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## PAPER

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## Introduction

Propylene ( $C_3H_6$ ) is one of the most critical chemical intermediates and an essential raw material used in the production of polypropylene, acrylonitrile, isopropanol, and propylene oxide.<sup>1</sup> In 2018, the global production of polypropylene, as the second most important synthetic plastic (second to polyethylene), was estimated at 56 Mt and will continuously increase to 88 Mt by 2026.<sup>2</sup> For most end uses, the propylene must have a purity of at least 99.5% (polymer-grade).<sup>3</sup> In industry, propylene is typically obtained by steam cracking of naphtha or during fluid catalytic cracking of gas oils in refineries, which involves propane ( $C_3H_8$ ) as a coproduct.<sup>4</sup> The production of polymer-grade  $C_3H_6$  involves the separation of  $C_3H_6$  from a  $C_3H_6/C_3H_8$  mixture. A conventional method for this separation mainly relies on cryogenic distillation, executed at about 243 K and 0.3 MPa in a column containing over 100 trays.<sup>5</sup> Evidently, such a heat-driven

## A metal-organic framework based propylene nano-trap with dual functionalities for highly efficient propylene/propane separation<sup>†</sup>

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Propylene/propane ( $C_3H_6/C_3H_8$ ) separation represents one of the most challenging and energy-intensive processes in the petrochemical industry due to their very similar sizes and physical properties. Most of the reported physisorbents still face the challenge of achieving simultaneously high  $C_3H_6$  uptake and selectivity with moderate adsorption enthalpy. Herein, we realize an efficient propylene nano-trap in a microporous MOF (ZJUT-2, Ni(pyz-SH)<sub>2</sub>SiF<sub>6</sub>) for highly efficient  $C_3H_6/C_3H_8$  separation. This MOF-based propylene nano-trap features a suitable pore cavity decorated with dual functionalities (–SH and SiF<sub>6</sub><sup>2–</sup>) to optimally interact with the  $C_3H_6$  molecule, affording both large  $C_3H_6$  capture capacity (123.5 cm<sup>3</sup> cm<sup>-3</sup> at 296 K and 0.5 bar) and high  $C_3H_6/C_3H_8$  selectivity of 17.2 achieved with moderate  $C_3H_6$  adsorption enthalpy (45 kJ mol<sup>-1</sup>). Theoretical calculations revealed that the appropriate pore cavity and dual functionalities synergistically construct an efficient nano-trap to match better with the  $C_3H_6$  molecule and thus provide stronger multipoint interactions with  $C_3H_6$  from  $C_3H_6/C_3H_8$  mixtures (50/50 and 10/90, v/v) under ambient conditions, affording both top-tier  $C_3H_6$  capture amount (2.6 mmol g<sup>-1</sup>) and dynamic selectivity of 10.

separation process is highly energy-intensive. It is highly demanded to develop alternative and energy-efficient separation technologies to potentially supersede traditional methods.<sup>6</sup>

Non-thermally driven processes, such as adsorptive separation by porous materials, have been considered to dramatically reduce the cost and energy required to purify olefins. In this regard, microporous metal-organic frameworks (MOFs) have been demonstrated to be promising adsorbents for gas separation and purification owing to their tunable pore size/shape and surface functionality.7-11 Amongst various gas separations,  $C_3H_6/C_3H_8$  separation represents one of the highest separation difficulties due to the subtle molecular size difference between the two components (<0.4 Å). A number of MOFs have been developed in recent years to show high C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation performance based on equilibrium-based, kinetic-based, molecular sieving or gating-opening mechanisms.12-30 Nevertheless, there commonly exists a trade-off challenge between uptake capacity and separation selectivity for most of the materials. For instance, several size-selective adsorbents with well-matched pore sizes (e.g., KAUST-7 and Co-gallate) enable complete size-exclusion of C3H8 from C3H6 to show record  $C_3H_6/C_3H_8$  selectivities but are commonly impaired by their relatively low gas uptakes.<sup>16,18</sup> In contrast, those large-pore MOFs (e.g., HKUST-1 and FeMIL-100) show high C<sub>3</sub>H<sub>6</sub> uptakes over 120 cm<sup>3</sup> g<sup>-1</sup>; however, large pores cannot efficiently discriminate the two similar molecules, resulting in low

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selectivity below 5.29 To overcome this trade-off dilemma, some specific MOFs with gating-opening or thermodynamic-kinetic effects have been realized for benchmark separation properties, while such kinds of materials are difficult to universally design in most cases.<sup>12-19</sup> Another more popular strategy is to immobilize strong open metal sites (OMSs) into MOFs for boosting preferential binding of C<sub>3</sub>H<sub>6</sub> over C<sub>3</sub>H<sub>8</sub>.<sup>25-29</sup> For example, the incorporation of high-density OMSs in MOF-74 or Ag(1) centers in MIL-101-SO<sub>3</sub>H can improve  $C_3H_6/C_3H_8$  selectivity up to *ca.* 40 while maintaining a high C3H6 adsorption amount.25-28 However, such high selectivities arise from ultra-strong metal-olefin interactions that are commonly greater than 60 kJ mol<sup>-1</sup>, leading to high regeneration energy. Evidently, there is a high demand to immobilize suitable functional sites with moderate binding affinity to boost  $C_3H_6/C_3H_8$  selectivity while maintaining high adsorption amounts.

Recent studies have shown that SIFSIX materials (SIFSIX = hexafluorosilicate  $(SiF_6^{2-})$  are very promising adsorbents for hydrocarbon separations because their pore size can be finely tuned and SiF<sub>6</sub><sup>2-</sup> anions have moderately strong interactions with hydrocarbon molecules.23,31 For example, two SIFSIX materials (GeFSIX-2-Cu-i and SIFSIX-2-Cu-i) with pore sizes of 4.5–4.7 Å exhibit the selective separation of  $C_3H_6$  over  $C_3H_8$ , while the relatively large pore sizes lead to the insufficient selectivity of below 5.23b Optimizing the pore size to 3.5 Å in NbOFFIVE-1-Ni can afford full molecular sieving toward C<sub>3</sub>H<sub>6</sub>/  $C_3H_8$  separation; however, the extremely small pore spaces severely delimit its C<sub>3</sub>H<sub>6</sub> uptake.<sup>16</sup> Therefore, simple control of pore sizes with single functionality in SIFSIX materials cannot fully address the trade-off dilemma to target both high C<sub>3</sub>H<sub>6</sub> adsorption and selectivity. Herein, we realized the immobilization of dual functionalities in a SIFSIX material (ZJUT-2,  $Ni(pyz-SH)_2SiF_6$ , pyz-SH = 2-mercaptopyrazine),<sup>34</sup> to construct an efficient C3H6 nano-trap for highly efficient C3H6/C3H8 separation. This MOF-based nano-trap features not only a small pore cavity with a suitable size of 3.9  $\times$  3.9  $\times$  7.5 Å<sup>3</sup> that matches better with a kinetic diameter of  $C_3H_6$  (4.0 Å) than  $C_3H_8$ (4.3 Å),<sup>12,18</sup> but also is decorated with dual functionalities (-SH and  $SiF_6^{2-}$ ) to optimally interact with the  $C_3H_6$  molecule. This material thus exhibits both top-tier C<sub>3</sub>H<sub>6</sub> capture capacity (123.5  $cm^3 cm^{-3}$  at 0.5 bar and 296 K) and  $C_3H_6/C_3H_8$  selectivity of 17.2 under ambient conditions, achieved by a moderate C<sub>3</sub>H<sub>6</sub> heat of adsorption (45 kJ mol<sup>-1</sup>). The C<sub>3</sub>H<sub>6</sub> uptake and selectivity of ZJUT-2a are obviously higher than those of the pristine SIFSIX-3-Ni (76.6  $\text{cm}^3$   $\text{cm}^{-3}$  and 6.6) and most of the top-performing materials reported. Highly efficient separation of C<sub>3</sub>H<sub>6</sub> from both 50/50 and 10/90 C3H6/C3H8 mixtures was confirmed by experimental breakthrough tests, providing both large  $C_3H_6$ uptake (2.6 mmol  $g^{-1}$ ) and high dynamic selectivity (10). Both values outperform or are comparable to those of some promising MOFs, such as Y-abtc (1.26 mmol  $g^{-1}$  and 8.3),<sup>17</sup> KAUST-7 (1.16 mmol g<sup>-1</sup> and 12),<sup>16</sup> and Ni-NP (2.3 mmol g<sup>-1</sup> and 9.6).<sup>22a</sup>

### Results and discussion

The powder sample of ZJUT-2 was prepared by the reaction of  $NiSiF_6$  and pyz-SH in methanol solution at 85 °C according to

the previously reported literature.<sup>34</sup> The phase purity and crystallinity of bulk ZIUT-2 were confirmed by powder X-ray diffraction (PXRD), which matched well with that of the simulated patterns (Fig. S1, ESI<sup>†</sup>). As shown in Fig. 1a, detailed structure analysis revealed that this material consists of twodimensional (2D) nets based on pyz-SH linkers and metal nodes, which are further pillared by  $SiF_6^{2-}$  anions to form the resulting 3D network. Each pore channel is separated by four  ${\rm SiF_6}^{2-}$  anions to form cylindrical nanocages with a size of 3.9  $\times$  $3.9 \times 7.5 \text{ Å}^3$ . From a kinetics point of view, the nanocage aperture of 3.9 Å matches better with the kinetic diameter of  $C_3H_6$  (4.0 Å) than  $C_3H_8$  (4.3 Å), making it an ideal singlemolecule trap for the capture of single C<sub>3</sub>H<sub>6</sub> molecules (Fig. 1b). Most importantly, the incorporated dual functionalities of -SH and SiF<sub>6</sub><sup>2-</sup> groups are located around the pore channels, which can create a multi-binding nano-trap to optimize the adsorption and recognition of C<sub>3</sub>H<sub>6</sub> molecules. Thus, the optimized nano-trap with a suitable size and dual functionalities may provide a single-molecule trap for highly selective capture of  $C_3H_6$  over  $C_3H_8$ .

The permanent porosity of ZJUT-2a was first confirmed using the CO<sub>2</sub> adsorption isotherms at 196 K (Fig. S2, ESI<sup>†</sup>), affording a Brunauer-Emmett-Teller (BET) surface area of 387.8 m<sup>2</sup> g<sup>-1</sup>. Single component gas adsorption isotherms of C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> for ZJUT-2a were collected at 296 K and 273 K up to 1 bar (Fig. 2a, S3 and S4, ESI<sup>†</sup>) and compared with those of pristine SIFSIX-3-Ni (Fig. S6, ESI†). As illustrated in Fig. 2a, ZJUT-2a exhibits a steep and high C<sub>3</sub>H<sub>6</sub> uptake at 296 K, which is larger than that of C<sub>3</sub>H<sub>8</sub> in the whole pressure region. Even at a low pressure of 0.1 bar, ZJUT-2a shows a very high C<sub>3</sub>H<sub>6</sub> uptake of 72.3 cm<sup>3</sup> cm<sup>-3</sup>, which is the highest among the reported MOFs relevant for C3H6/C3H8 separation except for the MOF-74 series (Fig. 2b).<sup>25-27</sup> In comparison, the  $C_3H_8$  uptake at 0.1 bar (11.9  $\text{cm}^3 \text{ cm}^{-3}$ ) is very low, affording a notably high  $C_{3}H_{6}/C_{3}H_{8}$  uptake ratio of 6.1 at 0.1 bar. Such high low-pressure C<sub>3</sub>H<sub>6</sub> uptake indicates that this MOF-based nano-trap can provide a stronger binding affinity with C<sub>3</sub>H<sub>6</sub> over C<sub>3</sub>H<sub>8</sub>, probably attributed to the suitable cage size and dual functionalities that match better with the size and shape of the  $C_3H_6$  molecule. When the pressure increases to 0.5 bar, the C<sub>3</sub>H<sub>6</sub> uptake amount can be improved to 123.5 cm<sup>3</sup> cm<sup>-3</sup>, which is higher than that of most relevant MOFs except for the MOF-74 series.<sup>25-27</sup> It is worth noting that this uptake is superior to that of SIFSIX-3-Ni (76.6 cm<sup>3</sup> cm<sup>-3</sup>) and most of the current best-performing materials reported (Fig. 2c), such as HIAM-301 (87.0 cm<sup>3</sup> cm<sup>-3</sup>),<sup>13</sup> UTSA-400 (85.5 cm<sup>3</sup> cm<sup>-3</sup>),<sup>14</sup> MFM-520 (74.6  $cm^{3} cm^{-3}$ ),<sup>20</sup> JNU-3a (69.3  $cm^{3} cm^{-3}$ ),<sup>12</sup> and KAUST-7 (46.0  $cm^{3}$ cm<sup>-3</sup>).<sup>16</sup> At 1 bar and 296 K, the C<sub>3</sub>H<sub>6</sub> uptake of ZJUT-2a can further increase to 138.9 cm<sup>3</sup> cm<sup>-3</sup>. These adsorption behaviors can be supported by the experimental isosteric heat of adsorption  $(Q_{st})$ , wherein the initial  $Q_{st}$  value of  $C_3H_6$  for ZJU-2a (45 kJ mol<sup>-1</sup>) is higher than that of  $C_3H_8$  (Fig. S9, ESI<sup>†</sup>). Further, as shown in Fig. S11 (ESI<sup>†</sup>), the initial Q<sub>st</sub> value of ZJUT-2 for C<sub>3</sub>H<sub>6</sub> is much higher than that of SIFSIX-3-Ni  $(38.7 \text{ kJ mol}^{-1})$ , indicating that the immobilization of -SH groups can strengthen the C<sub>3</sub>H<sub>6</sub> binding affinity. As shown in Fig. 2d, due to the lack of strong OMSs, the Q<sub>st</sub> value of ZJUT-2a

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**Fig. 1** Structure description of ZJUT-2. (a) Illustration of the square-shaped arrangement in the Ni–pyrazine (4,4') square grid that is further pillared by anion  $\text{SiF}_6^{2-}$  blocks to generate a 3D framework. (b) The pore channel structures of ZJUT-2, viewed along the *a/c*-axes and the *b*-axis, respectively. (c) The nanocages of ZJUT-2 that are separated by four  $\text{SiF}_6^{2-}$  anions along the *b*-axis. (d) View of the nano-trap with a size of  $3.9 \times 7.5 \text{ Å}^3$ , decorated with dual functionalities (–SH and  $\text{SiF}_6^{2-}$ ). Color code: F, red; Si, cyan; C, gray; H, white, N, blue; Ni, green; S, yellow.



**Fig. 2** (a) Adsorption isotherms of  $C_3H_6$  (red) and  $C_3H_8$  (black) for ZJUT-2a at 296 K. (b) Comparison of  $C_3H_6$  uptake capacity for ZJUT-2a and other best-performing materials at 0.1 bar and room temperature. (c) The absorption of  $C_3H_6$  at 0.5 bar and room temperature for ZJUT-2a compared to the indicated best-performing materials. (d) Comparison of heats of adsorption ( $Q_{st}$ ) of  $C_3H_6$  and  $C_3H_6$  uptake at 0.5 bar and room temperature for ZJUT-2a and room temperature for ZJUT-2a and room temperature for ZJUT-2a and other reported materials. (e) The IAST selectivity of 50/50 and 10/90  $C_3H_6/C_3H_8$  mixtures at 296 K. (f) Comparison of the  $C_3H_6$  uptake capacity at 0.5 bar and  $C_3H_6/C_3H_8$  selectivity for ZJUT-2a and other top-performing adsorbents reported.

is much less than that of the MOF-74 series with high-density OMSs (55–70 kJ mol<sup>-1</sup>).<sup>25</sup> Therefore, ZJUT-2a exhibits a remarkably top-tier  $C_3H_6$  uptake achieved by a moderate  $Q_{st}$  value, compared with all the indicated MOFs as evidenced in Fig. 2d and S12 (ESI†).

The adsorption selectivity of ZJUT-2a for 50/50 and 10/90 C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> mixtures was calculated by the ideal adsorbed solution theory (IAST) method. As indicated in Fig. 2e, ZJUT-2a shows a high selectivity of up to 17.2 and 20.9 for 50/50 and 10/ 90 C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> mixtures at 1 bar and 296 K, respectively, which are much higher than that of the pristine SIFSIX-3-Ni (6.6) and other SIFSIX materials such as SIFSIX-2-Cu-i (4.5),23b GeFSIX-2-Cu-i (4),<sup>23b</sup> and ZU-36-Ni (10.8).<sup>23a</sup> These values also outperform those of some promising MOFs including Ni-Np (10.5),<sup>22b</sup> MAF-23-O (8.8)<sup>19</sup> and MFM-520 (17),<sup>20</sup> but lower than those of molecular-sieving materials. It should be pointed out that this selectivity value is only for the qualitative comparison purpose. Besides gas selectivity, C<sub>3</sub>H<sub>6</sub> uptake capacity at partial pressure is also an important criterion to determine the final separation performance. As shown in Fig. 3f, we comprehensively compared C<sub>3</sub>H<sub>6</sub> uptake and selectivity of ZJUT-2a with some promising materials. Although those molecular-sieving MOFs exhibit the record-high selectivity due to the small pore sizes, their C<sub>3</sub>H<sub>6</sub> uptakes are relatively low. If we set the C<sub>3</sub>H<sub>6</sub> uptake and selectivity as concurrent objectives, most of the reported materials suffer from either unsatisfactory selectivity or inadequate uptake capacity. Evidently, ZJUT-2a, Co<sub>2</sub>(m-dobdc),<sup>25</sup> UTSA-400 (ref. 14) and HIAM-301 (ref. 13) exhibit more balance between adsorption uptake and gas selectivity for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub>

Fig. 3 Illustration of (a) and (b)  $C_3H_6$  adsorption sites in the nano-trap of ZJUT-2a, revealed by theoretical calculations. (c) Dense packing of the adsorbed  $C_3H_6$  molecules within the pore channel of ZJUT-2a, viewed along the *c* axis. Color code: F (red), Si (cyan), C (grey in ZJUT-2, orange in  $C_3H_6$ ), H (white), N (blue), Ni (green), S (yellow).

separation. Thus, both top-tier  $C_3H_6$  uptake capacity (123.5 cm<sup>3</sup> cm<sup>-3</sup> at 0.5 bar) and selectivity (17.2) along with moderate adsorption heat make this material among the best-performing materials reported for this separation.

To gain better insight into both high C<sub>3</sub>H<sub>6</sub> uptake and selectivity of ZJUT-2, grand canonical Monte Carlo (GCMC) simulations were performed to study the sorbate-sorbent interactions between the framework and gas molecules. The optimal adsorption sites for C3H6 and C3H8 in the pores of ZJUT-2a are approximated as shown in Fig. 3. Since the cavity size in ZJUT-2a matches well with the C<sub>3</sub>H<sub>6</sub> molecule, each nano-trap can only capture one C3H6 molecule through multiple hydrogen bonding and van der Waals (vdW) interactions between dual functionalities (-SH and SiF<sub>6</sub><sup>2-</sup>) and the C<sub>3</sub>H<sub>6</sub> molecule. As shown in Fig. 3a and b, each C<sub>3</sub>H<sub>6</sub> molecule interacts with four SiF<sub>6</sub><sup>2-</sup> anions through eleven C-H…F hydrogen bonds with the distances of 2.33-3.09 Å and also binds with four -SH groups through six C-H...S interactions (2.73–3.27 Å). Evidently, the immobilized  $SiF_6^{2-}$  and -SH groups synergistically contribute to enforcing the interactions with the C<sub>3</sub>H<sub>6</sub> molecule. Further, the dense distribution of these nanotraps within the framework enables the C<sub>3</sub>H<sub>6</sub> molecules to be in close proximity to each other with a contact distance of 4.16 Å along the b axis (Fig. 3c). Such observed contact distances in ZJUT-2a are notably shorter than those found in JNU-3a (4.53 Å), HIAM-301 (6.03 Å) and also comparable to the  $C_3H_6\cdots C_3H_6$ average distance in the crystalline C<sub>3</sub>H<sub>6</sub> (4.47 Å) collected at 65 K.15,32 This reveals that ZJUT-2a shows the dense packing of C<sub>3</sub>H<sub>6</sub> molecules within the pores, thus resulting in its high C<sub>3</sub>H<sub>6</sub> uptake capacity. In comparison, the overall H-bonding interactions between the pore surface and  $C_3H_8$  molecule are much less than that of C<sub>3</sub>H<sub>6</sub> (Fig. S14 and S15, ESI<sup>†</sup>). In addition, the cavity sizes of this nano-trap were found to be smaller than the kinetic diameter of C<sub>3</sub>H<sub>8</sub>. The weaker binding affinity and poor size match with the nano-trap may lead to partially populating the binding sites for C<sub>3</sub>H<sub>8</sub>. The above reasons thus afford both high C<sub>3</sub>H<sub>6</sub> uptake capacity and selectivity.

To evaluate the actual separation performance of ZJUT-2a, dynamic breakthrough experiments on binary  $C_3H_6/C_3H_8$  gas mixtures were carried out under ambient conditions. As presented in Fig. 4a, ZJUT-2a exhibited a clear separation for the 50/50 C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> mixture, wherein pure C<sub>3</sub>H<sub>8</sub> first eluted through the adsorption bed at 33 min, while C<sub>3</sub>H<sub>6</sub> was retained for a longer time of 65 min. During this breakthrough interval, the  $C_3H_6$  dynamic uptake was calculated to be 2.6 mmol g<sup>-1</sup>, which is 79% of the saturated uptake (3.3 mmol  $g^{-1}$ ) obtained from single-component adsorption isotherms at 296 K and 1 bar. This value is not only much higher than that of other reported SIFSIX materials (Fig. 4b), including SIFSIX-3-Ni  $(1.25 \text{ mmol } g^{-1})$ ,<sup>23*a*</sup> GeFSIX-2-Cu-i  $(2.2 \text{ mmol } g^{-1})$ ,<sup>23*b*</sup> and SIFSIX-2-Cu-i (2.0 mmol  $g^{-1}$ ),<sup>23b</sup> but also outperforms some topperforming MOFs such as JNU-3a (2.45 mmol  $g^{-1}$ ),<sup>12</sup> HIAM-301  $(2.07 \text{ mmol } \text{g}^{-1})^{13}$  and KAUST-7 (1.16 mmol  $\text{g}^{-1})$ .<sup>16</sup> Further, the dynamic C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivity was estimated to be up to 10, which exceeds that of SIFSIX-3-Ni (2.3)23a and most topperforming materials, such as Y-abtc (8.3),<sup>17</sup> Co-MOF-74 (6.5)<sup>25</sup> and Ni-NP (9.6).22a As shown in Fig. 4c, ZJUT-2a thus shows





Fig. 4 (a) Experimental breakthrough curves for a 50/50  $C_3H_6/C_3H_8$  mixture with a flow rate of 2 mL min<sup>-1</sup> under ambient conditions. (b) Comparison of  $C_3H_6$  dynamic uptake for ZJUT-2a and other benchmark materials. (c) Comparison of  $C_3H_6$  dynamic uptake and selectivity for ZJUT-2a and other benchmark materials. (d) Experimental breakthrough curves for a 10/90  $C_3H_6/C_3H_8$  mixture with a flow rate of 2 mL min<sup>-1</sup> under ambient conditions. (e) Cycling column breakthrough curves for 50/50  $C_3H_6/C_3H_8$  separation under ambient conditions. (f) Breakthrough curves of ZJUT-2a for 50/50  $C_3H_6/C_3H_8$  separation at 50% humidity.

a rare combination of simultaneously high C3H6 dynamic uptake and selectivity, placing it among the best-performing materials reported so far for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation. It should be noted that the feed gases in some production processes might contain only a small amount of C<sub>3</sub>H<sub>6</sub>, which requires adsorbents to efficiently capture C<sub>3</sub>H<sub>6</sub> at low partial pressures. Therefore, we performed the breakthrough experiments for 10/ 90 C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> mixtures (Fig. 4d). More difference in the breakthrough times of C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> was observed, with a high dynamic  $C_3H_6$  uptake of 1.5 mmol g<sup>-1</sup>, indicating the superior separation ability of ZJUT-2a for some gas mixtures with low  $C_3H_6$  content. Three continuous cycles on 50/50 and 10/90 mixtures showed the full retention of the separation performance and easy recyclability of ZJUT-2a (Fig. 4e and S20, ESI<sup>+</sup>). Given that water vapor is a ubiquitous component in industrial gas mixtures,<sup>33</sup> we conducted the breakthrough experiments for a wet C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> mixture at 50% relative humidity. As shown in Fig. 4f, the almost unchanged breakthrough times of both C<sub>3</sub>H<sub>6</sub> and C3H8 demonstrated the excellent moisture tolerance properties of ZJUT-2a, which can avoid the deleterious effect of water vapor on C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation performance. As inferred from the PXRD performed on associated samples (Fig. S22, ESI<sup>†</sup>), the framework of ZJUT-2a remains stable after multiple breakthrough experiments.

## Conclusions

In summary, we have realized the immobilization of dual functionalities into a suitable MOF to construct a single-

molecule nano-trap for highly efficient C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation. The incorporated bifunctional groups (-SH and  $SiF_6^{2-}$ ) combined with the appropriate cavity size/shape in ZJUT-2a can synergistically create multiple binding environments to densely and selectively trap the C<sub>3</sub>H<sub>6</sub> molecule, as revealed by theoretical calculations. This MOF-based nano-trap thus exhibited both top-tier  $C_3H_6$  capture capacity (123.5 cm<sup>3</sup> cm<sup>-3</sup> at 0.5 bar) and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> selectivity of 17.2 under ambient conditions, achieved by a moderate  $C_3H_6$  adsorption enthalpy (45 kJ mol<sup>-1</sup>). Breakthrough experiment data revealed both remarkably large  $C_3H_6$  dynamic uptake of 2.6 mmol g<sup>-1</sup> and high dynamic selectivity of 10 for the separation of actual C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> mixtures, surpassing most of the top-performing materials reported to date. This work provides some guidance to design porous materials with multiple soft functionalities to highly boost  $C_3H_6/C_3H_8$  separation performance through moderate gas adsorption enthalpy.

## Conflicts of interest

There are no conflicts to declare.

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