Porous Aromatic Frameworks as a Platform for Multifunctional Applications

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ABSTRACT: Porous aromatic frameworks (PAFs), which are well-known for their large surface areas, associated porosity, diverse structures, and superb stability, have recently attracted broad interest. Taking advantage of widely available building blocks and various coupling strategies, customized porous architectures can be prepared exclusively through covalent bonding to satisfy necessary requirements. In addition, PAFs are composed of phenyl-ring-derived fragments that are easily modified with desired functional groups with the help of established synthetic chemistry techniques. On the basis of material design and preparative chemistry, this review mainly focuses on recent advances in the structural and chemical characteristics of PAFs for potential utilizations, including molecule storage, gas separation, catalysis, and ion extraction. Additionally, a concise outlook on the rational construction of functional PAFs is discussed in terms of developing next-generation porous materials for broader applications.

INTRODUCTION

Porous materials are divided into inorganic porous materials (zeolites, carbon, etc.), inorganic–organic hybrid porous materials (MOFs, CPs, etc.), and organic porous materials in accordance with structural compositions.1 Emerging as a novel functional platform, organic porous materials are a new research hotspot in the fields of physics, chemistry, and material science.2 As a result of the combined advantages of both porous solids and polymers, organic porous materials are endowed with high surface areas, tunable architectures, well-defined porosities, and facile machinabilities.3–5 In addition, a variety of synthetic techniques facilitate the design and preparation of diverse organic porous materials that incorporate key physical properties and chemical functionalities into a porous skeleton or at the pore surface.6,7 To date, substantial advances have been made in the use of these materials in gas storage and separation,8–17 catalysis,18–23 energy storage,24–35 sustained drug release,36 and many other applications.37–47 Despite rapid progress, the variety of talents involved in this research encourage the preparation of a universal strategy to synthesize organic porous materials with tailor-made pore structures and specific functionalities.

Thanks to the continual developments of organic chemistry, organic porous materials can be customized with unique textures, such as crystalline structures and amorphous structures, through diverse coupling reactions. The crystalline materials are mainly classified as covalent organic frameworks (COFs),48–50 porous organic cages (CCs),51,52 and extrinsic porous molecules (EPMs).53–55 Typical amorphous structures in a timed sequence include hyper-cross-linked polymers (HCPs),56,57 polymers of intrinsic microporosity (PIMs),58,59 conjugated microporous polymers (CMPs) 60,61 covalent triazine frameworks (CTFs),62 and porous aromatic frameworks (PAFs),63 among others (Figure 1).64–75 In this Outlook, we focus on PAFs as a representative organic porous material to investigate the correlation between structure and function and propose some feasible strategies to guide the preparation and development of porous materials for practical applications.

PAFs are constructed by the effective assembly of organic building blocks through covalent coupling reactions, because they predominantly consist of 2D/3D periodic aromatic frameworks.76–79 Unlike conventional COFs, which are obtained by reversible organic condensation reactions, PAFs are prepared via irreversible cross-coupling reactions (generally, C–C coupling) and concomitantly possess high surface areas, open architectures, robust skeletons, and excellent...
stabilities. The free rotation of polyhedral monomers and uncorrected orientation of condensed oligomeric fragments leads to framework defects and an irregular internal structure. Sharing unordered structures, PAF materials featuring rigid building blocks, topology-oriented construction, short-range ordered structure, superb stability, and intrinsic porosity differ from other cross-linked polymers, such as HCPs, in an apparent manner. Obtained from the interlinked polymer chains after being untangled by the solvent, HCPs reveal conspicuous swelling and a complete disordered structure; PIMs, whose 1D rigid chains with contorted/disfigured aromatic fragments lose their ability to pack efficiently, render the solubility and intrinsic microporosity.

The groundbreaking work on PAFs is evaluated from computational studies that filled the C−C spaces of a diamond with multiple phenyl rings to produce highly porous architectures with theoretical surface areas ranging from 2000 to 6000 m² g⁻¹ (Figure 2).56,58,77 In 2009, Profs. Qiu and Zhu synthesized the porous aromatic framework PAF-1 via a one-step Ullmann polycondensation of a tetrahedral building block, tetrakis(4-bromophenyl)methane, and found that PAF-1 exhibits an ultrahigh specific surface area (BET: 5600 m² g⁻¹, Langmuir: 7100 m² g⁻¹) which is close to that of the ordered, crystalline versions.63 This high porosity is mainly attributed to the fact that the solvent templating effect of framework−solvent or solvent−solvent interactions prevents the structural interpenetration calculated using the Forcite module compared to the amorphous and disordered Models.76,80 PAF-1 reveals excellent stability and provides open and interconnected channels for guest molecules, making it useful for molecular storage; it can hold 29.5 mmol g⁻¹ of carbon dioxide at 298 K and 40 bar, 75.3 mg g⁻¹ of hydrogen at 77 K and 48 bar, or 1.86 g g⁻¹ of iodine vapor at 298 K and 40 Pa.81 Using the same coupling strategy, a series of PAFs with quadricovalent Si (PAF-3) and Ge (PAF-4) atoms in lieu of the C center were synthesized with high surface areas (up to 2932 m² g⁻¹).11 They possess considerable adsorption capacities for gas molecules, including hydrogen, methane, and carbon dioxide. Coincidentally, Prof. Zhou’s group replaced the central carbon of PAF-1 with other quadricovalent centers to develop porous structures that also illustrate exceptionally high surface areas.66

On the basis of this solid foundation, the target synthesis of functional PAF materials has harvested the rapid development by conditioning the surface area, pore size, and functionalization sites (Figure 3).82−88 Normally, the specific features can be regulated by the accommodation of building blocks with precise shape, size, hybridization, or heterocyclic units, followed by convenient synthetic methodologies to transform monomers into cross-linked textures, such as (1) ionization of porous frameworks or (2) molecularly imprinted porous aromatic frameworks. In regard to (1), the charges and electrostatically bound counterions along the channel walls result in a pore skeleton with intrinsic charge repulsion/affinity effects for guest molecules through polarization effects/chemical bonding.89−91 In regard to (2), using a PAF as a novel scaffold, the introduction of molecular imprinting technology into porous skeletons will endow polymeric matrices with selective recognition capabilities.92−94

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On the basis of our summary, a universal methodology is infeasible for the field to achieve high yields and great
homogeneity, multivariate behavior, surface area, and hybrid materials. As for the unique superiority of each strategy, this review focuses on the advantages of postsynthetic functionalization for preparing well-defined porous structures and addresses the ongoing efforts to establish function-oriented design methods for PAF products. Because of the amount of work that has been performed in this field, this article only builds upon representative works published after 2015.

**PAF-1 as a Platform.** A high surface area is a fascinating characteristic for porous materials that will provide accessible space for guest molecule storage. However, it is difficult to challenge the conventional routine for the construction of high porosity. Inspired by the study of PAF-1, our group designed and synthesized two PAF materials, named PAF-100 and PAF-101, via a strategy of engineering specific building units. PAF-100 and PAF-101 present high BET surface areas exceeding 5000 m² g⁻¹ together with uniform pore size distributions (Figure 4). PAF-100 and PAF-101 rendered high methane uptake values of 742 and 622 cm³ g⁻¹, respectively, at 298 K and 70 bar. A similar concept was investigated by Prof. Eddaoudi’s group, who implemented a molecular-building-block strategy to isolate three porous frameworks, namely, KPOP-1, KPOP-2, and KPOP-3 (KPOP = KAUST’s POP). KPOP-1 and KPOP-2 exhibit high specific BET surface areas (ca. 5120 and 5730 m² g⁻¹) and outstanding gravimetric methane storage properties (0.515 g g⁻¹ at 298 K and 80 bar).

Renowned for its ultrahigh surface area, PAF-1 demonstrates outstanding molecular adsorption capacities. Its periodic aromatic components constructed through covalent bonds possess high physicochemical stability even under extreme conditions (strong acid/base or organic solvent systems). Some attempts at postsynthetic functionalization, such as optimization of the pore sizes and modification of the existing constituents, have been exploited to improve the capabilities of this material.

Incorporating diarylethene (DArE) into PAF-1 modulates its channel environment to afford a new type of photodynamic material (DArE@PAF-1), as shown in Figure 5. The successful inclusion of DArE in the PAF framework was indicated by a reduction in the pore surface and pore size...
As a result of the confinement effect, the PAF-1 cavity provides a sterically hindered environment and inhibits the photocyclization of DArE molecules through aromatic stacking and H-bonding interactions. The photoswitching of DArE@PAF-1 enhances the binding affinity between DArE and CO$_2$, which triggers carbon capture and release. In addition, during the formation of a parallel $\sigma$-DArE conformer, the competition of DArE and CO$_2$ with PAF-1 weakens the intermolecular interactions between the adsorption sites and CO$_2$ molecules, resulting in the instantaneous CO$_2$ release. The modulation of the photoresponse in porous skeletons offers an advantageous route for the capture and release of gas molecules.

PAFs combine the substantial merits of inorganic materials and inorganic−organic hybrids, giving rise to a tunable pore environment and physicochemical stability. Their open pores are accessible to various functional groups or molecular assemblies for further decoration. The considerable stability and readily modified chemistry motivate the introduction of various desired chemical functionalities in a facile and dense manner. Upon postsynthetic functionalization, the phenyl skeletons of PAFs can be densely functionalized to allow advanced applications.\(^{78,82}\)

Hyperaccumulation of copper, an essential nutrient for life, in organisms is a sign of Wilson’s and Menkes diseases and other various neurodegenerative diseases. To create simple, selective, and sensitive diagnostic tools for copper monitoring, Profs. Long and Chang synthesized a robust three-dimensional PAF-1 that was densely functionalized with thioether groups (PAF-1−SMe).\(^{100}\) This material was able to selectively capture and concentrate copper ions from biological fluids and tissues (Figure 6). When combined with 8-hydroxyquinoline as a colorimetric indicator, PAF-1−SMe can be used in a noninvasive diagnostic technique to identify aberrant copper levels in urine or serum. Significantly, this work reveals a starting point to adopt functionalized porous materials for compatible, facile, and targeted diagnostic applications.

**Figure 5.** PAF-1 loaded with the diarylethene dye $\sigma$-DArE will release the adsorbed CO$_2$ under visible light (a). The reversible cyclization reaction of the dye (b). Reprinted with permission from ref 99. Copyright 2015, Wiley-VCH.

**Figure 6.** PAF-1−SMe as a selective capture material for copper detection. Reprinted with permission from ref 100. Copyright 2016, American Chemical Society.
Endowed with rapid kinetics and water/chemical stability, PAF-1 has also been utilized to address the energy demand associated with extracting uranium from seawater. PAF-1 was surface functionalized with poly(acrylonitrile) through atom-transfer radical polymerization. After conditioning with potassium hydroxide (KOH), the poly(acrylonitrile)-functionalized PAF-1 revealed a maximum capacity of 4.81 mg g\(^{-1}\) after 42 days of contact with the uranium-spiked seawater. Similarly, Prof. Ma functionalized a PAF-1 skeleton with noted uranyl-chelating amidoxime groups to obtain a PAF-1\(\text{CH}_2\text{AO}\) for uranium extraction from water (Figure 7). After PAF-1 was grafted, the resultant PAF-1\(\text{CH}_2\text{AO}\) exhibited a high uranium uptake capacity of 300 mg g\(^{-1}\) and a rapid enrichment speed (i.e., the uranium concentration decreased from 4.1 ppm to 1.0 ppb within 90 min). Postsynthetic functionalization of PAF-1 to obtain materials with enhanced capacities for guest molecules demonstrates a task-specific design strategy for the development of functional porous materials for advanced applications.

**PAF-11-Derived Functional Materials.** PAF-11 was polymerized through a facile Suzuki coupling reaction by using tetrakis(4-bromophenyl)methane (TBPM) and diboron acid as building units. The easily modified monomers and readily manipulated synthetic procedure allow dramatic structural transformations and the incorporation of different functional groups into porous materials to achieve isolated and stable functional sites for practical applications.

Previous investigations on porous aromatic frameworks modified with Bronsted acid groups manifest clear merits, such as indefinite stability in strong acids and bases, allowing for multiple adsorption/stripping cycles for ammonia capture. Because phenyl constituents in domain positions are suitable for targeted surface functionalization, Prof. Long presented a densely functionalized PAF structure with carboxylic groups, BPP-7 (Berkeley Porous Polymer-7). As a result of the appropriately sized binding pocket and dense carboxylic acid groups, BPP-7 displays stronger binding affinities for neodymium than strontium ions (Figure 8) and also exhibits excellent metal loading capacities, high adsorption selectivities, and desirable recyclability.

PAF-11 possesses hierarchical pore size distributions, and its mesopores can accommodate diverse organocatalysts for various reaction substrates. An amine-tagged PAF (PAF70–NH\(_2\)) can covalently immobilize large organocatalysts inside its mesopores to create the thiourea-containing PAF resultant PAF70–thiourea, which catalyzes N-bromosuccinimide (NBS)-mediated oxidation of alcohols and shows a higher catalytic activity than that of the homogeneous catalyst. Our group then adopted mesoporous PAF70–NH\(_2\) as a support to develop a palladium (Pd)-based molecular catalyst (PAF70-Pd). The unique porous skeleton of PAF allows an ultrahigh Pd content, and thus, PAF70-Pd has extremely high catalytic activity in Suzuki–Miyaura coupling reactions (Figure 9). The modified PAF solid manifests a perfect example of using PAF as an authentic scaffold for heterogeneous organocatalysis.

As a result of their facile preparation, good activity, and benign stability, bimetallic Ni–W and Ni–Mo sulﬁdes were ﬁxed on a PAF platform by decomposition of \([\text{(n-Bu)}_4\text{N}]_2[\text{Ni–(MeS}_4\text{)}_2\text{] (Me = W, Mo)}\) complexes to serve as sulﬁde catalysts. The activities of PAF catalysts have been investigated using naphthalene as a model substrate, and these catalysts show the highest reported naphthalene conversion rates in hydrogenation and can catalyze hydrocracking of naphthalene. Moreover, PAF supports can be extended to bifunctional catalysis systems that mediate multiple reactions in a single reaction platform. A rhodium complex and a pyrrolidine were combined to a PAF structure based on tetraphenyladamantane and tetraphenylmethane subunits (Figure 10). The new PAF compound catalyzes tandem Knoevenagel condensation and oleﬁn hydrogenation reactions. The obtained bifunctional PAF exhibits high activity.
and excellent stability in cascade reactions, and it can be recycled more than 10 times in a production process.

SUMMARY AND PERSPECTIVE

This Outlook summarizes the considerable progress in the construction of functional PAFs by postsynthetic functionalization techniques. In summary, several strategies allow rational design of PAFs aimed at specific applications. First, a high conversion degree of the coupling reaction and high purity of raw materials are essential to achieve a high polymerization degree and yield and large surface area of organic porous materials. A porous framework with a high surface area is a desirable scaffold, because it has a large amount of free space to accommodate guest molecules, facilitating condensation of active species packed inside pores. Second, the incorporation of units with optical, thermodynamic, or kinetic properties and precise shapes and sizes will afford porous skeletons with inherently high capacities. Therefore, some well-designed building blocks can be exploited for the unique features. Finally, easily modified constituents in open pores are advantageous for decorating PAFs with complementary functional groups to obtain advanced activities. After
postsynthetic functionalization, the hybrid skeleton with heteroatoms, nanoparticles, ionic groups, or chiral fragments will render multivariate behaviors in catalysis, energy conversions, and removal of contaminants.

In addition to their widely investigated applications, including molecular storage, gas separation, and catalysis, PAFs with tailorable compositions, structure, and pore environments can serve as advanced platforms for other far-reaching applications such as removal of pollutants and extraction of precious metals from an aquatic environment and catalysis under extreme (strong acid/alkali/oxidant) conditions. Moreover, the excellent stability and compatibility of PAFs lead to a great ease of operation and flexibility for large-scale coatings, films, and membranes in an antibiotic device, gas separation, nuclear material capture, and nuclear waste remediation applications. Further, efforts should be directed toward the scalable preparation of PAFs using mild and low-cost methods for industrial mass production.

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**Notes**
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