Facile one-pot synthesis of porphyrin based porous polymer networks (PPNs) as biomimetic catalysts†

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Stable porphyrin based porous polymer networks, PPN-23 and PPN-24, have been synthesized through a facile one-pot approach by the aromatic substitution reactions of pyrrole and aldehydes. PPN-24(Fe) shows high catalytic efficiency as a biomimetic catalyst in the oxidation reaction of 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) in the presence of $H_2O_2$.

The catalytic activity of metalloporphyrin complexes has been extensively studied since the discovery of the heme-containing enzymes, cytochrome P450.1 Inspired by the porphyrin core as the active site in cytochrome P450, many metalloporphyrin catalysts for hydroxylation, cyclopropanation, olefination, C–H insertion and N–H insertion have been explored.2 Using synthetic systems to mimic natural enzymes with high catalytic activity has been a sought-after goal in the past decade. Direct application of the metalloporphyrin complexes in aqueous solution is usually challenging due to the formation of catalytically inactive dimers in the oxidizing reaction media.3 With this consideration, various methods have been developed to heterogenize metalloporphyrin catalysts, including covalent bond formation, ion-pair formation, encapsulation or immobilization on supports such as zeolites, clays or mesoporous silica.4 However, these methods usually dilute the density of active sites,5 yield unwelcome interactions between the substrate and catalyst, and lead to leaching of the complexes from the substrate.6

As an alternative solution, advanced porous materials have been demonstrated as promising candidates to heterogenize metalloporphyrin because of their tuneable properties, high surface areas and controllable porosity. In the last two decades, metal–organic frameworks (MOFs), a novel category of porous materials, have been extensively investigated in scientific and technological research due to their potential application in many fields, such as gas storage,7 gas separation,8 sensors9 and catalysis.10 Recently, porphyrin derivatives have been introduced into MOFs by either linker modification or encapsulation.10,11 MOFs possess many advantages, such as large surface area, tuneable structures, and feasible platform for post-synthetic modifications. However, most MOFs, constructed with soft Lewis acids (metal ions) and hard Lewis bases (carboxylates), suffer from limited stability, which highly restrained their potential in industry applications. Porous polymer networks (PPNs), hyper-cross linked organic polymers based on covalent-bonds, have provided an alternative way to construct functional porous materials with extremely high chemical and thermal stability.12 Some research has been focused on synthesizing PPN materials with metalloporphyrin active centers utilizing pre-synthesized metalloporphyrin monomers via either C–C cross coupling reactions using a Pd catalyst or condensation with tetra(4-aminophenyl)methane.13 Nevertheless, their synthetic methodologies are usually not scalable due to the complicated synthesis procedure of the monomers and the requirement of expensive metal catalysts for polymerization. Preparation of porphyrinic porous organic polymers (POPs) with 2D planar structure via the bottom-up strategy has been initially reported by Bhaumik et al.14 However, incorporation of a porphyrinic active site into a 3D porous framework through the one-pot facile synthesis was absent thus far.

Herein, we report a facile one-pot synthetic method to produce large scale metalloporphyrin containing porous polymer networks, named PPN-23 and PPN-24 (Fig. 1), of which PPN-24 is the firstly reported 3D porphyrin based PPNs obtained by using this bottom-up synthetic strategy. This unique methodology is based on the extended condensation reaction between pyrrole and aromatic aldehydes including benzene-1,3,5-tri甲醛dehyde15 (PPN-23) and tetrakis(4-formylphenyl)silane16 (PPN-24). This condensation process yields black fluffy PPNs with high porosity, excellent thermal and chemical stability without the requirement of an inert atmosphere or expensive catalysts. Moreover, the synthetic procedure is very cost- and time-efficient and the final material can be easily...
functionalized with various metal ions, such as iron(II), zinc(II), copper(I) and cobalt(II), through an effortless post-synthetic modification reaction. The catalytic activity of PPN-24(Fe) has been demonstrated by catalytic oxidation of 2,2’-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) in the presence of H₂O₂. The catalytic activity of PPN-24(Fe) demonstrates the feasibility of precisely designing stable porous polymer materials to be applied for mimicking heme-based protein applications.

The synthesis was accomplished by treatment of pyrrole with benzene-1,3,5-tricaialdehyde (PPN-23) or tetrakis(4-formylphenyl)silane (PPN-24) in refluxed propionic acid media for 12 hours. Under acidic conditions, aromatic aldehydes were first activated through protonation, followed by electrophilic aromatic substitution of the activated carbon atoms of pyrrole, and further condensation to yield macrocyclic porphyrin building blocks with free aldehyde groups. This condensation process repeats until the completion of polymerization. After the reaction, black fluffy powder was collected, washed and dried to afford PPN-23 and PPN-24. FT-IR was employed to confirm the formation of porphyrin networks (in Fig. S6 and S7, ESI†). The bands corresponding to 1720–1740 cm⁻¹ (C=O stretching) are absent, suggesting that all the aldehyde starting materials have been consumed in the polymerization reaction. The strong bands observed at 3317 cm⁻¹ and 1625 cm⁻¹ (N–H bending) and 1563 cm⁻¹ (N–H stretching) are present, confirming the formation of microporous porphyrin networks. Field-emission scanning electron microscopy (FE-SEM) images show that PPN-23 and PPN-24 are composed of agglomerated sphere-shaped particles with sizes ranging from 1.0 to 3.2 μm in diameters (Fig. 2).

Porosities of these PPNs have been established from the N₂ sorption analysis at 77 K. Evident from Fig. 3, both PPN-23 and PPN-24 exhibit a type I isotherm, typical for microporous solids, where a steep gas uptake at low relative pressure and a mostly flat extrapolation in the intermediate sections of P/P° are observed. N₂ uptakes of 102 cm³ g⁻¹ and 187 cm³ g⁻¹ have been obtained for PPN-23 and PPN-24, respectively. The Brunauer–Emmett–Teller (BET) surface areas for PPN-23 and PPN-24 are 271 m² g⁻¹ and 478 m² g⁻¹, respectively (Langmuir surface areas are 426 m² g⁻¹ and 754 m² g⁻¹, respectively), suggesting permanent porosities of PPN-23 and PPN-24. Density Functional Theory (DFT) pore size distribution analysis based on the N₂ isotherms at 77 K indicates that the pore size of PPN-23 is uniformly distributed at around 13 Å, while PPN-24 is around 10 Å and 11.8 Å (Fig. S4 and S5, ESI†). Even though these materials do not possess a long-range spatial periodicity, the narrowly distributed pore size indicates that they have ordered arrangements in a short range with permanent porosity after activation.

PPN-24 was taken as an example for the stability test. The high thermal stability of PPN-24 was confirmed by thermogravimetric analysis (TGA) measurements (Fig. S8, ESI†). During the departure of the guest molecules below 70 °C, about 10% weight loss was observed. From the phase transition a decomposition temperature of around 320 °C was observed for the fresh sample. Moreover, the chemical stability was tested through treatment with water (Fig. S9, ESI†). After treatment with water for 36 hours, samples were measured by N₂ sorption at 77 K after typical activation procedures. Reduction of the N₂ sorption capacity of less than 15% was observed, suggesting only a slight destruction of the framework during these treatments. The excellent chemical stability can be ascribed to the strong covalent-bond connections, which endow the framework with high stability in aqueous solution. Both the thermal and chemical stabilities of PPN-24 boost their further applications, especially in biomimetic catalysis.
30 mM H$_2$O$_2$, 5.0 mg mL$^{-1}$ PCN-24(Fe) in citrate buffer at room temperature. The increase of the absorbance at 418 nm well demonstrates the biomimetic activity of PCN-24(Fe) in an aqueous environment. Meanwhile, we recorded the color change for the whole process, which changed from colorless to dark green in just 15 minutes (Fig. 4c).

In this context, we have successfully demonstrated a facile one-spot synthetic strategy to construct 3D, porous, highly stable PPN-24(Fe), which exhibits great catalytic activity for the oxidation of ABTS. The integration of the high porosity and enhanced thermal and chemical stability into PPN-24(Fe) is beneficial for future studies in the synthesis of biomimetic catalytically active PPN materials.

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**Notes and references**

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