Exploration of Advanced Porous Organic Polymers as a Platform for Biomimetic Catalysis and Molecular Recognition

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Exploration of Advanced Porous Organic Polymers as a Platform for Biomimetic Catalysis and Molecular Recognition

Pengcheng Zhang,[a] Sai Wang,[b,c] Shengqian Ma,[c] Feng-Shou Xiao,[b] Q. Sun*[a]

Nature has long been a dominant source of inspiration in the area of chemistry, serving as prototypes for the design of materials with proficient performance. In this Featured Article, we present our efforts to explore porous organic polymers (POPs) as a platform for the construction of biomimetic materials to enable new technologies to achieve efficient conversions and molecular recognition. For each aspect, we first present the chemical basis of nature, followed by depicting the principles and design strategies involved for functionalizing POPs along with a summary of critical requirements for materials, culminating in a demonstration of unique features of POPs. Our endeavours in using POPs to address the fundamental scientific problems related to biomimetic catalysis and adsorption are then illustrated to show their enormous potential and capabilities for applications ranged from concerned catalysis to radionuclide sequestration. To conclude, we present a personal perspective on the challenges and opportunities in this emerging field.

Introduction

Natural selection has resulted in the evolution of numerous processes, materials, and structures optimized for a broad range of functions.[1] The extremely efficient catalysis and molecular recognition by nature has inspired the researchers to imitate it. "Biomimetic chemistry" is a term introduced to describe chemistry, which attempts to utilize the fundamental principles and concepts used in biological systems to improve the artificial system's power.[2] After years of development, the field of biomimetic chemistry has encompassed several subfields that mainly include biomimetic catalysis, biomimetic reaction pathways, bioinspired molecular recognition, and bioinspired self-assembly.[3] Gaining inspiration or applying these design principles has proven to be a unique approach to addressing critical global challenges such as safe water and clean energy. Numerous synthetic biomimetic systems have been developed, including supramolecules,[4] metal-organic frameworks (MOF),[5] and porous organic materials.[6] In this Featured Article, we will present our efforts on biomimetic catalysis and molecular recognition, which generally refer to catalysis or adsorption that mimic certain key features of natural systems using porous organic polymers (POPs).
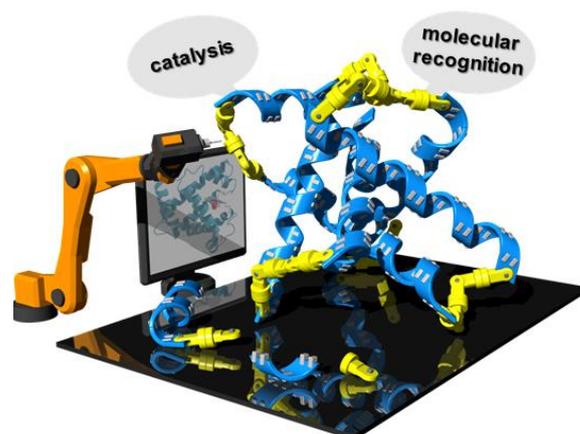
Fig. 1 Exploration of POPs as a platform for biomimetic catalysis and molecular recognition.

POPs are assembled by covalently linking organic molecules into two dimensional (2D) or three dimensional (3D) frameworks, having been leveraged for applications ranging from catalysis and environmental remediation to gas storage and separation.[7] According to the degree of long-range order, POPs can be separated into two categories: amorphous and crystalline, whereby the crystalline POPs are specifically named as covalent organic frameworks (COFs).[8] An endless number of organic struts can be connected *via* the expansive list of organic reactions to afford porous material with limitless structure types. Further tunability in these materials can be achieved by targeting mixed ligand frameworks and post-synthetic modification. The increasingly sophisticated synthetic strategies enable the precise spatial arrangement of chemical functionalities on the porous structures. Moreover, the functional space within the pores of polymers provides ideal

a. College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China.
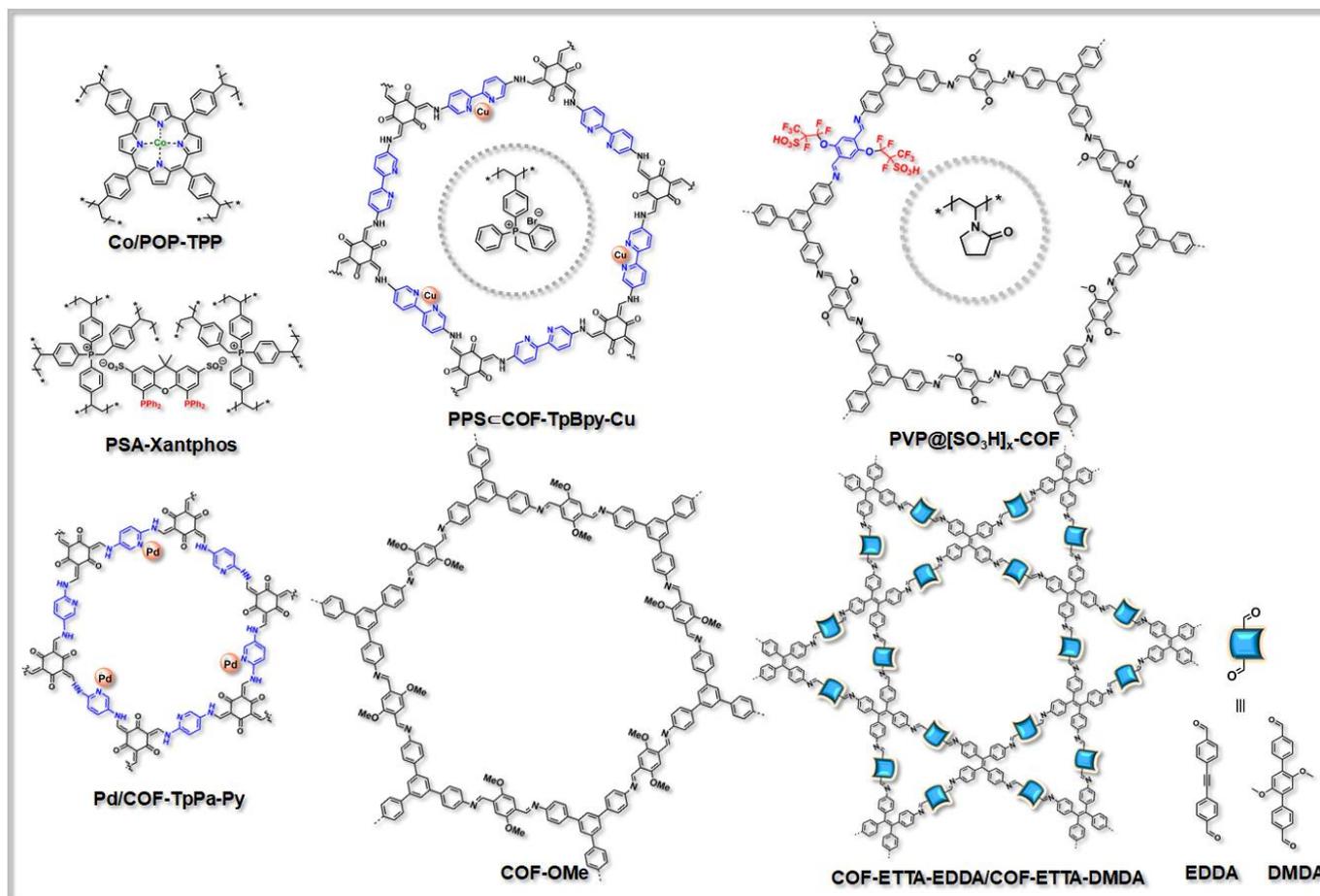b. Key Lab of Applied Chemistry of Zhejiang Province, Zhejiang University, Hangzhou, 310028, China.
c. Department of Chemistry, University of North Texas, 1508 W Mulberry St Denton, TX 76201, United States.
* Email: sunqichs@zju.edu.cn

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Fig. 2 Chemical structures of biomimetic POP-based catalysts mentioned in this Featured Article.

environment for hosting catalytic components, further diversifying the catalyst design. The tunable porous structure facilitates the mass transfer and adds new properties to the functionalities such as adjustable wettability. These attributes have allowed them to be used as an attractive platform for biomimetic material design. With the advent of POPs, great improvements have been made, as this type of materials simultaneously addresses the lack of designability of conventional materials, such as activated carbon, and the chemical stability issues that some advanced materials face, such as MOFs.

We have been working on exploring POPs for biomimetic catalysis and molecular recognition over the past several years (Fig. 1). In constructing biomimetic catalysis, we have focused on the enzyme mimicry, including cofactor, scaffold, reaction pathway, and reaction environment, on the POPs, as well as the cell mimics of the utilization of POPs for hosting enzymes to facilitate efficient catalysis. In an attempt to imitate some of the factors involved in biologic molecular recognition, we have

developed several strategies, such as employing the second-sphere interactions to reinforce the primary binding, enforcing the orientation of the ligands in the materials to improve their cooperation and, thus, the binding affinity, and increasing the flexibility of the functionalities to facilitate the formation of polydentate complexes. This Featured Article summarizes our progress on the design of biomimetic POPs for catalysis and molecular recognition.

Porous Organic Polymers as a Platform for Biomimetic Catalysis

Enzymes confer exquisite efficiency and selectivity to reactions by highly selective binding and activation of multiple components.[9] The unique ability of enzymes to facilitate chemical transformations has long been of interest to researchers. In this section, we exemplify our efforts in engineering the POPs for biomimetic catalysis (Fig. 2).

1. Cofactor mimics

A cofactor is a substance that increases the rate of enzymatic catalysis. Cofactor mimics encompass most of the current activities in biomimetic catalysis.[10] Porphyrins and their metalloderivatives are enzyme cofactors found ubiquitously throughout the natural world in all domains of life (Fig. 3).[11] Porphyrin-containing proteins are involved in plentiful central cellular processes, being referred to as the "pigments of life". For example, chlorophyll, a reduced magnesium porphyrin, is vital for photosynthesis to sustain life. Given their unique roles in light-harvesting and energy and electron transfers, porphyrin-based molecules have been extensively explored to mimic natural biological systems. Based on these efficient natural active species, many artificial porphyrin-based catalytic systems have been developed. However, molecular porphyrins are inclined to form catalytically inactive dimers, thereby showing much lower efficiency in comparison with their counterparts in nature. This concern can be effectively addressed via the incorporation of metalloporphyrin moieties into rigid porous solid materials resulting in the site isolation.[12]
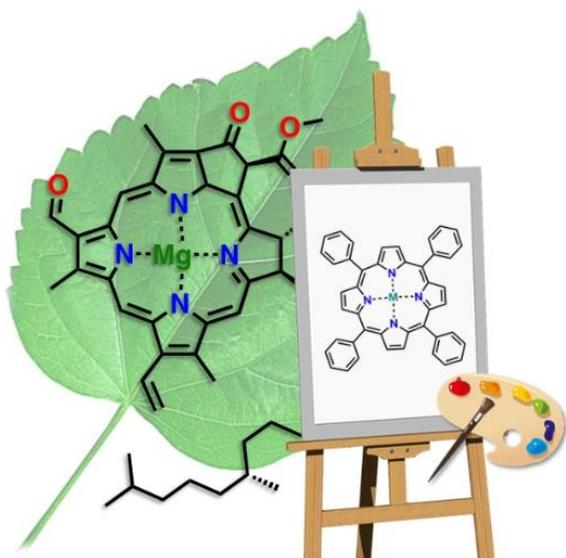

Fig. 3 Chemical structure of porphyrin of chlorophyll mimics.

Considering that extensive attention has been placed on the materials' development for the transformation of CO_2 into value-added products and that porphyrins and their related materials have shown considerable potential in this field,[13] we have constructed a series of metallated porphyrin moieties into porous frameworks and exploited the resulting materials to confer increased activity and stability in transformation process the CO_2.[14] As a representative sample, Co/POP-TPP, which was synthesized by the polymerization of tetrastyrylporphyrin, followed by the metalation of Co species, exhibited excellent performance in terms of activity and recyclability in the cycloaddition of epoxides with CO_2 in ambient conditions with the assistance of tetrabutylammonium bromide (n-Bu$_4$NBr). A wide array of electronically and structurally diverse epoxides can be converted efficiently at a reactant-to-catalyst molar ratio of around 2000, placing them among the top in the reported systems. Due to the site isolation of the porphyrin moieties in

Co/POP-TPP, which inhibits self-quenching, this material can be recycled for at least 18 times with negligible loss in activity. To further demonstrate the utility of Co/POP-TPP under practical conditions, flue gas which contains approximately 15% CO_2 at a total pressure of around 1 bar, was used as a source of CO_2. Co/POP-TPP afforded an epichlorohydrin conversion of 45.4% with a carbonate product selectivity of 88.7% after 48 hours, outperforming its homogeneous counterpart, which afforded the corresponding values of 37.4% and 81.0%, respectively, thus underscoring the great potential of Co/POP-TPP for CO_2 transformations.

2. Mimetic scaffold
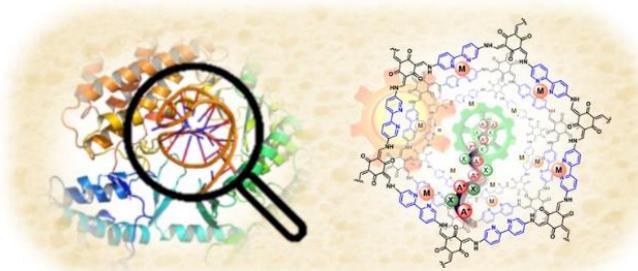
Fig. 4 Concept illustration of mimetic scaffold by the insertion of ionic linear polymers into a COF bearing Lewis acid, which enables heterogeneous concert catalysis.

Numerous proteins display functional promiscuity by the seamless integration of multiple partners, whereby, flexible loops surrounding the active sites play an essential role in substrate and cofactor organization in the catalysis, allowing for the cooperation of various functionalities.[15] The combination of multiple catalytically relevant elements into a single material has intrigued a great deal of interest. However, it remains a tremendous challenge to mimic the functional features of the secondary structures of enzymes, as, in the artificial system, these components are usually spatially isolated within rigid frameworks. Therefore, our strategy to improve the cooperation of various catalytic elements in POPs was underpinned by the impartment of flexibility onto the immobilized catalytic elements (Fig. 4). Considering the conformational variability and dynamism of linear polymeric chains, we took this advantage and proposed a valid strategy that was accomplished by host-guest assembly *i.e.*, the infiltration of catalytically active linear polymers in a porous solid catalyst to enable heterogeneous concerted catalysis. To achieve catalysis, composite materials bearing two catalytically active species (PPS⊂COF-TpBpy-Cu) were synthesized from the in-situ polymerization of linear ionic polymers with Br⁻ counter ions in a COF with Lewis acid sites.[16] The flexibility of the linear polymers enables two types of active sites to be proximate, facilitating the double-activation process. The high porosity and open one-dimensional pore channel of the resulting composite enable ready access of the reactants to the active sites. In the cycloaddition of the epoxides and CO_2, the composite's catalytic efficiency was enhanced for all substrates, with a notable 20-fold increase in activity towards carbonate product compared to single ones. Kinetic studies revealed that the cooperativity in the composites resulted in much lower activation energy than the physical mixtures of catalytic components in the fixation of CO_2.[17] The locally enriched concentration of the

catalytic species in the resulting composite catalysts led to a higher utilization efficiency, outperforming the benchmark catalytic system of the combination of the molecular ionic salt and the COF catalyst. To fully comprehend the flexibility of the linear polymers in catalysis, they were cross-linked, which led to a significant decrease in activity, indicating the flexibility matter. More significantly, the composite is robust and can be repeated used for at least ten cycles. These findings described the basis for a new design concept for achieving cooperation catalysis. Given that the involved strategy for targeting the composites is simple and effective, it will promote the development of materials for numerous applications.

3. Cascade catalysis
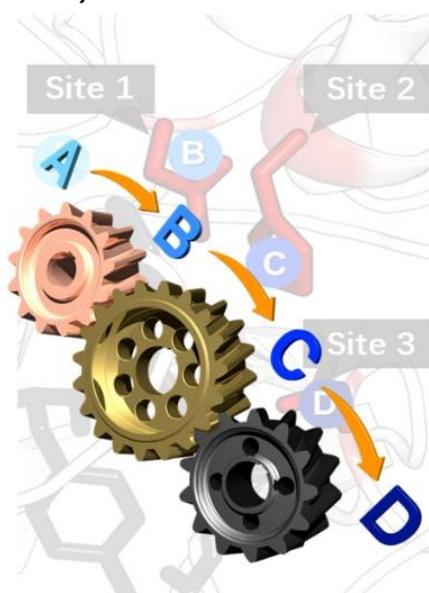
Fig. 5 Schematic illustration of cascade transformations, which are frequently adopted by nature.

Nature utilizes multicomponent catalytic systems to convert simple starting molecules into complex materials, during which the multistep reaction cascades of cellular metabolism are highly coordinated. The concept of cascade transformation was developed to mimic nature, referring to processes that combine various chemical steps in one pot without isolating the intermediates such that the operating time and costs, as well as the consumption of auxiliary chemicals and energy, can be drastically reduced (Fig. 5).[18] With these advantages, the design of catalytic cascade systems is at the forefront of synthetic chemistry. Proper spatial distribution of active sites is necessary for achieving an efficient cascade formulation. The unique architectures and tunability of 2D COFs, which allow the spatial arrangement of the functionalities being precisely managed, are expected to act as an ideal platform for the combination of multiple catalytic relevant elements to bring into effect the cascade catalysis. By virtue of the versatile catalytically related property of pyridine, which could serve as a nitrogen donor to incorporate metal species and a base catalyst, a pyridine-based COF (COF-TpPa-Py), synthesized by the condensation of triformylphloroglucinol and 2,5-diaminopyridine, was chosen for this study.[19] After being partially metalled the pyridine moieties in COF-TpPa-Py with

$Pd(OAc)_2$, the resulting bifunctional material, Pd/COF-TpPa-Py, showed high activities in the one-pot cascade synthesis involving Pd-catalyzed aerobic oxidation of alcohols to aldehydes and the subsequent base-catalyzed Knoevenagel condensation. The well-distributed and highly accessible catalytic species in Pd/COF-TpPa-Py are responsible for the observed superior performance. With these unique attributes, the COF-based cascade catalytic system outperformed the corresponding amorphous polymer and homogeneous analogues in terms of turnover frequency, highlighting that COFs give great promise for the design of heterogeneous cascade catalysis.

4. Mimic reaction environment

The catalytic performance of active sites is closely related to the microenvironment where they are situated. In the vast majority of enzymes, the catalytic center is surrounded by protein superstructure (Fig. 6). Non-covalent interactions are involved in most functions of enzymatic catalysis, such as (i) confining the active site, (ii) changing in solvation, and (iii) creating a hydrophobic pocket.[20] Activation of the reagent and stabilization of the intermediates are generally ascribed to the origins of the enhanced catalytic performance. Rather than altering active sites in a way that influences the catalytic elementary steps, the creation of a suitable microenvironment could be leveraged to specifically accomplish the target steps, without sacrificing reactivity elsewhere along the catalytic cycle. In this part, we present our efforts to control the reaction environment in the artificial catalysts, illuminating the development of genuinely competitive artificial enzymes.
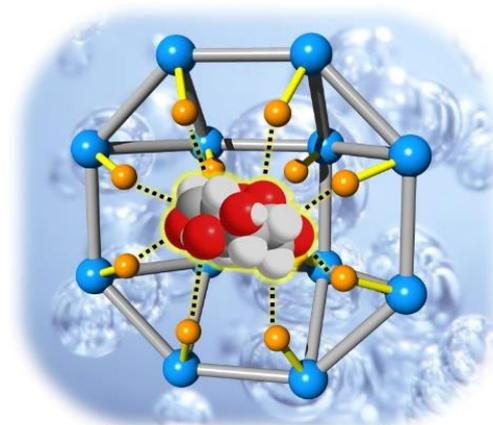
Fig. 6 Concept illustration of the biomimetic reaction environment, where the catalytic performance of the active sites could be regulated by the non-covalent interactions provided by the confined space.

(i) Confining the active site. The advent of supramolecular assemblies allows the performance of the encapsulated catalytically active species to be tuned by rational assembly host design.[4] However, it remains a remarkable challenge to precisely manipulate the outer-sphere environment around the catalytic centers in heterogeneous catalysts. By virtue of the well-defined confined environment of supramolecular assemblies, we advanced a new type of heterogeneous reaction vessel constructed by the supramolecular

ion pairs.[21] Using a cationic template equipped with polymerizable vinyl groups [(4-vinyl-benzyl)-tris-(4-vinyl-phenyl)-phosphonium chloride], a variety of anionic ligands (triphenylphosphine, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene, and 1,10-phenanthroline) can be confined in the resulting supramolecular assemblies, which were further polymerized to afford the corresponding porous frameworks named as PSA-PPh₃, PSA-Xantphos, and PSA-Phen, respectively. The created confined microenvironment, featuring hydrophilic ionic outer-sphere and hydrophobic ligand pocket, facilitates the enrichment of the substrate near the active sites, thus giving rise to superior activity and selectivity in the industrially relevant hydroformylation reaction, far outperforming the non-encapsulated complex.[22] In detail, in the hydroformylation of 1-octene, an aldehyde selectivity up to 98% was achieved with a linear to branched product ratio of 39 in the presence of Rh metallated PSA-Xantphos. Additionally, the assembly structures are stable during the reaction, as evidenced by the fact that the catalysts can be repeatedly used with maintained performance. These results collectively represent a way to emulate the enzyme to impart additional properties on the heterogeneous catalysts beyond current techniques. Given that the assembly catalyst system is readily tunable, this will stimulate new nano-objects with interesting catalytic properties.

(ii) Changing in solvation. Numerous research results suggest that the H_2O molecules and other polar residues are optimally organized to achieve stable transition states in the enzymatic catalysis, and consequently, the reaction efficiency.[23] Regarding the synthetic catalytic systems, it has long been known that the outcomes of chemical transformations are highly dependent on the solvation environment, and solvents are commonly used to control the reaction outcomes. Numerous catalytic transformations show superb results, being carried out in polar aprotic solvents, such as ionic liquids and dimethyl sulfoxide (DMSO). However, product isolation from these solvents is exceptionally complicated, usually accompanied by side reactions.[24] To tackle this challenge, the development of separation-friendly alternatives that could mimic the desired solvation environment to aid the accomplishment of those transformations is highly sought after. However, the transformation from the liquid phase to the solid-state realm remains a great challenge. It necessitates the precise control of the spatial distribution and dynamic interactions between the involved partners. We postulated that the development of POPs might provide a possible solution. The flexibility and tunability of polymer chains can offer a solvent-like reaction environment, wherein the catalytic sites could be readily incorporated in a designated way. To implement this strategy, we first equipped the solvent moieties (NMP, DMSO, and imidazolium-type ionic liquid) with vinyl groups for the potential construction of porous frameworks, with the yielded porous solid solvents (PSSs) named as PSS-NMP, PSS-DMSO, and PSS-IL, respectively.[25] Given the densely populated solvent moieties in the 3D nano space of PSSs, we envisioned that the solvation effect could be maintained in their solid state. To validate this hypothesis, we tested their ability to break the hydrogen-bonding network present in fructose crystals, as the hydrogen bond acceptors on these polymers are expected to coordinate with the hydroxyl group on fructose, reminiscent of that seen in dissolving. To do so, we mixed the PSSs with fructose and mechanical ground to

facilitate their interaction. The XRD peaks associated with fructose disappeared entirely in the resulting composites, indicating that the polymeric solvents retained the solvation effect of their liquid analogues. For the sake of imparting catalytic ability, monomer-bearing sulfonic-acid groups were incorporated *via* the co-polymerization of the vinyl-functionalized solvent monomers and the sodium *p*-styrene sulfonate in a specific ratio, followed by ion-exchange with 1 M HCl, yielding PSS-*x*IL-SO₃H. To test their catalytic efficiency, we evaluated their performance in the dehydration of fructose to produce 5-hydroxymethylfurfural (HMF). Encouragingly, these materials exhibited exceptional performance even when using THF as a readily separable reaction medium, giving rise to the HMF yield of 98.8%, which significantly exceeded the traditional acid catalytic system and was comparable to those operated in DMSO or ionic liquids. Therefore, we concluded that the densely populated solvent moieties around the acid sites could create a desired solvation environment in the confined nano space, leading to satisfied catalytic performance.

Nonetheless, the synthesis of the vinyl-functionalized solvent moieties is cumbersome, which significantly impedes their wide application. To circumvent this challenge, we proposed an alternative strategy, *i.e.,* the infiltration of the desired polymeric solvent analogues close to the active sites in porous catalytically active materials.[26] Considering that linear polymers are easy-to-get, this strategy dramatically simplifies the catalytic materials' synthetic procedure. By leveraging the benefits of both molecular and solid materials, the linear polymers confined in the pore channels enable them to create a solvation environment for the active sites anchored on the COF pore walls while providing the additional benefit of recyclability. To demonstrate the proof-of-concept, composite materials of sulfonic acid functionalized COFs and polyvinyl pyrrolidone linear polymers (PVP@[SO₃H]ₓ-COF) were synthesized to evaluate their performance in the aforementioned dehydration of fructose to yield HMF. Also, the resulting catalysts afforded HMF as the single product with nearly full conversion, placing them among the top systems reported thus far. Given the tunability, this strategy might provide a powerful toolbox for the design of efficient and green chemical processes.

(iii) Creating a hydrophobic pocket. Hydrophobic effects positively affect the enzymatic reaction by creating a reaction pocket where the hydrophobic substrates could be accumulated nearby the active sites and/or the reaction equilibrium could be broken by excluding the hydrophilic product, such as water, away from the catalytic pocket. Researchers have developed various hydrophobic cavities to mimic enzymes' remarkable abilities to achieve efficient chemical conversions. Additionally, increasing the hydrophobicity of solid materials represents a promising solution to combat failure associated with water absorptivity.[27] One issue that impedes the practical applications of plenty of efficient catalytic systems is their durability. Numerous efficient catalytic systems suffer from the inherent hydrolysis liabilities, and on various occasions, it is impossible to exclude the water from the systems entirely due to it being a common by-product in a wide range of reactions. To address these concerns, we demonstrated an effective strategy for stabilizing water-sensitive ligands through the construction of superhydrophobic

polymers. This was realized by the introduction of hierarchical porosities during polymerization processes.[28] We chose phosphite ligands to demonstrate this strategy, as they have proven to be efficient for various reactions, and the P-O bonds are inclined to hydrolyze. Through careful modification of the polymerization conditions, the vinyl-functionalized phosphite monomers were successfully transformed into a hierarchically porous structure (phosphite-POP), which renders them with superhydrophobicity, thus improving water resistance. After metalation, the resulting superhydrophobic porous catalyst exhibited significantly increased durability in the hydroformylation of internal olefins compared with the corresponding homogeneous analogues. In addition to being inhibited from entering into the reaction pocket, the water molecules generated in-situ within the scaffold can be effectively repelled, as demonstrated in the Pd-catalyzed dehydrative allylation. As such, the Pd metallated phosphite polymer remained active for at least 40 h, whereas the corresponding homogeneous analogues was deactivated within 8 h. Furthermore, due to the enrichment of the nonpolar reactants within the hydrophobic nanopores, the polymeric phosphite ligands showed an accelerated reaction rate compared to the homogeneous counterpart. Moreover, this strategy is generally applicable, which can be readily extended to other phosphite ligands with improved durability. Our work thus opens a new perspective to enhance the catalysts' water-resistance and activity simultaneously.

5. Cell mimics
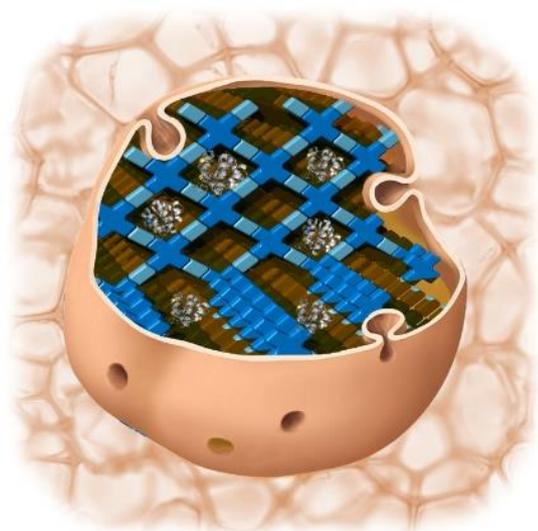
Fig. 7 Concept illustration of the COFs as cell mimics for hosting enzymes.

Due to the challenges associated with the operating range and durability, cell-free enzymes have not found wide use in industrial settings. To tackle these concerns, association enzymes with solid supports give a great promise.[29] We showed that COFs possess the right features relevant for hosting enzymes, namely tunability, porosity, crystallinity, and stability (Fig. 7).[30] With the tailorable composition, their pore environments can be readily regulated to favor specific interactions between COFs and enzymes to achieve the optimal reaction outcomes. The continuous and confined open channels could afford a high accessible interface surface area for the enzyme hosting while inhibiting their aggregation. With these merits, the COFs provided a higher affinity for the enzyme loading and a preferential microenvironment that offered orders-of-magnitude higher catalytic activities than that of using other types of porous hosts, silica and MOFs, as demonstrated in the kinetic resolution of racemic 1-phenylethanol with vinyl acetate. The COF-based biocomposites (lipase@COF-OMe) also exhibited superior performance compared to the composites made from their amorphous analogues, thus, underscoring the critical role of long-range order porous structures. In addition to the enhanced activity, it is shown that the resistance of enzymes towards various solvent/temperature conditions could be significantly improved after being infiltrated in the COFs, indicative of the enormous potential of the COFs for enzyme immobilization.

Given the divergent reaction's outcomes after associating the enzyme with various materials, fundamental elucidation of the role of the host's pore chemistry on the resulting composites' performance is critical for achieving more efficient formulations. However, it remains a significant challenge to establish the correction between the degree of freedom of the enzyme with the varied pore chemistry of the host materials. We showed that the combination of innovative technology of site-directed spin-labelling-electron paramagnetic resonance spectroscopy (SDSL-EPR) with the COF materials provides a powerful route to establishing such a structure-performance relationship.[31] By designing a set of isoreticular COFs with continuously varying levels of wettability, we revealed that increasing the host material's hydrophilicity results in more constrained conformations of lysozyme and decreased activity. We also demonstrated that the hydrophilic elements on the struts could be directly translated into the interaction between the resulting COF and the enzyme and that the extent of this effect is proportional to the density of the installed hydrophilic moieties. These findings suggest that altering the hydrophilicity of the host material provides a way to manipulate the performance of the resulting biocomposites.

The examples mentioned above demonstrated that the performance of the enzymes could be sophisticatedly optimized by regulating the wettability of isostructural 2D COFs, giving rise to orders of magnitude higher catalytic activities in comparison with the free enzymes. However, there is plenty of headroom when the following concerns are considered. The long reactants' transportation path results in the infiltrated enzymes being partly buried in the interior, which inevitably leads to the insufficient utilization of the enzymes. To alleviate such transport limitations, we designed two hydrophobic COF materials (COF-ETTA-EDDA and COF-ETTA-DMDA) with hierarchical pore structures, whereby the big pores are used for the immobilization of enzyme molecules, and the small pores are used explicitly for the acceleration of mass transfer,[32] such that, enzymes infiltrated in dual-pore COFs exhibited superior reactant accessibility and higher utilization efficiency, as well as more excellent resistance to denaturant than does that immobilized in COFs with single pore structures. Detailed kinetic evaluations reveal that pore heterogeneity facilitates the mass
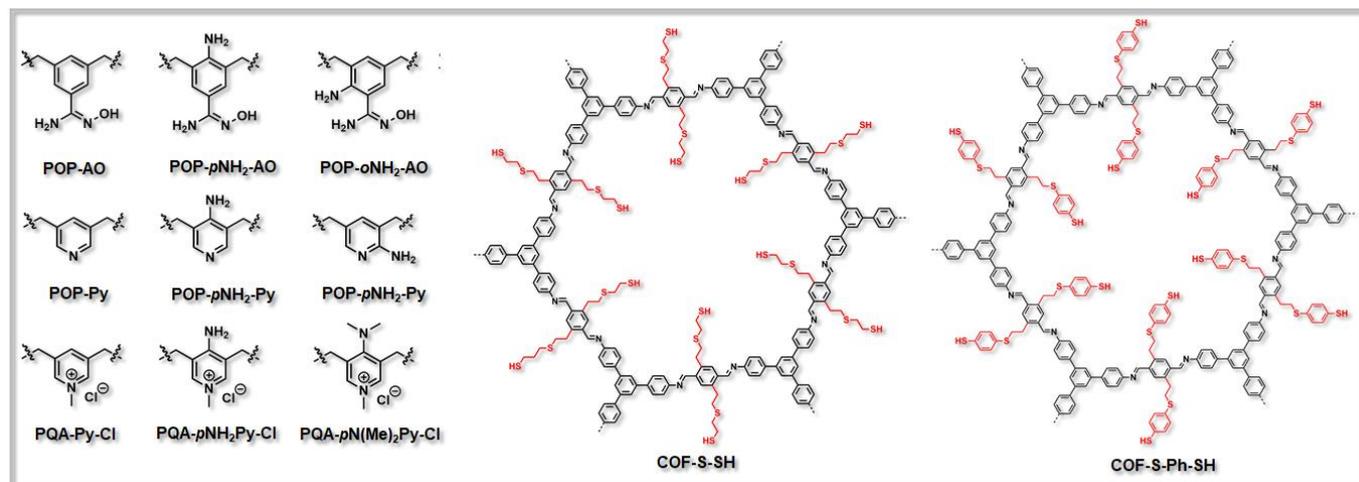
Fig. 8 Chemical structures of biomimetic POP-based adsorbents mentioned in this Featured Article.

transfer during the reaction, leading to rate enhancements of up to a three times per-enzyme molecule. Also, it was found that the enzyme associated with the dual-pore COFs was more tolerant towards a detrimental by-product of glycerol in the transesterification of triacylglycerides to fatty acid ethyl esters. The unparalleled versatility of COFs allows many aspects to be customized designed, lending credence to their prospect as next-generation host materials for enzymes.

## Porous Organic Polymers as a Platform for Biomimetic Molecular Recognition

Nature has produced strategies to recognize target ions with high selectivity over millennia of evolution.[33] Chemists have looked up to nature for the design of more efficient and selective adsorbents to enable challenging extraction. From the perspective of chemistry, general principles involved in nature to enhance the binding affinity include providing secondary sphere interactions to the distal sites off of the metal centers to enforce a correct geometry and exert charge stabilization, and preorganization of the binding sites to facilitate the cooperation.[33a] To use these concepts, our design strategies involved to achieve high-performance POPs include: introducing the hydrogen bond donors to reinforce the primary binding, enforcing the orientation of the binding sites to increase their accessibility and cooperation, and increasing the flexibility of the chelator to facilitate the formation of polydentate complexes. Prompted by the increased necessity of protecting freshwater supplies and deficiency of precious metal, the following section will present our progress in the deployment of POPs for radionuclide sequestration, heavy metal decontamination, and platinum group elements recovery, and unparalleled efficiency has been achieved by judicial implantation of the concepts mentioned above (Fig. 8).

The chemical toxicity and radioactivity of uranium pose severe environmental risks. In addition, the uranium deficiency in geological deposits provokes mining uranium from seawater,

the largest known resource, to safeguard the sustainable development of nuclear energy. Accomplishing these tasks requires the development of technology that can extract uranium economically and efficiently.[34] In order to enhance the affinity of chelators towards uranium, we were inspired by nature, in which the performance of the binding sites can be greatly boosted by the hydrogen bonding interaction contributed by the surrounding amino acid residues in the protein scaffold (Fig. 9). We postulated that the affinity of binding sites towards uranyl ions could be increased by incorporating a hydrogen bond donor orientated in a suitable position. Indeed, improvements in uranium capture with the sorbents bearing amidoxime group are evident with the addition of an amino, which can be further adjusted by their relative positions. The porous framework constructed by 2-aminobenzamidoxime (POP-oNH$_2$-AO) was exceptional in the decontamination of uranium polluted surface water and groundwater.[35] The uranium concentration can be rapidly decreased from 5 ppm to lower than 2 ppb within 5 min, far below the acceptable limit of 30 ppb for potable water set by the US Environmental Protection Agency (EPA). Nearly two and four times longer operation time is required for POP-pNH$_2$-AO and POP-AO (constructed by 4-aminobenzamidoxime and benzamidoxime, respectively) to reduce UO_2^{2+} ion concentrations to a similar level. Moreover, POP-oNH$_2$-AO can effectively extract trace quantities of uranium in seawater, affording an uptake capacity of 4.36 mg g^{-1}, which is three-fold more than the benchmark developed by the Japanese scientist. Collaborative experiments of spectroscopic, crystallographic, and DFT calculation revealed that the superb performance of POP-oNH$_2$-AO mainly stemmed from the fact that the amino group in close proximity to the amidoxime not only provides an additional hydrogen-binding site to enforce uranyl species in a favorable coordination mode but also lowers the overall charge on uranyl.

The efficiency of the strategy prompted us to apply in other system. Recovery tests for platinum group elements showed that incorporating of the amino group in the pyridine-based porous

polymers (POP-*p*NH$_2$-Py and POP-*o*NH$_2$-Py) could increase the nucleophilicity of the pyridine moiety for achieving a higher binding affinity toward Pd species.[36] Furthermore, as revealed by single-crystal results, due to hydrogen bonding between the added amino group and chloride ions coordinated on the Pd species, the amino group in the ortho position relative to the pyridine moiety produced a more robust complex with Pd species compared to its para counterpart, resulting in a higher recovery efficiency.
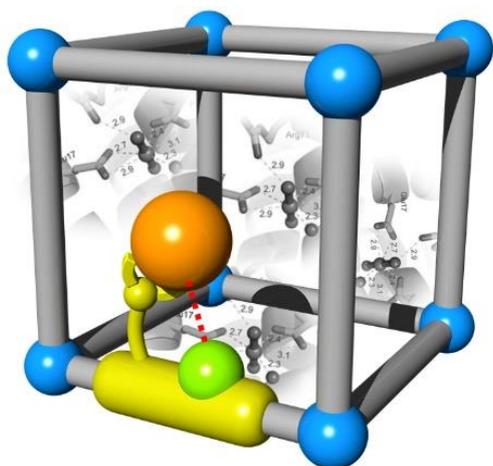

Fig. 9 Concept illustration of the introduction of the secondary sphere interactions to reinforce the primary binding.

To further illustrate the generality, we extended this strategy to the design of ion exchange materials. It was shown that the affinity of pyridinium-based anion nanotraps towards pertechnetate (TcO$_4^-$) could be altered by varying the substituted group on the pyridinium. Regulating the modifier enables the resulting anion nanotraps to possess intrigued properties as ideal TcO$_4^-$ scavengers (PQA-Py-Cl, PQA-*p*NH$_2$Py-Cl, and PQA-*p*N(Me)$_2$Py-Cl), which substantially overcome the tremendous challenge of TcO$_4^-$ removal under extreme conditions of strong irradiation field as well as super acidity and basicity.[37] The best material constructed by 4-(dimethylamino)-1-methylpyridin-1-ium chloride exhibited the highest sorption capacity and unprecedented extraction efficiencies under the conditions relevant to the used fuel reprocessing solution in 3 M nitric acid (97%), as well as legacy nuclear wastes from the Hanford tank wastes (95%) and from the Savannah River Sites (80%). This can be attributable to the fact that the addition of an electron-rich group of dimethylamino facilitates the formation of kinetically labile complexes, which allows for rapid guest exchange. Our insightful studies describe how slight modifications to the binding sites can greatly boost their performance, which could be readily extended to a multitude of applications.

Besides the local chemical environment, materials' pore structures also show great impact on sorption performance. Given the fact that a fraction of grafted chelators were found to be buried in the small and irregular pores and, thus, compromising overall efficiency, we delineated essential advances towards implementing 2D COFs for the construction of sorbent materials. Due to the unique pore structure of this type of material, the chelators are uncovered aligned in periodic arrays on the pore wall, which facilitate to trap ions by accelerating mass transfer and enabling cooperative binding (Fig. 10).

Increased uptake capacity and removal efficiency were observed for adsorbents designed using COF as a platform compared to their amorphous counterparts, as exemplified by uranium extraction. The COF-based sorbent (COF-TpDb-AO) prepared by the condensation of 2,5-diaminobenzonitrile with triformylphloroglucinol, followed by reacting with hydroxylamine outperformed the corresponding amorphous analogues in every aspect such as adsorption kinetics and uptake capacity.[38] More importantly, the convergent orientation of the amidoxime groups on the COF allows their cooperative binding with uranyl ions, unveiling by X-ray absorption fine structure (XAFS) spectroscopy, thus leading to the distribution coefficient value that is one order of magnitude higher than that of the amorphous counterpart.
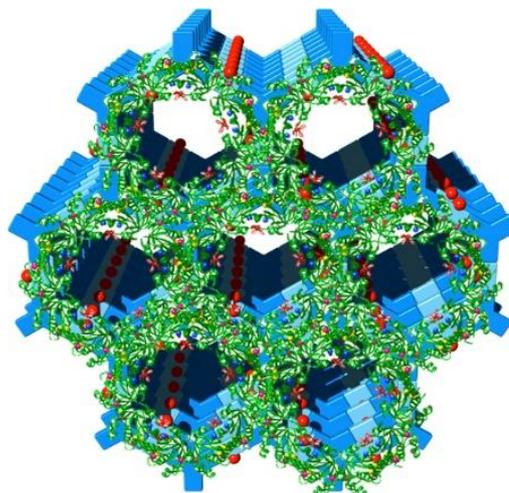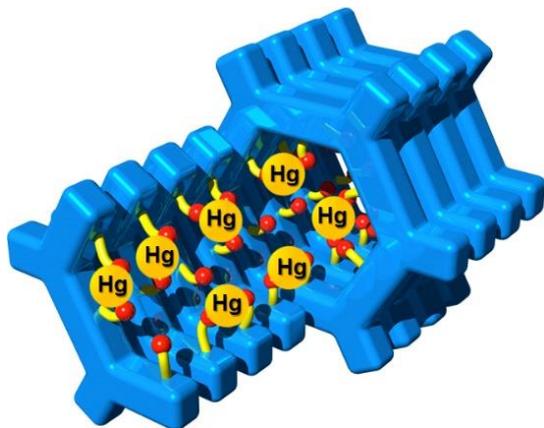

Fig. 10 Schematic illustration of chelating groups in COF materials, which are uncovered aligned in periodic arrays on the pore wall, favorable for ion trap by accelerating mass transfer and enabling cooperative binding.

It is well-known that most of the protein receptors are flexible, promoting the cooperative binding and, consequently, the accompanied efficiency (Fig. 11). Head-to-head comparisons were made with the COF decorated with flexible ligands (COF-S-SH) and rigid chelators (COF-S-Ph-SH) in the decontamination of mercury to gauge the importance of the flexibility of chelating groups for achieving high performance.[39] As expected, COF-S-SH outperformed COF-S-Ph-SH in both mercury removal kinetics and efficiency. In detail, the remaining mercury concentration after COF-S-SH treatment is under the detect limitation of inductively coupled plasma mass spectrometry (ICP-MS, 0.1 ppb), which is at least 10-fold lower than that treated by COF-S-Ph-SH (1.3 ppb). Given the similar compositions of COF-S-SH and COF-S-Ph-SH, their significant disparity in removal efficiency can be attributed to the different chelator properties. The flexible chelating arms in COF-S-SH allow metal ions to adopt a stable conformation by changing their conformations and, thus, the binding affinity. XAFS spectra confirmed that in COF-S-SH, each Hg was bound exclusively by two S, while only 78% of Hg species were bonded with two S atoms, rendering COF-S-SH with an unprecedentedly high binding affinity towards mercury. In addition to this, COF-S-SH also showed higher adsorption capacities than COF-S-Ph-SH, affording a saturation of Hg^{2+} ions and Hg^0 vapor uptake capacity of 1350 mg g^{-1} and 863 mg

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g^{-1}, respectively, which surpassed by far all of the thiol and thioether-based materials reported.

Challenges and Perspective

As discussed in the examples given above, POPs have been demonstrated to be excellent platforms for catalysis and molecular recognition from different biomimetic approaches, changing specific steps in these processes and, thus, giving rise to new results. One of

Fig. 11 Schematic illustration of increasing the flexibility of chelators for enhancing the cooperative binding and, thus, the binding affinity.

the main advantages observed is the improved stability of the catalytic species after immobilization. The unique scaffold protects them from deactivating pathways such as decomposition after being exposed to organic solvent or water. Furthermore, the provided confined environment and the introduced second-sphere interactions can induce substrate selectivity and binding affinity. Significant advances have been achieved in each aspect reviewed, auguring well for the future application of using POPs as a design platform for biomimetic approaches in solving various challenges encountered in catalysis and adsorption. Although we are just beginning to explore the possibilities in this field, it is clear that POPs give great promise in biomimetic applications, which can sometimes be challenging to achieve by traditional materials. Despite these successes, one hallmark of catalysis by nature in a complex tandem catalytic pathway is less explored: the ability of biomimetic materials to catalyze multistep reactions in one-pot sequences. The cell enables several chemically incompatible reactions to be accomplished in tandem. Such combinations are extremely challenging, necessitating various active species being compatible with each other to be operated under the same conditions with matched reaction rates. To achieve this goal, the understanding of precise operation mode of the biomimetic catalytic system is essential, which, in turn, promotes the development of more sophisticated catalysts. Also, with regard to molecule recognition, almost all of the current design strategy and computational optimization are based on small molecules, the structural properties of the synthesized polymer, however, evidenced to show a remark impact on the binding modes. Consequently, to establish a correct structure-property relationship, more efforts should be

placed on the systematic investigation of the adsorbents' textual parameters on the performance. Apart from these fundamental issues, to satisfy the requirements for real-world applications, the following challenges also need to be tackled. As a must for any future industrial-scale processes, the material synthesis should be cost-effective and straightforward, which remains a challenge for most POPs compared with industrially relevant zeolites and active carbon. In addition, most POPs share the drawback of other porous materials when it comes to shaping and processing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Exploration of Advanced Porous Organic Polymers as a Platform for Biomimetic Catalysis and Molecular Recognition

Pengcheng Zhang,[a] Sai Wang,[b,c] Shengqian Ma,[c] Feng-Shou Xiao,[b] Q. Sun,*[a]

[a] College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China.
[b] Key Lab of Applied Chemistry of Zhejiang Province, Zhejiang University, Hangzhou, 310028, China.
[c] Department of Chemistry, University of North Texas, 1508 W Mulberry St Denton, TX 76201, United States

*E-mail: sunqichs@zju.edu.cn

This Featured Article summarizes our progress on the design of biomimetic POPs for catalysis and molecular recognition with enhanced performance.