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# Efficient stacking of iso-butene in sulfonate functional metal–organic frameworks for efficient iso-butene/iso-butane separation†

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Separation of iso-butene and iso-butane is vital to producing high purity iso-butene feedstock, but is challenging because of their close molecular size and properties. Adsorptive separation using porous materials like metal organic frameworks (MOFs) is emerging as a potential energy-efficient alternative. But it's hindered by the lack of porous materials that exhibit satisfactory iso-butene/iso-butane separation performance. In this study, a novel sulfonate functionalized material, ZU-603, is reported to achieve the benchmark separation performance of iso-butene/iso-butane *via* exploiting the geometric difference of the carbon backbone between the planar iso-butene and tetrahedral iso-butane. Single-crystal analysis of ZU-603 loaded with iso-butene and simulation studies reveal that the sulfonate sites bound the iso-butene *via*  $S^{\delta-}\cdots H^{\delta+}=C$  interactions, meanwhile iso-butene molecules are efficiently stacked *via*  $\pi-\pi$  interactions within the confined space, realizing higher stacking efficiency of iso-butene than iso-butane. ZU-603 shows an exceptionally high iso-butene adsorption uptake of 2.30 mmol g<sup>-1</sup> (298 K, 1 bar) and a record high iso-butene/iso-butane uptake ratio of 2.77 at 1 bar, outperforming previously reported benchmarking materials (1.2). Fixed-bed breakthrough experiments confirm the impressive iso-butene/iso-butane dynamic separation ability of ZU-603. The work provides a potential shape-recognition strategy in designing functional materials for the efficient separation of hydrocarbons with similar physicochemical properties.

**Keywords:** Adsorptive separation; Hydrocarbon; Metal-organic frameworks; Iso-butene/iso-butane; Purification.

## 1 Introduction

Iso-butene (iso-C<sub>4</sub>H<sub>8</sub>) is an important feedstock in the petroleum industry, which could be utilized in producing butyl rubber, methyl methacrylate (MMA) and other high-performance materials.<sup>1–4</sup> One of the primary industrial sources of iso-C<sub>4</sub>H<sub>8</sub> is the catalytic dehydrogenation of iso-butane (iso-C<sub>4</sub>H<sub>10</sub>), the product of which typically consists of approximately equal mole fractions of iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> isomers due to the limited conversion rate.<sup>5–7</sup> To obtain high purity iso-C<sub>4</sub>H<sub>8</sub> from the mixture, an industrial practice is to react the mixture with methanol to convert iso-C<sub>4</sub>H<sub>8</sub> into methyl *tert*-butyl ether (MTBE).<sup>8–10</sup> Then MTBE is separated from iso-C<sub>4</sub>H<sub>10</sub> and cracked back into iso-C<sub>4</sub>H<sub>8</sub> and methanol.<sup>11</sup> This complicated purification process may be simplified by the more convenient technology of adsorption separation.<sup>12–14</sup> The potential application of adsorption separation has been widely investigated in separating chemicals with similar physicochemical properties.<sup>15–21</sup> The key to adsorption separation is the design and application of high-performance porous materials. In recent years, metal organic frameworks (MOFs) with their extremely variable pore structures and highly tunable nature have shown promising application potential in the separation of hydrocarbon gas mixtures with very close physicochemical properties,<sup>22–26</sup> including ethane/ethylene,<sup>27–31</sup> ethylene/acetylene,<sup>32–37</sup> propane/propylene,<sup>38–44</sup> C<sub>6</sub> isomers,<sup>45–48</sup> *etc.* HKUST-1 shows preferential adsorption of iso-C<sub>4</sub>H<sub>8</sub> over iso-C<sub>4</sub>H<sub>10</sub> in the very low-pressure range of 0.5 kPa. However, it demonstrates negligible selectivity at higher pressures, limiting its separation performance.<sup>49</sup> Other than that, little attention has been paid to investigating the adsorption separation of iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> using MOFs.

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The properties of iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> are very similar, where the most significant difference lies in the presence of a C=C double bond in the iso-C<sub>4</sub>H<sub>8</sub> molecule. As a result, the 4 carbon atoms of iso-C<sub>4</sub>H<sub>8</sub> are in the same plane while the 4 carbon atoms of the iso-C<sub>4</sub>H<sub>10</sub> molecule form a triangular pyramid. If this shape difference in the carbon backbone of the 2 isomers could be utilized to discriminate one another, the adsorption separation of iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> could be achieved with high selectivity. Shape selective materials have been developed in the literature for the separation of butadiene,<sup>50</sup> xylene isomers,<sup>51,52</sup> etc. A feasible strategy is to construct pore cages with limited space and suitable shape to accommodate the desired molecule. The single pore cage of the material could simultaneously accommodate multiple target molecules with suitable molecular shape when the molecules are densely packed. But for the undesired molecules with inappropriate molecular shape, a single pore cage could hardly accommodate multiple molecules, realizing the preferential adsorption of the target molecule.

In this work, a shape-recognizing sulfonate functional material, ZU-603, was found to be capable of separating the iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> mixture. Pure component adsorption isotherms show that ZU-603 exhibits higher adsorption affinity toward iso-C<sub>4</sub>H<sub>8</sub> over iso-C<sub>4</sub>H<sub>10</sub> with an iso-C<sub>4</sub>H<sub>8</sub>/iso-C<sub>4</sub>H<sub>10</sub> uptake ratio of 2.77, superior to previously reported HKUST-1 (1.2).<sup>49</sup> Fixed bed breakthrough experiments further prove the separation performance of ZU-603. The structures of single crystals loaded with iso-C<sub>4</sub>H<sub>8</sub> molecules were solved to unveil the adsorption behavior. Coupled with the DFT-D simulation, the separation mechanism was revealed.

## 2 Results and discussion

Mild conditions of ambient temperature and pressure are utilized for the synthesis of ZU-603, with methanol and water

as solvents. The mild synthesis conditions enable ZU-603 to be further scaled-up. The Cu metal node is coordinated with the 4,4'-dipyridyl disulfide ligand to form the pore windows of ZU-603, with an opening of approximately 5.2 Å × 5.2 Å (Fig. 1), close to the molecular dimensions of iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> (Fig. S1†). The sulfonate anion, 1,2-ethanedisulfonate, serves as the connecting unit of the pore windows, which further forms the pore cage (as illustrated by the orange sphere in Fig. 1) of ZU-603. It's revealed that the pore cages are connected to form a 2D layered structure (Fig. S2†). And then multiple 2D layered structures are stacked together to form the 3D structure of ZU-603, which endows it with the *sql* topology (Fig. S3†). The powder X-ray diffraction patterns of the synthesized samples match well with the simulated ones, confirming the high purity of the synthesized materials (Fig. 2f). Besides, the permanent porosity of ZU-603 is investigated *via* N<sub>2</sub> adsorption experiments at 77 K (Fig. S4†), which displays a Brunauer-Emmett-Teller (BET) surface area of 214 m<sup>2</sup> g<sup>-1</sup> (Fig. S5†). Thermogravimetric analysis shows that ZU-603 is stable up to 240 °C (Fig. S6†). The SEM image of ZU-603 shows a flake-like morphology with a narrow size distribution in the range of 0.9–1.2 μm (Fig. S7†).

To explore the adsorptive properties of ZU-603 for iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub>, pure component adsorption-desorption isotherms are collected at 298 K and 313 K (Fig. 2a and b and S8†). It's displayed that ZU-603 shows higher adsorption affinity toward iso-C<sub>4</sub>H<sub>8</sub> over iso-C<sub>4</sub>H<sub>10</sub> at both temperatures. At 298 K, ZU-603 exhibits a steep iso-C<sub>4</sub>H<sub>8</sub> uptake at the pressure as low as 0.003 bar. The iso-C<sub>4</sub>H<sub>8</sub> uptake is 2.30 mmol g<sup>-1</sup> at 1 bar. For iso-C<sub>4</sub>H<sub>10</sub>, the uptake at 1 bar is 0.83 mmol g<sup>-1</sup>. The iso-C<sub>4</sub>H<sub>8</sub>/iso-C<sub>4</sub>H<sub>10</sub> uptake at 1 bar is 2.77, higher than that of HKUST-1 (1.2).<sup>49</sup> Ideal adsorbed solution theory was applied to calculate the adsorption selectivity



**Fig. 1** The building blocks of the pore window of ZU-603 and the illustration of the pore window. The sulfonate anion is used to connect the pore window to construct the 3D framework of ZU-603, and the illustration of the pore cage is derived from the assembly of the pore window and the sulfonate anion. The van der Waals radius of hydrogen (1.1 Å) is deducted when taking the measurements (color code: silver, C; white, H; red, O; blue, N; yellow, S; pink, Cu; orange, illustration of the space within the expanded pore cage. The components that build a single contracted pore window and a single expanded pore cage are highlighted in red for clarity).





**Fig. 2** Pure component adsorption isotherms of *iso*-C<sub>4</sub>H<sub>8</sub> and *iso*-C<sub>4</sub>H<sub>10</sub> on ZU-603 at (a) 298 K and (b) 313 K; (c) *iso*-C<sub>4</sub>H<sub>8</sub>/*iso*-C<sub>4</sub>H<sub>10</sub> (50/50, v/v) IAST selectivity of ZU-603 calculated in the pressure range of 0–1 bar at 298 K and 313 K; (d) comparison of uptake ratio of *iso*-C<sub>4</sub>H<sub>8</sub> (0.5 bar)/*iso*-C<sub>4</sub>H<sub>10</sub> (0.5 bar) and *iso*-C<sub>4</sub>H<sub>8</sub> (0.5 bar) uptake of ZU-603 against other reported materials; (e) time dependent adsorption profiles of *iso*-C<sub>4</sub>H<sub>8</sub> and *iso*-C<sub>4</sub>H<sub>10</sub> at 298 K and 0.6 bar; (f) powder X-ray diffraction patterns (PXRD) of the activated sample and pattern simulated using the crystal structure of ZU-603.

(IAST selectivity). At infinity dilution, the IAST selectivity is 39 at 298 K and 14 at 313 K (Fig. 2c and S9 and S10<sup>†</sup>). It's noted that ZU-603 not only possesses a very high *iso*-C<sub>4</sub>H<sub>8</sub> uptake of 2.10 mmol g<sup>-1</sup> at 0.5 bar, but also shows the highest *iso*-C<sub>4</sub>H<sub>8</sub>/*iso*-C<sub>4</sub>H<sub>10</sub> uptake ratio of 3.33 at 0.5 bar compared with other reported materials (Fig. 2d): SD-65 (1.29),<sup>53</sup> Mg-gallate (1.27),<sup>54</sup> ZU-609 (1.20),<sup>55</sup> and HKUST-1 (1.23).<sup>49</sup> The time dependent adsorption profiles of both isomers were further measured to investigate the diffusion rate of *iso*-C<sub>4</sub>H<sub>8</sub> and *iso*-C<sub>4</sub>H<sub>10</sub> within the pores of ZU-603 (Fig. 2e). The diffusion time constants of *iso*-C<sub>4</sub>H<sub>8</sub> and *iso*-C<sub>4</sub>H<sub>10</sub> were calculated using the micropore diffusion model, which are  $7.42 \times 10^{-4}$  s<sup>-1</sup> and  $6.43 \times 10^{-4}$  s<sup>-1</sup> for *iso*-C<sub>4</sub>H<sub>8</sub> and *iso*-C<sub>4</sub>H<sub>10</sub>, respectively (Fig. S11 and S12<sup>†</sup>). The result indicates that both isomers show a close diffusion rate within the pores of ZU-603.

Grand Canonical Monte Carlo (GCMC) simulation was used to elucidate the preferential adsorption of *iso*-C<sub>4</sub>H<sub>8</sub> over *iso*-C<sub>4</sub>H<sub>10</sub> at a fixed pressure of 1 atm. Snapshots at different steps are taken to understand the adsorption process (Fig. S13 and S14<sup>†</sup>). The two images compare the adsorption behaviour of *iso*-C<sub>4</sub>H<sub>8</sub> and *iso*-C<sub>4</sub>H<sub>10</sub> in ZU-603 at 1 bar. *iso*-C<sub>4</sub>H<sub>8</sub> shows significantly higher uptake, with dense and progressive filling of the framework cavities from panel (1) to (10), while *iso*-C<sub>4</sub>H<sub>10</sub> adsorption remains sparse even at saturation. This contrast highlights ZU-603's selective adsorption driven by stronger interactions with the unsaturated *iso*-C<sub>4</sub>H<sub>8</sub> likely due to  $\pi$ -complexation or better shape compatibility. In addition, the low energy snapshot

of *iso*-C<sub>4</sub>H<sub>8</sub> also shows a higher packing density than that of *iso*-C<sub>4</sub>H<sub>10</sub> (Fig. S15<sup>†</sup>). The average loading of *iso*-C<sub>4</sub>H<sub>8</sub> is 0.77 molecules per unit cell and *iso*-C<sub>4</sub>H<sub>10</sub> is 0.21 molecules per unit cell, yielding an uptake ratio of 3.66 at 1 bar, which is very similar to the experimental result of 2.77. To further unveil the higher adsorption uptake of *iso*-C<sub>4</sub>H<sub>8</sub> over *iso*-C<sub>4</sub>H<sub>10</sub>, the structures of the single crystals loaded with *iso*-C<sub>4</sub>H<sub>8</sub> were successfully obtained. It's found that 2 *iso*-C<sub>4</sub>H<sub>8</sub> molecules could be simultaneously adsorbed within the same pore cage of ZU-603 (Fig. 3a). This allows the maximized occupation of the pore space. Further investigation into the packing diagram of the 2 *iso*-C<sub>4</sub>H<sub>8</sub> molecules adsorbed reveals the reason behind such a phenomenon. Due to the double bond of *iso*-C<sub>4</sub>H<sub>8</sub> molecules, the 4 carbon atoms of *iso*-C<sub>4</sub>H<sub>8</sub> are distributed in the same plane, which could be utilized to pack two *iso*-C<sub>4</sub>H<sub>8</sub> molecules in a space efficient way. In detail, the 2 *iso*-C<sub>4</sub>H<sub>8</sub> molecules are stacked in a confined pore cage of ZU-603 in a way that the aforementioned planes within each *iso*-C<sub>4</sub>H<sub>8</sub> run parallel to each other, with a distance of 3.4 Å between the two planes (Fig. 3b). This facilitates the space-efficient packing of *iso*-C<sub>4</sub>H<sub>8</sub> in the limited space of the pore cages within ZU-603, which could not be achieved by *iso*-C<sub>4</sub>H<sub>10</sub>. The O atoms of the sulfonate anions are the primary binding site of *iso*-C<sub>4</sub>H<sub>8</sub>, with the C-H...O hydrogen bond in the range of 1.7–2.9 Å (Fig. 3c). DFT-D calculation was applied to calculate the specific binding sites of *iso*-C<sub>4</sub>H<sub>10</sub> within ZU-603. The result show that like *iso*-C<sub>4</sub>H<sub>8</sub>, O atoms of the sulfonate anions are also the





**Fig. 3** (a) 2 iso-C<sub>4</sub>H<sub>8</sub> molecules adsorbed in one pore cage of ZU-603 as revealed by single crystal analysis; (b) the packing diagram of 2 iso-C<sub>4</sub>H<sub>8</sub> molecules adsorbed within one pore cage of ZU-603 as revealed by single crystal analysis; (c) the specific binding sites of iso-C<sub>4</sub>H<sub>8</sub> on ZU-603 as revealed by single crystal experiments; (d) the specific binding sites of iso-C<sub>4</sub>H<sub>10</sub> on ZU-603 as revealed by DFT-D calculations (color code: silver, C; white, H; red, O; blue, N; yellow, S; pink, Cu; orange, C of the adsorbed molecules).

main binding sites of iso-C<sub>4</sub>H<sub>10</sub>, where the C-H $\cdots$ O hydrogen bond is in the range of 2.6–2.9 Å (Fig. 3d).

A fixed bed breakthrough experiment with a gas mixture of iso-C<sub>4</sub>H<sub>8</sub>/iso-C<sub>4</sub>H<sub>10</sub> (50/50, v/v) was carried out to investigate the dynamic separation performance of ZU-603. The results show that ZU-603 could selectively adsorb iso-C<sub>4</sub>H<sub>8</sub> in the binary mixture with a breakthrough sequence of iso-C<sub>4</sub>H<sub>8</sub> < iso-C<sub>4</sub>H<sub>10</sub>. After the introduction of the gas mixture, both isomers were adsorbed within the column packed with ZU-603 until 23.5 min, where iso-C<sub>4</sub>H<sub>10</sub> first elutes. Iso-C<sub>4</sub>H<sub>8</sub> did not breakthrough until 50 min, with an effective dynamic adsorption capacity of 1.06 mmol g<sup>-1</sup>. The results show a good dynamic separation performance of ZU-603 for the binary mixture (Fig. 4a). Cycling adsorption experiments of pure component iso-C<sub>4</sub>H<sub>8</sub> show no obvious gas uptake loss

after 5 cycles, exhibiting the good cycling capacity of ZU-603 (Fig. 4b).

### 3 Conclusions

In summary, a novel sulfonate functionalized ultramicroporous material, ZU-603, was designed and it exhibits an excellent iso-C<sub>4</sub>H<sub>8</sub>/iso-C<sub>4</sub>H<sub>10</sub> separation performance because of its selective shape-recognizing ability toward iso-C<sub>4</sub>H<sub>8</sub> molecules over iso-C<sub>4</sub>H<sub>10</sub>. Through exploiting the C=C double bond and the planar configuration of iso-C<sub>4</sub>H<sub>8</sub>, ZU-603 with suitable pore size and distributed sulfonate functional sites induces the effective packing of 2 iso-C<sub>4</sub>H<sub>8</sub> molecules within the limited volume of 1 pore cage of the material *via* S<sup>δ-</sup> $\cdots$ H<sup>δ+</sup>=C interactions and  $\pi$ - $\pi$  guest-guest interactions. This work not only provides an



**Fig. 4** (a) Breakthrough experiment on ZU-603 using a gas mixture of iso-C<sub>4</sub>H<sub>8</sub>/iso-C<sub>4</sub>H<sub>10</sub> (50/50, v/v) with a mix gas flow rate of 0.8 mL min<sup>-1</sup> at 298 K and (b) cycling adsorption tests of iso-C<sub>4</sub>H<sub>8</sub> on ZU-603 at 298 K.



important case of iso-C<sub>4</sub>H<sub>8</sub>/iso-C<sub>4</sub>H<sub>10</sub> porous materials with both high capacity and selectivity, but also demonstrates the shape-recognizing strategy in the separation of C<sub>4</sub> hydrocarbons, which may also be applied in designing high-performance materials for other challenging separations.

## 4 Experimental section

### Materials

All chemicals were used as received without further purification. 4,4'-Dipyridyl disulfide (>97%) was purchased from TCI Chemicals, and 1,2-ethanedisulfonate disodium salt (98%) was purchased from Energy Chemical. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (AR) and methanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

### Synthesis of ZU-603 (powder)

4,4'-Dipyridyl disulfide (1 mmol, 0.220 g) is dissolved in 20 mL anhydrous methanol, yielding the ligand solution. Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.5 mmol, 0.121 g) and 1,2-ethanedisulfonate disodium salt (0.5 mmol, 0.117 g) are dissolved in 3 mL deionized water, after which 10 mL anhydrous methanol is added to the salt solution. The salt solution is then slowly added to the ligand solution under constant stirring. The composite is then stirred for 24 h at 25 °C. The purple product is obtained by filtration and purified by washing with 250 mL anhydrous methanol. The product is then soaked in anhydrous methanol for 3 days.

### Synthesis of ZU-603 (single crystal)

Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.02 g) and 1,2-ethanedisulfonate disodium salt (0.02 g) are dissolved in 20 mL deionized water. 4,4'-Dipyridyl disulfide (0.02 g) is dissolved in 20 mL methanol. Then the methanol solution is carefully layered onto the water solution at ambient temperature. The single crystals of ZU-603 are obtained after two weeks.

### Single crystal X-ray crystallography

The crystal structures of ZU-603 and iso-C<sub>4</sub>H<sub>8</sub> loaded ZU-603 are determined by single crystal X-ray diffraction experiments. The X-ray diffraction experiments are conducted using a Bruker D8 Venture diffractometer equipped with a PHOTONII/CMOS detector (GaK $\alpha$ ,  $\lambda = 1.34139 \text{ \AA}$ ). Data collection is performed using APEX3, and the dataset of each sample is integrated and reduced using SaintPlus 6.01. The space group of the material is determined using XPREP in APEX3. Structure solutions and refinements are carried out with SHELXS-201 and SHELXL-2018 with APEX3 for the samples described above. The CIF file of ZU-603 has been deposited at CCDC (2453159).

### Thermogravimetric analysis (TGA)

The thermal gravimetric analysis is performed on a TGA Q500 V20.13 Build 39. Experiments are carried out using a platinum pan under nitrogen atmosphere which is conducted

by a flow rate of 60 mL min<sup>-1</sup> nitrogen gas. The data are collected in the temperature range of 55 °C to 900 °C with a ramp of 10 °C min<sup>-1</sup>.

### Scanning electron microscopy (SEM)

The morphology of ZU-603 was characterized using a Hitachi SU-8010 scanning electron microscope.

### N<sub>2</sub> adsorption measurements

N<sub>2</sub> adsorption and desorption isotherms on activated materials are measured on a Micromeritics ASAP 2460 surface area analyzer at 77 K.

### C<sub>4</sub> gas equilibrium adsorption measurements

Iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> isotherms are collected on a Micromeritics ASAP 2050 surface area analyzer at 298 K.

### Kinetic adsorption measurement

The time-dependent adsorption profiles of different C<sub>4</sub> isomers on ZU-603 are measured using a BEL-SORP-max II at 0.6 bar and 298 K or 313 K. For the experiments at the specified pressure, a fixed amount of target gas is introduced into the sample chamber, and then the equipment monitors the pressure in the chamber until it becomes stable.

### Breakthrough experiments

The fixed-bed breakthrough experiments and cycling tests are carried out on dynamic gas breakthrough equipment. All experiments are conducted using stainless-steel columns with an inner diameter of 4.6 mm and a length of 10 cm. The ZU-603 sample packed in the column is 0.8409 g. The packing density is calculated to be 0.506 g cm<sup>-3</sup>, which remained the same after constant N<sub>2</sub> purging at 20 mL min<sup>-1</sup> for 24 hours. The gas mixture consists of 1:1 mole ratio iso-C<sub>4</sub>H<sub>8</sub>, and iso-C<sub>4</sub>H<sub>10</sub>. The column packed with porous materials are regenerated by purging dry N<sub>2</sub> with a flow rate of 20 mL min<sup>-1</sup> at 100 °C overnight.

### Grand Canonical Monte Carlo (GCMC) simulation

The gradual packing of iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> was determined through GCMC simulations in the sorption module. The framework of ZU-603 was first optimized by DFT-D calculations, and considered to be rigid during the simulation. The charges for atoms of ZU-603 were derived from Qeq method and Qeq\_charged 1.1 parameters. The simulations adopted the task of fixed pressure at 100 kPa, the Metropolis method in the sorption module, the universal force field (UFF) for ZU-603, and the configurational bias method in the sorption module. The interaction energy between the adsorbed molecules and the framework was computed through the Coulomb and Lennard-Jones 6–12 (LJ) potentials. The cutoff radius was chosen as 18.5 Å for LJ potential and the long range electrostatic interactions were handled using the Ewald summation method. The loading



steps and the equilibration steps were  $1 \times 10^7$ ; the production steps were  $1 \times 10^7$ .

### Dispersion-corrected density functional theory (DFT-D) calculations

The Quantum-Espresso package is applied for dispersion-corrected density-functional theory (DFT-D) calculations. The van der Waals interactions are accounted for by the addition of semi-empirical dispersive forces to conventional DFT-D. Vanderbilt-type ultrasoft pseudopotentials and generalized gradient approximation (GGA) with Perdew–Burk–Ernzerhof (PBE) exchange corrections are utilized. A cutoff energy of 544 eV and a  $3 \times 3 \times 3$   $k$ -point mesh (generated using the Monkhorst–Pack scheme) are enough for the total energy to converge within 0.01 meV per atom. The structure of ZU-603 is first optimized and the results are a good match for the experimentally determined crystal structure of the material. Iso-C<sub>4</sub>H<sub>10</sub> molecules are then introduced to various locations of the pore channels, followed by a full structural relaxation.

### Calculation of ideal adsorbed solution theory (IAST) selectivity

The software IAST++ is used for the calculation of IAST selectivity. Using the Dual-Site Langmuir–Freundlich (DSLFL) model, the adsorption isotherms of iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> on ZU-603 at 298 K are fitted. The fitted model parameters are input into the software to calculate the IAST selectivity at 298 K for an iso-C<sub>4</sub>H<sub>8</sub>/iso-C<sub>4</sub>H<sub>10</sub> mixture with a 0.5/0.5 composition ratio. The employed model equation is shown in eqn (1):

$$n(P) = q_1 \frac{(k_1 P)^{n_1}}{1 + (k_1 P)^{n_1}} + q_2 \frac{(k_2 P)^{n_2}}{1 + (k_2 P)^{n_2}} \quad (1)$$

where  $n(P)$  is the adsorption amount at pressure  $P$ ;  $P$  is the equilibrium pressure of the gas phase;  $q_1$ ,  $q_2$ ,  $k_1$ ,  $k_2$ ,  $n_1$ ,  $n_2$  are the fitted constants.

The equation for IAST selectivity is given by eqn (2):

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

where  $q_1$  and  $q_2$  are the molar amounts of the two components adsorbed, and  $p_1$  and  $p_2$  are the partial pressures of the two components in the gas phase.

### Calculation of diffusion time constants

The time dependent adsorption profiles of iso-C<sub>4</sub>H<sub>8</sub> and iso-C<sub>4</sub>H<sub>10</sub> on ZU-603 are fitted using the micropore diffusion model,<sup>56,57</sup> from which the diffusion time constant  $D_c/r_c^2$  of the gas was obtained. The specific equation is as follows:

$$\frac{q_t}{q_e} \approx \frac{6}{\sqrt{\pi}} \sqrt{\frac{D_c t}{r_c^2}} (q_t/q_e < 0.3) \quad (3)$$

where  $q_t$  is the amount of gas adsorbed at time  $t$ ;  $q_e$  is the equilibrium adsorption capacity;  $q_t/q_e$  is obtained from the instrument;  $D_c$  is the diffusion coefficient of a specific gas

component in ZU-603;  $r_c$  is the equivalent radius of the adsorbent particles.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

H. X. and L. Y. initiated and supervised the research. Z. Q., J. C., and D. Z. performed material synthesis and data collection. Z. Y. performed DFT-D calculation. Z. Q., J. C., L. Y., X. L., X. S., and X. C. engaged in data analysis. A. Z., X. S., X. C., and X. L., engaged in discussion and draft editing. Z. Q., J. C., L. Y. and H. X. engaged in manuscript preparation and revision.

## Conflicts of interest

The authors declare no conflict of interest.

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