

Kilogram-Scale Fabrication of A Robust Olefin-linked Covalent Organic Framework for Separating Ethylene from Ternary C₂ Hydrocarbon Mixture

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ABSTRACT: One-step adsorptive purification of ethylene (C₂H₄) from a ternary mixture of acetylene (C₂H₂), C₂H₄, ethane (C₂H₆) by a single material is of great importance but challenging in the petrochemical industry. Herein, a chemically robust olefin-linked covalent organic framework (COF), NKCOF-62, is designed and synthesized by melt polymerization method employing tetramethylpyrazine and terephthalaldehyde as cheap monomers. This method avoids most of the disadvantages of classical solvothermal methods, which enables the cost-effective kilogram fabrication of olefin-linked COFs in one pot. Furthermore, NKCOF-62 shows remarkably selective adsorption of C₂H₂ and C₂H₆ over C₂H₄ thanks to its unique pore environments and suitable pore size. Breakthrough experiments demonstrate that polymer-grade C₂H₄ can be directly obtained from C₂H₂/C₂H₄/C₂H₆ (1/1/1) ternary mixtures through a single separation process. Notably, NKCOF-62 is the first demonstration of the potential to use COFs for C₂H₂/C₂H₄/C₂H₆ separation, which provides a blueprint for the design and construction of robust COFs for industrial gas separations.

INTRODUCTION

Ethylene (C₂H₄), an important chemical feedstock and industrial gas, has been widely used to produce polymers (e.g., plastics) and other valued products in modern life.^[1-4] Currently, C₂H₄ is mainly produced by the thermal cracking of ethane (C₂H₆) or naphtha, with the inevitable presence of acetylene (C₂H₂) and C₂H₆ byproducts. Thus, separating C₂H₂ and C₂H₆ from these mixtures is an industrial necessity to obtain polymer-grade C₂H₄ (>99.9% purity), but remains a significant challenge because of their very similar physical properties, including boiling points, quadrupole moment, and kinetic diameter.^[5-8] Recently, as an alternative separation technology, the utilization of porous materials as sorbents for C₂H₄ purification has attracted widespread interest due to their high efficiency and environmental friendliness.^[9-13] In this regard, porous crystalline adsorbents such as metal-organic frameworks (MOFs)^[14-16] and hydrogen-bonded organic frameworks (HOFs)^[17-20] have been developed for C₂-gases mixture separation, significant progress has been devoted to addressing the efficient separation of C₂H₄ from binary C₂H₂/C₂H₄ and C₂H₆/C₂H₄ mixtures due to their well-defined structure, controllable pore size and modifiable pore environment. Because of the difficulty in designing and synthesizing materials that preferentially trap C₂H₂ and C₂H₆,

simultaneous removal of both C₂H₂ and C₂H₆ from ternary C₂H₂/C₂H₆/C₂H₄ mixtures in a one-step process is still underexplored. Besides, the reported MOF and HOF adsorbents generally suffer from poor chemical stability, high cost and unscalable products, which hamper their practical applications. Thus, developing inexpensive and chemically robust adsorbents with excellent C₂-gases mixture separation properties is urgently needed for the industrial purification of C₂H₄.

Covalent organic frameworks (COFs) are an emerging class of organic porous crystalline materials based on light elements interconnected through covalent bonds.^[21-25] Attributed to their predictable structures, high porosity, tunable pore sizes and high chemical stability, COFs have shown unique properties and great potential in gas storage and separation applications.^[26-30] Many experiments have been devoted to purify C₂H₄ from C₂-gases mixtures. In 2018, Zhu and co-workers used imide-linked COFs (PAF-110) to purify C₂H₄ from binary C₂H₂/C₂H₄ mixtures.^[31] Recently, our group reported that three-dimensional (3D) COFs with **bcu** topology could efficiently remove C₂H₆ from binary C₂H₂/C₂H₄ mixtures to produce polymer-grade C₂H₄. (Figure 1).^[32] To the best of our knowledge, COFs that can simultaneously and selectively remove both C₂H₂ and C₂H₆ from ternary C₂H₂/C₂H₆/C₂H₄ mixtures in a one-step process have not been reported, which

is in high industrial demand. The physical adsorption of C_2H_2 , C_2H_4 and C_2H_6 by COFs generally suffer poor C_2H_2/C_2H_4 or C_2H_6/C_2H_4 selectivity. These inherent contradictions make the design of a single COF to achieve C_2H_4 purification in one step from $C_2H_2/C_2H_4/C_2H_6$ ternary mixture a formidable challenge. Compared with reversible-linkage COFs (e.g., imine),^[33-36] olefin-linked COFs with nearly irreversible C=C linkage,^[37-44] as a rising star, is one of the promising candidates for gas separations at an industrial scale owing to their superb chemical stability, scalable synthesis and low production cost.^[45] Significantly, recent investigations also demonstrate that the melt polymerization method without adding organic solvent, pioneered by our group, can access a wide range of COFs, and enables the large-scale and low-cost fabrication of olefin-linked COFs,^[46] hence making olefin-linked COFs promising candidates to solve the formidable challenge of $C_2H_2/C_2H_4/C_2H_6$ separation.

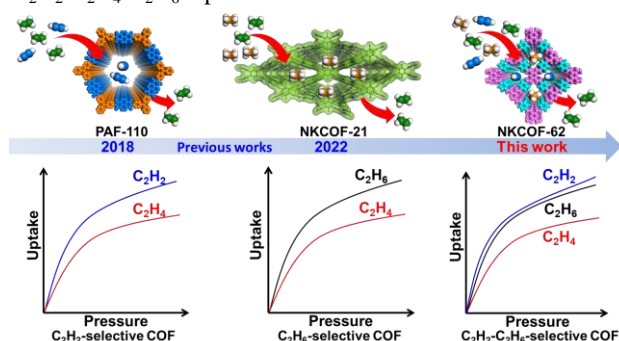


Figure 1. The brief development of one-step purification of C_2H_4 based on C_2H_2 - or C_2H_6 -selective COFs.

To address the above challenges, we discovered a new commercially available D_{2h} -symmetric monomer (tetramethylpyrazine), which has been widely used as an intermediate in flavoring agents, fragrances, pharmaceuticals and pesticides, showing great industrial application potential due to its extremely low cost (<\$90/kg). Herein, we constructed a new olefin-linked COF (denoted as NKCOF-62, NKCOF = Nankai covalent organic framework) with orthorhombic reticular topology from two cheap building blocks, tetramethylpyrazine (TMPZ) and terephthalaldehyde (TPA) (\$30/kg) through melt polymerization method. Notably, the melt polymerization strategy avoids using organic solvents and high operation pressure, making COFs easily scaled up to the hectogram level. Attributed to its relatively small pore size and unique pore environments, NKCOF-62 can preferentially trap C_2H_2 and C_2H_6 over C_2H_4 , leading to both high adsorption selectivities for C_2H_2/C_2H_4 and C_2H_6/C_2H_4 . Breakthrough experiments indicated that the polymer-grade C_2H_4 can be obtained not only from binary C_2H_2/C_2H_4 and C_2H_6/C_2H_4 , but also from ternary $C_2H_2/C_2H_4/C_2H_6$.

RESULTS AND DISCUSSION

We aimed to fabricate an olefin-linked COF by using commercially available tetramethylpyrazine, which can undergo a facile condensation reaction with terephthalaldehyde in the presence of benzoic anhydride and benzoic acid as modulator agents through the melt polymerization method (Figure 1b). To confirm the feasibility of this method, the model molecule

2,3,5,6-tetra(*E*-styryl)pyrazine was successfully synthesized by the condensation reaction of tetramethylpyrazine and benzaldehyde catalyzed by benzoic anhydride (Figure 1a, S1, S2 and Table S1). Subsequently, we screened the melt polymerization and solvothermal synthetic conditions, including the amount of benzoic acid and benzoic anhydride, reaction solvent, reaction temperature and time, to fabricate a highly crystalline COF (Figure S3-S10 and Table S2-S3). As we envisioned, TMPZ, TPA, benzoic acid and benzoic anhydride in a molar ratio of 1:2:4:4 were sealed in a glass tube and heated at 180 °C for 5 days, leading to the generation of NKCOF-62 (Figure S11). The formed COF monolith was washed with methanol and then dried at 80 °C to obtain the purified NKCOF-62 with a yield of ~75%.

The crystalline structure of NKCOF-62 was resolved by powder X-ray diffraction (PXRD) measurements and computational simulation. DFT-based geometry optimizations were performed with the CP2K software package.^[47] The CP2K input file in this work was generated with the help of the Multitwfn program.^[48] As shown in Figure 1c, the existence of high diffraction peaks in the PXRD pattern indicated that NKCOF-62 had a long-range ordered structure and crystalline nature, and three main diffraction peaks at 6.64 °, 13.49 ° and 24.88 ° were assigned to (110), (220) and (001) crystal facets, respectively. Pawley refinements were performed with the data from the experimental PXRD pattern to yield orthorhombic unit cell parameters of $a=18.65$ Å, $b=18.71$ Å, $c=3.45$ Å, $\alpha = \gamma = \beta = 90^\circ$ (residuals $R_p = 0.81\%$, $R_{wp} = 1.07\%$). Eclipsed (AA) stacking mode was constructed with the above unit cell parameter to generate corresponding diffraction patterns for comparison with experimental data, which agreed well with the simulated AA stacking model. Notably, similar PXRD patterns are common in olefin-linked COFs due to their irreversible C=C bond nature.^[40, 49-52]

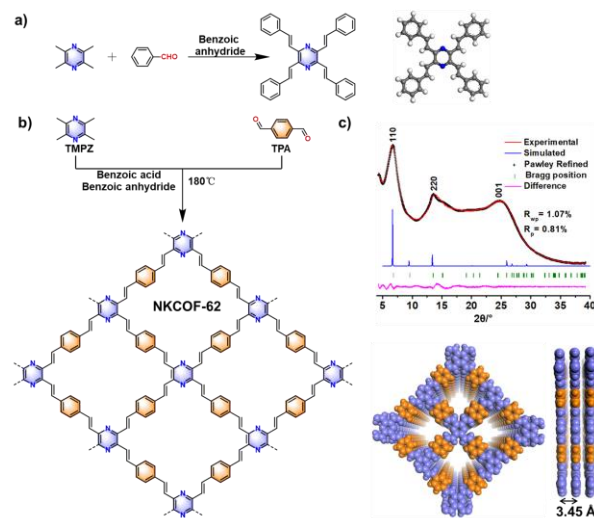


Figure 2. a) Synthesis of the model molecule and its single-crystal structure. b) Structure and synthesis of NKCOF-62. c) PXRD patterns of NKCOF-62, top and side views of the corresponding refined eclipsed AA stacking structure of NKCOF-62.

Various characterization approaches were employed to confirm the chemical component and structure of NKCOF-62. Fourier transform infrared spectra (FT-IR) showed a new characteristic absorbance at 962 and 1626 cm^{-1} , confirming the formation of the C=C bonds. The stretching vibration peak for methyl C-H of TMP monomer around 3000 cm^{-1} disappeared, and the stretching vibration peak for C=O of DFB monomer attenuated in the NKCOF-62, indicating their high polymerization degrees (Figure 3a). Comparing the ^{13}C solid-state nuclear magnetic resonance (NMR) spectrum of NKCOF-62 with the liquid ^{13}C NMR spectra of the model compound indicated that these signals well matched the corresponding carbon atoms. The carbonyl signals at around 123 and 136 ppm were typically arising from the olefin (C=C) carbon (Figure 3b), which further confirmed the formation of the olefin-linked COF. Scanning electron microscopy (SEM) image exhibited that NKCOF-62 was irregular morphology of the stacked blocks in the micro level. (Figure S12). High-resolution transmission electron microscopy images (HR-TEM, Talos F200X G2) of NKCOF-62 revealed the significant crystal lattice, and the lattice fringe spacing was about 0.34 nm, which corresponded to the (001) facet (Figure 3c). Thermogravimetric analysis (TGA) showed excellent thermal stability of NKCOF-62 (Figure S13), and there was no obvious weight loss up to 400 $^{\circ}\text{C}$ under N_2 atmosphere. In addition, the high chemical stability of NKCOF-62 was further investigated under different conditions, including boiling water, sodium hydroxide (NaOH, 10 M), and hydrochloric acid (HCl, 12 M). After soaking in the above solutions for 7 days, the crystallinity and skeletal structures were almost unchanged, as verified by FT-IR and PXRD (Figure S14 and S15), indicating the ultrahigh stability of NKCOF-62.

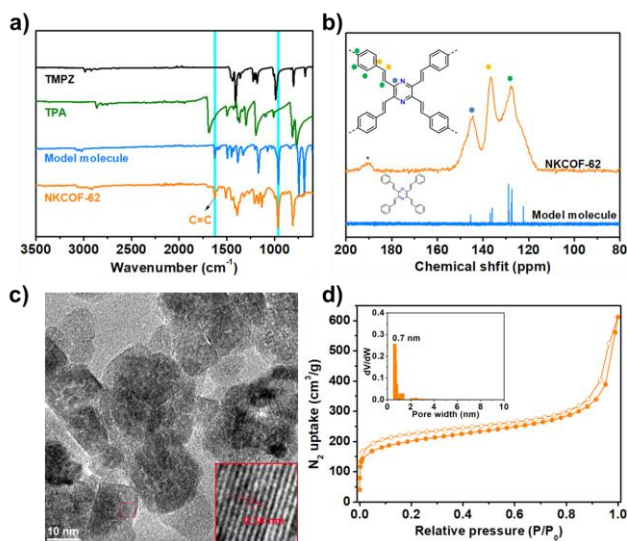


Figure 3. a) FT-IR spectra of NKCOF-62, corresponding monomers and model molecule. b) Liquid ^{13}C NMR spectra of the model molecule and ^{13}C solid-state NMR spectra of NKCOF-62. c) HR-TEM image of NKCOF-62. d) Nitrogen adsorption and desorption isotherms of NKCOF-62. Inset is the pore size distribution.

c) HR-TEM image of NKCOF-62. d) Nitrogen adsorption and desorption isotherms of NKCOF-62. Inset is the pore size distribution.

N_2 adsorption isotherm was conducted at 77 K to evaluate the permanent porosity of NKCOF-62. As shown in Figure 3d, NKCOF-62 showed a type I sorption isotherm, confirming its microporous structure. The Brunauer–Emmett–Teller (BET) surface area was calculated to be 654 m^2/g , and the total pore volume was 0.59 cm^3/g . Nonlinear density functional theory (NLDFT) cylindrical pore model-based pore size distribution analysis revealed a prominent pore size distribution profile centered at 0.7 nm, which was close to the calculated pore size (0.8 nm) for the eclipsed AA layer stacking model. Notably, NKCOF-62 possesses the smallest eclipsed pore among all orthorhombic 2D COFs (Figure S16).

Compared with the conventional solvothermal method, which is usually reacted in a sealed glass tube to obtain micrograms-scale COFs in the presence of organic solvent and hinder their practical applications, the melt polymerization strategy avoids most of the disadvantages of the solvothermal method, which is desirable for the large-scale production of materials. Therefore, we attempted to scale up the synthesis of NKCOF-62 using an autoclave by one-pot reaction, and a red cylinder shape (0.51 kg) was easily obtained under the same reaction condition (Figure 4). Notably, the BET surface area and crystallinity of the large-scale NKCOF-62 were comparable to that of the equivalent small-scale synthesis (Figure S17-S19). These results further demonstrated that NKCOF-62 could be easily scaled up to a large amount depending on the requirement in principle, which addressed the grand challenges of scalable COF synthesis that are inaccessible through traditional solvothermal approaches. Furthermore, the cost of preparing a kilogram of NKCOF-62 is $\text{75}\text{\\$/kg}$, far below most reported COFs (Table S4), which exhibits great potential for industrial production and application.

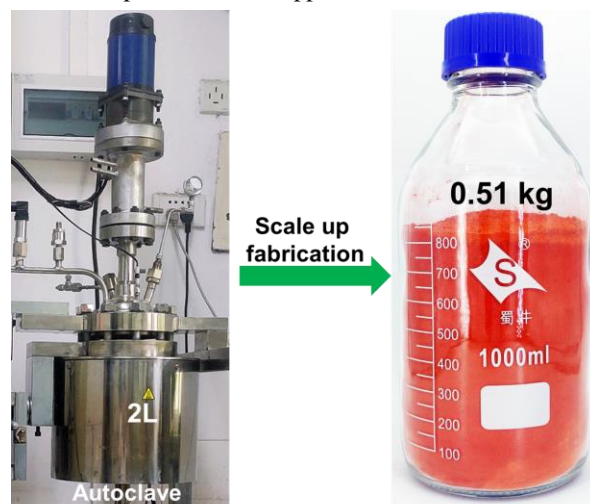


Figure 4. Photograph of scale-up fabrication of NKCOF-62.

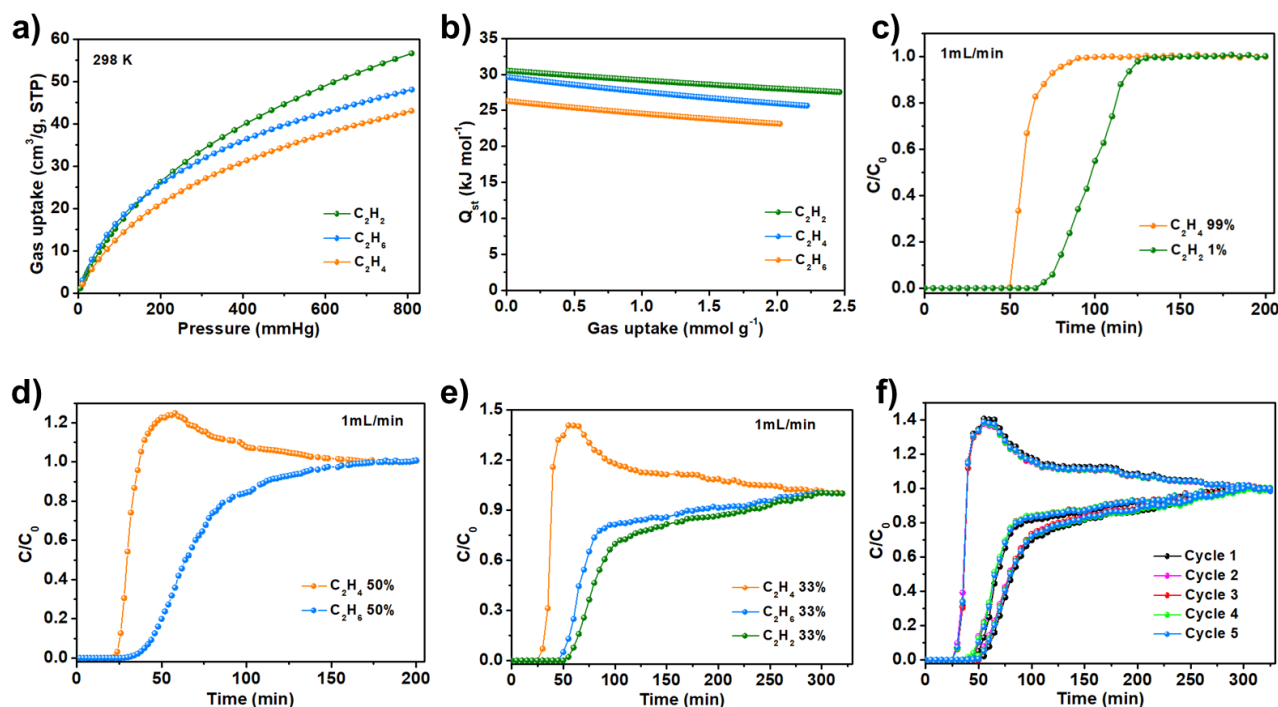


Figure 5. a) C_2H_2 , C_2H_4 , and C_2H_6 sorption isotherms of NKCOF-62 at 298 K. b) Isothermic heats of adsorption (Q_{st}) for C_2H_2 , C_2H_4 , and C_2H_6 . c) Experimental breakthrough curves of NKCOF-62 for C_2H_2/C_2H_4 (1/99, v/v) and (d) C_2H_6/C_2H_4 (50/50, v/v) binary mixtures with a total inlet flow rate of 1.0 mL/min. e) Experimental breakthrough curves for $C_2H_2/C_2H_4/C_2H_6$ (1/1/1, v/v/v) at 298 K and 1 bar. f) Five consecutive breakthrough cycles of $C_2H_2/C_2H_4/C_2H_6$ (1/1/1, v/v/v) for NKCOF-62.

The microporosity of NKCOF-62 prompted us to measure single-component C_2H_2 , C_2H_4 and C_2H_6 adsorption isotherms at 273 K and 298 K (Figure S5a and S20). The amount of adsorbed gas in activated NKCOF-62 decreased with increasing temperature. Interestingly, the adsorption capacity of NKCOF-62 for C_2H_2 and C_2H_6 was higher than that for C_2H_4 across the entire pressure range tested (0–100 kPa), implying selective adsorption of C_2H_2 and C_2H_6 over C_2H_4 . To evaluate the affinity of C_2 hydrocarbons with NKCOF-62, the coverage-dependent isosteric heat of adsorption (of Q_{st}) for C_2H_2 , C_2H_4 and C_2H_6 was calculated using the virial equation (Figure S21 and Table S5). As shown in Figure 5b, the order of Q_{st} values at zero coverage was C_2H_2 (30.5 kJ/mol) > C_2H_6 (29.6 kJ/mol) > C_2H_4 (26.3 kJ/mol), indicating that NKCOF-62 has the strongest affinity for C_2H_2 , followed by C_2H_6 and finally C_2H_4 which was useful in the separation and purification of C_2H_4 and consistent with the absorption amounts measured from the adsorption isotherms. Notably, the adsorption enthalpies of all three gases were lower than 35 kJ/mol, indicating that NKCOF-62 had a relatively low energy footprint for sorbent regeneration. To further evaluate the separation performance of NKCOF-62, the ideal adsorbed solution theory (IAST) was utilized to calculate the binary gas mixture 1/99 C_2H_2/C_2H_4 and 50/50 C_2H_6/C_2H_4 adsorptive selectivity. As shown in Figure S22 and S23, the predicted selectivity of C_2H_2/C_2H_4 and C_2H_6/C_2H_4 at pressure of 1 bar and 298 K were 1.30 and 1.37, respectively, which was comparable to most reported adsorbents for one-step C_2H_4 purification from a ternary $C_2H_2/C_2H_4/C_2H_6$ mixtures (e.g., NPU-1, NPU-2,^[53] UPC-612^[54] and Azole-Th-1^[55]), implying the feasibility of using NKCOF-62 to purify C_2H_4 from C_2H_2 and C_2H_6 in practical applications.

To further verify the practical separation performance of NKCOF-62, the transient fixed-bed column breakthrough ex-

periments of binary C_2H_2/C_2H_4 (1/99) and C_2H_6/C_2H_4 (50/50) mixtures, and ternary $C_2H_2/C_2H_4/C_2H_6$ (1/1/1) mixtures were performed at 298 K and ambient pressure with a total flow of 1 mL/min. As shown in Figures 5c and 5d, C_2H_4 was always first eluted through the column to obtain polymer-grade (> 99.95%) C_2H_4 , while C_2H_2 or C_2H_6 remained in the packed column for a certain time until reaching their saturation and breakthrough, indicating that NKCOF-62 could efficiently separate C_2H_4 from C_2H_2/C_2H_4 and C_2H_6/C_2H_4 binary mixtures. The breakthrough time was 15.4 min/g (C_2H_2/C_2H_4 , 1/99) and 8.2 min/g (C_2H_6/C_2H_4 , 50/50). Furthermore, NKCOF-62 could simultaneously capture both C_2H_2 and C_2H_6 from a $C_2H_2/C_2H_4/C_2H_6$ (1/1/1) ternary gas mixture and afforded polymer-grade C_2H_4 in a one-step separation process (Figure 5e). It was observed that C_2H_4 breakthrough occurred first at 26 min, followed by C_2H_6 at 45 min and C_2H_2 at 50 min, and the separation time was finally determined to be 19 min/g. Excitingly, this is the first case of a single COF adsorbent for one-step C_2H_4 purification from the ternary mixture of $C_2H_2/C_2H_4/C_2H_6$, and the C_2H_4 productivity of NKCOF-62 was higher than that of HIAM-210,^[56] NPU-1^[53] and even comparable to some top-performing materials like UiO-67-(NH_2),^[57] UPC-612^[54] and UPC-66^[58] (Table S6). Notably, NKCOF-62 could be easily scaled up to kilogram level, while these MOFs could not be prepared on a large scale. Furthermore, the cost of NKCOF-62 is far lower than those of benchmark MOFs, thus making NKCOF-62 great potential in the industrial-scale separation scenario. Additionally, the cycling dynamic breakthrough tests of $C_2H_2/C_2H_4/C_2H_6$ were conducted to assess the recyclability of NKCOF-62 under the same conditions (Figure 5f). The breakthrough time and the PXRD pattern remained almost unchanged with five continuous cycles, which indicated that it had outstanding stability and recyclability (Figure S24).

To better understand the selective adsorption behaviors of C_2H_2 and C_2H_6 over C_2H_4 , the grand canonical Monte Carlo (GCMC) simulation was performed to gain insight into the nature of the binding sites for C_2H_2 , C_2H_4 , and C_2H_6 in NKCOF-62. The simulated adsorption isotherms show a correct trend consistent with experiments that verify the reliability of the force field. As shown in Figure 6, C_2H_2 , C_2H_4 , and C_2H_6 were all distributed at similar positions with the orthorhombic one-dimensional channel of NKCOF-62. In addition, these gas molecules all interacted with the aromatic hydrogen of TPA. The order of interaction distances was C_2H_2 (2.71) < C_2H_6 (2.99) < C_2H_4 (3.28), and the corresponding adsorption energies were 38.81, 34.74, and 30.35 kJ/mol, respectively. These calculation results support the following trend in sorbent-sorbate interactions for NKPOC-62: $C_2H_2 > C_2H_6 > C_2H_4$, which is fully consistent with the experimental findings.

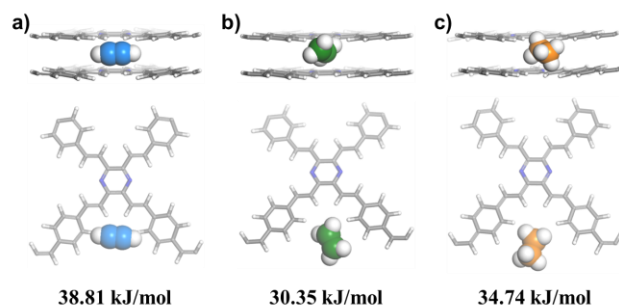


Figure 6. Preferential adsorption sites and corresponding adsorption energies for C_2H_2 , C_2H_4 , and C_2H_6 in the NKCOF-62.

CONCLUSIONS

In summary, we have demonstrated that a commercially available tetramethylpyrazine monomer can be used to create a new orthorhombic olefin-linked COF via the melt polymerization method. Notably, kilogram-level COF was firstly fabricated using an autoclave by one-pot reaction at a cost of <75\$/kg, which surpassed the most reported COFs and promoted the industrial application of olefin-linked COFs. This COF possessed the smallest eclipsed pore (~0.7 nm) among all orthorhombic 2D COFs, which afforded unique selective adsorption of C_2H_2 and C_2H_6 over C_2H_4 . Thereby, NKCOF-62 can be applied to purify C_2H_4 not only from C_2H_2/C_2H_4 and C_2H_6/C_2H_4 binary mixture, but also from challenging $C_2H_2/C_2H_4/C_2H_6$ ternary mixture. Furthermore, this case is the first time that a single COF is used to directly produce polymer grade C_2H_4 in one step from the ternary C_2 hydrocarbon gas mixture. Its separation performance is comparable to the top-performing MOFs, but with far lower cost. This work not only provides a new robust COF-based adsorbent for one-step C_2H_4 purification but also extensively facilitates the research of emerging cheap and efficient COF adsorbents for important industrial separations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

Z. Zhang and Z. Wang conceived and directed the project. Z. Wang and Y. Zhang designed and carried out the experiments and analyzed the data. Y. Zhang, E. Lin, S. Geng, M. Wang, J. Liu conducted the preparation of the starting materials. Z. Zhang, Z. Wang, Y. Chen, and P. Cheng discussed the results and wrote the paper.

‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Chuah, C. Y.; Goh, K.; Yang, Y.; Gong, H.; Li, W.; Karahan, H. E.; Guiver, M. D.; Wang, R.; Bae, T. H., Harnessing Filler Materials for Enhancing Biogas Separation Membranes. *Chem. Rev.* **2018**, *118*, 8655-8769.
- (2) Yang, L.; Qian, S.; Wang, X.; Cui, X.; Chen, B.; Xing, H., Energy-efficient separation alternatives: metal-organic frameworks and membranes for hydrocarbon separation. *Chem. Soc. Rev.* **2020**, *49*, 5359-5406.
- (3) Wang, Z.; Zhang, S.; Chen, Y.; Zhang, Z.; Ma, S., Covalent organic frameworks for separation applications. *Chem. Soc. Rev.* **2020**, *49*, 708-735.
- (4) Ebadi Amooghin, A.; Sanaeepur, H.; Luque, R.; Garcia, H.; Chen, B., Fluorinated metal-organic frameworks for gas separation. *Chem. Soc. Rev.* **2022**, *51*, 7427-7508.
- (5) Chen, K.-J.; Madden, D. G.; Mukherjee, S.; Pham, T.; Forrest, K. A.; Kumar, A.; Space, B.; Kong, J.; Zhang, Q.-Y.; Zaworotko, M. J., Synergistic sorbent separation for one-step ethylene purification from a four-component mixture. *Science* **2019**, *366*, 241-246.
- (6) Wu, Y.; Weckhuysen, B. M., Separation and Purification of Hydrocarbons with Porous Materials. *Angew. Chem. Int. Ed.* **2021**, *60*, 18930-18949.
- (7) Qazvini, O. T.; Babarao, R.; Shi, Z. L.; Zhang, Y. B.; Telfer, S. G., A Robust Ethane-Trapping Metal-Organic Framework with a High Capacity for Ethylene Purification. *J. Am. Chem. Soc.* **2019**, *141*, 5014-5020.
- (8) Kim, D.; Truong, B. N.; Jo, D.; Yoon, J. W.; Lee, S.-K.; Bae, Y.-S.; Ho Cho, K.; Lee, U. H., Single-step ethylene purification from ternary C_2 hydrocarbon mixtures in a scalable metal-organic framework. *Chem. Eng. J.* **2023**, *470*.
- (9) Sun, H.; Chen, F.; Chen, R.; Li, J.; Guo, L.; Liu, Y.; Shen, F.; Yang, Q.; Zhang, Z.; Ren, Q.; Bao, Z., Customizing Metal-Organic Frameworks by Lego-Brick Strategy for One-Step Purification of Ethylene from a Quaternary Gas Mixture. *Small* **2023**, *19*, e2208182.
- (10) Zou, X.; Zhu, G., Microporous Organic Materials for Membrane-Based Gas Separation. *Adv. Mater.* **2018**, *30*, 1700750.
- (11) Cui, W. G.; Hu, T. L.; Bu, X. H., Metal-Organic Framework Materials for the Separation and Purification of Light Hydrocarbons. *Adv. Mater.* **2020**, *32* (3), e1806445.
- (12) Su, K.; Wang, W.; Du, S.; Ji, C.; Yuan, D., Efficient ethylene purification by a robust ethane-trapping porous organic cage. *Nat. Commun.* **2021**, *12*, 3703.
- (13) Zhang, P.; Zhong, Y.; Zhang, Y.; Zhu, Z.; Liu, Y.; Su, Y.; Chen, J.; Chen, S.; Zeng, Z.; Xing, H.; Deng, S.; Wang, J., Synergistic binding sites in a hybrid ultramicroporous material for one-step ethylene purification from ternary C_2 hydrocarbon mixtures. *Sci. Adv.* **2022**, *8*, eabn9231.

- (14) Hao, H. G.; Zhao, Y. F.; Chen, D. M.; Yu, J. M.; Tan, K.; Ma, S.; Chabal, Y.; Zhang, Z. M.; Dou, J. M.; Xiao, Z. H.; Day, G.; Zhou, H. C.; Lu, T. B., Simultaneous Trapping of C₂H₂ and C₂H₆ from a Ternary Mixture of C₂H₂/C₂H₄/C₂H₆ in a Robust Metal-Organic Framework for the Purification of C₂H₄. *Angew. Chem. Int. Ed.* **2018**, *57*, 16067-16071.
- (15) Ding, Q.; Zhang, Z.; Zhang, P.; Yu, C.; He, C.-H.; Cui, X.; Xing, H., One-step ethylene purification from ternary mixture by synergetic molecular shape and size matching in a honeycomb-like ultramicroporous material. *Chem. Eng. J.* **2022**, *450*, 138272.
- (16) Wang, G. D.; Li, Y. Z.; Shi, W. J.; Hou, L.; Wang, Y. Y.; Zhu, Z., One-Step C₂H₄ Purification from Ternary C₂H₆/C₂H₄/C₂H₂ Mixtures by a Robust Metal-Organic Framework with Customized Pore Environment. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205427.
- (17) Yang, Y.; Li, L.; Lin, R.-B.; Ye, Y.; Yao, Z.; Yang, L.; Xiang, F.; Chen, S.; Zhang, Z.; Xiang, S.; Chen, B., Ethylene/ethane separation in a stable hydrogen-bonded organic framework through a gating mechanism. *Nat. Chem.* **2021**, *13*, 933-939.
- (18) Zhou, Y.; Chen, C.; Krishna, R.; Ji, Z.; Yuan, D.; Wu, M., Tuning Pore Polarization to Boost Ethane/Ethylene Separation Performance in Hydrogen-Bonded Organic Frameworks. *Angew. Chem. Int. Ed.* **2023**, *62*, e202305041.
- (19) Lin, Z. J.; Mahammed, S. A. R.; Liu, T. F.; Cao, R., Multi-functional Porous Hydrogen-Bonded Organic Frameworks: Current Status and Future Perspectives. *ACS Cent. Sci.* **2022**, *8*, 1589-1608.
- (20) Zhang, X.; Li, L.; Wang, J. X.; Wen, H. M.; Krishna, R.; Wu, H.; Zhou, W.; Chen, Z. N.; Li, B.; Qian, G.; Chen, B., Selective Ethane/Ethylene Separation in a Robust Microporous Hydrogen-Bonded Organic Framework. *J. Am. Chem. Soc.* **2020**, *142*, 633-640.
- (21) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M., Porous, Crystalline, Covalent Organic Frameworks. **2005**, *310*, 1166-1170.
- (22) Han, X.; Yuan, C.; Hou, B.; Liu, L.; Li, H.; Liu, Y.; Cui, Y., Chiral covalent organic frameworks: design, synthesis and property. *Chem. Soc. Rev.* **2020**, *49*, 6248-6272.
- (23) Zhao, S.; Jiang, C.; Fan, J.; Hong, S.; Mei, P.; Yao, R.; Liu, Y.; Zhang, S.; Li, H.; Zhang, H.; Sun, C.; Guo, Z.; Shao, P.; Zhu, Y.; Zhang, J.; Guo, L.; Ma, Y.; Zhang, J.; Feng, X.; Wang, F.; Wu, H.; Wang, B., Hydrophilicity gradient in covalent organic frameworks for membrane distillation. *Nat. Mater.* **2021**, *20*, 1551-1558.
- (24) Li, Y.; Chen, W.; Xing, G.; Jiang, D.; Chen, L., New synthetic strategies toward covalent organic frameworks. *Chem. Soc. Rev.* **2020**, *49*, 2852-2868.
- (25) Ma, T.; Kapustin, E. A.; Yin, S. X.; Liang, L.; Zhou, Z.; Niu, J.; Li, L.-H.; Wang, Y.; Su, J.; Li, J.; Wang, X.; Wang, W. D.; Wang, W.; Sun, J.; Yaghi, O. M., Single-crystal x-ray diffraction structures of covalent organic frameworks. *Science* **2018**, *361*, 48-52.
- (26) Guan, X.; Li, H.; Ma, Y.; Xue, M.; Fang, Q.; Yan, Y.; Valtchev, V.; Qiu, S., Chemically stable polyarylether-based covalent organic frameworks. *Nat. Chem.* **2019**, *11*, 587-594.
- (27) Xu, X.; Wu, X.; Xu, K.; Xu, H.; Chen, H.; Huang, N., Pore partition in two-dimensional covalent organic frameworks. *Nat. Commun.* **2023**, *14*, 3360.
- (28) Gui, B.; Liu, X.; Cheng, Y.; Zhang, Y.; Chen, P.; He, M.; Sun, J.; Wang, C., Tailoring the Pore Surface of 3D Covalent Organic Frameworks via Post-Synthetic Click Chemistry. *Angew. Chem. Int. Ed.* **2022**, *61*, e202113852.
- (29) Zhang, Z.; Kang, C.; Peh, S. B.; Shi, D.; Yang, F.; Liu, Q.; Zhao, D., Efficient Adsorption of Acetylene over CO(2) in Bioinspired Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2022**, *144*, 14992-14996.
- (30) Zeng, Y.; Zou, R.; Zhao, Y., Covalent Organic Frameworks for CO₂ Capture. *Adv. Mater.* **2016**, *28*, 2855-2873.
- (31) Jiang, L.; Tian, Y.; Sun, T.; Zhu, Y.; Ren, H.; Zou, X.; Ma, Y.; Meihaus, K. R.; Long, J. R.; Zhu, G., A Crystalline Polyimide Porous Organic Framework for Selective Adsorption of Acetylene over Ethylene. *J. Am. Chem. Soc.* **2018**, *140*, 15724-15730.
- (32) Jin, F.; Lin, E.; Wang, T.; Geng, S.; Wang, T.; Liu, W.; Xiong, F.; Wang, Z.; Chen, Y.; Cheng, P.; Zhang, Z., Bottom-Up Synthesis of 8-Connected Three-Dimensional Covalent Organic Frameworks for Highly Efficient Ethylene/Ethane Separation. *J. Am. Chem. Soc.* **2022**, *144*, 5643-5652.
- (33) Smith, B. J.; Parent, L. R.; Overholts, A. C.; Beaucage, P. A.; Bisbey, R. P.; Chavez, A. D.; Hwang, N.; Park, C.; Evans, A. M.; Gianneschi, N. C.; Dichtel, W. R., Colloidal Covalent Organic Frameworks. *ACS Cent. Sci.* **2017**, *3* (1), 58-65.
- (34) Gole, B.; Stepanenko, V.; Rager, S.; Grune, M.; Medina, D. D.; Bein, T.; Wurthner, F.; Beuerle, F., Microtubular Self-Assembly of Covalent Organic Frameworks. *Angew. Chem. Int. Ed.* **2018**, *57*, 846-850.
- (35) Jeong, K.; Park, S.; Jung, G. Y.; Kim, S. H.; Lee, Y.-H.; Kwak, S. K.; Lee, S.-Y., Solvent-Free, Single Lithium-Ion Conducting Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2019**, *141*, 5880-5885.
- (36) Diwakara, S. D.; Ong, W. S. Y.; Wijesundara, Y. H.; Gearhart, R. L.; Herbert, F. C.; Fisher, S. G.; McCandless, G. T.; Alahakoon, S. B.; Gassensmith, J. J.; Dodani, S. C.; Smaldone, R. A., Supramolecular Reinforcement of a Large-Pore 2D Covalent Organic Framework. *J. Am. Chem. Soc.* **2022**, *144*, 2468-2473.
- (37) Jin, E.; Asada, M.; Xu, Q.; Dalapati, S.; Addicoat, M. A.; Brady, M. A.; Xu, H.; Nakamura, T.; Heine, T.; Chen, Q.; Jiang, D., Two-dimensional sp² carbon-conjugated covalent organic frameworks. *Science* **2017**, *357*, 673-676.
- (38) Zhuang, X.; Zhao, W.; Zhang, F.; Cao, Y.; Liu, F.; Bi, S.; Feng, X., A two-dimensional conjugated polymer framework with fully sp²-bonded carbon skeleton. *Polym. Chem.* **2016**, *7*, 4176-4181.
- (39) Wang, Z.; Yang, Y.; Zhao, Z.; Zhang, P.; Zhang, Y.; Liu, J.; Ma, S.; Cheng, P.; Chen, Y.; Zhang, Z., Green synthesis of olefin-linked covalent organic frameworks for hydrogen fuel cell applications. *Nat. Commun.* **2021**, *12*, 1982.
- (40) Acharjya, A.; Pachfule, P.; Roeser, J.; Schmitt, F. J.; Thomas, A., Vinylene-Linked Covalent Organic Frameworks by Base-Catalyzed Aldol Condensation. *Angew. Chem. Int. Ed.* **2019**, *58*, 14865-14870.
- (41) Xu, S.; Richter, M.; Feng, X., Vinylene-Linked Two-Dimensional Covalent Organic Frameworks: Synthesis and Functions. *Acc. Mater. Res.* **2021**, *2*, 252-265.
- (42) Bi, S.; Zhang, Z.; Meng, F.; Wu, D.; Chen, J.-S.; Zhang, F., Heteroatom-Embedded Approach to Vinylene-Linked Covalent Organic Frameworks with Isoelectronic Structures for Photoredox Catalysis. *Angew. Chem. Int. Ed.* **2022**, *61*, e202111627.
- (43) Wang, S.; Li, X.-X.; Da, L.; Wang, Y.; Xiang, Z.; Wang, W.; Zhang, Y.-B.; Cao, D., A Three-Dimensional sp² Carbon-Conjugated Covalent Organic Framework. *J. Am. Chem. Soc.* **2021**, *143*, 15562-15566.
- (44) Li, Y.-J.; Cui, W.-R.; Jiang, Q.-Q.; Wu, Q.; Liang, R.-P.; Luo, Q.-X.; Qiu, J.-D., A general design approach toward covalent organic frameworks for highly efficient electrochemiluminescence. *Nat. Commun.* **2021**, *12*, 4735.
- (45) Zhang, P.; Wang, Z.; Yang, Y.; Wang, S.; Wang, T.; Liu, J.; Cheng, P.; Chen, Y.; Zhang, Z., Melt polymerization synthesis of a class of robust self-shaped olefin-linked COF foams as high-efficiency separators. *Sci. China Chem.* **2022**, *65*, 1173-1184.
- (46) Zhang, P.; Wang, Z.; Wang, S.; Wang, J.; Liu, J.; Wang, T.; Chen, Y.; Cheng, P.; Zhang, Z., Fabricating Industry-Compatible Olefin-Linked COF Resins for Oxoanion Pollutant Scavenging. *Angew. Chem. Int. Ed.* **2022**, *61*, e202213247.
- (47) Kühne, T. D.; Iannuzzi, M.; Del Ben, M.; Rybkin, V. V.; Seewald, P.; Stein, F.; Laino, T.; Khaliullin, R. Z.; Schütt, O.; Schiffmann, F.; Golze, D.; Wilhelm, J.; Chulkov, S.; Bani-Hashemian, M. H.; Weber, V.; Borstnik, U.; Taillefumier, M.; Jakobovits, A. S.; Lazzaro, A.; Pabst, H.; Müller, T.; Schade, R.; Guidon, M.; Andermatt, S.; Holmberg, N.; Schenter, G. K.; Hehn, A.; Bussy, A.; Belleflamme, F.; Tabacchi, G.; Glöckl, A.; Lass, M.; Bethune, I.; Mundy, C. J.; Plessl, C.; Watkins, M.; VandeVondele, J.; Krack, M.; Hutter, J. CP2K: An Electronic Structure and Molecular Dynamics Software Package -Quickstep: Efficient and Accurate Electronic Structure Calculations. *J. Chem. Phys.* **2020**, *152*, 194103.
- (48) Tian Lu, Feiwu Chen, Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580-592.
- (49) Cui, W.-R.; Zhang, C.-R.; Jiang, W.; Li, F.-F.; Liang, R.-P.; Liu, J.; Qiu, J.-D., Regenerable and stable sp² carbon-conjugated

covalent organic frameworks for selective detection and extraction of uranium. *Nat. Commun.* **2020**, *11*, 436.

(50) Pastoetter, D. L.; Xu, S.; Borrelli, M.; Addicoat, M.; Biswal, B. P.; Paasch, S.; Dianat, A.; Thomas, H.; Berger, R.; Reineke, S.; Brunner, E.; Cuniberti, G.; Richter, M.; Feng, X., Synthesis of Vinylene-Linked Two-Dimensional Conjugated Polymers via the Horner-Wadsworth-Emmons Reaction. *Angew. Chem. Int. Ed.* **2020**, *59*, 23620-23625.

(51) Li, S.; Geng, Y.; Teng, B.; Xu, S.; Petkov, P. S.; Liao, Z.; Jost, B.; Liu, Y.; Feng, X.; Wu, B.; Zhang, T., Nature-Inspired Pyrylium Cation-Based Vinylene-Linked Two-Dimensional Covalent Organic Framework for Efficient Sunlight-Driven Water Purification. *Chem. Mater.* **2023**, *35*, 1594-1600.

(52) Wei, S.; Zhang, F.; Zhang, W.; Qiang, P.; Yu, K.; Fu, X.; Wu, D.; Bi, S.; Zhang, F., Semiconducting 2D Triazine-Cored Covalent Organic Frameworks with Unsubstituted Olefin Linkages. *J. Am. Chem. Soc.* **2019**, *141*, 14272-14279.

(53) Zhu, B.; Cao, J. W.; Mukherjee, S.; Pham, T.; Zhang, T.; Wang, T.; Jiang, X.; Forrest, K. A.; Zaworotko, M. J.; Chen, K. J., Pore Engineering for One-Step Ethylene Purification from a Three-Component Hydrocarbon Mixture. *J. Am. Chem. Soc.* **2021**, *143*, 1485-1492.

(54) Wang, Y.; Hao, C.; Fan, W.; Fu, M.; Wang, X.; Wang, Z.; Zhu, L.; Li, Y.; Lu, X.; Dai, F.; Kang, Z.; Wang, R.; Guo, W.; Hu, S.; Sun, D., One-step Ethylene Purification from an Acetylene/Ethylene/Ethane Ternary Mixture by Cyclopentadiene Cobalt-Functionalized Metal-Organic Frameworks. *Angew. Chem. Int. Ed.* **2021**, *60*, 11350-11358.

(55) Xu, Z.; Xiong, X.; Xiong, J.; Krishna, R.; Li, L.; Fan, Y.; Luo, F.; Chen, B., A robust Th-azole framework for highly efficient purifi-

cation of C₂H₄ from a C₂H₄/C₂H₂/C₂H₆ mixture. *Nat. Commun.* **2020**, *11*, 3163.

(56) Liu, J.; Wang, H.; Li, J., Pillar-layer Zn-triazolate-dicarboxylate frameworks with a customized pore structure for efficient ethylene purification from ethylene/ethane/acetylene ternary mixtures. *Chem. Sci.* **2023**, *14*, 5912-5917.

(57) Gu, X. W.; Wang, J. X.; Wu, E.; Wu, H.; Zhou, W.; Qian, G.; Chen, B.; Li, B., Immobilization of Lewis Basic Sites into a Stable Ethane-Selective MOF Enabling One-Step Separation of Ethylene from a Ternary Mixture. *J. Am. Chem. Soc.* **2022**, *144*, 2614-2623.

(58) Wang, Y.; Fu, M.; Zhou, S.; Liu, H.; Wang, X.; Fan, W.; Liu, Z.; Wang, Z.; Li, D.; Hao, H.; Lu, X.; Hu, S.; Sun, D., Guest-molecule-induced self-adaptive pore engineering facilitates purification of ethylene from ternary mixture. *Chem* **2022**, *8*, 3263-3274.

