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Communication

Triptycene-Based Microporous Polymer Incorporating Thioamide Functionality: Preparation and Gas Storage Properties

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Abstract: Triptycene-based micorporous polymer was functionalized with thioamide moieties via post-polymerization using phosphorus pentasulfide as a thionating agent in the presence of sodium sulfite. Gas adsorption experiments indicate that the modification leads to a reduction in the BET surface area of the polymer, from 1640 m^2 g^{-1} for the parent TMP to 207 m^2 g^{-1} on 74% conversion of nitrile to thioamide, while the resulting micorporous polymer possesses high H_2 uptake capacity, reaching 101.1 $cm^3 g^{-1}$ (0.9 wt %) at 1.0 bar and 77 K, along with relatively high selectivity towards CO_2 over CH_4 and N_2. The microporous organic polymer presents a promising potential as efficient adsorbents in clean energy applications.

Keywords: micorporous polymer; triptycene; post-modification; thioamide; gas storage

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1. Introduction

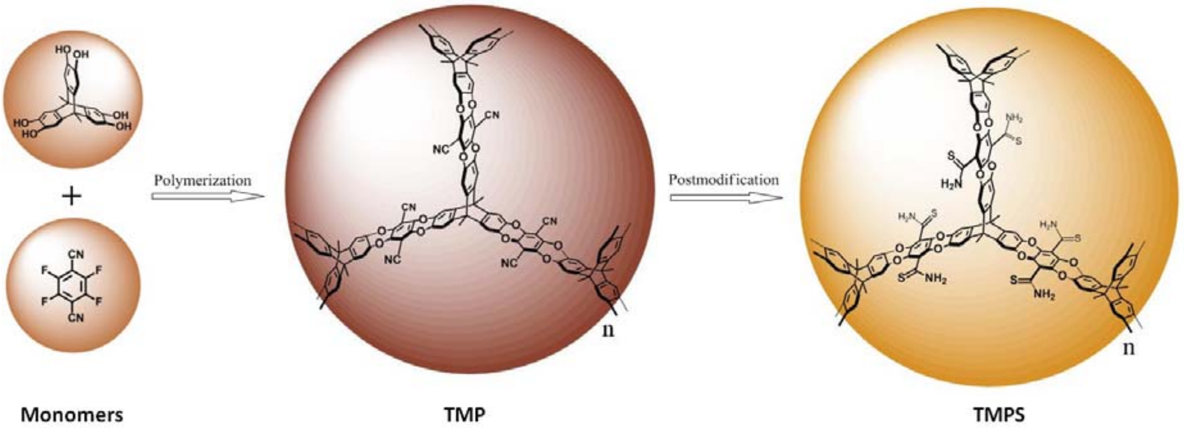
Advanced porous materials could play pivotal roles in the next generation clean energy technologies such as hydrogen storage for fuel cell in transportation, natural gas adsorbent for light-duty vehicle, and CO_2 separation and sequestration from the flue gas, etc [1-2]. A notable achievement in porous materials research is the development of micorporous organic polymers, which exhibit unique properties of large specific surface area, narrow pore size distribution, high chemical stability, low skeleton density, and the ability to be fine-tuned in their properties at the molecular level, allowing facile construction of porous materials with desired functionalities by appropriate choice of building block [3-5]. Such organic porous structure has flexibility of varying in designing organic functional monomers and pendant functional moieties, and can effectively combine the organic synthetic methodologies with processability of polymer, thus providing a unique opportunity for rational design and development of versatile microporous polymers for targeted applications. During the last decade, there are four well-known classes of micorporous organic polymers have been developed, including crosslinked polymer, hypercrosslinked polymers, polymers with intrinsic microporosity and covalent organic frameworks [6-7]. Although significant progress has been made in the area of micorporous organic polymers materials, only limited dimensionality, framework connectivity, and topologies of these promising materials have been explored [8]. In addition, better understanding on the effect of building block features on the target framework structures and properties is required.

In recent years, novel building blocks have been intensively investigated for the construction of three-dimensional microporous organic polymers, and the post-modification of microporous organic polymers also has been widely applied to synthesize novel microporous materials [9-10]. In previous publication [3], we reported the preparation of the triptycene-based micorporous polymer functionalized with CO_2-philic tetrazole moieties via $ZnCl_2$-catalyzed post-polymerization for CO_2-capture application. In this work, we extend the effort to seek high performance micorporous organic polymers - we are reporting the synthesis and gas storage properties of triptycene-based microporous polymer incorporating thioamide functionality. The polymer design employs triptycene and terephthalonitrile as the building blocks. The triptycene unit is rigid, which enables the preparation of permanently porous material. The fused-ring skeleton and threefold symmetry shape results in "internal molecular free volume," where the 3D spatial orientation reduces intermolecular contact between the extended planar struts of the rigid framework, thus reduces the packing within the solid [11]. In addition, the terephthalonitrile unit is rich in nitrile groups, which are the potential reaction sites for constructing diversified materials by post-modification, such as the carboxylated polymer and the polymer pending with tetrazole moieties [10]. In this study, the thioamide functionality by post-polymerization via the thionation of the aromatic nitriles are introduced to enhance the the polymer and gas species interactivity.

2. Results and Discussion

As shown in Scheme 1 in this study, the triptycene-based microporous polymer (TMP) were prepared from the nucleophilic aromatic substitution reaction between the 9,10-dimethyl-2,3,6,7,12,13-hexahydroxytriptycene monomer and commercially available 2,3,5,6-tetrafluoroterephthalonitrile according to the previous reports [3]. After the polymerization, the TMP was functionalized with thioamide moieties via post-polymerization using phosphorus pentasulfide as a thionating agent in the presence of sodium sulfite, leading to the desired triptycene-based microporous polymer with pending thioamide moieties (TMPS). The polymer structures of TMPS were confirmed by Fourier-transformation Infrared Spectroscopy (FTIR), ^{13}C solid-state NMR, and elemental analyses (EA). The TMPS showed the broad peaks around 3382 cm^{-1} and the emergence of two peaks at 1620 cm^{-1} and 860 cm^{-1} , which are the characteristic vibrations for the thioamide functionality [10]. The weak absorption at 2239 cm^{-1} assigned to nitrile stretching vibration indicated that not all the nitriles were converted in the reaction. In accordance with the results from the FTIR spectrum, the ^{13}C cross-polarization magic angle spinning (CPMAS) NMR spectrum provided further insight into the efficiency of the post-modification synthesis. The new peak at 191 ppm was ascribed to the carbon atoms present in the thioamide groups and the resonance locating at 139, 127, 109 and 17 ppm were originated from the carbon atoms of polymeric skeleton, respectively. The percentage conversion of nitrile to thioamide was estimated from the weight percent of sulfur determined by elemental analysis, which showed an 11.4 wt % of sulfur, corresponding to 74 % conversion of nitrile to thioamide. TMPS exhibited a relatively low thermal stability ($T_{dec} \approx 210$ °C) as evidenced by thermogravimetric analysis, which is in agreement with previous reports on the thioamide moiety [10]. The crystallinity and morphology of the micorporous polymer were investigated by powder X-ray diffraction (PXRD) and field-emission scanning electron microscopy (FESEM). The TMPS polymer network exhibited amorphous structures with some degree of crystallinity as indicated by powder X-ray diffraction studies. FE-SEM investigation also indicated the amorphous structures of the polymeric network.

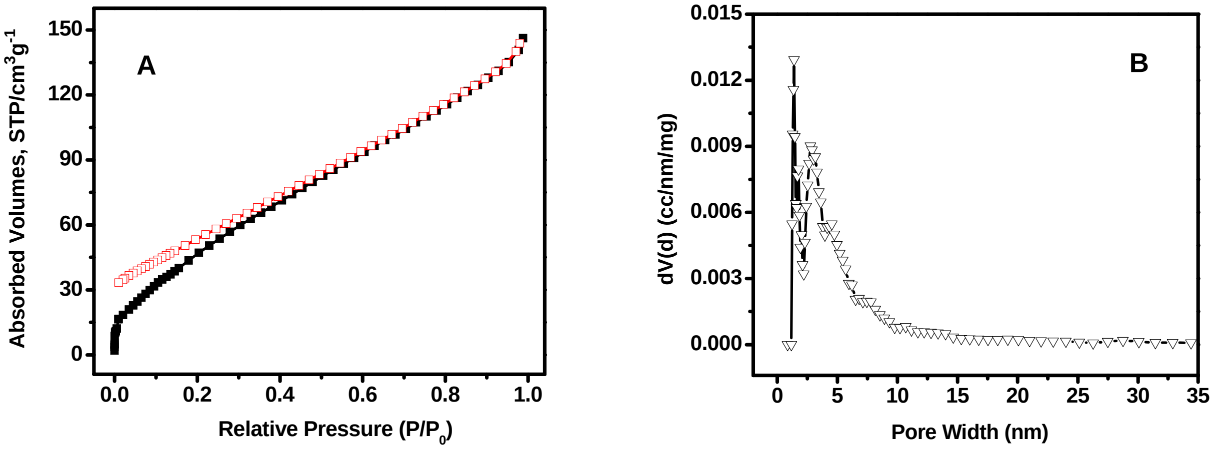
Scheme 1. Synthetic route to the triptycene-base microporous polymer TMPS. **(a)** Anhydrous DMF, anhydrous K_2CO_3, 80 °C, 24 h. **(b)** P_2S_5, Na_2SO_3, Ethanol, room temperature for 1 h; 1, 4- dioxane, reflux for 20 h.



The permanent porosities of TMPS were characterized by nitrogen adsorption/desorption isotherms of freshly activated samples at 77 K. As seen from Figure 1, N_2 sorption isotherm of the as synthesized polymeric network shows a steep gas uptake at relatively low pressure ($P/P_o < 0.001$) and an enhancement in N_2 uptake at $P/P_o > 0.1$. The Brunauere-Emmette-Teller surface area (S_{BET}), calculated from the adsorption branch of the nitrogen isotherms over a relative pressure range of 0.01-0.3 (P/P_o), indicate that the modification leads to a reduction in the BET surface area of the polymer, from 1640

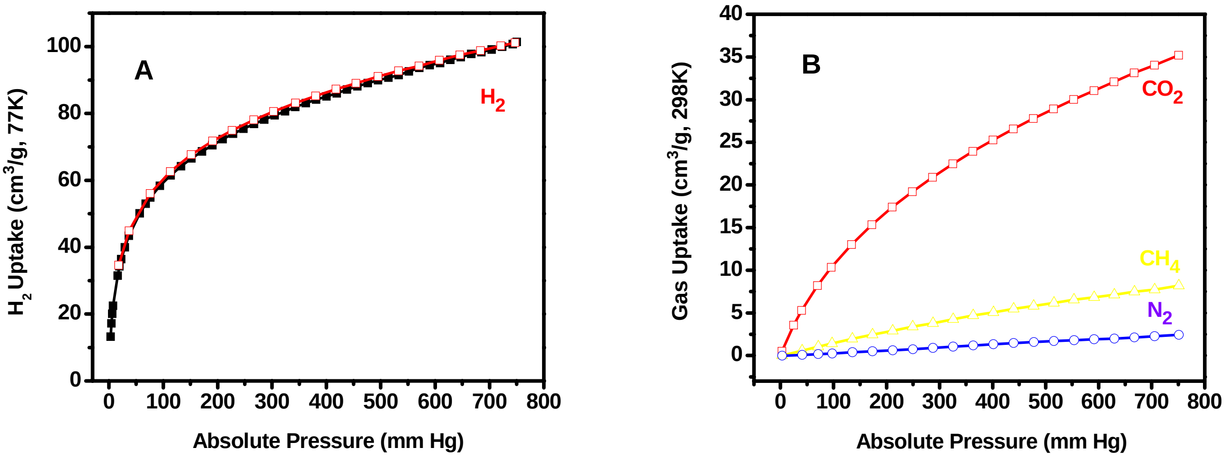
$m^2 g^{-1}$ for the parent TMP to 207 $m^2 g^{-1}$. This is consistent with previous reports, and there are various reasons why chemical modification may lead to a reduction in effective porosity. In the case of post-modification through the thionation of the nitriles, the thioamide is bulkier than the nitrile, occupying some of the free volume available in the parent polymer. In addition, the presence of groups which are capable of hydrogen bonding promotes intermolecular interactions between neighboring chains, resulting in a reduction in the polymer's free volume [10]. And the pore size distributions was derived using the entire range of the N_2 sorption isotherms measured at 77 K. Along with the decrease in surface area, the pore size distribution centered around 13 Å and 27 Å estimated by nonlocal density functional theory, still confirms the porosity of the post-modified triptycene-based polymeric network. As expected, the relatively narrow pore size distributions of the triptycene-based micorporous polymer TMPS should be related to the rigid spatial paddlewheel structure of triptycene units.

Figure 1. (a) N_2 sorption isotherms of triptycene-based microporous polymer TMPS. Filled cycles show adsorption isotherms and empty ones indicate desorption isotherms. P_0 is the saturated vapor pressure of the gas at 77 K. **(b)** Pore size distributions of triptycene-based microporous polymer TMPS calculated using nonlocal density functional theory.



Given the microporous nature and the narrow pore size distribution of the triptycene-based micorporous polymers TMPS, we next investigated its gas uptake capacities of small molecules. The H_2 (77 K), CO_2 (298 K), CH_4 (298 K) and N_2 (298 K) sorption isotherms were collected with the pressures up to 1.05 bar, respectively. What is noteworthy is that the microporous polymer network exhibits significant H_2 uptake capacities, 101.1 $cm^3 g^{-1}$ (0.9 wt %) at 1.0 bar and 77 K, as demonstrated in Figure 2a. The gradually increased curves suggest even higher H_2 uptake capacities upon further enhancing the pressures. On the other hand, the gas adsorption process is reversible in both cases as the desorption branch overlaps with the adsorption one. The obtained results indicate that the triptycene-based microporous polymer TMPS exhibits the comparable H_2 uptake value, making it among the family of high H_2 uptake polymer networks reported to date. Moreover, above experiment results verify the speculation of the theoretical study that the triptycene structure is suitable to adsorb H_2 [12]. In order to probe the performance of the material towards CO_2, N_2 and CH_4 uptake, gas sorption properties were evaluated by volumetric methods at the same conditions. For the sake of clarity, only adsorption isotherms are shown in Figure 2b. On the basis of these adsorption isotherms, we can find that the microporous polymer network TMPS exhibits the relatively high uptake capacity for CO_2 35.1 cm^3g^{-1} (6.4 wt %), and a low uptake capacities of CH_4 (8.2 cm^3g^{-1}, 0.6 wt %) and N_2 (2.4 cm^3g^{-1}, 0.3 wt %) at 1.0 bar and 298 K. Such saturation capacity of the microporous polymer towards CO_2 over CH_4 and N_2 presents another promising feature for gas purification.

Figure 2. (a) H_2 sorption isotherms of triptycene-based microporous polymer TMPS. Filled cycles show adsorption isotherms and empty ones indicate desorption isotherms. **(b)** Gas sorption isotherms of triptycene-based microporous polymer TMPS at 298 K.



3. Experimental Section

Synthesis of TMPS: A mixture of phosphorus pentasulfide (666 mg, 1.5 mmol) and sodium sulfite (189 mg, 1.5 mmol) in 7 mL ethanol was stirred at room temperature for 1 h. Then TMP (100 mg) and 1, 4-dioxane (60 mL) were added to the system. The resulting mixture was set to reflux and stirred for 20 h. On cooling, the mixture was poured into 60 mL water and stirred for another 4 h. The solvents were removed by rotary evaporation and the crude product was washed with DI water. The resulting brown solid was ground into the fine powder and dried in the vacuum oven at 80 °C for 24 h to give 0.96 g of TMPS. FTIR (KBr cm^{-1}): $\nu = 3382$ (s), 1620 (s), 1439 (s), 1224 (s), 860 (s). ^{13}C solid-state NMR (100 MHz, ppm): δ = 191, 139, 127, 109, 17. Elemental Analysis: Calculated for $C_{68}H_{42}N_6O_{12}S_6$: C 61.52, H 3.19, N 6.33, S 14.49, Found: C 59.34, H 2.73, N 6.03, S 11.45.

4. Conclusions

In this study, we have demonstrated the method of post-polymerization modification of triptycene-based micorporous polymer via the thionation of the aromatic nitriles. The thioamide moieties were introduced into the micorporous polymer leading to a reduction in the BET surface area of the polymer, while the resulting micorporous polymer still possesses high H_2 uptake capacity, reaching 101.1 cm^3g^{-1} (0.9 wt %) at 1.0 bar and 77 K. Such excellent performances make it promising candidate as effective adsorbent in clean energy application.

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Conflicts of Interest

The authors declare no conflict of interest.

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