

Regular Article

Heteroatom-rich porous organic polymers constructed by benzoxazine linkage with high carbon dioxide adsorption affinity



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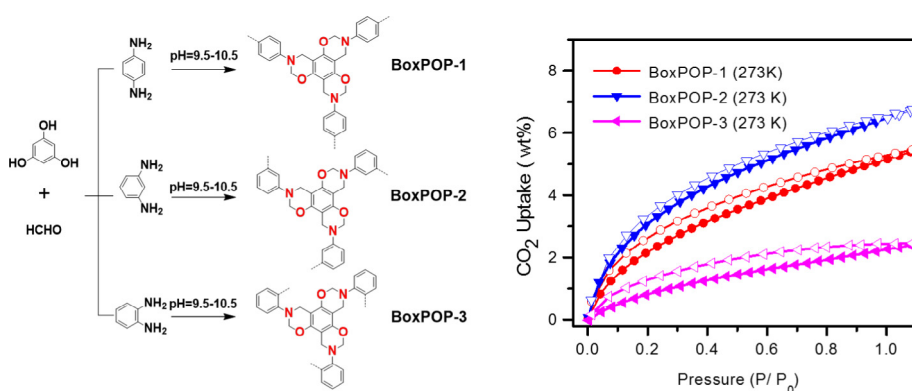
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GRAPHICAL ABSTRACT

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ABSTRACT

We report the synthesis and characterization of a new type of porous organic polymers linked by benzoxazine. The polymers were readily synthesized by condensation reaction of diamines, triphenol and paraformaldehyde. The formation of the linkage and porous structures were studied by infrared spectroscopy, solid-state ¹³C-CP MAS NMR and nitrogen sorption measurements. The porosity study revealed the resultant polymers are porous materials with surface area as high as 231 m² g⁻¹. Benzoxazine backbone endows the polymers with abundant heteroatoms (N and O), which makes these polymers promising candidates for carbon dioxide adsorption and storage. We found that the best polymer showing the highest carbon dioxide adsorption up to 6.81 wt% at 273 K and 1 bar, which is due to the most microporous structure and largest adsorption affinity. These results demonstrate a convenient approach to synthesize heteroatom-rich porous organic polymers for gas adsorption and storage.

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1. Introduction

Porous organic polymers (POPs), an emerging class of porous materials, are built by organic building blocks, which composed

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of light organic elements, such as C, O, N, B and others elements. Endowed with tuneable porosity and versatile building blocks, POPs are showing various promising applications in gas adsorption and storage, catalysis, sensor and optoelectronic areas [1,2]. According to formation reactions and structural characteristics, POPs can be mainly divided into following types: polymer of intrinsic microporosity (PIMs) [3,4], conjugated microporous polymers (CMPs) [5,6], hyper-crosslinked polymers (HCPs) [7], covalent organic frameworks (COFs) [8–10], etc. In order to achieve highly porous and functional POPs, a variety of polymerization methods have been developed. Schiff-base linkage [11], boronate linkage [12] and triazine linkage [13] are extensively employed for the synthesis of COFs. PIMs are obtained by condensation reactions using rigid twisted building units to endow the polymer with intrinsic porosities [14]. CMPs are constructed by a variety of coupling reactions, i.e. Suzuki-Miyaura coupling reactions [15], Yamamoto reactions [16] and Sonogashira coupling reactions [17]. Oxidative coupling reactions can also be employed to synthesize POPs, such as the coupling reaction of carbazole or thiophene building blocks [18–20]. Friedel-Crafts reaction is another very useful reaction to synthesize HCPs which features easy preparation and versatile starting materials, and thus show great promise for large-scale synthesis and practical applications [21–24]. Some other approaches for the creation of porous materials via condensation or polycyclization are also reported [25,26].

The heteroatom containing porous polymers represent as an important type of materials and have received wide attention to apply for gas adsorptions as well as other applications. In particular, heteroatom doped porous organic polymers can have enhanced adsorption ability for carbon dioxide adsorption. This is because CO₂ has much higher quadrupole moment as compared with other gases molecules and heteroatoms can provide the stronger adsorbate-adsorbent interactions [27]. Thus, we can improve the CO₂ capture by introducing heteroatoms doped building blocks that can give high isosteric heat of adsorption between sorbent and sorbate. For example, nitrogen, sulphur, oxygen atoms are often used to be introduced in the POPs to enhance the CO₂ adsorption ability [27]. By this principle, various type of POPs, including covalent triazine frameworks (CTFs), conjugated microporous polymers (CMPs), and hypercrosslinked polymers (HCPs) and so on, have been investigated for carbon dioxide adsorption [27]. At present, the highest CO₂ adsorption (HAT-CTF-450/600: 6.3 mmol g⁻¹ at 1 bar) was reported by using a CTF with an adsorption heat of 27 kJ mol⁻¹ [28]. Benzoxazine derivatives are also a type of interesting heteroatom containing materials that are formed from phenol, amine and formaldehyde by a condensation reaction, and have been shown to possess good thermal, electronic and mechanical properties as well as high stabilities [29–35]. The benzoxazine ring contains N and O atoms which located above and below the benzoxazine ring, and shows a distorted half chair conformation structure in space, enabling the six-ring structure possess certain rigidity [36]. Also, the benzoxazine ring could endow the materials with high level of nitrogen and oxygen content. Recently, some works on the preparation of functional porous materials based on polybenzoxazine resin via further ring-opening thermopolymerization or preparation of carbon materials using polybenzoxazine resin as carbonization precursors are reported [37–41]. However, the direct using of benzoxazine units as network linkage for porous organic polymers has not yet been developed.

Here, we reported a new type of porous materials connected by a benzoxazine linkage, which are synthesized using different diamine monomers condensed with paraformaldehyde and phloroglucinol to form three oxazine rings around benzene through Mannich reaction (Scheme 1). In contrast to the traditional benzoxazine resin polymers, which formed via further thermopolymerization and ring-opening reaction of benzoxazine units in the oligomers or

linear polymers, the resulting polymers in this work contains three oxazine rings connect to phenyls and these benzoxazine units further extend without ring-opening reaction, leading to porous network structures in the polymers [30,42]. The benzoxazine-linked porous polymers that are named as BoxPOP-1, BoxPOP-2 and BoxPOP-3, are obtained by polymerizing 1,3,5-trihydroxybenzene and paraformaldehyde with *p*-diaminobenzene, *m*-diaminobenzene and *o*-diaminobenzene, respectively. The BoxPOP-1, BoxPOP-2 and BoxPOP-3 are collected as insoluble solids in 86%, 83% and 26% yields, respectively. According to the reaction yields, the polymerization reactions of BoxPOP-1 and BoxPOP-2 are quite efficient. In contrast, BoxPOP-3 gives very low yield, which might be due to the large steric hindrance of proximal sites in *o*-diaminobenzene. Therefore, *o*-diaminobenzene may be not appropriate building block for high-level crosslinking polymer. The porous network structures were identified by nitrogen sorption measurements, which revealed the porous nature with pore sizes mainly distributed in the mesoporous regions. The ability of the BoxPOPs to adsorb carbon dioxide were studied by gas adsorption measurements and a capacity up to 6.8 wt% at 273 K and 1.0 bar and a high adsorption heat up to 29.8 kJ mol⁻¹ were revealed.

2. Experimental section

2.1. Materials and methods

Paraformaldehyde, 1,2-diaminobenzene, 1,3-diaminobenzene, 1,4-diaminobenzene, 1,3,5-trihydroxybenzene, 1,4-diethylene dioxide, and sodium hydroxide were obtained from National Medicines Corporation Ltd. of China, all of which were of analytical grade and used as received.

Nitrogen adsorption isotherm (77 K), pore size distributions, carbon dioxide adsorption were measured using Micromeritics ASAP 2020M surface area and porosity analyser. Before analysis, the polymer samples were pre-treated and degassed at 110 °C for 8 h under vacuum (10–5 bar). CO₂ sorption isotherms of these materials were collected at 273 K and 298 K, respectively. The isosteric heat of adsorption (Q_{st}) is calculated based on the CO₂ adsorption isotherms at 273 K and 298 K, by using the Clausius–Clapeyron equation.

2.2. Synthesis of BoxPOP-1, BoxPOP-2 and BoxPOP-3

A general synthetic procedure is as follows: a solution of 0.01 mol diaminobenzene in 20 mL dioxane was slowly added to a solution of 0.04 mol paraformaldehyde in 20 mL dioxane with two drops of sodium hydroxide (1 M), keeping the temperature at 5–10 °C. The mixture was allowed to stir for 90 min before 0.033 mol 1,3,5-trihydroxybenzene in 20 mL dioxane was added to the mixture. Then the reaction temperature was raised to 80 °C, and stirred for another 6 h. The precipitation in the solution were isolated by filtration and washed thoroughly to give the corresponding polymers (Scheme 1).

2.3. Structural characterization

FT-IR spectra were recorded under ambient conditions in the wave number range of 4000–400 cm⁻¹ using a Bruker VERTEX 70 FT-IR Spectrometer. Elemental analysis (EA) was determined using a Vario Micro cube Elemental Analyser (Elementar, Germany). Thermogravimetric analysis (TGA) measurements were conducted on a PerkinElmer Instruments Pyris1 TGA, thermobalance at a heating rate of 10 °C/min under nitrogen. The morphologies were investigated with a FEI Sirion 200 field emission scanning electron microscope (FE-SEM). The solid state ¹³C cross-polarization magic

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