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Porous organic cages for gas separations

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Gases have played a crucial role in various industries, spanning from manufacturing and medicine to electronics. In these industries, the attainment of pure gases through effective separation methods has been recognized as essential. Porous materials-based adsorption and separation technologies have garnered significant attention due to their advantageous features, including low energy consumption and simplified operational procedures. Among these materials, porous organic cages (POCs) have emerged as a promising class, constructed by individually designed macromolecules possessing inherent cavities that are tailor-made, soluble, easily regenerated, and amenable to precise modifications. Analogous to well-established porous framework materials like zeolites, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs), POCs have exhibited their intrinsic potential for gas separation applications in recent years. In this review, we delve into the progress achieved in the realm of POCs, with a particular focus on their utilization for selective gas separation. Moreover, we present an outlook on the future prospects of this field, along with the existing challenges that demand further attention.

1. Introduction

Separation technology is of paramount importance in contemporary society for various industries to extract pure substances from chemical mixtures. Examples of such applications include the separation of hydrocarbons from crude oil, alkenes from alkanes, greenhouse gases from dilute emissions, as well as the extraction of various derivatives and metals from different sources. Gases, in particular, play a fundamental role in the production of chemicals, including fuels, plastics, and polymers, as well as in the domains of petrochemicals, pharmaceuticals, and nuclear industries, where they serve as neutron moderators.² Traditional methods for gas separation rely on cryogenic distillation, which involves repetitive cycles of evaporation and condensation, 3,4 resulting in high energy consumption, environmental concerns, and potential generation of secondary byproducts. Consequently, alternative gas purification methods that are both cost- and energy-efficient are urgently needed.



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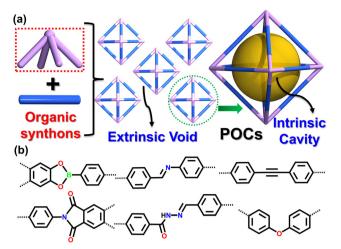


Fig. 1 (a) Synthesis and characteristics of POCs. (b) Common covalent linkages in construction of POCs.

In recent years, porous materials have emerged as a promising solution to address gas storage and separation challenges. Notable porous adsorbents encompass a range of materials, including metal-containing framework adsorbents like zeolites and metal-organic frameworks (MOFs), 5-10 porous organic adsorbents such as porous organic polymers (POPs), 11-13 covalent-organic frameworks (COFs), 14-16 and hydrogen-bonded organic frameworks (HOFs), 17-19 and molecular cage adsorbents like porous organic cages (POCs)²⁰ and metal-organic cages (MOCs).²¹ MOFs have witnessed the most rapid development in the field of gas separation due to their remarkable porosity, tunable pore structures, and unsaturated metal sites, leading to their successful applications in various separations such as carbon dioxide (CO₂) separation, ^{22,23} alkene purification,²⁴ noble gas separation,²⁵ and isotope separation.26 However, despite their accomplishments, MOFs face challenges concerning cost, regeneration, stability, and selectivity, making it crucial to explore alternative porous materials for gas separation. It is worth noting that the progress in the development of other porous materials has been notably slower compared to



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porous materials, including metal-organic cages, porous organic cages, and metal-organic frameworks.

MOFs, despite their inherent advantages. For instance, zeolites offer cost-effectiveness and easy availability, while porous organic materials possess a metal-free nature and native nonpolar/inert pore surfaces. POPs exhibit high stability, and HOFs and POCs allow for easy regeneration and tunability in fine-level pore sizes, respectively. Therefore, it is essential to investigate the gas purification capabilities of these materials to foster the advancement of diverse classes of porous materials in the field of gas separation.

Among the porous materials, POCs are constructed through covalent linkages of organic synthons to form discrete macromolecules with intrinsically hollow cavities (Fig. 1).27-34 This distinctive structure provides POCs with several advantages that include solution processing, regeneration, and post-synthesis modification, 35-42 compared to other porous framework materials. Organic cage compounds were first reported by the Nobel Prizewinning chemist Jean-Marie Lehn in 1969, who presented the first example of organic cage molecules constructed from crown ether for cation binding. 43 However, it was not until 2009 that Cooper's group confirmed the ability of isolated shape-persistent organic cages to serve as porous solids for gas storage. 44 Since then, there has been a rapid increase in the number of POCs with different topologies, shapes, and surface areas, attracting significant attention over the past decade. 45-73 The common methods used to synthesize POCs can be categorized into two types: irreversible bond formation and reversible bond formation, which mainly include several condensation reactions.²⁰ Both methods have been extensively reviewed in recent publications.

POCs, as a relatively new sub-class of porous materials, share many advantages with other porous materials including low density, high surface area and pore volume, tunable window and cavity sizes, and the ability for easy and precise modification. Additionally, POCs show promising potential for numerous applications such as molecular recognition, membranes, catalysis, and separation.⁷⁴⁻⁸⁵ Despite prior reviews covering several applications, there remains an insufficient amount of coverage regarding the efficient gas-selective separation achieved by POCs. Similar to zeolites, MOFs, and COFs, POCs also exhibit gas storage and separation capabilities, fundamental attributes of porous materials. However, POCs are distinct in their construction as discrete molecules held together by weak intermolecular interactions, which results in their porosity arising not only from intrinsic cavities but from extrinsic voids or channels that result from inefficient molecule packing in the solid state. This feature makes POCs vulnerable to structural changes that may significantly impact their porosity and performance in gas storage and separation. Over the last decade, the Brunauer-Emmett-Teller (BET) surface area of POCs has increased from 624 m² g⁻¹ to 3758 m^2 g^{-1} , displaying the ability to selectively store and separate gases such as CO2, hydrocarbons, noble gases, and isotope gases as shown on Fig. 2. Zhang et al. recorded the first shape-persistent prismatic molecular cage capable of high selectivity for CO₂ over N₂ adsorption in 2010.⁸⁶ Since then, Mastalerz et al. has developed several shape-persistent POCs that exhibit selective CO2 separation capabilities, 87 whereas Cooper et al. reported, in 2014, that an imine-linked tetrahedral POC (CC3) was effective in effectively separating noble gas

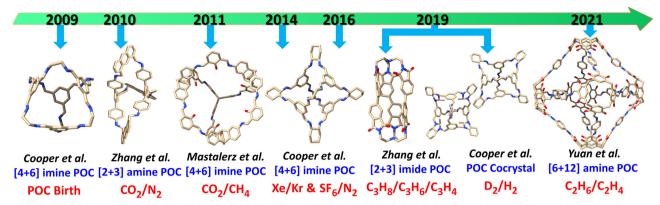


Fig. 2 Timeline of POCs for gas separation applications. Carbon is orange, oxygen red, nitrogen blue, and fluorine green. Hydrogen atoms and alkyl groups are omitted for clarity.

Xenon (Xe) and Krypton (Kr).88 Moreover, they showed successful separation of greenhouse gas sulfur hexafluoride (SF₆) and N₂ in 2016,89 and gaseous isotope mixtures (D2/H2) in 2019 by finetuning the internal cavities of POCs. 90 Furthermore, Zhang et al. achieved efficient separation of binary or ternary C3 hydrocarbon mixtures using a soft imide-based POC (NKPOC-1) with gateopening behavior in 2019.91 Yuan et al. developed a robust ethane-trapping POC (CPOC-301) in 2021, enabling one-step purification of high-purity ethylene (C2H4) from ethane (C2H6) and C₂H₄ mixture. 92 They also discovered the solvatomorphism, which influenced acetylene (C2H2) and CO2 separation in CPOC-101.93 In 2022, Mastalerz et al. fine-tuned the fluorinated sidechains on the windows of imine-linked POCs,94 subsequently improving the separation of fluorinated alkanes. This review aims to provide a comprehensive overview of the significant progress made by POCs in gas separation. It is divided into distinct sections covering CO₂ separation, hydrocarbon purification, rare gas separation, fluorinated greenhouse gas separation, and D2/H2 isotope separation. Additionally, we address remaining challenges and offer an outlook to stimulate further development of POCs in gas separation.

2. POCs for gas separations

Gas molecule separation is a challenging technological feat, particularly when the molecules possess similar sizes and shapes. However, highly porous materials utilized for adsorptive separation have become an alternative technology due to the lower energy consumption. POCs, with their exceptional characteristics, offer promising potential for highly efficient gas separation. In this section, we aim to provide an overview of the significant advancements made in POCs regarding the separation of various gases, such as CO₂, light hydrocarbons, Xe/Kr, fluorinated greenhouse gases and D₂/H₂.

2.1. CO₂ separation

The accelerated increase in atmospheric CO2 concentration caused by climate change has recently received substantial attention. In response, porous materials that use physical adsorption

are being considered as promising solutions for CO2 capture. POCs, as a new type of porous material, have also been successfully used in separating CO₂/N₂.95-98

In 2010, Zhang et al. published a study which reported the use of prismatic molecule cage 6 as an effective medium for CO₂ and N₂ separation.⁸⁶ They observed that CO₂ uptake capacity was 4.46 cm³ g⁻¹, while N₂ exhibited negligible adsorption at 0.061 cm³. The CO₂/N₂ adsorption selectivity was calculated to be 73, highlighting a profound affinity for CO2 over N2 during adsorption. Later, they successfully produced a series of new organic cage compounds (1-4) using a one-pot reversible imine condensation reaction between triamines and dialdehydes, 99 followed by hydride reduction of the resulting imine to amine bonds. The triamine moieties functioned as the top and bottom panels of a trigonal prism, while the dialdehyde moieties served as the three lateral edges. The N₂ adsorption isotherms at 77 K revealed that these materials had no pores for N2 gas, as indicated by a BET surface area of less than 10 m² g⁻¹. Cage 4 had the lowest N_2 uptake while also displaying a comparable adsorption capacity for CO2, resulting in the highest CO₂/N₂ adsorption selectivity with a ratio of 138/1. The selectivity in gas adsorption observed could be attributed to the density of amino groups within the cage molecule and the size of the cage cavity. The amino group density predominantly governed the uptake of CO2, whereas the capacity for N2 adsorption related to the dimensions of the molecular prisms.

Cooper et al. reported a new propeller-shaped organic cage known as CC6 in 2011, 100 produced via a one-step [2+3] cycloimination reaction between 1,3,5-tri(4-formylphenyl)benzene and 1,5-pentanediamine. The resulting CC6 had a moderate apparent BET surface area of 99 m 2 g $^{-1}$. Examination of the N $_2$ adsorption isotherm at 300 K and 1.2 bar revealed a low gas uptake of 0.08 mmol g^{-1} . Conversely, the CO_2 adsorption capacity of CC6 under the same conditions was determined to be 0.90 mmol g^{-1} . Using these isotherms, the ideal selectivity for CO₂/N₂ at 300 K and 1 bar was calculated to be 11.

In addition to reversible imine condensation, Zhang et al. successfully produced a tricyclooxacalixarene cage, named cage 1, in 2015 via a one-pot S_NAr reaction involving tetrahydroxytetraphenylethylene and 2,6-dichloropyridine-3,5-dicarbonitrile

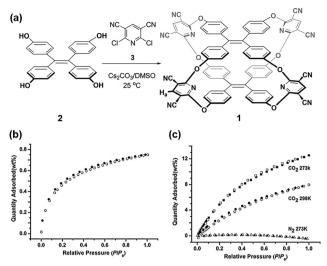


Fig. 3 (a) Synthesis of TPE-based tricyclooxacalixarene cage 1. (b) H₂ sorption isotherms at 77 K. (c) CO₂ and N₂ sorption isotherms at 273 K and 298 K. Reproduced with permission from ref. 101. Copyright 2015, Wiley.

(Fig. 3).¹⁰¹ This tricyclic cage had a grid-like porous architecture and demonstrated remarkable adsorption capacity for CO₂, accompanied by high selectivity towards CO₂/N₂. Despite having a moderate surface area (432 m² g⁻¹), cage 1 could adsorb $84 \text{ cm}^3 \text{ g}^{-1} (0.75 \text{ wt\%}) \text{ of H}_2 \text{ and } 62.7 \text{ cm}^3 \text{ g}^{-1} (12.5 \text{ wt\%}) \text{ of CO}_2$ at 1.0 bar. The superior CO2 adsorption performance of cage 1 can be attributed to the optimal congruence between its microporous structure and the dimensions of CO₂, as well as the electron-rich nature of nitrogen and oxygen atoms within the cage framework, which facilitate local-dipole/quadrupole interactions with CO₂. The analysis of the initial slopes of the adsorption isotherms yielded a calculated CO2/N2 selectivity of 80 for cage 1.

In 2018, a new cage (cage 5) was synthesized through a reaction between di(p-methylphenyl)-di(p-aminophenyl)ethylene and 2,6-pyridinediformyl chloride. 102 Cage 5 has a BET surface area of 347 m² g⁻¹ and displays considerable CO₂ uptake of 39.7 cm³ g⁻¹ at 273 K and 1 bar, equating to approximately six CO₂ molecules per cage, with each CO₂ molecule binding to one pyridyl ring. Moreover, the N2 adsorption under the same conditions was negligible, resulting in an excellent CO2/N2 selectivity of up to 32.

In 2020, Zhang et al. synthesized a triptycene-based cage (TC) using copper-mediated modified Eglinton-Glaser oxidative coupling reaction. 103 The initial structure of TC exhibited limited N2 adsorption at 77 K and a relatively low BET surface area of only 7 m 2 g $^{-1}$. However, by rapidly precipitating TC-rp from a methanol/dichloromethane solution, it transformed into a porous state, increasing the BET surface area to 653 m² g⁻¹. TC-rp also displayed noteworthy CO₂ uptake capacities, with values of 42.3 cm 3 g $^{-1}$ at 273 K and 33.6 cm 3 g $^{-1}$ at 298 K. Based on these measurements, the CO₂/N₂ selectivity of TC-rp was found to be 4.8 at 273 K.

Although it is primarily composed of methane (CH₄), natural gas often contains significant amounts of CO2 that must be

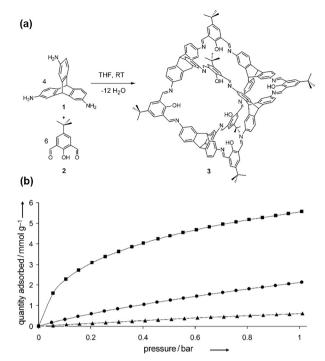
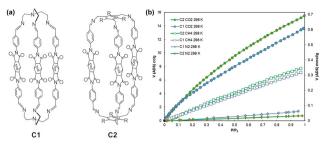


Fig. 4 (a) Synthesis of cage 3. (b) Gas adsorption isotherms of H₂ (square, 77 K), CO₂ (circle, 273 K), and CH₄ (triangle, 273 K) for cage compound 3. Reproduced with permission from ref. 87. Copyright 2011, Wiley.

extracted to increase its heating value and prevent pipeline corrosion. POCs have also been utilized in the separation of CO₂/CH₄. ^{104,105} In 2011, Mastalerz et al. examined the separation characteristics of CO₂/CH₄ using cage 3, which they synthesized through a one-pot Schiff base condensation reaction involving triamine and salicylbisaldehyde (Fig. 4).87 Cage 3 had a calculated BET surface area of 1375 m² g⁻¹ and a Langmuir surface area of 1566 m² g⁻¹. At 77 K and 1 bar, the H₂ adsorption capacity was 5.60 mmol g^{-1} . At the same conditions (273 K and 1 bar), the adsorption capacity of CO_2 was 2.10 mmol g^{-1} , while only 0.61 mmol g⁻¹ of CH₄ was adsorbed. The marked difference in adsorption capacity between CO2 and CH4 implies the usefulness of cage 3 in removing CO2 from natural gas and enhancing CH₄ content. The authors credit the hydroxy groups inside the cages for the high CO2/CH4 selectivity (10:1 w/w) of cage 3. Subsequently, a new exo-functionalized [4+6] cage 5 was reported, with a specific surface area of 919 m² g⁻¹, which exhibited high selectivity for CO2/CH4. At 273 K and 1 bar, cage 5 adsorbs 3.37 mmol g^{-1} CO₂ and only 0.66 mmol g^{-1} CH₄.⁹⁶

Yuan et al. recently introduced two POCs called CPOC-105 and CPOC-106 constructed using two C4RACHO atoms with four p-xylylenediamine and m-xylylenediamine linkers, ¹⁰⁶ respectively. The corresponding BET surface areas, calculated using CO2 sorption at 196 K, were 277 and 218 m² g⁻¹ for CPOC-105 and CPOC-106, respectively. At 298 K and 1 bar, CPOC-105 and CPOC-106 showed higher adsorption capacities for CO₂ than CH₄, with 44 cm³ g⁻¹ vs. 17 cm³ g⁻¹ for **CPOC-105** and 37 cm³ g⁻¹ vs. 20 cm³ g⁻¹ for CPOC-106. Using Ideal Adsorbed Solution Theory (IAST) results under 1 bar, the CO2/CH4 selectivity values were



(a) Sketches of C1 and C2 (R = ethyl). (b) Overlay of CO_2 , CH_4 , and N₂ adsorption isotherms, measured at 298 K. Reproduced with permission from ref. 107. Copyright 2022, Wiley.

calculated to be 4.5 for CPOC-105 and 3.1 for CPOC-106. Dynamic breakthrough experiments were used to validate the superior separation performance of CPOC-105.

Amendola et al. presented two novel imide/imine organic cages, named C1 and C2 (Fig. 5), 107 synthesized through a [2+3] imine condensation reaction using two distinct polyamines and a novel dialdehyde compound incorporating a rigid bicyclo[2.2.2] oct-7-ene-2,3,5,6-tetracarboxydiimide core. At 298 K, the CO₂ adsorption capacities of C1 and C2 were 0.61 mmol g⁻¹ and 0.69 mmol g⁻¹, respectively, while the adsorption capacities of CH₄ and N₂ were much lower. C1 and C2 demonstrated positive results in terms of CO2/N2 selectivity, with IAST selectivity values of 41 and 32, respectively, for CO₂/N₂ (15:85) mixtures. Moreover, both cages showed potential as fillers for mixed-matrix membranes (MMMs) in combination with polymers such as PEEK-WC and Matrimid[®] 9725. By incorporating C1 and C2 into Matrimid[®] 9725, CO₂/CH₄ selectivity was improved, and inclusion in PEEK-WC enhanced CO₂/N₂ selectivity.

In 2021, Mastalerz et al. conducted an investigation on chiral self-sorting of large cubic [8+12] salicylimine cages (Fig. 6). The cages formed via the condensation of eight chiral C_3 -symmetric TBTQ-tris(salicylaldehydes) with 12 p-phenylenediamine. Notably, only three isomers were observed: (P)-4, (M)-4, and (P,M)-4. The comparison between the two enantiomeric cages, (P)-4 and (M)-4, revealed that they had similar BET surface area of 1212 and

1126 m² g⁻¹, respectively. At 273 K and 1 bar, (P)-4 had an adsorption capacity of 61.1 cm³ g⁻¹ for CO₂ and 18.2 cm³ g⁻¹ for CH₄, while (M)-4 had an adsorption capacity of 63.6 cm³ g⁻¹ for CO₂ and 19.7 cm³ g⁻¹ for CH₄. (P)-4 had a CO₂/CH₄ selectivity of 7.6 and a CO2/N2 selectivity of 24.9, while (M)-4 had a CO2/CH4 selectivity of 7.4 and a CO₂/N₂ selectivity of 24.7. A comparison between (P,M)-4_1 and (P,M)-4_2 yields intriguing insights. While (P,M)-4 2 has higher crystallinity and a greater specific surface area, it shows lower selectivity. Specifically, it has selectivity values of 5 for CO₂/CH₄ and 12.3 for CO₂/N₂, compared to (P,M)-4_1, which has selectivity values of 7.1 for CO₂/CH₄ and 28.0 for CO₂/ N2. This finding emphasizes that a higher degree of crystallinity doesn't always mean superior material properties compared to an amorphous counterpart.

The structural stability of POCs is crucial in determining their gas separation performance. A highly acid and base-stable shape-persistent porous carbamate cage 3 was introduced in 2017. In addition, cage 3 is capable of stability even in hot 1 M hydrochloric acid and in concentrated hydrochloric acid at room temperature without decomposition. Despite its low specific surface area, cage 3 exhibited good selectivity towards CO₂/CH₄, adsorbing 58 cm³ g⁻¹ CO₂ and 21.8 cm³ g⁻¹ CH₄ at 273 K and 1 bar. In 2019, Mastalerz et al. synthesized a large shape-persistent [4+6] amide cage 4. The cages' chemical robustness enabled post-functionalization under harsh conditions, resulting in the formation of demethylated cage 7, brominated cage 8, and nitrated cage 9.110 Notably, all of these cages demonstrated similar CO2 adsorption capacities, measuring $47.8 \text{ cm}^3 \text{ g}^{-1} \text{ for cage 4, } 45.8 \text{ cm}^3 \text{ g}^{-1} \text{ for cage 7, } 46.3 \text{ cm}^3 \text{ g}^{-1} \text{ for }$ cage 8, and 45.8 cm 3 g $^{-1}$ for cage 9 at 273 K and 1 bar. Under the same conditions, the cages exhibited similar CH₄ adsorption capacities, measuring 13.7 cm³ g⁻¹ for cage 4, 11.2 cm³ g⁻¹ for cage 7, 12.1 cm 3 g $^{-1}$ for cage 8, and 12.0 cm 3 g $^{-1}$ for cage 9. Of these cages, cage 8 demonstrated the greatest selectivity for CO₂/ CH₄, with a value of 28.5.

Yuan et al. recently reported on sp² carbon-linked POCs (sp²c-POCs) that possess distinctive triangular prism structures through a one-step Knoevenagel reaction (Fig. 7). 111 The sp2c-POCs

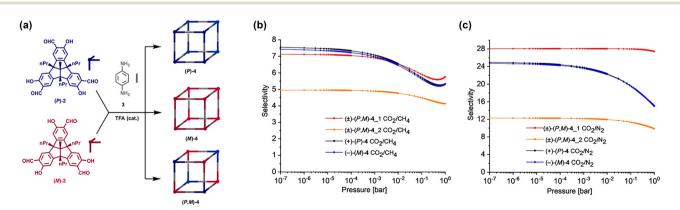


Fig. 6 (a) Condensation of the tri(salicylaldehyde) 2 with p-phenylenediamine 3 leading to the cubic [8+12] imine cage compounds (P)-4, (M)-4 and (P,M)-4. The cage compounds are represented schematically as cubes with the TBTQ-units at their vertices in blue for the (P)-enantiomer, in red for the (M)-enantiomer and the linear p-phenylenediimine linkers at the edges in grey. (b) IAST selectivity curves of the [8+12] cage compounds for CO₂/CH₄ (50:50) at 273 K and (c) for CO₂/N₂ (20:80) at 273 K. Reproduced with permission from ref. 108. Copyright 2021, Wiley.

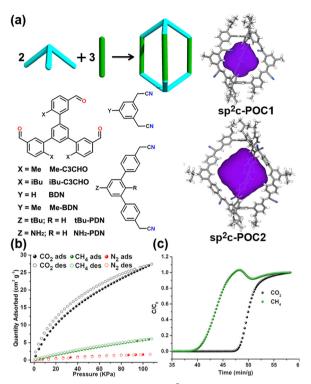


Fig. 7 (a) The synthetic route of [2+3] sp²c-POCs and their single-crystal X-ray structures. (b) CO_2 , CH_4 and N_2 adsorption isotherms of sp^2c -POC1 at 298 K. (c) Experimental breakthrough curves of an equimolar mixture of CO₂/CH₄ at 298 K and 1 bar over a packed bed of sp²c-POC1. Reproduced with permission from ref. 111. Copyright 2023, Chinese Chemical Society.

are highly stable, maintaining their structural integrity even in the presence of concentrated HCl, concentrated HNO3, or saturated NaOH solutions. Notably, sp²c-POC1 has the highest BET surface area (350 m 2 g $^{-1}$) among all sp 2 c-POCs. In addition, sp²c-POC1 can absorb 27.4 cm³ g⁻¹ of CO₂ and 6.1 cm³ g⁻¹ of CH₄, but has negligible affinity for N₂ at 298 K and 1 bar. The observed differences in gas uptake capacities imply that sp²c-POC1 can be useful in separating CO₂/N₂ and CO₂/CH₄ mixtures. The IAST selectivities of sp²c-POC1 were calculated, yielding values of 21 and 52 for CO₂/CH₄ (50:50) and CO2/N2 (15:85) mixtures, respectively. Breakthrough experiments have substantiated the excellent separation performance of sp²c-POC1 for CO₂/CH₄ and CO₂/N₂ gas mixtures. Moreover, the exceptional stability demonstrated by $sp^2c-POC1$ highlights its potential as a solid adsorbent for purifying and separating natural and flue gases.

The separation of CO2 and C2H2 is crucial in producing high-purity C₂H₂ by eliminating CO₂ impurities and poses significant challenges due to their similar molecular sizes and physical characteristics. It is imperative to study the gas sorption and separation behavior of CO₂ and C₂H₂ in POC with intrinsic porosity, abundant electron-rich π calix[4]-resorcinarene cavities, and oxygen and nitrogen sites. In 2021, Yuan et al. discovered a lantern-shaped calix[4]resorcinarene-based POC (CPOC-101) that exhibits eight distinct solvatomorphs when subjected to crystallization in different solvents, 93 presenting a significant breakthrough. Specifically, the CPOC-101α variant obtained

through crystallization in toluene/chloroform demonstrated an apparent BET surface area of up to 406 m² g⁻¹ as determined by nitrogen gas sorption at 77 K, which was much higher than other solvatomorphs of CPOC-101 with BET surface area below 40 m² g⁻¹. Most importantly, the **CPOC-101** α variant showed superior adsorption capacities for C₂H₂ and CO₂ and greater ability in C₂H₂/CO₂ separation than CPOC-101β, which served as the representative solvatomorph with low BET surface areas. At 298 K and 1 bar, the activation of CPOC-101α resulted in adsorption capacities of CO2 and C2H2 of up to 63 and 95 cm³ g⁻¹, respectively, while CPOC-101β resulted in lower adsorption capacities of 39 and 60 cm³ g⁻¹ under the same conditions. At ambient conditions, dynamic breakthrough experiments were conducted to verify the practical separation performance of C₂H₂/CO₂ using CPOC-101. The longer separation time of CPOC-101α compared to CPOC-101β indicates that it has a higher preference for trapping C₂H₂ over CO₂. Calculating the separation factors of C₂H₂/CO₂ for CPOC-101α and CPOC-101β using breakthrough experiments yields values of 2.2 and 2.0, respectively. Additionally, the stability of CPOC-101α was confirmed through recycling experiments where the breakthrough time remained consistent after four cycles.

In 2017, Yuan et al. reported the synthesis of seven waterstable hydrazone-linked POCs with four distinct assembly modes: HPOC-101, HPOC-102, HPOC-103, and HPOC-104. 112 These cages were synthesized via coupling reaction between C4RACHO and various dihydrazides (Fig. 8). The characterization of the porous organic cages revealed calculated BET surface areas ranging from 373 to 563 m² g⁻¹. Additionally, the cages' adsorption properties towards CO2 and C2H2 at room temperature were investigated, resulting in C2H2 capacities ranging from 31 to 47 cm 3 g $^{-1}$ and CO₂ capacities ranging from 24 to 33 cm 3 g $^{-1}$. These cages notably exhibited a preference for C₂H₂ adsorption over CO2. To assess their applicability in C2H2/CO2 separation, breakthrough experiments using a C₂H₂/CO₂ mixture (50:50), were specifically conducted for HPOC-102 and HPOC-104, which resulted in the effective separation of the C2H2/CO2 mixture. These breakthrough experiments highlight the promising performance of the cages in C₂H₂/CO₂ separation. Furthermore, HPOC-102 and HPOC-104 serve as pioneering examples of hydrazone-linked POC materials successfully achieving C₂H₂/ CO2 gas separation.

2.2. Light hydrocarbon purification

The separation of light hydrocarbons into individual components with the desired purity remains a significant objective in the petrochemical industry. Cryogenic distillation, a prevailing method, is expensive and energy-intensive, leading to the emergence of adsorption separation with porous materials as a promising alternative technology. Recently, a few POCs have been synthesized to achieve highly efficient separation of light hydrocarbons.

In 2018, Mastalerz et al. reported the synthesis of a small series of [4+6] boronic ester cages that varied in the degrees of fluorine content within the diboronic ester struts. 113 Of the fluorinated cages, cages 10* and 11* exhibited noteworthy

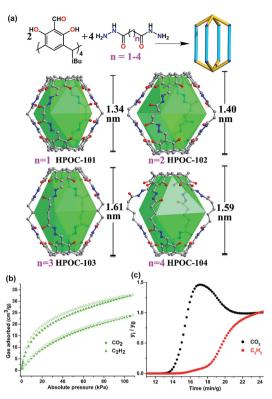


Fig. 8 (a) Schematic illustration of the assembly of [2+4] lanterns via hydrazone coupling of C4RACHO and alkanedihydrazides, along with their single-crystal X-ray structures and inner cavity heights. (b) CO₂ and C₂H₂ adsorption isotherms of HPOC-102 at 298 K. (c) Experimental breakthrough curves of an equimolar mixture of CO₂/C₂H₂ at 298 K and 1 bar over a packed bed of **HPOC-102**. Reproduced with permission from ref. 112. Copyright 2021, Royal Society of Chemistry.

properties. Notably, non-fluorinated cage 9* had an excellent specific surface area of 511 m² g⁻¹. Encouraged by this result, subsequent investigations concentrated on the adsorption and separation performance of cage 9* for small hydrocarbons. The gas adsorption capacity of cage 9* was found to be 2.52 mmol g⁻¹ for C_2H_6 , 2.50 mmol g^{-1} for C_2H_4 , and 2.53 mmol g^{-1} for C_2H_2 . The selectivities for C₂H₆/C₂H₄, C₂H₆/C₂H₂, and C₂H₄/C₂H₂ based on a hypothetical 1:1 mixture were evaluated to be 1.29, 1.52, and 1.17, respectively.

Zhang et al. subsequently reported the synthesis of a new class of soft porous crystals utilizing an [2+3] imide-based organic cage referred to as NKPOC-1 (Fig. 9).91 One intriguing characteristic of NKPOC-1 is its guest-induced breathing behavior, where it undergoes reversible transformations from a "closed" nonporous phase (α) to two distinct porous "open" phases (β and γ) upon exposure to various gas molecules. Notably, NKPOC-1-α exhibits remarkable selectivity for propyne (C₃H₄) adsorption over propylene (C₃H₆) and propane (C₃H₈) under ambient conditions. To evaluate its separation capabilities, dynamic breakthrough experiments were conducted using binary and ternary gas mixtures consisting of C_3H_4/C_3H_6 (2:1, v/v), C_3H_4/C_3H_8 (2:1, v/v), and $C_3H_4/C_3H_6/C_3H_8$ (2:1:1, v/v/v) at 298 K. **NKPOC-1-** α demonstrates exceptional separation efficiency in the case of binary C₃H₄/C₃H₆ and C₃H₄/C₃H₈ gas mixtures, with C₃H₄ saturation uptakes and

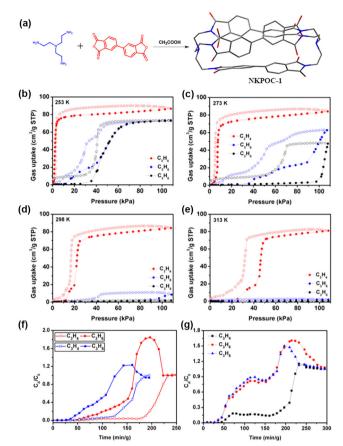


Fig. 9 (a) Synthesis of NKPOC-1 (C, gray; N, blue; O, red). Sorption isotherms of NKPOC-1- α for C_3H_4 , C_3H_6 , and C_3H_8 at (b)253 K, (c) 273 K, (d) 298 K, and (e) 313 K. Filled and open symbols represent adsorption and desorption, respectively. (f) Dynamic experimental fixedbed column breakthrough results of binary (2:1 v/v) C_3H_4/C_3H_6 and C_3H_4/C_3H_6 C_3H_8 gas mixtures in an absorber bed packed with activated **NKPOC-1-** α . (g) Ternary breakthrough experiment for a C₃H₄/C₃H₆/C₃H₈ (2:1:1 v/v/v) gas mixture. Reproduced with permission from ref. 91. Copyright 2019, American Chemical Society.

breakthrough retention times of 75.6 cm 3 g $^{-1}$ and 137 min g $^{-1}$, as well as 55.2 cm³ g⁻¹ and 100 min g⁻¹, respectively. Noteworthy, NKPOC-1-α also effectively removes C₃H₄ from a ternary gas mixture (C₃H₄/C₃H₆/C₃H₈, 2:1:1, v/v/v) under ambient conditions, based on a C_3H_4 retention duration of 135 min g^{-1} and a calculated C₃H₄ saturation uptake of 67 cm³ g⁻¹. This outstanding separation performance of NKPOC-1- α is attributed to its selective gate-opening effect for C3 hydrocarbons combined with the strength of the interactions once the gate is open.

Yuan et al. identified a promising POC, known as CPOC-301, which is composed of a highly porous [6+12] octahedral calix[4]resorcinarene structure (Fig. 10).92 It is important that CPOC-301 shows exceptional ability in selectively capturing C₂H₆ from mixtures with C2H4, resulting in the direct production of high-purity C_2H_4 . **CPOC-301** can adsorb up to 670 cm³ g⁻¹ of N_2 , a maximal capacity that corresponds to a calculated BET surface area of 1962 m² g⁻¹. A key finding is that, at 293 K, CPOC-301 selectively binds C₂H₆ more strongly (87 cm³ g⁻¹) than C₂H₄ (75 cm³ g⁻¹). The researchers calculated that the heat of adsorption

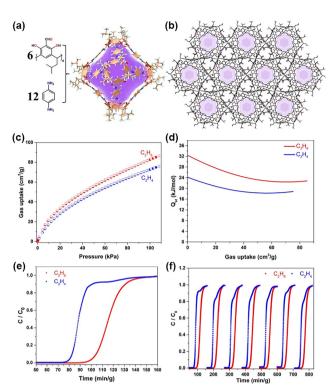


Fig. 10 (a) The X-ray crystal structure of CPOC-301. (b) The Solid-state molecular packing of CPOC-301 viewed from [001] direction, where H atoms are committed for clarity. Color codes: phenyl ring; orange, carbon; gray, oxygen; red, nitrogen; blue, and hydrogen; light turquoise. (c) Experimental C_2H_6 and C_2H_4 adsorption isotherms of **CPOC-301** at 293 K. (d) Isosteric heat of adsorption plots for the adsorption of C₂H₆ and C₂H₄ by **CPOC-301**. (e) Experimental breakthrough curves for equimolar mixture of C_2H_6/C_2H_4 at 298 K and 1 bar over a packed bed of **CPOC-301**. (f) The recyclability of CPOC-301 under multiple mixed gas column breakthrough tests. Reproduced with permission from ref. 92. Copyright 2021, Springer Nature.

 (Q_{st}) at zero coverage for C_2H_6 and C_2H_4 is 32.4 and 24.2 kJ mol⁻¹, respectively. This observation suggests that the host-guest interactions between CPOC-301 and C2H6 are much stronger than those with C2H4. The researchers attribute the stronger attraction of **CPOC-301** to C_2H_6 as a result of the creation of multiple $C-H\cdots\pi$ hydrogen bonds between C₂H₆ and the resorcin[4] arene cavities, demonstrated by first-principles dispersion-corrected density functional theory (DFT-D) calculations. Additionally, breakthrough experiments have validated the efficient isolation of C2H4 from C_2H_6/C_2H_4 mixtures using **CPOC-301**. The researchers provide the calculated separation factor for an equimolar mixture of C2H6/ C₂H₄, which is 1.3, a value that aligns well with the predicted IAST value. Further, researchers found that the CPOC-301 consistently maintains its separation performance over seven consecutive cycles, which demonstrates its robustness and positions it as a promising candidate for C₂H₄ purification purposes.

Recently, Yuan et al. explored the functionalities of the octahedral calix[4]resorcinarene-based hydrazone-linked porous organic cage (HPOC-401) as a prototype for post-synthetic metalation with different transition metal ions. 114 The study demonstrated that HPOC-401 has exceptional properties for this purpose, even under mild conditions. The BET surface areas of HPOC-401 after being metalated with various transition metal ions, namely HPOC-401-V, HPOC-401-Cu, HPOC-401-Zn, and HPOC-401-Mo, were significantly increased compared to pristine **HPOC-401.** The specific surface areas measured were 1456 m² g⁻¹ (HPOC-401-V), $1099 \text{ m}^2 \text{ g}^{-1}$ (HPOC-401-Cu), $983 \text{ m}^2 \text{ g}^{-1}$ (HPOC-**401-Zn**), and 710 m² g⁻¹ (HPOC-401-Mo), while HPOC-401 had a surface area of 474 m² g⁻¹. Furthermore, the metalated **HPOC-401** showed enhanced CO2, H2, and C2 hydrocarbon uptake capacity along with improved selectivity for C₂H₆/C₂H₄, compared to the pure HPOC-401. Specifically, HPOC-401-V and HPOC-401-Cu displayed an interesting preference for C₂H₆ over C₂H₄. However, HPOC-401 alone does not exhibit selective adsorption of C2H6. Remarkably, HPOC-401-V demonstrated an outstanding C₂H₆/ C₂H₄ selectivity of up to 2.3, which surpasses the selectivity values of other POCs. The breakthrough results indicate the potential of HPOC-401-V to achieve efficient one-step separation of C₂H₄ from an equimolar mixture of C2H6/C2H4.

2.3. Separation for Xe/Kr rare gases

Noble gases, including Kr and Xe, are widely used in diverse industries such as gas lasers, semiconductor, photography lighting, and medical fields. 115 However, unstable and hazardous radioisotopes of Kr and Xe, like ¹³³Xe and ⁸⁵Kr, can be generated by used nuclear fuel reprocessing facilities or nuclear accidents. When these radioisotopes escape into the atmosphere, they pose risks to the environment and living organisms.

Cooper et al. developed the first reported POC material for Xe/Kr separation with exceptional performance (Fig. 11).88 The team used a [4+6] tetrahedral POC called CC3, which is an imine-linked structure formed by the Schiff-base reaction of 1,3,5-triformylbenzene and 1,2-diaminocyclohexane in a 2:3 molar ratio. CC3 was chosen primarily because the largest inclusion sphere in the CC3 cavity measures 4.4 Å, which is close to the size of Xe (4.10 Å). Notably, the window diameter of CC3 observed in its static solid-state crystal structure is only 3.6 Å, which is theoretically too narrow to allow for Xe and Kr diffusion, with diameters of 4.10 Å and 3.69 Å, respectively. However, the flexibility of the cage structure, attributed to cage vibrations, results in temporary enlargement of the pore diameter. Despite being relatively soft since CC3 is assembled from discrete molecules, it exhibits structural deformations, such as window vibrations and packing changes under certain temperature and pressure conditions, allowing many gas molecules to access the pores of CC3. The simulations and experimental gas adsorption isotherms and molecular dynamics revealed that CC3 can accommodate both Xe and Kr, and it demonstrated a strong Xe preferential adsorption over Kr, as evidenced by calculations of the isosteric heat of adsorption. The calculated Xe/Kr selectivity for CC3 reached a value of 20.4, surpassing many MOF materials. To examine the practical separation performance of rare gases at low concentrations in the air, mimicking the spent nuclear fuels reprocessing, the researchers conducted experimental breakthrough measurements. They used gas mixtures containing Xe (400 ppm), Kr (40 ppm), and other elements of air (N2, O2, and CO2), which were passed through a packed column of CC3 crystals. The Kr

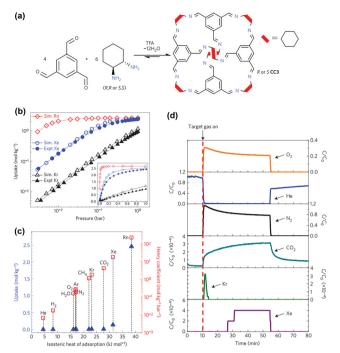


Fig. 11 (a) Schematic illustration of the assembly of CC3. (b) Predicted and experimental single-component gas adsorption isotherms for CC3 at 298 K. (c) Isosteric heat of adsorption calculations of noble and other gases at 298 K. (d) Breakthrough curves for CC3 by Xe, Kr, and common gas mixtures. Reproduced with permission from ref. 88. Copyright 2014,

gas was immediately detected in the effluent, while Xe gas was retained for more than 15 min, which is consistent with the observation of stronger host-guest interactions between Xe and the cage relative to Kr.

In 2016, Thallapally et al. reported the selective uptake of Xe by two previously reported POCs, 116 namely noria and PgC-noria. These POCs were prepared with an acid-catalyzed condensation reaction between glutaraldehyde and resorcinol (for **noria**) and pyrogallic acid (for **PgC-noria**), in the presence of concentrated hydrochloric acid. The isotherms for Xe and Kr adsorption were measured for both noria and PgC-noria. It was observed that both POCs showed selectivity towards Xe over Kr, with noria demonstrating greater Xe adsorption compared to PgC-noria. Furthermore, the IAST calculations demonstrated that noria displayed an exceptional Xe/Kr selectivity of 9.4 under dilute conditions. The remarkable Xe/Kr selectivity, coupled with the high thermal stability of noria implies that it could be a promising candidate for capturing Xe from the offgas produced during the reprocessing of used nuclear fuel.

2.4. Separation for fluorinated greenhouse gases

Manufactured fluorinated gases, including SF₆, perfluorocarbons (PFCs), and nitrogen trifluoride (NF₃), are widely utilized in modern industries such as refrigerants, propellants, and blowing agents.117-119 However, it is important to note that fluorinated gases are highly toxic and potent greenhouse gases whose global warming potentials are thousands of times higher than that of CO₂. Therefore, the development of porous adsorbents for selective adsorption of fluorinated gases, prioritizing them over other less harmful gases, is critical in both industrial and environmental domains. POCs have undergone development for the separation of fluorinated gases.

In 2016, Cooper et al. investigated whether four [4+6] iminelinked tetrahedral POCs (CC2, CC3, CC5, and CC13) could be potentially applied to separate SF₆ from N₂. 89 These POCs were synthesized through a Schiff-base reaction between diamine and tri-aldehyde in a 3:2 molar ratio. Adsorption experiments were conducted to evaluate their capability for SF₆ gas uptake, revealing that all four cages demonstrated SF₆ adsorption but at varying capacities due to their structural differences. It is important to note that the kinetic diameter of SF₆ (5.5 Å) exceeds the window diameters (~3.6 Å) of CC2, CC3, and CC13, suggesting that they are not capable of encapsulating SF₆. However, these POCs possess a flexible nature that enables them to adsorb SF₆ despite its larger size than the static window diameter. Further analysis of the adsorption isotherms indicated that $CC3\alpha$ exhibited a typical type I adsorption behavior characterized by sharp increases at low pressures, indicating its higher affinity for SF₆. This finding was supported by the calculated Qst values. Furthermore, CC3 showed the highest SF₆/N₂ selectivity among the four POCs, and activated CC3α achieved selectivities of 178 at 273 K and 74 at 298 K for a 10:90 SF₆:N₂ mixture, which exceeds those of many reported MOFs. Additional simulations suggested that cooperative diffusion and structural rearrangements within CC3 contribute to the near-ideal behavior of the host for SF₆ guest molecules. X-ray crystallography analysis provided insight into the location of SF₆ within the CC3 cavity, confirming the strong interaction between the CC3 host and SF₆ guest.

In 2022, Mastalerz et al. reported three isostructural [2+3] lantern-shaped POCs, including H-cage (with non-fluorinated *n*-butyl chains), **HF-cage** (with partially fluorinated *n*-butyl chains), and F-cage (with perfluorinated n-butyl chains), all with varying degrees of fluorinated side-chains (Fig. 12).94 Triamino triptycene and terphenyl-based bis-salicylaldehydes were used in a 2:3 molar ratio, catalyzed by trifluoroacetic acid to construct these POCs. The gas adsorption behavior of fluorinated and non-fluorinated alkanes was compared among these isomorphic crystalline states to evaluate the impact of different side chains on gas sorption properties. The study showed that the fluorinated POCs preferentially adsorbed fluorinated gases, whereas the non-fluorinated POCs demonstrated a preference for non-fluorinated gases. Specifically, F-cage exhibited the highest uptakes of PFCs, such as tetrafluoromethane (CF₄), hexafluoroethane (C₂F₆), and octafluoropropane (C₃F₈), compared to the other two POCs. IAST selectivities of CF₄/N₂, C₂F₆/N₂, and C₃F₈/N₂ were calculated under different compositions and conditions (273 K and 1 bar), indicating that F-cage had a high selectivity for fluorinated gases over N2. Additionally, F-cage showed the highest selectivity for fluorinated alkanes over non-fluorinated alkanes. Given its advantageous selective adsorption of PFCs, the researchers further investigated the sorption of octafluorocyclobutane

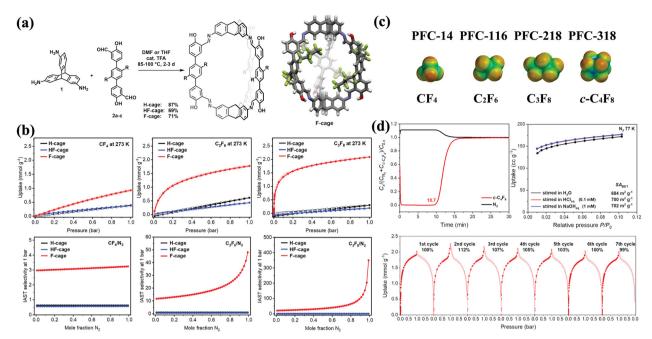


Fig. 12 (a) Synthesis of H-cage, HF-cage, and F-cage by imine condensation reactions of triamino triptycene and terphenyl bis-salicylaldehydes, and the single-crystal X-ray structure of F-cage. (b) PFC sorption properties of H-cage, HF-cage, and F-cage in comparison. (c) Space filling models of the fluorinated alkanes, including tetrafluoromethane (PFC-14), hexafluoroethane (PFC-116), octafluoropropane (PFC-218), and octafluorocyclobutane (PFC-318). (d) Applicability investigations of F-cage, including breakthrough curves and stablity tests. Reproduced with permission from ref. 94. Copyright 2022, Wiley.

(c-C₄F₈ or PFC-318) in more detail. F-cage demonstrated selectivity for c-C₄F₈/N₂ up to 41475. Experimental breakthrough analyses revealed that F-cage effectively separated c-C₄F₈ from N₂ mixtures with a breakthrough time of 107 minutes, and its separation performance remained consistent over seven consecutive cycles. Furthermore, F-cage demonstrated stability in neutral, acidic, and basic aqueous media as confirmed by ¹H and ¹⁹F NMR spectroscopy, thermogravimetric analysis (TGA), and N₂ sorption at 77 K, indicating that F-cage is robust enough for real-world applications.

2.5. Separation for D_2/H_2 gas isotopes

Deuterium is an irreplaceable raw material that finds widespread use in scientific research, including isotope tracing, neutron scattering, and proton nuclear magnetic resonance spectroscopy, as well as industrial applications, such as fuel in nuclear fusion reactors and for fusion reactions, and in medical uses like imaging and cancer therapy. To meet the growing global demand for deuterium, the development of a cost-effective and large-scale separation method is crucial. Two approaches for separating hydrogen isotopes using porous materials are kinetic quantum sieving (KQS), which utilizes nanoconfined space, and chemical affinity quantum sieving (CAQS), which relies on strong metal adsorption sites. Various porous materials, including activated carbons, zeolites, MOFs, and COFs, have been investigated in attempts to separate D₂ from H₂. 120-127 However, the selectivity of D₂/H₂ using these materials is often low, typically less than 2, for both separation strategies. Porous materials with ultra-fine pore apertures

 $(\sim 3 \text{ Å})$ are critical for achieving KQS but are challenging to obtain in activated carbons, zeolites, MOFs, and COFs.

Cooper et al. utilized PSM synthesis in 2019, which proved to be effective in modifying POCs' internal cavities and fine-tuning the pore sizes, resulting in outstanding quantum sieves.⁹⁰ Their work produced six internal functionalized POCs, namely 6ET-RCC3, 1PT-5FT-RCC3, 1AT-5FT-RCC3, 1ET-5FT-RCC3, 5FT-RCC3, and 6FT-RCC3, with PLE values ranging from 1.95 Å to 3.50 Å (Fig. 13). To achieve this, a post-synthetic "tying" and protection-deprotection strategy were utilized based on RCC3, a reduced derivative of CC3. The POCs demonstrated a trade-off behavior, where those with lower PLE values exhibited lower D2 adsorption capacities but higher selectivity while conversely, those with higher PLE values exhibited high D₂ adsorption capacities and lower selectivity. The upscaling of the internal functionalized POCs for practical applications presented significant challenges. Nonetheless, combining the small-pore and large-pore functionalized POCs through cocrystallization into a single solid resulted in a material with optimal separation performance, exhibiting excellent D₂/H₂ selectivity (8.0) and high deuterium uptake (4.7 mmol g^{-1}). In 2022, Vogel et al. used ab initio molecular dynamics (AIMD) simulations to explain how the internal functionalized POCs could manage D2 and H2 separation, leading to the targeted design of novel porous adsorbents for hydrogen isotope separation. 128

3. Conclusions

In summary, numerous POCs of different shapes, sizes, and functions have been designed and synthesized in the last

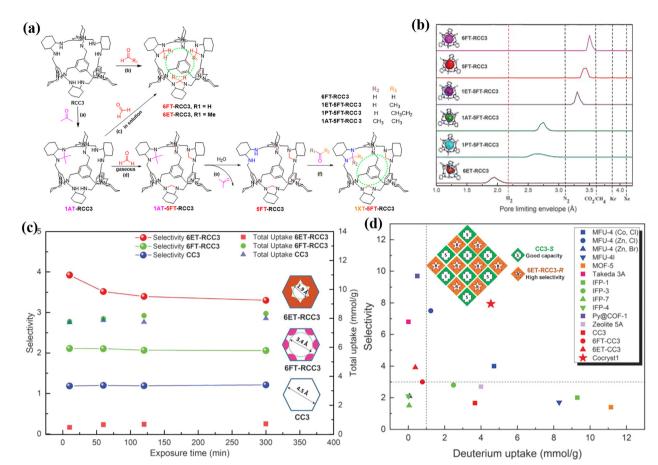


Fig. 13 (a) Full synthesis route for the internal functionalized POCs (including 6ET-RCC3, 1PT-5FT-RCC3, 1AT-5FT-RCC3, 1ET-5FT-RCC3, 5FT-RCC3, 5FT-RCC3, 1ET-5FT-RCC3, 1ET-5FT-RC3, 1ET-5FT-RC3, 1ET-5FT-RC3, 1ET-5FT-RC3, 1ET-5FT-RC3, 1ET-5FT-RC3, 1ET-5FT-RC3, 1ET-5FT-RC and 6FT-RCC3). (b) Representative single-crystal structures of the modified cages showing accessible cavities (colored), along with calculated PLEs for each system. (c) D₂/H₂ selectivities and gas uptakes as a function of exposure time at 30 K for CC3, 6FT-RCC3, and 6ET-RCC3. (d) Summary of hydrogen isotope KQS selectivities and adsorption capacities for various porous materials. Reproduced with permission from ref. 90. Copyright 2019, American Association for the Advancement of Science.

decade utilizing various organic synthons and covalent condensation reactions. However, only a few of these have been explored for gas separation. To our knowledge, POCs have only been examined in specific gas separation systems such as CO₂/ N₂, CO₂/CH₄, C₂H₂/CO₂, rare gases Xe/Kr, greenhouse SF₆/N₂, isotope separation D₂/H₂, and separation of industrially important C2 and C3 hydrocarbons through mixed gas experiments. These instances have been reviewed thoroughly. However, the gas separation applications of POCs are still in the early stage, and their uses have been limited to the aforementioned gas components in mixed gas experiments. Herein, we present some essential perspectives on the potential applications of POCs in gas separation.

(1) Developing stable POCs

Although many POCs have been assembled using dynamically reversible imine and boronate ester bonds, these components are sensitive to hydrolysis under acid, base, or even moisture conditions. This sensitivity often leads to POCs' decomposition, significantly hindering their practical use in gas separation studies considering the presence of acidic, basic, or water vapor gases in gas mixtures. Thus, there is a high demand for the development of robust covalent linkages to build chemically stable POCs using simple and cost-effective procedures. 111

(2) Separation of industrially important gases and multicomponent gas mixtures

POCs exhibit potential for exploring the applications of separating industrially important C4-C6 hydrocarbons as well as multicomponent gas mixtures. 129-131 POCs may exhibit unexpected and unique separation behavior compared to other extensively studied porous materials such as MOFs, zeolites, and POPs. "Soft" porous materials with flexible and adaptive pore structures have gained attention in recent years because of their capacity to adjust their structures to control gas mobility and diffusivity in their pores for efficient purification. 132-134 POCs possess the inherent attribute to serve as "soft" porous materials. They are constructed from small molecules that interact weakly in the solid-state, 39,94 allowing gas guests to gain pore access via structural deformations under specified conditions.

(3) Efficient and precise separation

Due to their discrete molecules, POCs can be designed with finely-tuned pore sizes at a remarkably precise level with selective interior functionalization. This level of control is challenging to achieve in other porous materials such as COFs and MOFs. Commonly, the strategy of tuning pores in MOFs and COFs involves systematically expanding or reducing the number of phenylene rings in the organic linker, resulting in coarse tuning increments or decrements of approximately 2.8 Å. This tuning method is not suitable for achieving finetuning of pores. Therefore, POCs have the potential to achieve high selectivity for the separation of gas mixtures with similar molecule shapes by designing appropriate pores through a finetuning approach. This fine-tuning method maintains high gas adsorption capacity while also maintaining the nearly unchanged original cavities.

(4) Gas separation using POC-based membranes

Membrane technology has emerged as an efficient and energysaving alternative for gas separation and purification processes. Leveraging the advantageous solubility and solvent processability of POCs, researchers have successfully developed pure POC-based membranes and mixed matrix membranes. These innovative membranes have demonstrated significant potential across various applications involving gases, ions and small organic molecules. 135-138 Therefore, it is imperative to emphasize the promising prospect of achieving high-performance membranes by precisely controlling both the intrinsic and extrinsic pores of POCs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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