



# Bifunctionalized conjugated microporous polymers for carbon dioxide capture



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## ABSTRACT

A novel kind of bifunctionalized conjugated microporous polymers containing sultone and hydroxyl groups has been synthesized via palladium-catalyzed Sonogashira–Hagihara cross-coupling reaction of bromophenol blue with 1,4-diethynylbenzene or 1,3,5-triethynylbenzene. The resulting polymers show high specific surface area up to 1470 m<sup>2</sup> g<sup>-1</sup> and good thermal stability. **BFCMP-2** exhibits a hydrogen uptake ability of 156 cm<sup>3</sup> g<sup>-1</sup> (~1.39 wt%) at 77 K/1.13 bar and a carbon dioxide uptake capacity of 2.77 mmol g<sup>-1</sup> at 273 K/1.13 bar. Compared with most other reported non-functionalized conjugated microporous polymers, both of the bifunctionalized polymer networks show relatively high isosteric heat of CO<sub>2</sub> adsorption (25 kJ mol<sup>-1</sup>) due to the introduction of the polar functional groups of sultone and hydroxy enhanced the binding affinity between the polymer networks and CO<sub>2</sub> molecules. The results demonstrate that the introduction of strong polar groups into a polymer skeleton is an efficient strategy to produce CO<sub>2</sub>-philic microporous organic polymers with enhanced binding affinity with CO<sub>2</sub> molecules.

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## 1. Introduction

Capture and separation of carbon dioxide (CO<sub>2</sub>) technologies have attracted increasing attention since the excessive emission of CO<sub>2</sub> produced from the burning of fossil fuels has led to global warming and some environment issues. The current leading CO<sub>2</sub> capture technology is amine-based wet scrubbing technology, which is the need for relatively high energy penalty to regenerate the amine solution after CO<sub>2</sub> capture [1]. A promising alternative to overcome the drawbacks of aqueous amine solutions is to use porous solid adsorbents, which physisorb CO<sub>2</sub> molecules via weak van der Waals forces making the regeneration of the materials energy much more efficient. Therefore, microporous organic polymers (MOPs), as a kind of advanced porous materials, are emerging as a promising class of gas adsorbent materials with notable potential to address many societal challenges relevant to energy and environment because of their high surface area, tunable pore properties, excellent physicochemical stability and low skeleton density. A particular advantage of MOPs is the potential to introduce synthetically a range of useful chemical functionalities into the polymer skeleton, which provides the polymer with special

functions and properties for specific applications [2–6], particularly for CO<sub>2</sub> capture [7–10]. In the past decade, a range of MOPs, such as polymers of intrinsic microporosity (PIMs) [11], conjugated microporous polymers (CMPs) [12], covalent organic frameworks (COFs) [13], porous aromatic framework (PAFs) [14], porous polymer networks (PPNs) [15], and hypercrosslinked porous polymers (HCPs) [16], have been intensively explored for capture of CO<sub>2</sub>.

However, most reported non-functionalized MOPs usually exhibited very low CO<sub>2</sub> uptake ability at ambient temperatures and pressures because of the low CO<sub>2</sub> adsorption enthalpies as a result of the lack of strong CO<sub>2</sub> binding sites. For example, CMP-1 showed a CO<sub>2</sub> uptake capacity of 2.15 mmol g<sup>-1</sup> at 273 K/1.13 bar [17], PAF-1 with ultrahigh surface area of 5460 m<sup>2</sup> g<sup>-1</sup> exhibited only a CO<sub>2</sub> uptake ability of 2.05 mmol g<sup>-1</sup> at 273 K/1.13 bar [18], and the benzene-based HCPs showed a CO<sub>2</sub> uptake ability of 3.61 mmol g<sup>-1</sup> at 273 K/1.13 bar [16]. To achieve the goal of high-performance CO<sub>2</sub> capture and storage, it is desirable to develop novel MOPs with rational modification of the skeletons and variable functionalities. Recently, it has been proved that the introduction of some CO<sub>2</sub>-philic polar groups into the solid adsorbents could enhance the binding affinity between the adsorbent and CO<sub>2</sub> molecules, which results in the increase of CO<sub>2</sub> capture capacity. For example, the carboxyl-functionalized porous aromatic framework PAF-26-COOH exhibited a CO<sub>2</sub> uptake capacity of 2.34 mmol g<sup>-1</sup> at 273 K/1.0 bar [19]. The binaphthol-based HCPs showed a CO<sub>2</sub> uptake capacity as

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high as 3.96 mmol g<sup>-1</sup> (273 K/1.0 bar) [20]. The porous organic polymer of SNU-C1-sca with carboxy and triazole groups exhibited a CO<sub>2</sub> uptake capacity as high as 4.38 mmol g<sup>-1</sup> (273 K/1.0 bar) [21]. The task-specific porous organic polymer TSP-2 with carbazole and triazine groups showed a CO<sub>2</sub> uptake capacity of 4.1 mmol g<sup>-1</sup> at 273 K/1.0 bar [22]. The sulfonate-grafted and polyamine-tethered porous polymer networks produced from PPN-6 by post modification exhibited exceptionally high CO<sub>2</sub> capture capacity [23–25]. These results demonstrated that such polar groups-functionalized MOPs have great potential to increase the CO<sub>2</sub> capture capacity.

Although the introduction of polar functional groups by post modification leads to the enhancement of binding affinity between the adsorbent and CO<sub>2</sub> molecules, the surface area of the modified MOPs is much lower than that of the parent materials because the functional groups introduced will occupy some pores [24,26–28], which makes the decrease of CO<sub>2</sub>-sorption capacity instead in some cases [17,26,29]. It has been proved that palladium-catalyzed Sonogashira–Hagihara cross-coupling polymerization is an efficient method to produce highly porous CMPs and functionalized CMPs with enhanced CO<sub>2</sub>-sorption capacity. For example, the conjugated microporous poly(aryleneethynylene) networks, as the first example of CMPs produced by Sonogashira–Hagihara cross-coupling polymerization, exhibited high surface area up to 834 m<sup>2</sup> g<sup>-1</sup> [12]. The hexabenzocoronene-based CMPs could adsorb CO<sub>2</sub> up to 2.05 mmol g<sup>-1</sup> at 273 K/1.0 bar [30]. The functionalized CMP-1 networks with different polar groups such as –COOH, –NH<sub>2</sub>, –(CH<sub>3</sub>)<sub>2</sub> and –OH showed enhanced heat of adsorption for CO<sub>2</sub> [17]. The cobalt/aluminium-coordinated CMPs exhibited outstanding CO<sub>2</sub> capture capacity up to 1.80 mmol g<sup>-1</sup> at 1.0 bar and 298 K [31]. The thienyl-phosphine functionalized CMPs exhibited the CO<sub>2</sub> uptake of 2.26 mmol g<sup>-1</sup> at 273 K/1.0 bar [32]. The CMP from post-synthetic amine functionalization exhibited a high CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity of 155 at 1 bar and 298 K [27].

We report here a bottom-up strategy for preparing bifunctionalized CMPs via one-pot palladium-catalyzed Sonogashira–Hagihara cross-coupling reaction of bromophenol blue with 1,4-diethynylbenzene or 1,3,5-triethynylbenzene. We hypothesized that the highly crosslinked polymer structure can substantially increase the surface area of the resulting polymer networks and, on the other hand, the incorporation of sultone and hydroxyl groups from the building block of bromophenol blue into the polymer skeleton could enhance the binding affinity between the adsorbent and CO<sub>2</sub> molecules, and thus lead to the increase of CO<sub>2</sub> capture capacity.

## 2. Experimental section

### 2.1. Chemicals

All the chemicals were commercial available and used as received. Bromophenol blue, CuI and 1,4-dioxane were purchased from Acros. 1,4-diethynylbenzene and 1,3,5-triethynylbenzene were purchased from TCI. Triethylamine (Et<sub>3</sub>N) and tetrakis-(triphenylphosphine)palladium(0) were purchased from J&K.

### 2.2. Synthesis of BFCMP-1

1,4-Diethynylbenzene (378 mg, 3.0 mmol), bromophenol blue (670 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (15 mg), and copper(I) iodide (10 mg) were dissolved in a mixture of 1,4-dioxane (6.0 mL) and Et<sub>3</sub>N (6.0 mL). The reaction mixture was heated to 100 °C and stirred for 36 h under a nitrogen atmosphere. Then, the mixture was cooled to room temperature and the precipitated polymer network was filtered and washed with methanol, water, chloroform and acetone to remove any unreacted

monomer or catalyst residues. Further purification of the polymer network was carried out by Soxhlet extraction from methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C (Yield based on bromophenol blue: 72.7%). Elemental combustion analysis (%) Calcd for (C<sub>39</sub>H<sub>18</sub>O<sub>5</sub>S)<sub>n</sub>: C 78.25, H 3.03, O 13.36, S 5.3; Found: C 82.52, H 4.17, S 3.24. The deviation of the elemental analysis from that expected could be attributed to the unreacted end groups as well as the trapped gases and water from air in the samples, which were not effectively removed by the outside analysis laboratory [33–35].

### 2.3. Synthesis of BFCMP-2

1,3,5-Triethynylbenzene (300 mg, 2.0 mmol), bromophenol blue (670 mg, 1.0 mmol), tetrakis-(triphenylphosphine)palladium(0) (15 mg), and copper(I) iodide (10 mg) were used in this polymerization, details as described for BFCMP-1. Yield based on bromophenol blue: 69.4%. Elemental combustion analysis (%) Calcd for (C<sub>35</sub>H<sub>14</sub>O<sub>5</sub>S)<sub>n</sub>: C 76.91, H 2.58, O 14.64, S 5.87; Found: C 80.15, H 3.26, S 2.33.

### 2.4. Characterization

The thermal properties of the polymer networks were evaluated using a thermogravimetric analysis (TGA) with a differential thermal analysis instrument (Q1000DSC + LNCS + FACS Q600SDT) over the temperature range from 30 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C/min. Elemental analysis was carried out on EURO EA30000 Elemental Analyzer. The FT-IR spectra were collected in transmission on a Tensor 27 FT-IR spectrometer (Bruker) using KBr disks. Solid state magic angle spinning <sup>13</sup>C CP/MAS NMR measurement was carried out on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz. Powder X-ray diffraction measurements (PXRD) was carried out on X-ray Diffractometer (D/Max-3c). The polymer morphology was achieved using a field-emission scanning electron microscopy (SEM) (JSM-7001F, JEOL, Tokyo, Japan). Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using an ASAP 2420-4 (Micromeritics) volumetric adsorption analyzer. The surface areas were calculated in the relative pressure (*P/P*<sub>0</sub>) range from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory (NL-DFT). Samples were degassed at 120 °C for 15 h under vacuum (10<sup>-5</sup> bar) before analysis. Gas sorption isotherms were measured on an ASAP 2420-4.

## 3. Results and discussion

Both of the bifunctionalized conjugated microporous polymers (BFCMPs) were synthesized via palladium-catalyzed Sonogashira–Hagihara cross-coupling reaction from bromophenol blue with 1,4-diethynylbenzene or 1,3,5-triethynylbenzene. The polymerization reactions were carried out at a fixed total molar monomer concentration (300 mmol/L) and a fixed reaction temperature and reaction time (100 °C/36 h). The molar ratio of ethynyl to bromine functionalities in the monomer feed was set at 1.5:1 based on the previous reports since this ratio was found to maximize surface area in this class of CMP networks [36,37]. The general synthetic routes to the BFCMPs and the notional polymer structures are shown in Scheme 1. The resulting polymers were insoluble in conventional organic solvents because of their highly crosslinked structures and the rigid skeleton. Both of the polymer networks exhibited almost the same thermal properties (Fig. S1), since they have the same functional groups and the main-chain structure. The

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