Conjugated macrocycle polymers

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Conjugated macrocycle polymers (CMPs) are an emerging class of organic porous materials with built-in supramolecular macrocycles in the conjugated skeleton through robust covalent bonds. Ideally, such an ingenious combination of extended \( \pi \)-conjugated networks and macrocycles with intrinsic cavities can offer enormous flexibility for molecular design to produce multiple binding sites and hierarchical aperture structures. CMPs can be constructed through kinetically controlled irreversible polymerization, which permits them to be tolerant to harsh conditions for customized functionalization. These features of CMPs make them promising candidates in many applications ranging from heterogeneous catalysis to molecule adsorption, separation, and sensing. Ever-increasing attention has been paid to the rapid expansion of this research area over the past few years, which has created a new interface in supramolecular chemistry and materials science. In this review article, the recent progress in CMPs will be explicitly presented, including their molecular design, synthesis, distinct functional exploration, and related applications. Finally, the outlook and challenges of this field will be discussed.

1. Introduction

Supramolecular chemistry, dominated by synthetic macrocycles and their self-assembly, offers an irreplaceable platform to depict molecular relationships and connections for the formation of complex and larger assemblies with programmed functions. The unique characteristics of these supramolecular macrocycles, such as confined space of inner cavities and conformational flexibility, enable them to accommodate a wide range of guests with inherently selective recognition properties. Accordingly, a number of strategies have been exploited to not only alter the cavity size, shape and electronic environment, but also install powerful functional groups, by which the additional affinity could be consolidated via the formation of specific donor–acceptor pairs.

Porous organic polymers (POPs) are established by knitting different organic units into extended two- or three-dimen-
sional (2D or 3D) networks possessing interconnected or closed pores, which have shown many superior properties in comparison with natural porous materials. The most fascinating feature of POPs is that their structures could be pre-designed based on a task-specific design strategy, taking advantage of the diversity of building blocks and linkages. Consequently, the aligned pore channels, tunable topological diagram and precise geometry prospect, originated from the inherent architectures of the building blocks with different shapes and sizes, could be systematically controlled. In particular, according to the diversity of organic units and linkages, POPs are categorized into covalent organic frameworks (COFs),\(^4\)–\(^6\) conjugated microporous polymers,\(^7\)–\(^8\) porous aromatic frameworks,\(^9\)–\(^10\) polymers of intrinsic microporosity,\(^11\)–\(^12\) covalent triazine frameworks\(^13\)–\(^14\) and hyper-crosslinked polymers.\(^15\) Research progress in POPs over the past decade demonstrated their great potential in a wide range of applications such as molecular adsorption and separation, catalysis, energy storage, bioengineering and environmental remediation.\(^16\)–\(^17\)

Development of novel POPs with enhanced properties and widespread applications is largely dependent on the selection of repeating precursors and synthetic strategies. Recently, precise reticulation of supramolecular macrocycles into a network of POPs has offered a conceptually fresh strategy to combine the bilateral advantages of both domains, such as permanent porosity, predictable structure and function, hosting ability for guest molecules, high chemical stability and ease of functionalization.\(^18\)–\(^20\) In order to find a new path for the cooperation of supramolecular chemistry and polymer materials, conjugated macrocycle polymers (CMPs) inherently incorporated with macrocyclic compounds that can be regarded as an important subclass of conjugated microporous polymers have been constructed by crosslinking macrocycles into conjugated networks (Fig. 1).\(^21\) There are several advantages of the newly designed CMPs integrated with macrocyclic entities: (i) reservation of the cavities can lead to the formation of intrinsic and extrinsic space originating from the macrocycles and the generation of a crosslinked polymeric backbone; (ii) immobilization of macrocycles can transfer the unique host–guest properties in solution to the solid porous skeleton, thus enabling the selective capture of potential guest molecules as additional anchoring sites; (iii) the robust network can prevent the self-aggregation-induced suppression of the inherent properties of \(\pi\)-conjugated co-planar aromatic macrocycles, as exemplified by metalloporphyrins or metallophthalocyanine-derived catalytic systems. Therefore, the marriage of macrocycles and conjugated microporous polymers can not only impart fascinating guest-responsive properties to solid-state materials, but also improve the accessibility of central active sites for guest transportation. Here, we review the recent advances in CMPs containing supramolecular macrocycles like crown ethers,\(^22\) porphyrins,\(^23\)–\(^26\) phthalocyanines,\(^24\)–\(^27\) pillar[n]arenes,\(^25\)–\(^26\) leaning tower[n]arenes (LT6) and [2]biphenyl-extended pillar[n]arenes (BpP6,\(^27\)–\(^30\) by presenting their synthetic approaches, structural features, properties and related functions, followed by an outlook on their possible future challenges and perspectives.

## 2. Design and synthesis of CMPs

Different synthetic routes have been exploited for the fabrication of advanced networks of CMPs, which could be similar to the classic synthetic procedures of other POPs. Among them, Pd-catalysed cross-coupling reactions, such as the Sonogashira–Hagihara cross-coupling reaction, are believed to serve as effective alternatives due to their obvious advantages such as high yield, easy preparation, facile separation and purification, as well as the enhanced stability of the cross-linked products.\(^21\),\(^31\) Certain other synthetic strategies have also been used including but not limited to the Knoevenagel condensation reaction, Schiff base reaction and electrophilic aromatic substitution (Chart 1).\(^32\)–\(^34\) However, there is also a lack of systematic and in-depth research on reaction conditions including solvents and their proportion, temperature, catalyst and polymerization time, which have direct influences on the resulting structures and properties, such as geometry, pore structure and BET surface areas. Meanwhile, supramolecular macrocycles are a special type of monomer due to their unique molecular recognition toward solvents, neutral and positive entities, or some inorganic elements, and thus bring about the potential self-assembly process via supramolecular interactions in the fabrication process. The self-assembly behaviour could cause a certain degree of uncontrollability that needs to be studied thoroughly. As a result, the potential host–guest interactions between the macrocycle- and non-macrocycle-derived subunits or the newly formed chemical bonds should be considered in terms of the structure–function relationship.

Another advantage of introducing macrocycles is that their facile rim functionalization can enable the tailorability and accessibility of intrinsic cavities. For example, alkylation-pillararene-based robust CMPs could be transformed into their quinone- or hydroxylated configuration, resulting in the flexible regulation of the coordination ability or improved hydrophilicity for more applications. Meanwhile, the target topology of CMPs could be determined by the symmetry and conformation of macrocyclic compounds. The rigid and pillar shaped pillararenes can serve as desirable \(C_9\) symmetry linkers to connect \(C_3\) or \(C_4\) symmetry cores to form crosslinked networks. Sometimes, the unique 3D ring architectures can also provide multi-fold crosslinking sites for the construction of 3D networks. As for porphyrin or phthalocyanine-derived functional systems, their conjugated electron co-planar structures make them potential four-connected rigid nodes, and the produced 2D sp\(^2\)-carbon-conjugated networks feature periodic arrangement for better electron delocalization.

## 3. Applications of CMPs

### 3.1 Adsorption and separation

In 2016, Coskun and co-workers reported on the synthesis of two pillar[5]arene-based conjugated microporous polymers (Fig. 2a)\(^31\) by a Pd-catalysed Sonogashira–Hagihara cross-coupling reaction between triflate functionalized pillar[5]arene and...
1,4-diethynylbenzene (or 4,4′-diethynylbiphenyl). The macrocyclic effect originated from the C–H⋯π interactions and the size match effect between propane and the pillar[5]arene cavity were responsible for primary thermodynamic adsorption of propane from a natural hydrocarbon gas mixture. As a result, the host–guest properties of pillar[5]arenes were brought into solid porous networks for selective adsorption and storage.

Very recently, we synthesized several CMP materials via a similar strategy, where LT6 and BpP6 were employed as emerging macrocyclic arenes with unique conformational architectures and attractive self-adaptation for guest capture.\(^{35}\) Triflate-
functionalized LT6 and BpP6 were used to crosslink with 1,4-diethynylbenzene or 4,4′-diethynylbiphenyl to form CMP-n (n = 1–4, Fig. 2b). Impressively, LT6-based CMP-4 demonstrated the highest iodine capture ability up to 208 wt% in vapor and 94% in aqueous solution due to their suitable pore size and numerous aromatic rings for iodine uptake via charge-transfer interactions. Meanwhile, CMP-2 based on BpP6 exhibited an ideal selectivity for CO2 over N2 and CH4 with the highest isosteric heats of adsorption (Qst) owing to the appropriate micropore size and the existence of triflate and abundant benzene linkers favourable for CO2 binding.

3.2 Catalysis

Zhao and co-workers obtained a series of crystalline COFs (CE-COFS) containing crown ethers of different sizes, such as 12-crown-4, 15-crown-5 and 18-crown-6, via solvothermal condensation of crown ether-functionalized p-triphenylene diamine monomers and 1,3,5-triformylbenzene (Fig. 3a).33 The powder X-ray diffraction (PXRD) patterns revealed the crystalline structures of the targeted COFs and nitrogen adsorption data confirmed the porous structure. However, the inherent cavities of crown ether units tend to block the pores due to the low Brunauer–Emmett–Teller (BET) surface areas (210, 59 and 47 m² g⁻¹ for 12C4-COF, 15C5-COF and 18C6-COF, respectively). Because crown ethers can bind inorganic metal ions of appropriate sizes, these crown ether-grafted COFs can be used as phase-transfer catalysts to transfer and activate the counter anions, proved by various nucleophilic substitution reactions.

Another supramolecular host–guest strategy for assisting selective photocatalytic oxidation was provided using a pillar[5]arene-based CMP system, which is indicative of the transfer of the host–guest properties of synthetic macrocycles from the solution phase to the solid network state for selective interaction with suitable guest molecules. In 2020, Wen and co-workers incorporated pillar[5]arene into a conjugated polymer network through crosslinking pillar[5]arene with 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine for heterogeneous photocatalysis in oxidizing guest-like sulfide derivatives (S-1) over non-guest-like substrates (S-2) as shown in Fig. 3b.36 In the case of conjugated organic polymers without pillar[5]arenes, no substrate selectivity was observed. Furthermore, the host–guest effect was confirmed as the main mechanism of selectivity by adding excess butanenitrile as a competitive guest in a competitive experiment, which led to an obvious decrease in the conversion yield of the oxidative products. A similar phenomenon has not been found for the conjugated organic polymer under identical conditions.

In 2019, we reported a nanoscale CMP, namely DMP[5]-TPP-CMP, by integrating alternating pillararene and porphyrin as typical strut and node components via a facile electrophilic aromatic substitution (Fig. 4a).34 In this work, double confine-
ment effects were introduced to exert enhanced control over the nucleation and seed growth of palladium nanoparticles (PdNPs) through coordination interactions with porphyrins and pillararenes in the CMP. Compared with the contrast polymer without pillararenes in the backbone, DMP[5]-TPP-CMP provided multiple active anchoring sites from two representative types of macrocyclic compounds and generated well-defined PdNPs of ca. 10 nm with better dispersibility and uniformity, which was closely related to its catalytic activity. Furthermore, the PdNP-loaded CMP (Pd@CMP) was used to catalyse the Suzuki–Miyaura coupling and the reduction of nitrophenol. The hybrid Pd@CMP not only showed good catalytic performance in facilitating the Suzuki–Miyaura coupling with 99% yield even under mild conditions (solvent: ethanol/water, reaction temperature: 60 °C), but also demonstrated a superior apparent kinetic rate constant (k_{app} of 1.9 × 10^{-2} s^{-1}) over most palladium supports in the reduction of nitrophenol.

Immobilization of co-planar aromatic macrocycles into the backbone of POPs is conducive to solving the self-aggregation problem caused by cofacially oriented π–π stacking, thus leading to better photoelectric activity. In 2018, Wu and co-workers constructed metallophthalocyanine-based POPs (CZJ-30) from four-branched tetra-amine FePc and three-con-

The construction of 2D conjugated COFs whose skeletons are linked by sp^2 carbon is still highly desired due to their high chemical stability. Wang and co-workers described a 2D sp^3 carbon-conjugated COF (Por-sp^3c-COF) based on porphyrin, which was synthesized from 5,10,15,20-tetrakis(4-benzaldehyde)porphyrin and 1,4-phenylenediacetonitrile via the Knoevenagel condensation reaction (Fig. 5a).^32^ Taking advantage of the unique photophysical and redox properties of porphyrin and the extended π-conjugated networks that can promote the electron delocalization along the framework, the Por-sp^3c-COF was successfully used in the photocatalytic aerobic oxidation of amines to imines under visible light. Significantly, both impressive reusability and prominent photocatalytic performance were observed in comparison with imine-linked analogous COFs.

Effective transformation of CO_2 represents a significant alternative approach to relieve the climate and ecological environment concerns. As a consequence, a great deal of attention has been paid to the fabrication of sustainable catalysts for the conversion of CO_2 to certain useful organic feedstock. For instance, McGrier and co-workers recently reported a ruthenium (Ru) porphyrin-based POP linked with benzo-bisthiazole (Ru-BBT-POP), which was synthesized by the reaction of building blocks premetalated Ru(II)-tetrakis(4-formylphenyl)porphyrin and 2,5-diamino-1,4-benzenedithiol dihydrochloride (Fig. 5b).^38^ This porphyrin-based POP was further utilized for the hydrosilylative reduction of CO_2 to produce pot-

In 2019, Gu and co-workers demonstrated another por-

In 2020, Zhang and co-workers designed a heterogeneous photo-Fenton catalyst, denoted as FePPOP-1, based on a metalloporphyrin-linked POP for organic pollutant degradation driven by visible light (Fig. 6b).^40^ The permanent porosity of the predictable polymeric network is believed to be responsible for the enhanced photocatalytic performance, which could achieve the total degradation of 70 ppm methylene blue in 50 mL of organic wastewater in the presence of 4 mg of FePPOP-1 within 80 min irradiation. The photocatalytic mechanism could be ascribed to the persistent reactive species \( \cdot \text{OH} \) and \( \cdot \text{O}_2 \) produced from the photo-Fenton reaction accelerated by FePPOP-1 and the photosensitive process of FePPOP-1, respectively. This work provides a promising direction for treating industrial wastewater.
3.3 Sensing

We prepared a luminescent CMP material (P[5]-TPE-CMP) with a well-defined alignment of pillar[5]arene and tetraphenylethylene (TPE) linked by an acetylene bond via the Sonogashira–Hagihara cross-coupling reaction (Fig. 7a).21 The integration of macrocycles and aggregation-induced emission (AIE) entities into a solid porous network is of considerable interest to combine the prefabricated macrocyclic cavities with a hosting ability and the fascinating emissive properties of AIEgens. Meanwhile, the interior accessibility, stability and recyclability of CMPs could be integrated into the functional materials. The experimental results indicated that P[5]-TPE-CMP could be used as a highly selective fluorescent sensor for Fe³⁺ with desirable recyclability and the carcinoogenic organic dye 4-amino azobenzene. Furthermore, we synthesized a counterpart CMP by replacing TPE with 2,4,6-tris(4-ethynylphenyl)-1,3,5-triazine and the obtained P[5]-TET-CMP without the AIE effect lacks the potential for sensing application.

In 2020, Zhang and co-workers used the peroxidase activity of metalloporphyrin-based POPs for quantitative, sensitive and rapid colorimetric sensing of sulfide ions (Fig. 7b).41 The crosslinking between tris(4-ethynylphenyl)amine and iron 5,10,15,20-tetrakis-(4′-bromophenyl)porphyrin was conducted via the Sonogashira cross-coupling reaction to produce the resulting polymer (FePPOPEPA) with a high BET surface area and abundant surface catalytically active sites. The peroxidase activity of FePPOPEPA was analyzed for the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB), a colorimetric substrate, in the presence of H₂O₂, where the color of the oxidation products is blue with obvious absorption at 652 nm. The addition of S²⁻ could enable the inhibition of the TMB oxidation process, thus leading to the decrease of the absorbance of the solutions with a good linear relationship versus the concentration of S²⁻. This work described a visual determination strategy for sulfide-ion sensing and achieved outstanding anti-interference performance with a low detection limit of 0.013 μM.

4. Overview and outlook

The past few years have witnessed the emergence of POPs built from macrocyclic compounds as multi-fold crosslinkers. Among them, CMPs inherently contain macrocycles with extended conjugated networks, showing many possibilities for flexible modular design for specific structures and functions. In this review, several types of CMPs synthesized by integrating crown ethers, porphyrins, phthalocyanines, pillararenes, LT6 and BpP6 have been summarized and discussed, and in the meantime their related applications in catalysis, adsorption...
and sensing have been showcased. Most of these examples are reported as classical POPs, such as COFs and conjugated microporous polymers. The participation of macrocycles in the construction of these smart CMPs gives rise to the generation of novel porous solid platforms with remarkable characteristics of supramolecular macrocycles and porous networks, such as structural integrity, guest-responsiveness and hierarchical apertures structures. Undoubtedly, the development of CMPs is still in its infancy and opportunities and challenges coexist in this promising field, for example:

(i) The polymerization process is largely dependent on the functionalization of synthetic macrocycles and exerts a great influence on the resulting geometry and connectivity. Consequently, new functionalization strategies and conformational optimization of macrocycles should be considered in further research, which are of great significance for connecting more types of macrocyclic compounds with these advanced backbones of CMPs.

(ii) Incorporation of macrocycles may block the pores and cause a decrease of specific BET surface areas to some extent. In some cases, penetration of the monomer into the cavities of macrocycles could lead to the formation of (pseudo)rotaxane structures, which are not favourable for the reservation of cavities as supplementary recognition sites. Screening reaction conditions and finding novel synthetic approaches are recommended to be fully explored to improve the porosity such as introducing effective templates to occupy the inner cavities of macrocycles. A possible solution to maintain the porosity permanently when macrocycles are immobilized into a 2D/3D network is to screen condensation conditions carefully including solutions, catalysts and temperature. Besides, suitable linkers also play significant roles in determining the connectivity and integrity of the pore channel.

Recent studies of the emerging CMPs have described the advantageous aspects of macrocycles in regulating the structures and properties of functional porous solid systems, which have provided constructive thinking for the development of future advanced functional materials. Although rapid progress has been made in CMPs, there is still a long way to go for the enrichment of CMP-based intelligent porous materials for broad applications, such as in treating concerning environmental and energy issues, which is far from the levels that have been fully explored.

Conflicts of interest
There is no conflict to declare.

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Notes and references