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Microporous Organic Polymers Based on Hexaphenylbiadamantane: Synthesis, Ultra-High Stability and Gas Capture

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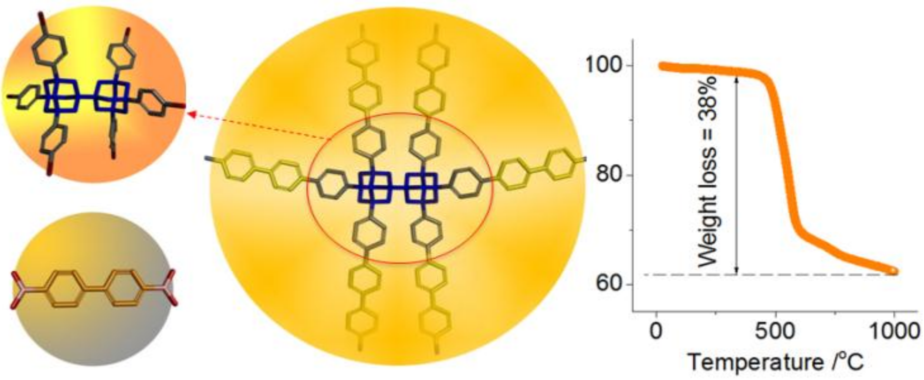
Abstract

Hexaphenylbiadamantane-based microporous organic polymers (MOPs) were successfully synthesized by Suzuki coupling under mild conditions. The obtained MOPs show high surface area (891 m^2 g^{-1}), ultra-high thermal (less than 40% mass loss at temperatures up to 1000 ^{o}C) and chemical (no apparent decomposition in organic solvents for more than 7 days) stability, gas (H_2, CO_2, CH_4) capture capabilities and vapor (benzene, hexane) adsorption. These combined abilities render the synthesized MOPs an attractive candidate as thermo-chemically stable adsorbents for practical use in gas storage and pollutant vapor adsorption.

Graphic Abstract



Keywords: Microporous material; Adamantane; Stability; Adsorption

1. Introduction

Great attention has been paid to porous materials in recent years as a consequence of their potential in a wide range of applications, such as gas adsorption [1], separation [2], storage [3] and catalysis [4]. Porous polymers having tailor-made functionality and being constructed from simple molecular synthons are now a major focus in this field. Microporous organic polymers (MOPs), in particular, have been intensively studied in an attempt to exploit their inherent internal cavities, which give rise to high surface area in the range of >600 m^2 g^{-1} [5-9].

High thermochemical stability is important for MOPs if they are to be employed in practical applications such as gas storage and hazardous vapor adsorption. Traditionally porous covalent organic frameworks have been reported to absorb a large amount of gas molecules especially CO_2 [10], yet they lack physicochemical stability, thus it is difficult to deploy them for long time storage or repeated use. Many porous metal-organic frameworks have also been shown to be unstable under harsh conditions due to the weak coordination bonds that compromise their macromolecular construct[11]. Typically, stable microporosity requires the use of rigid building blocks for synthesizing MOPs. Porous aromatic framework-1, for instance, has been found be stable and reusable, having extensive lifetime due to the use of somewhat ‘strong’ aromatic compounds as building units [12].

Adamantane, the simplest of the *so-called* diamondoid, is unique in that it is both rigid and virtually stress-free [13]. Motivated by our recent success in the synthesis of a diamondoid framework, 3,3’,5,5’,7,7’-hexakis(4-bromophenyl)-1,1'-biadamantane (**HBPBA**) [14] compromising a highly rigid biadamantane core surrounded by six phenyl groups, building macromolecular constructs from HBPBA would provide access to MOPs with desired stability. Herein we report the synthesis of highly stable MOPs containing 1,1’-biadamantane core and flanking aromatic linkers, using Pd-catalyzed coupling polymerization, showing superior thermo-chemical stability and capabilities in gas or hazardous vapor adsorption.

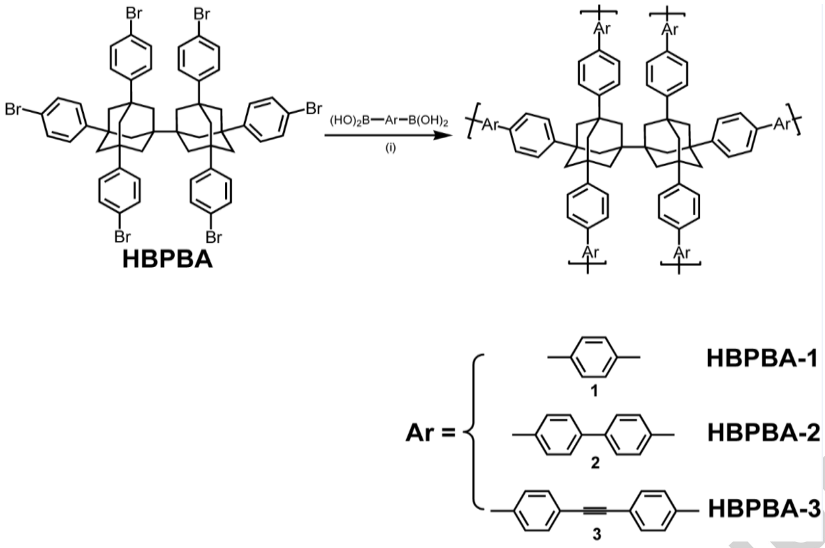
2. Experimental procedure

Hexakis (4-bromophenyl)-1,1'-biadamantane (e.g. 240 mg, 0.2mmol), diboronic acid (e.g. 3eq.), $Pd(PPh_3)_4$ (23 mg, 0.02mmol), NMP (dry, 20 mL) and 5 mL of a 2M aqueous Cs_2CO_3 solution were added into a 100 mL Schelenk flask and degassed by 3 freeze-thaw cycles. The mixture was then heated to 110 ^oC for 48h under Ar atmosphere. After cooling to room temperature, water was added and the solid polymer precipitate was collected by filtration. The residue was successively washed with water, acetone, chloroform and THF followed by extraction with THF (24 h) and chloroform (24h) and dried under vacuum, to obtain purified MOPs.

Solid-state ^{13}C CP/MAS NMR experiments were performed on a Bruker Avance III HD 400 spectrometer. Thermogravimetric analysis (TGA) was performed using STA-409 PC thermal analyzer system in the temperature range 30-1000 ^oC at heating rate of 10 $^oC/min$ under N_2 atmosphere. FT-IR spectra were measured within the 4000-400 cm^{-1} region using a Nicolet 380 Fourier transform spectrometer with KBr pellets. The nitrogen adsorption-desorption isotherms were measured on 3H-2000PM2 analyzer. Prior to gas sorption measurements samples were degassed at 150 ^oC in vacuum for 12h. BET surface areas were determined in a P/P_0 range from 0.05 to 0.1. The sorption of hydrogen, methane and carbon dioxide analyses was measured on 3H-2000PS2 apparatus at 77 K/1 bar (H_2) and 273 K/1 bar (CH_4 and CO_2). The benzene and hexane vapor adsorption isotherms were measured on 3H-2000PW apparatus at 298K and relative pressure P/P_0=0.8. Field emission scanning electron microscopy (SEM) was recorded using JSM-7001F with an acceleration voltage of 15.0 KV.

3. Results and discussion

Three HBPBA-based MOPs were prepared and the synthetic pathway is shown in Scheme 1. The synthesis of **HBPBA-1**, **-2** and **-3** was achieved by Suzuki polycondensation of HBPBA with 1,4-phenyldiboronic acid (**1**), 4,4'-biphenyldiboronic acid (**2**) and 4,4'-tolandiboronic acid (**3**), respectively, in a mixture of *N*-methyl-2-pyrrolidinone (NMP) and water (20%), using $Pd(PPh_3)_4$ as catalyst.



Scheme 1. Synthetic pathway towards the MOP networks. (i) *cat*. Pd(PPh_3)$_4$, Cs_2CO_3, NMP/H_2O (4/1), 110 °C.

The structures of the purified MOPs were analyzed by FT-IR, solid-state ^{13}C CP/MAS NMR, and SEM. FT-IR spectra (Figure S1) revealed that the polycondensation reaction was successful. Analysis of the C-Br region suggests the occurrence of the phenyl-phenyl coupling as the characteristic band at 1079 cm^{-1} belonging to bromine end-groups is hardly observed. The bands appeared at 2931 and 2855 cm^{-1} are characteristic vibrations of 1,1’-biadamantane (-CH_2-), band at 2211 cm^{-1} is attributed to C≡C stretching vibration for **HBPBA-3**, and peaks at 1605 and 1497 cm^{-1} belonging to the aromatic C=C stretching vibrations, are indicative of phenyl rings in HBPBA networks. NMR spectra (Figure 1) also confirmed the successful polycondensation. Detailed assignment of the resonances for particular carbon types in each compound is listed in Table S1.

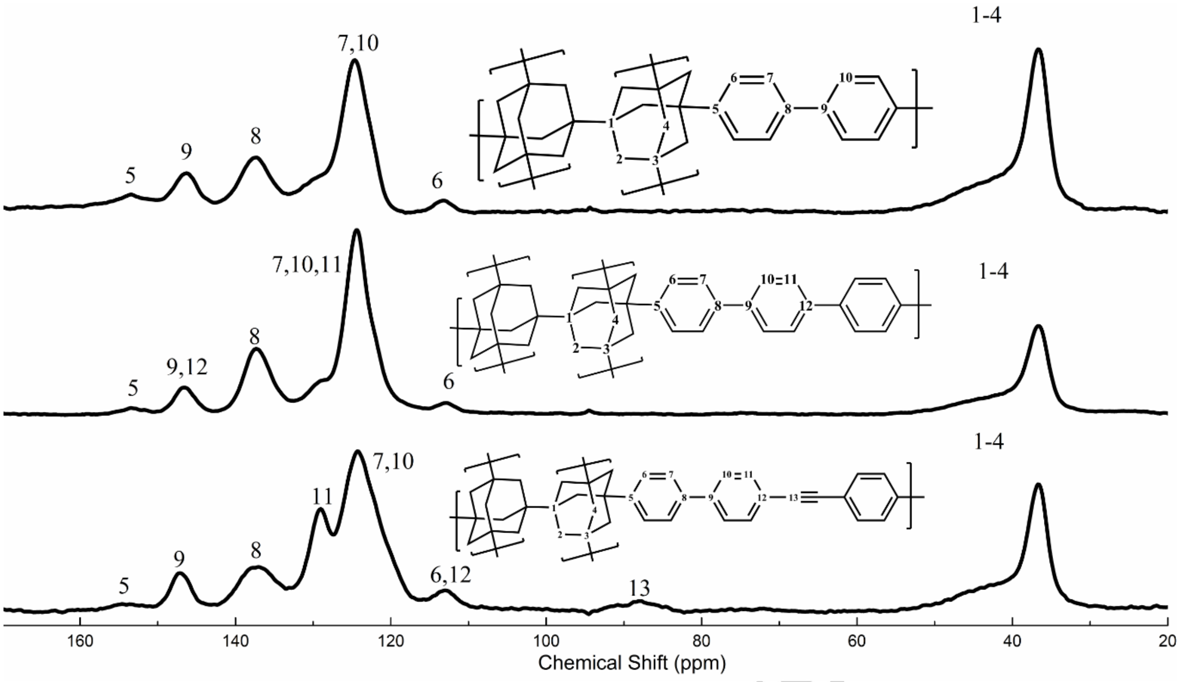


Figure 1. ^{13}C CP/MAS NMR spectra of the HBPBAs.

To reveal the porous structure of HBPBAs, nitrogen (N_2) sorption isotherms were measured at 77 K, as shown in Figure 2a. The steep uptake of N_2 at very low relative pressures suggests the existence of abundant micropores within samples. Furthermore, increase in N_2 adsorption above $p/p_0 = 0.9$ may result from interparticulate porosity [15], as seen from cavities between agglomerated nanospheres (Figure S2). The apparent BET surface area for **HBPBA-1**, **-2** and **-3**, is calculated to be 742, 760 and 891 $m^2\ g^{-1}$ respectively (Figure S3). Rather narrow pore size distributions (centered at 0.4-0.6 nm, Table S2) were found for all HBPBAs, according to nonlocal density functional theory .

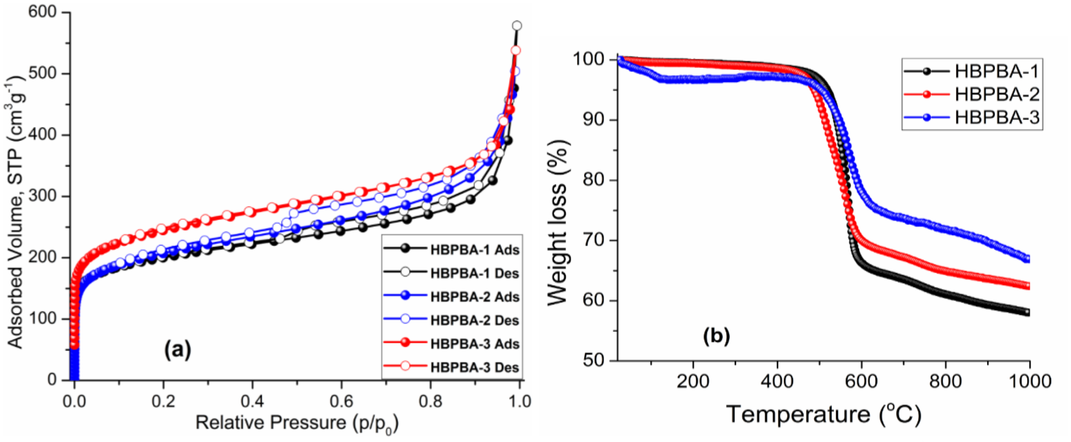


Figure 2. (a) N_2 adsorption (filled) and desorption (hollow) isotherms of the MOPs at 77 K. (b) TGA plots of weight loss.

All MOP samples possess extremely high thermal stability. TGA results (Figure 2b) show that the decomposition temperature is typically higher than 480 ^{o}C, with the maximum weight loss at about 570 ^{o}C. Surprisingly, the residual weights at 1000 ^{o}C for **HBPBA-1**, **-2** and **-3** were up to 58, 62, and 63wt% of its original weight, respectively, far more than any commonly known polymers would endure. Upon heating the samples at 300 ^{o}C in air for 2 h, we found no significant changes in structure (Figure S4) or N_2 physisorption properties (Table S3), further confirming their excellent thermal-performance, superior to most MOPs (Table S4) [7, 16, 17]. In addition to thermal stability, HBPBAs show superior chemical stability. For instance, they cannot be dissolved in common solvents such as THF, $CHCl_3$ and $CHCl_2$, even in boiling NMP and DMF for more than 7 days.

The combination of ultrahigh thermochemical stability, microporous nature and narrow pore sizes make the newly synthesized MOPs attractive candidates for gas-capture applications. We show in Figure 3 (a)-(c) the isothermal adsorption ability of the samples over gases of H_2, CH_4 and CO_2, and it came out that the HBPBAs possess capabilities of gas uptake in the high range values (Table S5). The total amount of CO_2 adsorbed by HBPBAs at 273K can reach >10wt% of sample mass, which is even better than some MOPs with ultrahigh surface area, such as PAF-1 (9.1 wt%, 5640 m^2 g^{-1}) [18] and COF-103 (7.6 wt%, 3530 m^2 g^{-1}) [19]. Similarly, the uptake of H_2 and CH_4 by HBPBAs are superior to other MOPs with comparable surface area. For instance, the HBPBAs adsorbed 1.11-1.16 wt% of H_2 at 77 K versus 1.04 wt% by PIM-1 having surface area of 760 m^2 g^{-1},[20] 1.01 wt% by CMP-1, 834 m^2 g^{-1} [21] and 1.12 wt% by CTC-COF, 1710 m^2 g^{-1} [22]. Values of 1.38-

1.76 wt% for CH_4 uptakes at 273K further confirm HBPBAs are good at gas capture [23]. Figure 4 (d) shows the vapor uptake isotherms at 298K of the HBPBAs. They can absorb a large number of vapor molecules of benzene/hexane, with the largest values up to 359.57 mg g^{-1} (benzene) and 306.69 mg g^{-1} (hexane), which is superior/comparable to MOPs[24, 25] (Table S6).

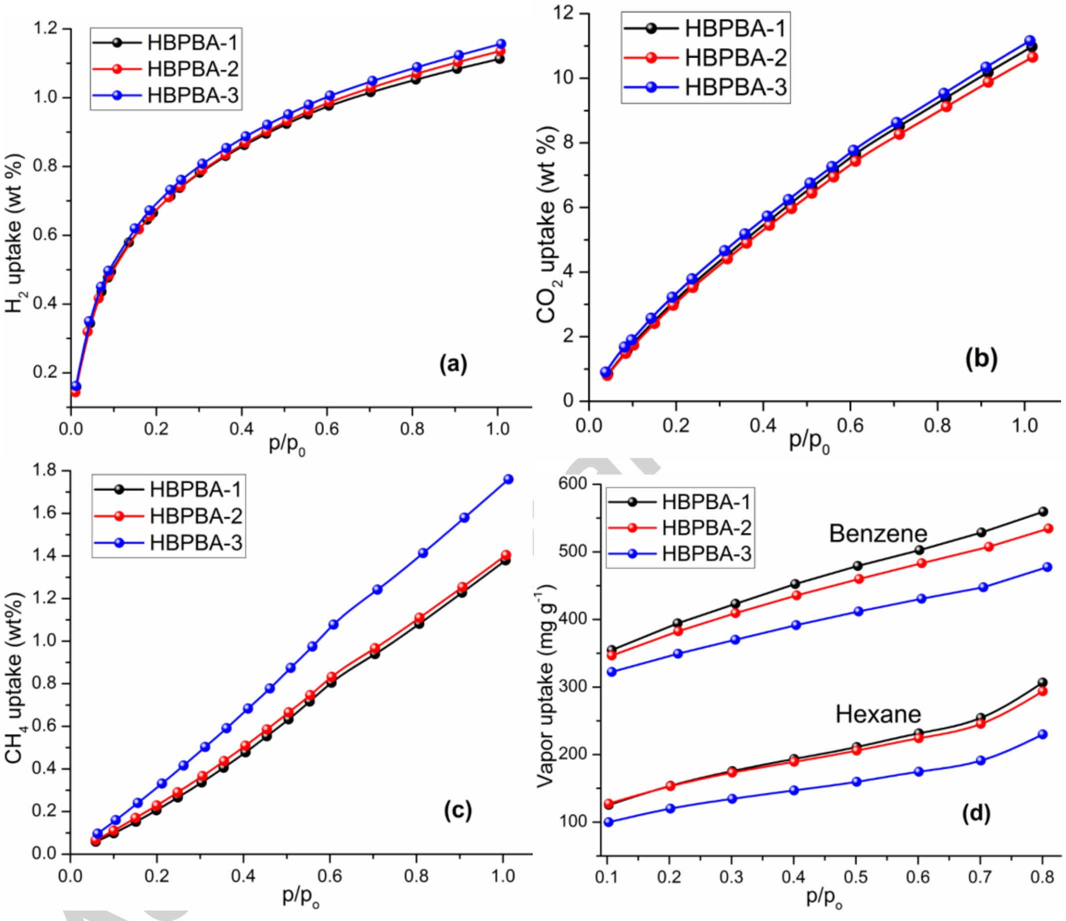


Figure 3. Adsorption isotherms of H_2 (a) at 77 K, CO_2 (b) and CH_4 (c) at 273K, benzene (values offseted) and hexane vapor (d) at 298K.

3. Conclusions

MOPs containing a hexaphenylbiadamantane building unit were successfully synthesized by Suzuki coupling by simple heating the solvated monomers. Microporous HBPBAs show high specific surface areas with narrow pore sizes, extremely high thermal and chemical stability, good adsorption ability towards hydrogen, methane, carbon dioxide, benzene and hexane vapor capture. These combined properties in our new MOPs open opportunities in gas storage and chemical pollutant collection in harsh environments.

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Highlights

- Microporous polymers containing adamantane core & aromatic linkers are synthesized.
- The rigid polymers display ultra-high thermal and chemical stability.
- Their adsorption capability towards gas and pollutant vapor is demonstrated.