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1. Introduction

Macrocycle-derived hierarchical porous organic polymers: synthesis and applications

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Porous organic polymers (POPs), as a new category of advanced porous materials, have received broad research interests owing to the advantages of light-weight, robust scaffolds, high specific surface areas and good functional tailorability. According to the long-range ordering of polymer skeletons, POPs can be either crystalline or amorphous. Macrocycles with inherent cavities can serve as receptors for recognizing or capturing specific guest molecules through host-guest interactions. Incorporating macrocycles in POP skeletons affords win-win merits, *e.g.* hierarchical porosity and novel physicochemical properties. In this review, we focus on the recent progress associated with new architectures of macrocycle-based POPs. Herein, these macrocycles are divided into two subclasses: non-planar (crown ether, calixarene, pillararene, cyclodextrin, cyclotricatechylene, *etc.*) and planar (arylene–ethynylene macrocycles). We summarize the synthetic methods of each macrocyclic POP in terms of the functions of versatile building blocks. Subsequently, we discuss the performance of macro-cyclic POPs in environmental remediation, gas adsorption, heterogeneous catalysis, fluorescence sensing and ionic conduction. Although considerable examples are reported, the development of macrocycle-based POPs.

Porous organic polymers (POPs) are an emerging class of multi-dimensional porous materials constructed from various

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^c College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China organic building blocks *via* strong covalent bonds.^{1–3} Depending on the degree of crystallinity, POPs can be divided into either amorphous or crystalline analogues. Amorphous POPs mainly include hyper-crosslinked polymers (HCPs), conjugated microporous polymers (CMPs), porous aromatic frameworks (PAFs), and polymers of intrinsic microporosity (PIMs), while covalent organic frameworks (COFs) represent the typical crystalline form of POPs.^{4–6} POPs have recently attracted a great deal of attention due to their merits of inherent porosity, light-weight, robustness, tuneable structures and tailor-made functionalities as well as their promising applications in gas



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The successful marriage between supramolecular chemistry and porous materials can offer great opportunities for the creation of new advanced materials with unique characteristics. Over the past several decades, macrocycles, such as crown ether (CE), cyclodextrin (CD), calix[n]arene (n = 4, 6, 8, CA), resorcinarene (RA) and pillar[n]arene (n = 5-10, PA), have been playing significant roles in supramolecular chemistry and materials science due to their intrinsic cavities capable of selectively accommodating guest molecules or ions. Although the intrinsic cavities of macrocycles make them promising host materials in a variety of applications, such as molecular recognition and separation, drug delivery, and enzyme mimetic catalysis,8 certain drawbacks such as low porosity and weak chemical stability restrain to some extent further improvements in their performance for specific applications. Recently, the scope of macrocyclic chemistry has expanded from discrete cavitands to rigid hierarchically porous organic frameworks which bear several advantages9-11 including but not limited to the following: (1) the preparation of macrocycle-based POPs opens up a promising approach to expand the structural diversities of POPs and generates hierarchically porous structures with high porosities; (2) the unique molecular recognition properties of macrocyclic moieties impart the resulting macrocycle-based POPs with specific functions via host-guest chemistry and non-covalent interactions; (3) the stimuli-responsive properties of macrocyclebased host-guest systems could mediate macrocyclic POPs to serve as fascinating and smart stimuli-responsive materials; (4) the crystalline macrocyclic COFs could facilitate the understanding of the structure-property relationship and the development of high-performance functional materials. Hence, the integration of supramolecular macrocycles into POPs could tailor specific functions of POPs, afford intriguing guest-responsive properties, and provide new possibilities for task-specific applications.^{12,13}

So far, several interesting reviews on POPs and their diverse applications have been documented.⁷ However, very few comprehensive overviews are focused on macrocycle-based POPs.^{9–13}



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focuses on the design and synthesis of 2D conjugated porous polymers for catalysis and energy-related applications. This review article will specifically highlight the macrocyclecontaining POPs and their synthetic strategies as well as promising applications. To clearly introduce the recent advances of macrocycle-based POPs, we classify the reported macrocyclic POPs based on the planarity of macrocycle building blocks (Fig. 1). Most of them are the nonplanar ones, which include conventional macrocycles (CE, CD, CA, RA and PA) as well as other types (e.g. cyclotricatechylene); they usually form amorphous POPs. On the other hand, planar macrocycles mainly include arylene-ethynylene macrocycles, porphyrin and phthalocyanine. Nevertheless, porphyrin- and porphyrinoid (phthalocyanine or corrole)-based POPs will not be discussed here because some recent and excellent reviews are available in the literature for readers' perusal.¹⁴⁻¹⁷ Furthermore, we emphasize the main applications of macrocycle-containing POPs, i.e. environmental remediation, gas adsorption/separation, heterogeneous catalysis, fluorescent sensors, and ionic conduction (Fig. 1). At the end, future prospects and remaining challenges of macrocycle-based POPs concerning technological synthesis and future practical applications are proposed, which might inspire further research in this specific field.

2. Amorphous macrocycle-based POPs

2.1 CE-based POPs prepared by Friedel-Crafts reaction

CEs represent the first explored macrocyclic hosts and their oxygen-rich binding sites and tuneable cyclic cavities can complex with various metal ions or organic cationic species.⁸ Hence, CE-functionalized materials have been intensively investigated in supramolecular chemistry.¹⁸ Liu and co-workers¹⁸ reported a triptycene and crown ether based POP (POP-TCE-15 in Fig. 2), which was prepared by a simple Friedel–Crafts alkylation reaction of triptycene, crown ether and formaldehyde dimethyl acetal (FDA). Powder X-ray diffraction (PXRD) analysis revealed that POP-TCE-15 was amorphous in nature. However, POP-TCE-15 showed a high surface area of 848 m² g⁻¹, good hydrophobicity and excellent chemical stability in both acidic and basic solutions.

2.2 Amorphous CD-based POPs

CDs are cone-shaped cyclic oligosaccharides and obtained from the enzymatic degradation of natural materials (*e.g.* corn starch). The main types of CDs are three naturally occurring ones, *i.e.*, α -, β - and γ -CDs, which contain six, seven or eight repeating glucopyranose units, respectively, linked by α -1,4-glycosidic bonds. The hydrophilic external surfaces render CDs easily soluble in aqueous systems but the hydrophobic internal cavities can accommodate various small organic molecules, metal ions or organometallic compounds such as ferrocene.⁸ The 2-, 3-, 6-hydroxyl groups of CDs can be facilely and selectively modified to introduce other functionalities. Traditional CD-based polymers synthesized from CDs and epichlorohydrin (EPI) (Fig. 3) usually exhibit low specific surface areas (<100 m² g⁻¹).¹⁹ Additionally, the environmentally hazardous EPI is potentially carcinogenic. Hence, exploring novel crosslinkers and synthetic strategies to improve the porosity of



Fig. 1 Structures of supramolecular macrocycles and main applications of macrocycle-based POPs discussed in this review.



CD-based polymers is highly desired. The following section

CD-based polymers is highly desired. The following section will mainly summarize the recent advances in the synthetic strategies and novel crosslinkers for preparing highly porous CD-based POPs.

2.2.1 CD-based HCPs prepared by Friedel-Crafts reaction. HCPs can be synthesized by Friedel-Crafts alkylation reaction of benzyl units, which feature high surface areas and good thermal stability.¹⁹ On the basis of this concept, Dai and co-workers¹⁹ reported a hyper-crosslinked β-CD porous polymer (BBnCD-HCPP) by Friedel-Crafts alkylation. Firstly, the fully benzylated β-CD (βBnCD) was prepared by a reaction of benzyl bromide with β -CD in dry DMF using NaH as the base. Then the resulting BBnCD was hyper-crosslinked using FDA as a crosslinker and anhydrous FeCl3 as the Lewis acid catalyst to afford BBnCD-HCPP (Fig. 3a). Compared to EPI-based CD-polymers, ßBnCD-HCPP exhibited a higher BET surface area (1225 $m^2 g^{-1}$) due to inefficient packing among rigid and contorted benzene rings and the inherent cavity of β -CD. Additionally, the excellent thermal stability of BBnCD-HCPP conferred exceptional performance in adsorbing aromatic pollutants. Subsequently, as shown in Fig. 3b,

Dai and co-workers further synthesized four CD-based HCPPs from α -CD and β -CD by a similar Friedel–Crafts alkylation reaction.²⁰ Interestingly, despite structural differences, all the four CD-based HCPs exhibited excellent thermal stability. Compared to α BnCD6OH-HCPP (871 m² g⁻¹) and β BnCD6OH-HCPP (880 m² g⁻¹), the BET surface areas of α BnCD-HCPP (989 m² g⁻¹) and β BnCD-HCPP (1225 m² g⁻¹) were higher owing to more benzene rings participating in hyper-crosslinking. Additionally, a series of BnCD-based HCPs by Friedel–Crafts alkylation of BnCD with other crosslinkers (DCX and BCMBP, Fig. 3c) were developed, which again showcased high BET surface areas, excellent thermal and chemical stability, and enhanced uptake of hydrophilic pollutants.^{21–23}

2.2.2 CD-based POPs prepared by nucleophilic aromatic substitution. Except Friedel–Crafts alkylation for the synthesis of β -CD based polymers, nucleophilic aromatic substitution (SNAr) reaction is another widely utilized approach to knit different CDs with rigid fluorinated aromatic cross-linkers. Dichtel and co-workers²⁴ made a breakthrough in developing β -CD containing polymers (TFN-CDP) with high specific surface areas. The TFN-CDP were prepared by a SNAr reaction between the hydroxyl groups of β -CD and rigid aromatic tetrafluoroterephthalonitrile (TFN, Fig. 4a). Importantly, the mesoporous TFN-CDP adsorbed a variety of organic micropollutants more rapidly than those of activated carbons and the non-porous β -CD polymer.

Although CD-based polymers showed good adsorption properties, the yields of the SNAr reaction were surprisingly low (18%), and the TFN : β -CD ratio of the isolated polymer (*ca.* 6 : 1) did not match with the monomer feed ratio (3 : 1). Dichtel and co-workers²⁵

reaction.



Fig. 3 CD-based POPs prepared by Friedel–Crafts reactions. (a) Left, synthesis of the β -CD polymer β BnCD-HCPP with high-surface-areas. Right, schematic representation of the β BnCD-HCPP structure. Adapted with permission from ref. 19. Copyright 2016 The Royal Society of Chemistry. (b) Synthesis of hyper-crosslinked CD-based HCPPs. (c) Some representative crosslinkers in the synthesis of CD-based POPs.

further demonstrated that a fluorine atom in TFN was substituted by a hydroxyl group by studying a model reaction between TFN and *n*-butanol. Therefore, phenolation and etherification are competing processes, and the level of phenolate incorporation can be controlled by varying the rate of base addition, monomer concentrations and the solvent (Fig. 4a). The results indicated that polymers with higher concentrations of negatively charged phenolic groups exhibited a higher binding capacity for heavy metal ions and a higher affinity for cationic micropollutants. This study paves the way for controllable synthesis of TFN-CDP in high yields.

Unfortunately, TFN-CDP with negatively charged phenolic moieties showed poor affinity for anionic per- and polyfluorinated alkyl substances (PFASs). To address this issue, Dichtel and co-workers²⁶ developed a new β-CD crosslinked polymer network (DFB-CDP) via a SNAr reaction between β-CD and the crosslinker (decafluorobiphenyl, DFB) with a higher fluorine content (Fig. 4b). Compared to TFN-CDP and activated carbon, DFB-CDP exhibited a higher affinity toward perfluorooctanoic acid (PFOA). This is because increasing fluorine content can decrease phenolate concentrations and increase the affinity. The low affinity of DFB-CDP towards anionic polyfluorinated alkyl substances except the one with a C7 alkyl chain is probably due to the size dependent hydrophobically driven binding mechanism of β -CD. The same group further reported a new strategy to improve the affinity for anionic PFASs by introducing a cationic functionality into a TFN-CDP.²⁷ The new cationic CDP were prepared by nitrile reduction of TFN-CDP into benzyl amine, which can form the cationic ammonium groups in neutral water (Fig. 4c). The combination of β-CD and protonated

amino groups showed a wider spectrum of PFAS remediation with different alkyl chains.

 α -CD can be utilized to remove special organic pollutants (*e.g.* dibutyl phthalate (DBP)) since it shows better guest affinity as compared with other CD analogues in this case.²⁸ Jana and co-workers²⁸ developed an α -CD-based molecularly imprinted polymer (MIP). Firstly, DBP formed a complex with α -CD (Fig. 5a), which could govern the mutual orientation of α -CD during the following polymerization process. Thereafter, the synthesis of the MIP involves a SNAr crosslinking reaction between TFN and the complex (Fig. 5a). The pristine α -CD MIP containing imprints of DBP in its polymeric network can selectively encapsulate DBP. With the optimal molar ratio of α -CD, TFN, and DBP at 1:3:9, the maximum binding capacity of 22 mg g⁻¹ was achieved with a high imprinting factor of 2.6.

In addition to direct introduction of CDs into polymer backbones, post-modification of POPs by CDs *via* SNAr reactions represents another efficient method. For example, Zhu and co-workers²⁹ reported a fully fluorinated porous aromatic framework (PAF-63). As shown in Fig. 5b, PAF-63 further reacted with α -, β -, and γ -CDs in K₂CO₃ and DMF to produce α -, β -, and γ -CD modified PAF-63, respectively. Compared to PAF-63 (2436 m² g⁻¹), CD-modified PAF-63 was nonporous, suggesting that flexible CD molecules occupied the channels of PAF-63, whereas the CD-PAF-63 can be used to protect the *ortho*-site of the aryl substrates in halogenation to selectively prepare the *para*-substituted compounds. Moreover, the selectivity can be obviously increased with the decreased size of the substrates.



Fig. 4 β-CD polymer networks derived from nucleophilic aromatic substitution reactions. (a) Top, synthesis of the high-surface-area porous TFN-CDP from β-CD and TFN. Down, schematic of the TFN-CDP structure. Adapted with permission from ref. 25. Copyright 2018 The Royal Society of Chemistry. (b) Synthesis of the DFB-CDP from β-CD and DFB. (c) Post-polymerization reduction of TFN-CDP yields amine functionalized TFN-CDP (reduced TFN-CDP). Reproduced with permission from ref. 27. Copyright 2019 Wiley-VCH.

The above-mentioned CD-POPs were usually synthesized in the organic phase, which might again cause secondary environmental pollution due to the use of organic solvents. Recently, Xie and co-workers³⁰ reported an eco-friendly strategy to prepare a new ultra-microporous and macroporous β-CD-based polymer (T-E-CDP) in aqueous solutions by simultaneously crosslinking β -CD with both flexible EPI and rigid TFN crosslinkers (Fig. 5c). Owing to the permanent porosity and abundant adsorption sites, T-E-CDP could effectively remove organic pollutants from water without being affected by the ionic strength and pH values, indicating great potential for water treatment. Furthermore, Xie and co-workers³¹ introduced 2,3-epoxypropyltrimethylammonium chloride (ETA) to the T-E-CDP by a similar preparation process. The quaternary amino-functionalized β -CDP can simultaneously and rapidly remove natural organic substances, organic micropollutants and detrimental microorganisms from water.



Fig. 5 CD-based porous polymers derived from nucleophilic aromatic substitution reactions. (a) Synthesis of the imprinted polymer MIP *via* the polymerization of α -cyclodextrin upon host–guest complexation with DBP, followed by the removal of DBP after polymerization. Adapted with permission from ref. 28. Copyright 2020 American Chemical Society. (b) Scheme of the preparation and the possible fragments of CD-PAFs. Adapted with permission from ref. 29. Copyright 2017 American Chemical Society. (c) Synthesis of T-E-CDP in the aqueous phase.

Other nucleophilic substitution reactions similar to the SNAr reaction have also been applied to prepare CD-based POPs. As shown in Fig. 6a, Liu and co-workers³² reported the preparation of macrocycle-containing polymer networks (TPECD) *via* the nucleophilic substitution of tetrakis(4-(bromomethyl)-phenyl)ethene (TPEBr) and β -CD. In the presence of an aggregation-induced emission (AIE) luminogen, *i.e.*, tetraphenylethene (TPE), and partially hydrophilic β -CDs, macrocycle-based POPs showcased prominent solid-state fluorescence and good water dispersibility. Moreover, the fluorescence of two β -CD-based POPs could be conveniently tuned from blue-green to red-orange *via* efficient fluorescence resonance energy transfer from TPE moieties to the encapsulated fluorophores in aqueous solutions. Yang and



Fig. 6 CD-based porous polymers derived from nucleophilic substitution reaction. (a) Synthetic routes to the TPECD polymer. (b) Synthetic routes to β -CDP-N and β -CDP-C.

co-workers³³ further used BCMBP (Fig. 3c) for nucleophilic substitution to prepare BCMBP-based β -CD polymers, which showed rapid and efficient removal of micropollutants from wastewater.

Ding and co-workers³⁴ successfully prepared two β -CD-based polymer networks (β -CDP-N and β -CDP-C) by simple nucleophilic substitution of the β -CD with 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine and 1,3,5-tris(*p*-bromomethylphenyl)benzene, respectively (Fig. 6b). Because β -CD can serve as the support for metal catalysts, these two β -CD based polymers were loaded with Au nanoparticles (NPs) through *in situ* reduction of NaAuCl₄·2H₂O to generate Au@ β -CDP-N and Au@ β -CDP-C. Transmission electron microscopy (TEM) suggested that Au NPs were well distributed in β -CDP materials. Additionally, the average sizes (4.2 \pm 1.3 nm) of Au NPs in β -CDP-N were smaller than that of Au@ β -CDP-C (5.6 \pm 2.3 nm), which was probably attributed to a synergistic role of the hydroxyl groups and N atoms of triazines in β -CDP-N, resulting in higher catalytic activities.

2.2.3 Ester-crosslinked CD-based POPs. In 2016, Peinemann and co-workers³⁵ reported an ester-crosslinked CD-based polymer by the polymerization of β -CD with terephthaloyl chloride (Fig. 7a). The authors optimized the preparation conditions to obtain continuous β -CD films on top of a commercial polyacrylonitrile porous support (Fig. 7b). The presence of hydrophobic cavities and hydrophilic ester linkages in the β-CD films results in high permeation for both polar and nonpolar solvents. Considering the diverse sizes of the three CDs and different internal and external polarities, Chung and co-workers³⁶ designed three freestanding molecular-sieving nanofilms derived from highly estercrosslinked networks through an interfacial reaction between the hydroxyl groups of CDs (α -, β -, and γ -CDs) and highly reactive acyl chloride groups of trimesoyl chloride using NaOH as the catalyst (Fig. 7c). The precise molecular sieving architectures with two kinds of channels similar to Janus pathways are constructed: the hydrophobic inner cavities of CDs provide a transport channel for apolar molecules, while the hydrophilic outer spaces between CDs



Fig. 7 (a) Interfacial polymerization of β -CD films on top of PAN porous supports. (b) SEM image of a β -CD film. Adapted with permission from ref. 35. Copyright 2016 Wiley-VCH. (c) Synthetic routes to the freestanding CD/TMC molecular sieving membranes.

facilitate the transport of polar molecules. Additionally, the intrinsic inner cavities of α -, β -, and γ -CDs can precisely adjust the pore size and thickness of the selective layer.

2.2.4 Imide-crosslinked CD-based POPs. Wooley and co-workers³⁷ reported a kind of imide-crosslinked CD-based POPs (CDPI, Fig. 8a), which were prepared by per-aminated β -CD-NH₂ with pyromellitic dianhydride in the presence of polar aprotic solvents containing acetic acid. The CDPI showed a Langmuir surface area of 155 m² g⁻¹ originating from hierarchical porosity. A wide distribution of mesopores was attributed to the π - π stacking of the pyromellitic dianhydride in the imide-crosslinked network. Scanning electron microscopy (SEM) indicated that large macroporous voids were generated in the gel framework. CDPI was stable in water and strongly acidic and alkaline aqueous solutions. Furthermore, a liquid filtration membrane (20 µm thick) was fabricated with a porous polyimide framework, which showed rapid separation of hydrophilic dyes in aqueous solution and toluene molecules in the vapor phase.

2.2.5 CD-based POPs prepared from isocyanates. In the above-mentioned synthesis, acid or base catalysts are necessary. In contrast, Zhang and co-workers³⁸ recently reported a series of



Fig. 8 Synthetic strategies for CD-based POPs: (a) polyimide-linked porous polymer CDPI. (b) Urea-linked aerogels CD-TTI200 and CD-HDI200 *via in situ* catalyst-free cross-linking of CDs with soft and rigid isocyanates. The cartoon picture is the porous structure of the CD aerogels (middle) and the photo images are the CD-TTI200 aerogel (murrey) and the CD-HDI200 aerogel (white). Adapted with permission from ref. 38. Copyright 2017 The Royal Society of Chemistry.

robust CD-based aerogels synthesized by in situ catalyst-free crosslinking of CDs with a soft isocyanate (hexamethylene diisocyanate, HDI) and a rigid isocyanate (triphenylmethane-4,4',4"-triisocyanate, TTI, Fig. 8b). The CD-based aerogels exhibited high BET surface areas (237 m² g⁻¹) owing to their hierarchically porous structures. In addition, the aerogels with a high Young's modulus (166 MP) can be compressed up to 70% without any observable cracking. The outstanding mechanical properties are beneficial for the applications of the CD-based aerogels in gas and liquid chromatography. Chang and co-workers³⁹ also reported a 3D polymer monolith synthesized by a catalyst-free polyaddition reaction of β -CD with 1,4-phenylene diisocyanate. The porous monolith could efficiently adsorb aromatic pollutants due to the hierarchical porosity and amphiphilicity. Furthermore, the materials embedded with TiO₂ can be used for photocatalytic degradation of aromatic pollutants.

2.3 Amorphous CA-based hierarchical POPs

CAs are a sort of well-known bowl-shaped cyclic oligomers with hydrophobic cavities constructed through methylene bridges at the *meta*-positions of phenol. This interesting hydrophobic cavity could serve as a powerful receptor for various guest molecules in supramolecular chemistry. By geometrical arrangement of the phenyl subunits, CAs, especially the calix[4]arene derivatives, can form four stable conformers with cone, partial cone, 1,2-alternate, or 1,3-alternate conformations.⁴⁰ The polar phenol units

or non-polar rims (aromatic rings) and the methylene bridges in CA can be easily modified to afford multifunctional supramolecular derivatives. Moreover, the structural rigidity of CA is propitious to be incorporated into the extended, porous reticulated architecture by robust covalent bonds. Compared to the discrete CA, the CA-based POPs displayed high surface areas and could selectively encapsulate various guests.

2.3.1 CA-based POPs prepared by Sonogashira–Hagihara reaction. CA only existed as side-chain pendants in conventional CA-contained polymers. The first CA-based reticulated polymer (CalP) with CA in the polymer backbone was reported by Trabolsi and co-workers in 2017.⁴¹ The CalP was prepared by hyper-crosslinking tetrabromo-calix[4]arene (1) with 1,4-diethynylbenzene *via* Sonogashira–Hagihara coupling.

Notably, the optimal concentrations of the monomers were crucial to produce a highly porous polymer in good yield. The obtained reticular structure exhibited excellent chemical and thermal stability under harsh conditions. The inherent cavity of CA and abundant intermolecular spaces endowed CalP with a high surface area of 596 m² g⁻¹ and a large pore volume of 0.73 cm³ g⁻¹, which enhanced the adsorption and removal of organic micropollutants.

Introducing π -electron rich alkyne units into the macrocyclic POPs can enhance both the rigidity and conjugation of the polymer skeleton, and results in high surface areas and improved adsorption capabilities. For example, Trabolsi and co-workers⁴²

further extended the family of CA-based POPs (CalPn, n = 2-4) by reacting 1 with three different acetylene-functionalized linkers (2, 3, and 4, Fig. 9a) via Sonogashira-Hagihara coupling. The IR and NMR spectra confirmed the successful formation of porous covalent calix[4]arene-based polymers. CalP4 showed a higher specific surface area (759 $m^2 g^{-1}$) than CalP2 (596 $m^2 g^{-1}$) and CalP3 (630 $\text{m}^2 \text{g}^{-1}$) due to more acetylene groups within CalP4. Incorporating lithiated phenols in calix[4]arenes can further enhance the adsorption performance of POPs via electrostatic interactions; in this respect, the lithiated polymers (CalP2-Li, CalP3-Li, and CalP4-Li) were synthesized by a reaction between the CA-based POPs and *n*-butyl lithium (Fig. 9a).⁴³ The disappearance of phenolic -OH stretching bands in FT-IR spectra and the chemical shifts ranging from 0.038 to 0.087 ppm in ⁷Li MAS NMR spectra confirmed the successful lithiation. The BET surface areas of CalP2-Li, CalP3-Li, and CalP4-Li were calculated to be 274, 308, and 445 m² g⁻¹, respectively. These values are smaller than those of the corresponding non-lithiated analogues, probably due to partial filling or collapse of the pores during lithiation.

Incorporating CA into 2D polymers is challenging due to the nonplanar and flexible CA rings. Trabolsi and co-workers⁴⁴ reported a template-free method to prepare 2D CA-based porous organic nanosheets (CX4-NS) from **1** and 4,4'-diethynyl-1,1'-biphenyl

(5, Fig. 9b). The obtained CX4-NS was a 2D flexible CA-containing network with weak interlayer attractions which facilitated layer exfoliation. Consequently, the bulk CX4-NS was exfoliated into fewlayered nanosheets (3.52 nm) in ethanol. The SEM, TEM and AFM images confirmed the thin sheet-like structures. The calculated results showed that the 1,2-alternate conformation of calix[4]arene could produce a two-dimensional pattern with the lowest energy.

The hydroxyl groups in CA can be facilely modified with other functions. Trabolsi and co-workers⁴⁵ rationally selected a thioether-crown-incorporating calix[4]arene derivative which further crosslinked with tetraacetylene pyrene (4) *via* Sonogashira-Hagihara reaction to produce the thioether-crown-rich CA-based mesoporous polymer S-CX4P (Fig. 10a). Despite the existence of large steric thioether-crown units, S-CX4P exhibits a high BET specific surface area of 547 m² g⁻¹. Except for calix[4]arene, a series of other CA-based POPs (CX4P, CX6P and CX8P)⁴⁶ were reported by the same group. The porosities of these materials were correlated with the cavity sizes of CAs. The specific surface areas of CX4P, CX6P and CX8P were 759, 725 and 635 m² g⁻¹, respectively. Interestingly, these three CA-based POPs exhibited outstanding adsorption capacities for paraquat.

Fluorine-rich linkers would enhance the interactions between the adsorbent and PFOA. Trabolsi and co-workers⁴⁷ recently developed two fluorine-rich calix[4]arene-based POPs



Fig. 9 Sonogashira–Hagihara cross-coupling approaches to the synthesis of CA-based POPs. (a) Synthetic routes to the polycalix[4]arene networks, CalPn, and their lithiated analogues, CalPn-Li (n = 2, 3, 4). (b) Schematic view of the network structure of CalP4. Adapted with permission from ref. 42. Copyright 2018 American Chemical Society. (c) Synthetic route to porous calix[4]arene nanosheets (CX4-NS) under solvothermal conditions. Adapted with permission from ref. 44. Copyright 2017 American Chemical Society.



Fig. 10 The Sonogashira–Hagihara cross-coupling approaches for synthesis of CA-based POPs. (a) Thioether-crown-rich calix[4]arene porous covalent polymer S-CX4P. Adapted with permission from ref. 45. Copyright 2019 American Chemical Society. (b) Non-fluorinated and fluorine-rich porous calix[*n*]arene polymers, CX4-P, CX4-BP, FCX4-P and FCX4-BP.

(FCX4-P and FCX4-BP) *via* Sonogashira–Hagihara reactions between **1** and the fluorinated linkers **6** and **7**, respectively (Fig. 10b). Non-fluorinated CA-based POPs (CX4-P and CX4-BP) were also synthesized by the same method starting from **1** and the nonfluorinated linkers (1,4-diethynylbenzene and 4,4'diethynyl-1,1'-biphenyl). The BET surface areas of fluorinated FCX4-P (417 m² g⁻¹) and FCX4-BP (451 m² g⁻¹) were slightly lower than those of non-fluorinated CX4-P (596 m² g⁻¹) and CX4-BP (468 m² g⁻¹) probably due to the channel occupied by fluorine atoms. Nevertheless, FCX4-P and FCX4-BP could more efficiently remove PFOA than the non-fluorinated POPs, which revealed that the F···F-C interactions between the fluorinated linkers and PFOA were essential for the excellent performance.

2.3.2 CA-based POPs prepared from a diazo-coupling reaction. Instead of using noble metal catalyzed Sonogashira–Hagihara cross-coupling, Trabolsi and co-workers⁴⁸ further reported two redox active POPs *via* diazo coupling between a nitro derivative of calix[4]arene (*p*TNC4A) and two different viologen diamines (Fig. 11a). The resulted COP1⁺⁺ and COP2⁺⁺ were amorphous and showcased modest BET surface areas of 17.9 and 51.8 m² g⁻¹, respectively. COP1⁺⁺ and COP2⁺⁺ could be reduced to stable radical cationic polymers due to the viologens, as proved by electron paramagnetic resonance (EPR) spectra. Moreover, the SEM and TEM images suggested that the morphologies of COP1⁺⁺ and COP2⁺⁺ were nanosheets owing to the partial cone structure of calix[4]arene.⁴⁰ Besides, both



Fig. 11 Alternative synthetic strategies for calixarene-based POPs. (a) Synthesis of COP1⁺⁺ and COP2⁺⁺ *via* diazo coupling. (b) Synthesis of pTC-SC4A films *via* interfacial polymerization with esterification.

cationic polymers showcased excellent chemical and thermal stability, and could effectively remove anionic azo-based dyes from water in a wide pH range of 2–10.

2.3.3 CA-based POPs prepared from interfacial polymerization. It is widely accepted that the pore sizes of porous materials significantly affect their performances on mass transport. To develop efficient porous materials with hierarchical pore distribution, Liu and co-workers⁴⁹ reported two mesoporous polymer films through interfacial polymerization on the surfaces of commercial porous membranes by a reaction between terephthaloyl chloride and pillar[5]arene or sulfonatocalix[4]arene (SC4A), respectively (Fig. 11b). The polymer films displayed two types of pores, one from the polymer network and the other from the cavity. Thanks to the ultrahigh permeability and strong host–guest interaction, both polymers could effectively remove cationic dyes by simple vacuum filtration.

2.3.4 CA-based POPs prepared from nucleophilic aromatic substitution. Nucleophilic aromatic substitution can be also employed in the synthesis of CA-based POPs. Zhang and coworkers⁵⁰ reported four CalCOPs via nucleophilic aromatic substitution between amino calix[4]arene with different alkyl chains and triazine derivatives (Fig. 12a). The BET surface areas of CalCOP1, CalCOP2, CalCOP3 and CalCOP4 were 280, 31.5, 18.4, and 1.6 m² g⁻¹, respectively, which were reduced with increasing the lengths of alkyl chains from ethyl to butyl. Zhang and co-workers51 also reported a series of amino-bridged covalent organic polycalix[4]arenes (CaCOPs) prepared via nucleophilic aromatic substitution of a modified calix[4]arene intermediate with different aromatic diamines. The BET surface areas increased from CaCOP1 (10.86 $m^2 g^{-1}$) to CaCOP2 (20.16 $m^2 g^{-1}$) to CaCOP3 $(81.09 \text{ m}^2 \text{ g}^{-1})$ with increasing the number of benzene rings and extending the conjugated networks. Although the surface areas were quite low, these electron-rich networks exhibited excellent iodine adsorption capacity. Yuan and co-workers52 reported a new cationic CA-based POP (CalCOP-1) by nucleophilic aromatic substitution of calix[4]arene with imidazolium units (Fig. 12b). The morphological characterization indicated that CalCOP-1



Fig. 12 Synthesis of CA-based POPs by nucleophilic substitution. (a) Synthetic route to triazine-based covalent organic polycalix[4]arenes, CalCOPs. (b) Synthetic route to the cationic calix[4]arene polymer CalCOP-1. (c) Synthetic routes to TPE-SC4A polymers.

was composed of nanospheres. The BET surface area of CalCOP-1 was low (46 m² g⁻¹), while it could adsorb CO₂ with moderate adsorption capacity up to 19 cm³ g⁻¹ at 273 K. Liu and co-workers³² also reported CA-based POPs (TPE-SC4A) *via* the nucleophilic substitution of TPEBr and SC4A (Fig. 12c). TPE-SC4A similar to TPECD (Fig. 6a) exhibited efficient fluorescence resonance energy transfer due to the presence of TPE.

2.4 RA-based hierarchical POPs

RAs is another kind of commonly used architecture in supramolecular chemistry, similar to CAs. They are also typical bowlshaped macrocycles with eight phenolic groups in their upper rims, allowing functionalization and preparation of various supramolecular hosts. In addition, these hydrophobic π -rich cavitands enable the encapsulation of various guest compounds. However, only a few examples of calix[4]resorcinarene-based POPs were reported.^{53–56} The early calix[4]resorcinarene-containing POPs were prepared using Bakelite type chemistry through condensation of calix[4]resorcinarenes with formaldehyde.^{53,54} The phenolic hydroxyl groups were further functionalized by incorporating *N*-propyl sulfamic acid as the catalyst. However, the surface areas of these polymers after treatment with sulfamic acid were relatively low (179 m² g⁻¹).⁵³

2.4.1 RA-based POPs prepared from diazo-coupling reactions. Yuan and co-workers⁵⁴ reported a series of calix[4]resorcinarenebased POPs (CalPOF-1, CalPOF-2 and CalPOF-3) by diazo coupling reactions of 4,4'-biphenyldiamine and C-alkyl calix[4]resorcinarenes (RsC*ns*; *n* stands for the number of carbon atoms of the alkyl chain, Fig. 13a) under mild conditions. Interestingly, tailoring the lengths of the alkyl chains on the methylene groups of RA could tune the porosity of the resulted polymers. The BET surface areas of CalPOF-1 (303 m² g⁻¹), CalPOF-2 (154 m² g⁻¹) and CalPOF-3 (91 m² g⁻¹) decreased with increasing alkyl chain length from methyl through ethyl to propyl, respectively.

2.4.2 RA-based POPs prepared by nucleophilic aromatic substitution. Dichtel and co-workers⁵⁵ reported another strategy to afford two cavitand-containing polymers (CP-TFIN and CP-TFN, Fig. 13b) *via* nucleophilic aromatic substitution between fluorinated aromatic monomers (TFIN and TFN) and the phenolic groups of calix[4]resorcinarenes (Fig. 13b). The polymerization efficiencies for diarylether formation were optimized by regulating the reaction temperature and monomer concentrations. The surface areas of CP-TFIN and CP-TFN reached values up to 1190 and



Fig. 13 Alternative synthetic strategies for RA-based POPs. (a) Synthesis of azo-bridged calix[4]resorcinarene-based porous organic frameworks, CalPOFs, *via* the diazo-coupling reaction. (b) Synthetic schemes of CP-TFIN and CP-TFN by nucleophilic aromatic substitution.

1081 m² g⁻¹, respectively. The combustion analysis and ¹⁹F MAS NMR spectroscopy demonstrated that CP-TFIN and CP-TFN consisted of fully fused and partially fused cavitands, which were beneficial for host-guest interactions. Furthermore, compared to activated carbon and a commercial resin (Ambersorb 560), CP-TFIN showed a higher affinity toward toxic halomethanes and 1,4-dioxane.

2.4.3 RA-based POPs prepared by Sonogashira-Hagihara coupling reaction. Patra and co-workers⁵⁶ reported three calix-[4]resorcinarene-based hierarchical POPs (RN4-Az-OH, RN4-F and RN4-OH) synthesized by three different methods, i.e., diazo-coupling reaction, nucleophilic aromatic substitution and Sonogashira coupling reaction, based on the different functional groups in the macrocycles and the specific aromatic linkers (Fig. 14). The length and functionality of the linker governed the physicochemical properties of the RN4-based POPs. All the POPs featured excellent chemical stability in many organic solvents and aqueous solutions. The SEM images showed that both RN4-Az-OH and RN4-OH displayed sphere-shaped morphology, but RN4-F contained large aggregated particles. Interestingly, RN4-Az-OH was hydrophilic, whereas both RN4-OH and RN4-F were hydrophobic due to the alkyne- and fluorine-rich linkers. The BET specific surface areas were also different. Compared to RN4-Az-OH (340 m² g⁻¹) and RN4-OH (720 m² g⁻¹), RN4-F showed a much higher surface area (1230 m² g⁻¹) owing to the smaller length and more crosslinkable sites of the F-rich linker. These results demonstrated that selecting appropriate crosslinkers and functional groups could facilitate the understanding of the



Fig. 14 Synthetic strategies of *C*-phenylresorcin[4]arene-based POPs. RN4-Az-OH: diazo coupling reaction, RN4-OH: Sonogashira–Hagihara cross-coupling reaction, and RN4-F: aromatic nucleophilic substitution reaction. Adapted with permission from ref. 56. Copyright 2017 American Chemical Society.

structure-property relationship and promote the development of task-specific porous materials.

2.5 PA-based hierarchical POPs

PAs, similar to calixarenes, are constructed by methylene bridges with hydroquinone units in the *para*-positions, as first reported by Ogoshi and co-workers in 2008.⁵⁷ They feature symmetric pillarshaped structures and π -electron rich cavities, which endow them with extensive adsorption properties for cationic and neutral guests. Moreover, PAs are facilely prepared in different solvents to yield pillar[5]arene (PA[5]), pillar[6]arene (PA[6]), or other PA homologs, with linear oligomers as side products. The alkoxy groups in PAs can be easily deprotected and further modified with various functional groups.

2.5.1 PA-based POPs prepared by Sonogashira-Hagihara coupling reaction. PA[5]-based conjugated microporous polymers (P5-CMPs) were first reported by Coskun and co-workers⁵⁸ (Fig. 15a). P5-CMPs were prepared by Sonogashira coupling reaction between triflate functionalized PA[5] and 1,4-diethynylbenzene (P5-CMP-1) or 4,4'-diethynyl-1,1'-biphenyl (P5-CMP-2). P5-CMP-1 and P5-CMP-2 showed BET surface areas of 400 and 345 m^2 g⁻¹, respectively. P5-CMPs were obtained as grey powders and were completely insoluble in common organic solvents, indicating the formation of crosslinked networks. In addition, P5-CMPs also showed high stabilities in strong acids and bases. Besides the fully functionalized P5-CMPs, Yang and co-workers⁵⁹ reported partially functionalized PA[5]-based CMPs (P[5]-TPE-CMP and P[5]-TET-CMP, Fig. 15b), which were synthesized from di-triflate functionalized PA[5] and AIE-active TPE or 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine via Sonogashira coupling. P[5]-TPE-CMP was a greenish-black powder with excellent stability against diluted acidic and basic solutions, and was absolutely insoluble in common organic solvents. However, both P[5]-TPE-CMP (6.99 m² g⁻¹) P[5]- and TET-CMP $(22.05 \text{ m}^2 \text{ g}^{-1})$ exhibited small specific surface areas.

In addition to the traditional PA, Yang and co-workers⁶⁰ prepared two novel PA[6] analogues, [2]biphenyl-extended PA[6] (BpP6) and leaning tower[6]arenes (LT6). The hydroxyl groups of LT6 and BpP6 can further react with trifluoromethanesulfonic anhydride to afford triflate functionalized derivatives (LT6-OTf and BpP6-OTf). Furthermore, the authors synthesized four CMPs (CMP-n, n = 1-4) by Sonogashira coupling between LT6-OTf or BpP6-OTf and 1,4-diethynylbenzene or 4,4'-diethynylbiphenyl (Fig. 15c). All four CMPs were amorphous in nature with similar layered structures. The BET surface areas of CMP-1, CMP-2 and CMP-4 were 16.1, 20.2, and 9.5 $m^2 g^{-1}$, respectively, which were relatively lower than that of CMP-3 (284.6 $m^2 g^{-1}$). This was likely attributed to the interpenetration and tilted cavities of biphenyl linkers leading to micropores in CMP-1, CMP-2 and CMP-4. Owing to the presence of the acetylene linkage and proper cavity size of LT6 and BpP6, the four CMPs exhibited excellent chemical and thermal stability as well as outstanding I₂ affinity.

2.5.2 PA-based POPs prepared by nucleophilic substitution reaction. Besides Sonogashira coupling, Huang and co-workers⁶¹ synthesized a PA-based chiral 3D polymer (TADP5) by a nucleophilic



Fig. 15 Sonogashira–Hagihara cross-coupling approaches to the synthesis of pillararene-based POPs. (a) Synthetic routes to the pillar[5]arene-based conjugated microporous polymers P5-CMPs. (b) Synthesis of the luminescent conjugated macrocycle polymer P[5]-TPE-CMP. (c) Synthetic routes to catcher-type CMPs (CMP-n, n = 1-4).

substitution reaction between the (*R*,*R*)-tetraaryl-1,3-dioxolane-4,5-dimethanol derivative (TADDOL-OH) and per-(2-bromoethyl)pillar[5]arene (DBEP5). TADP5 was further modified with excessive Ti(Oi-Pr)₄ to obtain the active catalyst TADP5Ti (Fig. 16a). After Ti-loading, the morphology of TADP5Ti was similar to that of TADP5, indicating the structural stability. The chiral catalytic sites were well distributed over the frameworks due to the rigid architecture and numerous substituents, and TADP5Ti could efficiently convert aryl aldehydes into chiral secondary alcohols with high ee values in a wide substrate scope. Ma and co-workers⁶² also reported two PA[*n*]-based POPs (P-PAP[5] and P-PAP[6]) through nucleophilic substitution between TFN and PA[5] or PA[6] (Fig. 16b). The BET specific surface areas of these new materials were 529 and 533 m² g⁻¹ for P-PAP[5] and P-PAP[6], respectively, with micropores of 5 Å size, which suggested that they might be potential adsorbents.

The functionalization on the lateral periphery of PA[5] is challenging. Liu and co-workers⁶³ reported a novel and facile method to render laterally functionalized methylene bridges of dimethoxypillar[5]arene by means of *N*-bromosuccinimide to generate the bromo-PA[5] (BDMP5, Fig. 16c). The resulting BDMP5 further served as a building block to cross-link with alkyl diamines with different lengths to produce polymer nano-capsules or 2D polymer films. When the chain length of alkyl diamines is longer, for example, hexane-1,6-diamine, cystamine

dihydrochloride and 1,4-diaminobutane, the polymerization could more easily form uniform nanocapsules. However, when employing ethane-1,2-diamine as a crosslinker only 2D polymer films were formed probably due to the high bending rigidity of PA[5] and short linkers. Furthermore, the hydrophilicity of nanocapsules could be improved by decorating with 2-(2-(2-(2bromoethoxy))ethoxy)-ethan-1-ol. The decorated nanocapsules have promising potential in drug encapsulation and release.

2.5.3 PA-based POPs prepared by Friedel–Crafts reaction. Ma and co-workers⁶⁴ further reported a PA[5]-based POP (PPA) *via* the Friedel–Crafts reaction between PA[5] and *p*-xylylene dichloride. Due to the easy functionalization of PA[5], fully quinone-functionalized PPQ (Fig. 17a) was obtained *via* the oxidation of methoxy groups on PA[5], and it served as the host for Pd loading to produce Pd-PPQ. The BET surface area of PPA was 400 m² g⁻¹, while the surface area of PPQ (272 m² g⁻¹) decreased after oxidation. Upon Pd-loading, the surface area further reduced to 202 m² g⁻¹ due to the partial occupancy of the porous structure by Pd NPs. The average size of Pd-clusters was about 0.75 nm as observed from the TEM image. The uniform size of Pd NPs was beneficial to catalysis.

2.5.4 PA-based POPs prepared by amidation reactions. Huang and co-workers⁶⁵ firstly synthesized carboxyl-functional PA[5],



Fig. 16 Nucleophilic substitution approaches to the synthesis of pillararenebased POPs. (a) Synthesis of chiral 3D polymer networks TADP5 and TADP5Ti. (b) Synthetic procedures of porous pillar[*n*]arene polymers P-PAP[*n*]s. (c) The mechanism of covalent self-assembling into polymer nanocapsules and 2D polymer films from BDMP5. Adapted with permission from ref. 63. Copyright 2017 The Royal Society of Chemistry.

which subsequently reacted with *p*-phenylenediamine (PPD) to prepare the 3D polymer network P5-P. P5-P was further *in situ* functionalized with hydrophilic 1-(3-dimethylaminopropyl)-3ethylcarbodiimide hydrochloride (EDC) groups to promote its hydrophilicity (Fig. 17b). Although the surface area (7.69 m² g⁻¹) of the modified P5-P was negligible, the SEM and TEM results suggested that the 3D polymer network had large voids ranging from several hundred nanometres to several micrometres, which was beneficial to water flow through P5-P and enhanced its contact with micropollutants. Therefore, it could remove a wide range of micropollutants from water.

2.5.5 PA-based POPs prepared by electrophilic aromatic substitution. Electrophilic aromatic substitution has also been applied to construct PA-based POPs as heterogeneous catalysts. Yang and co-workers⁶⁶ explored a novel and facile approach to prepare PA-based CMP NPs (DMP[5]-TPP-CMP NPs) by electrophilic aromatic substitution between pyrrole and dibenzaldehyde functionalized PA[5] (P[5](PhCHO)₂, Fig. 18a). Pyrrole could directly react with aldehyde groups to generate porphyrin. Given the abundant methoxy groups in PA rings and the strong coordination ability of porphyrin, DMP[5]-TPP-CMP could be well deposited on palladium NPs to prepare Pd@CMP. Both DMP[5]-TPP-CMP NPs



Fig. 17 Alternative synthetic strategies for PA-based POPs. (a) Synthetic route to the pillar[5]arene-based porous polymer PPA by Friedel–Crafts reaction, pillar[5]quinone-based PPQ, and the Pd-loaded heterogeneous catalyst Pd-PPQ (quinone acted as a loading ligand). Adapted with permission from ref. 64. Copyright 2017 Wiley-VCH. (b) The 3D network polymer P5-P derived from amidation reactions.

and Pd@CMP were black powders and showed outstanding thermal stability. Additionally, Pd@CMP exhibited remarkable catalytic activity in nitrophenol reduction reactions. Furthermore, Ning and co-workers⁶⁷ also employed P[5](PhCHO)₂ with melamine to synthesize PA-containing POPs (PAN-FPP5, Fig. 18b). The BET surface area of PAN-FPP5 is 788 m² g⁻¹. The total pore volume and micropore volume of PAN-FPP5 were 0.84 and 0.15 cm³ g⁻¹, respectively. The proportion of the micropore volume in the total pore volume of PAN-FPP5 was 17.9%, which exhibited advantages for the adsorption of small gas molecules.

2.5.6 PA-based POPs prepared by mechanochemical synthesis. Recently, Dai and co-workers⁶⁸ developed a mechanochemical approach for preparing MHP-P5Q by ball milling of triptycene hexamine (THA) with pillar[5]quinone (P5Q, Fig. 19). The BET surface area was calculated to be 296 m² g⁻¹ for MHP-P5Q with three micropore distributions of 0.76, 1.19, and 1.30 nm. Remarkably, the pore size at 0.76 nm was consistent with the cavity size of PA[5] (0.62 nm),⁵⁷ indicating that the robust framework with PA[5] was successfully prepared. Mechanochemical synthesis is a rapid and environmentally friendly approach, which opens a new pathway toward large-scale industrial production.

2.6 Other amorphous macrocycle-based hierarchical POPs

In addition to the above-summarized conventional supramolecular macrocycles, some special macrocycles such as the cyclotricatechylene (CTC)-based macrocycle and TPE-based oxacalixarene macrocycle (TOM) have also been used as building blocks for the construction of POPs. The corresponding macrocycle-based POPs were synthesized by nucleophilic aromatic substitution, Suzuki coupling, Sonogashira–Hagihara coupling, Yamamoto-type Ullmann cross-coupling and click reactions.

2.6.1 CTC-based POPs prepared by different crosslinking reactions. CTC is a rigid pyramidal macrocyclic molecule, with a bowl-shaped shallow cavity. CTC-based derivatives such as cyclotriveratrylene (CTV), CTV-Br₃ and CTV-alkyne were reported as building blocks for preparation of CTC-based POPs. McKeown and co-workers⁶⁹ synthesized CTC-network-PIM *via* the nucleophilic aromatic substitution between CTV and TFN (Fig. 20a). The CTC-based PIMs exhibited a high BET surface area (830 m² g⁻¹) and excellent adsorption capacity for H₂.

Zheng and co-workers⁷⁰ further explored CTC-based POPs (CTV-CMP-1,⁷⁰ CTV-CMP-2,⁷⁰ Click-POPs-1⁷¹ and Click-POPs-2⁷¹). Among them, CTV-CMP-1 was obtained *via* Suzuki coupling reaction between CTV-Br₃ and benzene-1,4-diboronic acid (BDBA, Fig. 20b). CTV-Br₃ could also react with 1,4-diethynylbenzene through Sonogashira–Hagihara coupling to afford CTV-CMP-2 (Fig. 20b). Click-POPs-1 and Click-POPs-2 were facilely prepared by click reactions between the CTV-alkyne and azide-1 or azide-2 (Fig. 20c), respectively. However, these methods are expensive and unsafe due to the use of precious metals and azides, which require further improvement.

2.6.2 TOM-based POPs prepared by Yamamoto-type Ullmann cross-coupling. Zhang and co-workers⁷² synthesized a TOM *via* a SNAr reaction between the TPE phenolic compound and tetra-chloropyridine. Subsequently, the authors polymerized the TOM through Yamamoto-type Ullmann cross-coupling to afford pTOM with blue-greenish fluorescence (Fig. 21). Compared to the



Fig. 18 Alternative synthetic strategies for PA-based POPs. (a) Synthetic routes to DMP[5]-TPP-CMP by electrophilic aromatic substitution. (b) Synthetic routes to the nitrogen-rich microporous polymer PAN-FPP5 through Schiff base chemistry.



Fig. 19 Schematic representation of the synthesis of MHP-P5Q using P5Q and THA *via* mechanochemistry. Adapted with permission from ref. 68. Copyright 2020 Nature publishing group.

nonporous packing frameworks of TOM, pTOM showed higher BET surface area (268 m² g⁻¹) and CO₂ capture capacity (33.6 cm³ g⁻¹ at 273 K/1.0 bar). Interestingly, the fluorescent pTOM can realize white-light emission by accommodating the tris(bipyridine)ruthenium luminophore *via* effective Förster resonance energy transfer.

3. Crystalline macrocycle-based COFs

COFs represent an emerging class of crystalline POPs which can be predesigned and constructed by precise reticulation of functional organic building blocks into extended 2D or 3D lattices via robust covalent linkages.73-75 Compared to the amorphous macrocycle-based POPs, incorporating macrocyclic compounds into the ordered frameworks is beneficial to unveil the structure-property relationship between the macrocycle building blocks and the corresponding COFs. Moreover, the preparation and the post-modification of macrocycle-based COFs is more convenient and avoids the use of noble metal catalysts. Additionally, the specific surface areas of macrocyclebased COFs are usually higher than those of the amorphous counterparts. However, most supramolecular macrocycles are nonplanar and flexible, which are difficult to prepare long range ordered frameworks. Therefore, only a few examples of crystalline COFs containing macrocycles have been reported. This section will summarize the representative macrocyclic COFs including CE-, CD-, CA- and the unconventional CTCand arylene-ethynylene macrocycle (AEM)-based COFs.

3.1 CE-based hierarchical COFs

3.1.1 Imine-linked CE-based COFs. Three crystalline CE-based COFs (CE-COFs) were firstly developed by Zhao and co-workers⁷⁶ starting from three CE-based *p*-terphenyl-4,4"-diamine monomers (CE-TBPA, Fig. 22a) and 1,3,5-triformylbenzene under solvothermal conditions. The crystalline structures of the corresponding COFs (12C4-COF, 15C5-COF, and 18C6-COF) were determined by PXRD



Fig. 20 Alternative synthetic strategies for CTC-based POPs. (a) Synthetic route to CTC-network-PIM by using the benzodioxane-forming reaction. (b) Synthesis of CTV-CMP-1 and CTV-CMP-2 by a palladium-catalyzed C–C coupling reaction. (c) Synthesis of Click-POP-1 and Click-POP-2 *via* click reactions.

analysis. The BET surface areas of 12C4-COF, 15C5-COF and 18C6-COF were 210, 59, and 47 m² g⁻¹, respectively. Interestingly, these CE-COFs exhibited excellent performance as phase-transfer catalysts (PTCs) in various nucleophilic substitution reactions such as esterification, etherification and cyanation.

To improve the porosity and crystallinity of CE-based COFs, Liu and co-workers⁷⁷ prepared two CE-based aldehydes



Fig. 21 Synthesis of the fluorescent macrocycle-based POP pTOM by Ullmann cross-coupling reaction. Adapted with permission from ref. 72. Copyright 2018, American Chemical Society.

(B₁₈C₆ and B₂₄C₈), which were subsequently condensed with 4,4',4",4"'-(pyrene-1,3,6,8-tetrayl)tetraaniline (Py) to afford two new CE-based COFs (Py-B18C6-COF and Py-B24C8-COF) *via* Schiff base reactions under solvothermal conditions (Fig. 22b). The BET surface areas of Py-B18C6-COF and Py-B24C8-COF were 1356 and 862 m² g⁻¹, respectively. Additionally, these two CE-based COFs exhibited good crystallinity and excellent stability under harsh conditions. Notably, these two CE-based COFs can selectively capture alkali metal ions (K⁺ and Cs⁺) owing to the intrinsic ion binding affinity of the corresponding CEs.

3.1.2 Olefin-linked CE-based COFs. It is very challenging to prepare olefin-linked COFs due to the irreversible -C=-C- linkage. Cui and co-workers⁷⁸ prepared a chiral building block of tetrabenzaldehyde-based dibinaphthyl-22-crown-6 (BINOL²-C). The authors used the BINOL²-C to react with 2,2'-(1,4-phenylene)-diacetonitrile or 2,2'-(biphenyl-4,4'-diyl)diacetonitrile to prepare two chiral olefin-linked CE-based COFs (CCOF17 and CCOF18) through Knoevenagel condensation (Fig. 22c). The BET surface areas of these two sp²c-CCOFs were low owing to the distorted frameworks containing flexible CE.

Furthermore, the C—C bonds of the CCOFs were reduced into C–C single bonds. The reduced CCOFs could maintain high crystallinity and porosity as well as high chemical stability under harsh conditions. These results confirmed the crystal-tocrystal transformation and open a new pathway for designing and preparing COFs with new linkages.



Fig. 22 Alternative synthetic strategies for CE-based COFs. (a) The construction of imine-linked CE-COFs by the "bottom-up" strategy. (b) Scheme of the synthesis of Py-B18C6-COF and Py-B24C8-COF *via* Schiff base reaction. (c) Synthesis of the olefin-linked chiral COFs (CCOF17 and CCOF18) by Knoevenagel polycondensation reaction and the reduced chiral COFs (CCOF17-R and CCOF18-R). Adapted with permission from ref. 78. Copyright 2021, American Chemical Society.

3.1.3 Acylhydrazone-linked pseudorotaxane-based COFs. To prepare single- or few-layer sheets of COFs by weakening

the strong interlayer interactions is still highly challenging. Loh and co-workers 79 prepared CE-based building blocks bearing



Fig. 23 Synthesis of macrocycle- and pseudorotaxane-based COFs via Schiff base reactions. Adapted with permission from ref. 79. Copyright 2020 Nature Publishing Group.

either ditopic hydrazides (CyHz0) or tetratopic hydrazides (CyHz1, Fig. 23). As shown in Fig. 23, these CE-based building units (CyHz0 and CyHz1) directly reacted with 2,4,6-triformylphenol (Sa) to afford the [2+3] and [4+3] acylhydrazone 2D COFs. Both the experimental and simulated PXRD analyses confirmed the two acylhydrazone CE-based 2D COFs stacked in antiparallel conformations due to the strong interlayer dipole interactions. To suppress the non-covalent interaction, the authors utilized CE moieties as hosts for encapsulating viologens to form pseudorotaxanes. Viologens with pyridinium cations were added in situ during the COF synthesis and served as interfering agents to weaken the strong interlayer interactions by steric hindrance and electrostatic repulsion to increase the interlayer distance and finally realize the self-exfoliation of the acylhydrazone 2D COFs. Owing to the existence of viologens, the pseudorotaxane RCOF-1 was well dispersed in solvents and can be readily exfoliated.

3.2 Crystalline CD-based COFs

3.2.1 Spiroborate-linked CD-based COFs. Wang and co-workers⁸⁰ reported the first 3D anionic γ -CD-based COFs with different counterions connected *via* spiroborate linkages.

The authors first employed γ -CD to react with B(OMe)₃ and LiOH (Li⁺ as the counterion) under microwave-assisted solvothermal conditions to afford a 3D anionic CD-COF-Li in a good yield (Fig. 24a). CD-COF-Li showed high crystallinity and BET surface area of 760 m² g⁻¹. Furthermore, CD-COF-DMA and CD-COF-PPZ were obtained by changing the proton acceptor to dimethylamine (DMA) or piperazine (PPZ). The BET surface areas of CD-COF-DMA and CD-COF-PZZ were 934 and 494 m² g⁻¹, respectively. The high porosities of γ -CD-based COFs mainly stemmed from frameworks by spiroborate linkages. Based on the PXRD analysis and simulation, these three CD-COFs belonged to a **rra** topology. The exploitation of 3D anionic γ -CD-based COFs enriched the diversity of crystalline COFs with "soft" struts and open a new pathway for developing host–guest chemistry.

3.2.2 Imine-linked CD-based COFs. Feng and co-workers⁸¹ reported a β -CD COF with imine linkage through Schiff base condensation between heptakis(6-amino-6-deoxy)- β -CD (Am7CD) and terephthaldehyde (TPA). Interestingly, the crystalline β -CD COF was obtained by polymerizing Am7CD and TPA in the presence of acetic acid as the catalyst in water and ethanol at room temperature (Fig. 24b). In contrast, when using ammonia



Fig. 24 Alternative synthetic strategies for CD-based COFs. (a) Boronatelinked first 3D anionic COF, CD-COFs. Adapted with permission from ref. 80. Copyright 2017 Wiley-VCH. (b) Imine-linked β -CD COF.

as the catalyst, the polycondensation was much faster and the resulted precipitate was an amorphous polymer (β -CD NCP). Interestingly, the morphology of the crystalline β -CD COF was a cubic structure, while the β -CD NCP adopted a spherical morphology, indicating that the selection of catalysts largely affects the crystallite shape and morphology of the COF. The BET surface area of the crystalline β -CD COF (79.2 m² g⁻¹) was higher than that of the amorphous β -CD NCP, suggesting that the ordered framework might improve adsorption performance.

3.3 Crystalline imine-linked CA-based COFs

The synthesis of crystalline calix[4]arene-based COFs is still challenging due to the flexible conformation of bowl-shaped CA. Trabolsi and co-workers very recently reported the first examples of CA-based COFs prepared through Schiff base condensation between tetrakis(p-formyl)calix[4]arene (CX4-CHO) and benzidine (BD) (Fig. 25).82 Interestingly, two different CA-based COFs (CX4-BD-1 and CX4-BD-2) with different morphologies and topologies were selectively obtained by different synthetic methods from the same monomers. CX4-BD-1 adopting a crystalline biaxial interpenetrated topology was prepared at the chloroform-water interface (Fig. 25) and exhibited a dimeric capsule-like morphology. In contrast, CX4-BD-2 prepared under highly diluted conditions in the presence of chloroform and methanol displayed unique noninterpenetrated 2D stacking modes. Owing to interlayer voids and surface potential charge, both COFs showcased excellent adsorption capacities for cationic dyes such as methylene blue and rhodamine B in aqueous solutions.

3.4 Crystalline CTC-based COFs

3.4.1 Borate-linked CTC-based COFs. Besides the development of CTC-based amorphous polymers, Zheng and co-workers^{83–86} further reported CTC-based crystalline COFs (CTC-COFs). CTC-COF-1⁸³ was synthesized under solvothermal conditions by co-condensation of CTC and BDBA at 95 °C for 4 days (Fig. 26a).



Non-interpenetrated CX4-BD-2 COF

Fig. 25 Synthesis of the calix[4]arene-based COFs from CX4-CHO and benzidine (BD) using different approaches: interfacial synthesis and infinite dilution conditions. Adapted with permission from ref. 82. Copyright 2021 American Chemical Society.

Similarly, another two CTC-COF analogues (CTC-COF-2 and CTC-COF-3) with larger pore sizes were synthesized by the same group using CTC and biphenyldiboronic acid (BPDA) or pyrenediboronic acid (PDBA) as monomers.⁸⁴ The BET surface areas are 541 and 1013 m² g⁻¹ for CTC-COF-2 and CTC-COF-3, respectively. It is worth noting that the experimental PXRD results indicate an eclipsed packing structure irrespective of the nonplanar conformation of the CTC macrocycle. The wavy structure makes CTC-COFs exhibit small pore size distribution and improved gas uptake capacity.

3.4.2 Imine-linked CTC-based COFs. Imine-linked COFs are less susceptible to moisture than the boronate-linked counterparts. Zheng and co-workers⁸⁵ reported two imine-linked CTCbased COFs (CTV-COF-1 and CTV-COF-2) synthesized from triformylcyclotrianisylene (f-CTV) and aromatic amines under solvothermal conditions (Fig. 26b). Both highly crystalline CTV-COFs adopted eclipsed stacking modes despite the bowl-shape of f-CTV. The BET surface areas of CTV-COF-1 (1245 $m^2 g^{-1}$) and CTV-COF-2 (1170 $m^2 g^{-1}$) were higher than those of the boronate CTC-COFs. Moreover, both CTV-COFs possessed high hydrolytic stability under water. However, the solubility of f-CTV was poor, and synthetic steps for f-CTV were complicated with a low overall yield (3%), which impeded the large-scale synthesis of CTV-based imine COFs. Thus, Zheng and co-workers⁸⁶ further developed an amino-substituted cyclotrianisylene (aCTV) which subsequently reacted with four aromatic aldehydes to produce aCTV-based COFs, (aCTVCOF1 to aCTV-COF4, Fig. 26c). All four aCTV-COFs possessed high crystallinities and large BET surface areas from 636 to 1428 m² g⁻¹. The methoxy groups in aCTV-COF3 and the hydroxyl groups in aCTV-COF4 exerted significant influences on their physicochemical properties. For example, aCTV-COF3 and aCTV-COF4 exhibited better



Fig. 26 Alternative synthetic strategies for CTC-based COFs. (a) Synthetic routes of boronate-linked CTC-COFs. (b) Synthetic routes of CTV-COF-1 and CTV-COF-2 *via* Schiff base reaction. (c) Synthetic routes of aCTV-COF-n (n = 1-4) *via* Schiff base reaction.

hydrolytic stability than the non-substituted aCTV-COF1 and aCTV-COF2.

3.5 Planar macrocycle-based COFs

3.5.1 Boronate ester-linked planar macrocycle-based COFs. Besides the non-planar macrocycle, planar macrocycle-based COFs were also reported. Jiang and co-workers⁸⁷ synthesized a C_3 -symmetric 9,10-hydroxyphenanthrene cyclotrimer (HPTC) which consisted of six hydroxyl units (Fig. 27a). Three starshaped 2D HPCT-based COFs (Star-COF 1, Star-COF-2, and Star-COF-3) were prepared by polycondensation of HPTC with three diboronic acids (BDBA, PDBA, and BPDA) under solvothermal conditions. These three planar macrocycle-based COFs exhibited high BET surface areas (582, 1538, and 1489 m² g⁻¹ for Star-COF-1, Star-COF-2, and Star-COF-3, respectively). Moreover, the Star-COFs adopted AA-stacking modes with periodically aligned π -columns and oriented mesoporous 1D channels, which conferred enormous potentials in optoelectronics.

AEMs are also a kind of planar and rigid macrocycles. Zhang and co-workers⁸⁸ proposed a "macrocycle-to-framework" strategy and synthesized two AEM-based building blocks (AEM-1 and AEM-2) through acyclic diyne metathesis macrocyclization with a multidentate triphenolsilane-based Mo(vi) carbyne complex as the catalyst. Subsequently, AEM-COF-1 and AEM-COF-2 were prepared under solvothermal or microwave conditions by reacting AEM-1 and AEM-2 with BDBA (Fig. 27b and c). The BET surface areas of AEM-COF-1 and AEM-COF-2 were 1445 and 1487 m² g⁻¹, respectively. The strong π - π interactions between rigid arylene–ethynylene backbones mediated AEM-COFs to exhibit eclipsed packing and ordered open channels.

The "macrocycle-to-framework" strategy was further utilized by McGrier and co-workers.⁸⁹ They reported two C₃-symmetric π -conjugated dehydrobenzoannulenes (DBA[12] and DBA[18]). The crystalline DBA-COF 1 and DBA-COF 2 were further synthesized by polycondensation of DBA[12] and DBA[18] with BDBA (Fig. 27b and d). Interestingly, owing to the coplanar arrangement of DBA[12], DBA-COF 1 exhibited strong fluorescence even in the solid state. Furthermore, McGrier and co-workers90 prepared a crystalline multiple-component macrocycle-based COF, Py-MV-DBA-COF (Fig. 27e). The Py-MV-DBA-COF was obtained by boronate ester reaction among DBA[12], DBA[18] and PDBA under solvothermal conditions. Meanwhile, the authors also synthesized homogeneous DBA-vertex-based COFs, Py-DBA-COF 1 and Py-DBA-COF 2 (Fig. 27b and d). Py-DBA-COF 1 exhibited ball-shaped and needle-shaped morphologies, while Py-DBA-COF 2 and Py-MV-DBA-COF featured cauliflower-like crystallites.

Incorporating metals into the vertices of DBA-based COFs can greatly enhance the binding performance for gas storage. As shown in Fig. 27f, McGrier and co-workers⁹¹ constructed a 3D DBA-COF (DBA-3D-COF 1) by a boronate ester reaction between DBA[12] and tetra(4-dihydroxyborylphenyl)methane (TBPM). Subsequently, DBA-3D-COF 1 was reacted with Ni(COD)₂ to afford the metalated Ni-DBA-3D-COF. Surprisingly, the BET surface area of DBA-3D-COF 1 was up to 5083 m² g⁻¹ with a very low density (0.13 g cm⁻³). Moreover, Ni-DBA-3D-COF still maintained a high BET surface area of 4763 m² g⁻¹. Compared to the DBA-3D-COF 1, the gas uptake capacity of metalated Ni-DBA-3D-COF for ethane and ethylene was slightly increased probably due to the open Ni(0) sites.

3.5.2 Azine-linked planar DBA-based COFs. Azine can serve as a linkage to prepare macrocycle-based COFs owing to better

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Fig. 27 Boronate ester-linked planar macrocycle-based COFs. (a) Chemical structures of star-shaped 2D COFs. (b–d) Chemical structures of AEM-COF-1 (or DBA-COF 1), AEM-COF-2, DBA-COF 2, Py-DBA-COF 1 and Py-DBA-COF 2. (e) Chemical structures of Py-MV-DBA-COF with small and large triangular vertices. (f) Synthesis of DBA-3D-COF and Ni-DBA-3D-COF.

robustness compared to the boronate ester linkage. McGrier and co-workers⁹² synthesized an azine-linked 2D DBA-based COF (DBA-COF 5) by a Schiff base reaction between DBA[12]-CHO and hydrazine under solvothermal conditions (Fig. 28). DBA-COF 5 was further reacted with Ni(COD)₂ to produce a dark green crystalline Ni-DBA-2D-COF in dry toluene. It is worth noting that the colour of DBA-COF 5 changed from bright yellow to dark green for the Ni-DBA-2D-COF owing to the charge





Fig. 29 Synthesis of ionic COFs ICOF-1 and ICOF-2 and porous coordination polymers Ti-PCP *via* the transesterification reaction.

Fig. 28 Synthesis of DBA-COF 5 using DBA[12]-CHO and hydrazine monomers followed by metalation with Ni(COD)₂ to produce Ni-DBA-2D-COF.

transfer effect upon Ni doping. Additionally, the BET surface area (1565 m² g⁻¹) of the Ni-DBA-2D-COF was slightly reduced compared to DBA-COF 5 (1643 m² g⁻¹). Moreover, the Ni-DBA-2D-COF maintained high crystallinity, indicating that DBA-COF 5 featured excellent stability.

3.5.3 Spiroborate-linked planar macrocycle-based COFs. In addition to the C3-symmetric macrocycles, Zhang and co-workers93 used the D_4 -symmetric square-shaped AEM as the building block to condense with trimethyl borate in the presence of dimethyl amine or LiOH as counterions to generate spiroborate-linked ionic COFs, ICOF-1 and ICOF-2 (Fig. 29). ICOF-2 exhibited higher crystallinity than ICOF-1 probably due to the low solubility of LiOH during the reaction. The BET surface area of ICOF-1 $(210 \text{ m}^2 \text{ g}^{-1})$ was also lower than that of ICOF-2 (1022 m² g⁻¹). The results suggest that the size and solubility of different bases as counterions can exert a significant influence on both the crystallinity and porosity of the resulting ICOFs. Importantly, the spiroborate-linked COFs remained nearly intact after immersing in water or a basic solution for two days, indicating excellent resistance to hydrolysis. Additionally, the same groups replaced the metal ions with Ti(OⁱPr) to produce the porous coordination polymers Ti-PCP (Fig. 29). The PXRD analysis of Ti-PCP still exhibited multiple peaks indicating a certain structural order. More importantly, Ti-PCP possessed a high surface area (1029 $m^2 g^{-1}$) and outstanding thermal stability. Owing to the presence of titanium, Ti-PCP could

capture CO_2 and serve as a catalyst for the synthesis of organic carbonates from epoxides and CO_2 .⁹⁴

4. Applications

Incorporating macrocycles into organic porous materials may create two kinds of porosity: one is from the extended porous frameworks knitted by covalent bonds; the other is the intrinsic cavities from the macrocycles. The hierarchical macrocyclebased POPs not only bridge the traditional porous materials with supramolecular chemistry, but also enhance the hostguest interactions. The following section mainly summarizes the application potentials of macrocycle-based POPs in environmental remediation, gas adsorption/separation, fluorescence sensing, heterogeneous catalysis, and ionic conduction.

4.1 Environmental remediation

With the development of human civilization and industry, our ecological environment has been severely polluted by heavy metal ions, organic micropollutants, radioactive elements and so on. Therefore, how to efficiently remove these pollutants is an urgent topic. At present, adsorption and separation of pollutants by means of porous materials has been widely studied due to the advantages of low cost, convenient operation and high efficiency. Traditional porous materials,⁹⁵ *e.g.* molecular sieves and activated carbon, are not easy to modify, which hinders further improvement of their adsorption and separation performance. Even though MOFs as pollutant removers have been investigated, they display poor chemical stabilities⁹⁶ and the toxic metals generated after structural decomposition of MOFs



render the secondary contamination. Hence POPs are promising candidates that are different from the conventional counterparts. Macrocycle-based POPs exhibited unique and excellent performance in environmental remediation due to their hierarchical porosities, host–guest interactions, facile structure-and-function tuneability and high chemical stabilities.

4.1.1 Organic micropollutants. Organic micropollutants (Chart 1) in waters are difficult to be degraded and seriously damage the ecosystem and endanger human life and health.⁹⁷ For example, bisphenol A (BPA) as a common component in epoxy-resin-based plastics was regarded as an endocrine disruptor. BPA is used as a model pollutant to evaluate the pollutant-removal performance of macrocycle-based POPs. Dichtel and co-workers²⁴ reported porous TFN-CDP (Fig. 4a) with high surface areas (263 m² g^{-1}), which could remove ~95% of BPA after reaching equilibrium in 10 s. However, the conventional EPI-CDP only removed 22% of BPA under the same conditions and reached the adsorption equilibrium after 1 h. The nonporous NP-CDP also required 30 min to reach the equilibrium. What's more, the BPA adsorption rate constant (k) of TFN-CDP was 1.5 mg g^{-1} min⁻¹, which outperformed the widely utilized activated carbon. The maximum adsorption capacity of TFN-CDP at equilibrium $(q_{\text{max,e}})$ was 88 mg g⁻¹, which was higher than that of the EPI-CDP (84 mg g^{-1}). As shown in Table 1, the BET surface areas of CD-POPs seem to have no correlation with their maximum adsorption capacity. However, BnCD-DCX²¹ with a BET surface area of 1209 m² g⁻¹ exhibited the highest maximum adsorption capacity (278 mg g^{-1}) among other reported CD-POPs. These results suggest that suitable porosity is one of the indispensable factors to improve the adsorption performance. In addition to

CDs, other macrocyclic POPs were also investigated as adsorbing materials for BPA. For example, the CA-POPs⁴² (CalP4, Fig. 9a) showed outstanding adsorption performance toward BPA (403 mg g⁻¹, Table 1), which might have originated from the rigid cavity of CA and the high π -electron density from alkyne and pyrene moieties.

PFASs, such as PFOA and perfluorooctanesulfonic acid (PFOS), are refractory organic contaminants from the production of polytetrafluoroethylene and film forming foam (Chart 1). The health advisory level of PFOA and PFOS set by the U.S. Environmental Protection Agency is 70 ng L^{-1} .²⁶ Selection of a suitable adsorbent is the key for removing PFASs. The fluorinated DFB-CDP²⁶ (Fig. 4b) can fast absorb over 95% of the total PFOA after 13.5 h and the PFOA concentration was decreased from 1 μ g L⁻¹ to 10 ng L⁻¹. Although the BET surface area of DFB-CDP was low ($<10 \text{ m}^2 \text{ g}^{-1}$), the $q_{\text{max,e}}$ was 34 mg g⁻¹ and the kinetic performance was 2.88 g mg⁻¹ min⁻¹, which was higher than that of granular activated carbon. Furthermore, the same group²⁷ aimed to improve the affinity for all anionic PFASs. TFN-CDP was reduced to the primary amines, which can form the cationic amino groups in water and rapidly eliminate 80-98% of 10 anionic PFASs at environmentally relevant concentrations after 30 min (Fig. 4c).

Organic dyes as a typical class of organic micropollutants are also difficult to be decomposed by nature and are toxic and carcinogenic to human beings. According to the charge states, organic dyes can be classified into anionic dyes, for example, methyl blue (MeB), methyl orange (MO), Congo red (CR), etc., and cationic dyes, e.g. methylene blue (MB), rhodamine B (RhB), etc., as well as the neutral dyes (Chart 2 and Fig. 30d). According to the charge states and sizes of the dye molecules, reasonable design and preparation of porous materials for selective adsorption and separation of dye molecules have been developed. As summarized in Table 2, the CE-based POPs (POP-TCE-15)¹⁸ can effectively adsorb cationic dyes. The $q_{\text{max},e}$ values for MB and RhB are 787.4 and 421.9 mg g^{-1} , respectively, while the $q_{\text{max,e}}$ value of POP-TCE-15 for MO is only 64.8 mg g⁻¹. The abundant O atoms from CE can contribute excellent adsorption capacity for cationic dyes deriving from the electrostatic interaction between the electron lone pairs on the O atoms of benzo-15-crown-5 and the positively charged dyes. The CA-based POPs also showed high capture performance. For example, CalP1⁴¹ displayed highly efficient and fast adsorption for both

Table 1 The BPA removal performance of representative macrocycle-based POPs in this review

Macrocycle	Macrocycle- based POPs	BET surface area $(m^2 g^{-1})$	$K (g mg^{-1} min^{-1})$	$Q_{ m max} \ (m mg\ g^{-1})$	Ref.
CD	BnCD-DCX	1209	_	278	21
CD	TFN-CDP	263	1.5	88	24
CD	T-E-CDP	0.31	1.99	128	30
CD	β-CDP	8.8	_	103	31
CD	CD-TTI200	233	_	37.5	38
CD	β-CD COF	108.2	6.8	20	81
CA	CalP4	759	2.12	403	41
PA	P5-P	7.69	0.16	14.2	65



Chart 2 Chemical structures of dyes discussed in this review.



Fig. 30 (a) The rejection of dyes with different molecular weights through CD/TMC/Matrimid nanofilm composite membranes. Inset: Photographs of the feed and filtrate solutions. (b) Photographs of the feed and filtrate of the mixed dye solution. (c) Schematic diagram of the molecular sieving mechanism through CD/TMC nanofilms. (d) The molecular structures of the dyes MO, IC, RBB, BBR and RhB. Adapted with permission from ref. 36. Copyright 2018 Wiley-VCH.

 Table 2
 The organic dye removal performance of representative macrocycle-based POPs covered in this review

Macrocycle	Macrocycle- based POPs	BET surface area $(m^2 g^{-1})$	$Q_{\max} \pmod{(\mathrm{mg g}^{-1})}$	Contaminant	Ref.
CE	POP-TCE-15	848.27	787.4	MB	18
CE	POP-TCE-15	848.27	421.9	RhB	18
CE	POP-TCE-15	848.27	64.8	MO	18
CD	CD-TTI200	233	86.7	RhB	38
CD	CD-TTI200	233	29.5	MO	38
CA	CalP	596	625	MB	41
CA	CalP	596	484	RhB	41
CA	CalP	596	673	CR	41
CA	COP1 ⁺⁺	17.9	928	CR	48
PA	P5-P	7.69	909	MO	65
CA	CX4-BD-1	_	35	MB	82
CA	CX4-BD-1	_	25	RhB	82
CA	CX4-BD-2	_	37	MB	82
CA	CX4-BD-2	_	40	RhB	82

anionic ($q_{\text{max},e}$: CR = 673 mg g⁻¹) and cationic dyes ($q_{\text{max},e}$: MB = 625 mg g⁻¹ and $q_{\text{max},e}$: RhB = 484 mg g⁻¹, Table 2), benefiting from the π -conjugated network, host–guest interaction of CA, and the large porosity.

In addition to selective adsorption, selective separation of organic dyes using macrocycle-based POP membranes has also been explored. For example, Chung and co-workers³⁶ prepared a series of freestanding CD-based POP (CD/TMC) membranes by the reactions between TMC and α -, β -, or γ -CDs, respectively (Fig. 7b). Fig. 30a suggests that the rejections of dyes through these three CD/TMC membranes increased with the increasing molecular weights of dyes, namely, Rose Bengal ($M_{w_{RB}} = 1018$) > Brilliant Blue R ($M_{w_{BBR}} = 826$) > Remazol Brilliant Blue ($M_{w_{RBB}} = 626$) > Indigo carmine ($M_{w_{IC}} = 466$) > MO ($M_{w_{MO}} = 327$).

The molecular weight cutoff follows the trend of α -CD/TMC/ Matrimid (320 Da) < β -CD/TMC/Matrimid (400 Da) < γ -CD/ TMC/Matrimid (550 Da), which is consistent with the cavity size (α -CD < β -CD < γ -CD). When a mixed solution of MO (orange) and RBB (blue) was passed through the β -CD/TMC membrane, the yellow solution only containing MO (14.9 × 4.8 Å) without RBB (15.8 × 11.9 Å) was obtained, which was confirmed by the UV absorption spectra. The reason was that the short diameter (4.8 Å) of MO was smaller than those of the inner cavities (6.0–7.8 Å) and the outer spaces (6.3–9.4 Å) of β -CD/TMC membranes, which selectively transported MO through the pore channels (Fig. 30b and c).

4.1.2 Heavy metal ions. Mercury and lead ions are the most common toxic heavy metal ions existing in the wastes, and are easily accumulated in the human body and cause cancer. TFN-CDP²⁵ (Fig. 4a) containing the negatively charged phenolation can effectively remove Pb^{2+} ions. But the $q_{max,e}$ value of TFN-CDP was only 16.4 mg g^{-1} due to the low surface area. To improve the uptake capacity of the β-CD-based POPs, Kong and co-workers⁹⁸ synthesized a β -CD polymer with a higher surface area (270.8 m² g⁻¹) by a reaction between β -CD and TFN. This polymer showed a higher uptake capacity (215 mg g^{-1}) of Pb²⁺ ions. Additionally, the β -CD polymer could remove other heavy metals like Cu^{2+} ($q_{max,e} = 192.8 \text{ mg g}^{-1}$) and Cd^{2+} ions $(q_{\text{max},e} = 163.2 \text{ mg g}^{-1})$. The adsorption mechanism investigated by Dichtel et al. and He et al. both suggested that the hydroxyl groups, especially negatively charged phenolates, were the key sites for binding of metal ions.

For the removal of highly toxic Hg²⁺, sulphur-containing porous materials are usually considered. Generally, the sulphur atoms can bind with mercury ions to generate insoluble chelates to



Fig. 31 Illustration of the structure of S-CX4P and the reversible process of adsorbing Hg^{2+} . Adapted with permission from ref. 45. Copyright 2019 American Chemical Society.

achieve efficient removal of Hg^{2^+} . A thioether-crown-functionalized CA-based POP (S-CX4P, Fig. 10a) was applied for highly efficient and fast uptake of Hg^{2^+} .⁴⁵ The superior uptake capacity of Hg^{2^+} reached 1686 mg g⁻¹ and the fastest initial adsorption rate was 278 mg g⁻¹ min⁻¹. Notably, even interfered by other competitive ions (Ca²⁺, Mg²⁺, Cu²⁺, and Zn²⁺) at high concentrations, S-CX4P can still effectively remove Hg^{2^+} from an initial high concentration (5 ppm) to a quite low level (2 ppb) within 5 min. The authors attributed the superior performance to the high specific surface area (547 m² g⁻¹) and the host–guest interactions between sulphur atoms in the thioether-crown moieties and Hg^{2^+} (Fig. 31).

4.1.3 Adsorption of iodine. Iodine allotropes, *i.e.*, ¹²⁹I and ¹³¹I, are typical radioactive elements with half-lives of up to millions of years, both of which are mainly generated from nuclear fuel. Once the radioactive iodine is released, it will cause serious damage to the ecological environment, water and organisms. Therefore, effective disposal and permanent storage of iodine are extremely important for sustainable development of nuclear energy and ecological protection. It is demonstrated that porous materials could effectively adsorb iodine under simulated real conditions. Host-guest interactions within macrocycles and π -conjugated porous skeletons including alkyne, diazo and triazine units are beneficial to improve the adsorption of iodine molecules. The alkyne-linked CA-based POPs⁴³ (CalP2–CalP4, Fig. 9a) exhibited a good iodine adsorption capacity of 88-220 wt%. To further improve the performance, the phenolic hydroxyl groups of calix[4]arenes were lithiated to afford CalP2-Li and CalP4-Li, respectively. Among them, CalP4-Li displayed the highest iodine adsorption capacity of 312 wt% (Table 3). This is because CalP4-Li possesses the most aromatic rings and alkynes per repeat unit as well as highest BET surfaces area (445 m² g⁻¹), which provides abundant lithium sites for iondipole interactions.

Diazo-linked RA-based POPs (CalPOF-1 to CalPOF-3, Fig. 13a) could also effectively absorb I₂ (Table 3).⁵⁴ Among them, CalPOF-1 exhibited the highest uptake capacity (477 wt%). The excellent performance on environment remediation originated from the permanent porosities and abundant sorption sites including macrocyclic π -rich cavities, azo (-N=N-) groups and phenolic units in the skeleton. Iodomethane is another radioactive and highly toxic methylation reagent. PA-based POPs

Table 3 The I_2 removal performance of representative macrocycle-based POPs in this review

Macrocycle	Macrocycle- based POPs	BET surface area $(m^2 g^{-1})$	$Q_{ m max}\ (m wt\%)$	Ref.
CA	CalP2	596	88	42
CA	CalP2-Li	274	108	42
CA	CalP3	630	196	42
CA	CalP3-Li	308	248	42
CA	CalP4	759	220	42
CA	CalP4-Li	445	312	42
CA	CX4-NS	468	114	43
CA	CalCOP1	280	232	50
CA	CaCOP1	10.86	240	51
CA	CaCOP2	20.16	281	51
CA	CaCOP3	81.09	310	51
RA	CalPOF-1	303	477	54
RA	CalPOF-2	154	406	54
RA	CalPOF-3	91	353	54
PA	CMP-1	16.1	151	60
PA	CMP-2	20.2	177	60
PA	CMP-3	284.6	131	60
PA	CMP-4	9.5	208	60
PA	PAN-FPP5	788.0	222.5	67

(MHP-P5Q, Fig. 19)⁶⁸ showed high adsorption capacity (80.3 wt%) and long-term storage of CH₃I. While the uptake capacities of the pristine P5Q (27.6 wt%) and the analogous polymer MHP without P5Q were much lower (62.2 wt%). This is because MHP-P5Q provides multiple ways to interact with the guest molecules including host-guest interactions, the halogen bond ($-I \cdots N = C$ -) and chemical adsorption.

Recently, four catcher-type CMPs (CMP-n (n = 1-4)) designed by Yang and co-workers⁶⁰ (Fig. 15c) were applied in I₂ adsorption under ambient pressure at 75 °C. Among these four CMPs, CMP-4 with suitable pore size and numerous aromatic rings exhibited the largest capacity of iodine adsorption (208 wt%, Fig. 32a and b). Moreover, adsorption experiments were also conducted in aqueous iodine solutions. As shown in Fig. 32c, the yellow solution gradually became colourless upon addition of CMP-4 and a high removal efficiency of 94% was realized.

4.2 Gas adsorption and separation

4.2.1 H₂ adsorption. Macrocycle-based POPs have large specific surface areas and tuneable pore sizes and pore environment, which show unique advantages in gas adsorption and separation (Tables 4 and 5). As a kind of clean energy with a high energy density, hydrogen is of great importance to ameliorate the critical global problems, *i.e.*, the shortage of energy resources and environmental pollutions triggered by excessive combustion of fossil fuels. In this respect, safe and efficient storage of hydrogen is a thorny technological challenge to be solved, in which effective adsorption of hydrogen represents one of the most important issues. Among the developed strategies, macrocycle-based POPs have been demonstrated as promising platforms for adsorption of hydrogen.⁶⁹ The efficiency of adsorption of hydrogen is mostly determined by the specific surface area, pore size distribution, and functionality of macrocycle-based POPs as well as the external pressure and temperature. For example, the CTC-network-PIM (Fig. 20a) with a high BET surface area (830 m² g⁻¹) and an



Fig. 32 (a) The adsorption maximum of iodine in CMP-1, CMP-2, CMP-3 and CMP-4 at 348 K. (b) Illustration of CMP-4 for efficient adsorption of I₂. (c) Iodine adsorption efficiency determined by time-dependent UV-Vis absorption spectroscopy of the I₂/H₂O solution (1 mM) upon addition of CMP-4. Inset: Photographs of iodine solutions; adapted with permission from ref. 60. Copyright 2021 Wiley-VCH.

 $\label{eq:table_table_table} \begin{array}{ll} \mbox{Table 4} & \mbox{The H_2 adsorption performance of representative macrocycle-based POPs in this review} \end{array}$

Macrocycle	Macrocycle- based POPs	BET surface area $(m^2 g^{-1})$	Pore size (nm)	H ₂ uptake ^{<i>a</i>} (wt%)	Ref.
CTC	CTC-network-PIM	830	0.6	$1.43^{b}/1.7^{c}$	69
CTC	CTV-CMP-1	314	0.7	0.81^{d}	70
CTC	CTV-CMP-2	218	0.7	0.51^{d}	70
CTC	Click-POP-1	342	1.27	0.46^{e}	71
CTC	Click-POP-1	317	1.35	0.46^{f}	72
CTC	CTC-COF	1710	2.26	1.12^{g}	83
CTC	CTV-COF-1	1245	1.48	$1.3^{h}/1.23^{i}$	84
CTC	CTV-COF-2	1170	2.16	0.75^{h}	84
CTC	aCTV-COF1	1132	1.7	0.5^{i}	85
CTC	aCTV-COF2	1428	2.2	0.8^{i}	85
CTC	aCTV-COF3	698	14	1.1^{i}	85
CTC	aCTV-COF4	636	14	1.0^{i}	85
^{<i>a</i>} Temperat ^{<i>e</i>} 0.53 bar. ^{<i>j</i>}	ure: 77 K; external ; ^f 0.60 bar, ^g 1.066 h	pressure. ^b 1.0 par. ^h 1.097 bay	bar. ^c 10. r. ⁱ 1.013 l	0 bar. ^d 1.13 oar.	bar.

ultramicroporous pore size (*ca.* 0.6 nm) achieved a maximum uptake for H_2 of 1.43 wt% at 1 bar and 1.70 wt% at 10 bar at 77 K (Table 4).⁶⁹

Zheng and co-workers reported a series of amorphous CTC-based POPs (Fig. 20b and c) and crystalline CTC-based COFs (Fig. 26a–c), which also exhibited excellent H₂ adsorption properties. As summarized in Table 4, compared to the amorphous CTC-based POPs (CTV-CMP-1, CTV-CMP-2, Click-POP-1, and Click-POP-1),^{69,70} the crystalline CTC-based COFs^{82,84,85} with higher BET specific surface areas exhibited better H₂ adsorption performance (Table 4). Even though the specific surface areas of aCTV-COF3 and

aCTV-COF4 are relatively small, the uptake capacities of aCTV-COF3 (1.1 wt%) and aCTV-COF4 (1.0 wt%) are higher than those of other aCTV-COFs (aCTV-COF1 and aCTV-COF2). This is ascribed to the microporosity and interactions of H_2 with the methoxy and hydroxyl groups in aCTV-COF3 and aCTV-COF4.

4.2.2 CO_2 adsorption. Carbon dioxide (CO_2) represents the most notorious greenhouse gas. The massive emission of CO_2 has significantly triggered the global warming, melting of glaciers and rise of sea level, which pose a great threat to the survival of terrestrial organisms.⁹⁹ Therefore, efficiently capturing CO_2 is very important. Unlike other gases, CO_2 is a quadrupole molecule.⁹⁹ Enhancing the interaction of macrocycle-based POPs with CO_2 is beneficial to improve the adsorption performance.

Owing to the effective affinity of hydroxyl groups to CO_2 , Dai and co-workers²⁰ reported four α - and β -CD-based HCPs (Fig. 3b). Among them, the α BnCD6OH-HCPP and β BnCD6OH-HCPP with free hydroxyl groups exhibited higher selectivity of CO_2/N_2 than the fully benzylated BnCD-HCPPs (Table 5). But BnCD-HCPPs showed higher CO_2 adsorption capacities than the BnCD6OH-HCPPs with free hydroxyl groups. More benzene rings led to the formation of more micropores and resulted in higher BET surface areas, thus enhancing the CO_2 adsorption capability.

A PA-based POP (PAN-FPP5, Fig. 18b)⁶⁷ exhibited the highest CO_2 adsorption capability (12.5 wt% at 273 K and 9.9 wt% at 298 K) and the highest selectivity of CO_2/N_2 (55.6) (Table 5). This could be associated with the "macrocycle effect" of PA. Additionally, MHP-P5Q (Fig. 19) could not only capture CH_3I , but also exhibit outstanding CO_2 adsorption capability (11.56 wt% at 273 K and 9.18 wt% at 298 K, Table 5). This was attributed to the hierarchical microporosity of the POP (0.76, 1.19 and 1.30 nm) and the affluent CO_2 -philic surface sites, including unreacted C=O sites and nitric sites in MHP-P5Q.⁶⁷

4.2.3 Propane/methane separation. Propane as a hazardous but highly value-added hydrocarbon is usually obtained by selective separation from natural gases; efficient separation of propane is of great importance to protect the environment and increase the utilization efficiency of natural gas. Coskun and co-workers58 reported two alkyne-linked P5-based CMPs (P5-CMP-1 and P5-CMP-2, Fig. 15a) for propane/methane separation. The size of micropores (6 Å) of P5-CMPs matched well with the kinetic diameter of propane (4.3 Å). Among them, P5-CMP-1 showed the highest methane and propane uptake capacities of 0.177 and 1.12 mmol g^{-1} , respectively, at 298 K. The selectivity toward the propane/methane mixture (10:90)was calculated by using the ideal adsorbed solution theory (IAST). The selectivities of P5-CMP-1 and P5-CMP-2 were determined to be 180 and 189, respectively, at 298 K and 1 bar. The high affinity of P5-CMPs for propane is attributed to the strong supramolecular host-guest interactions and multiple C-H/ π interactions from the "macrocyclic effect" of P5 in contact with matched propane.

4.3 Fluorescent sensors

Introducing macrocycles into fluorescent POPs is an efficient approach to constructing fluorescence sensors for the detection of specific metal ions or chiral molecules. Cui and co-workers⁷⁸

Table 5 The CO₂ adsorption performance of representative macrocycle-based POPs in this review

		PET surface		CO_2 upta	ıke (wt%)	CO ₂ /N ₂ s	electivity	
Macrocycle	Macrocycle-based POPs	area $(m^2 g^{-1})$	Pore size (nm)	273 K	298 K	273 K	298 K	Ref.
CD	αBnCD-HCPP	989	_	2.38	1.38	35	38	20
CD	αBnCD6OH-HCPP	871	_	2.32	1.36	41	32	20
CD	βBnCD-HCPP	1225	_	2.45	1.41	26	18	20
CD	βBnCD6OH-HCP	880	_	2.01	1.17	47	30	20
RA	HRN4	156	2.8	6.1	_	_	_	56
RA	RN4-Az-OH	340	2.8	9.0	_	_	_	56
RA	RN4-OH	720	1.4	9.9	_	_	_	56
RA	RN4-F	1230	0.7	11.4	_	_	_	56
PA	PAN-FPP5	788.0	0.52/1.25	12.5	9.9	_	55.6	67
PA	MHP-P5Q	296	0.76/1.19/1.30	11.56	9.18	—	—	68

reported two chiral olefin-linked CE-based COFs (CCOF17 and CCOF18, Fig. 22c) which exhibited strong fluorescence with quantum yields (Φ_{PL}) of 5.8% and 6.5%, respectively. Higher quantum yields could be achieved by further reducing the -C=-C- bonds of CCOF17 and CCOF18 to -C--C- single bonds to afford the corresponding CCOF17-R and CCOF18-R (Φ_{PL} : 19.0% and 20.5% for CCOF17-R and CCOF18-R, respectively). This is because the π -conjugated structures of sp² c-CCOFs were destroyed to hinder the non-radiative energy transfer pathway. These four fluorescent chiral COFs were employed to recognize chiral amino alcohols including phenylglycinol (PGL), phenylalaninol (PAL) and tryptophanol (TPL), through fluorescence enhancement or quenching mechanisms (Fig. 33). The enantioselectivity



Fig. 33 (a) Operating principle of the CCOF sensor. (b) Fluorescence emission spectra of (*R*)-CCOF 17 with increasing concentration of p-phenylglycinol in solution. (c) Benesi–Hildebrand plots of the fluorescence emissions of (*R*)-CCOF 17 enhanced by p- and L-phenylglycinol. (d) The comparative EFs/QRs of the (*R*)-P-BINOL²-C and (*R*)-CCOFs for three amino alcohols. (e) Structures of the examined amino alcohols and (*R*)-P-BINOL²-C. Adapted with permission from ref. 78. Copyright 2021 American Chemical Society.

factor (EF) or quenching ratio (QR) was used to evaluate the sensitivity toward these amino alcohols. The results suggested that the QR/EF values of CCOF17 and CCOF 18 were higher than those of CCOF17-R and CCOF 18-R (Fig. 33d), indicating that the olefin-linked CCOFs were more sensitive to chiral amino alcohols. This could be ascribed to the reduced structures with a discrete π -conjugated system, which suppressed the transmission and expression of chiral information in the 2D CCOF systems.

Yang and co-workers⁵⁹ reported another two fluorescent PA-based CMPs (P[5]-TPE-CMP and P[5]-TET-CMP, Fig. 15b). Owing to the AIE feature of TPE, P[5]-TPE-CMP showed distinct two-photon fluorescence, while the P[5]-TET-CMP without AIEgens exhibited no fluorescence. The fluorescence quantum yield of P[5]-TPE-CMP was 25.6%. Interestingly, the strong fluorescent P[5]-TPE-CMP was sensitive to metal ions. When P[5]-TPE-CMP was suspended in the solutions of different ions, only Fe³⁺ made remarkable fluorescence quenching (92.9%). The mechanistic study suggested that the good affinity of the methoxy group and the size matching effect of P[5] toward Fe³⁺ are the main reasons for fluorescence quenching. Furthermore, the fluorescence of P[5]-TPE-CMP was quenched by 98.5% in the presence of 4-amino azobenzene. These results indicate that P[5]-TPE-CMP can serve as a potential fluorescence sensor for Fe³⁺ and amide-based organics with high selectivity and fast response.

4.4 Ionic conduction

Ion transport in nanopores is critical for energy storage and conversion. For example, efficient proton and lithium-ion conductors are the key materials for fuel cells and lithium-ion batteries.⁹³ Zhang and co-workers demonstrated that the chemically stable spiroborate-linked arylene–ethynylene-based ICOF2 containing Li⁺ can serve as a solid-state electrolyte (Fig. 29).⁹³ The electrochemical tests showed that ICOF-2 had an ionic conductivity of 3.05×10^{-5} S cm⁻¹ and an average Li⁺ transference number of 0.80 ± 0.02 at room temperature.

Recently, Wang and co-workers⁸⁰ reported the first 3D ionic γ -CD-based COF (CD-COF-Li, Fig. 24a) which also showed a prominent conductivity of Li⁺ (Fig. 34). The ionic conductivity tests based on pellet samples indicated that CD-COF-Li exhibited an ionic conductivity of 2.7 mS cm⁻¹. The rapid transport of Li⁺ might be the synergistic result of the anionic feature of the spiroborate linkage, the flexible and dynamic nature of CD as



Fig. 34 Li ion conductivity tests. (a) Arrhenius plot of the CD-COFLi \supset LiPF6-EC-DMC ionic conductivity. (b) Schematic representation of Li ion transport in the channels of CD-COF-Li. Adapted with permission from ref. 80. Copyright 2017 Wiley-VCH.

well as the high capability for entrapping the electrolytes in the confined channels (Fig. 34b). The preparation of high-performance ionic COFs provides a new approach for the development of solid electrolytes.

4.5 Heterogeneous catalysis

4.5.1 Metal-free heterogeneous catalysts. Macrocycles, such as CA and RA, have external polarity due to the hydroxyl groups, which can function as catalytic sites for CO₂ fixation. For example, Yuan and co-workers⁵² reported the cationic CalCOP-1 (Fig. 12b) with CA and imidazolium moieties, which exhibited excellent catalytic activities for converting epoxides into cyclic carbonates without solvents at atmospheric pressure. This is because the cationic POPs have abundant hydrogen binding sites from the hydroxyl groups of phenol segments and nucleophilic bromide anions. This pioneering work provides a new way for designing ionic CA-based POPs as green heterogeneous catalysts for CO₂ fixation. RA-based POPs (RN4-Az-OH, Fig. 14)⁵⁶ also exhibited outstanding catalytic performance with a high conversion yield (95%) for transformation of CO2 into cyclic carbonates. This excellent performance is associated with a large number of CO2-philic functionalities including diazo and phenolic -OH groups.

4.5.2 Metal-loaded heterogeneous catalysts. The hydrophobic inner cavity of macrocycles can load metal ions with catalytic activities, such as Pd, Ni and Au (Fig. 35). For example, the reported CD-based HCP (BnCD-HCPP, Fig. 3a)¹⁹ can support Au NPs to generate the Au@BnCD-HCPP catalyst composite. The catalytic activity of Au@BnCD-HCPP was assessed by the reduction of 4-nitrophenol into 4-aminophenol. Notably, the colourless 4-nitrophenol turned into yellowish 4-nitrophenolic

ions after adding NaBH₄. When Au@BnCD-HCPP was added, the catalytic reaction rapidly completed within 3 min. The yellow mixture became colourless with the production of 4-aminophenol. The rapid reaction is attributed to the outstanding affinity of the BnCD-HCPP for 4-nitrophenol, the facilely diffused pores as well as high surface area (1225 m² g⁻¹) of BnCD-HCPP.

Pd-loaded macrocycle-based POPs can be used as heterogeneous catalysts for Suzuki-Miyaura coupling reaction. Quinone can efficiently coordinate with Pd NPs to generate the Pd-catalyst. Ma and co-workers⁶⁴ reported quinone-containing PA-based POPs (PPQ, Fig. 17a) as solid support for efficient loading of Pd NPs. The catalytic activity of the obtained Pd-PPQ was evaluated by the Suzuki-coupling reaction between 4-bromotoluene and phenylboronic acid (Fig. 35c). The results suggested that the turnover frequency (TOF) of Pd-PPQ was 97 times larger than that of the commercial Pd/C under the same reaction conditions, probably due to the highly dispersed Pd NPs in Pd-PPQ. Yang and co-workers⁶⁶ also designed a Pd-loaded CMP (Fig. 18a and Fig. 35a) with PA and porphyrin as the catalyst for Suzuki-Miyaura coupling and nitrophenol reduction reaction (Fig. 35c and d). The confinement and the sufficient anchoring sites of dual macrocycles (PA and porphyrin) exerted significant effects on controlling nucleation and seed growth of Pd NPs with a narrow size distribution.

Planar arylene–ethynylene based macrocycles, such as triangular-shaped dehydrobenzoannulene (DBA), can be used as ligands for complexation with Ni(0). McGrier and co-workers⁹²



Fig. 35 (a) Schematic representation of the metal-immobilized conjugated macrocycle-based polymer, Pd@DMP[5]-TPP-CMP. Adapted with permission from ref. 66, Copyright 2019 Wiley-VCH. (b) Schematic representation of the covalent organic framework Ni-DBA-2D-COF and (c–e) the corresponding catalytic reactions.

reported the outstanding catalytic activity of the metalated Ni-DBA-2D-COF (Fig. 35b) for reductively cleaving the aryl C–S bonds of various aryl thioethers in the presence of dimethylethylsilane as the reducing agent (Fig. 35e). The desulfurization of organosulfur compounds using Ni-doped DBA-COF as a catalyst is a rare example, indicating the unique advantages of metalated DBA-COFs as supporting platforms for metal species in catalytic transformations.

5. Conclusion and perspectives

In this review article, we have summarized the main strategies for constructing supramolecular macrocycle-based POPs, which include Friedel-Crafts reaction, nucleophilic substitution, Schiff base condensation, Sonogashira-Hagihara coupling, diazo coupling, and mechanochemical synthesis. Subsequently, the applications of these macrocycle-based POPs are discussed and classified into environmental remediation, gas adsorption and separation, heterogeneous catalysis, etc. A comparative analysis of the data suggests that the excellent performances of macrocyclederived POPs in heterogeneous catalysis and chemical adsorption are attributed to the unique host-guest interactions offered by supramolecular macrocycles. In addition, post-modified macrocycle-based POPs (e.g. lithiation of hydroxyl groups within macrocycles) exhibited a much more improved performance compared to the pristine materials. Macrocycle-based POPs can be further processed into membranes for separating polar and non-polar organic compounds, demonstrating good mechanical strength. Although the introduction of macrocycles into POPs sometimes leads to decreased surface areas, their gas adsorption selectivity and affinity are surprisingly improved. Compared to the traditional POPs, macrocycle-based POPs at least feature several advantages: (1) a better accommodating ability for guest molecules; (2) multifunctional POPs can be further obtained via facile post-modification of the macrocycles; (3) the obtained macrocycle-based POPs have good structural stability due to the highly cross-linked structures resistant to strong acids/bases and high temperatures.

Despite the various advantages of macrocycle-based POPs, many challenges still remain. Firstly, besides the traditional macrocycles (CDs, CEs, CAs, PAs, etc.), it is intriguing to develop new macrocycles to expand the diversity of macrocycle-based POPs. Recently, some novel macrocycles, such as cyanostars,^{100,101} triazolophane^{102,103} and cyclotetrabenzil,¹⁰⁴ have been developed. Among them, cyanostars and triazolophane have received increasing attention due to the facile synthesis with high yields and their potential applications in environmental and industrial sequestration. However, covalently linked cyanostar- or triazolophane-based POPs have not yet been documented. Interestingly, the very recently reported cyclotetrabenzil-based POPs¹⁰⁴ exhibited high CO₂ affinity and featured an excellent CO₂/N₂ selectivity (CO₂/N₂: 137) at 273 K. However, the harsh synthetic conditions for cyclotetrabenzil-based POPs might limit their practical applications. Therefore, more efforts should be devoted to developing novel and high-performance macrocycle-based POPs via green and efficient methods.

Secondly, although many amorphous macrocycle-based POPs have been reported, examples of crystalline macrocycle-based COFs are still rare. In addition, the advantages of macrocycles can be better utilized for other applications if they can be successfully introduced into COFs. In fact, the construction of macrocycle-based COFs is challenging due to several aspects: (1) in general, the construction of 2D-COFs needs planar monomers, but many macrocycles possess 3D configurations; for instance, CA and their derivatives exhibit cone, partial cone, 1,2-alternate, and 1,3-alternate stable conformations, which, on the other hand, could be used to build 3D COFs after tackling the challenges of synthesis, separation and purification of each conformer of CA; (2) some macrocycles, such as cucurbiturils and PA, cannot be easily functionalized to synthesise COFs. (3) Many macrocycles with complex structures have been used for COF synthesis, but always afford poor crystallinities or amorphous materials. Anyway, new reactions for COF synthesis are continually developed, and the obstacles to expand these macrocycle-based COFs might be eventually solved in the future.

Thirdly, macrocycle-based POPs have already been demonstrated with great application potential. For instance, CD-based POPs have been systematically studied for adsorption of organic micropollutants in waste waters, which sets an example for the practical applications of other macrocycle-based POPs in water purification. However, in terms of gas adsorption and separation, it is necessary to consider how to enhance the specific surface areas of macrocycle-based POPs; the efficiency of heterogeneous catalysis can also be improved after addressing this issue. Although COF-based materials exhibit many promising applications in gas adsorption and separation, environmental remediation, heterogeneous catalysis, photoelectric devices, sensing, energy storage and conversion, macrocycle-based COFs are still in their infancy. As highlighted in a very recent perspective article,¹⁰⁵ promising and diverse industrial applications (like batteries, molecular separation, and heterogeneous catalysis) could be expected when COFs are integrated with other stateof-the-art polymeric, metallic and carbonaceous materials (e.g. graphene and metal oxides) to afford new-generation hybrid materials. The current challenges also indicate that many new research topics in this field could be evoked in the near future.

In summary, we provided a comprehensive overview of the synthetic strategies and applications of macrocycle-derived hierarchical POPs. This review emphasizes the merits of the marriage between macrocycles and POPs, which not only inherit the features of the intrinsic cavity and unique host-guest interactions from the macrocyclic building blocks, but also can form hierarchical porous structures, and thus improve both the porosity and the performance in specific applications. Macrocyclic POPs will be further developed along with emerging synthetic chemistry, characterization technologies and material engineering.^{106,107} We envision that the current challenges in macrocyclic porous materials can be properly addressed and more innovative and high-performance macrocycle-based POPs could be developed in the near future. We hope that the current review would provide some valuable references and insights into the

design and synthesis of new macrocyclic POPs to accelerate the PPZ progress of this emerging field.

Abbreviations

]
POPs	Porous organic polymers	ł
HCPs	Hyper-crosslinked polymers	f
CMPs	Conjugated microporous polymers	â
PAFs	Porous aromatic frameworks]
PIMs	Polymers of intrinsic microporosity	ł
COFs	Covalent organic frameworks	1
CE	Crown ether]
CD	Cyclodextrin	ł
CA	Calix[n]arene ($n = 4, 6, 8$)	1
RA	Resorcinarene	1
PA	Pillar[n]arene (n = 5-10)	(
FDA	Formaldehyde dimethyl acetal	1
PXRD	Powder X-ray diffraction	ł
EPI	Epichlorohydrin]
BET	Brunauer–Emmett–Teller]
DCX	Dichloroxylene	I
BCMBP	4,4'-Bis(chloromethyl)-1,1'-biphenyl]
SNAr	Nucleophilic aromatic substitution	7
TFN	Tetrafluoroterephthalonitrile	(
PFAS	Per- and poly-fluorinated alkyl substance]
DFB	Decafluorobiphenyl]
DBP	Dibutyl phthalate	1
MIP	Molecularly imprinted polymer]
ETA	2,3-Epoxypropyltrimethylammonium chloride	(
TPEBr	Tetrakis(4-(bromomethyl)-phenyl)ethene]
AIE	Aggregation-induced emission	I
TPE	Tetraphenylethene	
NPs	Nanoparticles	
TEM	Transmission electron microscopy	(
SEM	Scanning electron microscopy	-
HDI	Hexamethylene diisocyanate	1
TTI	Triphenylmethane-4,4',4"-triisocyanate	
AFM	atomic force microscopy	1
EPR	Electron paramagnetic resonance	
SC4A	Sulfonatocalix[4]arene	1
PA[5]	Pillar[5]arene	I
PA[6]	Pillar[6]arene	1
BpP6	[2]Biphenyl-extended PA[6]	8
LT6	Leaning tower[6]arenes	I
TADDOL-OH	(<i>R</i> , <i>R</i>)-Tetraaryl-1,3-dioxolane-4,5-dimethanol	
EDC	1-(3-Dimethylaminopropyl)-3-	I
	ethylcarbodiimide hydrochloride	
THA	Triptycene hexamine	
P5Q	Pillar[5]quinone	
CTV	Cyclotriveratrylene	
CTC	Cyclotricatechylene	
AEM	Arylene–ethynylene macrocycle	
Ру	4,4',4",4"'-(Pyrene-1,3,6,8-tetrayl)tetraaniline	
Sa	2,4,6-Triformylphenol	
DMA	Dimethylamine	

PPZ	Piperazine
Am7CD	Heptakis(6-amino-6-deoxy)-β-CD
TPA	Terephthaldehyde
CX4-CHO	Tetrakis(<i>p</i> -formyl)calix[4]arene
BD	Benzidine
BPDA	Biphenyldiboronic acid
PDBA	Pyrenediboronic acid
f-CTV	Triformylcyclotrianisylene
aCTV	Amino-substituted cyclotrianisylene
HPTC	9,10-Hydroxyphenanthrene cyclotrimer
BDBA	Benzene-1,4-diboronic acid
TBPM	Tetra(4-dihydroxyborylphenyl)methane
BPA	Bisphenol A
PFOS	Perfluorooctanesulfonic acid
MeB	Methyl blue
МО	Methyl orange
CR	Congo red
MB	Methylene blue
RhB	Rhodamine B
RB	Rose bengal
BBR	Brilliant blue R
RBB	Remazol brilliant blue
IC	Indigo carmine
TMC	Trimesoyl chloride
CO_2	Carbon dioxide
PGL	Phenylglycinol
PAL	Phenylalaninol
TPL	Tryptophanol
EF	Enantioselectivity factor
QR	Quenching ratio
TOF	Turnover frequency
DBA	Dehydrobenzoannulene

Conflicts of interest

There are no conflicts to declare.

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