



Microporous frameworks based on adamantane building blocks: Synthesis, porosity, selective adsorption and functional application



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ABSTRACT

Two microporous organic frameworks based on adamantane (hereafter denoted as **MF-Ads**) were fabricated through Sonogashira-Hagihara coupling polycondensation of aryl halides and alkynes. Results show that both types of **MF-Ad** networks had similar porous properties and exhibited excellent CO₂ uptake capacity (72.5 cm³ g⁻¹) and CO₂/N₂ selectivity (59.1) at 273 K and 1.0 bar. Taking advantage of the superhydrophobic wettability of the resulting **MF-Ad** networks, wire mesh scaffolds were used to fabricate superhydrophobic films with polydimethylsiloxane (PDMS) acting as a binder. These films displayed excellent instant hydrocarbon/water separation efficiency (up to 99.6%), which was maintained at a constant level after five repeated cycles. This work provides a novel insight into the fabrication of microporous organic frameworks and extends their applicability to carbon capture and absorption of hazardous organic pollutants.

1. Introduction

During the past decade, considerable research effort has been devoted to the development of advanced materials for capturing CO₂ efficiently, adsorbing hazardous organic pollutants and preventing further decline of our environment [1–3]. Work has recently revealed that most frameworks with abundant porous structure, such as metal organic frameworks (MOFs) [4], covalent organic frameworks (COFs) [5] and microporous organic polymers (MOPs) [6], to name a few, are promising adsorbents for capturing CO₂ due to their remarkably high surface area, large adsorption capacity and tunable chemical composition. Interestingly, in contrast to most reported MOFs and COFs which commonly suffer from poor chemical and thermal stabilities, MOPs are fabricated through C–C covalent bonds which provide better thermal and physicochemical stability. These improved properties make MOPs more suitable candidates than MOFs and COFs for carbon capture and storage (CCS) at high temperatures or in harsh environments [7, 8]. For example, Woo and Manoranjan synthesized azo-linked polymers with ultrahigh CO₂ adsorption capacity (up to 195 mg g⁻¹) with a weight loss of 10% up to between 280 and 305 °C, depended on the network [9]. Kundu and Bhaumik reported a nitrogen- and sulfur-rich hyper-cross-linked microporous poly(triazine-thiophene) copolymer (HMC-1), which exhibited a CO₂ uptake of 462 mg g⁻¹ at 273 K and 3.0 bar, but gave a weight loss of 10% at 220 °C [1]. Conversely, for reported MOPs,

Janiak et al. carried out a mixed-linker approach to obtain a triazine-based framework (Ad2L1), which had good CO₂ adsorption capacity (77.3 mg g⁻¹ at 273 K and 1.0 bar) and CO₂/N₂ selectivity (up to 13). Importantly, the Ad2L1 framework showed remarkable thermal stability (stable up to 400 °C) [10]. Chang et al. reported microporous hydrocarbon particles based on adamantane building blocks, which exhibited high BET surface area (up to 665 m² g⁻¹) and narrow pore size distribution (0.6 nm) [11]. Zulfiqar et al. synthesized a nanoporous amide network based on tetraphenyladamantane (NAN-1), which exhibited ultrahigh thermal stability (stable up to 500 °C) and good CO₂ adsorption capacity (55.7 mg g⁻¹ at 273 K and 1.0 bar) [12]. These excellent physicochemical and hydrothermal stabilities may be attributed to the exclusively aromatic structure and the sole presence of C–C covalent bonds within the framework of these MOP materials [13, 14]. However, compared with MOFs and COFs, most of reported MOPs typically exhibit higher thermal stability but with lower CO₂ adsorption capacity and selectivity over N₂. Furthermore, the large adsorption capacity of microporous frameworks is another significant parameter for their use in CCS. Therefore, there is a need, yet significant challenge, to develop new strategies to synthesize MOPs with higher CO₂ adsorption capacity and selectivity over N₂.

On the other hand, to date, all of the reported microporous organic polymers are found in powder form with poor processability, which has severely limited their application in gas storage/separation. The

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development of MOPs with better processability and chemical inertness is beneficial to expand the potential of these microporous frameworks. Recently a small number of novel strategies has received great attention to tackle these challenges [15–18]. However, it is still difficult to fully address these limitations for any industrial application due to the inefficiency of these strategies.

With these considerations in mind, herein, we report the synthesis of microporous frameworks based on adamantane (**MF-Ad-1** and **MF-Ad-2**) via Sonogashira-Hagihara coupling between 4,4'-diethynylbiphenyl and aryl halides. The gas-adsorption properties of these microporous frameworks have been evaluated and exhibit excellent selectivity for CO₂ over N₂. More interestingly, these microporous frameworks also showed superhydrophobicity when coated with polydimethylsiloxane (PDMS), which were particularly useful for the separation of hydrocarbons/water. These studies elegantly extend the applications of microporous organic frameworks, particularly in CCS and adsorbing hazardous organic pollutants.

2. Experimental

2.1. Materials

Unless otherwise stated, all starting materials were purchased from Guoyao Chemical Reagent Co., Ltd. (China). Tetrahydrofuran (THF, anhydrous, 99.5%), triethylamine (TEA, anhydrous, 99.5%), dimethyl formamide (DMF, anhydrous, 99%), toluene (99%) and rhodamine B (99%) were purchased from Shanghai Macklin Biochemical Co., Ltd. (China). 1,3-Dibromobenzene (anhydrous, 99.5%), 2-methyl-3-butyn-2-ol, 4,4'-dibromobiphenyl, copper(I) iodide [CuI], tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄] and dichlorobis(triphenylphosphine)palladium(II) [Pd(PPh₃)₂Cl₂] were all purchased from Sigma-Aldrich Co., Ltd. (UK). 4,4'-diethynylbiphenyl (**DPE**) was synthesized according to the published method except that 2-methyl-3-butyn-2-ol was used instead of trimethylsilylacetylene [6]. 3,3',5,5',7,7'-Hexakis(4-bromophenyl)-1,1'-biadamantane (**HBPBA**) was synthesized according to published methods [19]. The PDMS (Sylgard 184) was obtained from Dow Corning Co., Ltd. (China). The stainless-steel meshes (30 mm × 40 mm) with a mesh opening size of 0.55 mm were obtained from Anping Park Lin Metal Wire Mesh Co., Ltd. (China). The stainless-steel meshes were pretreated by washing with hydrochloric acid (2.0 M), water and acetone for three times and then dried at 80 °C.

2.2. Synthesis of 1,3,5,7-tetrakis(1,3-bromophenyl)adamantane (TBBPA)

1,3-dibromobenzene (70 mL) was added to a mixture of 1,3,5,7-tetrabromoadamantane (5.0 g, 11.1 mmol) and AlCl₃ powder (4.0 g, 30.0 mmol), at 0 °C. The mixture was then stirred at ambient temperature for 36 h. After quenching the reaction by adding ice water, the organic layer was diluted with chloroform and filtered. The filtrate was washed with deionised water and brine and then dried over magnesium sulfate. After evaporation to remove volatiles, 1,3,5,7-tetrakis(1,3-bromophenyl)adamantane was obtained as a white solid from the crystallization in chloroform (9.6 g, 81% yield). ¹H NMR (DMSO-*d*₆, 400 MHz): δ (ppm) 7.80 (s, 8H), 7.69 (s, 4H), 2.05 (s, 12H); ¹³C NMR (CDCl₃-*d*₃, 400 MHz): δ (ppm) 150.7, 131.5, 126.2, 122.4, 45.3, 38.3. Anal. Calcd for C₃₄H₂₄Br₈: C, 38.10; H, 2.26; Found: C, 38.11; H, 2.21.

2.3. Synthesis of networks MF-Ad-1 and MF-Ad-2

For **MF-Ad-1**, a mixture of HBPBA (480.0 mg, 0.4 mmol), DPE (242.4 mg, 1.2 mmol), Pd(PPh₃)₂Cl₂ (28.1 mg, 0.04 mmol), CuI (152.4 mg, 0.08 mmol), dimethyl formamide (DMF) (60 mL) and triethylamine (TEA) (60 mL) were stirred in a 250 mL Schlenk flask and then heated to 90 °C for 48 h under argon atmosphere. After cooling to ambient temperature, the mixture was filtered, and the precipitate was

washed with hot THF, DMF, 2.0 M hydrochloric acid, 2.0 M sodium hydroxide, water and methanol in succession. Importantly, the polymer was rigorously stirred at 2000 rpm during acid and base immersions for 30 min and the process was repeated 3 times. After filtration, the insoluble powder was dried under vacuum at 100 °C for at least 24 h to give **MF-Ad-1** (492 mg, 93% yield) as a light yellow fluffy powder. Anal. Calcd for C₁₀₄H₇₂: C, 94.54; H, 5.46. Found: C, 92.12; H, 5.75.

The synthetic procedure of **MF-Ad-2** was similar to that of **MF-Ad-1**, except that the linker (knot) used was TBBPA (321.6 mg, 0.3 mmol), instead of HBPBA (480.0 mg, 0.4 mmol), which also afforded a light yellow fluffy powder (382 mg, 94% yield). Anal. Calcd for C₈₀H₅₄: C, 94.67; H, 5.33. Found: C, 91.83; H, 5.57.

2.4. Preparation of superhydrophobic MF-Ad-based mesh films

The following is an example for **MF-Ad-1**: **MF-Ad-1** (0.2 g) was added to a mixture of PDMS and toluene (at a total ratio of PDMS/toluene/**MF-Ad-1** of 1.1/10/0.2, w/w/w), at room temperature, and then the mixture was treated by ultrasonic tip-sonication for 30 min. A stainless-steel mesh was immersed into the mixture, dried at 85 °C, then repeated 20 times until the **MF-Ad**-based mesh films had successfully formed.

2.5. Characterization

Fourier transform infrared (FTIR) spectra were obtained using a Thermo Electron Nicolet-6700 spectrometer. ¹H NMR, ¹³C NMR and solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker AVANCE III 400 MHz Superconducting Fourier in deuterated chloroform (CDCl₃) or dimethyl sulfoxide-*d*₆ (DMSO-*d*₆). Powder X-ray diffraction (XRD) data were collected on a Bruker X'pertpro multipurpose diffractometer (MPD). Samples were mounted on a sample holder and measured using Cu Kα radiation with 2θ range of 5° to 70°. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere on a NETZSCH STA 409 PC thermal analyzer with a heating rate of 10 °C min⁻¹ from ambient temperature to 800 °C. The nitrogen adsorption-desorption isotherms were measured on a 3H-2000 PM2 analyzer and the adsorption of hydrogen, methane and carbon dioxide was measured on 3H-2000PS2 apparatus at 77 K/1.0 bar (H₂) and 273 K/1.0 bar (N₂, CH₄ and CO₂). SEM analysis was performed on a Hitachi S-3400N scanning electron microscope to investigate the surface morphology of the polymers. Elemental analysis was performed with a Perkin Elmer Series II 2400 elemental analyzer. All samples were dried at 100 °C for 24 h under vacuum prior to measurement.

3. Results and discussion

The synthesis of two microporous organic frameworks, **MF-Ad-1** and **MF-Ad-2**, was accomplished via Pd(0)/CuI-catalyzed Sonogashira-Hagihara cross coupling polymerization. These frameworks were constructed using two different 3D building links (or 'knots'), HBPBA and TBBPA, as illustrated in Scheme 1. All of the building units dissolved in the solvent, leading to good yields (93% for **MF-Ad-1** and 94% for **MF-Ad-2**) under mild reaction conditions. After the reaction, however, these frameworks were found to be insoluble in conventional organic solvents, such as methanol, chloroform and tetrahydrofuran, suggesting the formation of crosslinked structures.

3.1. Structural characterization

¹H NMR and ¹³C NMR spectra (Figs. S1 and S2, ESI) indicate the successful synthesis of the building knot (TBBPA). Additionally, the molecular structure of the **MF-Ad** networks was confirmed by FTIR and ¹³C CP/MAS solid-state NMR spectroscopies. As shown in Fig. 1, the two **MF-Ad** networks showed bands at 3031 and 1599 cm⁻¹, arising

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