



# Synthesis and properties of organic microporous polymers from the monomer of hexaphenylbenzene based triptycene



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## ABSTRACT

An expanded triptycene (hexaphenylbenzene based triptycene) monomer was synthesized from triiodotriptycene. Using this monomer, two kinds of organic microporous polymers **HTP-A** and **HTP-B** were prepared by Friedel–Crafts and Scholl reactions. Their structure and properties were characterized by FT-IR, solid <sup>13</sup>C NMR, powder XRD, SEM, TEM and gas absorption. Nitrogen sorption analysis displayed that the BET surface areas are 569 and 914 m<sup>2</sup> g<sup>-1</sup> for **HTP-A** and **HTP-B**, respectively. For **HTP-B**, they can reversibly absorb 1.09 wt % H<sub>2</sub> (1.0 bar and 77 K) and 10.3 wt% CO<sub>2</sub> (1.0 bar and 273 K), respectively.

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## 1. Introduction

Because of their potential applications in gas storage [1], separation [2], catalysis [3], sensor [4] and drug delivery [5], organic microporous polymers (OMP) have attracted great interest with the characteristics of low mass density, easy functionality and high stability. During the last decade, OMPs have been developed into different kinds, such as covalent organic frameworks (COFs) [6–8], hypercross-linked polymers (HCPs) [9], polymers of intrinsic microporosity (PIMs) [10], and conjugated microporous polymers (CMPs) [11,12]. The design and synthesis of novel building blocks has been recognized as one of the most important driving forces for the great advance in OMP. So far, some landmark research results of OMPs have been reported by utilization of three-dimensional building blocks, such as tetraphenyl methane and tetraphenyl silane [13,14].

Triptycene and its derivatives [15,16], a class of interesting

compounds with three-dimensional rigid framework, have been found to have attractive applications in supramolecular chemistry [17–24]. Recently, more and more research groups have proved that triptycenes are useful building blocks for construction of microporous polymers. Swager and co-workers [25,26] have prepared a series of triptycene-based linear poly(aryl ether)s with specific surface area of 400 m<sup>2</sup> g<sup>-1</sup>. The specific surface area of McKeown's three-dimensional triptycene-based PIMs [27,28] and Han's triptycene-based microporous poly-(benzimidazole) networks [29] can be up to 1760 and 600 m<sup>2</sup> g<sup>-1</sup>, respectively. Zhao used triptycene scaffold and prepared a polymeric 2D monolayers [30]. Our group synthesized a series of microporous polymers based on triptycene and demonstrated that triptycenes are a kind of promising building blocks in construction of porous materials [31–34].

Hexaphenylbenzenes (HPBs) [35] with propeller-like structure, are attractive building blocks for the synthesis of microporous organic polymers. HPB-PIM and HPB-based porous organic polymers (HPOP)s were reported by McKeown [36] and Han [37], respectively. Recently, we designed and synthesized a novel microporous polymer from hexaphenylbenzene based triptycene monomer by nickel (0)-catalyzed Ullmann cross-coupling reaction,

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which displayed good ability for gas absorption [38].

Herein, we employed two Tan's cost-effective and versatile synthetic strategies [39,40] to crosslink hexaphenylbenzene based triptycene monomers to obtain two kinds microporous polymers (**HTP-A** and **HTP-B**), which displayed high surface area, thermal stability and good CO<sub>2</sub> adsorption.

## 2. Experimental section

### 2.1. Materials and synthesis

2, 6, 14-triiodotriptycene was synthesized according to our previous work [41]. Other chemicals, and solvents were commercial and used as received.

#### 2.1.1. Synthesis of **2**

To a mixture of triiodotriptycene **1** (200 mg, 0.315 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (37 mg, 0.036 mmol) and CuI (11.6 mg, 0.061 mmol) in Et<sub>3</sub>N (20 mL) was dropwise added a Et<sub>3</sub>N (20 mL) solution of phenylacetylene (200 μL, 0.99 mmol), the resulting mixture was stirred for 24 h at 70 °C under argon, then Et<sub>3</sub>N was removed by rotary evaporator. The residue was dissolved with dichloromethane (10 mL), and washed with hydrochloric acid solution (1 M, 20 mL × 2). The aqueous solution was extracted with dichloromethane (2 × 50 mL). The organic extracts were combined, washed successively with aqueous NaHCO<sub>3</sub> (2 × 50 mL) and brine (2 × 50 mL), dried with Na<sub>2</sub>SO<sub>4</sub>, concentrated, and chromatographed on silica gel eluted with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:3) to give the product **2** as a white solid. Yield: 68.0%. M.p. 184–185 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.45 (s, 1H), 5.46 (s, 1H), 7.25 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.33–7.37 (m, 9H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.50–7.53 (m, 6H), 7.60 (d, *J* = 1.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 53.4, 53.5, 88.8, 89.4, 120.49, 120.42, 123.3, 123.77, 123.80, 126.9, 128.2, 128.3, 129.1, 131.6, 144.47, 144.49, 144.51, 144.57. EI-MS: *m/z* 555 (M<sup>+</sup>). Anal. Calcd for C<sub>44</sub>H<sub>26</sub>: C, 95.28; H, 4.72. Found: C, 95.01; H, 5.08.

#### 2.1.2. Synthesis of hexaphenylbenzene based triptycene (**HT**) monomers **3**

To a mixture of tetraphenylcyclopentadienone (215 mg, 0.560 mg) and **2** (100 mg, 0.181 mmol) was added diphenyl ether (1.5 mL), and the resulting mixture was refluxed for 48 h under argon, the reaction mixture was poured into MeOH (200 mL). A precipitate thus formed was collected by filtration and subjected to column chromatography on silica gel with dichloromethane and petroleum ether (1:3) as eluent to give the product **3** as a white solid. Yield: 52.0%. M.p. >300 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.05 (s, 1H), 4.28 (s, 1H), 6.29–6.36 (m, 9H), 6.48–6.61 (m, 9H), 6.72–6.82 (m, 66H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 52.8, 53.0, 121.6, 125.02, 125.10, 125.3, 125.4, 126.1, 126.4, 126.5, 126.67, 126.73, 128.0, 128.1, 129.89, 129.92, 131.2, 131.3, 131.4, 131.58, 131.64, 131.72, 135.8, 136.3, 139.7, 140.0, 140.12, 140.19, 140.23, 140.33, 140.37, 140.40, 140.46, 140.49, 140.68, 140.72, 140.78, 140.82, 142.4, 143.1, 143.7, 143.9. MALDI-TOF-MS: *m/z* 1647 (M + Na<sup>+</sup>), 1663 (M + K<sup>+</sup>). Anal. Calcd for C<sub>128</sub>H<sub>86</sub>: C, 94.66; H, 5.34. Found: C, 95.02; H, 5.50.

#### 2.1.3. Synthesis of **HTP-A**

HPB-Triptycene (240 mg, 0.15 mmol, 1.0 equiv.) and formaldehyde dimethyl acetal (171 mg, 2.25 mmol, 15.0 equiv.) were dissolved in 1,2-dichloroethane (20 mL) in a round-bottom flask, FeCl<sub>3</sub> (365 mg, 2.25 mmol, 15.0 equiv.) was added. The reaction mixture was magnetically stirred and heated to 80 °C for 24 h. Then after cooling to room temperature, 80 mL methanol was added and stirred for another 2 h. The crude product was filtered, washed with methanol and further purified by soxhlet extraction in methanol for 24 h. Dried in vacuo at 60 °C for 24 h, an orange-brown powder was

obtained. Yield: >100%.

#### 2.1.4. Synthesis of **HTP-B**

HPB-Triptycene (195 mg, 0.12 mmol, 1.0 equiv.) was dissolved in chloroform (10 mL) in a round-bottom flask with magnetic stirring at 60 °C, AlCl<sub>3</sub> (480 mg, 3.60 mmol, 30.0 equiv.) was added. The reaction was proceed at the same temperature for 48 h. Then after cooling to room temperature, 10 mL H<sub>2</sub>O was added slowly to quench the reaction. The crude product was filtered, washed with ethanol once, HCl–H<sub>2</sub>O (*v/v* = 2/1) twice, ethanol once and further purified by soxhlet extraction in ethanol for 48 h. Dried in vacuo at 70 °C for 24 h, a brown powder was obtained. Yield: 91.7%.

### 2.2. Physical measurements of **HTPs**

Elemental analyses were performed on a Perkin–Elmer 240 elemental analyzer. TGA measurements were performed on Pyris1 TGA at a heating rate of 10 °C min<sup>-1</sup> to 800 °C under a nitrogen atmosphere and the flow rate was 10 mL min<sup>-1</sup>, an empty Al<sub>2</sub>O<sub>3</sub> crucible was used as reference. IR spectra were measured on a Tensor 27 OPUS (Bruker) FTIR spectrometer with KBr pellets. Field-emission scanning electron microscopy (FE-SEM) images were obtained on a FEI Sirion 200 instrument. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G220 instrument. X-Ray powder diffraction (XRD) patterns were recorded on X'Pert PRO X-ray diffractometer with Cu–K radiation with a wavelength of 0.1542 nm. The <sup>13</sup>C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp 100) and pulse delay of 3 s. Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Sample was degassed at 110 °C for 15 h under vacuum before analysis. Hydrogen isotherms were measured at 77 K up to 1.0 bar and CO<sub>2</sub> isotherms were measured at 273 K up to 1.0 bar using a Micromeritics ASAP 2020 volumetric adsorption analyzer with the same degassing procedure.

## 3. Result and discussion

Synthesis of the HT monomer is outlined in Scheme 1. Starting from triiodotriptycene **1**, its palladium-catalyzed Sonogashira coupling reactions with ethynylbenzene in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, CuI, and Et<sub>3</sub>N afforded triethynylation products **2** in good yields, which were then subjected to Diels–Alder reactions with cyclopentadienone to result in the HT monomer **3** in 52% yields. The intermediate **2** and HT monomer **3** were purified with silica gel chromatography and their structures were determined by NMR, MS spectra and elemental analysis.

The synthesis of polymers was carried out following Tan's low-cost synthetic strategies. For **HTP-A**, The polymerization of HT **3** with 3 equiv of formaldehyde dimethyl acetal (FDA) produced brown, insoluble powder with yield in excess of 100%, which may be due to the trapping of iron residues within the networks. For **HTP-B**, the Scholl coupling reaction of HT monomer under the condition of AlCl<sub>3</sub> afford brown powder with yield of 91.7%.

The structures of **HTPs** were initially characterized by FT-IR analysis (Fig. S5 in Supporting Information). The FT-IR spectra of **HTPs** showed similar absorption peaks in the range of the aromatic C–H out-of-plane bending vibration (650–950 cm<sup>-1</sup>) compared with the HT monomer, which suggested that the hexaphenylbenzene structure were kept in the **HTPs** networks. <sup>13</sup>C cross-polarization magic-angle spinning (CP/MAS) NMR analysis confirmed the successful growth of a microporous networks. As shown in Fig. 1, the resonance peaks at δ = 143, 132, 127 and 55 ppm can be assigned to the substituted phenyl carbons (a, b, e, f, i), the

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