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# High-capacity sieving of C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> by a copper-based MOF with interconnected gourd-shaped channels

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Targeting the challenging purification of electronic-grade C<sub>3</sub>F<sub>8</sub>, we report the size-sieving separation of C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> by a robust copper-based metal–organic framework, CuHTPO, that features a distinctive interconnected “gourd”-shaped pore architecture. This compound completely excludes C<sub>3</sub>F<sub>8</sub> while strongly adsorbing C<sub>3</sub>F<sub>6</sub>, achieving an adsorption capacity as high as 71.3 cm<sup>3</sup> g<sup>−1</sup> at 298 K and 100 kPa. Dynamic breakthrough experiments demonstrate the direct production of ultra-high-purity C<sub>3</sub>F<sub>8</sub> (>5N) from a C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> (10 : 90, v/v) gas mixture. The underlying size-sieving-based separation mechanism is corroborated by *in situ* infrared spectroscopy and density functional theory calculations.

## Introduction

Perfluoropropane (C<sub>3</sub>F<sub>8</sub>), owing to its unique carbon-to-fluorine ratio (C/F = 0.375) and favorable thermodynamic properties, exhibits an excellent process window in HARC (high aspect ratio contact) etching and CVD (chemical vapor deposition) chamber cleaning.<sup>1</sup> However, as process nodes approach near-zero defect tolerance, the purity requirement for C<sub>3</sub>F<sub>8</sub> has been elevated to above 99.999% (5N).<sup>2–5</sup> Beyond the electronics industry, C<sub>3</sub>F<sub>8</sub> plays an irreplaceable role in the medical field particularly in complex vitreoretinal surgeries, where similarly stringent purity standards are required.<sup>6</sup> The presence of any toxic impurities may lead to irreversible damage to the retinal neuroepithelium or unintended elevation of intraocular pressure,<sup>7,8</sup> potentially resulting in severe clinical complications. C<sub>3</sub>F<sub>6</sub> is one of the most ubiquitous impurities encountered during both industrial purification and exhaust gas recovery of C<sub>3</sub>F<sub>8</sub>.<sup>9–13</sup> Owing to the small boiling point difference between C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> ( $\Delta T_b \approx 7.3$  K), achieving >5N purity *via* cryogenic distillation requires exceptionally high reflux ratios and oversized distillation columns, resulting in prohibitive energy consumption and capital costs.<sup>14–16</sup> Consequently, the development of efficient and low-energy separation strategies for C<sub>3</sub>F<sub>6</sub> removal from C<sub>3</sub>F<sub>8</sub> is of critical industrial importance.

Adsorptive separation utilizing porous materials has emerged as a compelling alternative to cryogenic distillation, driven by its superior energy efficiency and lower capital expenditure.<sup>17</sup> Conventional adsorbents, exemplified by activated carbon and zeolites, have demonstrated the potential for physical discrimination of C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>.<sup>18–23</sup> Metal–organic frameworks (MOFs), exhibiting remarkable tunability in pore size, topology, and surface chemistry, hold particularly promise for precise separation of physicochemically similar molecules.<sup>24–31</sup> Given the ultrahigh purity requirement of electronic-grade C<sub>3</sub>F<sub>8</sub>, molecular sieving is widely considered the most desirable separation mechanism for removing trace C<sub>3</sub>F<sub>6</sub> and directly producing high-purity C<sub>3</sub>F<sub>8</sub>. However, achieving precise size-dependent discrimination is frequently accompanied by a significant reduction in adsorption capacity. Recent strategies involving framework flexibility,<sup>31,32</sup> pore environment engineering,<sup>33,34</sup> electrostatic modulation,<sup>35</sup> and biomimetic design<sup>36</sup> have largely mitigated this limitation, nevertheless, sieving-based MOFs with high adsorption capacity remains highly needed.

In this work, we demonstrate high-capacity sieving of C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> using a MOF featuring large cages accessible through narrow windows. This architecture allows for the maximal packing of guest molecules within the internal voids while maintaining strictly defined apertures for size-selective discrimination.<sup>37–42</sup> The robust copper-based MOF, CuHTPO (H<sub>3</sub>TPO = tris-(4-carboxylphenyl) phosphine oxide), featuring interconnected “gourd”-shaped pore channels, effectively overcomes the “trade-off” between adsorption capacity and size-sieving precision. CuHTPO completely excludes C<sub>3</sub>F<sub>8</sub> while its large internal cavities provide abundant adsorption sites for C<sub>3</sub>F<sub>6</sub>. As a result, it exhibits negligible uptake of C<sub>3</sub>F<sub>8</sub> but a record-high C<sub>3</sub>F<sub>6</sub> adsorption capacity of 71.3 cm<sup>3</sup> g<sup>−1</sup> at 298 K

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and 100 kPa. Dynamic breakthrough experiments further demonstrate the direct production of high-purity  $C_3F_8$  (>5N) from a  $C_3F_6/C_3F_8$  (10:90, v/v) mixture with excellent cycling stability, while *in situ* infrared spectroscopy and density functional theory calculations provide insight into the underlying separation mechanism.

## Results and discussion

**CuHTPO** was synthesized *via* a slightly modified procedure based on a previously reported method,<sup>43</sup> with detailed synthetic protocols provided in the SI. Briefly,  $Cu(NO_3)_2 \cdot 3H_2O$  and  $H_3TPO$  were subjected in a mixed solvent of *N,N*-dimethylformamide/ $H_2O$ /methanol, and the subsequent solvothermal reaction afforded crystals of **CuHTPO** (Fig. S1 and S2). It crystallizes in the orthorhombic crystal system with the space group *Pbcn*. The framework is constructed from phosphine oxide ligand  $HTPO^{2-}$  coordinated to classical paddlewheel-type  $Cu_2(COO)_4$  secondary building units (SBUs) (Fig. 1a). Each  $HTPO^{2-}$  ligand laterally bridges two copper clusters through two carboxylate groups, while a phosphine oxide moiety coordinates monodentately to a copper center along the axial direction; notably, the non-coordinated carboxylic acid groups engage in hydrogen-bonding interactions with carboxylate groups from neighboring ligands (Fig. 1b). **CuHTPO** assembles into a robust three-dimensional network, featuring pore channels extending along the *a* axis that exhibit a characteristic gourd-like architecture composed of alternating large

cavities of approximately 6.9 Å and narrow pore apertures of about 5.5 Å (Fig. 1c). Distinct from conventional one-dimensional gourd-shaped channels,<sup>44,45</sup> the pores of **CuHTPO** form a two-dimensional interconnected “gourd”-shaped channel system propagating along the *ac* plane, in which large cavities are interconnected by four narrow apertures (Fig. 1d). This unique pore topology not only mitigates the intrinsic trade-off between selectivity and adsorption capacity in molecular sieving but also provides multiple and efficient diffusion pathways for guest molecules within the framework.

The phase purity of as-synthesized **CuHTPO** was confirmed by powder X-ray diffraction (PXRD). As shown in Fig. S3, the PXRD patterns of the as-synthesized and methanol-exchanged samples match well with the simulated pattern derived from single-crystal data. Notably, the activated sample and the sample after adsorption measurements retain identical diffraction features, indicating full preservation of crystallinity throughout activation and adsorption processes. Thermogravimetric analysis (TGA) of the as-synthesized sample reveals continuous mass loss upon heating, whereas the methanol-exchanged sample exhibits an extended plateau up to 320 °C (Fig. S4). Furthermore, the chemical and thermal stability of **CuHTPO** were systematically investigated. The material was immersed in various organic solvents and aqueous solutions with pH values ranging from 3 to 9 for seven days. PXRD analyses reveal that the framework structure is largely preserved in different organic solvents (Fig. S5), while maintaining good structural integrity in mildly acidic aqueous media (Fig. S6).

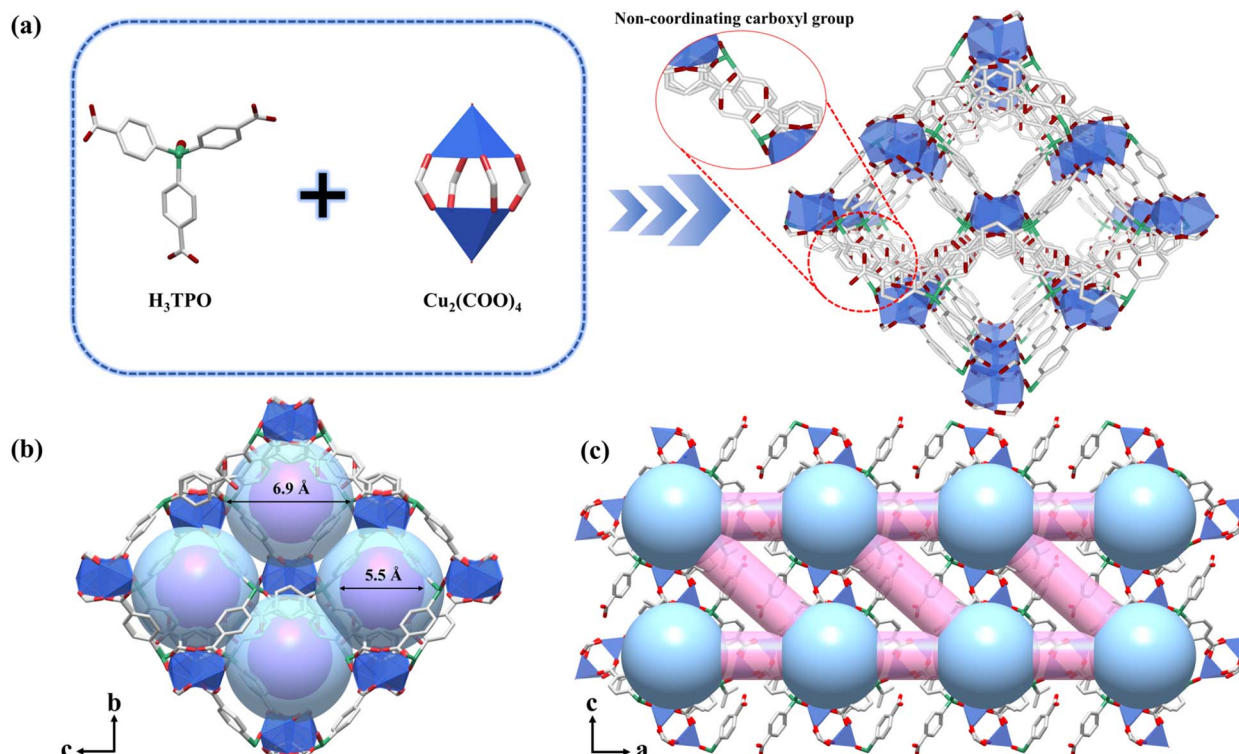


Fig. 1 Crystal structure of CuHTPO. (a) 3D structure built from  $H_3TPO$  and  $Cu_2(COO)_4$ . (b and c) Cavities and 2D channels of CuHTPO. Color scheme: Cu, blue; O, red; C, gray; P, green.



This stability is particularly relevant considering that industrial production of  $C_3F_8$  typically introduces trace amounts of acidic impurities,<sup>46</sup> rendering the crude product weakly acidic. Therefore, materials exhibiting resistance to mildly acidic environments are better suited for practical separation processes in such systems. In addition, variable-temperature *in situ* PXRD measurements under a nitrogen atmosphere demonstrate that the crystalline structure of **CuHTPO** remains essentially intact up to 320 °C (Fig. S7). Combined with its stability in various solvents, this robustness enables the use of more rigorous yet efficient solvent-exchange and activation procedures. The permanent porosity of **CuHTPO** was evaluated by  $N_2$  adsorption at 77 K, revealing two types of pores with diameters of 5.5 and 6.8 Å, respectively (Fig. 2a and S8), in good agreement with the crystal structure. The adsorption displays an  $N_2$  uptake of  $239 \text{ cm}^3 \text{ g}^{-1}$ , and a corresponding Brunauer–Emmett–Teller (BET) surface area of  $1000.3 \text{ m}^2 \text{ g}^{-1}$  (Fig. S9).

The robust framework and precisely defined pore dimensions of **CuHTPO** prompted us to evaluate its adsorption and separation performance toward  $C_3F_6$  and  $C_3F_8$ . Single-component adsorption isotherms for  $C_3F_6$  and  $C_3F_8$  were measured at 273, 298, and 308 K (Fig. 2b). Across this temperature range, **CuHTPO** exhibits negligible adsorption of  $C_3F_8$ , whereas a typical type-I adsorption profile is observed for  $C_3F_6$ .

At 298 K and 100 kPa, **CuHTPO** delivers a substantial  $C_3F_6$  uptake of  $71.6 \text{ cm}^3 \text{ g}^{-1}$  ( $3.2 \text{ mmol g}^{-1}$ ). These results clearly demonstrate that **CuHTPO** is capable of completely excluding the bulkier  $C_3F_8$  while efficiently adsorbing  $C_3F_6$ , highlighting its potential for purifying  $C_3F_8$  by removing trace  $C_3F_6$ . Notably, the  $C_3F_6$  adsorption capacity of **CuHTPO** surpasses previously reported molecular-sieving-based benchmark MOFs for  $C_3F_6/C_3F_8$  separation, including Ca-tcpb<sup>31</sup> ( $44.8 \text{ cm}^3 \text{ g}^{-1}$ ), Ni(INA)<sub>2</sub>-NH<sub>2</sub> (ref. 33) ( $56.7 \text{ cm}^3 \text{ g}^{-1}$ ), Zr-PMA<sup>34</sup> ( $59.1 \text{ cm}^3 \text{ g}^{-1}$ ), Zn-bzx-CF<sub>3</sub> (ref. 35) ( $47.0 \text{ cm}^3 \text{ g}^{-1}$ ), and CoFA<sup>36</sup> ( $44.8 \text{ cm}^3 \text{ g}^{-1}$ ) (Fig. 2d and Table S3). Adsorption kinetics measurements reveal that **CuHTPO** takes up  $C_3F_6$  quickly, whereas  $C_3F_8$  remains essentially being excluded, confirming its selective molecular exclusion behavior (Fig. 2c). The calculated diffusion time constant for  $C_3F_6$  ( $3.3 \times 10^{-3} \text{ s}^{-1}$ ) surpasses that of  $C_3F_8$  ( $6.4 \times 10^{-5} \text{ s}^{-1}$ ) by a factor of over 50 (Fig. S10). We attribute this precise size-sorting to the optimal pore window of the large-cavity-small-aperture architecture of **CuHTPO**.

To quantitatively evaluate the binding strength of  $C_3F_6$  and  $C_3F_8$  within the **CuHTPO** framework, differential scanning calorimetry (DSC) measurements were performed at 298 K. The adsorption enthalpy ( $\Delta H_{\text{ads}}$ ) for  $C_3F_6$  was determined to be  $43.02 \text{ kJ mol}^{-1}$ , whereas the value for  $C_3F_8$  was negligible (Fig. 3a). Furthermore, the isosteric heat of adsorption ( $Q_{\text{st}}$ )

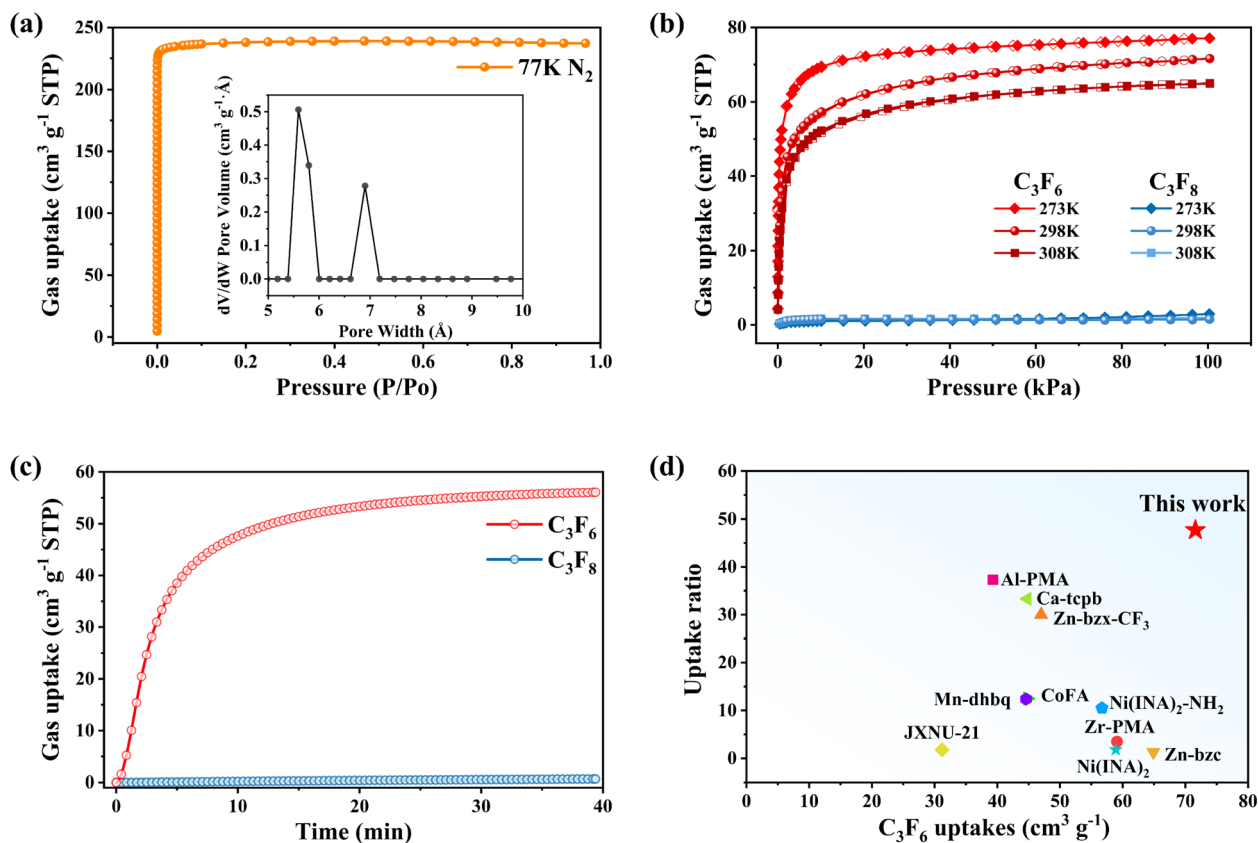


Fig. 2 (a)  $N_2$  adsorption isotherms of **CuHTPO** measured at 77 K (inset: pore size distribution derived from the DFT method). (b) Single-component adsorption isotherms of  $C_3F_6$  and  $C_3F_8$  on **CuHTPO** measured at different temperatures. (c) Adsorption kinetics of  $C_3F_6$  and  $C_3F_8$  obtained at 298 K and a partial pressure of 0.5 bar. (d) Comparison of the  $C_3F_6/C_3F_8$  uptake ratio and the  $C_3F_6$  uptake at 298 K and 100 kPa for **CuHTPO** and representative benchmark material.



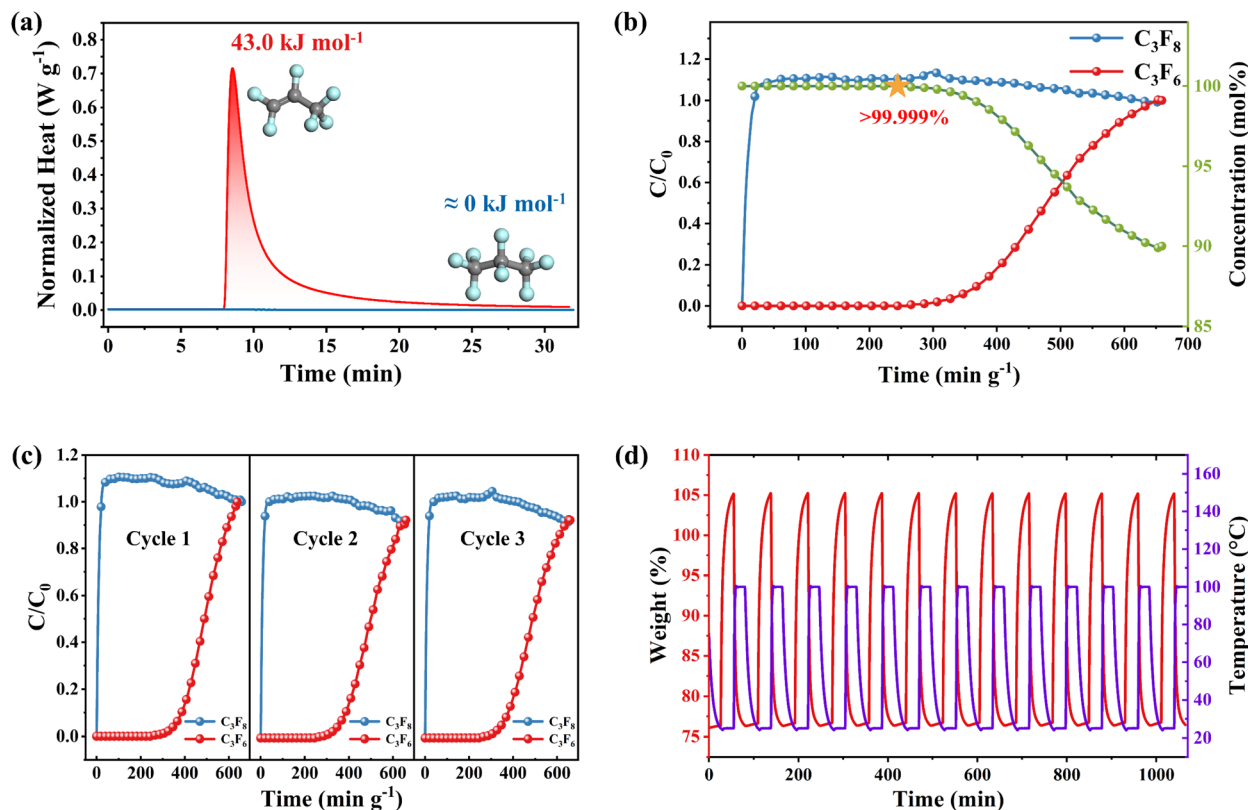


Fig. 3 (a) Differential scanning calorimetry (DSC)-derived adsorption enthalpies of CuHTPO toward  $C_3F_6$  and  $C_3F_8$ . (b) Binary breakthrough curves of a  $C_3F_6/C_3F_8$  (10 : 90, v/v) mixture recorded at 298 K using a fixed-bed column packed with CuHTPO; The purity of  $C_3F_8$  exceeded 99.999% before the breakthrough of  $C_3F_6$ . (c) Comparison of three consecutive dynamic separation cycles. (d)  $C_3F_6$  adsorption-desorption cycling performance of CuHTPO over 10 consecutive cycles at 298 K.

calculated from the  $C_3F_6$  isotherms at various temperatures is  $\approx 38.7 \text{ kJ mol}^{-1}$  (Fig. S11–S16), generally matching the adsorption enthalpy measured by DSC. On this basis, the dynamic separation performance of CuHTPO toward the  $C_3F_6/C_3F_8$  mixture was further evaluated at 298 K using a fixed-bed column packed with CuHTPO under a feed composition of  $C_3F_6/C_3F_8$  (10 : 90, v/v). As shown in Fig. 3b,  $C_3F_8$  eluted immediately upon introduction of the gas mixture, whereas  $C_3F_6$  was retained in the column and did not break through until approximately  $240 \text{ min g}^{-1}$ , thereby enabling the production of ultrapure  $C_3F_8$  (>99.999%) with a high yield of  $323.65 \text{ cm}^3 \text{ g}^{-1}$ . Furthermore, subsequent adsorption-desorption breakthrough cycling experiments, in which the column was regenerated under a He flow at 423 K, revealed nearly identical breakthrough profiles over three consecutive cycles (Fig. 3c), demonstrating the excellent recyclability and cycling stability of CuHTPO.

In addition, to systematically assess its long-term recyclability, temperature-swing adsorption-desorption cycling tests were conducted, during which the sample was exposed to pure  $C_3F_6$  at 298 K followed by regeneration under an  $N_2$  atmosphere at 373 K. Notably, no discernible loss in uptake capacity was observed over 10 consecutive cycles (Fig. 3d), highlighting the structural stability and reusability of CuHTPO.

To gain deeper insights into the adsorption mechanism of perfluorinated gases within the CuHTPO framework, *in situ*

infrared (IR) spectroscopy measurements were performed (Fig. 4a and b). Upon activation, approximately 20 Torr of pure  $C_3F_6$  or  $C_3F_8$  was introduced into the IR cell, and difference spectra at various time intervals were obtained by subtracting the activated-state spectrum from the adsorption spectra. As shown in Fig. 4a and b, upon introduction of  $C_3F_6$ , a red shift of approximately  $5 \text{ cm}^{-1}$  was observed in the  $1193\text{--}1178 \text{ cm}^{-1}$  region, which can be assigned to the asymmetric C–F stretching vibration ( $\nu_{\text{as}}$ ) of  $C_3F_6$ , while a distinct negative band appears around  $1000 \text{ cm}^{-1}$ , attributed to the in-plane bending vibration of aromatic C–H ( $\delta$ ), indicating that this mode is sensitive to guest occupancy and suggesting the presence of specific host-guest interactions dominated by C–H $\cdots$ F hydrogen bonding between  $C_3F_6$  and the framework; in contrast, upon exposure to  $C_3F_8$ , no significant changes were observed in the aromatic C–H in-plane deformation region and only gas-phase C–F vibrational features were detected near  $1000 \text{ cm}^{-1}$ . These results directly demonstrate, at the molecular level, that CuHTPO discriminates  $C_3F_6$  from  $C_3F_8$  through a molecular sieving mechanism.

Density functional theory (DFT) calculations further corroborated the conclusions drawn from the *in situ* IR experiments. As illustrated in Fig. 4c,  $C_3F_6$  preferentially resides in the corner regions of the pore, where the dominant interactions arise from multiple C–F $\cdots$ H hydrogen bonds formed between fluorine atoms of  $C_3F_6$  and hydrogen atoms on the phenyl rings



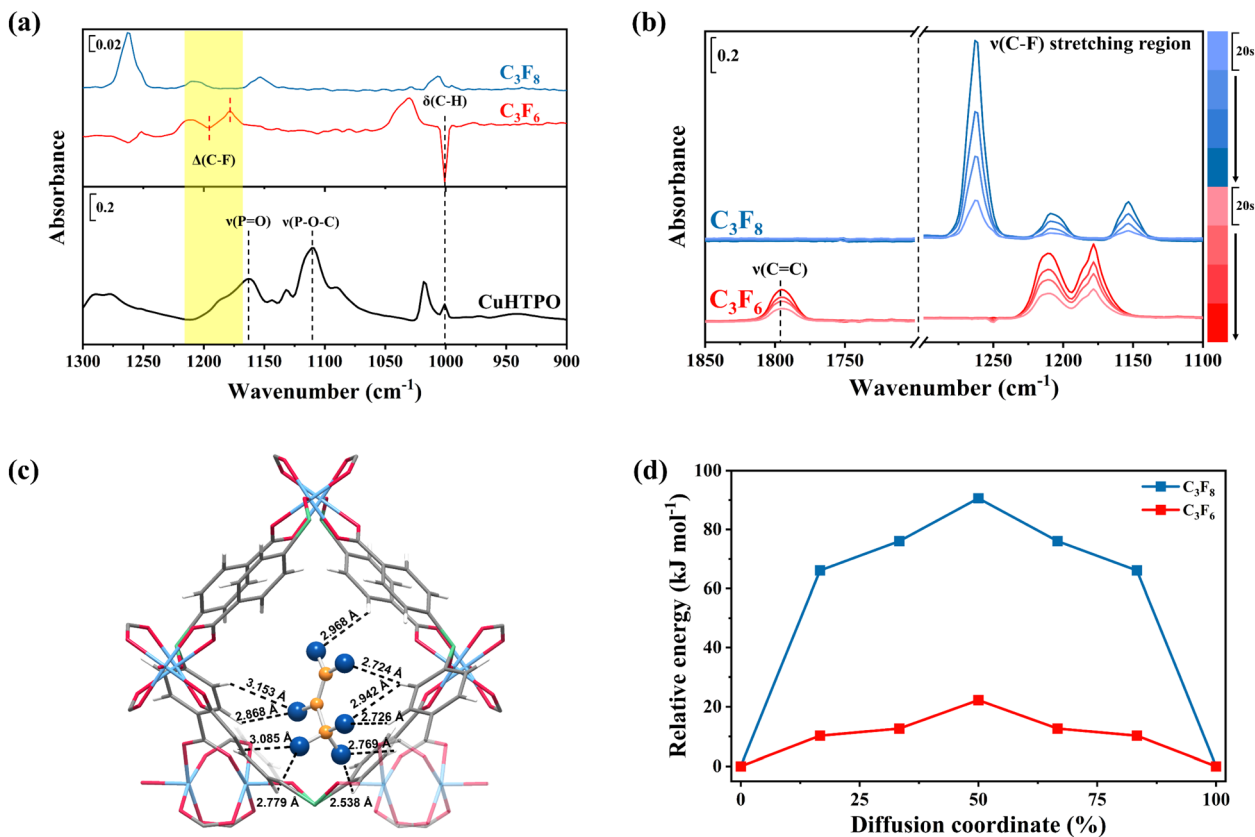


Fig. 4 IR difference spectra of CuHTPO upon loading  $C_3F_6$  and  $C_3F_8$  ( $\approx 20$  Torr) at 298 K: (a) referenced to the activated sample under vacuum, with gas-phase signals subtracted and (b) time-resolved spectra collected at 20 min intervals. (c) The optimal adsorption sites of  $C_3F_6$  on CuHTPO. (d) DFT-calculated energy profiles and relative energies for  $C_3F_6$  and  $C_3F_8$ .

of the framework, with  $F\cdots H$  interaction distances ranging from 2.538 to 3.153 Å (indicated by black dashed lines). To further validate the molecular sieving mechanism of CuHTPO toward  $C_3F_6$  and  $C_3F_8$ , diffusion energy barrier calculations were performed. The calculated energy barrier for  $C_3F_6$  is  $22.2 \text{ kJ mol}^{-1}$ , whereas that for  $C_3F_8$  is as high as  $90.6 \text{ kJ mol}^{-1}$  (Fig. 4d), confirming that the diffusion of  $C_3F_8$  is essentially prohibited. In addition, the calculated binding energy of  $C_3F_6$  is  $40.76 \text{ kJ mol}^{-1}$ , which is in good agreement with the results obtained from DSC measurements. The charge density difference analysis reveals pronounced electron redistribution around the pore apertures and metal–ligand coordination sites upon  $C_3F_6$  adsorption, indicating strong host–guest interactions accompanied by significant molecular polarization (Fig. S18). Consistently, electrostatic potential calculations show an overall positively charged framework and a negatively charged  $C_3F_6$  molecule, confirming a favorable electrostatic affinity between the guest and the framework (Fig. S19). These theoretical results are in excellent agreement with the experimental adsorption behavior, further confirming that the optimal pore aperture of CuHTPO enables effective size-exclusive molecular sieving for  $C_3F_6/C_3F_8$  separation.

## Conclusions

We have demonstrated here the high-capacity size-sieving separation of  $C_3F_6$  and  $C_3F_8$  by a stable and robust copper-based metal–organic framework, CuHTPO. The unique coordination mode between the phosphine oxide-carboxylate ligand and copper nodes not only significantly enhances the structural stability of CuHTPO, but also constructs a distinctive interconnected “gourd”-shaped pore architecture, in which large cavities are connected through narrow pore apertures. This pore configuration effectively breaks the trade-off between selectivity and adsorption capacity commonly observed in conventional molecular-sieving MOFs, while simultaneously maintaining excellent framework robustness. Binary dynamic breakthrough experiments demonstrate that CuHTPO can stably produce ultra-high-purity  $C_3F_8$  (>99.999%) over multiple cycles. Furthermore, *in situ* infrared spectroscopy combined with density functional theory calculations elucidates the interaction strengths of  $C_3F_6$  and  $C_3F_8$  within CuHTPO at the molecular level and reveals the underlying separation mechanism. This work provides important structure–performance relationship insights for the development of high-performance adsorbents for  $C_3F_6/C_3F_8$  separation under stringent purity requirements.



## Author contributions

H. Wang and L. Yu conceived and designed the project. M. Gao provided conceptual guidance. Z. Wang synthesized the compounds and performed PXRD analysis, stability tests, adsorption measurements, and breakthrough experiments. M.-Y. Zhou performed theoretical calculations. S. Li and X. Zhou provided technical support for the breakthrough tests. Y. Wu and F.-A. Guo conducted the *in situ* infrared spectroscopy experiments. Z. Wang, S. Mao, and L. Yu wrote the first draft of the manuscript. All authors contributed to the discussion of the results and the revision of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

CCDC 2544357 contains the supplementary crystallographic data for this paper.<sup>47</sup>

Data associated to the article are available in the supplementary information (SI). Supplementary information: experimental methods, PXRD analysis, TGA curves, additional adsorption isotherms, calculation adsorption selectivity and heat for CuHTPO. See DOI: <https://doi.org/10.1039/d6sc01756h>.

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## Notes and references

- 1 K. Kim, C. Oh, N.-E. Lee, J. Kim, J. Bae, G. Yeom and S. Yoon, *J. Vac. Sci. Technol. B*, 2004, **22**, 483–488.
- 2 M. B. Chang and J.-S. Chang, *Ind. Eng. Chem. Res.*, 2006, **45**, 4101–4109.
- 3 F. Illuzzi, H. Thewissen and J. Integr, *Environ. Sci.*, 2010, **7**, 201–210.
- 4 W.-T. Tsai, H.-P. Chen and W.-Y. Hsien, *J. Loss Prev. Process Ind.*, 2002, **15**, 65–75.
- 5 R. S. Prabhakar, T. C. Merkel, B. D. Freeman, T. Imizu and A. Higuchi, *Macromolecules*, 2005, **38**, 1899–1910.
- 6 S. Chang, H. A. Lincoff, D. J. Coleman, W. Fuchs and M. E. Farber, *Ophthalmology*, 1985, **92**, 651–656.
- 7 N. C. Steinle, D. S. Dhoot, C. Q. Ruiz, A. A. Castellarin, D. J. Pieramici, R. F. See, S. C. Couvillion, M. a. A. Nasir and R. L. Avery, *Retina*, 2017, **37**, 643–650.
- 8 I. A. Rodrigues, A. N. Stangos, D. A. McHugh and T. L. Jackson, *Am. J. Ophthalmol.*, 2013, **155**, 270–276.
- 9 M. Basu, *Understanding Fluoride and Fluorocarbon Toxicity: An Overview*, Springer Nature Singapore, Singapore, 2024.
- 10 R. D. Chambers, *Fluorine in organic chemistry*, John Wiley & Sons, New York, 2004.
- 11 Y. Oda, R. Suzuki, T. Mori, H. Takahashi, H. Natsugari, D. Omata, J. Unga, H. Uruga, M. Sugii and S. Kawakami, *Int. J. Pharm.*, 2015, **487**, 64–71.
- 12 G. Casini, P. Loiudice, S. De Cillà, P. Radice and M. Nardi, *Int. J. Retina Vitreous*, 2016, **2**, 10.
- 13 S. M. McClintic, J. D. Grodsky and G. G. Emerson, *Retin. Physician*, 2025, **22**, 8–10.
- 14 X. Cao, R. Liu, Y. Lu, S. Jia and X. Yuan, *Sep. Purif. Technol.*, 2021, **279**, 119813.
- 15 D. S. Sholl and R. P. Lively, *Nature*, 2016, **532**, 435–437.
- 16 F. Fang and J. Joffe, *J. Chem. Eng. Data*, 1966, **11**, 376–379.
- 17 J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869–932.
- 18 P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864.
- 19 W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133.
- 20 M. Menk, C. Bläker, C. Pasel and D. Bathen, *Microporous Mesoporous Mater.*, 2025, **402**, 113988.
- 21 Z. Du, Z. Wu, X. Li, W. Zhang, J. Huang, Y. Wu, L. Zhu and J. Xiao, *Sep. Purif. Technol.*, 2026, **383**, 136249.
- 22 Y. Fu, L. Sheng, W. Xia, G. Hai, J. Yan, L. Chen, Q. Yang, Z. Zhang, Q. Ren and Z. Bao, *Ind. Chem. Mater.*, 2025, **3**, 567–577.
- 23 X. Wei, S. Du, Y. Zheng, J. Peng, G. miao, X. Meng, X. Li, X. Li and J. Xiao, *AlChE J.*, 2026, **72**, e70155.
- 24 O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401–10402.
- 25 B. M. Ji, D. Y. Zhang, R. Liang, G. H. Kang, Q. Y. Zhu and D. S. Deng, *Cryst. Growth Des.*, 2021, **21**, 482–489.
- 26 P. A. P. Mendes, P. Horcajada, S. Rives, H. Ren, A. E. Rodrigues, T. Devic, E. Magnier, P. Trens, H. Jobic, J. Ollivier, G. Maurin, C. Serre and J. A. C. Silva, *Adv. Funct. Mater.*, 2014, **24**, 7666–7673.
- 27 S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5415–5418.
- 28 H. Furukawa, K. E. Cordova, M. O’Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.
- 29 L. Lan, S. J. Wei, W. Xia, Q. Zhang, Y. Liu, C. Bao, M. Cheng, Z. Y. Qian, L. L. Wang, Y. L. Li, M. Feng, Z. Bao and T. L. Hu, *Angew Chem. Int. Ed. Engl.*, 2026, **72**, e6037453.
- 30 H.-F. Ma, X.-P. Fu, H.-P. Xiao, L. Chen, Q.-Y. Liu and Y.-L. Wang, *Sci. China Chem.*, 2026, DOI: [10.1007/s11426-025-3177-3](https://doi.org/10.1007/s11426-025-3177-3).
- 31 W. Xia, Y. Yang, L. Sheng, Z. Zhou, L. Chen, Z. Zhang, Z. Zhang, Q. Yang, Q. Ren and Z. Bao, *Sci. Adv.*, 2024, **10**, eadj6473.
- 32 L. Sheng, W. Xia, Y. Fu, J. Yan, Z. Zhou, F. Zheng, F. Shen, L. Chen, Z. Zhang, Q. Yang, Q. Ren and Z. Bao, *ACS Mater. Lett.*, 2025, **7**, 2080–2087.
- 33 X. Lv, M. Zheng, Z. Jiang, H. Huang, Z. Bao and C. Zhong, *Chem. Eng. J.*, 2025, **522**, 168005.
- 34 W. Xia, Z. Zhou, C. Xia, L. Chen, L. Sheng, F. Zheng, Z. Zhang, Q. Yang, Q. Ren and Z. Bao, *Angew. Chem., Int. Ed.*, 2025, **64**, e202503505.



- 35 M. Zheng, W. Xue, T. Yan, Z. Jiang, Z. Fang, H. Huang and C. Zhong, *Angew. Chem., Int. Ed.*, 2024, **63**, e202401770.
- 36 W. Xia, Z. Zhou, L. Sheng, L. Chen, F. Shen, F. Zheng, Z. Zhang, Q. Yang, Q. Ren and Z. Bao, *Nat. Commun.*, 2024, **15**, 8716.
- 37 J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477–1504.
- 38 H. Wang and J. Li, *Acc. Chem. Res.*, 2019, **52**, 1968–1978.
- 39 X.-W. Zhang, D.-D. Zhou and J.-P. Zhang, *Chem*, 2021, **7**, 1006–1019.
- 40 H. Wang, Y. Liu and J. Li, *Adv. Mater.*, 2020, **32**, 2002603.
- 41 L. Li, J. G. Bell, S. Tang, X. Lv, C. Wang, Y. Xing, X. Zhao and K. M. Thomas, *Chem. Mater.*, 2014, **26**, 4679–4695.
- 42 B. Van de Voorde, B. Bueken, J. Denayer and D. De Vos, *Chem. Soc. Rev.*, 2014, **43**, 5766–5788.
- 43 W. R. Lee, D. W. Ryu, W. J. Phang, J. H. Park and C. S. Hong, *Chem. Commun.*, 2012, **48**, 10847–10849.
- 44 L. Yu, X. Dong, Q. Gong, S. R. Acharya, Y. Lin, H. Wang, Y. Han, T. Thonhauser and J. Li, *J. Am. Chem. Soc.*, 2020, **142**, 6925–6929.
- 45 L. Yu, S. Ullah, H. Wang, Q. Xia, T. Thonhauser and J. Li, *Angew Chem. Int. Ed. Engl.*, 2022, **61**, e202211359.
- 46 Y. W. Alsmeyer, W. V. Childs, R. M. Flynn, G. G. I. Moore and J. C. Smeltzer, *Electrochemical Fluorination and Its Applications*, Springer US, Boston, 1994.
- 47 CCDC 2544357: Experimental Crystal Structure Determination, 2026, DOI: [10.5517/ccdc.csd.cc2rdm1v](https://doi.org/10.5517/ccdc.csd.cc2rdm1v).

