Pillararene-based molecular-scale porous materials

Meng-Hao Li,† Xin-Yue Lou† and Ying-Wei Yang†,*

This review discusses the design and syntheses of molecular-scale pillar[n]arene-based porous materials with promising applications and summarises the development of using pillar[n]arenes as the building blocks of porous materials. From the perspective of "role of participation" in the syntheses of molecular-scale pillar[n]arene-based porous materials, the content can be divided into pillar[n]arenes serving as supramolecular nanovalves on surfaces and as ligands for metal–organic frameworks and covalent organic polymers. By integrating pillararenes, which possess rigid pillar-like structures, electron-rich cavities and desirable host–guest properties, with porous polymers of large surface areas and abundant active sites, applications of the resulting materials in drug release platforms, molecular recognition, sensing, detection, gas adsorption, removal of water pollution, organic photovoltaic materials and energy storage can be realised simultaneously and efficiently. Finally, in the conclusions and perspectives part, we put forward the challenges and viewpoints of the current research on pillar[n]arene-based porous materials. We hope this article can provide a timely and valuable reference for researchers interested in synthetic macrocycles and porous materials.

Introduction

As an essential addition to the natural inorganic porous materials in nature, the development of synthetic inorganic/organic porous materials has a history of hundreds of years. Extensive attention has been attracted by porous materials benefitting from their outstanding properties, including permanent porosity, tunable structure, higher thermal stability, water stability, and chemical stability, and their great potential has been demonstrated in research fields such as sensing,1,2 catalysis,3,4 detection,5 gas adsorption,6 separation,7 and energy storage.8

The earliest discovery of microporous inorganic porous materials can be traced back to 1756 when the Swedish mineralogist A. F. Cronstedt discovered and proposed the definition of zeolite. However, with the progress of materials science, research focused on porous materials is no longer limited to inorganic materials. In recent decades, the areas of porous materials have gradually emerged and flourished, including mesoporous silica nanoparticles (MSNs),9,10 metal–organic frameworks (MOFs),11,12 covalent organic frameworks (COFs),13 and conjugated microporous polymers (CMPs).14 However, it is worth mentioning that the design and construction of porous polymers possessing various functions are tricky. A typical method is to immobilise functional organic entities onto the surfaces of inorganic/hybrid porous materials to indirectly achieve improved properties via the specific heterojunctions between their functional groups.15,16 By this means, the performance of the materials can be significantly optimised. Another direct and effective strategy is introducing macrocyclic molecules into the polymers/porous polymers to generate more active sites for enhanced functionalities.17–19 Notably, the physical and chemical properties of the polymers can be tuned mainly by directly modifying the macrocyclic structure of the polymers. Because of the multiple benzene rings in the macrocycle skeletons, pillar[n]arenes possess multiple active sites that can be functionalised and modified, which provide infinite possibilities in tuning their physical and chemical properties.10,17,20,21,22,23 So far, relatively mature synthetic methods and functionalisation strategies of pillar[n]arenes and their derivatives have been developed. Additionally, the research scope is no longer limited to the rigid pillar[n]arenes. Still, it has been extended to analogues, such as leaning pillar[n]arenes, enriching the family of pillar[n]arene species.24,25,26

In this review, we discuss various types of porous materials based on pillar[n]arenes. According to the “role of participation” of pillar[n]arenes in porous materials, we present two main sections where pillar[n]arenes are used either as the moving elements of supramolecular nanovalves on surfaces or ligands for MOFs and COFs. On the one hand, pillar[n]arenes can be effectively modified through non-covalent interactions on the surface of porous materials, including MSNs,20 MOFs and...
inorganic nanoparticles (NPs). On the other hand, pillar[n]-arenes can also be used as linker units of porous materials to directly synthesise polymers, such as supramolecular one/two-dimensional (1D/2D) polymers. We will also introduce various applications based on pillar[n]arene-based porous materials, including drug release platforms, fluorescent probes, sensing, detection, adsorption, pollution treatment, and photocatalysis. Finally, we will discuss the existing problems that still require more attention and remain to be overcome in both academic researches and real-world applications in the scope of pillar[n]arene-based porous materials.

**MSNs installed with pillararene nanovalves**

It is generally believed that the outstanding properties of MSNs, such as high surface areas, large pore volumes, uniform and tunable sizes, good biocompatibility, and modifiable internal and external surfaces, are vital prerequisites for serving as ideal drug containers. Supramolecular switches are defined as molecular ensembles consisting of at least two entities associated with noncovalent interactions. Particularly, host–guest interactions between the macrocyclic cavities and the guest stalks usually realise the construction of supramolecular switches with stimuli responsiveness and specificity that can be equipped onto porous materials. Pillar[n]arenes, as the main body of the new synthetic macrocyclic ring, due to their suitable and tunable host–guest interaction and other properties, make them perfect candidates for the crucial tasks of constructing supramolecular switches. On this basis, the mechanised MSNs integrated with nanovalves have received wide attention from scientists because of their tunable and controllable release of trapped cargo in the pores of MSNs.

The first demonstration of the use of pillar[n]arenes in the fabrication of supramolecular switches was reported by our research group in 2013. In this work, the supramolecular switch anchored on the MSNs can be activated by pH variation and the competitive binding between carboxylatopillar[5]arene (CP5) and acetylcholine. Subsequently, Du and co-workers used carboxylatopillar[6]arenes (CP6) to construct nanovalves on the mechanised MSNs for the controlled release of drug molecules. Two types of guest molecules, dimethylbenzimidazolium (DMBI) or bipyridinium (BP), were used as the stalks for the host–guest complexation with CP6 to seal the MSN pores. Since CP6 and stalks are entangled together through supramolecular interactions, multi-responsive controlled release can be achieved. Under acidic conditions, CP6 will be protonated, leading to reduced negative charges and solubility, which results in the weakened electrostatic interaction between CP6 and DMBI/BP stalks and directly causes detachment of CP6 from the functionalised stalks and the drug release. In addition, since the binding affinity of divalent metal ions toward CP6 is stronger than the electrostatic interaction between CP6 and DMBI/BP stalks, the carboxylate groups at each end of CP6 can be preferentially coordinated to divalent metal ions, which weakens the host–guest binding, thus opening the CP6-based nanovalves. Similarly, since 1,10-dimethyl-4,4′-bipyridinium (methyl viologen, MV) has a high binding affinity with CP6, the competitive binding of MV molecules toward CP6 can also lead to the release of drugs in MSNs.

Du and co-workers employed phosphonated pillar[5]arenes (PP5) to construct nanovalves with choline (Ch)/pyridinium (Py) as the stalks. On this basis, the mechanised MSNs integrated with nanovalves have received wide attention from scientists because of their tunable and controllable release of trapped cargo in the pores of MSNs.
quaternary ammonium stalks minimises the probability of premature release of the drug. The same PP5-valved Ch/Py-MSNs can also achieve multiple stimuli-response. When the anti-tumour drug doxorubicin (DOX) is encapsulated in MSNs, PP5 will detach from the Ch/Py stalks due to tumour cells with lower internal pH, achieving the purpose of the targeted release of the drug. In addition, the phosphate of PP5 can weaken the host–guest interactions between PP5 and the Ch/Py stalks by sequestering Zn$^{2+}$ ions, releasing loaded drugs and achieving the purpose of treating Alzheimer’s disease. Besides, the PP5-based nanovalves can also release loaded drugs upon activation of competitive binding of MV in the solution. The authors also embedded gold nanorods (AuNRs) into MSN cores (AuNRs@MSNs). Thanks to the hybridisation of MSNs and gold nanorods, AuNRs@MSNs have a photothermal effect under near-infrared (NIR) irradiation, weakening the host–guest interactions of the PP5 nanonanowires and the Ch/Py stalks and releasing the loaded cargo from MSN pores.

In 2016, we built a drug delivery system based on MSNs functionalised with quaternary ammonium salt (MSN-Q) and CP5-modified Au NPs (AuNPs) (Fig. 1C), which can be activated by competitive binding and temperature variation. This is the first example of integrating host–guest properties of pillar[n]-arenes and photothermal conversion capability of AuNPs in one drug delivery platform. CP5 ring can encircle the quaternary ammonium salt (Q) stalks through host–guest interactions so that AuNPs can cover the MSN aperture and seal the loaded cargo inside the pores. Thus, effective cargo release can be achieved in response to competitive agent ethylenediamine (EDA) and alleviated temperatures.

With the foundation of previous researches, therapeutic applications as expanded research of pillar[5]arene-modified NPs as gate-keepers for MSNs, our research group designed and manufactured a new type of multifunctional supramolecular drug delivery platform using hollow MSNs (HMSNs) modified with pyridinium (Py-P) as the drug carrier (HMSN-Py-P) and CP5-functionalized CuS NPs (CP5–CuS) as the gatekeepers (Fig. 2A). Similar to CP5–AuNPs, CP5–CuS can be attached to Py-P stalks through host–guest interactions with CP5 rings. The HMSNs loaded with anticancer drug doxorubicin (DOX) were capped with CP5–CuS and further coated with folic acid (Fa)-conjugated polyethylene glycol layer (Fa-mPEG) via electrostatic interaction as antennas to target tumour cells, affording the final material FaPCH NPs as a highly integrated therapeutic nanoplatform. Quadruple stimuli, including temperature, pH, competitive binding, and NIR irradiation, can open the nanovalves and drug release. Both in vivo and in vitro experiments have verified that FaPCH NPs exhibited efficient tumour inhibition through synergistic chemophotothermal therapy. This work provides bright prospects in the development of precise nanomedicine for cancer treatment.

Fig. 2  (A) Schematic diagram of the preparation of FaPCH NPs and their application in synergistic chemo-photothermal therapy. Reproduced with permission from ref. 29. Copyright 2020, Ivyspring International Publisher. (B) Schematic diagram of the preparation of DF-MSNB and their application in GSH/pH dual responsive drug delivery. (a and b) TEM images of MSNB. Reproduced with permission from ref. 30. Copyright 2019, Royal Society of Chemistry. (C) Schematic diagram of GA3-HMSN/Fe₃O₄ preparation, magnetic manipulation and multi-stimulus response to hormone release. Reproduced with permission from ref. 31. Copyright 2019, Royal Society of Chemistry and Chinese Chemical Society 2019. (D) Schematic representation of the preparation of MSNPs. (c) Alkali-triggered release profiles of HMAP from MSNPs. (d) Partial 2D ROESY of CP5 and APy-HDA under neutral conditions and (e) alkaline conditions. Reproduced with permission from ref. 33. Copyright 2016, Royal Society of Chemistry.
The creation and application of novel MSN species with multiple functions and enhanced performances are seminal in developing mesoporous silica materials. Thus, our research group constructed a difunctional bean-shaped mechanised mesoporous silica materials, DF-MSNBs, as a drug delivery platform (Fig. 2B). It not only achieved high-efficiency drug release but also showed fluorescence “turn-on” for tumour cell imaging. The functionalised mesoporous silica nanobeans (MSNBs) were prepared by a one-pot co-condensation method so that MSNBs possessed both functional groups –NH₂ and –SH. Tetraphenylethylene (TPE), a broadly-used fluorescent molecule with aggregation-induced emission property, was modified on the MSNB surface by coupling with the –NH₂ group. The 1,3-dimethyl-benzimidazolium (MBM) stalks on the MSNBs through disulfide bond were encircled by linking pillar[n]arenes (AWLP6) via host–guest complexation to block the channels of MSNBs. Under acidic conditions, the host–guest interaction between AWLP6 and MBM stalks of the material can be destroyed, releasing the loaded drug. Meanwhile, glutathione (GSH), as a typical reducing agent, would result in the breakage of the disulfide bond connecting MBM and the departure of MBM. Thus, the electron transfer between TPE and MBM no longer persisted, leading to enhanced fluorescence emission of TPE for tumour cell imaging.

Besides the applications in biomedicine, MSNs with pillar[n]arene-based supramolecular nanocarriers can also be used in other fields, including agriculture and alloy anticorrosion. For example, from the perspective of promoting plant growth, HMSNs gated by CP5 functionalised Fe₃O₄ NPs (CP5–Fe₃O₄) were prepared to deliver a plant growth modulator phenone (HMAP) can be released under the stimulation of Mg²⁺ inhibitor encapsulated in MSNPs, 2-hydroxy-4-methoxy-aceto-cinerea.32

MOFs based on the functional modification of pillararenes

MOFs are a new type of porous metal–organic hybrid materials that have recently emerged and attracted broad interest due to their uniform structure, high specific surface areas, permanent porosity, and biocompatibility. So far, reported research focusing on the integration of MOFs and pillar[n]arenes usually concerned using pillar[n]arenes as the host molecules to encircle guest moieties on MOF exteriors to construct molecular-scale porous materials for drug delivery. Additionally, researches have also emerged where pillar[n]arenes are introduced as backbone monomers/ligands to obtain new MOF species.

In 2015, our research group reported the first case of a drug delivery platform combining pillar[n]arene and MOFs, providing strong support for developing new targeted drug carriers (Fig. 3A). Positively charged stalks 1-(6-bromohexyl)pyridinium bromide (Py-N) were bound to the surface of UMCM-1-NH₂ by post-synthetic modification (PSM), and CP5 was selected to encapsulate the drug/cargo through host–guest complexation with Py-N. The drug delivery system exhibited outstanding features such as extremely low biological toxicity and high cell compatibility, along with dual-stimuli responsiveness concerning the changes in pH and competitive agents.

Based on the above work, our group chose another Zr-based MOF UiO-66-NH₂ as the solid scaffold for drug loading and positively charged quaternary ammonium salt Q stalks on the surface of UiO-66-NH₂ (UiO-66-NH₂-Q) capped by CP5 as nanocarriers for the control release of loaded cargoes (Fig. 3B). Based on the excellent characteristics of the modified UiO-66-NH₂ MOFs, our research group also chose UiO-66-NH₂-Q as the drug carriers and CP5 sodium salts as the gatekeepers of the drug loading platform for bone regeneration and cancer therapy (Fig. 3C). While retaining the original dual stimuli-responsive behaviour of the system in thermal heating and pH conditions, our research group also studied the effect of Ca²⁺ concentration on the platform release of drugs, the results of the study showed that with the increase of Ca²⁺ concentration, the release concentration and rate of 5-fluorouracil (5-Fu) would increase. This gratifying discovery makes this system applicable to the treatment of bone tumour diseases since the presence of bone tumour cells will lower the cell pH, so osteolysis will occur and increase the Ca²⁺ concentration.

Based on the previous work, UiO-66-NH₂ was selected as a shell to wrap the surface of the polypyrrole NPs core (PPy NPs) to afford a core–shell structure (PU NPs), with Py-N stalks modified on its surface for further host–guest interaction with CP6 and Py-N stalks to encapsulate 5-Fu in the system. To improve the targeting and biocompatibility of the drug delivery platform, the system’s surface was modified with polyethyleneimine modified with folic acid to form layer-by-layer assembled PPy@UiO-66@CP6@PE-Fa NPs (PUWPFa NPs) (Fig. 3D). Because PPy NPs are typical organic photothermal reagents, the system responds to pH, temperature stimulation and NIR irradiation. In another work, our research group synthesised a new drug loading platform, Fe₃O₄@UiO-66@CP6, with Fe₃O₄ NPs.
as the core and identical MOF shell and CP6 supramolecular nanovalves (Fig. 4A). This platform has expanded the application to magnetic hyperthermia and magnetic resonance imaging (MRI) in theranostics. Recently, our research group also constructed an intelligent plant hormone system based on the supramolecular host–guest interaction of MOFs modified with quaternary ammonium stalks (PCN-Q) and carboxylated leaning tower\[6\]arene (CLT6) to promote plant growth. The nanoplatform (CLT6@PCN-Q) loaded with GA3 can realise triple-stimuli-responsive release in pH, temperature and competitive agent spermine. 

Zeolitic imidazolate frameworks (ZIFs) are one of the dazzling branches of MOFs, composed of multiple tetrahedral units where each unit comprises one divalent metal cation (usually Zn\(^{2+}\)) and four imidazolate anions. Pei and co-workers chose Zn(2-methylimidazole)\(_2\) (ZIF-8) as the main framework (ZIF-8@DOX) for loading drugs with CP6 bonded to the surface of ZIF-8@DOX through the coordination between the carboxyl groups and the metal nodes (ZIF-8@DOX@CP6). Then galactose derivative (G) was introduced on the surface of ZIF-8@DOX@CP6 (ZIF-8@DOX@CP6@G) via the host–guest complexation with CP6 (Fig. 4B). In addition, because of original design concepts, the host–guest function between CP6 and G in ZIF-8@DOX@CP6@G is mainly a modifier, which improves the water dispersibility and targeting of ZIF-8@DOX. This material can achieve pH stimuli-responsiveness.

Pillar[\(\text{n}\)]arenes can also be used as ligands to synthesise MOF, forming molecular-scale porous materials. In 2012, Stoddart and co-workers reported the first study using functionalised pillar[5]arene (PSA) as ligands to synthesise pillar[\(\text{n}\)]-arene-based MOFs (rac-PSA-MOF-1). This result has attracted significant attention. It is worth noting that the chiral PSA-MOF-1 exists as a racemate because of the mixed planar chirality of PSA ligands. In addition, the result of PSA-MOF-1 single crystal data analysis was not enough to represent the clear framework solid structure of MOF itself due to the free rotation of the PSA molecules around each terphenyl junction in the extended network and the random distribution of the

Fig. 3 (A) Schematic diagram of the preparation of functionalised UMCM-1-NH\(_2\) with Py-N stalks and its response to multiple stimuli. Release profiles of the Rh6G-loaded, CPS-capped UMCM-1-NH-Py-N operated by (a) competitive binding. (b) pH changes. (c) Release profiles of the DOX-loaded, CPS-capped UMCM-1-NH-Py-N operated by pH activation. Reproduced with permission from ref. 37. Copyright 2015, Royal Society of Chemistry. (B) Schematic diagram of the preparation of UiO-66-NH\(_2\) MOFs functionalised with positively charged quaternary ammonium salt (Q) stalks and pillararene[2]pseudorotaxanes-coated UiO-66-NH\(_2\)-Q MOFs. Release profiles of the Fu-loaded, CPS-capped UiO-66-NH\(_2\)-Q operated by (d) competitive binding with Zn\(^{2+}\) and (e) thermal activation. Reproduced with permission from ref. 38. Copyright 2015, Wiley-VCH. (C) Schematic diagram of the preparation of functionalised Zr-MOFs with Q stalks and UiO-66-NH\(_2\)-Q MOFs coated with carboxylatopillar[5]arene. Release profiles of the 5-Fu-loaded, CPS-capped UiO-66-NH\(_2\)-Q. (f) pH changes. (g) Thermal activation. (h) Operation by Ca\(^{2+}\) addition. Reproduced with permission from ref. 39. Copyright 2018, Royal Society of Chemistry. (D) Schematic diagram of the preparation of PUWPFa nano-platform and their application in dual-targeted chemo-photothermal therapy for cervical cancer. (i) Release profiles of 5-Fu from 5-Fu-loaded PUWPFa NPs and PUNPs (aqueous media of pH 7) at different temperatures. (j) Monitoring of 5-Fu release in the case of temperature change in a simulated pathological environment (pH 5). (k) Pulsatile release profile of 5-Fu from 5-Fu-loaded PUWPFa NPs (aqueous media of pH 7) under periodic 808 nm NIR laser on/off irradiation. Reproduced with permission from ref. 41. Copyright 2018, American Chemical Society.
chiral P5A molecules. In the subsequent work of the same group, the enantiomers were converted into diastereomers by adding a chiral auxiliary to the racemate mixture P5A ligands. They obtained purely separated enantiomers (SP)-1 and (RP)-1 by the normal phase chromatography (Fig. 5). Subsequently, (SP)-1 and (RP)-1 were further coordinated with Zn\(^{2+}\) to synthesise homotypic chiral porous framework SP-P5A-MOF-1 and RP-P5A-MOF-1, respectively. Inspired by the work of predecessors, our research group prepared a luminescent molecular crystal (P5bipy) and a Cu(i)-coordinated luminescent nanocrystal (Cu(i)-P5bipy) concurrently using one pyridine-conjugated pillar[5]arene. Interestingly, P5bipy showed enhanced blue luminescence in its single crystal form, while Cu(i)-P5bipy nanocrystals exhibited long-lifetime luminescence and tunable emission properties under different solvent conditions.\(^{48}\)

**Functionalised metal NPs based on pillararenes**

In addition to pillar[n]arene-capped MSN/MOF as multifunctional platforms for drug delivery, pillar[n]arene-modified NPs are also a hot spot in biomedical fields.\(^{49}\) Although the action mechanism of pillar[n]arene-equipped NPs in drug delivery, photocatalysis and bioimaging, still lies in the host–guest
interaction between the pillar[n]arene cavities and guest molecules, pillar[n]arenes are directly or indirectly (via ligand exchange) capped on the surface of NPs in the form of covalent bond, instead of treating the pillar[n]arenes as supramolecular nanovalves.

Considering the broad prospects of photothermal therapy in clinical applications, we have developed a series of NPs that can respond to NIR irradiation. Through our previously reported one-pot synthesis method, CP5-terminated CuS NPs (CuS@CP) were successfully prepared (Fig. 6A). Guest molecules with hepatocyte targeting ability (G) were installed on the surface of CuS@CP through the interaction of its pyridinium salt moiety and CP5 cavity (CuS@CPG). Finally, DOX molecules were loaded on the CuS@CPG surface (CuS@CPG-DOX) through electrostatic interaction. The drug loading efficiency of CuS@CPG-DOX can be as high as 48.4%. Experimental studies in vivo and in vitro have shown that CuS@CPG-DOX can simultaneously achieve tumour targeting and dual responsiveness including pH, and NIR irradiation, confirming its good biocompatibility and tumour suppressing effect. The integration of AuNRs and pillar[n]arenes to afford a multifunctional theranostic system is reported by our research group in collaboration with Tang and co-workers (Fig. 6B). While retaining highly efficient photodynamic therapy (PDT) and photothermal therapy (PTT) of AuNRs, it also realises the characteristics of dense fluorescence imaging and photoacoustic imaging (PAI). A facile ligand-exchange method to exchange CTAB to CP5 was used to avoid the instability and aggregation of AuNRs and keep their unique photothermal properties, which also reduced the cytotoxicity of AuNRs (CP5@AuNR).

Besides researching precious metal NPs, we also combine rare-earth upconversion NPs (UCNPs) with pillar[n]arenes. UCNPs are inorganic phosphors doped with lanthanide ions, which can be used in photocatalysis, bioimaging, and fluorescent biological probes. Generally, in the preparation of UCNPs, a water-insoluble coating layer (oleic acid OA) is formed on the surface of NPs. Yet, the NPs (OA-UCNPs) are not conducive to organisms. The OA layer was exchanged with a simple ligand exchange strategy using water-soluble phosphoryl-functionalized pillar[5]arene (4C-PP5) ligands. The modified β-NaYF4:Yb/Er NPs (4C-PP5-UCNPs) have good water dispersity and excellent controlled release and cell imaging capabilities (Fig. 6C). Experiments confirmed that at a pH of 7.4, 4C-PP5-UCNPs@RhB could release up to 72% of the cargo. While at
pH 5.0 and 1.9, the release rates were only 17% and 2%. This is because the relatively stable host-guest interaction between 4C-PP5 and RhB dominates when the pH is 1.9. However, when the pH increases (pH 5.0–7.4), the phosphate group of 4C-PP5 will preferentially carry a single negative charge and continue to deprotonate, which will lead to an increase in the electrostatic repulsion between the negatively charged PP5 and RhB. This system feature indicates that it can be used as an oral drug to treat inflammatory bowel disease. Moreover, the cells treated by the system were found to emit bright green light under NIR irradiation, confirming that it can achieve the purpose of cell imaging. Sun and co-workers developed a new supramolecular upconversion nanosystem (CP5 ⊳ 1-UCNPs) (Fig. 7A). On the one hand, the nanosystem possesses the up-conversion luminescence (UCL) imaging of the UCNPs. On the other hand, by coating the surface of NaYF₄:Yb/Er NPs with NaGdF₄ shells, the NaYF₄:Yb/Er@NaGdF₄ NPs (OA-UCNPs@NaGdF₄ NPs) could be used in MRI. It is also necessary to remove the OA ligand on the surface. Distinct from our design, Sun et al. obtained OA-free UCNPs through a series of more complicated operations and modified the surface of UCNPs with 15-carboxy-\textit{N},\textit{N},\textit{N}-tri-alkylpentadecan-1-ammonium bromide (1-UCNPs). The electron-rich cavity of CP5 can interact with the ammonium bromide stalk on the surface of 1-UCNPs to form a CP5 ⊳ 1-UCNPs nanosystem. pH responsiveness of the nanosystem was achieved in human cervical cancer (HeLa) cells and exhibited effective inhibition for cancer cell proliferation.

Pillar\textit{n}arene-modified NPs also show great promise in adsorption, sensing, and catalysis. In 2013, we successfully synthesised protonated carboxylatopillar[\textit{5}]arene (CP5H)-functionalised Fe₃O₄ magnetic NPs (Fe₃O₄/CP5H NPs) (Fig. 7B). Fe₃O₄/CP5H NPs were selected as magnetic solid-phase extraction sorbents. They can identify residual pesticides in beverages through the CP5H cylindrical hollow and the pseudo-cavities.
on the surface of different CP5H and NPs, showing high selectivity and recovery rate. Based on this work, we subsequently prepared CP5-modified Fe₃O₄ magnetic NPs (CP5-MNPs) via the newly developed one-pot solvothermal strategy for the first time (Fig. 7C).⁶⁰

Due to the strong complexation between the CP5 cavity and the guests and the magnetic responsiveness, CP5-MNPs can adsorb and separate organic cationic dyes (methylene blue, crystal violet, and dimethyl viologen salt, etc.). These results also further confirmed the tolerance of CP5-MNPs to pH and inorganic salt interference, providing a reliable theoretical basis for their further application in environmental protection such as sewage treatment.

As for the application of pillar[n]arene-modified NPs in sensing, our research group first synthesised CP5-modified AuNPs (Fig. 8A).⁶¹ Due to the strong host–guest interaction between CP5 and viologen, a small amount of viologen can cause CP5-modified AuNPs to undergo 1D and three-dimensional (3D) assembly. The experimental result shows that CP5-modified AuNPs can be used as an optical probe for herbicide detection. Our research group also developed a series of pillar[n]arene modified AuNPs for sensing and catalysis (Fig. 8B).⁶² We used the reverse Turkevich method to synthesise medium-sized functional AuNPs (CP6–AuNPs-RT, AuNPs is 6–10 nm), where CP6 not only acts as a stabiliser on the surface of AuNPs but also serves as a reducing agent, which has been widely reported and replied.⁵² The –COO⁻ groups will undergo hydrolysis to increase the pH to 7.0–8.0. In a weakly alkaline environment, Au(III) can be immediately reduced to many Au(0) nuclei by –COO⁻. Importantly, CP6-AuNPs-RT can perform high-efficiency label-free detection of herbicides (paraquat) with a low detection limit and a wide detection concentration range. Interestingly, CP6–AuNPs-RT can also effectively catalyse the reduction of nitrophenols.

### Functionalised graphene modified by pillararenes

Graphene, a single-atom layered porous carbon material, has a 2D planar structure and active sites of multi-functional groups on the surface with various physical and chemical properties.⁶³,⁶⁴ To improve the performance and function of graphene, introducing the graphene 2D surface into hybrid molecules has been proven to hold considerable scientific significance and practical applications.⁶⁵,⁶⁶ Through π–π interaction, electrostatic forces, hydrogen bonding, host–guest interactions, and the covalent bonding of EDC–NHS coupling, pillar[n]arenes with good water solubility and recognition ability can be functionalised on the 2D surface of graphene,⁶⁷ thus improving their stability and dispersion in water and expands the applications in sensing detection, bio-friendliness, and environmental protection.⁶³,⁶⁸,⁶⁹

Diao and co-workers reported the first example of pillar[n]arene-functionalized graphene hybrid material.⁷⁰ In this work, an amphiphilic pillar[5]arene (AP5) was modified on the reduced graphene oxide (RGO) surface (RGO–AP5) under the dual support of covalent bonds (amide bonds) and non-covalent bonds (π–π interaction) (Fig. 9A). Compared with unmodified graphene oxide (GO), the modified RGO–AP5 can be better dispersed in water. Due to the uniform distribution of AP5 on the surface of RGO, AuNPs can assemble on the surface of RGO–AP5 (RGO–AP5–AuNPs) through amide groups of AP5 to afford ternary nanocomposites, which can be applied in sensing because of the good selective guest recognition and enrichment capabilities. Glassy carbon electrodes coated with RGO–AP5 and RGO–AP5–AuNPs were subjected to cyclic voltammetry (CVs) to recognise guest molecules, suggesting that both had good recognition ability toward electroactive substances such as dopamine,
4-acetaminophen, uric acid, methylene blue, tryptophan, and imidacloprid. Due to the multifunctional synergy of the ternary hybrid system, including guest recognition ability of AP5, catalytic properties of AuNPs, and the excellent electrochemical properties of RGO, RGO–AP5–AuNPs exhibits superior sensing ability for dopamine, which is manifested in a wide linear detection range and a low detection limit. In the follow-up work, the same research group made fine adjustments to the synthesis of CP5H–AgNPs/GO, mainly through non-covalent bonding (hydrogen bonds, π–π interaction) to combine CP5H–AgNPs with GO surface (Fig. 9B). Glassy carbon electrodes coated with CP5H–AgNPs were used to detect MV via CVs.\(^7\) For the application of functionalised RGO to detect dopamine, ascorbic acid, and uric acid, Kang and co-workers used the per-hydroxylated pillar[5]arene (P5) and GO connected by covalent bonding to afford functionalised graphene (GO–P5), where the film consisted of GO–P5 and thionyl chloride was coated on the electrode surface and irradiated by UV light to form the final RGO–P5 (Fig. 9C).\(^7\) The detection limit of RGO–P5 for dopamine is as low as \(2 \times 10^{-7}\) M, and the linear response range is from \(6 \times 10^{-6}\) M to \(9 \times 10^{-5}\) M.

Based on previous research, our research group developed another pillar[5]arene-functionalised RGO nanosheets (RGO–CP5H) and applied them in fluorescence sensing of aromatic dyes (Fig. 9D). Using the EDC–NHS coupling reaction, CP5H was bound to the surface of the RGO via ester bonds with the hydroxyl groups on the surface of the RGO to construct RGO–CP5H nanosheets. Fluorescence experiments proved that RGO–CP5H maintained the hydrophobic patches on the surface of RGO and possessed the host–guest recognition function of CP5H macrocycles. Under this dual effect, planar aromatic compounds can more easily adhere to these plaques through π–π stacking interactions, resulting in fluorescence quenching of RGO–CP5H for rhodamine 6G and neutral red.

Li and co-workers provided new ideas for pillar[\(n\)]arene-graphene in the applications of fluorescence sensing by introducing an indirect detection method to realise the recognition of acetaminophen (AP) (Fig. 9E).\(^7\) Acridine orange (AO) was
selected as the fluorescent probe loaded on the surface of RGO–AP5 via noncovalent bonding with RGO–AP5. The host–guest complexation between AO and AP5 macrocyclic cavity will cause fluorescence quenching of AO. After adding the competitive agent AP, AO can be detached from AP5 with its fluorescence turned on. Interestingly, AP can cause the fluorescence to increase exclusively since other competitive agents, such as ascorbic acid, potassium chloride, 4-nitrophenol, 4-aminophenol, and hydroquinone, can only cause minor changes in fluorescence. Another similar example was reported by Cao and co-workers, where AO was still selected as the fluorescent probe for binding the pyridine-functionalized pillar[n]arene (PCP6) on the surface of RGO to construct a hybrid material PCP6–RGO for the detection of trinitrophenol (TNP) (Fig. 9F).68

Because of the excellent biocompatibility and low toxicity of pillar[n]arene–GO/RGO hybrid materials, they can also be applied in biological fluorescence imaging, in which pillar[n]-arenes act as stabilisers for graphene materials in aqueous solutions. In 2014, Zhao and co-workers used strong hydrogen bond interactions for loading water-soluble pillar[5]arenes bolaamphiphile (P1) and tadpole-like amphiphile (P2) on the surface of GO to synthesise two functionalised GOs (P1-GO, P2-GO) (Fig. 10A).69 The nanomaterials were further endocytosed by HeLa cells for in vitro dual-mode Raman imaging. In addition, when the fluorescent guest molecule, bipyridinium derivative (Y1), was introduced into the P1-GO and P2-GO suspensions, the P1-GO-Y1 and P2-GO-Y1 not only maintained their original stability but could be endocytosed by HeLa cells to achieve the purpose of in vitro fluorescence imaging as well.

Pillar[n]arene–GO/RGO hybrid materials can also be targeted for identification and in vivo fluorescence imaging through the host–guest interaction. For example, Li and co-workers anchored hydrazine-pillar[5]arene (HP5) to the surface of graphene through covalent bonds via a typical EDC/NHS reaction (HP5-G), and safranine T was selected as the indicator of fluorescence imaging for the host–guest complexation with HP5 to construct the hybrid material safranine T/HP5-G (Fig. 10B).75 The host–guest complexation can cause fluorescence resonance energy transfer (FRET) between safranine T and graphene to quench the fluorescence of safranine T. Both in vitro HeLa cells and in vivo experiments in mice have confirmed that the paraquat can replace the Safranine T molecules and turn on the fluorescence, thus achieving the purpose of targeted imaging in living organisms.

Another excellent example of biosensing is the label-free fluorescence measurement of insulin through the supramolecular recognition between cationic pillar[6]arene (PC6) and insulin.76 Li and co-workers synthesised a new graphene hybrid material incorporated with pillar[6]arene (PC6–RGO). Similarly,
insulin can compete with the probe molecule RhB to recognise PC6–RGO, leading to the disappearance of the FRET phenomenon and “turning on” the fluorescent signal (Fig. 10C).

PAI combined with ultrasound and optical imaging has the advantages of deeper tissue penetration and higher spatial resolution. Chen and co-workers developed a hybrid supramolecular nanomaterial GO@WP6B ⊍ PyNS by modifying the host–guest complex WP6B ⊍ PyNS between pillar[5]arene with 12 tertiary amine groups (WP6B) and an amphiphilic molecule (PyNS) containing a pyrene unit on GO surface (GO@WP6B ⊍ PyNS) via π–π interaction between GO and PyNS, which can be used as a photoacoustic (PA) signal and ultrasound (US) signal nanoamplifier (Fig. 10D).77 Moreover, mediated by NIR irradiation, the bicarbonate on the surface of GO@WP6B ⊍ PyNS can be decomposed into CO2 nanobubbles as a “molecular experiment” to enhance PA and US signals.

Lee and Xu used pillar[5]arenes with different branches to synthesise new hybrid materials MoS2/C1/Zn–RGO and MoS2/C1/Zn–RGO–P10 (Fig. 10E).78,79 Because the amphiphilic pillar[n]arene can regulate the charge incompatibility, P5 and P10 were incorporated into the porous nanosheets of MoS2 and RGO to ease the charge incompatibility of the hybrid composite. Due to the intervention of pillar[n]arene, the hybrid materials have higher specific capacitance and better cycle performances than the original MoS2 materials, showing application potentials in lithium-ion storage and anode materials for lithium batteries.

**Supramolecular polymers based on coordination of pillararenes and metals**

Supramolecular organic polymers based on pillar[n]arenes are typical and widely-investigated molecular-scale porous polymers. They are mainly self-assembled through non-covalent bonds.80 In the process of supramolecular self-assembly, disordered organic monomers will orderly drive the construction of 1D/2D/3D skeletons through specific supramolecular interactions.81–83 Interestingly, Supramolecular organic polymers possess optimised properties thanks to the highly tuneable supramolecular interactions, including tunable luminescence range,84 reversible supramolecular dynamic balance,85 and multiple stimuli-response,86 providing attractive prospects for their applications in sensing, detection, and biomedicine-related fields.

Yao and co-workers reported a fluorescent pillar[5]arene supramolecular polymer based on coordination with Zn(n) (X12–Zn–X2)n (Fig. 11A).86 The expansion of the polymer was mainly based on the coordination of the terpyridyl group (X1) attached to one end of the pillar[5]arene with Zn2+, as well as the interaction between the cavity of the macrocyclic molecule and the guest molecule containing two triazole groups at both ends (X2). It can be considered that component X1–Zn is an AA-type monomer, and component X2 is a BB-type monomer. The two monomers interacted to form a linear supramolecular terpolymer. Interestingly, when the concentration of the supramolecular polymers (X12–Zn–X2)n in CH3CN/CHCl3 (v/v = 1/1) increased, they were reversibly converted into glue-like viscous liquid at 42–46 °C. On the other hand, (X12–Zn–X2)n also exhibited alkali responsiveness. When the concentration of OH− increases, the original coordination effect of polymer can be destroyed, and the generated zinc hydroxide can cause the polymers to dissociate into a transparent solution. Another similar example was reported by the Jing group and involved a supramolecular polymer based on the coordination of pillar[10]arene (P10) and Zn2+ (Fig. 11B).84 In this work, the supramolecular organic framework (SOF) presented a vertical 2D layered structure based on horizontal linear expansion. While the host–guest interaction between the cavity of the P10 and the guest molecule (X3) occurred, the X3 was also used to coordinate with Zn2+/Ag+ since the ends of X3 were modified by a terpyridine group and an imidazolium group with an alkyl chain, respectively. Thus, 2D supramolecular polymers (X32–Zn–P10/Ag)n, were formed using the strong coordination effect of the pyridine groups with Zn2+, the imidazole groups with Ag+, and the host–guest complexation of P10 and two alkyl chains. Similarly, (X32–Zn–P10/Ag)n exhibited reversible glue-sol phase transitions during heating and cooling. In addition, the (X32–Zn–P10/Ag)n glue can be stimulated by light irradiation and the competitive guest X4 with the original host-guest function of (X32–Zn–P10/Ag)n destroyed, causing the glue-sol phase transition.

Coordination metals in the supramolecular polymers have a significant influence on the properties of the material. Besides the Zn2+ above, lanthanide metals have been widely used in optoelectronics, materials science, and medical diagnosis because of their outstanding photophysical properties, such as narrow bandgap, high quantum yield, and longer fluorescence lifetime.87 Shi et al. selected EuII as the coordination metal for coordinated supramolecular polymer (Fig. 11C).88 The AA type “exo-wall” monomer was prepared by the π–π interaction between two ethylated pillar[5]arene (EtP5) molecules and N,N′-bis(n-butyl)pyromellitic diimide (X5) (EtP5–X5). The BB type two-position monomer (X62–Eu) was synthesised by the coordination of EuII and two bromoalkylated pyridines (X6). The macrocyclic cavity of EtP5–X5 and the bromoalkyl chain of X62–Eu can form a host–guest complex to self-assemble into a linear supramolecular polymer (EtP5–X5-X62-Eu)n. By using a relatively simple one-pot mixing method, the linear supramolecular polymer can be easily obtained. More interestingly, because of the changes in the coordination geometry of the coordination metals, the diffusion coefficient of the supramolecular polymer can also be adjusted. Jiang and co-workers designed and synthesised a discrete hexagonal metallacycle M containing tris[2]pseudorotaxane moiety (Fig. 11D).89 Through the host–guest complexation of pillar[5]arene dimer (PD) and M to prepare a new cross-linked supramolecular polymer (M ⊍ (PD)n), M ⊍ (PD)n can show redox responsive behaviour when the redox state of the coordination metal changes. Furthermore, when the coordination geometries of [Cu(phen)]+ and [Cu(phen)]2+ changed, the diffusion ability of supramolecular polymers can be reversibly adjusted. This attractive property of the materials can promote their applications in stimuli-responsive polymers.
Because supramolecular polymers are superior stimuli-responsive materials, Lin et al. fabricated a new type of SOF (SOF-AMP) for hypersensitivity (Fig. 12A). For the framework, a pillar[5]arene modified with a bis-naphthalimide group at both ends was selected as the host molecule (APA5) for the host–guest complexation with bis-ammonium functionalised pillar[5]arene (MJP5). Through the cation–π interaction between the macrocyclic cavity of APA5 and ammonium cation of MJP5, a 1D linear supramolecular polymer was first formed, followed by the formation of a 2D layered supramolecular polymer through π–π interaction of the naphthalene rings at both ends of APA5 (SOF-AMP). Interestingly, a stable supramolecular gel (SOF-AMP-G) can be formed in cyclohexanol, achieving an ultra-sensitive fluorescence response to the competing agent Fe^{3+}. Moreover, when H_{2}PO_{4}^{−} was added to Fe^{3+} coordinated SOF (MSOF-Fe), it can cause recovered fluorescence because of the hypersensitivity of H_{2}PO_{4}^{−}. Under the dual actions of H-bonding and “exo-wall” π–π stacking interactions between thioacethydrazine functionalised pillar[5]arene (MTP5) and 2,2'- (1,4-butanediyl)-bis(1H-benzimidazole) (HB), a new type of fluorescent supramolecular polymer (MTP5-HB) was synthesised (Fig. 12B). MTP5-HB can realise ultra-sensitive recognition of Cu^{2+} and Fe^{3+}. In addition, the in situ generated MTP5-HB-Cu can specifically detect CN^{−}, and the dry gel of MTP5-HB-Cu can effectively remove CN^{−} in an aqueous solution with a removal rate of 94.40%, providing solid support for the detection and removal toward CN^{−} in water.
resources. Yang et al. also reported a supramolecular polymer (H₂ ⊸ G₂) capable of exhibiting a dual stimuli-responsive fluorescence transition under the stimulation of a competitive guest (adiponitrile) and a halide anion (tetrabutylammonium bromide) (Fig. 12C). A bipyridine monomer (G₁) was synthesised with alkyl chain cyano groups at both ends and TPE group in the centre. A ditopic ligand (X₇) was selected for the 1:1 coordination with G₁ to self-assemble into a diamond-shaped metal ring G₂. Subsequently, the new supramolecular polymer (H₂ ⊸ G₂) was synthesised through the host–guest interaction between G₂ and pillar[5]arene dimer (H). By using the kinetic properties of the coordination bonds and the host–guest interactions, fluorescence responsiveness toward adiponitrile and tetrabutylammonium bromide can be achieved. Another interesting example was reported by Lin where bis-thioacethydrazine modified pillar[5]arene (DPSH) was selected as the host for the host–guest complexation and hydrogen bonding interaction with bis-bromohexane functionalised pillar[5]arene (DPHB) to construct a 2D SOF (SOF-THBP) (Fig. 12D). Using the same design concept, our research group also designed and synthesised a pillar[6]arene-based SOF (P₆-SOF-2). Each P₆ adopted C₂ symmetric chair-like conformation, and P₆-SOF-2 also had 3D interconnection channels and larger pore volume. Affected by the amorphous cavity size of P₆ and van der Waals interaction, P₆-SOF-2 can preferentially adsorb CO₂, followed by C₂H₂ and C₂H₄ (CO₂ > C₂H₂ > C₂H₄).

Conjugated porous organic polymers based on pillararenes

CMPs represent another typical porous organic polymers completely connected by covalent bonds. Their most extraordinary charm lies in the fine design of the repetition unit and the use of fixed and stable unit repetitions. Compared with MOFs, their skeleton structures can be controlled more accurately, which means that CMPs have the advantages of permanent porosity, structural tunability, and high thermal and chemical stability.
which provides firm support for their use in adsorption separation,\textsuperscript{97} environmental protection,\textsuperscript{98} gas and energy storage,\textsuperscript{99} heterogeneous catalysis,\textsuperscript{100} etc. Pillar[\(n\)]arenes as macrocycle monomers anchored into the conjugated organic framework can introduce molecular recognition capabilities into the microporous framework, increasing the heterogeneity of the extrinsic pores and providing additional driving forces and more specific sites for gas adsorption, molecular catalysis, etc.\textsuperscript{101–103} In addition, according to their topological structure, conjugated organic porous materials based on pillar[\(n\)]arenes can also be divided into 1D linear and cross-linked conjugated polymers.\textsuperscript{104,105}

Considering the molecular symmetrical chemical structures of pillar[\(n\)]arenes, 1D rigid oligomers/polymers based on pillar[\(n\)]arenes can be produced preferentially. Such materials can be more vividly understood as “alternative carbon nanotubes”.\textsuperscript{106} Due to the planar chirality and cylindrical chemical structures, pillar[\(n\)]arenes modified with bulky functional groups are generally used as the monomers for building polymers. This can effectively prevent the rotation of the heterocyclic aromatic hydrocarbons and prevent the expansion of the polymer in multiple directions.\textsuperscript{18} For example, Coskun and co-workers selected triflate functionalised pillar[5]arene and 1,4-diethynylbenzene/4,4’-diethynyl-1,1’-biphenyl as the linkers of the skeleton (Fig. 13A). The first 1D conjugated organic frameworks (EP5-CMP-1 and EP5-CMP-2) were synthesised with the participation of pillar[\(n\)]arenes based on the Sonogashira–Hagihara cross-coupling reaction.\textsuperscript{107} The BET surface areas of EP5-CMP-1 and EP5-CMP-2 were 400 and 345 m\(^2\) g\(^{-1}\), respectively. Compared with methane, the series of EP5-CMPs showed very high affinity and selectivity for propane. This can be attributed to the influence of the host–guest interaction of the macrocycles on the adsorption selectivity, which is also confirmed by the higher isotactic heat of adsorption (\(Q_{st}\)). At 0 °C, the \(Q_{st}\) of propane can remain as high as 53 kJ mol\(^{-1}\) and decrease with the increase of propane loading. These facts showed that EP5-CMPs could separate saturated hydrocarbons with low polarizability via the host–guest interaction with the pillar[5]arenes.

Pillar[\(n\)]arene-CMPs are also widely used in the uptake of carbon dioxide and iodine. Ning and co-workers prepared a new type of macrocyclic nitrogen-rich CMP (PAN-FPP5) via the condensation reaction between two benzaldehyde-modified pillar[5]arenes (FPP5) and melamine (Fig. 13B).\textsuperscript{101} Compared with its counterpart without pillar[5]arenes, PAN-FPP5 had comparable BET surface areas (788 m\(^2\) g\(^{-1}\)), excellent CO\(_2\) adsorption capacity (12.5 wt\% vs. 9.9 wt\%, 273 K/1 bar) and CO\(_2\)/N\(_2\) selectivity (55.6 vs. 39.9, 298 K). It is worth emphasising that even when compared with porous polymers with higher BET surface areas (COF-102, 3620 m\(^2\) g\(^{-1}\), 6.9 wt\%; COF-103, 3530 m\(^2\) g\(^{-1}\), 7.6 wt\%, PAF-1, 5640 m\(^2\) g\(^{-1}\), 9.1 wt\%),\textsuperscript{108,109} under the same test conditions, the CO\(_2\) adsorption of PAN-FPP5 still exceeds that of many porous polymers. PAN-FPP5 also exhibited excellent iodine adsorption properties in both the solution and gas phases because of the nitrogen-rich characteristics. This can be attributed to the electron transfer
between the lone pair electrons of the N atom, which makes the iodine molecules polarised into polyiodides (I\textsubscript{3}\textsuperscript{-}, I\textsubscript{5}\textsuperscript{-}). As another exciting example of iodide capture, Huang and co-workers selected triptycenehexamine (THA) with unique internal volume characteristics as a triple crosslinking agent to react with ten times pillar\[5\]quinone (P5Q) for preparing a new type of microporous organic polymer (MHP-P5Q) (Fig. 13C).

MHP-P5Q exhibited an adsorption survival curve of 3 distinct steps, and its BET surface area was 296 m\textsuperscript{2} g\textsuperscript{-1}. MHP-P5Q also showed excellent capture and storage capabilities of radioactive iodide (\text{CH}_3\text{I}), which can be attributed to the additional host–guest binding sites provided by rigid P5Q and the halogen bonds (\text{I} \cdot \cdot \cdot \text{N} = \text{C}).

Although pillar\[\pi\]arene-CMPs have excellent adsorption capacities in iodine and iodides, it is undeniable that the columnar spatial structure of conventional pillar\[\pi\]arene will increase the spatial resistance of the framework synthesis. To tackle this problem, our research group has prepared two new CMPs (CMP-LT1, CMP-LT2) via the Sonogashira–Hagihara cross-coupling reactions of trifluoromethane-functionalized leaning tower\[\pi\]arene (LT6-OTF) and 1,4-diethynylbenzene (DEP)/4,4’-diethynylbiphenyl (DEBP) (Fig. 13D).

Interestingly, CMP-LT1/2 exhibited an outstanding I\textsubscript{2} adsorption capacity because of the matched cavity sizes in the skeleton and the host–guest interaction of LT6-OTF. The adsorption capacity in steam can be as high as 208%, and the removal efficiency can be as high as 94% in the aqueous solution. We also synthesised similar structures of microporous polymers (CMP-BP1, CMP-BP2) based on trifluoromethane-functionalized pillar\[\pi\]arenes (Bp6-OTf). CMP-BP2 synthesised by Bp6-OTf and DEBP can specifically capture CO\textsubscript{2} under environmental conditions. Further, besides the adsorption of iodine and its derivatives, different pillar\[\pi\]arene-CMPs can also achieve high-efficiency and rapid adsorption and removal of various contaminants in water, such as low molecular weight alkylamines, carboxylic acids, bisphenol A, and herbicides.

Pillar\[\pi\]arene-CMPs also have a wide range of applications in fluorescence detection and sensing. Klaus and co-workers synthesised a new type of functionalised pillar\[5\]arene bearing two alkynyl groups (DP\[5\]). A 1D linear “fishing rod-like” conjugated polymer (DP\[5\]-PR) was synthesised via the Sonogashira–Hagihara cross-coupling reaction of DP\[5\] and di-halogenated benzene (iodine) (Fig. 14A). The polymer extended toward a benzene ring in the pillar\[5\]arene (direction of benzene ring functionalised with two alkynyl groups) and can emit blue fluorescence. The fluorescent properties of DP\[5\]-PR lay the foundation for applying pillar\[\pi\]arene-CMPs in fluorescent sensing. Another interesting example of a 1D conjugated polymer, Cao and co-workers synthesised a new type of CMPs (TP\[5\]-DPP) through Sonogashira–Hagihara cross-coupling reaction of thiophene-methoxypillar\[5\]arene (TP\[5\]) and diketopyrrolopyrrole (DPP) (Fig. 14B). The introduction of DPP gave TP\[5\]-DPP a large extinction coefficient at 519 nm (\textit{ε} = 1.1 × 10\textsuperscript{4} M\textsuperscript{-1} cm\textsuperscript{-1}) and strong fluorescence emission at 587 nm. TP\[5\]-DPP’s unique host–guest binding performance and fluorescence properties can be successfully and effectively used for the adsorption and detection of adiponitrile in water. Our research group used trifluoromethanesulfonic acid-functionalised pillar\[5\]arene (FP5) and 1,1,2,2-tetakis(4-ethynylphenyl)ethylene as framework linkers to construct a new type of CMP with intriguing fluorescence property (FP\[5\]-TPE-CMP) via Sonogashira–Hagihara cross-coupling reaction (Fig. 14C).

Interestingly, although the excitation wavelength varied from visible light to near-infrared, the emission peak of FP\[5\]-TPE-CMP remained at 537 nm, which suggested that FP\[5\]-TPE-CMP had a strong and satisfactory light stability. The material also...
showed detection performance for Fe$^{3+}$ ions and carcinogenic organic dyes (e.g., 4-amino azobenzene).

Pillar[n]arene-CMPs have also been applied to the field of catalysis. Our research group has innovatively synthesized reproducible and controllable particle size CMP NPs (DMP[5]-TTP-CMP NPs) (Fig. 14D).$^{102}$ The DMP[5]-TTP-CMP NPs were loaded with palladium (Pd@CMP) by a simple post-processing method. The Pd@CMP exhibited excellent catalytic activity for the Suzuki–Miyaura coupling reaction of borohydride (4-formylphenylboronic acid and para-substituted bromobenzene) the reduction of nitrophenol, and at the same time showed outstanding dynamic performance. Wen and co-workers recently reported two conjugated organic frameworks (FP[5]-TEPT, FP[5]-TEB) based on ditriflate-functionalized pillar[5]arene and applied them to the field of photocatalytic oxidation of sulfides, where the photocatalytic activity of FP[5]-TEPT and FP[5]-TEB on guest sulfide molecules was much higher than that of non-guest sulfide molecules (Fig. 14E).$^{114}$ Recently, our research group applied pillar[n]arene-CMPs containing sulfur heteroatoms (DMP[5]-TZ-CP) to photodegradation of organic dyes in solutions. Experimental results confirmed that DMP[5]-TZ-CP displayed an effectively photocatalytic activity in RhB solution within four hours due to the conjugated structure, broad visible-light absorption range after introducing heteroatoms, higher reactive oxygen species generation efficiency, and large contact area (Fig. 14F).$^{115}$ These works enriched the applications of conjugated macrocyclic polymers and inspired new research on catalytic mechanisms.

Conclusions and perspectives

In summary, this review focuses on the syntheses and application of a variety of pillar[n]arene-based molecular-scale porous materials, including pillar[n]arene-MSNs, pillar[n]arene-MOFs, pillar[n]arene-NPs, pillar[n]arene-GO/RGO, pillar[n]arene-CMPs, etc. Since Ogoshi et al. proposed the chemistry of pillar[n]arene in 2008, pillar[n]arenes have received extensive attention because of their intriguing properties. The highly symmetrical pillar-shaped structure, internal cavity diameter, and modifiable rims of the pillar[n]arenes are conducive to constructing molecular-scale regular porous materials. The internal electron-rich macrocyclic cavity can provide active sites by exerting unique host–guest interactions, which makes it easier to improve the physical and chemical properties of porous materials, and further expands the application fields of the polymers, such as drug delivery platforms, molecular recognition, fluorescence imaging and sensing, pollutant removal, gas adsorption, electrode materials, heterogeneous catalysis, and many other aspects. However, some problems still need more attention and require solutions to emerge in future research. (1) The mixed planar chirality of MOFs/CMPs materials based on pillar[n]arene ligands and the determination of the framework structure still need to be resolved; (2) so far, most of the pillar[n]arenes widely used in porous materials are pillar[5]arenes/pillar[6]arenes, and pillar[n]arene-porous polymers with different cavity sizes and connecting units should be designed and prepared. (3) New types of pillar[n]arene hydrocarbon-porous materials still need further exploration. For example, there have been few reports on the crystalline porous materials of pillar[n]arene-COFs prepared based on covalent bonds, and only some reports on the porous materials constructed by the host–guest interactions between pillar[n]arenes and COFs surface. Given this, molecular-scale porous materials based on pillar[n]arenes still need more in-depth research and future developments.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge the National Natural Science Foundation of China (21871108) and the Jilin Province University Cooperative Construction Project-Special Funds for New Materials (SXGJSF2017-3) for financial support.

Notes and references