

## RESEARCH ARTICLE

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## Size exclusion propyne/propylene separation in an ultramicroporous yet hydrophobic metal–organic framework†

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Propyne/propylene separation is important in the petrochemical industry but challenging due to their similar physical properties and close molecular sizes. Herein, we present two isorecticular ultramicroporous Zn(II)-MOFs,  $Zn_2(ATZ)_2(TPDC)$  (**BUT-305**,  $H_2TPDC = [1,1':3',1''\text{-terphenyl}]$ -4,4''-dicarboxylic acid,  $HATZ = 3\text{-amino-1,2,4-triazole}$ ) and  $Zn_2(ATZ)_2(MeTPDC)$  (**BUT-306**,  $H_2MeTPDC = 5'\text{-methyl-}[1,1':3',1''\text{-terphenyl}]$ -4,4''-dicarboxylic acid). The pore aperture of **BUT-306** ( $\sim 1.6 \text{ \AA}$ ) is smaller than that of **BUT-305** due to the presence of extra gate-like methyl groups in the 1D channels of the former. With a narrow and hydrophobic pore aperture, **BUT-306** exhibits high hydrophobicity and hydrolytic stability and adsorbs  $C_3H_4$  but excludes  $C_3H_6$  in a wide temperature range. The  $C_3H_6$  and  $C_3H_4$  adsorption capacities of **BUT-306** at 298 K and  $\sim 1$  bar were 2.4 and 29.6  $\text{cm}^3 \text{ g}^{-1}$ , respectively. Dynamic column breakthrough experiments confirmed the high capability of **BUT-306** to remove  $C_3H_4$  from the equimolar binary gas mixture of  $C_3H_4$  and  $C_3H_6$ . The  $C_3H_4/C_3H_6$  separation performance of **BUT-306** was largely retained even when the binary  $C_3H_4/C_3H_6$  gas for breakthrough experiments was pre-saturated with water vapor. In addition, the single-crystal structure of  $C_3H_4$ -loaded **BUT-306** was determined, which revealed that the adsorbed  $C_3H_4$  molecules were located in the center of channel cavities and interacted with the MOF by multiple weak  $C^\delta-\dots-C^\delta+$  dipole–dipole interactions and  $C-H\dots\pi$  interactions. This work demonstrates the high potential of an ultramicroporous, hydrophobic, and hydrolytically stable MOF in the removal of  $C_3H_4$  from the  $C_3H_4/C_3H_6$  gas mixture by size exclusion adsorption. The structure and gas adsorption studies shed light on the design and synthesis of new adsorbents for the separation of light hydrocarbons.

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## Introduction

Propylene ( $C_3H_6$ ), as a raw material of many chemical products, plays a key role in the petrochemical industry.<sup>1</sup>  $C_3H_6$  is mostly produced from the cracking of large hydrocarbon molecules or crude oil in the petrochemical industry commonly accompanied by propyne ( $C_3H_4$ ) as an undesirable byproduct, which can poison the catalysts for propylene polymerization.<sup>2</sup> Efficient removal of  $C_3H_4$  from the  $C_3H_4/C_3H_6$  mixture is thus of high importance. Traditional  $C_3H_4/C_3H_6$  separation methods, such as cryogenic distillation or catalytic partial hydrogenation, suffer from high cost and high energy

penalties.<sup>3,4</sup> The physical adsorption method based on porous materials is attractive for gas separation owing to its environmentally friendly processes and energy efficiency.<sup>5–11</sup> Highly efficient  $C_3H_4/C_3H_6$  separation using traditional porous materials (such as zeolites and activated carbons) remains challenging because of highly similar physical properties, molecular sizes ( $C_3H_6$ :  $4.65 \times 4.16 \times 6.44 \text{ \AA}^3$  and  $C_3H_4$   $4.01 \times 4.16 \times 6.51 \text{ \AA}^3$ ) and kinetic diameters ( $C_3H_6$ : 4.68  $\text{\AA}$  and  $C_3H_4$ : 4.76  $\text{\AA}$ ) of the two hydrocarbons.<sup>12</sup>

As a class of newly emerged porous materials, metal–organic frameworks (MOFs)<sup>13–20</sup> have been widely used for gas separation owing to their structural diversity,<sup>21–26</sup> adjustable pore size<sup>27–30</sup> and designable adsorption sites.<sup>31–37</sup> Most reported MOFs used for  $C_3H_4/C_3H_6$  separation are based on their open metal sites or functional groups which can strongly interact with  $C_3H_4$ . For example, the MOF-74 series (Mg, Co, Ni, and Fe-MOF-74)<sup>38</sup> with open metal sites and the SIFSIX series (SIFSIX-3-Ni,<sup>39</sup> SIFSIX-1-Cu,<sup>40</sup> and SIFSIX-2-Cu-<sup>i</sup><sup>19</sup>) with  $SiF_6^{2-}$  anion pillars can afford high adsorption capacity and strong interaction for  $C_3H_4$ .<sup>34</sup> However, these MOFs allow

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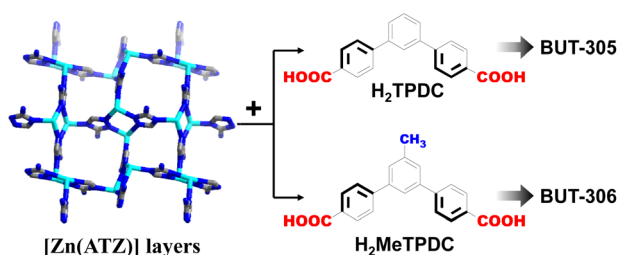
diffusion of both  $C_3H_4$  and  $C_3H_6$  into their pores,<sup>2,34,41–46</sup> resulting in a compromised separation efficiency. In addition, the regeneration processes are relatively energy-intensive due to the high affinity of these MOFs to  $C_3H_4$ . Therefore, the development of adsorbents with high performance in selective adsorption of  $C_3H_4$  over  $C_3H_6$  primarily relying on the molecular sieving effect would be complementary. However, among the reported MOFs, only UTSA-200 showed molecular sieving  $C_3H_4/C_3H_6$  separation performance with a high adsorption selectivity of over 20 000.<sup>32</sup> In addition, stability and recyclability are also important for porous materials in gas separation applications,<sup>47</sup> especially when the gas mixtures to be purified contain reactive non-hydrocarbon impurities, *e.g.* water, which is ubiquitous.

Herein, we report two ultramicroporous MOFs,  $Zn_2(ATZ)_2(TPDC)$  (**BUT-305**,  $H_2TPDC = [1,1':3',1''\text{-terphenyl}]$ -4,4''-dicarboxylic acid, HATZ = 3-amino-1,2,4-triazole) and  $Zn_2(ATZ)_2(\text{MeTPDC})$  (**BUT-306**,  $H_2\text{MeTPDC} = 5'$ -methyl-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid), which are 3D framework structures consisting of 2D  $[Zn(ATZ)]$  layers pillared by  $TPDC^{2-}$  and  $\text{MeTPDC}^{2-}$  ligands (Scheme 1), respectively. The difference between the two isorecticular MOFs is that there are extra gate-like methyl groups in the 1D channels of **BUT-306**. Owing to its narrow and hydrophobic pore aperture, **BUT-306** exhibits high hydrolytic stability, hydrophobicity, and potential in the removal of  $C_3H_4$  from the  $C_3H_4/C_3H_6$  mixture. In addition, the location of  $C_3H_4$  molecules inside the pore of **BUT-306** and the host-guest interactions have been elucidated by single-crystal structural analyses.

## Results and discussion

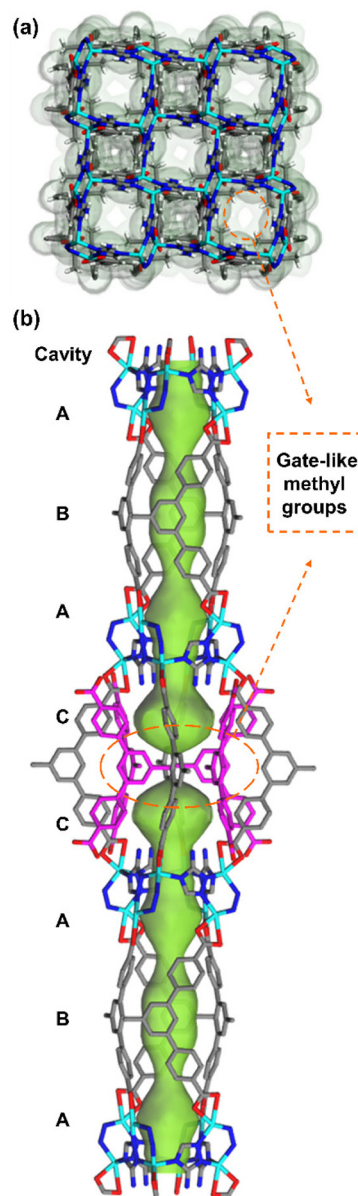
### Single-crystal structures and chemical stability

As-synthesized crystals of **BUT-305** and **-306** were obtained through the solvothermal reactions of zinc salt and organic ligands (HATZ and  $H_2TPDC$  or HATZ and  $H_2\text{MeTPDC}$ ) in the mixture of DMF and a small amount of aqueous  $\text{HBF}_4$  solution. The as-synthesized crystals were guest-exchanged in MeOH solvent for 3 days at 120 °C followed by heating at 120 °C for 18 hours to remove guest molecules, resulting in the formation of **BUT-305** and **-306** samples. The SCXRD measurement of **BUT-306** revealed that it crystallizes in the tetragonal  $I4/m$  space group (Table S1†) and it is isorecticular to



**Scheme 1** The construction and building blocks of **BUT-305** and **-306**.

$Zn_2(ATZ)_2(\text{iPA})$  ( $H_2\text{iPA} = \text{isophthalic acid}$ ) as reported by Chen and co-workers.<sup>48</sup> The 2D  $[Zn(ATZ)]$  layers are linked by the  $\text{MeTPDC}^{2-}$  pillars to form a 3D pillar-layered framework with 1D channels along the crystallographic *c*-axis (Fig. 1a). The cross-sectional diameters of the channel are estimated to be 1.6 to 5.0 Å by Materials Studio.<sup>49</sup> It is worthy of note that the channel is highly tortuous with three types of cavities (A, B, and C), and it is divided into parts by sets of gate-like methyl groups, each set of which are from 4 neighboring  $\text{MeTPDC}^{2-}$  ligands (Fig. 1b). The aperture defined by the 4 gate-like methyl groups is only about 1.6 Å in diameter. Regardless of



**Fig. 1** The crystal structure of **BUT-306**: (a) the 3D framework view along the *c* axis and (b) side-view of the channel. Color codes: Zn, turquoise; O, red; N, blue; C, grey; H, white; and Connolly surface (probe radius 1.7 Å), green. The ligands coordinated with the metal ions on the walls of neighboring channels are shown in pink for clarity.

the small aperture size, **BUT-306** is still potentially porous as the total potential solvent area volume accounts for 23.6% of the unit cell volume of **BUT-306** and the pore volume is estimated to be  $0.17 \text{ cm}^3 \text{ g}^{-1}$  by Platon.<sup>50</sup>

Due to the thin-plate-like shape of **BUT-305** crystals, attempts to determine their structure by SCXRD failed. The PXRD pattern of **BUT-305** resembled that of **BUT-306**, suggesting that **BUT-305** is likely isorecticular to **BUT-306** (Fig. 2a). Indexing and Pawley refinement results for the PXRD pattern of **BUT-305** showed that it also crystallizes in the same space group ( $I4/m$ ) with a slightly larger unit cell relative to that of **BUT-306** (Fig. 2b and Table S2†). Due to the absence of methyl groups on the ligands of **BUT-305**, it is expected that the channels of **BUT-305** are larger than those of **BUT-306**. The difference in the channels of the two MOFs results in their distinctive gas separation performance, which will be discussed in detail below. The PXRD patterns of **BUT-305** and **-306** samples well matched the simulated one from the single-crystal structure of **BUT-306** (Fig. 2a), which confirmed that

the prepared **BUT-305** and **-306** samples were pure phases. In addition, the PXRD measurements showed that the highly crystalline structures of **BUT-305** and **-306** samples remained essentially unchanged after they were treated with methanol at  $120 \text{ }^\circ\text{C}$  for 3 days (Fig. S1†) or treated with water at room temperature for 24 hours (Fig. 2a), demonstrating their high hydrolytic stability.

### Adsorption studies

To verify the accessibility of their pores,  $\text{N}_2$  adsorption isotherms of **BUT-305** and **-306** were recorded at  $77 \text{ K}$  (Fig. S2†). Although the calculated pore volumes of the two MOFs are over  $0.17 \text{ cm}^3 \text{ g}^{-1}$ , type I  $\text{N}_2$  adsorption isotherms were not obtained. The  $\text{N}_2$  uptake at  $P/P_0 \approx 1$  was only  $1.2 \text{ cm}^3 \text{ g}^{-1}$  for **BUT-306**, suggesting that  $\text{N}_2$  molecules could not diffuse into its channels at  $77 \text{ K}$ . The  $\text{N}_2$  uptake of **BUT-305** gradually increased as the pressure is increased with an  $\text{N}_2$  uptake of  $77.1 \text{ cm}^3 \text{ g}^{-1}$  at  $P/P_0 \approx 1$ , which might result from the comparable size of the  $\text{N}_2$  molecule and the pore of **BUT-305**. The  $\text{CO}_2$  adsorption isotherms of **BUT-305** and **-306** at  $195 \text{ K}$  were then recorded. As shown in Fig. S3,† the two MOFs showed an abrupt increase in  $\text{CO}_2$  uptake (to  $\sim 70 \text{ cm}^3 \text{ g}^{-1}$ ) at low pressures ( $P/P_0 < 0.1$ ). At higher pressures, the  $\text{CO}_2$  uptake of **BUT-306** only slightly increased, while that of **BUT-305** increased to  $193 \text{ cm}^3 \text{ g}^{-1}$  at  $P/P_0 \approx 1$  by two additional stepwise increases, indicating the presence of some difference in the pore size, shape and/or flexibility of the two MOFs. According to the adsorption data at low pressures, the BET surface areas of **BUT-305** and **-306** were estimated to be  $351$  and  $305 \text{ m}^2 \text{ g}^{-1}$ , respectively. Water adsorption isotherms were also recorded for the MOFs at  $298 \text{ K}$ . Type III water adsorption isotherms were obtained for both MOFs (Fig. 3a and S4†), and the water uptakes at  $P/P_0 \approx 1$  were  $160$  and  $80 \text{ cm}^3 \text{ g}^{-1}$  for **BUT-305** and **BUT-306**, respectively. These results indicated that the two MOFs were capable of accommodating small molecules and their pore surface was relatively hydrophobic.

Encouraged by the high stability, accessible porosity and small pore apertures of the two MOFs, we explored their performances in light hydrocarbon separations. Adsorption isotherms for  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_4$ ,  $\text{C}_3\text{H}_6$ , and  $\text{C}_3\text{H}_8$  were recorded at  $298 \text{ K}$ , as shown in Fig. S5.† The adsorption capacities of **BUT-305** for  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  at  $\sim 1$  bar were similar ( $42.3$ – $44.6 \text{ cm}^3 \text{ g}^{-1}$ ), and its adsorption capacities for  $\text{C}_3\text{H}_4$  ( $44.4 \text{ cm}^3 \text{ g}^{-1}$ ) and  $\text{C}_3\text{H}_6$  ( $43.9 \text{ cm}^3 \text{ g}^{-1}$ ) at  $\sim 1$  bar were also close, but that for  $\text{C}_3\text{H}_8$  ( $33.8 \text{ cm}^3 \text{ g}^{-1}$ ) was lower. These results suggested that all these hydrocarbons could enter the pore of **BUT-305**, and the differences in adsorption capacities of **BUT-305** for these hydrocarbons were not profound. In contrast, strong size exclusion effects were observed in the hydrocarbon adsorption isotherms of **BUT-306**. For  $\text{C}_2$  hydrocarbons, the uptake of **BUT-306** for  $\text{C}_2\text{H}_2$  ( $36.6 \text{ cm}^3 \text{ g}^{-1}$ ) or  $\text{C}_2\text{H}_4$  ( $30.3 \text{ cm}^3 \text{ g}^{-1}$ ) was obviously higher than that for  $\text{C}_2\text{H}_6$  ( $11.0 \text{ cm}^3 \text{ g}^{-1}$ ) at  $\sim 1$  bar. Moreover, the uptakes of **BUT-306** for  $\text{C}_3\text{H}_6$  ( $2.4 \text{ cm}^3 \text{ g}^{-1}$ ) and  $\text{C}_3\text{H}_8$  ( $0.33 \text{ cm}^3 \text{ g}^{-1}$ ) at  $\sim 1$  bar were nearly negligible (Fig. S5d†), but a type I-like  $\text{C}_3\text{H}_4$  adsorption isotherm was obtained for **BUT-306** with a relatively high

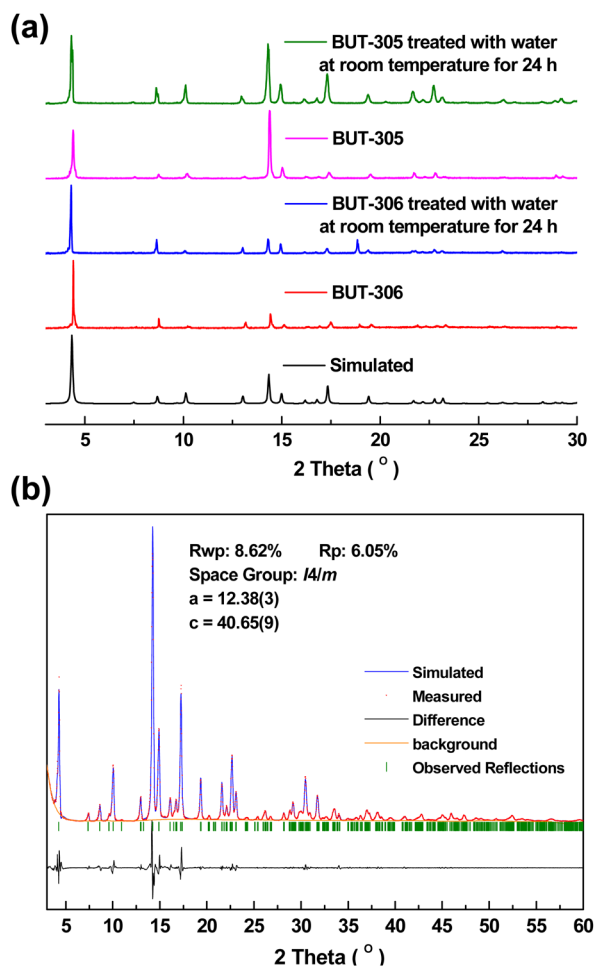
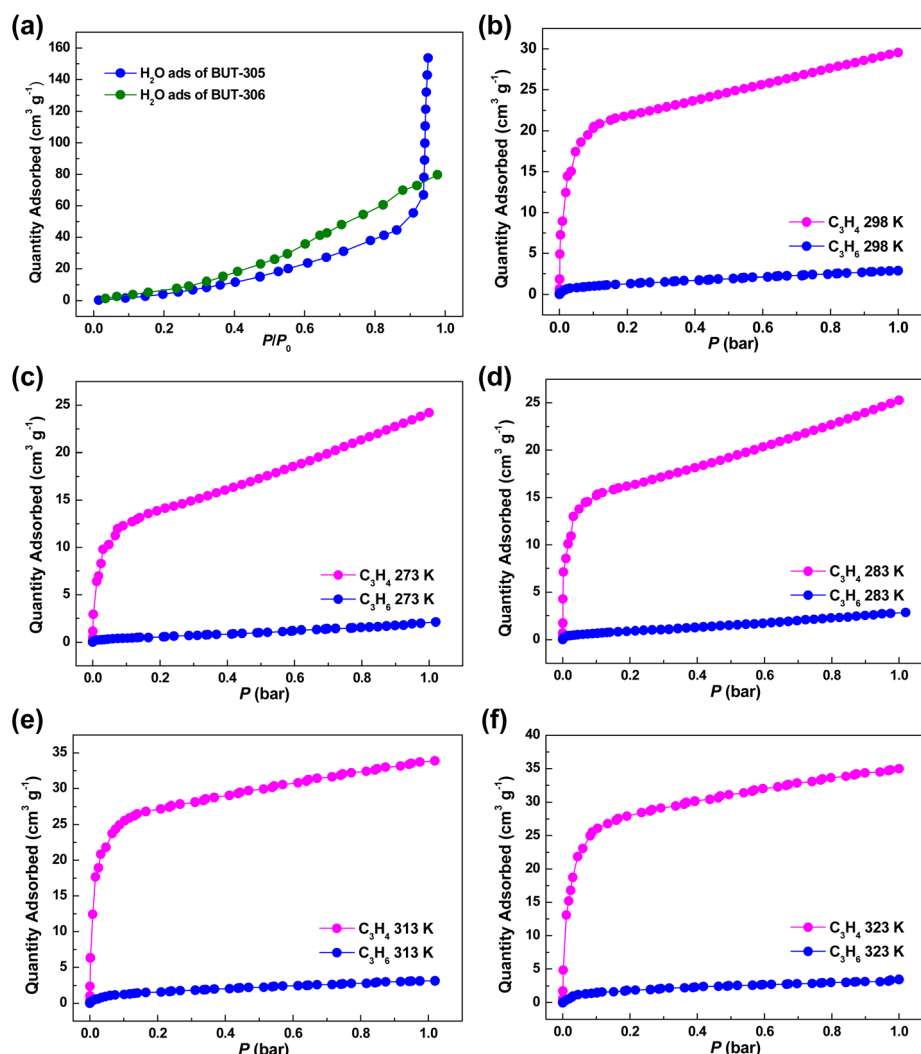


Fig. 2 (a) The PXRD patterns of **BUT-305** and **BUT-306**. (b) The results of Pawley refinement for the PXRD data of **BUT-305**. For comparison, the space group and cell parameters of **BUT-306** are as follows:  $I4/m$ ,  $a = 12.3420(2) \text{ \AA}$ , and  $c = 40.6826(9) \text{ \AA}$ .



**Fig. 3** Adsorption and separation performance of BUT-306. (a) The  $\text{H}_2\text{O}$  adsorption isotherms of BUT-305 and -306 at 298 K. Single-component  $\text{C}_3\text{H}_4$  and  $\text{C}_3\text{H}_6$  adsorption isotherms of BUT-306 at (b) 298 K, (c) 273 K, (d) 283 K (e) 313 K and (f) 323 K, respectively.

uptake of  $29.6 \text{ cm}^3 \text{ g}^{-1}$  at  $\sim 1$  bar (Fig. 3b and S6<sup>†</sup>), indicating its potential in the removal of  $\text{C}_3\text{H}_4$  from the  $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$  mixture. Although the  $\text{C}_3\text{H}_4$  adsorption capacity of BUT-306 is lower than those of some reported MOFs under similar conditions, *e.g.*, SIFSIX-2-Cu-i ( $84.4 \text{ cm}^3 \text{ g}^{-1}$ ), UTSA-200 ( $80.2 \text{ cm}^3 \text{ g}^{-1}$ ) and ELM-12 ( $62.1 \text{ cm}^3 \text{ g}^{-1}$ ), BUT-306 hardly permits the entrance of  $\text{C}_3\text{H}_6$  molecules into its pores. The  $\text{C}_3\text{H}_6$  adsorption capacity of BUT-306 was only  $2.4 \text{ cm}^3 \text{ g}^{-1}$  at  $\sim 1$  bar and 298 K, significantly lower than those of the reported MOFs (Table S3<sup>†</sup>),<sup>32,51,52</sup> including SIFSIX-2-Cu-i ( $58.9 \text{ cm}^3 \text{ g}^{-1}$ ), UTSA-200 ( $26.9 \text{ cm}^3 \text{ g}^{-1}$ ), and ELM-12 ( $32.0 \text{ cm}^3 \text{ g}^{-1}$ ). The size exclusion effects of BUT-306 on the adsorption of  $\text{C}_3\text{H}_4$  over  $\text{C}_3\text{H}_6$  should be related to the small apertures defined by gate-like methyl groups in its 1D channels.

For a better comparison, the uptake ratios of BUT-306 for  $\text{C}_3\text{H}_4$  over  $\text{C}_3\text{H}_6$  at 0.99 bar or at 0.01/0.99 bars (0.01 bar for  $\text{C}_3\text{H}_4$  and 0.99 for  $\text{C}_3\text{H}_6$ ) and 298 K were calculated, being 10.75 and 3.67, respectively, which are much higher than

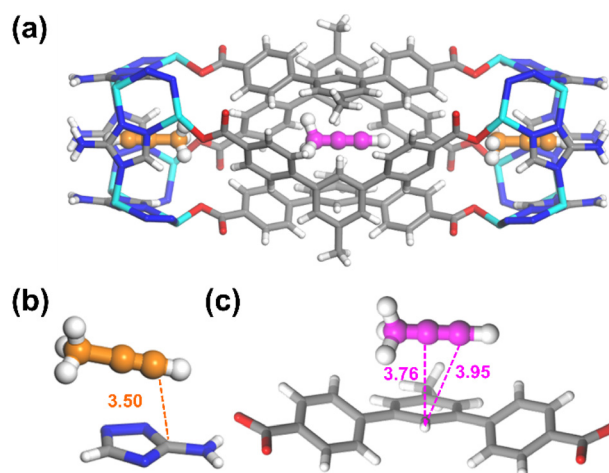
those of the reported porous materials (1.05–3.07 at 0.99 bar; 0.03–2.49 at 0.01/0.99 bars) under similar conditions (Table S3<sup>†</sup>). Furthermore, ideal adsorbed solution theory (IAST) was used to predict the  $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$  adsorption selectivity of BUT-306. Assuming the gas mixture with  $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$  ratios (v/v) of 1:1, 1:9 and 1:99, the IAST  $\text{C}_3\text{H}_4/\text{C}_3\text{H}_6$  adsorption selectivities of BUT-306 at  $\sim 1$  bar and 298 K were calculated to be 636, 717, and 989, respectively (Fig. S7<sup>†</sup>).

To explore the adsorption performances of BUT-306 for  $\text{C}_3\text{H}_4$  and  $\text{C}_3\text{H}_6$  in a broader temperature range,  $\text{C}_3\text{H}_4$  and  $\text{C}_3\text{H}_6$  adsorption isotherms were measured at 273, 283, 313 and 323 K, respectively. As shown in Fig. 3c–f, type I-like adsorption isotherms were obtained for  $\text{C}_3\text{H}_4$  at all four temperatures, and the adsorption capacities at  $\sim 1$  bar were all over  $25 \text{ cm}^3 \text{ g}^{-1}$ , while the  $\text{C}_3\text{H}_6$  uptakes were all relatively low ( $< 5 \text{ cm}^3 \text{ g}^{-1}$ ). It is indicated that the size exclusion adsorption behavior of BUT-306 is not highly sensitive to the temperature. The adsorption capacity of BUT-306 for  $\text{C}_3\text{H}_4$  or  $\text{C}_3\text{H}_6$  gradually

increased as the temperature increased from 273 to 323 K. For example, the  $C_3H_4$  uptake at  $\sim 1$  bar increased from  $24.2 \text{ cm}^3 \text{ g}^{-1}$  at 273 K to  $35.0 \text{ cm}^3 \text{ g}^{-1}$  at 323 K. The adsorption data at these temperatures were further verified by repeated adsorption isotherm measurements (Fig. S8<sup>†</sup>). It is not common because physisorption is essentially exothermic, and the adsorption capacities at a certain equilibrium pressure should decrease when increasing the adsorption temperature for typical physical adsorption adsorbents. The abnormal adsorption behavior suggests the existence of structural flexibility in **BUT-306**.<sup>53,54</sup> To verify this, SCXRD measurements were carried out for the same one single crystal of **BUT-306** at 273 K, 313 K and 298 K, respectively. As shown in Fig. S9 and Table S1,<sup>†</sup> the unit cell parameters were nearly unchanged and no obvious structural change was observed during varying the measurement temperatures, indicating that the structural flexibility was induced by the adsorption of hydrocarbons rather than the change of temperature. Otherwise, according to the static equilibrium crystal structure of **BUT-306**, the narrowest pore aperture is too small (diameter:  $1.6 \text{ \AA}$ ) to let the hydrocarbon molecules diffuse into the channels. The increase of measurement temperature should be beneficial for the diffusion of  $C_3H_4$  molecules into **BUT-306** as there is an energy barrier between the guest-free state and the guest-included state originating from the structural flexibility of **BUT-306**, which leads to the uncommon adsorption behavior of **BUT-306** as mentioned above.

For a better understanding of the  $C_3H_4$  adsorption process of **BUT-306**, the single-crystal structure of  $C_3H_4$ -loaded **BUT-306** was determined. A single crystal of **BUT-306** preheated at  $50 \text{ }^\circ\text{C}$  under an  $N_2$  atmosphere for 6 hours was exposed to the atmosphere of  $C_3H_4$  at ambient pressure and temperature for 30 minutes to load the hydrocarbon molecules, which was then mounted on a single-crystal X-ray diffractometer under a low-temperature  $N_2$  flow bath ( $200 \text{ K}$ ) for data collection. Structure determination and refinement results revealed that the framework of **BUT-306** was essentially unchanged after  $C_3H_4$  loading (Fig. S9 and Table S1<sup>†</sup>) and two crystallographically independent  $C_3H_4$  molecules were found inside its channels. As the framework was retained, the narrowest channel apertures defined by the methyl groups of  $\text{MeTPDC}^{2-}$  ligands kept unchanged after  $C_3H_4$  loading, indicating that there was a transient structural variation to open the gate-like apertures when  $C_3H_4$  molecules diffused into the channels. The transient gate-opening might have resulted from the swing or distortion of the  $\text{MeTPDC}^{2-}$  ligands.

The two types of  $C_3H_4$  molecules are located inside cavities A and B with a linear molecular shape along the 4-fold rotation axis, respectively (Fig. 4a). The C–C triple bond and single bond of the  $C_3H_4$  molecule located at cavity A ( $C_3H_4\text{-A}$ ) are  $1.08(8)$  and  $1.54(8) \text{ \AA}$ , respectively. The  $C_3H_4$  molecule located at cavity B ( $C_3H_4\text{-B}$ ) is normal to the reflection plane crossing its center C atom. Due to the symmetry-imposed disorder, the two C–C bonds of  $C_3H_4\text{-B}$  are same in length, being  $1.24(8) \text{ \AA}$ , close to the average length of a C–C triple bond and a C–C single bond. Occupations of the two  $C_3H_4$  molecules were set

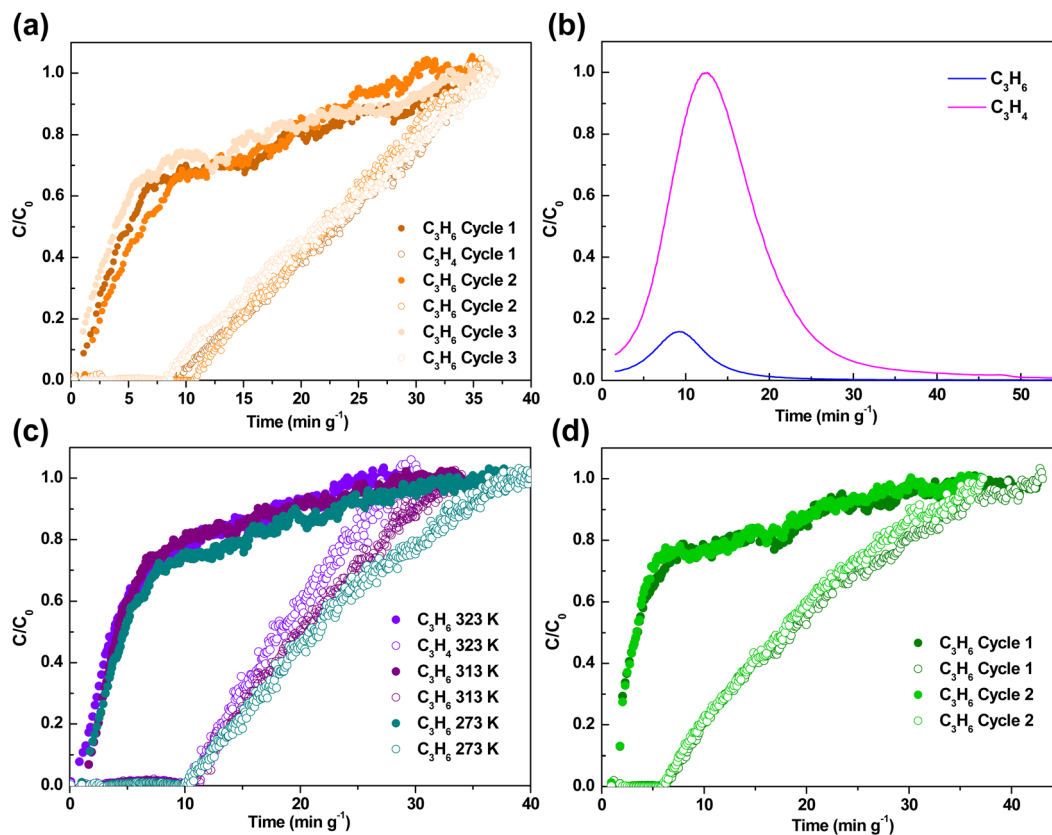


**Fig. 4** (a) The two types of  $C_3H_4$  adsorption sites in the cavities of **BUT-306**. The interaction between the **BUT-306** framework and the  $C_3H_4$  molecules located in cavity A (b) and in cavity B (c). Color codes: Zn, turquoise; O, red; N, blue; C, grey; and H, white. For clarity, the C atoms of  $C_3H_4\text{-A}$  and  $C_3H_4\text{-B}$  are in gold and pink colors, respectively.

to be 20%, and no geometrical restraints were used in the structure refinements. The  $C_3H_4$  molecules are confined inside the cavities by multiple weak host–guest interactions with the framework. Specifically, the distance between the terminal sp-hybridized C atom (with a negative charge) of  $C_3H_4\text{-A}$  and the 3-position C atoms (with a positive charge) of four neighboring  $\text{ATZ}^-$  ligands on the channel walls is  $3.50 \text{ \AA}$  (Fig. 4b), slightly larger than the van der Waals radii of two C atoms ( $1.7 \times 2 \text{ \AA}$ ), indicating the presence of weak  $C^{\delta-} \cdots C^{\delta+}$  dipole–dipole interactions. In addition, there are fourfold weak C–H $\cdots\pi$  interactions between  $C_3H_4\text{-B}$  and the aromatic H atoms of four neighboring  $\text{MeTPDC}^{2-}$  ligands ( $C_{C_3H_4} \cdots H$  distances:  $3.76$ ,  $3.95 \text{ \AA}$ ;  $\langle C\text{-H} \cdots C$  angles:  $85.9$ ,  $86.1^\circ$ ) (Fig. 4c). Though every single interaction is weak, the overall interactions between  $C_3H_4$  and MOF should be moderate because each  $C_3H_4$  molecule is interacting with four neighboring channel walls simultaneously. Assuming that the two adsorption sites are fully occupied, the calculated  $C_3H_4$  uptake of **BUT-306** is  $26.8 \text{ cm}^3 \text{ g}^{-1}$ , which is slightly lower than the experimentally observed uptake ( $29.6 \text{ cm}^3 \text{ g}^{-1}$ ) at  $\sim 1$  bar and  $298 \text{ K}$ . It is noteworthy that  $C_3H_4$  uptake of **BUT-306** at  $\sim 1$  bar gradually increased from  $24.2$  to  $35.0 \text{ cm}^3 \text{ g}^{-1}$  as the temperature increased from  $273$  to  $323 \text{ K}$ . This fact suggests that the adsorbed  $C_3H_4$  molecules could be also located inside the cavity C besides cavities A and B. When each of the cavities is occupied by one  $C_3H_4$  molecule, the calculated  $C_3H_4$  uptake of **BUT-306** is  $35.7 \text{ cm}^3 \text{ g}^{-1}$ , close to the uptake ( $35.0 \text{ cm}^3 \text{ g}^{-1}$ ) observed at  $\sim 1$  bar and  $323 \text{ K}$ , further justifying the assignment of adsorption sites.

#### Dynamic column breakthrough studies

Dynamic column breakthrough experiments of a binary gas of  $C_3H_4/C_3H_6$  ( $1:1$ , v/v) were carried out at ambient pressure and temperature to further evaluate the separation performance of **BUT-306** for a real gas mixture. As the binary gas flowed



**Fig. 5** Dynamic column breakthrough curves of **BUT-306** for a binary  $C_3H_4/C_3H_6$  (1 : 1, v/v) gas (a) at room temperature, (c) at 273, 313 and 323 K, and (d) under RH  $\approx$  100% at room temperature, respectively. (b) The MS signal peaks of  $C_3H_4$  and  $C_3H_6$  at the outlet when the MOF column was purged with a He gas flow at 393 K after a breakthrough test at room temperature.

through the column packed with **BUT-306**, purified  $C_3H_6$  was detected in the outlet of the column, while  $C_3H_4$  was trapped in the column until the retention time reached  $\sim 10 \text{ min g}^{-1}$  (Fig. 5a). After saturation of gas adsorption, the MOF was regenerated at 393 K under a He gas flow. Meanwhile, the gas eluted from the outlet was monitored. As shown in Fig. 5b, the peak area of desorbed  $C_3H_4$  was significantly larger than that of desorbed  $C_3H_6$ , indicating the high adsorption selectivity of  $C_3H_4$  over  $C_3H_6$ . The dynamic  $C_3H_4$  productivity is estimated to be  $0.87 \text{ mol kg}^{-1} \text{ h}^{-1}$  with a purity of 90.3% by analyzing the breakthrough and desorption curves. It is important to note that during the  $C_3H_4/C_3H_6$  separation process, the fewer the  $C_3H_6$  molecules the adsorbent adsorbs, the higher the  $C_3H_6$  purification productivity and efficiency. The **BUT-306** sample was regenerated and used for the  $C_3H_4/C_3H_6$  breakthrough experiment for two more cycles, and its separation performance essentially unchanged (Fig. 5a), which indicated that **BUT-306** could be fully regenerated for repeated use in the removal of  $C_3H_4$  from the  $C_3H_4/C_3H_6$  mixture. Breakthrough experiments were also carried out at 273, 313 and 323 K. As shown in Fig. 5c, the final retention times of  $C_3H_4$  nearly kept unchanged after varying the measurement temperatures. Since **BUT-306** shows high hydrolytic stability and hydrophobicity, the effect of water vapor on its  $C_3H_4/C_3H_6$  separation perform-

ance was also investigated. The breakthrough experiments were carried out with the binary  $C_3H_4/C_3H_6$  gas pre-saturated with water vapor (RH  $\approx$  100% at ambient temperature). It was found that the separation performance of **BUT-306** was not lost under such a high humidity (Fig. 5d). The retention time of  $C_3H_4$  was  $\sim 6 \text{ min g}^{-1}$ , about 60% of that under dry conditions. The breakthrough experiment under humid conditions was repeated after regeneration of the MOF, and the two breakthrough curves obtained from the two successive runs well overlapped, suggesting the high and stable separation performance of **BUT-306** due to its ultramicroporous, stable and hydrophobic nature.

## Conclusions

Two new MOFs **BUT-305** and **-306** with isorecticular ultramicroporous structures have been synthesized. The pore aperture of **BUT-306** ( $\sim 1.6 \text{ \AA}$ ) is smaller than that of **BUT-305** due to the presence of extra gate-like methyl groups in the channels of the former. This structural feature endows **BUT-306** with a high adsorption selectivity of  $C_3H_4$  over  $C_3H_6$ . The  $C_3H_6$  and  $C_3H_4$  adsorption capacities of **BUT-306** at 298 K and  $\sim 1 \text{ bar}$  were  $2.4$  and  $29.6 \text{ cm}^3 \text{ g}^{-1}$ , respectively, indicating a size exclu-

sion adsorption behavior. Based on the single-component gas adsorption isotherms, the IAST C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> adsorption selectivity at 298 K and 1 bar was calculated to be 636 for an equimolar mixture of C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>. Dynamic column breakthrough experiments of a binary gas confirmed the high capability of **BUT-306** to remove C<sub>3</sub>H<sub>4</sub> from a real C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> mixture. Thanks to its high hydrolytic stability and hydrophobicity, the C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> separation performance of **BUT-306** was largely retained even when the binary C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> gas for breakthrough experiments was pre-saturated with water vapor. In addition, the single-crystal structure of C<sub>3</sub>H<sub>4</sub>-loaded **BUT-306** revealed that the adsorbed C<sub>3</sub>H<sub>4</sub> molecules were located in the center of channel cavities and interacted with the MOF by multiple weak C<sup>δ-</sup>...C<sup>δ+</sup> dipole-dipole interactions and C-H...n interactions. In short, this study reports an ultramicroporous, hydrophobic, and hydrolytically stable MOF with high performance in the removal of C<sub>3</sub>H<sub>4</sub> from a C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> gas mixture by size exclusion adsorption. Its structure and gas adsorption studies shed light on the design and synthesis of new adsorbents for light hydrocarbon separations.

## Experimental section

### Materials and characterization

All general reagents and solvents (AR grade) were purchased commercially and used directly. The single-crystal X-ray diffraction data (SCXRD) of **BUT-306** (at 273, 298, and 313 K) and C<sub>3</sub>H<sub>4</sub>-loaded **BUT-306** (at 200 K) were collected on a Rigaku Supernova CCD diffractometer equipped with a graphite-monochromatic enhanced Cu-K $\alpha$  radiation source ( $\lambda = 1.54184 \text{ \AA}$ ). These SCXRD data for **BUT-306** have been deposited in the Cambridge Crystallographic Data Centre (CCDC accession numbers: 2168051–2168054 $\dagger$ ). The PXRD pattern (2 $\theta$  range: 3–60 $^\circ$ ) of **BUT-305** was measured with a Bruker D8 Advance X-ray powder diffractometer and Pawley refinement<sup>55</sup> of the PXRD data was performed in Materials Studio. The peak profiles, background, zero-shift, asymmetry, and unit cell parameters were together refined. The final Pawley refinement results are shown in Fig. 2a and Table S2. $\dagger$  The simulated PXRD pattern was obtained from single-crystal data of **BUT-306** *via* the Mercury program.<sup>56</sup> The other experimental PXRD data were recorded on a Rigaku SmartLab3 X-ray powder diffractometer that was equipped with a Cu sealed tube ( $\lambda = 1.54178 \text{ \AA}$ ) with a scanning rate of 10 $^\circ \text{ min}^{-1}$ . The gas sorption measurements were performed using a Micromeritics ASAP 2020 surface area and pore analyzer.

### Synthesis and activation

A mixture of HATZ (18 mg), H<sub>2</sub>MeTPDC (30 mg) or H<sub>2</sub>MeTPDC (32 mg) and Zn(CH<sub>3</sub>COO)<sub>2</sub>·(90 mg) was dissolved in 18 mL of DMF and placed in a 20 mL glass vial containing 720  $\mu\text{L}$  of 48% aqueous HBF<sub>4</sub> solution. Then the mixture sealed in the vial was heated in an oven to 120  $^\circ\text{C}$  for 48 hours and the as-synthesized colorless crystals of **BUT-305** or **-306** were obtained. After the solution was cooled, the crystals were col-

lected and washed several times with CH<sub>3</sub>OH and dried under vacuum.

The as-synthesized samples of the two MOFs were first soaked in fresh DMF at 60  $^\circ\text{C}$  for 12 hours to remove the excess organic ligands and metal salts. Then, these samples were immersed in MeOH for 3 days at 120  $^\circ\text{C}$ . In order to ensure the activation effect, the extract was replaced with fresh methanol three times a day. Finally, the samples in MeOH were collected and dried at 120  $^\circ\text{C}$  under vacuum for 18 hours for gas adsorption measurements.

### Gas adsorption measurements

The N<sub>2</sub> adsorption isotherms of **BUT-305** and **-306** were measured at 77 K, while their water adsorption isotherms were recorded at 298 K. Single-component gas (C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub>) adsorption isotherms of the two MOFs were measured at 298 K. In addition, the C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> adsorption isotherms of **BUT-306** were also recorded at 273, 283, 313 and 323 K, respectively. The C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> adsorption isotherms of **BUT-306** at 298 were fit by the Langmuir-Freundlich equation, respectively (Fig. S10 $\dagger$ ). Then, based on the single-component gas adsorption isotherms of **BUT-306** for C<sub>3</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> at 298 K, ideal adsorbed solution theory (IAST) was used for the prediction of adsorption equilibria of the binary gas mixtures.<sup>57</sup> The selectivity of preferential adsorption of component 1 (C<sub>3</sub>H<sub>4</sub>) over 2 (C<sub>3</sub>H<sub>6</sub>) in a mixture containing 1 and 2 can be formally defined as an equation (eqn (1)), where  $q_1$  and  $q_2$  are the absolute loadings at the partial pressures  $p_1$  and  $p_2$ , respectively. To calculate the C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> adsorption selectivity of **BUT-306** for gas separation, the gas mixture composition is assumed to be 1 : 99, 1 : 9 and 1 : 1, respectively.

$$S_{1,2} = \frac{q_1/q_2}{p_1/p_2} \quad (1)$$

### Breakthrough experiments

The breakthrough experiments for the binary C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> gas mixture (1 : 1, v/v) were carried out using a setup as shown in Fig. S11. $\dagger$  A powder sample of **BUT-306** (330 mg) was packed in a quartz tube (o.d. 6 mm, i.d. 3 mm, and length 150 mm). The temperature of the MOF sample packed in the quartz tube was controlled by a heating jacket (298, 313, 323, and 393 K) or by an ice/water bath (273 K). The gas mixture flow rate was set to be 2 mL min<sup>-1</sup> by the mass flow controllers (MFC). The outlet gas compositions from the column were determined continuously using a mass spectrometer (MS, Hiden, HPR-20). For the breakthrough experiments with a humid gas mixture, the C<sub>3</sub>H<sub>4</sub>/C<sub>3</sub>H<sub>6</sub> mixture was pre-saturated with water vapor (relative humidity (RH)  $\approx$  100% at room temperature) by bubbling it through deionized water before it passed through the MOF column. The sample was regenerated for repeated tests under a He flow for 4 hours at 393 K.

## Conflicts of interest

The authors declare no conflict of interest.

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