A Benzoquinone-Derived Porous Hydrophenazine Framework for Efficient and Reversible Iodine Capture

<table>
<thead>
<tr>
<th>Journal</th>
<th>ChemComm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>CC-COM-09-2018-007529.R1</td>
</tr>
<tr>
<td>Article Type</td>
<td>Communication</td>
</tr>
</tbody>
</table>
A Benzoquinone-Derived Porous Hydrophenazine Framework for Efficient and Reversible Iodine Capture

Kecheng Jie, Hao Chen, Pengfei Zhang, Wei Guo, Meijun Li, Zhenzhen Yang and Sheng Dai

A type of benzoquinone-derived porous organic polymer with hydrophenazine linkages, porous hydrophenazine frameworks, were developed. Their application in iodine capture from both air and solution was investigated.

Porous organic polymers (POPs) are a fascinating class of materials with the features of high surface areas, synthetic diversity, low densities, and great thermal/chemical stabilities. In light of these unique advantages, there has been rapid development of POPs to explore their wide applications in catalysis, separations, gas storage, environmental treatment, and so on. To fabricate stable POPs, it is typically necessary to use rigid building blocks (repeating units) to prevent the collapse of the framework and fill the volume space in a more periodic manner. The rigidity of POPs is normally based on the rigid repeating aromatic units. Meanwhile, the chemical bonds that connect the lightweight aromatic units should also be rigid enough to avoid framework shrinkage.

Chemists and materials scientists have applied numerous organic synthetic strategies to form rigid chemical bond linkages in the synthesis of POPs. To date, these have been mostly realized by polymerization or polycondensation through C–X (X=C, O, N) bond formation strategies, such as metal-mediated couplings, oxidative coupling, imine/amide/imide-based condensation, aromatic nucleophilic substitution, radical polymerization, cyclotrimerization, hyper-crosslinking processes by Lewis acids, and so on. Benefiting from these processes, the chemistry of POPs have been greatly expanded and the targeted engineering of POPs with specific requirements related to surface area, pore size, surface affinity, and target functional group have been successfully achieved. Given the abundance of organic synthetic procedures, the exploration of new synthetic strategies to construct POPs with simple building blocks is still meaningful to enrich the POP class with unique functions.

Scheme 1. (a) The synthetic procedure of a model compound (MC) using o-phenylenediamine and benzoquinone (BQ). (b) The illustration of the synthesis of a porous hydrophenazine framework (PHF-1) using triptycenehexamine (THA) and BQ via a solvothermal Method. (c) Synthesis of cationic PHF-1-Ct by protonation of PHF-1 with diluted HCl.

In this study, we developed a novel class of POPs with hydrophenazine linkages. Derived from benzoquinone (BQ) and triptycenehexamine (THA), porous hydrophenazine frameworks (PHFs) were successfully synthesized via a catalyst-free aza-ring formation reaction between ortho-diamine and BQ (Scheme 1a and 1b). To the best of our knowledge, such a synthetic strategy has never before been used in the synthesis of POPs. The preparation of PHFs did not require strict reaction conditions (an anhydrous and oxygen-free environment) or catalysts and took only a few hours to complete the reaction. The resultant neutral PHF (PHF-1) had a high Brunauer-Emmett-Teller (BET) specific surface area (1046 m²/g) as well as good thermal and physiochemical stability. The nitrogen-rich...
PHF-1 also displayed an exceptional CO₂ adsorption capacity. Furthermore, the neutral PHF-1 was easily protonated with dilute hydrochloride (HCl) to become positively charged PHF-1-Ct because of the existence of aniline groups on the hydrophenazine rings. The protonation resulted in a decrease in the BET surface area and the CO₂ adsorption capacity. Intriguingly, the positively charged PHF-1-Ct with lower BET surface area displayed an efficient iodine capture capacity (4.05 g/g) higher than that of the neutral PHF-1 (3.05 g/g) and was the highest among the amorphous POPs.18-24 The higher iodine loading amount in PHF-1-Ct was ascribed to the multiple binding sites for both neutral iodine molecules and polyiodide anions. Moreover, the PHFs were recycled many times without losing their iodine capture ability.

We began the study with the synthesis of an aza-fused hydrophenazine-like model compound (MC-1) using o-phenylenediamine and BQ. The 2:1 reaction with BQ dropwise added into the o-phenylenediamine solution afforded MC-1 with a yield of over 95% within 30 min (Scheme 1a, Fig. S4-S7). Thus, an efficient rigid-ring formation reaction may be suitable for the synthesis of POPs. Replacing o-phenylenediamine with THA, a rigid threefold symmetric building block, resulted in a 2-dimensional (2D) shape-persistent hydrophenazine-linked framework with inherent periodic honeycomb-like structures (PHF-1) after a solvothermal reaction. The yield of the polymeric product was increased from 30% to 88% by an extension of the reaction time from 8 to 16 h (Scheme 1b). The PHF-1 polymer network was chemically stable and was insoluble in common organic solvents such as DMF, acetone, and alcohols.

The structure of PHF-1 was first characterized by solid state ¹³C cross-polarization magic-angle spinning (CP/MAS) nuclear magnetic resonance (NMR) at the molecular level (Fig. 1a). The solid-state ¹³C CP-MAS NMR spectrum revealed eight carbon peaks with chemical shifts of 52.8, 80.6, 113.3, 122.4, 132.9, 140.6, 170, and 201.9 ppm, which were assigned to the sp² bridge carbon (a), the aromatic (sp²) carbons (b, d, e, f, g, h), and the edge carbonyl (C=O) groups (c), respectively (Fig. 1a). X-ray photoelectron spectroscopy (XPS) was performed to probe the nitrogen bonding nature in PHF-1 (Fig. 1b). The peaks at 398.78 eV and 400.28 eV were attributed to the characteristic imine nitrogen atoms and aniline nitrogen atoms,25 respectively, revealing the formation of hydrophenazine rings in the PHF-1 structure (Fig. 1b). The Fourier-transform infrared spectrum showed several peaks at 3345 cm⁻¹/3180 cm⁻¹, 2160 cm⁻¹, 1186 cm⁻¹/1210 cm⁻¹, and 1620 cm⁻¹, corresponding to the stretching vibrations of N-H, C=N, and C-N and the in-plane bending vibrations of N-H, respectively (Fig. 1c). This was in good agreement with the XPS results. Thermogravimetric analysis (TGA) showed an apparent weight loss began at temperatures as high as 580 °C, indicating the high thermal stability of PHF-1 (Fig. 1d).

To investigate the long-range ordering of the PHF-1 structure, a powder x-ray diffraction (PXRD) experiment was performed. No sharp peaks were observed in the PXRD spectrum, indicating the loss of long-range crystallographic ordering of PHF-1 (Fig. S10). The bulk morphologies of PHF-1 were visualized with field-emission scanning electron microscopy (FE-SEM). The SEM images showed that PHF-1 consisted of relatively uniform solid sub-micron spheres (Fig. 1e and 1f). These fused polymer masses without well-defined shapes also implied the loss of long-range order. The fluffy sample may be favourable for good porosity, especially the mesoporosity or macroporosity that exists among the micro-spheres.
Ct was 690 m$^2$/g with a total pore volume of 0.44 cm$^3$/g—lower than that of PHF-1. We deduced that the presence of chloride anions in PHF-1-Ct led to a decrease in the accessible pores for N$_2$. Meanwhile, the level of microporosity was assessed by the ratio of micropore volume to the total pore volume ($V_{\text{micro}}/V_{\text{total}}$). The $V_{\text{micro}}/V_{\text{total}}$ values of PHF-1 and PHF-1-Ct were 0.57 and 0.59, respectively, indicating the good microporosity of the two porous polymers (Table 1).

**Fig. 2.** (a) N$_2$ adsorption and desorption isotherms at 77 K and (b) CO$_2$ adsorption isotherms of PHF-1 and PHF-1-Ct at 273 K.

The two nitrogen-rich porous materials also showed superb CO$_2$ uptake capacities. Uptakes of 4.55 mmol/g (20.0 wt %) and 3.28 mmol/g (14.4 wt %) at 1 bar and 273 K were obtained for PHF-1 and PHF-1-Ct, respectively (Fig. 2b). The results revealed that PHF-1 with a larger BET surface area had a better CO$_2$ capture performance than PHF-1-Ct with a lower BET surface area. Moreover, the CO$_2$ uptake in PHF-1 was comparable to that of many reported POPs. The reason can be ascribed to the synergistic effects of rich microporosity and abundant CO$_2$-philic surface sites, including unreacted peripheral C=O sites and nitric sites.

**Table 1. Porosity Parameters of PHFs**

<table>
<thead>
<tr>
<th>PHFs</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_{\text{total}}$ (cm$^3$/g)</th>
<th>$V_{\text{micro}}$ (cm$^3$/g)</th>
<th>$V_{\text{micro}}/V_{\text{total}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHF-1</td>
<td>1046</td>
<td>0.61</td>
<td>0.35</td>
<td>0.57</td>
</tr>
<tr>
<td>PHF-1-Ct</td>
<td>690</td>
<td>0.44</td>
<td>0.26</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Radiological iodine species such as $^{129}$I and $^{131}$I are common nuclear volatile fission wastes formed during the production of nuclear power. They need to be efficiently captured and reliably stored. The two PHFs, with their features of good porosity, high electron density, and abundant aromatic/aza rings may also have exceptional iodine capture capabilities. To explore this question, iodine vapor adsorption experiments were first performed. Fig. S14 shows that the colors of both PHF-1 and PHF-1-Ct became darker after adsorption of iodine vapor. This phenomenon indicated that iodine molecules were not only adsorbed onto the surface but also loaded into the intrinsic pores of the two porous polymers. Iodine uptake capacities were measured by gravimetric methods that depend on the differences of sample weights before and after exposure to iodine vapor. Upon reaching equilibrium, one gram of PHF-1-Ct and PHF-1 adsorbed approximately 4.05 g and 3.05 g of iodine, respectively (Fig. 3a). TGA results showed that the weight losses below 300 °C of PHF-1-Ct and PHF-1 after adsorption of iodine were 80% and 75%, respectively, corresponding to the iodine capture capacity of 4.0 g/g and 3.0 g/g (Fig. S15 and S16). The results thus agreed well with gravimetric measurements. It was worth noting that the iodine loading capacity of PHF-1-Ct was the highest among the POPs and the second-highest among all reported materials (Table S1). SEM images showed that iodine-loaded PHF-1 consisted of large nanoparticles, whereas iodine-loaded PHF-1-Ct consisted of nanorods, both of which were different from their original morphologies (Fig. S17). This implied that the mesopores or macropores between the small spheres of PHF-1 or PHF-1-Ct were filled with iodine, resulting in the morphology change. It should be mentioned that PHF-1-Ct, with a lower BET surface area, had a better iodine capture performance than PHF-1 with a higher BET surface area, which was contrary to the CO$_2$ capture results. The mechanism behind this result was verified by XPS. Iodine species adsorbed in PHF-1 with only a valence of zero were detected, confirming that iodine remained as neutral I$_2$ (Fig. 3b). This finding revealed a purely physical adsorption process of iodine in PHF-1. However, iodine species of both neutral I$_2$ and polyiodide anion I$_3^-$ were detected in PHF-1-Ct, indicating that some adsorbed iodine molecules were transformed to I$_3^-$ by PHF-1-Ct (Fig. 3c). Moreover, the positively charged nitrogen-fused aromatic PHF-1-Ct produced multiple supramolecular interactions with iodine, such as typical charge transfer interactions between phenyl rings and iodine molecules, and electrostatic interactions between positively charged ammonium group and I$_3^-$, thereby increasing the adsorption amount for iodine.

**Fig. 3.** (a) Time-dependent iodine vapor capture capacities of PHF-1 and PHF-1-Ct. 1 3d XPS spectra: (b) PHF-1 and (c) PHF-1-Ct after capture of iodine vapor. (d) Photographs and (e) time-dependent UV/vis absorption spectra when 25 mg of PHF-1-Ct were placed in 2 mL iodine aqueous solution. (f) Iodine capture efficiency after PHF-1 and PHF-1-Ct were recycled five times. PHF-1-Ct was also able to capture iodine dissolved in solution. Upon the addition of PHF-1-Ct to an iodine n-hexane solution, the purple solution faded over time and turned completely colorless after 60 minutes (Fig. S18a). A time-dependent ultraviolet–visible spectroscopy (UV/Vis)
experiment (Fig. S18b) showed that the iodine concentration decreased over time to nearly zero after 120 min. This means that PHF-1-Ct captured iodine from n-hexane with a final concentration of iodine below 1 ppm. Moreover, PHF-1-Ct was capable of capturing iodine in aqueous solution, which has only rarely been demonstrated by porous materials, such as metal-organic frameworks, because of their moisture instability (Fig. 3d). It also took about 60 min to completely adsorb iodine in a saturated aqueous iodine solution, a somewhat faster rate than that in n-hexane (Fig. 3e).

To be practically useful, an adsorbent should be reused over multiple cycles without loss of performance. When iodine-loaded PHF-1 or PHF-1-Ct was exposed to ethanol, the transparent solvent soon became yellow, indicating the spontaneous release of iodine (Fig. S19). After being immersed in ethanol for 5 hours, the PHFs were collected, washed with ethanol, and dried for the next use. The recovered PHFs were still able to capture iodine without an apparent loss of iodine loading capacity after five cycles (Fig. 3f).

In conclusion, we for the first time employed a catalyst-free aza-Diels-Alder reaction between BQ and ortho-diamines to prepare a novel class of porous organic polymers with hydrophenazine linkages—PHFs. The neutral PHF-1 had a higher BET surface area and CO₂ adsorption capacity. However, the positively charged PHF-1-Ct with a lower BET surface area displayed an efficient iodine capture capacity that was higher than that of the neutral PHF-1 and was the highest among all reported amorphous POPs. The high iodine loading capacity of PHF-1-Ct was ascribed to the multiple binding sites for both neutral iodine molecules and polyiodide anions. Compared with other iodine adsorbents, PHFs have several advantages beside their high loading capacity. For example, the preparation of PHFs from BQ is extremely simple and cost-effective. Moreover, because of their moisture and thermal stability, PHFs can capture not only volatile iodine in the air but also iodine dissolved in organic and aqueous solutions. Finally, they can be reused many times without an apparent loss in performance. Given the abundance of building blocks containing diamines or BQs, various PHFs will be developed via this synthetic method for targeted applications in the near future. Particular interest may be focused on the construction of hydrophenazine-linked crystalline covalent organic frameworks.

Conflicts of interest
There are no conflicts to declare.

ACKNOWLEDGMENT
This work was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy.

Notes and references