



Facile one-pot synthesis of glycoluril-based porous organic polymers



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ARTICLE INFO

Article history:

Received 23 September 2014

Received in revised form

13 December 2014

Accepted 31 December 2014

Available online 13 January 2015

Keywords:

Porous organic polymers

Glycoluril

Carbon dioxide uptake

ABSTRACT

Several polymers are constructed through a facile one-pot approach connecting glycoluril with different aldehydes using *p*-toluenesulfonic acid as both catalyst and solvent in a sealed tube at high temperature. Fourier transform infrared and solid-state ¹³C CP/MAS NMR spectroscopy are used to elucidate the final structure of the glycoluril based porous organic polymers. The materials, with Brunauer–Emmet–Teller (BET) specific surface area up to 1010 m² g⁻¹, possess a high carbon dioxide uptake (up to 12.2 wt% (273 K) and 8.3 wt% (298 K) at 1.0 bar) while a methane uptake up to 4.2 wt% (273 K) at 1.0 bar. Furthermore, the polymers exhibit a hydrogen uptake capacity up to 1.37 wt% (77 K) at 1.0 bar.

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1. Introduction

The researches on porous materials are attracting a great deal of attention from the scientific community owing to their promising potential in gas storage and separation [1], catalysis [2,3], and production of carbon materials [4,5]. By merging the advantages of both porous materials and polymers, porous organic polymers exhibit some unique characteristics in comparison with the metal–organic frameworks (MOFs) because of replacement of the coordination bonds employed in MOFs [6,7] with strong covalent bonds, from which porous polymers would possess better thermal and hydrothermal stabilities [8]. Up to now, a wide variety of porous organic materials have been synthesized through Sonogashira–Hagihara coupling reaction [9], Suzuki–Miyaura cross-coupling chemistry [10], Glich coupling reaction [11], self condensation of aromatic nitriles [12], and benzoin condensation [13]. However, most of these reactions are catalyzed by metal-containing catalysts such as Pd, Cu, Ni, and Zn, which are not environmentally friendly and may induce the water and soil pollution. Meanwhile, a majority of the monomers are synthesized through multiple steps at high cost. Thus, inexpensive and convenient raw materials and facile routes with non-metallic catalysts are essential for the preparation of porous polymer.

The synthesis of glycoluril was achieved by Schiff in 1877 through a condensation reaction of urea and glyoxal [14]. During the past several decades, glycoluril, as a derivative of the simple

compound of urea, has played a promising role in the construction of characteristic structures in both covalent and supramolecular ways [15]. Great attention has been paid for the purpose of making use of the intriguing molecule to fabricate versatile materials such as cucurbit[6]uril [16] and its complexes [17,18]. A lot work has been done to pave the way for broaden the application of cucurbituril homologues and derivatives on the basis of the supramolecular assembling [19]. Some researches focus on other host–guest complexes and their binding dynamics in recent years [20–22]. However, there seems no report on glycoluril-based porous polymer so far.

Herein, we demonstrate a simple way to produce porous material from glycoluril. The obtained glycoluril-based porous organic polymers (**GPOPs**) are constructed through the reaction between glycoluril and different aldehydes at high temperature. *p*-Toluenesulfonic acid (TSA) is used as an effective non-metallic acidic catalyst according to the reports [23]. The **GPOPs** possess a high BET specific surface area up to 1010 m² g⁻¹, and a carbon dioxide uptake up to 12.2 wt% (273 K) and 8.3 wt% (298 K) at 1.0 bar, respectively. Given the excellent gas adsorption performance and high BET specific surface area, **GPOPs** may be a competitive candidate for the gas storage and separation materials.

2. Experimental

2.1. Materials

Anhydrous potassium carbonate, anhydrous sodium sulfate, 1,3,5-tribromobenzene, 4-bromobenzaldehyde, 4-formylphenylboronic

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acid, terephthalic aldehyde (**M1**), and *p*-toluenesulfonic acid were purchased from Beijing Chemical Reagent Company. Terephthalic aldehyde was purified by recrystallization in ethanol. The detailed synthesis procedures of 4,4'-biphenyldicarboxaldehyde (**M2**) and 1,3,5-tri(4-formylphenyl)benzene (**M3**) are included in the Supplementary Information. Ethyl acetate, petroleum ether, dichloromethane, acetone, tetrahydrofuran and other chemical reagents were used as received. All condensation reactions to produce **GPOPs** were operated using standard Schlenk line technique.

2.2. Preparation of **GPOPs**

Glycoluril (50.0 mg, 0.35 mmol), terephthalic aldehyde (47.0 mg, 0.35 mmol), and *p*-toluenesulfonic acid (2.0 g) were mixed in a glass tube. The mixture was degassed by at least three freeze–pump–thaw cycles. The tube was frozen at 77 K (liquid nitrogen bath) and evacuated to high vacuum and flame-sealed. After 180 °C for 24 h, the reaction mixture gave a solid product (denoted as **GPOP-1**), which was filtrated and washed with acetone, dichloromethane, and ethanol subsequently. Further purification of the polymer was carried out by Soxhlet extraction with water, ethanol, and dichloromethane for 24 h to give the final product, which was dried *in vacuo* at 120 °C for more than 12 h.

Similar to the preparation of **GPOP-1**, 4,4'-biphenyldicarboxaldehyde (**M2**) and 1,3,5-tri(4-formylphenyl)benzene (**M3**) were used to afford **GPOP-2** and **GPOP-3** respectively.

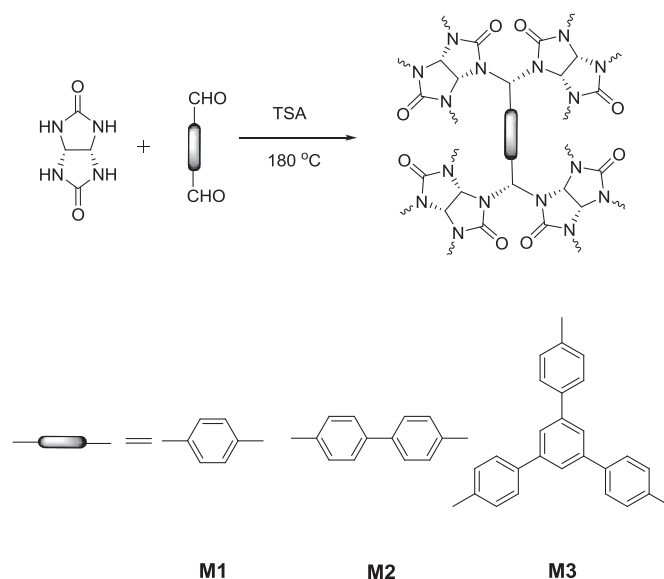
2.3. Instrumental characterization

¹H NMR spectra were recorded on a Bruker DMX400 NMR spectrometer, with tetramethylsilane as an internal reference. Solid-state ¹³C CP/MAS NMR measurements were performed on a Bruker Avance III 400 spectrometer. Elemental analysis for carbon, nitrogen and hydrogen was carried out in duplicate on a Vario EL II elemental analyzer (Elementar). Thermogravimetric analysis (TGA) was performed on a Pyris Diamond thermogravimetric/differential thermal analyzer by heating the samples at 10 °C min⁻¹ to 800 °C in the atmosphere of nitrogen. Infrared (IR) spectra were recorded in KBr pellets using a Spectrum One Fourier transform infrared (FT-IR) spectrometer (PerkinElmer Instruments Co. Ltd, USA). The sample was prepared by dispersing the polymers in KBr and compressing the mixtures to form disks, and 15 scans were signal-averaged. Field-emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope (Hitachi, Japan) operating at an accelerating voltage of 6.0 kV. SEM samples were prepared by dropping an ethanol suspension of **GPOP-1**–**GPOP-3** on a silicon wafer and left to dry in air. Energy dispersive X-ray (EDX) detector was used to analyze the chemical elements of the samples. Nitrogen adsorption–desorption and hydrogen adsorption experimentations were conducted using an ASAP 2020M + C accelerated surface area and porosity analyzer (Micromeritics, USA) at 77 K. Carbon dioxide and methane uptake experimentations were performed by using a TriStar II 3020 accelerated surface area and porosity analyzer (Micromeritics, USA). Before measurement, the samples were degassed *in vacuo* at 120 °C for more than 12 h. The specific surface area value was calculated from the nitrogen adsorption branch by Brunauer–Emmett–Teller (BET) analysis in the relative pressure (*P/P*₀) range from 0.01 to 0.10 (see the Supplementary Information), whereas pore size and pore size distribution were estimated through the original density function theory (DFT). Total pore volume was calculated from nitrogen adsorption–desorption isotherms at *P/P*₀ = 0.95, whereas micropore volume was calculated from nitrogen adsorption isotherm using the *t*-plot method.

3. Results and discussion

The **GPOPs** were prepared by the reaction of glycoluril with multi-formyl compounds. Both dialdehydes and trialdehyde in **Scheme 1** were used to form C–N bonds through nucleophilic addition reaction of carbonyl groups. Müllen group has already used the Schiff base chemistry to fabricate a microporous network with melamine and terephthalaldehyde at high temperature [24]. The monomers (**M2** and **M3**) were synthesized by Suzuki coupling reaction of aromatic halides with formylphenylboronic acid. It is well-known that amino group is a nucleophilic reagent owing to the lone electron pair of nitrogen atom. With acid as a catalyst, the positively charged carbonyl group of aldehyde could be attacked by amino group to form imine group and sequentially imine would react with another amine group for the formation of aminal. Finally, a cross-linked, aminal-type polymer is constructed. The glycoluril and formyl-containing compounds are mixed with *p*-toluenesulfonic acid that is used as both catalyst and solvent in a glass tube. After reaction in sealed tube at 180 °C for 24 h, several polymers are formed. Elemental analysis for carbon, nitrogen, and hydrogen was used to calculate the composition of the materials. It is showed that carbon exhibits a large proportion about 74.9–80.9 wt% and nitrogen accounts for 0.64–0.91 wt% while the content of hydrogen is about 4.71–4.92 wt% for **GPOPs**. (Table S1, Supplementary Information). All the polymers are stable and insoluble in common organic solvents such as dichloromethane, ethanol, and acetone. Additionally, the obtained polymers show a high thermal stability from the results of TGA (Fig. S1, Supplementary Information). The weight loss below 5% up to 150 °C can be ascribed to the evaporation of trapped solvent and adsorbed water or carbon dioxide, which cannot be cleaned up from the micropores during the post-treatment and drying procedure. All of the materials will maintain their stability when heated until 300 °C.

FT-IR spectroscopy can be used to investigate the changes of the secondary amine and aldehyde groups in the monomers. It is shown in all the spectra (Fig. 1 and Fig. S2, Supplementary Information) that the characteristic stretching vibration mode of N–H at ~3200 cm⁻¹ fades away in **GPOP-2**. The signals at 1600 and 1200 cm⁻¹ are related to the stretching vibration mode of C=O and C–N from the glycoluril, indicating the structure of glycoluril is



Scheme 1. Schematic representation of the possible structures of glycoluril-based porous organic polymers.

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