



Phosphine-containing microporous networks: High selectivity toward carbon dioxide to methane



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ABSTRACT

Two phosphine-containing microporous organic networks TPPDEB-O and TPPDEB-S were designed and synthesized via Sonogashira–Hagihara coupling condensation reaction. The electronic structures and the adsorption characteristics of the polymers can be tailored by facile oxidation and vulcanization modification of the nucleophilic phosphorus atom node. Nitrogen adsorption–desorption isotherms of TPPDEB-O and TPPDEB-S showed the Brunauer–Emmet–Teller specific surface areas were $712.51 \text{ m}^2 \text{ g}^{-1}$ and $677.02 \text{ m}^2 \text{ g}^{-1}$, respectively. The two frameworks have strong affinity for CO_2 and the isosteric heats of sorption were excess 25 kJ mol^{-1} at the whole loading range. Furthermore, their selectivity toward CO_2/CH_4 exceeded most of porous organic polymers and the surfaces functionalized by $\text{P}=\text{O}$ or $\text{P}=\text{S}$ showed a large different capacity on the CO_2/CH_4 separation (TPPDEB-O and TPPDEB-S at 273 K is 15.9, 5.5 and at 298 K is 9.3, 4.3, respectively).

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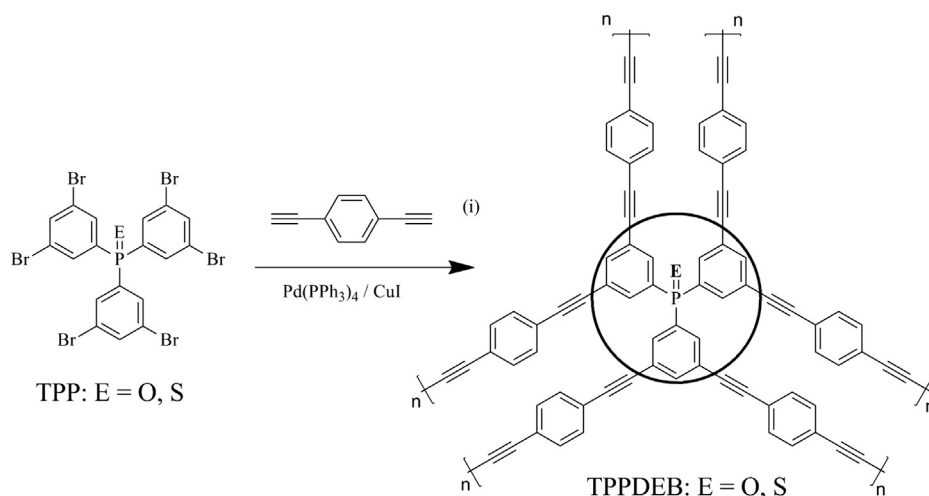
1. Introduction

Rapid consumption of hydrocarbon fuels caused CO_2 concentration increased quickly in the atmosphere thus generating the problem of global-warming and some climate change issues, which lead scientific community had drawn much attention and concern in recent two decades [1]. The way of CO_2 capture and sequestration (CCS) in physical process provides a less energy penalty and cost associated with state-of-the-art gas uptake, which is a potential short-term strategy for the fossil sources continue using until green energy technologies mature. High physical CO_2 uptake capacity, low regeneration energy consumption and synthetic diversification make porous materials excellent for CCS [2–4]. Microporous organic polymers (MOPs), a new class of porous materials which are composed of light, non-metallic elements with high chemical and thermal stability have attracted significant interest in academic and economic application. Versatile MOPs such as covalent organic frameworks (COFs) [5–7], polymers of intrinsic microporosity (PIM) [8,9], porous aromatic framework (PAF) [10,11], hypercrosslinked polymers (HCPs) [12,13], crystalline triazine-based organic frameworks (CTFs) [14,15], and conjugated

microporous polymers (CMPs) [16,17], have been exhibited high CO_2 capture and separation capacities.

In the past few years, a significant research effort has been directed at synthesizing specific chemical and physical properties materials use in CCS. As a good example, the different main group elements of C, N, Si as the node of the MOPs' frameworks had showed excellent performance in CCS. Cooper and Holst J [18], reported the C node polymer with Brunauer–Emmet–Teller (BET) specific surface area up to $3160 \text{ m}^2 \text{ g}^{-1}$, CO_2 uptake up to 6.54 wt% at 298 K, 1.13 bar and Lu W [19], reported the C node network PPN-1 with the selective of CO_2/CH_4 up to 7 at 80 bar. The Si-containing frameworks with BET area up to $1102 \text{ m}^2 \text{ g}^{-1}$, and CO_2 uptake up to 4.01 wt% at 298 K and 1.13 bar [18]. Jiang J. reported the N-containing microporous polymers (NCMPs) based on poly(-triethylphenyl)amine with BET specific surface areas in the range $500\text{--}1100 \text{ m}^2 \text{ g}^{-1}$, but no CO_2 uptake experiment was reported [20]. Phosphorus is another light element in nature and with facile chemical modifying property, however, the MOPs using it as the node had got less attention [21]. Mohanty P. and Landskron K. reported the inorganic hexachlorocyclotriphosphazene-containing frameworks PECONF-4 has the high selectivity toward CO_2/CH_4 to 12 at 273 K [22]. The versatile chemical reactivity and electronic nature of phosphorus (which can easily chemically modified by H_2O_2 , S_8 , Se, BH_3 , AuCl, $[\text{RH}(\text{COD})\text{Cl}]_2$, $\text{Fe}_2(\text{CO})_9$, $\text{W}(\text{CO})_5$) [23] offer great opportunities for novel materials design, such as inorganic

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Scheme 1. Synthetic route towards the polymers of TPPDEB-O and TPPDEB-S, (i) Cat. Pd(PPh₃)₄, CuI, DMF/Et₃N (1/1), 80 °C.

electronics (organic solar cells, organic light-emitting diodes, organic thin-film transistors) [24,25] and porous chemistry (metal-organic frameworks) [26]. It is an attractive work to intercalate the phosphorus group into the skeleton and modify it to functionalize the MOPs, and then to explore their discrepancy in gas storage and separation.

In this manuscript, two phosphine-containing frameworks TPPDEB-O and TPPDEB-S were prepared for the first time from triphenylphosphine (TPP) derivatives TPP-O and TPP-S. The two building blocks are significantly cheaper than most monomers of CMPs typically used so far. The phosphorous node with lone pair electrons in building block can be facilely modified by H₂O₂ and S₈. The versatile chemical reactivity properties provide an easy way to change the steric configuration of the TPP building block and functionalize the surface of the porous materials. The gas adsorption results showed that only replacing the O atom by S atom in the backbone, the performance of TPPDEB-O and TPPDEB-S had a large difference in the selectivity toward CO₂ to CH₄.

2. Experimental section

2.1. Materials and synthesis

All chemical reagents were commercially available unless otherwise stated. 1, 3, 5-Tribromobenzene, 1, 4-diethynylbenzene, and tetrakis(triphenylphosphine)palladium(0) were purchased from J&K. Triphenylphosphine derivatives were prepared according to reported methods [27], respectively.

2.1.1. Synthesis of triphenylphosphine oxide (TPP-O) and triphenylphosphine sulfur (TPP-S)

TPP-O: n-BuLi (6.49 mL, 2.4 M, 0.015 mmol) was slowly added in a solution of 1, 3, 5-tribromobenzene (4.9 g, 0.015 mmol) in ether (250 mL) at -78 °C. After addition the solution was stirred at -78 °C for 30 min before the temperature was warmed to room temperature, then cooled it down below -30 °C, phosphorus trichloride (467 μ L, 0.005 mmol) in ether (20 mL) was added to the reaction mixture and stirred at room temperature for 2 h. The reaction mixture was extracted with ethyl acetate and dried with MgSO₄, then evaporated the solvent and dissolved the residue in 50 mL CH₂Cl₂, excess H₂O₂ was added dropwise to the reaction mixture and stirred for 3 h at room temperature. The crude product

was washed with water and dried over MgSO₄, evaporated the solvent and the residue was purified by column chromatography on silica gel to give white solid, yield 89%. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.93 (s, 3H), 7.68–7.66 (d, 6H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 138.84, 134.89, 134.22, 133.06, 132.99, 124.40, 124.29. ³¹P NMR was tested using 85% H₃PO₄ as an external standard at 242.9 MHz in CDCl₃: δ (ppm) 22.6.

TPP-S: same procedure with TPP-O just except oxidant using sulfur to give white solid, yield 79%. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.89 (s, 3H), 7.71–7.68 (d, 6H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm) 138.33, 135.64, 135.10, 133.30, 133.22, 124.23, 124.12. ³¹P NMR (242.9 MHz, CDCl₃): δ (ppm) 40.27.

2.1.2. Synthesis of polymers TPPDEB-O and TPPDEB-S

TPPDEB polymers were prepared by palladium-catalyzed Sonogashira–Hagihara coupling condensation reaction between TPP-O, TPP-S with 1, 4-diethynylbenzene, respectively. A representative preparation for TPPDEB-O is given in details as follows.

TPP-O (150.3 mg, 0.2 mmol), 1, 4-diethynylbenzene (117.1 mg, 0.9 mmol), tetrakis(triphenylphosphine)palladium(0) (11.6 mg) and copper(I) iodide (1.9 mg) were added into the solvent of dimethyl formamide (2.5 mL) and triethylamine (2.5 mL), and the mixture was degassed by the freeze–pump–thaw cycles under mixture gas (N₂/H₂) atmosphere (in order to rigorously exclude oxygen and to prevent the homo-coupling of the alkyne monomers). The resulting mixture was slowly heated to 80 °C and stirred for 72 h. After cooled to room temperature, the brown precipitate was filtered and washed with chloroform, water, acetone and methanol to remove any unreacted monomers or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with methanol for 24 h. The product was then dried under vacuum for 24 h at 80 °C to give 226 mg brown powder. Elementary analysis for TPPDEB-O, Calcd: C 91.57, H 3.84. Found: C 89.45, H 3.79.

TPPDEB-S: same procedure to prepare it. Calcd: C 90.15, H 3.78, S 3.09. Found: C 89.62, H 3.64, S 3.49.

Spectroscopy. Solid state magic angle spinning ¹³C CP/MAS NMR measurement was carried out on a Bruker Avance III model 400 MHz NMR spectrometer at a MAS rate of 5 kHz. FT-IR spectra were collected in attenuated total reflection (ATR) mode on a Thermo Nicolet 6700 FT-IR Spectrometer. Scanning electron microscopy (SEM) was recorded using a Hitachi S-4800 with

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