Knitting hypercrosslinked conjugated microporous polymers with external crosslinker

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ABSTRACT

A new series of hypercrosslinked polymers were efficiently synthesized by knitting rigid aromatic building blocks using a novel external crosslinker (1,4-dimethoxybenzene, DMB) which result in a conjugated microporous structure. This knitting hypercrosslinked conjugated microporous polymers (HCCMPs) are predominantly microporous and exhibit high surface area of up to 800 m^2 g^{-1}, which also show comparable gas uptake properties reaching 1.14 wt. % H_2 adsorption at 1.13 bar/77 K, and 12.72 wt. % CO_2 adsorption at 1.13 bar/273 K, respectively. The extended π-conjugated structure and the three-dimensional network of $\pi-\pi$ stacked aryl rings enable these HCCMPs good luminescence properties and high electrical conductivity.

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1. Introduction

Conjugated microporous polymers (CMPs) combining permanent microporosity with extended π-conjugated skeletons have been the subject of much interest in a wide range of applications including catalysis [1], CO_2 capture [2], separation [3], energy storage [4], light harvesting [5], luminescence [6] and sensing [7]. Considering the structure demanded, most CMPs and related networks are based on rigid aromatic building blocks that must be covalently linked by a π-conjugated bond via the carbon—carbon coupling reactions [8,9]. Therefore, a large number of challenges exist in spite of the successful examples, the most important aspects are as follows: (i) the monomers designed to obtain specific electrical or optoelectronic properties are expensive and hard to prepare, (ii) the transition metal catalysts or noble metal catalysts used in C—C coupling methods are expensive and very rare.

Hypercrosslinked polymers (HCPs) [10—12] are a class of low-cost scalable porous materials that have been produced commercially for some years [13]. These materials are predominant microporous and mainly prepared by the Friedel—Crafts alkylation reaction [14—16]. The porosity in these materials derived from the interspace between non-close-packed polymer chains is due to the extensive crosslinking reaction [17,18]. The highly crosslinked nature provides these materials high surface area, good thermal and chemical stability as well as lightweight property. Breakthrough in this field is the invention of the "knitting" polymers [12] which were synthesized by a simple one-step Friedel—Crafts alkylation of low functionality aromatic monomers using a formaldehyde dimethyl ether crosslinker. Indeed, the monomer can be as simple and inexpensive as benzene, and the mild synthesis conditions as well as the cheap solvent should allow economical and larger-scale production of such materials. This strategy is versatile and flexible and a wide range of possible structural building block can be employed in the synthesis of functional materials with diverse pore structures and unique properties for tremendous applications in CO_2 capture [19,20], separation [21,22], heterogeneous catalysis [23,24], drug release [25] and so on. Despite the advantage of synthetic diversification, there is still a drawback that should not be ignored. The FDA crosslinker acts as a bridge to link the neighbouring aromatic rings but remained methylene groups in the resulting networks which interdicted the extension of the conjugate structure from the monomers. This defect limited the potential application in electric/photoelectric materials that should be of

prime importance in the energy fields. Recently, a cost-effective approach was reported presenting a facile construction of conjugated structure which involves the elimination of two aryl-bound hydrogen atoms accompanied by the formation of a new aryl–aryl bond based on the Scholl reaction [26]. This general bottom-up approach abandoned the usage of crosslinker and directly linked a variety of rigid functionalized monomers without destroying the conjugated topology. However, this strategy prescribe a limit to the variety of the monomer that no functional groups can be existed on the aromatic rings. Besides, the harsh reaction conditions and complex experimental operation are difficult to achieve in the real industrial production.

Here, we report a simple method for the preparation of hypercrosslinked conjugated microporous polymers by taking in the concept of "knitting". Instead of the methylene kind crosslinker, we choose a new external crosslinker (1,4-dimethoxybenzene, DMB) which contains the benzene ring. During the hypercrosslinking reaction, 1,4-dimethoxybenzene serves as the bridge to link with other benzene derivatives and benzene rings were introduced among aromatics to extend the long-range conjugated structure in the resulting networks. We hypothesized that polymerization of aromatic monomer with this novel crosslinker would be an effective strategy for generating conjugated HCPs with electric/photoelectric properties.

2. Experimental section

2.1. Materials

Benzene, biphenyl, methylbenzene, chlorobenzene, phenol, $FeCl_3$ (anhydrous), methanol and nitrobenzene were obtained from National Medicines Corporation Ltd. of China, all of which were of analytical grade and were used as received. *p*-Dimethoxybenzene (DMB, Aladdin, 98%) and 1,3,5-triphenylbenzene (Alfa Aesar, 98%) were also used as received.

2.2. Synthesis of hypercrosslinked conjugated microporous polymers

2.2.1. Synthesis of HCCMPs-1 (benzene network)

Typically, anhydrous ferricchloride (2.44 g, 15.02 mmol) was added to a mixture solution of benzene (0.13 g, 1.67 mmol) and DMB (0.69 g, 4.99 mmol) in nitrobenzene (15 ml) with magnetic stirring at room temperature for several minutes to get a homogeneous mixture. After which the solution was heated at 80 °C for 5 h to form a primary network, and then heated at 120 °C for 24 h to complete the reaction and produced a microporous polymer (condenser was used for reflux). After the reaction, the resulting solid material was washed with hydrochloric acid and methanol for several times until the filter liquor was practically colourless. And then, the remained product was Soxhlet extracted in methanol for 24 h following by a drying process in a vacuum oven at 60 °C for 24 h. Yield: ~118% (Equation S1, Supporting Information).

2.2.2. Synthesis of HCCMPs-2 (biphenyl network)

This HCCMPs-2 was prepared by treating biphenyl (0.10 g, 0.67 mmol), DMB (0.69 g, 4.99 mmol) and anhydrous ferricchloride (2.44 g, 15.02 mmol) in 15 ml nitrobenzene. Yield: ~139% (Equation S1, Supporting Information).

2.2.3. Synthesis of HCCMPs-3 (1,3,5-triphenylbenzene network)

This HCCMPs-3 was prepared by treating 1,3,5-triphenylbenzene (0.15 g, 0.49 mmol), DMB (0.69 g, 4.99 mmol) and anhydrous ferricchloride (2.44 g, 15.02 mmol) in 15 ml nitrobenzene. Yield: ~130% (Equation S1, Supporting Information).

2.2.4. Synthesis of HCCMPs-4 (methylbenzene network)

This HCCMPs-4 was prepared by treating methylbenzene (0.16 g, 1.73 mmol), DMB (0.69 g, 4.99 mmol) and anhydrous ferricchloride (2.44 g, 15.02 mmol) in 15 ml nitrobenzene. Yield: ~148% (Equation S1, Supporting Information).

2.2.5. Synthesis of HCCMPs-5 (chlorobenzene network)

This HCCMPs-5 was prepared by treating chlorobenzene (0.19 g, 1.68 mmol), DMB (0.69 g, 4.99 mmol) and anhydrous ferricchloride (2.44 g, 15.02 mmol) in 15 ml nitrobenzene. Yield: ~107% (Equation S1, Supporting Information).

2.2.6. Synthesis of HCCMPs-6 (phenol network)

This HCCMPs-6 was prepared by treating phenol (0.16 g, 1.70 mmol), DMB (0.69 g, 4.99 mmol) and anhydrous ferricchloride (2.44 g, 15.02 mmol) in 15 ml nitrobenzene. Yield: ~170% (Equation S1, Supporting Information).

2.2.7. Synthesis of HCCMPs-7 (crosslinker network)

This HCCMPs-7 was prepared by treating DMB (0.69 g, 4.99 mmol) only and anhydrous ferricchloride (2.44 g, 15.02 mmol) in 15 ml nitrobenzene. Yield: ~152% (Equation S1, Supporting Information).

2.3. Characterizations

Polymer surface areas, N_2 adsorption isotherms (77 K), pore size distributions, CO_2 uptake volumetric analysis (up to 1.13 bar, 273 K/ 298 K) and H_2 uptake volumetric analysis (up to 1.13 bar, 77 K) were measured using Micromeritics ASAP 2020 M surface area and porosity analyser. Before analysis, the samples were degassed at 110 °C for 8 h under vacuum (10^{-5} bar). The surface areas were calculated from nitrogen adsorption data by Brunauer–Emmett–Teller (BET) or Langmuir analysis. Pore size distributions were calculated by DFT methods via the adsorption branch. FT-IR spectra were recorded under ambient conditions in the wave number range of 4000–400 cm^{-1} using a Bruker VERTEX 70 FT-IR Spectrometer. Solid-state NMR spectra were obtained on a Bruker Avance II WB 400 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp100) and pulse delay of 3 s. Elemental analysis (EA) was performed on a VarioMicro cube Elemental Analyser (Elementar, Germany). Thermogravimetric-analysis (TGA) measurements were performed on a PerkinElmer Instruments Pyris1 TGA from room temperature to 800 °C with a heating rate of 10 °C/min under nitrogen flow. Transmission electron microscopy (TEM) images were taken on a Tecnai G20 microscope (FEI Corp. USA) instrument operated at an accelerating voltage of 200 kV. Polymer morphologies were investigated with a FEI Sirion 200 field emission scanning electron microscope (FE-SEM). Before measurement, the samples were sputter coated with platinum. Fluorescence excitation and emission spectra were obtained at solid state using a FP-6500 fluorescence spectrometer (Jasco, JPN). Fluorescence images were observed in solution under a UV lamp and the samples were well suspended in THF in quartz cuvettes.

2.4. HCCMPs dispersed THF solution

A typical procedure to get the THF solution was as followed: 10 mg of each sample was suspended in 10 ml THF solvent, after ultrasonic dispersion for several minutes, the insoluble sample was separated from the solution by centrifugation. Finally, the solid sediment was removed to get a clear THF solution of polymer networks.