Cavitand and Molecular Cage-Based Porous Organic Polymers

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ABSTRACT: Supramolecular cavitands and organic cages having a well-defined cavity and excellent host–guest complexing ability have been explored for a myriad of applications ranging from catalysis to molecular separation to drug delivery. On the other hand, porous organic polymers (POPs) having tunable porosity and a robust network structure have emerged as advanced materials for molecular storage, heterogeneous catalysis, water purification, light harvesting, and energy storage. A fruitful marriage between guest-responsive discrete porous supramolecular hosts and highly porous organic polymers has created a new interface in supramolecular chemistry and materials science, confronting the challenges related to energy and the environment. In this mini-review, we have addressed the recent advances (from 2015 to the middle of 2020) of cavitand and organic cage-based porous organic polymers for sustainable development, including applications in heterogeneous catalysis, CO\textsubscript{2} conversion, micropollutant separation, and heavy metal sequestration from water. We have highlighted the “cavitand/cage-to-framework” design strategy and delineated the future scope of the emerging new class of porous organic networks from “preporous” building blocks.

1. INTRODUCTION
Molecular hosts, such as cavitands, capsules, cages, the “Lego” blocks of supramolecular chemistry, having aesthetically appealing architecture, possess large cavities to accommodate small molecules or ions. The confined space of these molecular hosts with excellent guest recognition property leads to multifarious applications ranging from catalysis to molecular separation, sensing, enzyme mimetic catalysis, and development of artificial molecular machines. On the other hand, zeolites, porous carbons, metal–organic frameworks (MOFs), and porous organic polymers (POPs) possess open, continuous one-dimensional (1D) channels or two-dimensional (2D) or three-dimensional (3D) rigid porous networks. Among the aforementioned porous materials, POPs have attracted significant attention in the past few years due to (i) superior chemical, thermal, and hydrothermal stabilities arising from strong covalent bonds, (ii) structural and functional tunability, (iii) lightweight because of B\textsubscript{2}, C\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, and H-based building blocks, and (iv) \(\pi\)-conjugated network structure in conjugated microporous polymers (CMPs).

The intrinsic pores of molecular hosts become isolated (0D pores) in the solid state due to the closed packing, which inhibits facile mass transfer for the bigger substrates. After the guest removal, the supramolecular structures of these molecular hosts are often collapsed. On the other hand, amorphous POPs lack guest selectivity due to the hierarchical pore size distribution. Hence, the marriage of discrete molecular cavitands/cages and polymeric porous organic materials provides a hydrothermally stable robust structure and high porosity, as well as fascinating guest-responsive properties. A new interface of supramolecular chemistry and porous organic materials emerged by knitting the cavitands or cage molecules with suitable aromatic linkers, leading to task-specific POPs with enhanced solid-state guest-responsive properties.

1.1. Cavitand/Cage-to-Framework Design Strategy. A judicious design strategy for developing a cavitand/cage-based host matrix for solid-state applications is a worthy problem to address. In this regard, various approaches have been demonstrated, such as (i) integrating the cavitands/cages into the supramolecular network polymers through the reversible host–guest interactions, (ii) fabrication of cavitand/cage-based porous molecular solids through crystallization, (iii) cross-linking the molecular host through flexible alkylic linkers, and (iv) knitting the molecular containers through covalent linkages with the rigid aromatic linkers. Herein, we focus on the fourth design strategy, where the guest recognition properties and porosity due to the molecular hosts (cavitands, cages) and the rigid aromatic linkers are augmented in the resultant covalently linked networks polymers leading to task-specific applications.

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2. CAVITAND-BASED POROUS ORGANIC POLYMERS

According to Cram’s definition, cavitands are “synthetic organic compounds that contain enforced cavities large enough to accommodate simple molecules or ions.” These “cavities” are constructed by the macroyclic rings with a range of topologies from concave or bowl-shaped features to fully capsular molecular surfaces. Herein, we have focused our discussion on some of the well-explored bowl-shaped organic cavitands, such as cyclodextrins, calix[n]arenes, calix[4]-resorcinarenes, and pillar[n]arenes, as building blocks for developing crystalline and amorphous POPs.

2.1. Building Block: Cyclodextrin. Cyclodextrins (CDs) have toroidal, rigid structures composed of D-glucopyranose subunits connected by α-1,4-glycosidic bonds. They exhibit a high amphiphlicity owing to the outer hydrophilic surface made of a large number of –OH groups and interior hydrophobic cavity with diameters 0.57 (α-CD), 0.78 (β-CD), and 0.95 (γ-CD) nm. CDs have been heavily explored in supramolecular chemistry due to the excellent host–guest complexation ability. A high aromatic linker, tetrafluoro-biphenol A. The rate of adsorption was 15–200 times higher than that of the well-known carbon-based commercial adsorbents (Brita AC, GAC, NAC) as well as the nonporous β-CD-based polymers (EPI-CDP). The thermodynamic

In 2011, Zhang and co-workers first demonstrated the strategy for the development of the cross-linked polymers by connecting the “preporous” building blocks such as cages through the covalent attachment (Figure 1). In this approach, porous molecular hosts acting as building blocks are linked with different organic linkers to form the framework. The benefit of the “cavitand/cage-to-framework” strategy is to incorporate the dimensional and functional features of the “preporous” building units into the final framework architecture. A similar design strategy was also discussed in inorganic porous molecular hosts acting as building blocks are linked through the covalent attachment (Figure 1). In this approach, porous molecular hosts acting as building blocks are linked with different organic linkers to form the framework. The benefit of the “cavitand/cage-to-framework” strategy is to incorporate the dimensional and functional features of the “preporous” building units into the final framework architecture.

Figure 1. Schematic illustration depicting the progressive development of organic cage and cavitand-based porous organic polymers for multifarious applications. From left to right: first demonstration of “cage-to-framework” design strategy,8 triazine cage for selective CO₂ adsorption and separation,9 β-cyclodextrin-based porous polymer for micropollutant removal from water,10 pillar[5]arene-based conjugated microporous polymers for propane/methane separation,11 γ-cyclodextrin-based covalent organic frameworks for Li-ion storage,12 calix[4]arene-based porous polymer for water purification and oil–water separation,13 resorcin[4]arene-based POPs for iodine sequestration,14 αβγ-cyclodextrin-based postmodified porous aromatic framework for heterogeneous catalysis,15 sulfonated calix[4]arene-based POPs for solid-state tuning of photoluminescence,16 deep-cavity resorcin[4]arene-based POPs for halof orm removal from water,17 D₃h-symmetric triazine cage for selective CO₂ sorption,18 C-phenyIresorcin[4]arene-POPs for size/charge-selective molecular separation and, catalytic CO₂ fixation.19 CD-COF-Li and cage-COF figures adapted with permission from ref 7d (copyright 2017 John Wiley and Sons) and ref 7j (copyright 2019 American Chemical Society).
analysis of micropollutant adsorption suggested most of the \( \alpha \)-CD units in the polymer can form 1:1 complexes with bisphenol A at equilibrium.

TFN-CDP mostly exhibited a high affinity for cationic and neutral micropollutants.\(^9\) The formation of anionic phenolate groups through a competing side reaction between TFN and potassium carbonate during the polymerization (zeta-potential: \(-28.9 \pm 0.7\) mV) favors adsorption of cationic analytes.\(^9\) Upon reducing the nitrile groups of TFN-CDP to amines in TFN-CDP-red, the polymer shows high affinity toward anionic guests, including polyfluorinated alkyl substances (PFASs).\(^9\) The multiscale porous networks (micropores to macropores) were fabricated by employing high internal-phase emulsion (HIPE) radical polymerization. PDC-CDP rapidly uptakes a variety of organic solvents and adsorbs micropollutants due to the amphiphilic \( \alpha \)-CD moieties along with the multiscale porosity (Figure 2d). Upon being embedded with titanium dioxide (TiO\(_2\)) nanoparticles, PDC-CDP-HIPE exhibited photocatalytic degradation of organic pollutants with excellent recyclability. The pictorial representation of the catalytic activity indicates the facile mass transport through the internal macrochannels of PDC-CDP-HIPE (Figure 2d). \( \beta \)-CD moieties having a microporous cavity facilitate the rapid uptake of micropollutants. Upon irradiation with UV light (365 nm), homogeneously distributed TiO\(_2\) nanoparticles produce reactive oxygen species (ROS) to degrade the adsorbed molecules with excellent efficiency.

Cyclodextrins are also well-known as “molecular reaction vessels” for enzyme mimetic catalysis.\(^1\) Recently, CD-based porous polymers have emerged as excellent heterogeneous catalysts for selective chemical transformations. Zhu and coworkers prepared a highly fluorinated porous aromatic framework (PAF, \( S_{\text{BET}}\): 2436 m\(^2\) g\(^{-1}\)) with a hierarchical porosity (Figure 3a).\(^8\) The postsynthetic covalent modification with different cyclodextrins (\( \alpha \), \( \beta \), \( \gamma \)-CDs) led to CD-PAFs demonstrating selective encapsulation of a diverse range of micropollutants.
of aryl compounds based on their molecular sizes (Figure 3a–d). α-CD-PAF showed the highest selectivity toward p-chlorination over o-chlorination compared to β-CD-PAF because of preferential blocking of the o-position of the substrates (Figure 3b–d). The selectivity is due to the reduction of cavity size from γ- to α-CD. Again, with the decrease in the substrate size (head diameter: 0.58 nm, tail diameter: 0.97 to 0.41 nm), the uptake capacity of the α-CD-PAF increases (Figure 3d). Pristine PAF did not show any selectivity. On the other hand, only CDs showed good selectivity but poor recyclability. Hence, CD-PAFs bridge the gap between both types of materials, showing excellent selectivity and recyclability. Dai and co-workers developed a highly porous hyper-cross-linked polymer BnCD-HCP (Figure 3e) through Friedel–Crafts alkylation using dimethoxy methane as an external cross-linker; Au nanoparticle-doped BnCD-HCP exhibited high catalytic activity for nitrophenol reduction. (f) Condensation of γ-CD with trimethyl borate (B(OMe)₃) in the presence of lithium hydroxide (LiOH), dimethylamine (DMA), or piperazine (PPZ) under microwave conditions to afford crystalline γ-CD-covalent organic frameworks (CD-COFs) with different counterions. CD-COFs were employed for selective CO₂ adsorption and Li⁺ ion storage. Panel d and f were adapted with permission from ref 7g (copyright 2017 American Chemical Society) and ref 7d (copyright 2017 John Wiley and Sons).

Further, Au nanoparticle-doped BnCD-HCP was employed as a heterogeneous catalyst for nitrophenol reduction in water.

Wang and co-workers first developed γ-CD-based covalent organic frameworks (COFs) through a thermodynamically controlled transesterification reaction employing trimethyl borate (Figure 3f). The use of a 3D preporous building block resulted in the formation of a finely crystalline COF with well-defined nanochannels. The Brunauer–Emmett–Teller (BET) specific surface area was tuned from 494 to 760 to 934 m² g⁻¹ by exchanging the countercations of negatively charged tetrahedral tetrakis(spiroborate) linkages, respectively, with protonated piperazine (H₂PPZ⁺), Li⁺ ion, and protonated dimethylamine (HDM⁺⁺) (Figure 3f). A significantly high Li⁺ ion conductivity of 2.7 mS cm⁻¹ was observed for CD-COF-Li (20 wt % Li⁺) at 30 °C.

2.2. Building Block: Calix[n]arene. Calix[n]arenes are chalice-like phenol-based cavands having a hydrophobic cavity with phenolic–OH decorated polar rim. The host–guest complexation property of β-CD was used to encapsulate various phenolic pollutants. Further, Au-nanoparticle-doped BnCD-HCP was employed as a heterogeneous catalyst for nitrophenol reduction in water.

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the alkyne-linked porous organic polymers (CalPs) in 2017 (Figure 4a).\textsuperscript{7e} Pd(II)-catalyzed Sonogashira–Hagihara cross-coupling of tetrabromocalix[4]arene and 1,4-diethynylbenzene led to CalP2 ($S_{\text{BET}}$: 596 m$^2$ g$^{-1}$), exhibiting efficient sequestration of organic micropollutants and oil from water. Condensation with tri- and tetra-alkyne-substituted linkers resulted in CalP3 and CalP4 having BET specific surface areas of 630 and 759 m$^2$ g$^{-1}$, respectively (Figure 4a).\textsuperscript{11a} CalP4 having tetraethynylpyrene linkers showed a bisphenol A uptake rate 2.12 mg g$^{-1}$ min$^{-1}$, significantly higher than that observed in commercially activated carbons. Various factors were invoked for the high separation efficiency exhibited by CalPs. Phenolic–OH containing a polar rim of calix[4]arene facilitates dipolar and H-bonding interactions with micropollutants. The nonpolar electron-rich hydrophobic cavity of calix[4]arene provides a suitable environment to accommodate hydrophobic guests. Additionally, alkyne linkages endow hydrophobicity as well as rigidity to the network to achieve a superhydrophobic highly porous polymer.

Lithiation of the calixarene-based polymers by deprotonating phenolic–OH groups by $n$-butyl lithium led to the ionic porous polymers (Figure 4a).\textsuperscript{11b} CalP4-Li showed enhanced iodine capture (312 wt %) attributed to dipole–dipole, ion–dipole, and van der Waals interactions (Figure 4b).\textsuperscript{11b} For the sequestration of inorganic pollutants such as heavy metal ions, Hg(II) from water, the Trabolsi group developed a novel cavitand, thioether-crown-calix[4]arene-based porous organic polymers (S-CalP4, $S_{\text{BET}}$: 547 m$^2$ g$^{-1}$).\textsuperscript{11c} S-CalP4 exhibited an unprecedented high uptake capacity of Hg$^{2+}$ (1686 mg g$^{-1}$) and fast kinetics, decreasing the mercury level below the acceptable limit for drinking water (2 ppb) within 60 min. The record-high uptake of Hg(II) is due to the high intrinsic sulfur content and soft–soft interactions with thioether-crown-calix[4]arene units.

Trabolsi and co-workers recently demonstrated fine-tuning of the cavitand size of calix[n]arenes ($n$ = 4, 6, 8) in the POPs governing the removal efficiency of micropollutants, such as the toxic cationic herbicide paraquat (PQ).\textsuperscript{11d} Calix[8]arene, having a large cavity size (1.17 nm) along with more effective cation–π interactions with the guest, is likely to be more effective than calix[4]arene (0.3 nm) or calix[6]arene (0.76 nm). Molecular modeling studies showed the complete inclusion of the cationic PQ in the calix[8]arene. Tetraethynylpyrene and calix[8]arene-based POP, CX8P, exhibited a BET specific surface area (635 m$^2$ g$^{-1}$) lower than that of CX4P (759 m$^2$ g$^{-1}$) and CX6P (725 m$^2$ g$^{-1}$). However, CX8P showed the highest uptake capacity ($Q_{\text{max}}$: 419 mg g$^{-1}$) with 100% removal of PQ from water in 60 min owing to the exceptional complexation ability.
Liu and co-workers connected sulfonatocalix[4]arenes (SC4A) by tetraphenylethylene derivative (TPE) as a linker (Figure 1). The resultant mesoporous polymer, TPE-SC4A (S BET: 91 m2 g−1), showed solid-state photoluminescence (λ max: 500 nm) and guest encapsulation properties. Watersoluble yellow emitting dye 4-[4-(dimethylamino)styrly]-1-methylpyridinium iodide (DASPI, λ max: 580 nm) was encapsulated into the TPE-SC4A polymer matrix. The emission color was tuned from bluish-green to reddish-orange by varying the adsorbed amount of DASPI. Upon excitation of the dye-encapsulated network at 365 nm, two emission peaks around 500 and 580 nm corresponding to TPESC4A and the dye-encapsulated network at 365 nm, two emission peaks by varying the adsorbed amount of DASPI. Upon excitation of the dye-encapsulated network at 365 nm, two emission peaks around 500 and 580 nm corresponding to TPESC4A and the dye-encapsulated network at 365 nm, two emission peaks

2.3. Building Block: Resorcin[4]arene. Resorcin[4]arenes are a unique class of flexible host, which can change the conformation and cavity size depending on reaction conditions as well as guest molecules. In contrast to calix[4]arene, calix[4]resorcinarene possesses a greater number of phenolic −OH groups that provide multiple propagating sites for polymerization. In 2018, Yuan and co-workers first incorporated a series of C-alkylcalix[4]resorcinarene cavitands into the porous organic frameworks (CalPOFs) through facile metal-free diazo coupling reaction (Figure 1). The BET specific surface areas of calix[4]resorcinarene derivatives with an increase in the alkyl chain length from methyl to ethyl to propyl decreased from 303 to 154 to 91 m2 g−1 for CalPOF-1, CalPOF-2, and CalPOF-3, respectively. The results were anticipated due to the pore-blocking effect associated with the flexible alkyl chains. The network polymers showed outstanding iodine vapor adsorption capacity with increasing surface area, CalPOF-1 (477 wt %) > CalPOF-2 (406 wt %) > CalPOF-3 (353 wt %). The presence of azo (N=N−N=−) groups, π-electron-rich cavities, and phenolic −OH units of calix[4]resorcinarene and permanent porous structures contributed to ultrahigh uptake of iodine vapor.

The pore-blocking effect of C-alkylresorcin[4]arenes can be circumvented by replacing alkyl groups by rigid aromatic groups in the resorcin[4]arene (RN4) core. Patra and co-workers fabricated a series of RN4-based POPs by employing C-phenylresorcin[4]arene derivatives through three different fabrication strategies, such as (i) Pd(II)-catalyzed Sonogashira cross-coupling (RN4-OH), (ii) diazo coupling (RN4-Az−OH), and (iii) aromatic nucleophilic substitution reactions (RN4-F, Figure 5a). The azo-linked, highly dispersible, hierarchically mesoporous, RN4-Az−OH (S BET: 340 m2 g−1) exhibited a remarkable catalytic activity with high recyclability for metal-free cycloaddition of CO2 with a series of epoxides under solvent-free, mild reaction conditions (Figure 5b). The mechanistic investigation revealed the activation of substrate epoxides through H-bonding with phenolic −OH groups of C-phenylresorcin[4]arene units (Figure 5c).

Alkyne-linked microporous RN4-OH (S BET: 720 m2 g−1) showed high H2 storage capacity (10 mmol g−1, 2 wt %) at 1 bar and 273 K. The fluorine-rich hydrophobic POP (RN4-F, S BET: 1230 m2 g−1) exhibited efficient charge-specific and size-selective removal of organic micropollutants from water (Figure 5d). RN4-F having pore sizes of 0.7 and 1.4 nm
effectively adsorbed cationic and neutral micropollutants with comparable molecular dimensions, such as cresyl violet (1.48×0.83 nm), methylene blue (1.55×0.73 nm), rhodamine B (1.50×1.44 nm), rhodamine 101 (1.54×1.33 nm), β-naphthol (0.82×0.62 nm) and p-nitrophenol (0.79×0.55 nm). On the contrary, larger anionic molecules with multiple charges, such as methyl blue (2.41×1.76 nm) and Congo red (2.74×0.87 nm), were poorly sequestered. Moreover, RN4-F can selectively separate cationic methyl blue from the equimolar aqueous solution of methyl blue and anionic methyl orange (Figure 5e). Efficient fluorine−cation, π−cation, as well as phenolate−cation interactions are assumed to be responsible for the charge-specific molecular separation. In all aspects, RN4-derived POPs outperformed the pristine 0D porous building units in terms of activity as well as recyclability.

Recently, Dichtel and co-workers developed the deep-cavity resorcinarene-based porous organic polymer (CP-TFIN, S_BET: 1190 m^2 g\(^{-1}\)) employing tetrafluoroisocyanonitride (TFIN), believed to be a less sterically hindered linker compared to tetrafluoroterephthalonitrile (TFN), through base-catalyzed nucleophilic aromatic substitution reactions (Figure 1).\(^{15}\) Deep-cavity resorcin[n]arene derivatives are well-known hosts for various halomethanes and 1,4-dioxane. CP-TFIN was employed for the effective removal of halomethanes and 1,4-dioxane from drinking water. CP-TFIN outperformed commercially available activated carbons and resins in terms of affinity and fast removal kinetics for halomethanes and 1,4-dioxane.

2.4. Building Block: Pillar[n]arene. Ogoshi and co-workers in 2008 developed a symmetrical, rigid, and electron-rich supramolecular pillar-shaped cavitand, known as pillar[n]arene.\(^{14}\) Pillar[n]arene has been explored heavily due to the high yield compared to other pillar[n]arenes. Coskun and co-workers, in 2016, first introduced pillar[n]arene into the alkyne-linked conjugated porous polymers through cross-coupling of triflate substituted pillar[n]arene with 1,4-diethynylbenzene (P5-CMP-1, S_BET: 400 m^2 g\(^{-1}\)) and 4,4′-diethyl-1,1′-biphenyl (P5-CMP-2, S_BET: 345 m^2 g\(^{-1}\)) (Figure 6a).\(^{7c}\) P5-CMPs exhibit unimodal pore size distribution mainly in the micropore region with a pore diameter of 6 Å. Interestingly, the value is in good agreement with the reported inner cavity of pillar[n]arene. P5-CMP-1 was found to be an excellent material for the separation of propane from a mixture of propane and methane. Intriguing separation of nonpolar gases was due to the matching kinetic length of propane (4.3 Å) with the diameter of the cavity (6 Å) in P5-CMP-1, termed as the “macrocyclic effect”.

The guest encapsulation property of pillar[n]arene was further used for the micropollutant removal from the aqueous phase through the fabrication of a semipermeable membrane. A mesoporous membrane (pTC-PSA) with high permeability was designed through interfacial polymerization between benzoyl chloride and pillar[n]arene at the hexane−water interface where the pore dimensions (~3.4 nm) were large enough to facilitate easy movement of the organic/aqueous phase, maintaining the selectivity due to host−guest
interactions involving the cavitand (Figure 6b).\textsuperscript{13a} PSA has a specific affinity to cationic guests due to the electron-rich cavity. As shown in Figure 6b, cationic malachite green oxalate was effectively separated from anionic sulforhodamine B by the pTC-PSA film through the nanofiltration of the aqueous solution of the dyes.

Recently, Dai and co-workers demonstrated the mechanochemical synthesis of pillar[5]quinone (P5Q)-derived micro-porous organic polymers (MHP-P5Q, $S_{\text{BET}}$: 296 m$^2$ g$^{-1}$) for removal and storage of CH$_3$I from the radioactive waste (Figure 6c–e).\textsuperscript{13b} The design strategy involves incorporating two rigid building blocks, pillar[5]arene and triptycinehexamine (THA), into the porous 3D network. MHP-P5Q displayed a unique three-step N$_2$ sorption isotherm with three distinct pore size distributions at 0.76, 1.19, and 1.30 nm. The pore size of 0.76 nm is attributed to the pillar[5]arene intrinsic cavity in the networks. MHP-P5Q was demonstrated to have a superior performance in radioactive iodomethane (CH$_3$I, 80.3 wt %) capture and storage compared to the analogous network polymer, excluding P5Q (CH$_3$I, 62.2 wt %) and the pristine cavitand perethylated pillar[5]arene (27.6 wt %). The high rate of adsorption of iodomethane in MHP-P5Q is due to the C−H···π intermolecular interactions, leading to efficient host−guest complexation (Figure 6d). The phenazine framework formed an N−CH$_3$ bond through amine nitrogen (Figure 6e). Additionally, the H$_2$C−I···N=C−interactions involving the imine functionality of networks stabilized the chemisorptive intermediate. Thus, the synergistic effects of multiple supramolecular forces enhance the adsorption capacity of the cavitand-based POPs.

3. ORGANIC CAGE-BASED POROUS ORGANIC POLYMERS

Shape-persistent organic cages have a rigid regular geometric topology with a well-defined interior, large enough to accommodate guest molecules.\textsuperscript{1b} Unlike cavitands, cage molecules have multiple windows that allow the guest molecules to access the intrinsic void space. For example, imine cages have four triangular windows.\textsuperscript{1b,d} In the solid state, these cage molecules are closely packed in different alignments, such as window-to-window or window-to-arene.\textsuperscript{13d} Window-to-window arrangement provides interpore connectivity, leading to porous molecular solid, whereas window-to-arene packing often blocks the intrinsic voids of the cage and limits the diffusion kinetics of the guest molecules. The bottleneck associated with the accessibility of the cage voids in the solid state can be circumvented by the “cage-to-framework” design strategy.\textsuperscript{13a} Moreover, the frameworks are also enriched by the guest recognition properties of pristine molecular cages.

Zhang and co-workers first demonstrated the “cage-to-framework” design strategy via Sonogashira cross-coupling between 3D molecular cage and 1,4-diethynylbenzene in 2011.
The resultant cage-based framework showed CO$_2$ sorption capacity 4 times higher than that of the pristine cage. Later on, a series of organic cage frameworks (OCFs) through microwave-assisted Sonogashira cross-coupling employing various diacytylene linkers was developed. Interestingly, the secondary pore volume due to the extrinsic pores (i.e., between the cages) rises with the increase of linker length. It resulted in the amplification of the gas uptake capacity of the OCFs. On the other hand, the linker with a polar electron-rich triethylene glycol methyl ether pendent group endowed strong intermolecular interactions, with CO$_2$ leading to selective adsorption of CO$_2$ over N$_2$ (up to 213/1) at 1 bar and 293 K. Thus, a judicious choice of linkers with varying sizes and chemical functionalities, and 3D-structure impeded due to the cage alter the gas adsorption property and selectivity of the frameworks.

Coskun and co-workers fabricated a series of porous cage frameworks (pCAGES) using a shape-persistent triazine cage as a building block through a catalyst-free polymerization route. The frameworks, pCAGE-1 ($S_{\text{BET}}$: 629 m$^2$ g$^{-1}$), pCAGE-2 ($S_{\text{BET}}$: 711 m$^2$ g$^{-1}$), and pCAGE-3 ($S_{\text{BET}}$: 844 m$^2$ g$^{-1}$), were obtained by varying the size and topology of the linkers, namely, hydrazine (1D), 1,3,5-tri(4-aminophenyl) benzene (2D), and tetrakis(4-aminophenyl)adamantane (3D), respectively (Figure 1). Owing to the triazine moieties in the building units, the pCAGES showed superior affinity toward CO$_2$ adsorption (up to 4.2 mmol g$^{-1}$, 18.5 wt % at 1 bar, 273 K) with a $Q_a$ value of 42.9 kJ mol$^{-1}$ at high loading. The affinity of pCAGES toward CO$_2$ arises from ultramicroporosity, i.e., the intrinsic porosity of triazine cage building blocks termed “cage effect”. A control network using a “half-CAGE” molecule (without having the cage void) as a monomeric unit was synthesized. The resulting polymer showed a $Q_a$ value (25.2 kJ mol$^{-1}$) substantially lower than that of the pristine CAGE (39.4 kJ mol$^{-1}$) as well as pCAGES, indicating the importance of the cage effect.

Zhang and co-workers synthesized a fluorescent cage-based polymeric framework (pTOC) by using tetrphenylethylene-based oxalilarenecage (TOC) via nickel (0)-catalyzed Yamamoto-type Ullmann coupling reaction (Figure 7a). In TOC, the two propeller-like TPE units are fixed by four pyridine units through oxo bridges, resulting in a quadrangular prismatic cage structure (Figure 7a). The TOC showed “window-to-arene” packing mode in the solid state, leading to nonconnective lattice voids (illustrated by the blue Connolly surface, Figure 7b). The packing mode of TOC resulted in a nonporous crystalline solid ($S_{\text{BET}}$: 8 m$^2$ g$^{-1}$). However, knitting the discrete cage molecules by covalent bonds into a framework structure gave rise to pTOC. Resolving the issue of “window-to-arene” stacking, pTOC exhibited permanent porosity with a high BET specific surface area (929 m$^2$ g$^{-1}$), pTOC showed a high CO$_2$ uptake capacity of 49.3 cm$^3$ g$^{-1}$ (9.7 wt %) at 273 K, 1 bar, and strong green fluorescence under excitation of UV light at 365 nm (Figure 7c). Upon bubbling CO$_2$ into the methanolic dispersion of pTOC for 5 min led to 30% enhancement in the fluorescence (Figure 7d). CO$_2$ molecules (kinetic diameter: 3.3 Å) are able to fit into the cavities (5.8 Å) of pTOC and interact with heteroatoms in the cage skeleton through local dipole/quadrupole interactions. Hence, the rotation and vibration of phenyl rings of the TPE moieties are further restricted, blocking the nonradiative decay channels, resulting in fluorescence enhancement. Again, after the addition of NH$_3$·H$_2$O into the dispersion, CO$_2$ was removed from the cavity, and the initial fluorescence intensity of pTOC was regained (Figure 7e).

Wang and co-workers synthesized the extended crystalline COFs using porous organic cages as building units (Figure 8). The rigid, $D_{6h}$-symmetric triazine-based molecular cage consists of three V-shaped electron-deficient cavities. The hexagonal COF skeletons were fabricated taking the cage as a $C_5$-symmetric knot with p-phenylenediamine and benzidine as linkers for cage-COF-1 ($S_{\text{BET}}$: 1237 m$^2$ g$^{-1}$) and cage-COF-2 ($S_{\text{BET}}$: 667 m$^2$ g$^{-1}$), respectively (Figure 8a). The unique structure of cage COFs originated due to the antidirectional diimine linkages with vertically aligned aromatic linkers, resulting in a rippled layer with staggered ABC packing (Figure 8b,c). Integration of triazine cages into the crystalline frameworks led to the significantly high CO$_2$ uptake of 43.8 (8.6 wt %) and 37.3 cm$^3$ g$^{-1}$ (7.3 wt %) for cage-COF-1 and cage-COF-2, respectively, at 273 K and 1 bar. Integrating the shape-persistent porogenic organic cages into the crystalline porous frameworks via dynamic covalent chemistry is promising for cooperative sorption with enhanced efficiency and selectivity. Recently, Cooper and co-workers introduced a trigonal prismatic cage (Cage-6-NH$_2$) as a novel 3D building block with six propagating sites for the construction of the 3D imine linked COF. The cage-based 3D COF (3D-CageCOF-1, $S_{\text{BET}}$: 1040 m$^2$ g$^{-1}$) adopts an unprecedented topology with a two-fold interpenetration. Due to the flexibility in the cage knot, 3D-CageCOF-1 showed unique reversible switching between a large-pore structure and a small-pore structure in
the presence and absence of dimethylformamide, respectively. The presence of a N,O-decorated backbone with hydrophilic pore environment helped to harvest water with a maximum capacity of 33 wt % at low humidity conditions (<40%) at 298 K.

4. FUTURE SCOPE AND CONCLUSION

The present mini-review sheds light on various aspects of supramolecular hosts as building units for developing amorphous and crystalline porous organic materials. We presented the whole gamut of recent research based on the structure–property relationship of supramolecular host-based POPs for task-specific applications, such as selective gas adsorption, water purification, heavy metal sequestration, as well as heterogeneous catalysis. Since the genesis, we have witnessed excellent progress in the field in the last 5 years. However, there are considerable scopes to employ these materials for state-of-the-art applications.

(i) Some cavitands/cages, even though having excellent guest recognition properties, are seldom used for polymerization either due to their multistep synthetic routes with low yields or because they lack suitable functionalities for polymerization. Therefore, introducing well-crafted, green, and high-yielding fabrication methodology is desirable to integrate novel cavitand/cage-building blocks into the porous polymers. We envision cucurbit[n]urils, tubularenes, imine cages, porphyrin boxes, etc. to have tremendous application potential as building units in the near future.

(ii) Processability is a bottleneck for the cavitand/cage-based POPs in real-time applications. Making the cavitand/cage-based polymers solution-processable and retaining their porosity is a formidable challenge. Such processable POPs may find novel applications in light harvesting, surface coating, and dip catalysis, etc. Cavitand/cage-based POPs not only sequester toxic pollutants from the aqueous phase but also can be used in protective equipment, such as in masks to filter the air from toxic gases, volatile organic compounds, and microbes.

(iii) Development of innovative design strategies for supramolecular host-based POPs to augment guest-responsive property and porosity for the fabrication of drug delivery vehicles, stimuli-responsive smart materials, sensors, and artificial molecular machines to enzyme mimetic catalysis are some of the exciting avenues for further research.

Recent studies on cavitand/cage-based POPs, as outlined in this mini-review, provide numerous promising scopes for sustainable developments, including environmental remediation. Thus, the emerging class of materials stemmed from the marriage of molecular container and porous polymer, if explored adequately, can turn out to be the “materials for tomorrow”.

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Notes
The authors declare no competing financial interest.

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