Porous Aromatic Frameworks

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Highly Efficient Enrichment of Volatile Iodine by Charged Porous Aromatic Frameworks with Three Sorption Sites

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Abstract: *The targeted synthesis of a series of novel charged porous aromatic frameworks (PAFs) is reported. The compounds PAF-23, PAF-24, and PAF-25 are built up by a tetrahedral building unit, lithium tetrakis(4-iodophenyl)borate (LTIPB), and different alkyne monomers as linkers by a Sonogashira–Hagihara coupling reaction. They possess excellent adsorption properties to organic molecules owing to their "breathing" dynamic frameworks. As these PAF materials assemble three effective sorption sites, namely the ion bond, phenyl ring, and triple bond together, they exhibit high affinity and capacity for iodine molecules. To the best of our knowledge, these PAF materials give the highest adsorption values among all porous materials (zeolites, metal–organic frameworks, and porous organic frameworks) reported to date.*

The demand for developing alternative source of fossil energy is growing rapidly. Although nuclear energy is considered as an efficient and a non-carbon-emitting power source,[1,2] an urgent issue of safety concern behind nuclear power production is the management of waste products generated from the nuclear fission of uranium.[3,4] The nuclear waste stream contains volatile radionuclides such as ^{129}I, ^{131}I, ^{3}H, and ^{85}Kr. One radionuclide that attracts particular attention is radiological iodine, mainly because it has a very long radioactive half-life (1.57×10^{7} years) and can be incorporated into the human metabolic system.[5] Therefore, to facilitate the future development of nuclear energy, effective methods for capture and storage of radiological iodine are highly desired.

Currently the prevalent technique for iodine capture is utilizing natural or synthetic metal-exchanged zeolites as iodine sorbents.[6,7] These materials are chemically and hydrothermally stable; however, their limited adsorption capabilities lead to low adsorption of iodine. Therefore, scientists are currently investigating alternative iodine capturing materials that have higher affinity, higher loading capacity, and lower overall cost. Up to now, several examples of iodine inclusion into inorganic porous materials[8–11] and metal–organic frameworks (MOFs)[12–24] are known, with the loading weight ratio varying from 8 % to 175 %. By contrast, studies focused on enrichment and detection of iodine by porous organic frameworks (POFs) are rare.[25–28] Furthermore, selectivity and durability are also critical features for materials that are used for selective adsorption and storage of long-term radioactive waste. Considering the high thermal and chemical stabilities, excellent sorption properties, and unique skeleton structures of POFs, we aimed at exploring novel materials towards the effective capture and storage of iodine.

Herein, we present the design and synthesis of a series of charged porous aromatic frameworks (PAF-23, PAF-24, and PAF-25). As illustrated in Figure 1, PAF-23, PAF-24, and PAF-25 are built up by a charged tetrahedral lithium tetrakis(4-iodophenyl)borate (LTIPB),[29] and different alkyne monomers were successfully produced by a Sonoga-

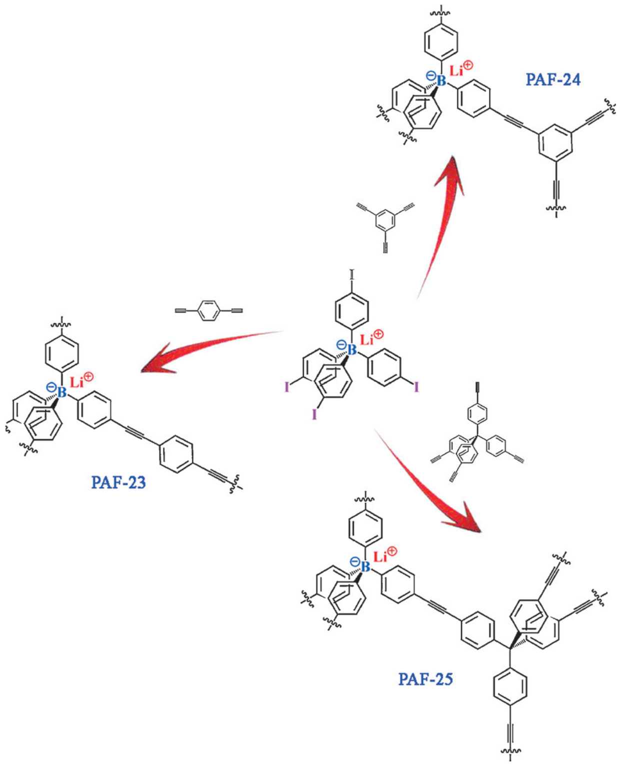

Figure 1. Synthetic routes for polymers PAF-23, PAF-24, and PAF-25 by a Sonogashira–Hagihara coupling reaction.

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shira–Hagihara coupling reaction. These PAF materials combine three effective sorption sites, an ionic bond, phenyl ring, and triple bond together, and exhibit very high affinity for iodine owing to their special aromatic networks. As far as we know, PAF-23, PAF-24, and PAF-25 possess the highest reported iodine adsorption capability to date.

Synthesis of these charged PAF materials was accomplished by a Sonogashira–Hagihara coupling reaction (Experimental Section). FTIR spectra indicate the completion of the cross-coupling reactions (Supporting Information, Figure S1). PAF-23, PAF-24, and PAF-25 do not exhibit the terminal alkyne C$-$H stretching vibration of the monomers near 3300 cm^{-1}. No C$-$I vibration band is visible in the IR spectra of PAF networks (LTIPB: 480 and 506 cm^{-1}). Furthermore, a new peak near 2200 cm^{-1} in the final product appears, which is corresponding to the alkyne $-$C$\equiv$C$-$ stretching vibration mode. The formation of the expected bonds demonstrated the success of the cross-coupling reactions.

The structures of three PAF networks were characterized at the molecular level by solid-state ^{13}C CP/MAS NMR spectroscopy (Supporting Information, Figure S2), ^{11}B MAS NMR (Figure 2) and ^{7}Li MAS NMR (Supporting Information, Figure S3). The carbon resonances with chemical shifts in the range of 115–146 ppm are associated with aromatic carbon atoms in the framework-building phenylene groups (Supporting Information, Figure S2). Meanwhile, resonance of ethynylene $-$C$\equiv$C$-$ units in the frameworks have been observed at around 90 ppm. Furthermore, the only resonance at around -26 ppm seen in the ^{11}B MAS NMR spectra can be attributed to the central B atoms in the framework units (Figure 2, black curve), indicating that the building units retain their configuration after the reactions. Moreover, the chemical shift at around 1.2 ppm in the ^{7}Li MAS NMR spectra (Supporting Information, Figure S3) corresponds to the Li$^+$ ions surrounding the central B atoms of the frameworks, and the results also show that the LTIPB building units keep intact during the coupling reaction and work-up.

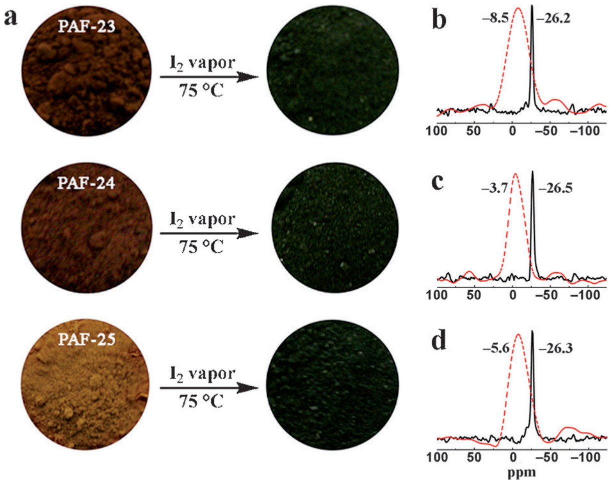


Figure 2. a) Photographs showing the color change before and after iodine capture for polymer networks PAF-23, PAF-24, and PAF-25. b)–d) Solid-state ^{11}B MAS NMR spectrum of PAF-23 (b), PAF-24 (c), and PAF-25 (d) (black curves) and after iodine capture (red dotted curves).

The thermal and chemical stabilities of the PAF frameworks were also investigated. Thermogravimetric analysis (TGA) of PAF-23, PAF-24, and PAF-25 networks indicate their excellent thermal stability up to 400 °C in air atmosphere (Supporting Information, Figure S4). Furthermore, these polymer networks also exhibit high chemical stability, which is verified by the lack of dissolution or decomposition in common organic solvents such as THF, acetone, CHCl$_3$, DMF, and DMSO.

Powder X-ray diffraction (PXRD) patterns of the three PAF materials (Supporting Information, Figure S5) show a characteristic broad peak and indicate their amorphous nature, which is consistent with most of the previously reported conjugated microporous polymer (CMP) networks.[30–32] Scanning electron microscopy (SEM) images show that the obtained PAFs were composed of fused polymer masses without well-defined shape (Supporting Information, Figure S6a–c). Simultaneously, high-resolution transmission electron microscopy (HRTEM) (Supporting Information, Figure S6d–f) also reveals the amorphous texture of the PAFs, but uniform pores are observed in the images.

To characterize the porous properties of PAF-23, PAF-24, and PAF-25 networks, the carbon dioxide sorption isotherms are performed on the activated samples at 195 K. All of the porous materials possess a rapid rise at low relative pressure ($P/P_0 < 0.1$), and followed by a slow increase (Supporting Information, Figure S7). The values of their surface areas are 82, 136, and 262 m^2 g^{-1}, respectively, as interpreted by the BET model. Their pore sizes centered at around 0.44, 0.50, and 0.47 nm, respectively, as calculated by the Horvath–Kawazoe (HK) method.

Further investigation on the porosity properties of these PAF materials were carried out by characterizations of their sorption selectivity between methanol and H$_2$O at 298 K. PAF-23, PAF-24, and PAF-25 were excellent hydrophobic materials, as illustrated by their selective adsorption of methanol over H$_2$O (Supporting Information, Figure S8). The methanol adsorption isotherms of these PAF networks steadily increase accompanying the rise of liquid vapor pressure, and are still unsaturated at $P/P_0 \approx 1$. The methanol uptake at 298 K and 1 bar is 273 mg g^{-1}, 321 mg g^{-1}, and 403 mg g^{-1} for PAF-23, PAF-24, and PAF-25, respectively. The large hysteresis between adsorption and desorption isotherms suggest strong interactions between the methanol molecules and the pore surface, which indicates a solvent-induced structural modification and further reveals the soft and dynamic characteristics of these PAF networks. As with other MOFs and porous polymers, these materials can swell in solvents.[33–37]

The specific “breathing” dynamic frameworks of these PAFs prompted us to further investigate their adsorption properties for other molecules. We successfully carried out highly efficient iodine enrichment based on PAF-23, PAF-24, and PAF-25 by the approach of exposing the powdered samples to iodine vapor, the molecular dimension of which is 0.335 nm. For each measurement, the PAF powder was loaded in a pre-weighed glass vial. The vial and excess solid iodine were together in a closed system at 75 °C and ambient pressure, which is a typical nuclear fuel reprocessing condition. As time went on, the color of the solid powder became progressively darker (Figure 2 a). Iodine uptake was measured by the gravimetric method. No further change in the iodine loading amount was observed after 48 h, implying that the adsorption equivalent had been established. The adsorptive capacities were obtained from the differences of sample weights before and after being exposed to iodine vapor. One gram of PAF-23, PAF-24, and PAF-25 can adsorb approximately 2.71 g, 2.76 g, and 2.60 g of iodine, respectively. These PAF materials give the highest sorption values among all porous materials (zeolites, MOFs, and POFs) reported to date (Supporting Information, Table S1). The charged aromatic frameworks with conjugated π-electrons could produce multiple interactions with iodine, thereby increasing the adsorption amount for iodine.[20,28,38] X-ray photoelectron spectroscopy (XPS; Supporting Information, Figure S9) indicated that the valence of the iodine adsorbed on the surface of PAFs is zero, confirming it remains as neutral I_2. After I_2-loaded PAFs were washed with ethanol three times, the iodine encapsulated into the pores in the ionic state, which verified that the iodine species exists as I_3^-. For the I_2-loaded PAF-23, PAF-24, and PAF-25 samples, the TGA analysis showed similar behavior for all of the samples (Supporting Information, Figure S10), where an obvious mass loss step is observed from 90 to 400 °C (I_2 subl. = 184 °C). The mass loss associated with surface desorption started at 90–170 °C, and a further loss range at 170–400 °C was associated with release of adsorbed iodine inside the pores.

Herein, we have shown that PAF-23, PAF-24, and PAF-25 materials have very high affinity and capacity for iodine. We suggest that there are three main reasons leading to such high iodine sorption capacity for these PAF materials. First, the central boron atom in polymer frameworks shows a strong affinity with iodine molecules, which is further supported by the ^{11}B MAS NMR spectra of I_2-loaded PAF materials (Figure 2, red dotted curve). Compared with the PAFs in ^{11}B MAS NMR spectra (Figure 2, black curve), the resonance of tetrahedral central boron atom shifts from −26 ppm to −5 ppm after iodine capture. Moreover, the profile of boron signal visibly becomes broader in the ^{11}B MAS NMR spectra of PAFs after iodine capture. The changes of the ^{11}B MAS NMR indicate that the central boron atom in networks shows high affinity with iodine molecules. Second, the plentiful phenyl rings in the polymer networks lead to an enhancement for their interactions with iodine molecules compared with other zeolites or MOFs (Figure 3 a).[20] Third, the triple-bond linkages in polymer frameworks also play an important role for such a high iodine enrichment behavior of PAF materials.[28]

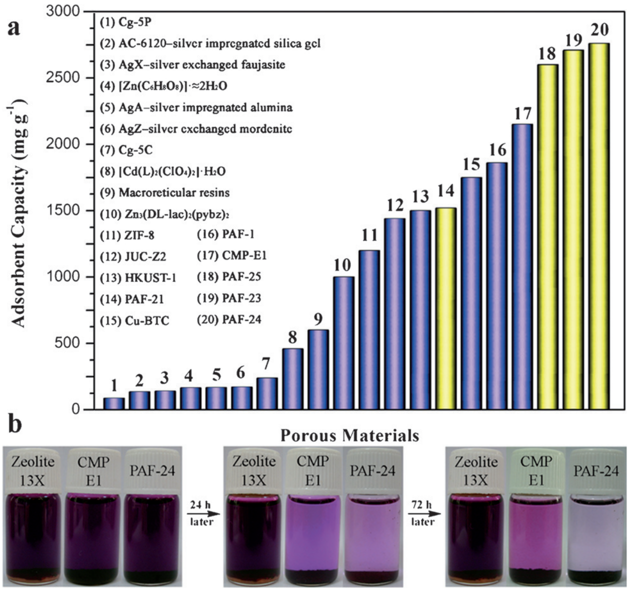
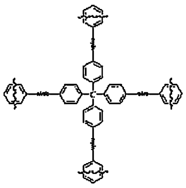
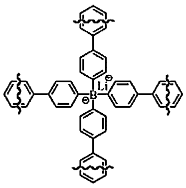
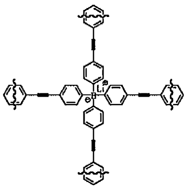
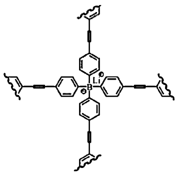
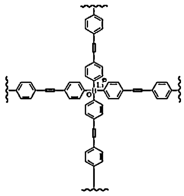


Figure 3. a) Comparisons of iodine adsorption capacities of different porous materials. The yellow columns represent new synthetic charged porous aromatic frameworks in this work, and the purple columns represent the other porous materials. b) Photographs show the different adsorption capacities of PAF-24, CMP-E1, and zeolite 13X. The same weights of different adsorbents (30 mg) immersed in a hexane solution of I_2 (0.02 mol L^{-1}, 3 mL) at room temperature.

To verify this proposal, another two polymer frameworks, charged PAF-21 (Supporting Information, Figures S11, S12) and uncharged CMP-E1,[31] were synthesized and their iodine enrichment behaviors were investigated. At the same conditions, 1 g of PAF-21, CMP-E1, and PAF-23 can adsorb approximately 1.52 g, 2.15 g, and 2.71 g of iodine, respectively. An illustration of different structures is shown in Table 1.

Table 1: Calculation of iodine sorption properties of each functional site.

	CMP-E1	**PAF-21**	**PAF-23**	**PAF-24**	**PAF-25**
structure segment					
phenyl rings	6	6	6	5.3	8
triple bonds	4	0	4	4	4
ionic bonds	0	1	1	1	1
I_2 capacity [mg g^{-1}]	2150	1520	2710	2760	2600

PAF-21 has a similar structure to PAF-23, except for the absence of the acetylenic bond in the framework. This is probably the reason for the lower iodine uptake of PAF-21. In the CMP-E1 structure, the central atom of the framework is carbon instead of the boron atom in the PAF-23 network, which may lead to the lower iodine uptake of CMP-E1. This study demonstrates that the plentiful phenyl rings, the skeleton central boron atom, and the acetylenic bond could be responsible for high iodine sorption capacity in these PAF materials.

Furthermore, we found that the iodine sorption of PAF-23, PAF-24, and PAF-25 are all reversible. Further studies indicated that the captured iodine could be readily removed from the polymer frameworks by immersing the I_2-loaded PAFs in organic solvents (Supporting Information, Figure S13). Herein, the I_2-loaded PAF-23, PAF-24, and PAF-25 were immersed in EtOH for 24 h at room temperature. The color of the solution changed gradually from colorless to dark brown (Supporting Information, Figure S13), which distinctly indicates that the iodine is dissociating from the polymer frameworks. This result indicates that these PAF networks are recyclable and could be regenerated for the use of iodine enrichment, which is important in practical applications.

The iodine sorption of PAF-23, PAF-24, and PAF-25 were further investigated using an iodine solution, and the results demonstrated that these PAF materials are capable of trapping iodine in organic solvent. When the PAFs were immersed in a hexane solution of iodine ($0.01\ \mathrm{mol\,L^{-1}}$) in a small sealed vial at room temperature, it was observed that the dark purple solutions of iodine fade slowly to very pale red and finally colorless (Supporting Information, Figure S14), which indicated that the iodine was encapsulated into the PAF networks to successively generate iodine-loaded systems in solution. The same weights of different adsorbents (PAF-24, CMP-E1, and zeolite 13X) were immersed in a hexane solution of iodine ($0.01\ \mathrm{mol\,L^{-1}}$) at room temperature for comparison. The photographs in Figure 3b reveals the different inclusion rates and capability of PAF-24 in comparison with CMP-E1 and zeolite 13X. The uptake of iodine on PAF-24 is very efficient, and clearly exceeds that of CMP-E1 and zeolite 13X[39] in the hexane solution. These results indicate that there is an obvious difference compared to conventional iodine capture materials lacking an accessible interaction between the host and iodine. The exceptional affinity of PAF materials for iodine may lead to the result of different uptakes of iodine.

In summary, we have presented a series of novel charged porous aromatic frameworks, PAF-23, PAF-24, and PAF-25. The resulting polymers display high thermal and chemical stabilities, and excellent sorption abilities to iodine molecules. According to our experimental and theoretical analysis, we demonstrated that the ionic bond, phenyl ring, and triple bond are the effective sorption sites to iodine at 75 °C. To the best of our knowledge, the loading amounts of these PAFs are the highest adsorption values of iodine uptake among all porous materials (zeolites, MOFs, and POFs) reported to date. We anticipate that this study will increase awareness and impact the use of PAFs in the application of capturing related fossil products.

Experimental Section

To synthesize PAF-23, lithium tetrakis(4-iodophenyl)borate (0.5 mmol, 415 mg), 1,4-diethynylbenzene (1.5 mmol, 189 mg), tetrakis(triphenylphosphine)palladium (30 mg) and copper(I) iodide (10 mg) were added to an oven-dried round-bottom flask. PAF-24 and PAF-25 were synthesized similarly, replacing 1,4-diethynylbenzene with 1,3,5-triethynylbenzene (1.0 mmol, 150 mg) for PAF-24, and tetrakis(4-ethynylphenyl)methane (0.75 mmol, 312 mg) for PAF-25. Anhydrous DMF (8 mL) and anhydrous diisopropylamine (8 mL) were added through a syringe. The reaction mixture was heated to 80 °C under N_2 atmosphere and reacted for 72 h. After cooling to room temperature, the product was filtered and washed with excess chloroform, tetrahydrofuran and acetone and then Soxhlet extracted with methanol overnight to remove any unreacted monomers and metal catalyst residues. The final products were dried in vacuum for 24 h at 60 °C to give PAF-23 (91 % yield), PAF-24 (97%), and PAF-25 (88%).

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Keywords: charged frameworks · iodine enrichment · ionic bonds · phenyl rings · triple bonds

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