Stable benzimidazole-incorporated porous polymer network for carbon capture with high efficiency and low cost

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ABSTRACT

Porous Polymer Networks (PPNs) are an emerging category of advanced porous materials that are of interest for carbon dioxide capture due to their great stabilities and convenient functionalization processes. In this work, an intrinsically-functionalized porous network, PPN-101, was prepared from commercially accessible materials via an easy two-step synthesis. It has a BET surface area of 1095 m^2/g. Due to the presence of the benzimidazole units in the framework, its CO_2 uptake at 273 K reaches 115 cm^3/g and its calculated CO_2/N_2 selectivity is 199, which indicates its potential for CO_2/N_2 separation. The great stability, large CO_2/N_2 selectivity and low production cost make PPN-101 a promising material for industrial separation of CO_2 from flue gas. Its H_2 and CH_4 uptake properties were also investigated.

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Elimination of CO_2 from mixed component gas streams has gained a tremendous amount of attention due to a growing concern of the environmental and climatic impact of greenhouse gas emissions [1]. Many environmental problems, such as global warming and ocean acidification, have been primarily attributed to the escalating level of atmospheric CO_2. In order to reduce anthropogenic CO_2 emissions, various Carbon Capture and Sequestration (CCS) techniques have been investigated as means to selectively remove CO_2 from the flue gas of fossil-fuel-powered plants and then store it underground [2]. Aqueous alkanolamines, such as monoethanolamine (MEA) solutions, have been utilized due to their large CO_2 capacity and selectivity [3]. Nevertheless, this process suffers from a series of complications that have substantially limited their industrial applications, such as the high regeneration cost arising from the large heat capacity of aqueous MEA solutions, the toxicity, the unpleasant smell and the corrosive nature of amine compounds [4].

As an alternative solution, many solid adsorbents have been shown to be promising candidates to overcome the downsides of aqueous alkanolamine solutions. For the past few decades, advanced porous materials [5] have been extensively investigated in scientific and technological research due to their capability to adsorb and interact with atoms, ions and molecules [6]. The

functionalities and prospective applications of the porous materials are largely dependent on their pore size distribution and pore surface properties. Under the motivation of achieving larger surface area and better framework properties, metal-organic frameworks (MOFs) [7,8] and porous polymer networks (PPNs) [9] emerged as novel categories of porous materials and are widely applied in areas such as such as gas storage [9,10], gas separation [11,12], catalysis [13,14], sensors [15], and other applications. Even though MOFs possesses many advantages such as enormous surface area, tunable structures and convenient post-synthetic modifications, most MOFs suffer from a limited stability, which restrained their practical applications [16]. PPNs, appearing as hyper-crosslinked organic polymers, have provided an alternative solution to the construction of ultra-porous materials with high thermal and chemical stability [17]. Unlike crystalline Covalent Organic Frameworks (COFs) [18], PPNs are amorphous materials with Brunauer–Emmett–Teller (BET) surface areas as large as 6461 m^2/g (in PPN-4), which is the largest PPN BET surface area to date [9]. Regardless of the enormous surface area and improved stability, those PPNs suffer from several shortcomings that generally hamper them from being practically implemented. First, their synthesis involves the coupling of tetrahedral monomers via the Yamamoto homo-coupling reaction [17], which requires an extremely expensive and air-sensitive reagent, Bis(cyclooctadiene)nickel ($Ni(cod)_2$). This has significantly increased the production cost of PPNs and prevented their large-scale synthesis for industrial use. Second, many applications of porous materials require the functionalization of the inner pore surfaces. Being constructed primarily from phenyl rings

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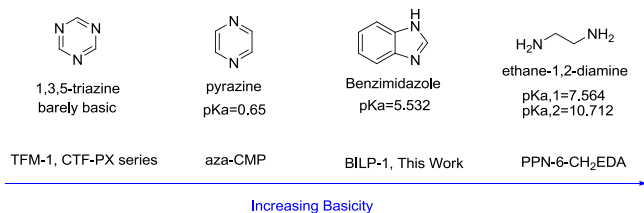
Scheme 1. The basicity of the basic units that have been incorporated into PPNs.
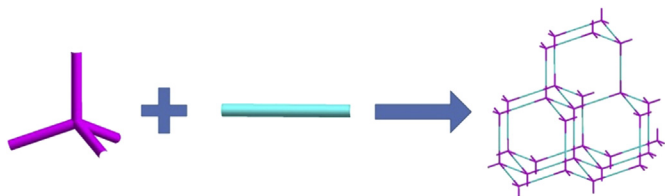

Fig. 1. The conceptual illustration of an ideal network that incorporates tetrahedral nodes and linear nodes. Ideally, this will give rise to a network with diamondoid topology.

or alkyne bridges, the lack of internal functionalization of those PPNs has significantly limited their applications, especially for the purposes of carbon dioxide sequestration. Post-synthetic modifications (PSM) of those PPNs appear as an efficient way to improve their functionality [4,19]; however, the PSM process has not only drastically impaired their porosity but also further increased their production cost. It is highly desirable to synthesize functionalized PPNs with considerably large porosities and reasonable production costs for industrial CCS processes.

Incorporation of Lewis bases into MOFs [20] and PPNs [4] has been demonstrated as an effective way to improve CO_2 uptake and CO_2/N_2 selectivity. These moieties can be incorporated into the struts of the PPN framework, or can be introduced by post-synthetic modification. Pyrazine [21], triazine [22,23] and polyamines [4] have been successfully incorporated into PPNs. However, none of these materials can remove CO_2 from flue gas with both high efficiency and low cost. Despite the interesting electronic properties resulting from the conjugate system; the CO_2/N_2 selectivity of the pyrazine-incorporated PPN, Aza-CMP, was not

investigated, probably due to the low porosity (BET surface area of 24 m^2/g when activated at 300 °C) and complicated activation procedure of this material [21]. The incorporation of triazine into PPN frameworks, as shown in TFM-1 [22] and CTF-PX series [23], was demonstrated as a moderately efficient way to improve the CO_2/N_2 selectivity; however, the selectivity was restrained by the limited basicity of the triazine units. It is conceivable that incorporation of a more basic unit could further improve the CO_2/N_2 selectivity and CO_2 adsorption enthalpy due to the acidic nature of CO_2. The incorporation of polyamines into PPNs [4] was demonstrated as an efficient way to improve the CO_2/N_2 selectivity; however, Ni(cod)$_2$ was required in the synthesis, and the PSM process further increased the cost of this PPN. In spite of the high efficiency of CO_2 removal in polyamine PPNs, the overall production cost remains largely problematic. Herein, we introduce a stable benzimidazole-incorporated porous polymer network, PPN-101, which has a BET surface area of 1096 m^2/g, CO_2 uptake of 226.2 mg/g at 273 K, and CO_2/N_2 selectivity of around 200. The significantly reduced cost and highly efficient separation of CO_2 from N_2 make it a promising material for industrial separation of CO_2 from flue gas with both high efficiency and low cost.

Scheme 1 illustrates a few basic units that have been successfully incorporated into PPNs. Benzimidazole incorporation into the frameworks can be used to improve the CO_2/N_2 selectivity. Polybenzimidazoles (PBIs) have been widely used in other areas, such as in proton-exchange membranes in fuel cells [24]. However, few of the PBIs turn out to be suitable materials for industrial separation of CO_2/N_2 due to their very limited porosity. El-Kaderi and coworkers [25] published the first benzimidazole-incorporated PPN named as BILP-1 (Benzimidazole Linked Polymer) by condensation of tetrakis(4-formylphenyl)methane and 2,3,6,7,10,11-hexaaminotriphenylene, with the BET surface area of 1172 m^2/g and CO_2 uptake of around 180 mg/g at 273 K, which makes it the first benzimidazole-incorporated PPN with considerable porosity for selective CO_2 removal. However, the laborious syntheses of both the aldehyde [26] and amine [27] monomers significantly increased the production cost of BILP-1 and hindered its synthesis in large quantities. After the discovery of BILP-1, they have provided a series of benzimidazole-incorporated PPNs where expensive monomers were utilized [28–30]. In this work, PPN-101 was prepared from a synthetically-accessible silicon-centered aldehyde monomer [31] and a commercially available amine monomer, which has significantly brought down
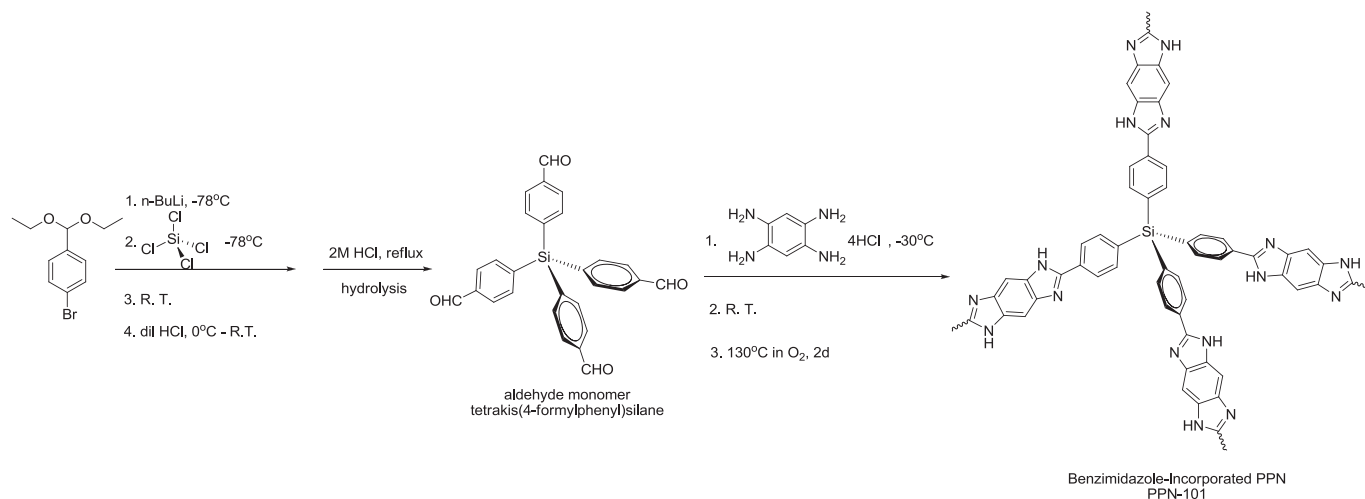
Scheme 2. The syntheses of aldehyde monomer (tetrakis(4-formylphenyl)silane) and PPN-101. This PPN can be synthesized within two steps from commercially available compounds, and no extremely expensive reagent is involved.