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Design and synthesis of conjugated polymers of tunable pore size distribution

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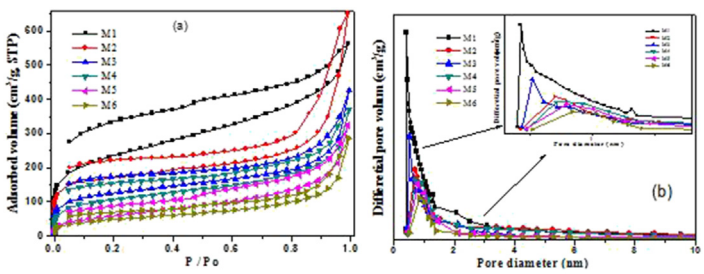
HIGHLIGHTS

- Microporous conjugated polymers were prepared by Yamamoto coupling.
- Pore structure of microporous polymers could be tuned by chaining monomers.
- H_2 and CO_2 storage properties of microporous polymers were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Conjugated microporous polymers of tunable pore size distribution were synthesized by Yamamoto homo-coupling or co-coupling of 1,3,5-tris(4-bromophenyl)benzene with five chaining monomers of different strut length, respectively. Conjugated microporous polymers with apparent BET surface area in the range from 172 to 820 $m^2\ g^{-1}$ were prepared. The materials were found to have excellent microporosity, which could be accurately tuned by changing the strut length of chaining monomers. It was revealed that copolymerization of the core monomer and several chaining monomers with different strut length was an effective strategy to fine-tuning properties of the materials. Moreover, the incorporation of "flexible" double bonds into the chaining monomers could further promote this strategy. H_2 and CO_2 adsorption capacity of conjugated microporous polymers were also systematically investigated.

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1. Introduction

Porous organic polymers (POPs) have drawn considerable attentions owing to their potential applications in the fields such as in catalysis, sensing, optoelectronics, light harvesting as well as gas storage and separation [1–10]. According to the IUPAC classification [11], microporous polymers are defined as polymeric materials with pore diameter smaller than 2 nm. Up to now, various porous polymer materials such as covalent organic frameworks (COFs) [12,13], covalent trianzine frameworks (CTFs) [14,15], conjugated microporous polymer networks (CMPs) [16,17], porous aromatic frameworks (PAFs) [18,19], polymers of intrinsic microporosity (PIMs) [20,21], porous polymer networks (PPNs) [22] and hypercrosslinked porous polymers (HCPs) [23,24] were successfully prepared in the past decade years. Yaghi and co-workers [12] successfully synthesized COF-103 with BET surface area of 4210 m^2/g. Based on tetraphenylmethane subunits, Zhu group [22] designed and prepared microporous polymers with BET surface areas of

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5640 m^2/g. Moreover, another polymers PPN-4 from Zhu group [25] exhibited permanent porosity with extremely high BET surface area of 6461 m^2/g. POPs have excellent properties such as light weight, high porosity, physicochemical stability, microporosity tunability and physichemical functions, which make it show great advantages over metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZTFs), active carbon.

Organic chemistry provides many excellent direct synthesis protocols for the generation of porous polymer materials. For example, Sonogashira-Hagihara cross-coupling reaction has been applied to prepare tetrathiafulvalene-conjugated microporous polymers [26], and Suzuki coupling reaction were also used for the production of core–shell conjugated microporous polymers [27]. Carbazole-based conjugated microporous polymers have been prepared via oxidative polymerization in the presence of $FeCl_3$ or $AlCl_3$ as Lewis catalysts [28,29]. Microporous polymers PS4AC1/PS4AC2 derived from the trimerizations of acetylinic compounds in the presence of $Co_2(CO)_8$ as catalyst was reported by Yu and co-works [30]. However, the application of transition metal catalysis inevitably leaves the metal elements in the materials.

On the other hand, Yamanoto coupling technique is also an interesting route to prepare CMPs. Yamanoto reaction are often carried out by coupling halogen-functionalized monomers with bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)) as a catalyst [31]. In the present work, we described the preparation and the characterization of several novel CMPs with controllable pore size distribution. The coupling reaction were conducted by using 1,3,5-tris(4-bromophenyl)benzene as a core monomer and several dibromo-compounds with different length as the chaining monomers. H_2 and CO_2 storage capacity of the materials were also systematically investigated and discussed.

1.1. Characterization

Nitrogen sorption porosimetry was performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer. The experiments were carried out at the temperature of liquid nitrogen (77.3 K). The samples were first heated in a tube under vacuum at 120 °C for 20 h to remove adsorbed materials from the surface. The related data were manipulated using the software supplied to yield the relevant porosity parameters. Pore size distribution curves and the pore volumes of CMPs were derived from the adsorption branches of the isotherms using the nonlocal density functional theory (NL-DFT).

FT-IR spectra were collected in transmission mode in KBr pellets at room temperature on a FTIR-2000 spectrometer (Perkin-Elmer in America). All spectra were measured with 16 scans at a resolution of 4 cm^{-1} using a blank KBr disk as background followed by baseline correction.

^{13}C cross-polarization, magic angle spinning (CP/MAS) nuclear magnetic resonance spectra were recorded on a AVANCE III 400 MHz spectrometer (BRUKER Inc., Switzerland) equipped with a 4-mm HXY T3 PENCIL probe. CP/MAS NMR experiments were carried out at an MAS rate of 10.0 kHz operating at 100.61 MHz for ^{13}C, and 400.13 MHz for ^{1}H. The samples packed into a standard 4-mm (external diameter) zirconia rotor with a volume of 160 μL and capped by a Teflon spacer. All the spectra were obtained at the spinning rate of 10 kHz.

The elemental analysis was carried out on X-ray photoelectron spectroscopy (XPS), which have 180° double hemisphere analyzer with 128 channel detector and aluminum Ka micro gathered monochromator to obtain a facula of size in the range of 5 μm–400 μm. The energy of ion gun can be tuned from 100 to 4000 eV and the resolution of XPS can reach 0.5 eV.

Powder X-ray diffraction data were collected on a Bruker X'pert pro multipurpose diffractometer (MPD). Samples were mounted on a high-throughput Al plate and measured in transmission mode using Cu Kα radiation with a 2θ range of 5°–30°.

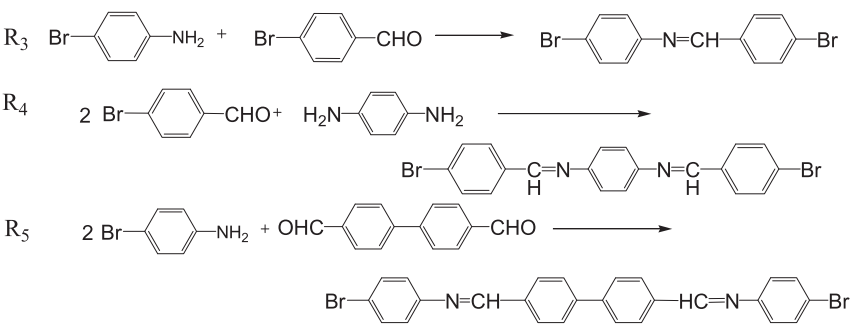
2. Experimental section

2.1. Materials

Tetrahydrofuran (THF) and dimethylformamide (DMF) were purified by distillation with CaH_2. 1,3,5-Tris(4-bromophenyl)benzene (TBPB, **Z1**) was synthesized with slight modification according to the method reported by Wang et al. [32] (Ni(COD)), 2,20027-bipyridyl, 1,5-cyclooctadiene, 4-bromoaniline, *p*-bromo benzaldehyde, *p*-phenylenediamine, benzidine, 1,4-Dibromobenzene (**R_1**), 4,4′-dibromo biphenyl (**R_2**), and various solvents were all purchased from commercial sources (Aladdin, Sigma-Aldrich) and used without further purification.

2.2. Synthesis of chaining monomers

4-bromoaniline (0.01 mmol, 1.7203 g), *p*-bromo benzaldehyde (0.01 mmol, 1.8502 g) or *p*-bromo benzaldehyde (0.01 mmol, 1.8502 g), *p*-phenylenediamine (0.005 mmol, 0.5407 g) or *p*-bromo benzaldehyde(0.01 mmol, 1.8502 g), and benzidine (0.005 mmol 0.9212 g) were dissolved in 50 mL ethanol, and the solution was added into a 100-mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser. The mixture was heated to reflux for 6 h. The precipitates were separated and washed with the de-ionized water to obtain the chaining monomers **R_3** (white tabular crystal in 85% yield), **R_4** (khaki powder in 83% yield) or **R_5** (faint yellow blocky particle in 78% yield). (The NMR spectra of the chaining monomers were provided in Fig. S1 in Supporting Information).



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