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Hydrogen bond unlocking-driven pore structure control for shifting multi-component gas separation function

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Purification of ethylene (C₂H₄) as the most extensive and output chemical, from complex multi-components is of great significance but highly challenging. Herein we demonstrate that precise pore structure tuning by controlling the network hydrogen bonds in two highly-related porous coordination networks can shift the efficient C₂H₄ separation function from C₂H₂/C₂H₄/C₂H₆ ternary mixture to CO₂/C₂H₂/C₂H₄/C₂H₆ quaternary mixture system. Single-crystal X-ray diffraction revealed that the different amino groups on the triazolate ligands resulted in the change of the hydrogen bonding in the host network, which led to changes in the pore shape and pore chemistry. Gas adsorption isotherms, adsorption kinetics and gas-loaded crystal structure analysis indicated that the coordination network Zn-fa-atz (2) weakened the affinity for three C₂ hydrocarbons synchronously including C₂H₄ but enhanced the CO₂ adsorption due to the optimized CO₂-host interaction and the faster CO₂ diffusion, leading to effective C₂H₄ production from the CO₂/C₂H₂/C₂H₄/C₂H₆ mixture in one step based on the experimental and simulated breakthrough data. Moreover, it can be shaped into spherical pellets with maintained porosity and separation performance.

Separation of valuable components for multicomponent mixtures in one step without preconcentration is one of the most challenging tasks in separation science. In the process of C₂H₄ production, the product compositions of the thermal decomposition are complicated, and the conversion of dehydrogenation is only *ca.* 50%–60%. Therefore, the resulting C₂H₄ usually contains a variety of impurities, among which carbon dioxide (CO₂), acetylene (C₂H₂) and ethane (C₂H₆) are the most difficult ones to separate because of very similar physical and chemical

properties with C₂H₄^{2,3}. To obtain polymer-grade C₂H₄ (>99.9%), multi-step processes are needed to remove the impurities, including chemical absorption, catalytic hydrogenation, cryogenic distillation, etc.⁴. The stepwise purification processes result in huge equipment costs and energy consumption⁵.

Using recyclable physisorbents, the adsorptive separation can be a promising approach for high-purity C₂H₄ thanks to the simple operation processes and lower energy requirements^{6–10}. Metal-organic

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frameworks (MOFs), or porous coordination polymers (PCPs)/metal-organic materials (MOMs), with tunable pore structures^{11–15}, have shown great potential for binary C2 hydrocarbons separation, such as C₂H₂/C₂H₄^{16–23}, C₂H₄/C₂H₆^{24–31}, and C₂H₂/CO₂^{32–36}. Compared with the multi-step separation process, purification of C₂H₄ in one-step from complex systems is more valuable in terms of energy utilization and chemical process. However, limited by the physicochemical properties of four gas molecules (kinetic diameter: CO₂ ≈ C₂H₂ < C₂H₄ < C₂H₆; quadruple moment: C₂H₂ > CO₂ > C₂H₄ > C₂H₆)^{37–39}, it is extremely difficult to separate C₂H₄ from the quaternary CO₂/C₂H₂/C₂H₄/C₂H₆ in one step. Although a few of studies have achieved the one-step preparation of C₂H₄ from the ternary C₂H₂/C₂H₄/C₂H₆^{40–48} or more difficult four-component separation^{2,49,50}, the understanding of such a complex systems and the corresponding principle of structural design are far from sufficiency⁵¹.

Herein, we show that unlocking the framework hydrogen bonding can affect the pore size/shape and pore chemistry, and weaken the affinity to C2 hydrocarbons, especially C₂H₄ (Fig. 1). The fine turning of pore structure shifts the multi-component gas separation function, enabling one-step production of high-purity C₂H₄ in the quaternary CO₂/C₂H₂/C₂H₄/C₂H₆.

Results

Structure and adsorption properties of Zn-fa-datz (1)

[Zn₂(fa)(datz)₂] (Zn-fa-datz (1), H₂fa = fumaric acid, Hdatz = 1H-1,2,4-triazole-3,5-diamino) was initially selected⁵², because of its high stability in moisture conditions (Supplementary Fig. 5), ultramicroporous nature and polar pore surface without open-metal coordination sites, based on our previously raised general rule⁵¹. Zn-fa-datz (1) is a pillared-layer coordination network with **pcu** topology (Supplementary Fig. 1). Each Zn²⁺ ion is saturated by three N atoms from three datz⁻ ligands and one O atom from a fa²⁻ ligand, forming a 3D pillar-layered network with accessible 1D ultramicroporous channels (Fig. 2a and Supplementary Fig. 2). The purity and porosity were confirmed by powder X-ray diffraction (PXRD) pattern and 195 K CO₂ adsorption isotherm, respectively (Fig. 3a, Supplementary Fig. 3 and Supplementary Table 1). Note that, because N₂ diffuses extremely slowly in Zn-fa-datz (1) (Supplementary Fig. 4), 195 K CO₂ adsorption isotherm was conducted for the study of the porosity. As we expected, Zn-fa-datz (1) features stronger affinity for C₂H₂ (34.7 kJ mol⁻¹) and C₂H₆ (39.4 kJ mol⁻¹) than C₂H₄ (33.6 kJ mol⁻¹) at the low loading (Fig. 3d, Supplementary Figs. 6–9 and Supplementary Table 2). The equimolar C₂H₂/C₂H₄/C₂H₆ mixture breakthrough experiment shows that C₂H₄

eluted preferentially with high purity (99.9%) from three gases in the fixed-bed adsorber (Fig. 5a), thus further demonstrating that Zn-fa-datz (1) can achieve one-step purification of C₂H₄ in the ternary C2 hydrocarbon mixture. However, due to the lower CO₂ affinity (24.0 kJ mol⁻¹) than for C₂H₄ (33.6 kJ mol⁻¹) (Fig. 3c, d and Supplementary Table 2), Zn-fa-datz (1) failed to produce C₂H₄ in one-step from the equimolar CO₂/C₂H₂/C₂H₄/C₂H₆ quaternary mixture (Fig. 5b).

Regarding the thermodynamic aspect, the adsorption affinity for C₂H₄ should be the lowest among the four adsorbates in order to achieve one-step purification of C₂H₄ from the CO₂/C₂H₂/C₂H₄/C₂H₆ quaternary mixture⁴⁹. For Zn-fa-datz (1), the narrow cavity ensures that the larger C₂H₆ molecule (kinetic diameter = 4.44 Å) can fully contact the pore surface and achieve a higher interaction than the smaller C₂H₄ (kinetic diameter = 4.16 Å). Nevertheless, it also causes C₂H₄ to bind slightly more strongly to the network than the smaller CO₂ (kinetic diameter = 3.30 Å)⁵³. We speculated that by fine tuning the pore structure to achieve a more optimized CO₂ adsorption environment, it is possible to reverse the adsorption affinity of C₂H₄ and CO₂ without affecting the adsorption sequence of C₂H₂/C₂H₄/C₂H₆. After carefully analyzing the Zn-fa-datz (1) network, it can be observed that the pore wall of 1D channel is constituted by fa²⁻ ligands and both two amino groups of datz⁻ ligands through four tight hydrogen-bonding interactions (O-H...N = 1.95–2.12 Å, ∠O-H...N = 138.8–170.4°) (Fig. 2d and Supplementary Fig. 12). The hydrogen bonds restrict the swing of ligands and determine the arrangement of adsorption sites and size/shape of the channel. Hence, we predict that precise pore structure control could be achieved by regulating the hydrogen bonds via different amino side groups (i.e., replacing the diamino datz⁻ with unilateral-amino 3-amino-1,2,4-triazolate, atz⁻).

Synthesis and characterization of Zn-fa-atz (2)

Solvothermal reaction of Zn(NO₃)₂·6H₂O with H₂fa and Hatz in a DMF/MeOH/water mixed solvent gave a pillared-layer coordination network with 1D channels, [Zn₂(fa)(atz)₂] (Zn-fa-atz (2)) (Fig. 2b). Single-crystal structure analysis at 298 K revealed that Zn-fa-atz (2) crystallizes in the orthorhombic *Pbca* space group (Supplementary Table 3), isorecticular with previous Zn-fa-datz (1). Both Zn²⁺ ions in Zn-fa-atz (2) exhibit tetrahedral coordination. Each Zn²⁺ ion is coordinated with three N atoms from three atz⁻, and one O atom from fa²⁻ (Supplementary Fig. 13). Similar to Zn-fa-datz (1), Zn-fa-atz (2) also exhibits **pcu** topology, which is constructed by the Zn-atz layer based on the dinuclear [Zn₂(atz)₂] unit and the fa²⁻ pillar, but there is an obvious slip between the pillar and the layer (Supplementary Figs. 1–2). The porosity of

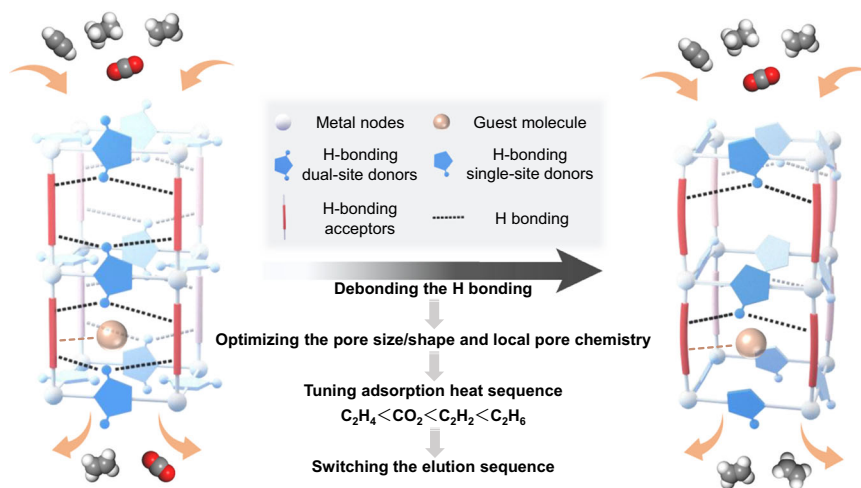


Fig. 1 | Illustration of strategy. Illustration of hydrogen bond unlocking-driven pore size/shape and chemistry control to shift multi-component separation (Color code: metal nodes, white; guest molecule, orange; H-bonding single-site/dual-site

donors, blue; H-bonding acceptors, red; H bonding, black dotted line; weak interaction, orange dotted line; the direction of gas flow, orange row; derivation of structure-function relationship, black row).

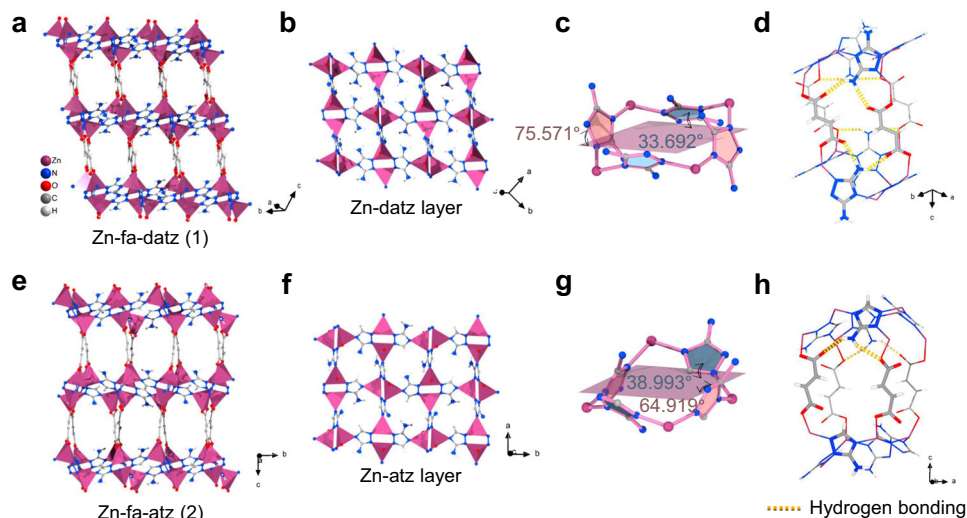


Fig. 2 | Crystal structures. Perspective view of the structure along the 1D channels of Zn-fa-datz (1) (a) and Zn-fa-atz (2) (e). Zinc-aminotriazolate layer of Zn-fa-datz (1) (b) and Zn-fa-atz (2) (f). Dihedral angles in Zn-fa-datz (1) (c) and Zn-fa-atz (2) (g)

between atz/datz⁻ and Zn-atz/datz layers. Front views of pore walls with highlighted (yellow) H-N...O interactions of Zn-fa-datz (1) (d) and Zn-fa-atz (2) (h). Color code: Zn, purple; C, gray; O, red; N, blue; H, white.

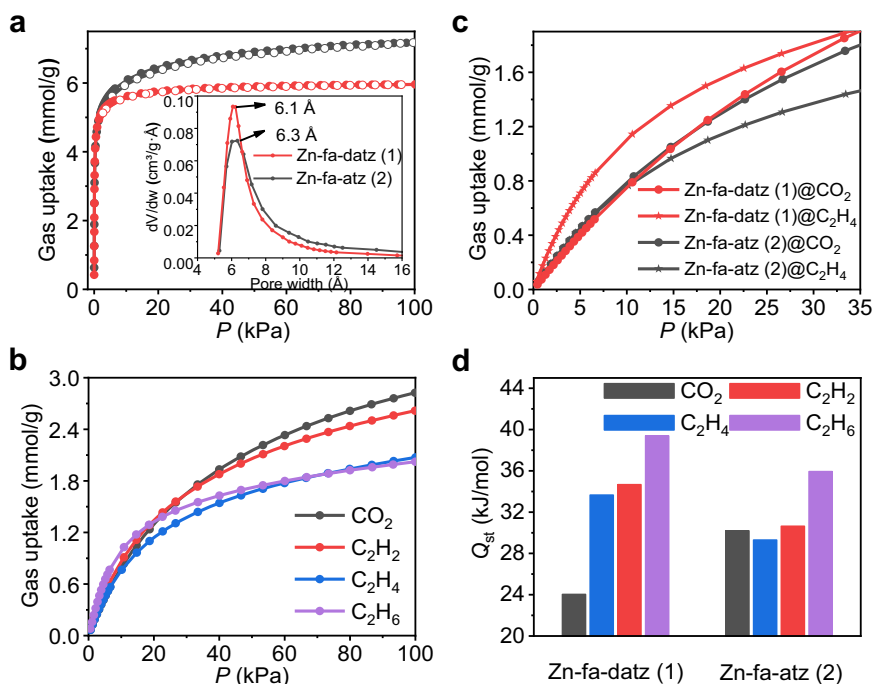


Fig. 3 | Gas adsorption properties of Zn-fa-datz (1) and Zn-fa-atz (2). a CO₂ adsorption isotherms at 195 K (solid: adsorption; open: desorption) and corresponding pore size distributions calculated based on the CO₂ isotherm at 195 K according to the Horvath-Kawazoe model (pore geometry: cylinder) (insert) for Zn-fa-datz (1) (red) and Zn-fa-atz (2) (black). b Adsorption isotherms of Zn-fa-atz (2) for

CO₂ (black), C₂H₂ (red), C₂H₄ (blue) and C₂H₆ (purple) from 0–100 kPa and 298 K. c Comparison of CO₂ (point) and C₂H₄ (star) adsorption isotherms of Zn-fa-datz (1) (red) and Zn-fa-atz (2) (black) from 0 to 35 kPa and 298 K. d Comparison of adsorption enthalpies (Q_{st}) of four gases in Zn-fa-datz (1) and Zn-fa-atz (2).

Zn-fa-atz (2) was calculated to be 46.3% (by PLATON⁵⁴) which is larger than that of Zn-fa-datz (1) (38.9%) (Supplementary Table 1). Furthermore, due to the reduction of amino groups, there are fewer hydrogen bonds on the pore walls than Zn-fa-datz (1). For Zn-fa-atz (2), only one side of atz⁻ ligands are tied to fa²⁻ ligands through two O-H...N hydrogen bonding interactions (O-H...N = 2.12–2.47 Å, ∠O-H...N = 135.6–170.4°) (Fig. 2h and Supplementary Fig. 12). But in Zn-fa-datz (1), both sides of datz⁻ ligand can connect with fa²⁻ ligands by four hydrogen bonds. When the diagonals between four adjacent O atoms

from different fa²⁻ ligands were used to compare the pore sizes of the two structures (minus the van der Waals radius of O atom of 1.52 Å) (Supplementary Fig. 2)⁵⁵, it can be seen that the difference in aperture between Zn-fa-atz (2) (5.5 × 4.9 Å) and Zn-fa-datz (1) (5.4 × 4.6 Å) is very small. In fact, debonding the hydrogen bonds causes the rotation of the five-member ring of atz⁻ ligand, resulting in different dihedral angles between atz⁻/datz⁻ and Zn-atz/datz layers (Fig. 2c, g). Therefore, the greater difference between the Zn-fa-atz (2) and Zn-fa-datz (1) is reflected in the size/shape of the pore and the local pore chemistry.

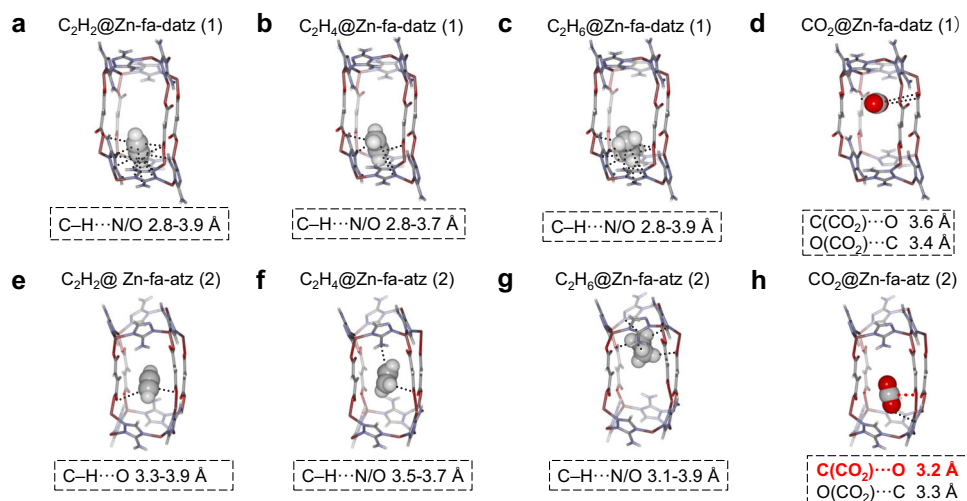


Fig. 4 | The host-guest structures of Zn-fa-datz (1) and Zn-fa-atz (2) revealed by powder diffraction data from Rietveld refinement analysis. a The C_2H_2 binding site, **(b)** C_2H_4 binding site, **(c)** C_2H_6 binding site and **(d)** CO_2 binding site in gas-loaded Zn-fa-datz (1). **e** The C_2H_2 binding site, **(f)** C_2H_4 binding site, **(g)** C_2H_6 binding

site and **(h)** CO_2 binding site in gas-loaded Zn-fa-atz (2). Color code: Zn, purple; C, gray; O, red; N, blue; H, white. The graphical representation is created with iRASPA⁶¹.

Thermogravimetry and PXRD data showed that Zn-fa-atz (2) can be fully exchanged with MeOH (Supplementary Figs. 3 and 6). The 195 K CO_2 adsorption isotherm for Zn-fa-atz (2) shows a quasi-type-I characteristic. The pore volume was calculated to be $0.285 \text{ cm}^3 \text{ g}^{-1}$ and $0.283 \text{ cm}^3 \text{ g}^{-1}$ using the CO_2 and N_2 uptake measured at $P/P_0 = 0.96$ and 0.95 , respectively, which is comparable with the value calculated from single-crystal diffraction data at 195 K ($0.319 \text{ cm}^3 \text{ g}^{-1}$) (Fig. 3a, Supplementary Fig. 14 and Supplementary Table 1). Besides, it is worth to mention that Zn-fa-atz (2) can remain the crystalline and porosity after treated with water or exposed to moisture (ca. 35% RH) (Supplementary Fig. 15). The pore size distribution analysis based on the Horvath-Kawazoe model also reveals that the 1D channels of Zn-fa-atz (2) (6.3 \AA) comparable with that of Zn-fa-datz (1) (6.1 \AA), which is consistent with single-crystal analysis.

Adsorption and separation performances of Zn-fa-atz (2)

Single-component adsorption isotherms for CO_2 , C_2H_2 , C_2H_4 , and C_2H_6 in Zn-fa-atz (2) were measured at 273 K and 298 K (Fig. 3b and Supplementary Fig. 7). At low pressure and 298 K, similar with Zn-fa-datz (1), Zn-fa-atz (2) shows higher uptake for C_2H_6 and C_2H_2 than C_2H_4 , indicating the selective adsorption of both adsorbates over C_2H_4 . However, the CO_2 uptake for Zn-fa-atz (2) is higher than that for C_2H_4 , while the opposite was observed for Zn-fa-datz (1). At 298 K, the adsorption amount sequences of Zn-fa-atz (2) at 14 kPa, 25 kPa and 33 kPa are followed as $C_2H_6 > C_2H_2 > CO_2 > C_2H_4$, $C_2H_2 \approx CO_2 > C_2H_6 > C_2H_4$, and $CO_2 \approx C_2H_2 > C_2H_6 > C_2H_4$, respectively (Supplementary Fig. 16). For Zn-fa-atz (2), the trend in the adsorption enthalpy (Q_{st}) at the low loading is as the following: C_2H_6 (35.9 kJ mol^{-1}) $>$ C_2H_2 (30.6 kJ mol^{-1}) $>$ CO_2 (30.2 kJ mol^{-1}) $>$ C_2H_4 (29.3 kJ mol^{-1}) (Fig. 3d, Supplementary Figs. 7–9 and Supplementary Table 2), while the Q_{st} order of Zn-fa-datz (1) is following as C_2H_6 (39.4 kJ mol^{-1}) $>$ C_2H_2 (34.7 kJ mol^{-1}) $>$ C_2H_4 (33.6 kJ mol^{-1}) $>$ CO_2 (24.0 kJ mol^{-1}). Interestingly, when compared with Zn-fa-datz (1), the $C_2H_2/C_2H_4/C_2H_6$ Q_{st} for Zn-fa-atz (2) decreased synchronously and maintained the same sequence, while the CO_2 Q_{st} showed a significant increase—that is, Zn-fa-atz (2) reversed the C_2H_4/CO_2 adsorption selectivity (Fig. 3c, Supplementary Figs. 10–11 and Supplementary Table 2). Although each of the ideal adsorbed solution theory (IAST) selectivity of the three gases to C_2H_4 are not very high ($CO_2/C_2H_4 = 1.4$, $C_2H_2/C_2H_4 = 1.5$, $C_2H_6/C_2H_4 = 1.4$) (Supplementary Table 2), it is rare to achieve the preferential adsorption of $CO_2/C_2H_2/C_2H_6$ over C_2H_4 at the same time, especially for components with the

very close physicochemical properties. The IAST selectivities of Zn-fa-datz (1) and Zn-fa-atz (2) were compared with the best-performing sorbents in the $C_2H_2/C_2H_4/C_2H_6$ three-component system, and $C_2H_2/C_2H_4/C_2H_6/CO_2$ four-component system (Supplementary Table 4). Both Zn-fa-datz (1) and Zn-fa-atz (2) show moderate selectivity for C_2H_2/C_2H_4 , C_2H_6/C_2H_4 and CO_2/C_2H_4 . In fact, it is very difficult to maintain the lowest selectivity for C_2H_4 among the four gas components, because the physicochemical properties of the four gases are too similar. In general, for ultramicropores without specific binding sites (e.g., open-metal sites), the adsorption affinity mainly comes from the combination of various weak interactions (e.g., van der Waals forces and hydrogen bonding) between the guest molecule and the network in multiple orientations. Consequently, even a slight change in the pore size/shape and local pore chemistry can significantly affect the affinity. In case of Zn-fa-datz (1) and Zn-fa-atz (2), based on the SCXRD analysis, different amino groups not only change the local chemical environment of the pore, but also affect hydrogen bonds in the framework which further leads to the change in the size/shape of the channel (the spatial arrangement of the adsorption sites) (Fig. 2 and Supplementary Figs. 2 and 12).

Host-guest structure studies

To further understand the role of pore structure tuning, the host-guest structures of Zn-fa-datz (1) and Zn-fa-atz (2) were studied by the PXRD analyses and corresponding refinements (Fig. 4, Supplementary Figs. 17–20 and Supplementary Table 5). The eight studied host-guest systems showed that all the gas molecules preferentially localized within the pockets enclosed by four triazolate moieties and four fa^{2-} ligands. For $C_2H_2/C_2H_4/C_2H_6$, the host-guest interactions are mainly contributed by weak $O/N \cdots H-C$ hydrogen bonding interactions from multiple orientations. C_2H_2 , C_2H_4 , and C_2H_6 are all confined in the relatively spacious positions in the cavities of Zn-fa-datz (1) and Zn-fa-atz (2), but the molecular orientations change due to the difference in pore shape and pore chemistry. As shown in Fig. 4 and Supplementary Table 5, most measured $O/N \cdots H-C$ distances in Zn-fa-atz (2) are slightly longer than that in Zn-fa-datz (1), which is consistent with the synchronous decrease of the Q_{st} for the three C_2 hydrocarbons in Zn-fa-atz (2). For CO_2 in Zn-fa-atz (2) (Fig. 4), the optimal position has changed when compared with that in Zn-fa-datz (1), and the O atom from the framework can contact closely with the C atom in CO_2 , yielding a relative strong

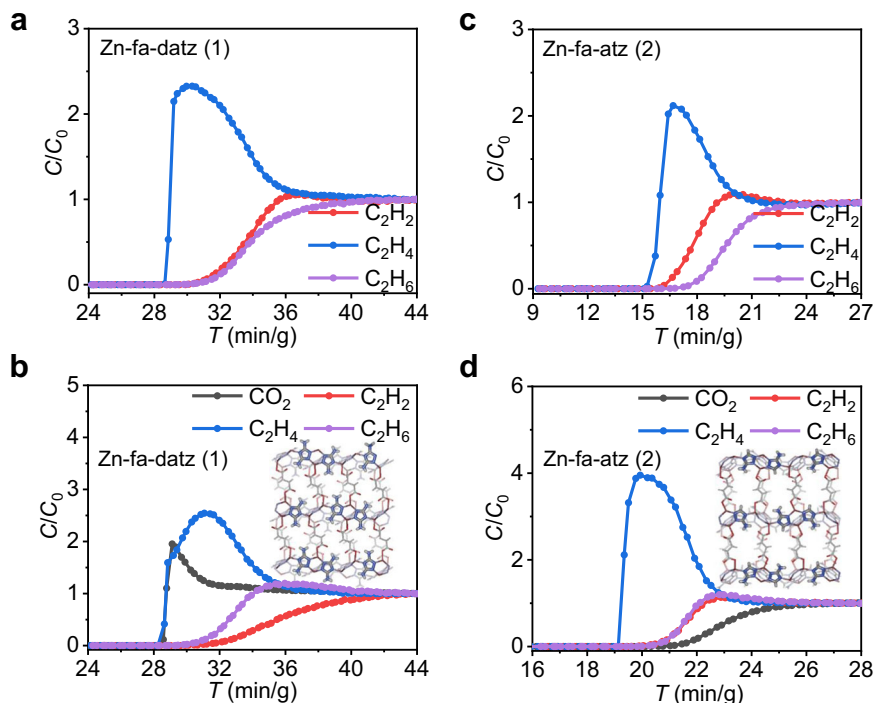


Fig. 5 | Experimental breakthrough experiments. Experimental column breakthrough curves at 298 K for: Zn-fa-datz (1) powder using a mixture of (a) $C_2H_2/C_2H_4/C_2H_6/He$ (1:1:1:4, total gas pressure of 1 bar, total flowing rate of 3.5 mL/min), and an equimolar mixture of (b) $CO_2/C_2H_2/C_2H_4/C_2H_6$ (1:1:1:1, total gas pressure of 1 bar,

total flowing rate of 2 mL/min). Zn-fa-atz (2) powder using (c) $C_2H_2/C_2H_4/C_2H_6/He$ (1:1:1:4) and (d) $CO_2/C_2H_2/C_2H_4/C_2H_6$ (1:1:1:1). Color code: Zn, purple; C, gray; O, red; N, blue; H, white.

interaction ($C\cdots O = 3.231 \text{ \AA}$) that cannot be observed in Zn-fa-datz (1), resulting in higher CO_2 Q_{st} than that of Zn-fa-datz (1).

Dynamic breakthrough experiments of Zn-fa-atz (2) and Zn-fa-atz (2)/PES composite beads

To evaluate the gas separation performance, breakthrough experiments were performed with Zn-fa-atz (2). At 298 K and ambient pressure, $C_2H_2/C_2H_4/C_2H_6/He$ and equimolar $CO_2/C_2H_2/C_2H_4/C_2H_6$ mixtures were passed through the column packed with Zn-fa-atz (2) powder (Fig. 5). The outlet gases were monitored by the online gas chromatography. As shown in Fig. 5c, d, C_2H_4 breaks through first from the column at 15 min g^{-1} and 19 min g^{-1} , respectively, which is consistent with the adsorption isotherms. Before the impurities flowed out, the purity of C_2H_4 at the outlet reached that of polymer grade ($>99.9\%$) (Supplementary Fig. 21), demonstrating that Zn-fa-atz (2) achieved the one-step purification of C_2H_4 from both the $C_2H_2/C_2H_4/C_2H_6/He$ and $CO_2/C_2H_2/C_2H_4/C_2H_6$ mixtures. It is worth mentioning that the different gas elution orders of three- and four-component separation are related to the order of adsorption capacity of each gas at different partial pressures (Supplementary Table 6). In contrast, Zn-fa-datz (1) can only realize one-step C_2H_4 production from ternary $C_2H_2/C_2H_4/C_2H_6$ mixture. To test the recycling performance of Zn-fa-atz (2), three cycles of breakthrough and following desorption experiments were conducted (Supplementary Figs. 22–23). There was no significant change in the C_2H_4 retention time and the separation performance, revealing the favorable recyclability and facile regeneration of Zn-fa-atz (2). Moreover, the highly consistent breakthrough data from three different batches of samples also fully verified the reproducibility of the samples and experiments (Supplementary Fig. 24). The simulated breakthrough curves were conducted to further validate the feasibility of Zn-fa-atz (2) for the separation performance (Supplementary Fig. 25), which is highly consistent with our experimental results. However, when Zn-fa-atz (2) was exposed to wet quaternary mixtures (ca. 36% RH), the breakthrough curves showed

that Zn-fa-atz (2) can maintain the elution sequence, but the retention times and the shape of the breakthrough curves have changed significantly, indicating the competitive adsorption of water with the other four gases (Supplementary Fig. 26).

To verify the competitive adsorption during the breakthrough experiments, we calculated the actual uptakes of Zn-fa-datz (1) and Zn-fa-atz (2) for the four gases using the reported method (Supplementary Figs. 27–28 and Supplementary Tables 7–8)^{56–58}. The results show that the actual selectivities are little different from that of IAST selectivities. For Zn-fa-atz (2), the adsorption amount order of each gas is followed as $CO_2 > C_2H_2 > C_2H_6 > C_2H_4$, being similar with the isotherms, but the selectivity changed in CO_2/C_2H_4 ($S_{breakthrough} = 2.17 > S_{IAST} = 1.4$). For Zn-fa-datz (1), the adsorption amount order for each gas is followed as $C_2H_2 > C_2H_6 > CO_2 > C_2H_4$, which is inconsistent with that of the isotherms ($C_2H_2 > C_2H_6 > C_2H_4 > CO_2$), and the selectivity of CO_2/C_2H_4 also changed ($S_{breakthrough} = 1.27 > S_{IAST} = 0.8$). Obviously, both Zn-fa-atz (2) and Zn-fa-datz (1) have different degrees of increase in the adsorption of CO_2 in the breakthrough experiments. Therefore, the diffusion coefficients of the four gases through the adsorption kinetic profiles at 298 K (Supplementary Fig. 29) were calculated. The results showed that the diffusion of CO_2 (0.3874) was significantly higher than that of C_2H_4 (0.1191), C_2H_2 (0.0820), and C_2H_6 (0.0478), indicating CO_2 diffused much faster than other three gases during the breakthrough experiments. Therefore, the larger uptakes of CO_2 are the result of the synergistic effect of adsorption thermodynamics and kinetics.

In addition, for practical industrial applications, the Zn-fa-atz (2) crystals were shaped into spherical pellets, with addition of organic polymer binder. In presence of 20 wt% of poly-ether sulfone (PES) as the binder, the Zn-fa-atz (2)/PES composite beads with a diameter of ca. 2.5 mm were successfully fabricated via the phase inversion method (Supplementary Fig. 30). The scanning electron microscope (SEM) images show Zn-fa-atz (2) crystals (ca. 500 nm) are well embedded within the inner polymer matrix (Supplementary Fig. 30b, c). The CO_2 adsorption isotherm at 195 K of Zn-fa-atz (2)/PES also

shows a quasi-type-I characteristic, indicating the microporosity of the beads (Supplementary Figs. 30d, e and 31). The pore volume was calculated to be $0.265 \text{ cm}^3 \text{ g}^{-1}$ at $P/P_0 = 0.96$ (7% lower than that of pure Zn-fa-atz (2) crystal sample), suggesting that Zn-fa-atz (2)/PES retains most of the porosity. Further, the kinetic adsorption profiles for C_2H_6 were measured at 298 K and 1 atm. The diffusional rate constants (k)⁵⁹ for C_2H_6 in Zn-fa-atz (2)/PES was calculated to be 1.1437, which is within the vicinity of that for the Zn-fa-atz (2) powder ($k = 1.2706$), meaning that compositing has little effect on the gas diffusion (Supplementary Fig. 32). The equimolar $\text{CO}_2/\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ mixture breakthrough experiment was further tested with Zn-fa-atz (2)/PES beads-packed column at room temperature. As shown in Supplementary Fig. 30f, C_2H_4 breakthrough first at 18 min g^{-1} , following by C_2H_6 , CO_2 , and C_2H_2 , indicating the effective one-step C_2H_4 production ability from quaternary mixture after shaping Zn-fa-atz (2) into PES-based spherical pellets.

Discussion

In conclusion, fine-tuning pore size/shape and local pore chemistry by regulating the network hydrogen bonding interactions in two related coordination networks can precisely control the adsorption selectivity of C_2H_4 in the complex separation systems. The reported ultramicroporous adsorbent, Zn-fa-atz (2), can achieve the effective one-step purification of C_2H_4 from $\text{CO}_2/\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ quaternary mixture. Design principle presented here could be helpful to advance the new-generation physisorbent synthesis and application for more complex industry-related separation system.

Methods

Synthesis of Zn-fa-datz (1)

According to the reported procedures with a little modification⁵². $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.298 g), fumaric acid (H_2fa , 0.5 mmol, 0.058 g), 1*H*-1,2,4-triazole-3,5-diamino (Hdatz , 1.0 mmol, 0.099 g) were dissolved in 10 mL DMF/MeOH/ H_2O mixed solution (4:4:2, $v/v/v$). After 30 min of sonication treatment, the resulting solution was sealed in a 25 mL Teflon-lined stainless-steel autoclave and heated at 130 °C under autogenous pressure for 72 h. After slowly cooling down to room temperature, the colorless crystals of Zn-fa-datz (1) were washed with DMF/MeOH (1:1, v/v) mixed solution for three times, and dried at room temperature (yield = 48% based on Zn). The obtained sample was exchanged with fresh MeOH three times daily for three days.

Synthesis of Zn-fa-atz (2)

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.298 g), fumaric acid (H_2fa , 0.5 mmol, 0.058 g), 3-amino-1,2,4-triazole (Hatz , 1.0 mmol, 0.084 g) were dissolved in 10 mL DMF/MeOH/ H_2O mixed solution (4:4:2, $v/v/v$). After 30 min of sonication, the resulting solution was sealed in a 25 mL Teflon-lined stainless-steel autoclave and heated at 130 °C under autogenous pressure for 72 h. After slowly cooling down to room temperature, the colourless crystals of Zn-fa-atz (2) were washed with fresh DMF/MeOH (1:1, v/v) mixed solution for three times, and dried at room temperature (yield = 52% based on Zn). The obtained sample was exchanged with fresh MeOH three times daily for three days.

Gas adsorption measurements

The thermodynamic adsorption isotherms for CO_2 , C_2H_2 , C_2H_4 , and C_2H_6 were conducted on 3FLEX (Micromeritics). Before the N_2 (77 K)/ CO_2 (195 K) adsorption measurement, Zn-fa-atz (2) powder, Zn-fa-datz (1) powder and Zn-fa-atz (2)/PES beads (~100 mg) were evacuated under a dynamic vacuum at 75 °C for 4 h to remove the guest molecules.

Dynamic breakthrough experiments

Before breakthrough experiments, the samples were packed in a column and activated in-situ by heating at 75 °C for 20 h in a He flow with

rate of 20 mL/min, and then cooled to room temperature. Then the gas flow is switched to the desired gas mixture ($v(\text{He})/v(\text{C}_2\text{H}_2)/v(\text{C}_2\text{H}_4)/v(\text{C}_2\text{H}_6) = 58:14:14:14$, $v(\text{CO}_2)/v(\text{C}_2\text{H}_2)/v(\text{C}_2\text{H}_4)/v(\text{C}_2\text{H}_6) = 25:25:25:25$). The dynamic breakthrough data were recorded on a homemade apparatus at room temperature and 1 atm. The gas stream concentration at column outlet was continuously detected by using a chromatographic analyzer (TCD-Thermal Conductivity Detector, detection limit 0.1 ppm). After equilibrium, desorption curves of Zn-fa-atz (2) in Supplementary Fig. 23 was collected under a He flow of 20 mL/min at 70 °C.

Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability

For full characterization data including detailed sorption and breakthrough experiments data see the Supplementary Methods 3 and 5. All data supporting the finding of this study are available within this article and its Supplementary Information. Crystallographic data for Zn-fa-atz (2) reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2176255-2176256. Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. Source data of the PXRD patterns, TGA curves, sorption tests; gas adsorption enthalpies and selectivities, Rietveld refinement of powder X-ray diffraction tests and breakthrough tests that support the findings of this study are provided as a Source Data file (ref. 60. Rong, Y. (2023): Source data of Zn-fa-datz (1) and Zn-fa-atz (2) that support the findings of this study.xlsx. Data sets. figshare <https://doi.org/10.6084/m9.figshare.24864540>). Source data are provided with this paper.

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Author contributions

K.-J.C. designed the project. R.Y., Y.W., J-W.C., T.G., X.-O.X. and Q.-H.Y. synthesized the compounds, J.-W.C., X.J., R.Y., Y.W. and T.G. collected all adsorption data. T.P. and K.A.F. participated in the separation mechanism discussion. R.Y., Y.W. and J-W.C. collected the experimental breakthrough data. R.K. carried out the breakthrough simulation. H.C. and L.Li participated in the breakthrough simulation discussion. Y.W. and

T.G. collected the SEM data. R.Y. and Y.W. analyzed the adsorption data and experimental breakthrough data. Y.W., B.-K.L. and T.Z. analyzed the single crystal data, Y.W. and Z.-M.Y. collected and analyzed the powder refinement data. Y.W., R.Y. and K.-J.C. wrote the paper, and all authors contributed to revise the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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