

Polyamine-Tethered Porous Polymer Networks for Carbon Dioxide Capture from Flue Gas**

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One of the most pressing environmental concerns of our age is the escalating level of atmospheric CO₂, which is largely correlated to the combustion of fossil fuels. For the foreseeable future, however, it seems that the ever-growing energy demand will most likely necessitate the consumption of these indispensable sources of energy. Carbon capture and sequestration (CCS), a process to separate CO₂ from the flue gas of coal-fired power plants and then store it underground, has been proposed to reduce the anthropogenic CO₂ emissions. Current CO₂ capture processes employed in power plants worldwide are post-combustion “wet scrubbing” methods involving the chemical adsorption of CO₂ by amine solutions such as monoethanolamine (MEA). The formation of carbamate from two MEA molecules and one CO₂ molecule endows the scrubber with a high capacity and selectivity for CO₂. However, this process suffers from a series of inherent problems, such as high regeneration costs that arise from heating the solution (ca. 30 % of the power produced by the plant), fouling of the equipment, and solvent boil-off.^[1]

To sidestep the huge energy demand, corrosion problem, and other limitations of traditional wet scrubbers, intensive efforts have been made to investigate the use of solid adsorbents as an alternative approach.^[2] Compared to wet scrubbing, in which a large amount of water (70 % w/w) must be heated and cooled during the regeneration of the dissolved amines, the solid adsorbent approach has the tremendous advantage of improving the energy efficiency of the regeneration process by eliminating the need to heat water.

Porous materials, such as MOF-210,^[3] NU-100,^[4] and PPN-4,^[5] have been deemed to be viable storage alternatives

because of their high porosity and, therefore, significantly increased accessible contact area with gas molecules. This could be advantageous because separation and regeneration could be performed under relatively mild conditions compared to amine wet scrubbing systems. Unfortunately, the record high storage capacities do not translate to high selectivities and only moderate CO₂-uptake capacities were observed under carbon capture conditions.

The polarizability and large quadrupole moment of CO₂ can be taken advantage of by introducing CO₂-philic moieties that create strong interactions between the material surface and the CO₂. This will improve the loading capacities and selectivity of CO₂ over other gases. Indeed, this approach has already been proven to be very successful in enhancing the enthalpy of CO₂ adsorption,^[6] which can be calculated from CO₂ sorption isotherms at different temperatures and used to quantify the interaction between the material and CO₂. It is worth pointing out that the porosity of the material will be compromised by the introduction of functional groups. CO₂ loading capacities at ambient conditions are dependent on the adsorption enthalpy and porosity (both surface area and pore volume), which must be balanced to achieve high loading.

Besides the loading capacity, another important factor when quantifying how well a material will perform is CO₂ selectivity over N₂. Taking amine scrubbing as the model, aminated porous materials that have been synthesized usually exhibit very large adsorption enthalpies for CO₂ and high CO₂/N₂ selectivities. Recently, Long and co-workers demonstrated the incorporation of *N,N*-dimethylethylenediamine (mmen) at exposed metal centers of CuBTtri (H₃BTtri = 1,3,5-tri(1*H*-1,2,3-triazol-4-yl)benzene), with the new compound mmen-CuBTtri showing drastic enhancement of CO₂ uptake at low pressure, as well as CO₂/N₂ selectivity. It has the highest heat of adsorption for CO₂ (96 kJ mol⁻¹) and one of the highest CO₂/N₂ adsorption selectivities (*S*_{LAST} = 327 at 25 °C) reported to date.^[7] Despite its large isosteric heat of CO₂ adsorption, mmen-CuBTtri could easily be regenerated at 60 °C.

It is always important to keep physicochemical stability in mind for practical applications. Purely organic porous polymers are a class of adsorbents that exhibit surface areas comparable to those of metal-organic frameworks (MOFs), but have much higher physicochemical stability because of the entirely covalently bonded network.^[6a,8]

The key to obtaining porous polymers with high amine loading is to judiciously select efficient reactions and starting materials with ultrahigh surface areas. PPN-6^[9] (PPN stands for porous polymer networks), which has an exceptionally high surface area and an extremely robust all-carbon scaffold

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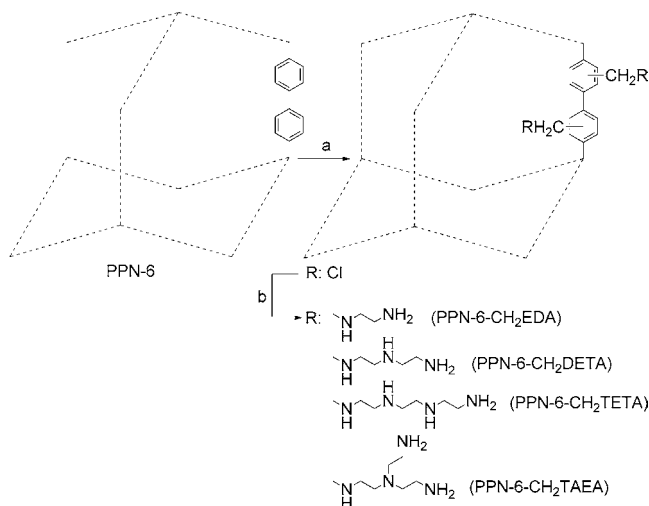
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based on biphenyl rings, is ideal for the introduction of CO₂-philic groups under harsh reaction conditions. PPN-6 (also known as PAF-1, first reported by Ben et al.^[8a]) was synthesized by using a modified Yamamoto homocoupling polymerization procedure.^[10] It has a Brunauer–Emmett–Teller (BET) surface area as high as 4023 m² g⁻¹, and takes up 1.3 mmol g⁻¹ (5.4 wt %) CO₂ at 295 K and 1 bar. The polyamine-tethered PPNs (Scheme 1, and see Experimental Section) show dramatic increases in CO₂-uptake capacities at low pressures, and exceptionally high CO₂/N₂ adsorption selectivities under ambient conditions.

Nitrogen gas adsorption/desorption isotherms were collected at 77 K (Figure 1 a). The calculated BET surface areas were 1740, 1014, 663, 634, and 555 m² g⁻¹ for PPN-6-CH₂Cl, PPN-6-CH₂EDA, PPN-6-CH₂TAEA, PPN-6-CH₂TETA, and PPN-6-CH₂DETA respectively. Notably, the huge adsorption/desorption hysteresis in PPN-6-CH₂Cl disappeared into a nearly type I isotherm for the polyamine-tethered PPNs. Along with the decrease in surface area, the pores are smaller after tethering, which supports the reaction occurring within the cavities (see Figure S4 in the Supporting Information).

The efficiency of amine substitution was confirmed by elemental analysis (see Table S5 in the Supporting Informa-



Scheme 1. Synthetic route to polyamine-tethered PPNs. a) CH₃COOH/HCl/H₃PO₄/HCHO, 90 °C, 3 days; b) amine, 90 °C, 3 days.

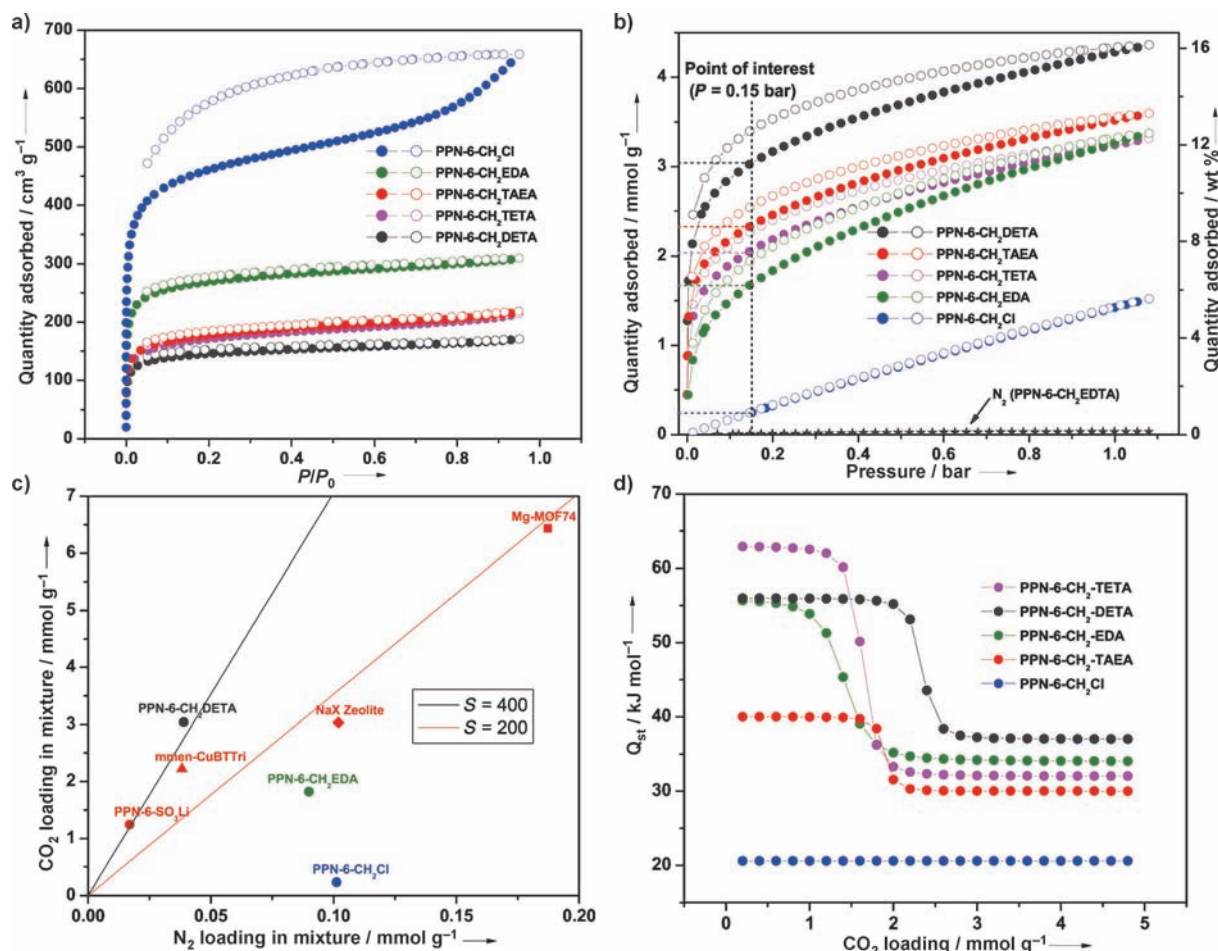


Figure 1. a) N₂ adsorption (●) and desorption (○) isotherms at 77 K. b) CO₂ adsorption (●) and desorption (○) isotherms, as well as PPN-6-CH₂DETA N₂ adsorption, at 295 K. c) The component loadings of N₂ and CO₂ calculated by IAST with bulk gas-phase partial pressures of 85 kPa and 15 kPa for N₂ and CO₂, respectively, with PPN-6-CH₂DETA, PPN-6-CH₂EDA, PPN-6-CH₂Cl, PPN-6-SO₃Li,^[9] NaX zeolite,^[9] MgMOF-74,^[10] mmen-CuBTtri.^[7] Loadings for calculated selectivities of 200 and 400 are shown as a guide. d) Isothermic heats of adsorption Q_{st} for the adsorption of CO₂, calculated using the dual-site Langmuir isotherm fits.

tion). The chlorine content of 14.42 % in PPN-6-CH₂Cl was reduced to only trace amounts in the polyamine-tethered PPNs. PPN-6-CH₂DETA had the highest nitrogen content of 11.95 % (see Table S5 in the Supporting Information), which corresponds to a loading of 0.3 functional groups per phenyl ring.

The introduction of polyamine groups in PPN-6 resulted in materials with excellent CO₂ adsorption characteristics at 295 K and low pressures (Figure 1b). The trend of improvement in CO₂ adsorption in terms of tethered polyamine groups was DETA > TAEA > TETA > EDA. Although PPN-6-CH₂DETA has the lowest surface area, it exhibits the highest CO₂-uptake capacity of all the polyamine-tethered PPNs. This finding indicates that the CO₂-uptake capacity is closely correlated to amine loading instead of surface area under these conditions, and the result is consistent with previous findings of Dawson et al.^[8f] At 295 K and 1 bar, PPN-6-CH₂DETA exhibits exceptionally high CO₂ uptake (4.3 mmol g⁻¹, 15.8 wt %), possibly because of the accessibility of the alkylamine chain. To the best of our knowledge, this value is one of the highest of all the microporous organic polymers reported so far,^[8f,9] including top-performing N-containing ones, such as N-TC-EMC^[11] (4.0 mmol g⁻¹), BILP-4^[12] (3.6 mmol g⁻¹), and MFB-600^[13] (2.25 mmol g⁻¹).

Coal-fired power plants emit flue gas that contains approximately 15 % CO₂ at total pressures of around 1 bar; thus, CO₂-uptake capacity at about 0.15 bar (partial pressure of CO₂ in flue gas) is more relevant to realistic post-combustion applications. At 295 K and 0.15 bar, PPN-6-CH₂Cl only takes up 0.25 mmol g⁻¹ CO₂ (1.1 wt %), whereas PPN-6-CH₂DETA takes up 3.0 mmol g⁻¹ of CO₂ (11.8 wt %). This latter value is comparable to other top-performing materials, such as mmen-CuBTTr^[7] (9.5 wt % at 298 K) and MgMOF-74^[14] (22.0 wt % at 293 K), but PPN-CH₂DETA stands out with respect to its physicochemical stability arising from the covalent bonding in the framework. The increase in the volumetric uptake capacity upon tethering of the polyamine chain is even more significant: from 1.3 g L⁻¹ for PPN-6-CH₂Cl to 37.5 g L⁻¹ for PPN-6-CH₂DETA at 295 K and 0.15 bar (the tap densities were measured to be 0.12 and 0.28 g cm⁻³ for PPN-6-CH₂Cl and PPN-6-CH₂DETA, respectively; see Table S6 and Figure S2 in the Supporting Information).

At 295 K, the polyamine-tethered PPNs adsorb less N₂ than PPN-6-CH₂Cl (see Figure S3 in the Supporting Information). PPN-6-CH₂DETA is especially interesting, with an uptake of less than 0.1 wt % N₂ at 1.0 bar, approximately one third of that of PPN-6-CH₂Cl. It is possible that the added polar sites in the former may enhance N₂ adsorption, but that this is totally offset by the significant loss of surface area. Conversely, the CO₂ uptake is significantly enhanced because the strong interactions play a more significant role.

To evaluate the CO₂/N₂ selectivity of the materials under flue-gas conditions with single-gas isotherms, we used the ideal adsorbed solution theory (IAST) model of Myers and Prausnitz^[15] along with the pure component isotherm fits to determine the molar loadings in the mixture for specified partial pressures in the bulk gas phase. Figure 1c presents the

component loadings of N₂ and CO₂ for PPN-6-CH₂Cl, PPN-6-CH₂EDA, PPN-6-CH₂DETA, PPN-6-SO₃Li, MgMOF-74, NaX zeolite, and mmen-CuBTTr calculated by IAST with bulk phase equilibrium partial pressures of 85 kPa (N₂) and 15 kPa (CO₂). Two factors that define a material for efficient separation of CO₂ are a high CO₂ loading and a high selectivity over N₂. Figure 1c clearly shows both factors, and highlights the high loading on PPN-6-CH₂DETA and its exceptional selectivity of CO₂ over N₂ (the better the material, the closer to the top left corner of the graph). We note that CO₂ loading is highest for MgMOF-74; however, PPN-6-CH₂DETA has a much lower N₂ uptake than MgMOF-74, thereby leading to an unprecedented selectivity compared to any reported material (see Table S7 in the Supporting Information). The poor N₂ adsorption with PPN-6-CH₂DETA can be attributed to low porosity (pore volumes are 0.573 and 0.264 cm³ g⁻¹ for MgMOF-74^[14] and PPN-6-CH₂DETA, respectively).

To better understand the adsorption properties, the isosteric heats of adsorption (Q_{st}) were calculated from dual-site Langmuir fits of the CO₂ isotherms at 273, 284, and 295 K. Figure 1d shows a plot of the adsorption enthalpies as a function of loading. Particularly noteworthy are the strong inflections for all the polyamine-tethered PPNs. As can be seen from Figure 1d, PPN-6-CH₂DETA retains its strong CO₂ interactions to a relatively high CO₂ loading (ca. 2.0 mmol g⁻¹), which is consistent with its large CO₂-uptake capacity. The temperatures of flue-gas streams emitted from power plants, however, are much higher than 295 K. To be practically useful for CO₂ capture under realistic flue-gas conditions, the preservation of high isosteric heats of adsorption is essential for solid adsorbents so as to maintain high CO₂-uptake capacity at elevated temperatures. Assuming full regeneration, the quantity adsorbed at 0.15 bar could be considered as the full capacity. From 295 K to 313 K, the CO₂-uptake capacity of PPN-6-CH₂DETA at 0.15 bar only dropped slightly from 11.8 to 10.0 wt % (see Figure S5 in the Supporting Information); thus, this porous material holds considerable promise for realistic post-combustion carbon-capture applications.

The advantages of solid adsorbents with high heats of adsorption include high selectivity and large CO₂ capacities at low partial pressures; however, concerns about material regeneration are often raised. To test the cyclability of PPN-6-CH₂DETA we simulated temperature and vacuum swings with an ASAP2020 analyzer, by saturating with CO₂ up to 1.1 bar at 273 K followed by a high vacuum for 100 min at 80 °C. After 20 cycles, there was no apparent loss in capacity (Figure 2), thus indicating complete desorption during each regeneration cycle. Compared to mmen-CuBTTr, PPN-6-CH₂DETA shows higher energy demands for regeneration, possibly because of the large percentage of primary amines in PPN-6-CH₂DETA as opposed to only secondary amines in mmen-CuBTTr—primary amines have been shown to form stronger bonds with CO₂. Despite the high adsorption enthalpies of these materials, the regeneration energies would still be substantially lower than for amine solutions, in which the chemisorption interactions (ca. 50–100 kJ mol⁻¹) necessitate heating the solutions containing about 70 % water

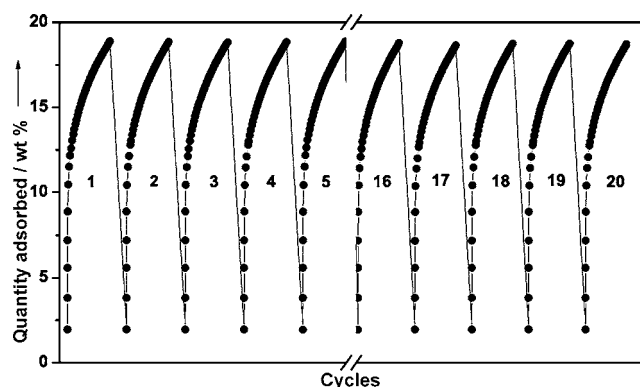


Figure 2. Twenty cycles of CO₂ uptake at 273 K. After saturation, the sample was regenerated with a temperature swing to 80 °C and then under vacuum (0.1 mmHg) for 100 min. Data were collected with an ASAP2020 analyzer.

to around 100 °C. In the latter case, the energy consumption is directly linked to the high heat capacity of water (4.15 J g⁻¹ K⁻¹).

Compared to aqueous alkanolamines, which not only boil off but also degrade below 140 °C, higher decomposition temperatures were observed when these amines were fixed into PPNs. Thermogravimetric analysis (TGA) suggests polyamine-tethered PPNs to be thermally stable in air up to 200 °C (see Figure S6 in the Supporting Information).

Physicochemical stability, high CO₂ capacity, high selectivity, and low regeneration costs are the criteria by which new adsorbents for post-combustion CO₂ capture will be evaluated. The results presented herein demonstrate that aromatic chloromethylation of PPN-6 and a subsequent polyamine substitution bestows the materials with significantly enhanced CO₂-uptake capacity but much lowered N₂-uptake capacity at low pressures. PPN-6-CH₂DETA exhibits an exceptionally high binding affinity and the largest selectivity for CO₂ of any porous material reported to date. Given the outstanding physicochemical stability and mild regeneration requirements, this material has great potential for practical application in a post-combustion CO₂ capture technology.

Experimental Section

Synthesis of PPN-6: Tetrakis(4-bromophenyl)methane (205 mg, 0.32 mmol) was added to a solution of 2,2'-bipyridyl (226 mg, 1.45 mmol), bis(1,5-cyclooctadiene)nickel(0) ([Ni(cod)₂]; 400 mg, 1.45 mmol), and 1,5-cyclooctadiene (cod; 0.18 mL, 1.46 mmol) in anhydrous DMF/THF (30 mL/30 mL), and the mixture was stirred overnight at room temperature under argon. 6 M HCl (20 mL) was added, and the resulting mixture was stirred for 6 h. The precipitate was collected by filtration, then washed with methanol and water, and dried in vacuo to produce PPN-6 as an off-white powder (85 mg, 85 %).

Synthesis of PPN-6-CH₂Cl: A resealable flask was charged with PPN-6 (200 mg), paraformaldehyde (1.0 g), glacial AcOH (6.0 mL), H₃PO₄ (3.0 mL), and conc. HCl (20 mL). The flask was sealed and heated to 90 °C for 3 days. The resulting solid was collected, washed with water and methanol, and then dried in vacuo to produce PPN-6-CH₂Cl as a brown powder in quantitative yield.

General procedure for the introduction of polyamine groups (with the synthesis of PPN-6-CH₂DETA as an example): A resealable

flask was charged with PPN-6-CH₂Cl (200 mg) and diethylenetriamine (DETA, 20 mL). The flask was sealed and heated to 90 °C for 3 days. The resulting solid was collected, washed with water and methanol, and then dried in vacuo to produce PPN-6-CH₂DETA as a brown powder in quantitative yield.

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