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# Fine-tuned ultramicroporous carbon materials *via* CO<sub>2</sub> activation for molecular sieving of fluorinated propylene and propane†

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Ultramicroporous carbon materials with precisely engineered pore structures offer a promising pathway for the challenging separation of fluorinated gases with similar physicochemical properties, such as C<sub>3</sub>F<sub>6</sub> (fluorinated propylene) and C<sub>3</sub>F<sub>8</sub> (fluorinated propane). In this work, we report the synthesis of CO<sub>2</sub>-activated porous carbon adsorbents derived from a precursory resin and systematically investigate their molecular sieving behavior for C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> mixtures. Through controlled thermal pyrolysis and stepwise CO<sub>2</sub> activation, we tailored ultramicropore size distributions to selectively exclude or admit target molecules. Adsorption studies reveal that optimal CO<sub>2</sub> activation yields pore sizes that enable effective separation of C<sub>3</sub>F<sub>6</sub> from C<sub>3</sub>F<sub>8</sub>, achieving efficient molecular sieving due to size exclusion effects. Excessive activation, however, generates larger pores that diminish selectivity due to nonspecific affinity for both gases. The findings highlight the importance of ultramicropore control for energy-efficient separation of fluorinated hydrocarbons and provide insights for designing advanced adsorbents for industrial gas purification.

Keywords: Electronic specialty gas (ESGs); Adsorption separation; Phenolic resin-derived carbon; Molecular sieving; C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub>.

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## 1 Introduction

The semiconductor industry, serving as the foundational infrastructure for artificial intelligence (AI) and 5G ecosystems, has achieved atomic-scale fabrication breakthroughs that critically depend on ultrapure electronic specialty gases (ESGs). These gases enable advanced manufacturing processes,<sup>1</sup> with their purity demonstrating a direct correlation to process yield metrics as semiconductor nodes evolve.<sup>2</sup> Perfluoropropane (C<sub>3</sub>F<sub>8</sub>), a plasma etching and chemical vapor deposition (CVD) chamber-cleaning agent, is widely employed due to its etch selectivity and nanoscale aspect ratio control.<sup>3,4</sup> However, industrial production of C<sub>3</sub>F<sub>8</sub>, typically achieved through the fluorination of hexafluoropropylene (C<sub>3</sub>F<sub>6</sub>), invariably results in the presence

of 1–10 mol% impurities.<sup>5,6</sup> The minimal boiling point differential ( $\Delta T_{bp} = 5.7$  K) between C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> renders conventional distillation economically unsustainable for achieving semiconductor-grade purity (5 N/6 N), necessitating energy-intensive multi-column configurations.<sup>7,8</sup>

Adsorptive molecular sieving has emerged as an innovative alternative to fluorocarbon distillation, circumventing thermodynamic limitations through pore-size precision engineering.<sup>9,10</sup> This approach necessitates precise control of pore sizes within the 5.0–8.0 Å range, positioned between the three-dimensional dimensions of C<sub>3</sub>F<sub>6</sub> (7.3 Å × 6.2 Å × 5.1 Å) and C<sub>3</sub>F<sub>8</sub> (7.6 Å × 5.3 Å × 5.1 Å).<sup>11</sup> However, commercial zeolite adsorbents exhibit limited tunability in pore aperture dimensions at the angstrom scale. Moreover, their inherent cation polarization fields promote strong  $\pi$ -complexation with C<sub>3</sub>F<sub>6</sub>,<sup>7,12,13</sup> resulting in energy-intensive, high-temperature regeneration requirements and an increased risk of undesirable olefin polymerization.<sup>14–16</sup> In contrast, although a select group of metal–organic frameworks (MOFs) including Al-PMA,<sup>17</sup> Zn-bzc-CF<sub>3</sub> (ref. 18) and CoFA<sup>19</sup> have demonstrated sieving separation for C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> *via* programmable pore environments, their practical application is constrained by metastable coordination bonds, elevated synthesis costs, and irreversible framework collapse during processing.<sup>20–22</sup> By comparison, carbon molecular

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sieves (CMS) leverage defect-engineered architectures to facilitate physisorption dominated by van der Waals interactions, thereby enabling simplified desorption.<sup>23–25</sup> Their well-developed porosity and tailorable pore architectures position them as industrial benchmarks for the high-efficiency separation of  $C_3F_6$  and  $C_3F_8$  through molecular sieving mechanisms.

Traditional carbon-based adsorbents, such as those derived from coal, suffer from significant structural heterogeneity attributed to variable feedstock compositions, stochastic pyrolysis, and uncontrolled etching during activation, leading to broad pore size distributions.<sup>26–28</sup> Such intrinsic limitations preclude effective molecular sieving for near-isomorphous fluorocarbons like  $C_3F_6/C_3F_8$ . Conversely, synthetic resin-derived carbons offer improved structural predictability due to their periodic crosslinked networks.<sup>29–31</sup> Notably, phenolic resin-derived carbons have demonstrated the potential to engineer microporosity for industrial-scale air ( $N_2/O_2$ ) and  $CO_2/N_2$  separation,<sup>32–34</sup> inspiring efforts to develop targeted narrow-pore architectures for  $C_3F_6/C_3F_8$  separation.

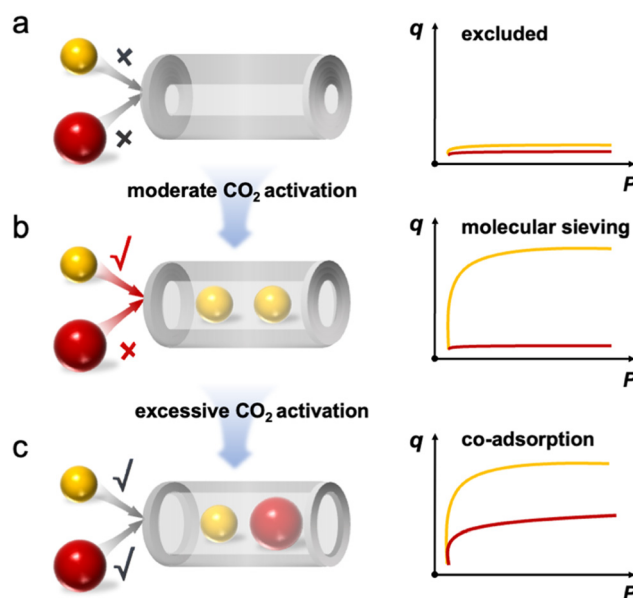
Nevertheless, the inherent pore size distribution in resin-derived carbons restricts the separation of larger fluorocarbon molecules. Additionally, ultra-micropores with narrowly confined dimensions often result in sluggish adsorption kinetics and protracted equilibration times.<sup>35–37</sup> To address this, recent strategies have focused on directionally modulating pore structures to optimize the balance between molecular sieving and diffusivity. For instance, the incorporation of hierarchical mesopores has been explored to expand pore networks and enhance gas diffusion in carbon matrices.<sup>38</sup> Xiao *et al.* demonstrated that hydrothermal temperature modulation enables the synthesis of GC-x materials with tailored micropore expansion, promoting accelerated  $C_3H_6$  diffusion kinetics while preserving effective  $C_3H_8$  exclusion.<sup>39</sup> Such defect-engineered, pore-expansion strategies quantitatively resolve the trade-off between selectivity and diffusion efficiency, offering a universal framework for industrial gas separations with carbon molecular sieves.

Common chemical activation methods are often associated with significant environmental and operational challenges, such as toxic emissions, hazardous waste production, and severe equipment corrosion.<sup>40</sup> Instead, physical activation provides a more environmentally benign alternative.<sup>41</sup> For example, Li's group employed a synergistic  $CO_2$ -steam activation strategy for pore size regulation, wherein  $CO_2$  primarily governs micropore expansion and optimizes pore architectures.<sup>42</sup> Inspired by these insights, we report herein a series of phenolic resin-derived carbon molecular sieves (PRC) synthesized *via*  $CO_2$  physical activation, enabling precise modulation of surface characteristics and pore architecture. By carefully tuning the  $CO_2$  concentration (5–25 vol%) during pyrolysis, we produce carbon materials exhibiting monodisperse ultra-micropores (5.6–8.0 Å) and graded porosity. The resulting

appropriate pore size facilitated precision size-sieving of  $C_3F_8$  concomitant with accelerated kinetic diffusion of  $C_3F_6$  (Scheme 1). The optimized PRC-15 $CO_2$  achieves an exceptional  $C_3F_6$  adsorption capacity (2.34 mmol  $g^{-1}$  at 100 kPa), outstanding dynamic breakthrough performance, and complete  $C_3F_8$  exclusion under ambient conditions—marking the first carbon material to achieve efficient  $C_3F_6/C_3F_8$  sieving separation, surpassing even state-of-the-art MOFs. Additionally, these slightly expanded micropore channels enhance mass transfer kinetics, while ultra-high selectivity is corroborated by molecular dynamics (MD) simulations. The industrial viability of these materials is further substantiated by their cyclic stability, batch-to-batch reproducibility, scalable synthesis, and cost-effectiveness. The successful integration of precision pore engineering with sustainable activation methodologies thus establishes carbon molecular sieves as a disruptive technology for the purification of semiconductor-grade fluorocarbons, addressing critical challenges in next-generation electronics manufacturing.

## 2 Results and discussion

Phenolic resin (PR) was synthesized *via* an emulsion polymerization method by following the previously reports with some modification.<sup>43</sup> Subsequent carbonization under controlled  $CO_2/N_2$  atmospheres (0–25 vol%  $CO_2$ ) yielded



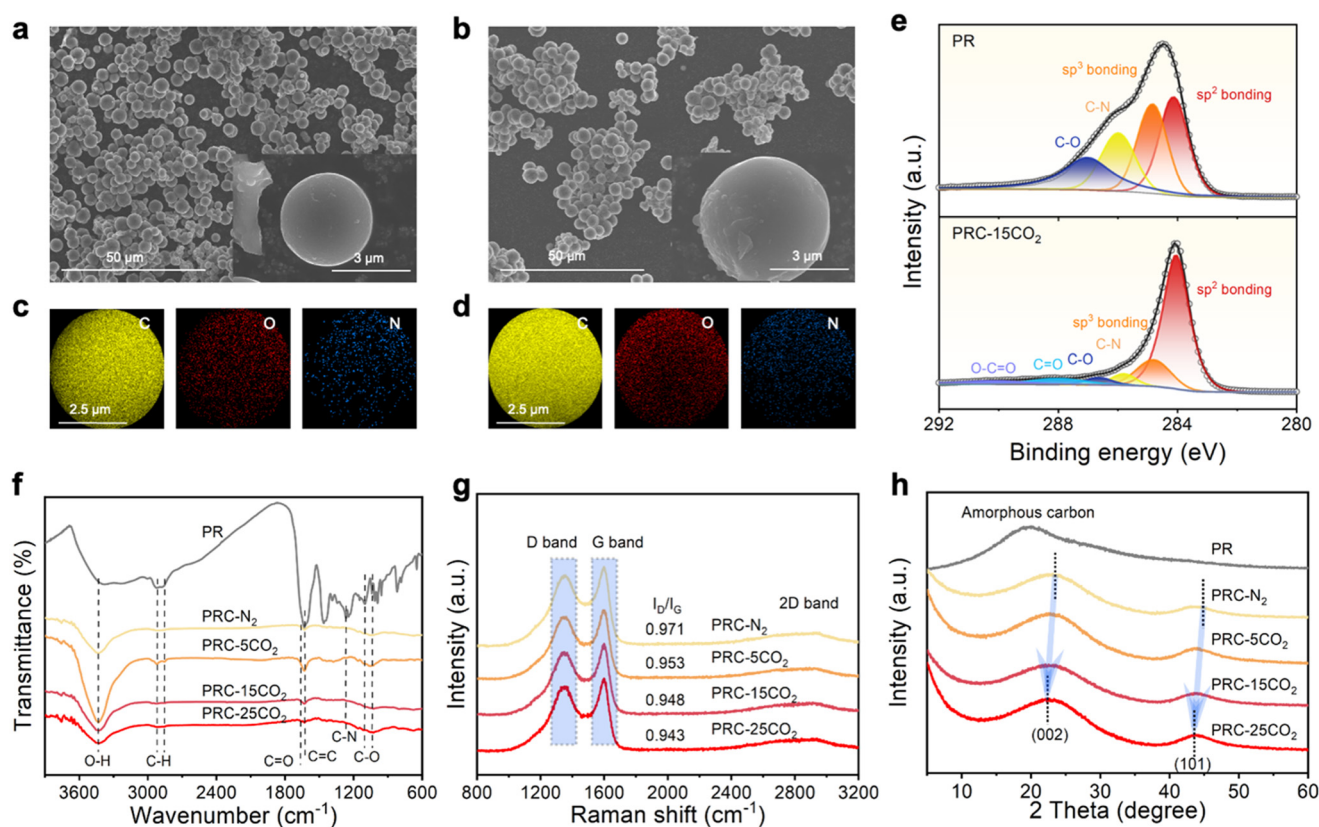
**Scheme 1** Schematic illustration of the synthesis of  $CO_2$ -activated phenolic resin-derived carbon adsorbents and the proposed mechanism of controlled thermal pyrolysis for the development of ultramicropores tailored for  $C_3F_6$  (yellow spheres)/ $C_3F_8$  (red spheres) molecular sieving separation: (a) narrow pores exclude both  $C_3F_6$  and  $C_3F_8$ ; (b) appropriately sized pores, obtained through moderate  $CO_2$  activation, enable the selective molecular sieving of  $C_3F_6/C_3F_8$ ; (c) excessively large pores, resulting from extensive  $CO_2$  activation, display strong affinity toward both  $C_3F_6$  and  $C_3F_8$ , thereby reducing selectivity.



spherical carbon particles with uniform particle size distributions (2–5  $\mu\text{m}$ ), as evidenced by scanning electron microscopy (SEM) (Fig. 1a and b). The progressive evolution of surface roughness, attributed to  $\text{CO}_2$ -mediated etching, clearly demonstrates the active role of  $\text{CO}_2$  in modulating both the chemical composition and the topology of the carbon structures. This is further substantiated by energy-dispersive X-ray spectroscopy (EDS) depth profiling, revealing a volcano-shaped dependence of the C/O ratio on  $\text{CO}_2$  concentration (Fig. 1c and d and Table S1†). Furthermore, X-ray photoelectron spectroscopy (XPS) elucidated a coordinated surface reconstruction process, wherein native C–O (286.9 eV) and C–N (285.0 eV) groups are converted to C=O (288.6 eV) and O–C=O (290.0 eV) species. The observed inconsistency between nitrogen content (higher in elemental analysis, Table S1†) and oxygen functional group abundance (higher in XPS, Table S2†) originated from intrinsic bulk-surface differences in carbon materials. Specifically, nitrogen atoms distribute uniformly throughout the bulk matrix, whereas oxygen-containing functional groups preferentially accumulate at surfaces. This discrepancy is further amplified by XPS's collective detection of multiple oxygen functionalities (C–O, C=O, and O–C=O). The total content of C=O and O–C=O peaks at 5 vol%  $\text{CO}_2$  (Fig. 1e and S1 and Table S2†), mirroring Fourier-transform infrared

spectroscopy (FTIR) observations of quinoid group formation (Fig. 1f) and high-resolution O 1s XPS spectra (Fig. S2 and Table S3†). Newly formed quinone-type C=O groups ( $1670\text{ cm}^{-1}$ ) emerged, with oxygen functionalities displaying a marked volcano-shaped trend (maxima at 5 vol%  $\text{CO}_2$ ), highlighting the dual function of  $\text{CO}_2$  as both etchant and oxidizer. Moreover, the apparent contradiction between the reduced FTIR features (Fig. 1f) and higher oxygen content (Table S1†) in highly activated samples (PRC-15 $\text{CO}_2$  and PRC-25 $\text{CO}_2$ ) is attributed to graphitization-induced peak broadening, the low IR-activity of stable oxygen groups, and conductivity-related background interference.<sup>44–46</sup> In parallel, the carbon matrix exhibited increased ordering, as evidenced by an elevated  $\text{sp}^2/\text{sp}^3$  hybridization ratio and the appearance of graphitic nitrogen species (Fig. S3 and Table S4†), collectively enhancing  $\pi$ -electron delocalization across the carbon lattice.

The observed non-monotonic behavior in structural evolution originates from a dual mechanism paradigm governed by the  $\text{CO}_2$  partial pressure. At  $\text{CO}_2$  concentrations below 5 vol%, selective oxidation prevails, effectively removing metastable oxygen functionalities (C–O–C and C=O) while preserving graphitic domains. This is reflected in Raman spectral analysis by a decrease in the  $I_D/I_G$  ratio from 0.971 to 0.943 (Fig. 1g), indicative of enhanced



**Fig. 1** SEM images of (a) PRC-N<sub>2</sub> and (b) PRC-15CO<sub>2</sub>; elemental mapping images of C, O and N of (c) PRC-N<sub>2</sub> and (d) PRC-15CO<sub>2</sub>; (e) high-resolution spectra of C 1s for phenolic resin and PRC-15CO<sub>2</sub>; (f) FTIR spectra, (g) Raman spectra and (h) X-ray diffraction patterns of phenolic resin precursor and its derived carbon molecular sieves (PRC-N<sub>2</sub>, PRC-5CO<sub>2</sub>, PRC-15CO<sub>2</sub>, and PRC-25CO<sub>2</sub>).



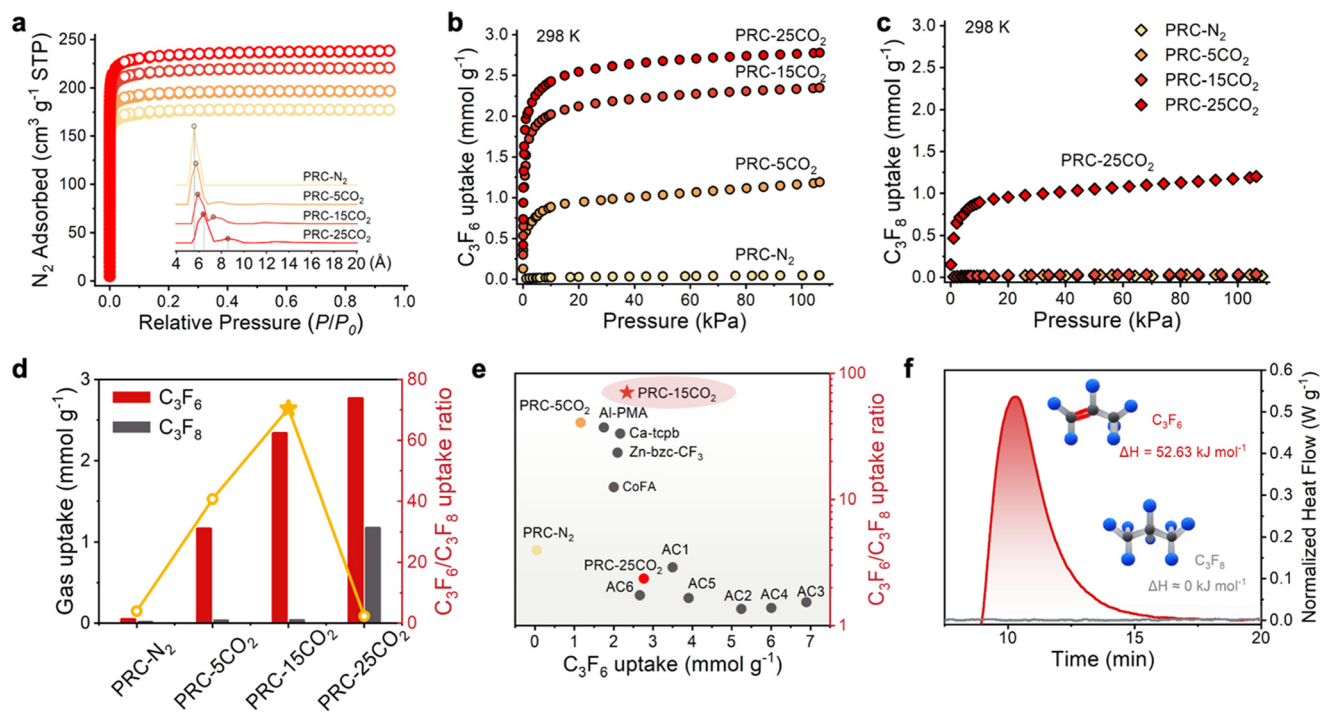


structural order. In contrast, above 5 vol% CO<sub>2</sub>, the Boudouard equilibrium becomes thermodynamically favorable, leading to framework gasification and the generation of microstructural defects. This transition is evidenced by significant increases in specific surface area ( $\Delta S_{\text{BET}} = +202.43 \text{ m}^2 \text{ g}^{-1}$ ) and pore volume expansion ( $\Delta V_{\text{pore}} = +0.090 \text{ cm}^3 \text{ g}^{-1}$ ) (Fig. S4 and Table S5†), demonstrating the concentration-dependent shift in CO<sub>2</sub>'s role from selective etchant to bulk oxidizer. Complementary powder X-ray diffraction (PXRD) analysis (Fig. 1h) further delineates crystallographic evolution: the inclusion of CO<sub>2</sub> induces a continuous shift of the (002) and (101) Bragg reflections toward lower angles, corresponding to lattice expansion. This structural reorganization, driven by preferential etching of amorphous carbon regions, aligns with Raman data indicating improved graphitic ordering.

The diverse physicochemical transformations prompted by varying CO<sub>2</sub> treatments motivated detailed investigation of pore structural evolution using N<sub>2</sub> adsorption-desorption measurements at 77 K (Fig. 2a). All PRC materials exhibited type I isotherms with fully reversible adsorption-desorption profiles (no hysteresis), confirming dominant microporosity. The resulting specific surface area and pore volume clearly reflect the role of CO<sub>2</sub> activation in pore expansion. Narrow pore size distribution (PSD) profiles (Fig. 2a) reveal the prevalence of ultra-micropores (5–7 Å), strategically matched to the kinetic diameters of

C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>. Notably, CO<sub>2</sub>-activated carbon molecular sieves maintain PSD profiles akin to N<sub>2</sub>-annealed variants (PRC-N<sub>2</sub>), although with distinct evolutionary trends: PRC-5CO<sub>2</sub> exhibits initial micropore expansion with the appearance of a broader shoulder (7–9 Å), which becomes more prominent in PRC-15CO<sub>2</sub> ( $V_{>7\text{\AA}} = 0.039 \text{ cm}^3 \text{ g}^{-1}$ ) (Table S5†) due to Boudouard reaction-driven oxidation. This CO<sub>2</sub> concentration-dependent pore architecture integrates ultra-micropores (5–7 Å) for molecular sieving and progressively expanded micropores (7–9 Å) for enhance diffusion, correlating strongly with improved C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> separation efficiency.

Adsorption isotherms for C3 fluorocarbons (Fig. 2b and c) quantitatively assess the influence of CO<sub>2</sub> partial pressure on gas uptake. PRC-25CO<sub>2</sub> exhibits the highest C<sub>3</sub>F<sub>6</sub> saturation capacity (2.77 mmol g<sup>−1</sup> at 100 kPa), but with significant co-adsorption of C<sub>3</sub>F<sub>8</sub> (1.17 mmol g<sup>−1</sup>). This underscores a thermodynamic trade-off: excessive framework etching compromises selectivity by permitting target product loss, emphasizing the necessity for precise pore engineering. In contrast, PRC-5CO<sub>2</sub> and PRC-15CO<sub>2</sub>, achieve nearly exclusive C<sub>3</sub>F<sub>8</sub> exclusion (0.02–0.03 mmol g<sup>−1</sup>), while maintaining substantial C<sub>3</sub>F<sub>6</sub> uptake (1.16 and 2.34 mmol g<sup>−1</sup>, respectively). The almost negligible adsorption observed with PRC-N<sub>2</sub> confirms that CO<sub>2</sub>-mediated pore expansion is essential for generating channels (>5.6 Å) accessible to fluorocarbons. Under saturation, PRC-15CO<sub>2</sub> attains an



**Fig. 2** (a) N<sub>2</sub> adsorption-desorption isotherms at 77 K (the curves from top to bottom correspond to PRC-25CO<sub>2</sub>, PRC-15CO<sub>2</sub>, PRC-5CO<sub>2</sub> and PRC-N<sub>2</sub>) and pore size distributions of phenolic resin-derived carbon molecular sieve materials; adsorption isotherms of (b) C<sub>3</sub>F<sub>6</sub> and (c) C<sub>3</sub>F<sub>8</sub> at 298 K on PRC materials; (d) adsorption isobars (100 kPa) for C<sub>3</sub>F<sub>6</sub> (red) and C<sub>3</sub>F<sub>8</sub> (grey), along with the uptake ratio of C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> (yellow) for PRC materials; (e) adsorbent properties for C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> separation at 298 K and 100 kPa; (f) adsorption heats for C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> on PRC-15CO<sub>2</sub> as determined by TG-DSC.



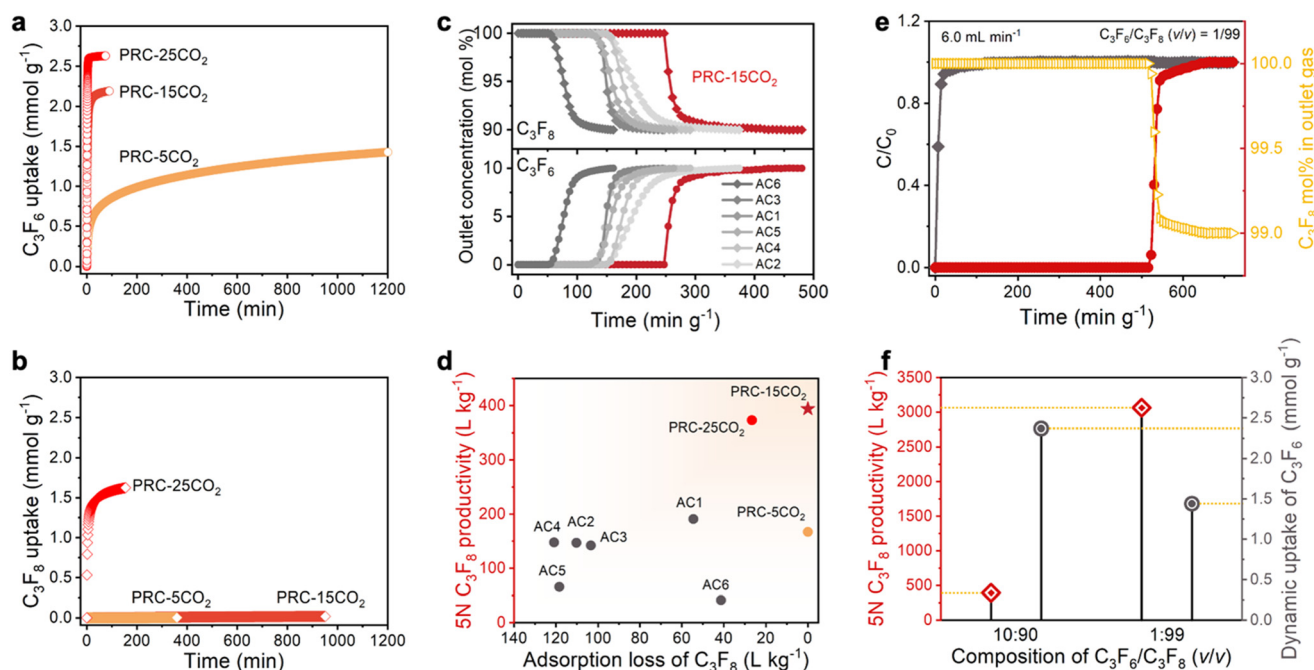
exceptional uptake ratio of 70.48, well exceeding that of PRC-5CO<sub>2</sub> (40.72) and PRC-25CO<sub>2</sub> (2.36) (Fig. 2d). This hierarchy affirms that optimal CO<sub>2</sub> activation (15 vol%) achieves a fine balance between pore expansion and molecular sieving, averting the capacity-selectivity trade-off manifest in over-etched materials.

A comparative assessment against commercial carbon adsorbents (Fig. 2e and S5 and Table S6†) revealed systemic limitations of these materials, characterized by pervasive co-adsorption behavior that significantly undermines both selectivity and process economics. For instance, activated carbon AC3 exhibited the highest C<sub>3</sub>F<sub>6</sub> adsorption capacity (6.90 mmol g<sup>-1</sup>) but demonstrated marginal selectivity (1.53). Among the evaluated carbons, AC1 achieved the highest uptake ratio (2.90), which remains orders of magnitude inferior to that of PRC-15CO<sub>2</sub>. Moreover, PRC-15CO<sub>2</sub> surpassed all reported MOFs in uptake ratio, outperforming CoFA (12.5), Zn-bzc-CF<sub>3</sub> (23.5) and Ca-tcpb (33.3) under identical conditions (298 K and 100 kPa). This dual parameter superiority in both capacity and selectivity establishes PRC-15CO<sub>2</sub> as a disruptive alternative to coordination polymers for fluorocarbon purification.

The observed disparities in adsorption behavior can be rationalized by differences in affinity between adsorbents and adsorbates, as evaluated through thermogravimetry-differential scanning calorimetry (TG-DSC). The heat of adsorption ( $Q_{st}$ ) for C<sub>3</sub>F<sub>6</sub> on PRC-15CO<sub>2</sub> was precisely determined to be 52.63 kJ mol<sup>-1</sup>, while C<sub>3</sub>F<sub>8</sub> exhibited

undetectable interaction, attributable to size exclusion imposed by the micropores of PRC-15CO<sub>2</sub> (Fig. 2f). This moderate  $Q_{st}$  surpasses those of other commercial carbons (Fig. S6 and S7†), positioning PRC-15CO<sub>2</sub> as a readily regenerable adsorbent suitable for industrial separation processes.

To further validate kinetic sieving capabilities, time-dependent uptake profiles for C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> were recorded (Fig. 3a and b). Adsorption equilibrium times for C<sub>3</sub>F<sub>6</sub> decreased markedly with increasing CO<sub>2</sub> concentration, from 1200 min for PRC-5CO<sub>2</sub> to 34 min for PRC-25CO<sub>2</sub>. Correspondingly, the diffusion time constant ( $D'$ ) followed the order PRC-5CO<sub>2</sub> ( $7.49 \times 10^{-5} \text{ s}^{-1}$ ) < PRC-15CO<sub>2</sub> ( $9.15 \times 10^{-4} \text{ s}^{-1}$ ) < PRC-25CO<sub>2</sub> ( $3.42 \times 10^{-3} \text{ s}^{-1}$ ) (Fig. S8 and Table S7†). Given the non-polar nature of the carbon pore interface, differences in diffusion rates primarily arise from variations in pore size. Pore expansion enhances mass transfer efficiency and reduces diffusion energy barrier by synergistically increasing porosity, average pore size, and the proportion of effective micropores (<7 Å). Meanwhile, the higher density of delocalized  $\pi$  electrons creates stronger van der Waals and  $\pi$ - $\pi$  interaction sites for C<sub>3</sub>F<sub>6</sub>, imposing surface diffusion limitations. Although PRC-25CO<sub>2</sub> exhibits excessive pore expansion, it still maintains a C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> kinetic selectivity of 8.51, indicating preserved albeit reduced separation capability. However, the co-adsorption of C<sub>3</sub>F<sub>8</sub> on PRC-25CO<sub>2</sub> remains significant, whereas PRC-15CO<sub>2</sub> achieves complete C<sub>3</sub>F<sub>8</sub> exclusion. These results demonstrate that



**Fig. 3** Time-dependent uptake profile of (a) C<sub>3</sub>F<sub>6</sub> and (b) C<sub>3</sub>F<sub>8</sub> on PRC-5CO<sub>2</sub>, PRC-15CO<sub>2</sub> and PRC-25CO<sub>2</sub> at 298 K and 100 kPa; (c) comparison of the dynamic breakthrough performance of these carbon-based adsorbents for C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> mixtures (10/90, v/v) at 298 K and 100 kPa; (d) comparative analysis of C<sub>3</sub>F<sub>8</sub> adsorption loss and the yield of high purity C<sub>3</sub>F<sub>8</sub> (>5 N) from a single breakthrough experiment using the aforementioned adsorbents; (e) experimental breakthrough curves for C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> (1/99, v/v) on PRC-15CO<sub>2</sub> at 298 K and 100 kPa; (f) comparison of the dynamic adsorption capacity for C<sub>3</sub>F<sub>6</sub> and the yield of 5 N C<sub>3</sub>F<sub>8</sub> obtained by PRC-15CO<sub>2</sub> following breakthrough with different feed gases.



precision micropore engineering fundamentally dictates optimal separation performance.

To assess industrial applicability, dynamic breakthrough experiments were conducted under conditions representative of crude distillation mixtures ( $\text{C}_3\text{F}_6/\text{C}_3\text{F}_8$ , 10/90, v/v). In PRC-15 $\text{CO}_2$  columns,  $\text{C}_3\text{F}_8$  eluted immediately, whereas  $\text{C}_3\text{F}_6$  was retained for 218.82 min  $\text{g}^{-1}$  (Fig. 3c). During this period, effluent  $\text{C}_3\text{F}_6$  concentration remained below 0.001%, enabling the production of ultra-high purity  $\text{C}_3\text{F}_8$  (>5 N, 99.999%) with a yield of 393.88 L  $\text{kg}^{-1}$ . This performance surpasses that of other commercial carbon materials (e.g., AC1: 190.91 L  $\text{kg}^{-1}$ , AC2: 147.01 L  $\text{kg}^{-1}$ ) and other PRC materials (Fig. 3d and S9–S11; Tables S8 and S9†). Under more dilute impurity conditions ( $\text{C}_3\text{F}_6/\text{C}_3\text{F}_8$ , 1/99, v/v), RC-15 $\text{CO}_2$  maintained sharp separation, yielding 3063.73 L  $\text{kg}^{-1}$  of 5 N-grade  $\text{C}_3\text{F}_8$  (Fig. 3e and f). Moreover, implementation of multi-column units operating in series facilitates continuous production of high-purity  $\text{C}_3\text{F}_8$ .

Mechanistically, a multilayer carbon model with controlled interlayer spacings (5.6, 6.5, 8.0 Å), mimicking the pore size distribution, was constructed to elucidate the molecular sieving mechanism. Molecular dynamics (MD) simulations conducted at 298 K and 0.1 MPa tracked diffusion of a binary  $\text{C}_3\text{F}_6/\text{C}_3\text{F}_8$  (10/90, v/v) mixture through these engineered architectures. Time-resolved adsorption snapshots (Fig. 4a–c and S12–S14†) reveal progressive differentiation in molecular transport. Within the initial 1000 ps,  $\text{C}_3\text{F}_6$  molecules adsorbed preferentially *via* quadrupole moment interactions, while  $\text{C}_3\text{F}_8$  showed no adsorption. Between 1000 and 10000 ps,  $\text{C}_3\text{F}_6$  rotated and diffused through 6.5 Å interlayer channels (PRC-15 $\text{CO}_2$ ), with

complete exclusion of  $\text{C}_3\text{F}_8$  (kinetic diameter  $\phi = 7.6$  Å > slit width) (Fig. 4e). By 10000 ps, full  $\text{C}_3\text{F}_6$  permeation and absolute  $\text{C}_3\text{F}_8$  exclusion was achieved, theoretically ensuring 5 N-grade  $\text{C}_3\text{F}_8$  purity. Simulations across different interlayer spacings further highlighted critical pore size thresholds: 5.6 Å slits (PRC-5 $\text{CO}_2$ ) caused molecular bottlenecks due to diffusion barriers, precluding passage of both species (Fig. 4d), whereas 8.0 Å slits (PRC-25 $\text{CO}_2$ ) allowed unselective passage, confirming the importance of controlled  $\text{CO}_2$ -mediated activation (Fig. 4f). The presence of strategically incorporated oxygen functionalities coupled with optimized pore sizes in PRC-15 $\text{CO}_2$  supports a dual-function mechanism facilitating both molecular sieving precision and adsorption enhancement, as corroborated experimentally and by MD simulations.

Material stability and regenerability are critical for industrial deployment. After five consecutive static/dynamic adsorption–desorption cycles (180 °C degassing for 4 h), PRC-15 $\text{CO}_2$  retained 99.5% of initial  $\text{C}_3\text{F}_6$  adsorption capacity while consistently producing 5 N-grade  $\text{C}_3\text{F}_8$  ( $3063.73 \pm 15.21$  L  $\text{kg}^{-1}$ ), exhibiting negligible degradation (Fig. S15† and 5c). Thermogravimetric analysis under  $\text{N}_2$  atmosphere revealed high thermal stability with minimal mass loss, contrasting markedly with the phenolic resin precursor (Fig. S16†), and maintained exceptional stability in air. Thus,  $\text{CO}_2$ -modulated carbonization effectively suppresses deleterious side reactions, preserving graphitic domain integrity. Furthermore, the engineered hydrophobicity increased progressively with  $\text{CO}_2$  concentration, reflecting enhanced graphitization and a reduction in hydrophilic oxygen species (C–O). Achieving a water contact angle of 129.6°, governed by the Cassie–

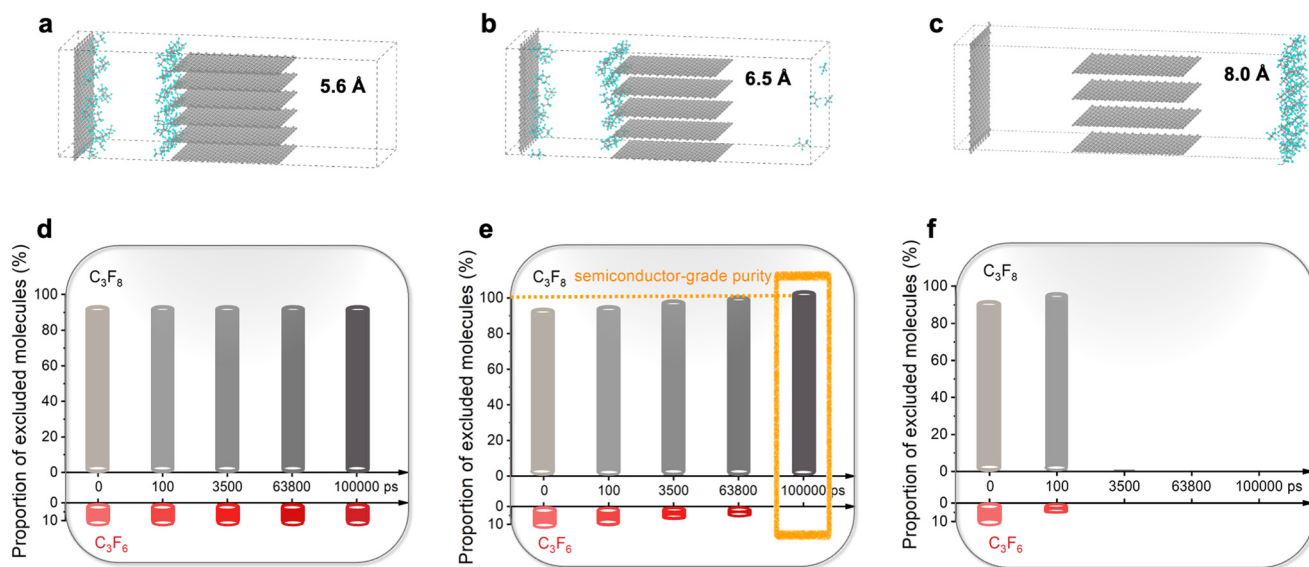
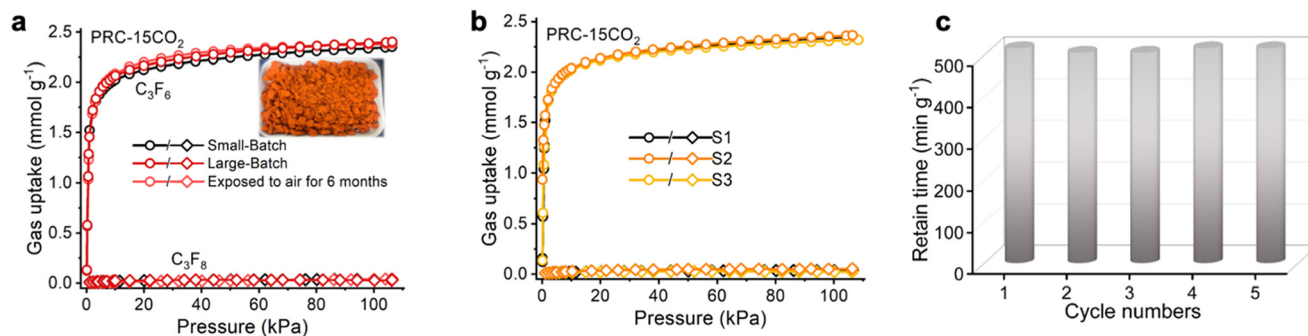


Fig. 4 MD simulation snapshots of the adsorption process for a  $\text{C}_3\text{F}_6/\text{C}_3\text{F}_8$  (10/90, v/v) mixture in (a) PRC-5 $\text{CO}_2$ , (b) PRC-15 $\text{CO}_2$  and (c) PRC-25 $\text{CO}_2$  models at the final simulation time; (d–f) proportion of excluded gas molecules in the inlet stream over time for (d) PRC-5 $\text{CO}_2$ , (e) PRC-15 $\text{CO}_2$ , and (f) PRC-25 $\text{CO}_2$ , respectively (the Y-axis represents the proportion of  $\text{C}_3\text{F}_6$  or  $\text{C}_3\text{F}_8$  molecule in the total number of molecules at the entrance).







**Fig. 5** (a) Comparison of the adsorption isotherms for C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> at 298 K on PRC-15CO<sub>2</sub> synthesized under varying conditions; (b) adsorption isotherms of C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> at 298 K on phenolic resin-derived carbon molecular sieve materials synthesized across different batches; (c) multicycle dynamic breakthrough curves of C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> (1/99, v/v) gas mixtures using a packed column bed with PRC-15CO<sub>2</sub> at 298 K and 100 kPa, illustrating the retention times over five dynamic cycles.

Baxter model, this super-hydrophobicity and elevated H<sub>2</sub>O adsorption barriers confer significant moisture resistance (Fig. S17†).

Scaling synthesis was demonstrated through seamless transition from laboratory to pilot-scale synthesis (10-fold precursor scale-up), yielding kilogram-scale batches that retained performance and met industrial stability benchmarks, including extended shelf life ( $\Delta q < 1.5\%$  loss after 6 months) (Fig. 5a and S18†). Furthermore, batch-to-batch reproducibility across three production lots exhibited minimal variation in C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> uptake, attributable to precision pyrolysis protocols and defect engineering *via* controlled CO<sub>2</sub> etching optimizing microporosity (Fig. 5b and S19†). This holistic integration of surface chemistry control, statistical process management, and scalable manufacturing establishes PRC-15CO<sub>2</sub> as a paradigm-shifting material that overcomes longstanding challenges in carbon molecular sieve industrialization by synchronizing atomic-scale functionality with macroscopic production robustness.

## 3 Conclusions

In summary, we demonstrate that careful regulation of ultramicropore dimensions in CO<sub>2</sub>-activated carbon adsorbents is essential for achieving effective molecular sieving of fluorinated propylene (C<sub>3</sub>F<sub>6</sub>) from fluorinated propane (C<sub>3</sub>F<sub>8</sub>). The results show that moderate CO<sub>2</sub> activation produces tailored pore structures that selectively favor C<sub>3</sub>F<sub>6</sub> over C<sub>3</sub>F<sub>8</sub>, whereas excessive activation generates larger pores with reduced selectivity. This work not only underscores the pivotal role of ultramicroporous engineering in boosting separation performance, but also provides a rational strategy for the development of advanced adsorbents for challenging small-molecule separations in industrial settings. The CO<sub>2</sub> activation method offers a scalable route for the preparation of molecular sieves tailored to specific separation needs, advancing the sustainable purification of valuable fluorinated gases.

## 4 Experimental section

### 4.1 Materials

All reagents, solvents and gases were purchased from commercial sources and used as received without further purification. Resorcinol (C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>, 99.5%), anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, 99.5%), polyethylene glycol (PEG-2000, CP), hexamethylenetetramine (HMTA, C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, 98.0%) and formaldehyde solution (AR, containing polymerization inhibitor) were supplied by Sinopharm Chemical Reagent Co., Ltd. Activated carbons AC1 (general adsorption use), AC2 (electroplating decolorization grade), AC3 (BPL), AC4 (100CTC3070), AC5 and AC6 (coconut and fruit shells origins) were provided by Calgon Carbon Corporation. High-purity gases including N<sub>2</sub>, He, CO<sub>2</sub>, C<sub>3</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub> (all 99.999%), as well as premixed gas blends of CO<sub>2</sub>/N<sub>2</sub> (5/95, 15/85, 25/75, v/v) and C<sub>3</sub>F<sub>6</sub>/C<sub>3</sub>F<sub>8</sub> (10/90, 1/99, v/v) were supplied by Zhejiang Quzhou City Julun Gas Co., Ltd.

### 4.2 Preparation of materials

**4.2.1 Synthesis of phenolic resin (PR).** Phenolic resin (PR) was synthesized *via* a modified emulsion polymerization method. Specifically, resorcinol (10.00 ± 0.05 g) was dissolved in 200 mL deionized water within a 500 mL three-neck flask under vigorous stirring (500 rpm) at 353 K. After complete dissolution, Na<sub>2</sub>CO<sub>3</sub> (0.05 g), PEG-2000 (1.00 g) and HMTA (12.00 g) were sequentially added. The mixture was homogenized, then 20 mL of formaldehyde aqueous solution was introduced dropwise. The reaction was maintained under reflux for 24 h with precise temperature control (±1 °C). The resulting PR was isolated by hot filtration, followed by washing with deionized water and ethanol to remove residual monomers and surfactants. The purified product was vacuum-dried at 348 K for 12 h, yielding orange-yellow PR powder with moisture content below 0.5%.

**4.2.2 Scale-up synthesis of PR.** Scaling the above protocol tenfold, resorcinol (100.0 g) was dissolved in 3 L deionized water in a 5 L reactor under identical agitation and thermal conditions. Na<sub>2</sub>CO<sub>3</sub> (0.50 g), PEG-2000 (10.00 g) and HMTA



(120.00 g) were added, followed by the controlled dropwise addition of 200 mL formaldehyde solution over 30 min. The reaction time was extended to 72 h under reflux to accommodate scale kinetics. Post-reaction purification entailed gravitational sedimentation (six cycles, 2 h per cycle) with water replacement to remove colloidal impurities, ethanol washing ( $5 \times 200$  mL) and vacuum drying at 348 K for 12 h, yielding PR powder with consistent physicochemical properties.

#### 4.2.3 Synthesis of phenolic resin-derived carbon (PRC).

Precisely 2.00 g of PR powder was loaded into a quartz boat located at the isothermal zone of a horizontal tubular furnace. Carbonization was conducted with a heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  from ambient temperature to  $900\text{ }^{\circ}\text{C}$  under varied atmospheres: PRC- $\text{N}_2$  (pure  $\text{N}_2$ , 99.999%), PRC- $5\text{CO}_2$  ( $\text{CO}_2/\text{N}_2$ , 5/95, v/v), PRC- $15\text{CO}_2$  ( $\text{CO}_2/\text{N}_2$ , 15/85, v/v), and PRC- $25\text{CO}_2$  ( $\text{CO}_2/\text{N}_2$ , 25/75, v/v) at a total gas flow rate of  $75\text{ mL min}^{-1}$ , followed by natural cooling to below  $50\text{ }^{\circ}\text{C}$ .

#### 4.3 Characterization of PRC

Surface topography and elemental composition were analyzed using a field-emission scanning electron microscope (Hitachi Regulus 8230) equipped with EDS attachment. Powder X-ray diffraction (PXRD) was performed on a PANalytical X'Pert PRO diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.542\text{ \AA}$ ), scanning  $5\text{--}60^{\circ}$  with a step size of  $0.02^{\circ}$ . Raman spectroscopy was performed on a Horiba LabRAM Odyssey spectrometer with a  $532\text{ nm}$  laser source covering  $500\text{--}4000\text{ cm}^{-1}$ . XPS was carried out using a Kratos AXIS Supra+ spectrometer with monochromatic  $\text{Al K}\alpha$  X-rays ( $1486.6\text{ eV}$ ). FT-IR spectra were recorded in attenuated total reflectance (ATR) mode on a Bruker INVENIO R system ( $4000\text{--}600\text{ cm}^{-1}$ ,  $2\text{ cm}^{-1}$  resolution, 32 scans). Thermogravimetric analysis (TGA) was investigated on a Pyris 1 TGA Thermogravimetric analyzer (TA Instruments Corp., USA) to  $900\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  or air at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ . Nitrogen adsorption-desorption isotherms at  $77\text{ K}$  were collected on a Micromeritics ASAP 3Flex analyzer after degassing at  $200\text{ }^{\circ}\text{C}$  under vacuum for 24 h, yielding BET surface areas and pore size distributions. Elemental analysis employed an Elementar Vario MAX cube analyzer.

#### 4.4 Gas adsorption measurements

Single-component adsorption isotherms of  $\text{C}_3\text{F}_6$  and  $\text{C}_3\text{F}_8$  were measured using a Micromeritics ASAP 2020 PLUS gas sorption analyzer at  $298.0 \pm 0.1\text{ K}$  over pressures from 0 to 100 kPa. Approximately  $0.100 \pm 0.005\text{ g}$  of sample was degassed at  $250\text{ }^{\circ}\text{C}$  under vacuum for 6 h prior to analysis. Samples were transferred under protected atmosphere to prevent contamination. PRC adsorbents exhibited negligible  $\text{C}_3\text{F}_8$  uptake ( $<0.05\text{ mmol g}^{-1}$  at 100 kPa), enabling use of equilibrium adsorption capacity ratios as primary selectivity indicators.

#### 4.5 Measurements of adsorption heats ( $Q_{\text{st}}$ )

Adsorption heats ( $Q_{\text{st}}$ ) were quantified using coupled thermogravimetric-differential scanning calorimetry (TGA-DSC, STD 650). Approximately  $10.0 \pm 0.2\text{ mg}$  of sample was loaded into a platinum crucible and degassed *in situ* under  $\text{N}_2$  ( $50\text{ mL min}^{-1}$ ) with a linear heating ramp ( $10\text{ K min}^{-1}$ ) to  $473\text{ K}$ , followed by thermal equilibration. Thermal equilibration was maintained until mass fluctuation fell below  $0.01\% \text{ min}^{-1}$ . The system was cooled to  $313\text{ K}$  at  $5\text{ K min}^{-1}$  under continuous  $\text{N}_2$  flow and stabilized for 30 min before alternate introduction of  $\text{C}_3\text{F}_6$  and  $\text{C}_3\text{F}_8$  gases. Mass change and heat flow were monitored, equilibrium was defined as DSC signal variation  $<2\text{ }\mu\text{W}$  over 300 s.

#### 4.6 Dynamic multicomponent breakthrough experiments

Degassed samples ( $200\text{ }^{\circ}\text{C}$ , 24 h) were packed into stainless steel columns ( $50\text{ mm} \times 4.6\text{ mm I.D.}$ ) inside an argon-filled glovebox ( $\text{H}_2\text{O} < 0.1\text{ ppm}$ ,  $\text{O}_2 < 0.5\text{ ppm}$ ) to prevent contamination. Columns were thermally conditioned at  $200\text{ }^{\circ}\text{C}$  under helium purge for 6 h, then integrated into a temperature-controlled breakthrough apparatus maintained at  $298\text{ K}$ . Gas mixtures of  $\text{C}_3\text{F}_6/\text{C}_3\text{F}_8$  (10/90, v/v) and (1/99, v/v) were introduced at flow rates of 2.0 and  $6.0\text{ mL min}^{-1}$ , respectively. Effluent composition was monitored by a Shimadzu GC-2010 Pro gas chromatography. Regeneration involved thermal desorption at  $200\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  flow for 12 h.

#### 4.7 Adsorption kinetic experiments

Kinetic uptake curves were recorded using an Intelligent Gravimetric Analyzer (IGA-001) with a high-resolution microbalance. Samples ( $50.0\text{--}80.0\text{ mg}$ ) were pre-activated *in situ* under dynamic vacuum at  $200\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$  until mass stabilization, then equilibrated at  $298.0 \pm 0.1\text{ K}$  *via* closed-loop thermostatic control. Following adsorbate introduction, gravimetric data acquisition continued until saturation. Transport diffusivities and kinetic selectivities were derived from time-dependent uptake profiles.

#### 4.8 Molecular dynamics (MD) simulations

Molecular dynamics (MD) simulations employed the GROMACS platform,<sup>47</sup> parameterized with the generalized Amber force field (GAFF). Atomic partial charges were assigned *via* the restrained electrostatic potential (RESP) method, and long-range van der Waals and electrostatic interactions were treated using the particle mesh Ewald (PME) algorithm.<sup>48,49</sup> Systems were energy-minimized to a convergence of  $0.01\text{ kcal mol}^{-1}$ , then equilibrated at  $298\text{ K}$  in the NVT ensemble using a Nosé-Hoover thermostat.<sup>50,51</sup> Production runs spanned 100 ns with 1 fs timestep, incorporating a 10.3 MPa transmembrane pressure gradient to model gas permeation dynamics while maintaining molecular stochasticity.





#### 4.9 Vapor adsorption measurements

Moisture adsorption characteristics were evaluated on a Belsorp-max II vapor sorption analyzer. Prior to analysis, samples underwent standardized degassing protocols. Measurements were conducted isothermally at 303 K.

#### 4.10 Stability tests

Adsorption stability was assessed through five consecutive C<sub>3</sub>F<sub>6</sub> adsorption-desorption cycles and five consecutive dynamic breakthrough adsorption-regeneration cycles under controlled experimental conditions.

### Data availability

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

### Author contributions

Yiwen Fu: data curation, investigation, writing – original draft and review. Liangzheng Sheng: methodology, data curation, validation and writing – original draft. Guangtong Hai: methodology, data curation and validation. Jialei Yan: validation, investigation and data curation. Lihang Chen: validation, investigation, review, editing, supervision and funding acquisition. Zhiguo Zhang: resources, project administration and funding acquisition. Qiwei Yang: resources, project administration and funding acquisition. Qilong Ren: resources, project administration and funding acquisition. Zongbi Bao: conceptualization, editing, supervision, resources, project administration and funding acquisition.

### Conflicts of interest

The authors declare no conflict of interest.

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