

# 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 CO<sub>2</sub>, 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 CO<sub>2</sub> from the flue gas of coal-fired power plants and then store it underground, has been proposed to reduce the anthropogenic CO<sub>2</sub> emissions. Current CO<sub>2</sub> capture processes employed in power plants worldwide are post-combustion “wet scrubbing” methods involving the chemical adsorption of CO<sub>2</sub> by amine solutions such as monoethanolamine (MEA). The formation of carbamate from two MEA molecules and one CO<sub>2</sub> molecule endows the scrubber with a high capacity and selectivity for CO<sub>2</sub>. 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.<sup>[1]</sup>

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.<sup>[2]</sup> 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,<sup>[3]</sup> NU-100,<sup>[4]</sup> and PPN-4,<sup>[5]</sup> 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 CO<sub>2</sub>-uptake capacities were observed under carbon capture conditions.

The polarizability and large quadrupole moment of CO<sub>2</sub> can be taken advantage of by introducing CO<sub>2</sub>-philic moieties that create strong interactions between the material surface and the CO<sub>2</sub>. This will improve the loading capacities and selectivity of CO<sub>2</sub> over other gases. Indeed, this approach has already been proven to be very successful in enhancing the enthalpy of CO<sub>2</sub> adsorption,<sup>[6]</sup> which can be calculated from CO<sub>2</sub> sorption isotherms at different temperatures and used to quantify the interaction between the material and CO<sub>2</sub>. It is worth pointing out that the porosity of the material will be compromised by the introduction of functional groups. CO<sub>2</sub> 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 CO<sub>2</sub> selectivity over N<sub>2</sub>. Taking amine scrubbing as the model, aminated porous materials that have been synthesized usually exhibit very large adsorption enthalpies for CO<sub>2</sub> and high CO<sub>2</sub>/N<sub>2</sub> selectivities. Recently, Long and co-workers demonstrated the incorporation of *N,N*-dimethylethylenediamine (mmen) at exposed metal centers of CuBTtri (H<sub>3</sub>BTtri = 1,3,5-tri(1*H*-1,2,3-triazol-4-yl)benzene), with the new compound mmen-CuBTtri showing drastic enhancement of CO<sub>2</sub> uptake at low pressure, as well as CO<sub>2</sub>/N<sub>2</sub> selectivity. It has the highest heat of adsorption for CO<sub>2</sub> (96 kJ mol<sup>-1</sup>) and one of the highest CO<sub>2</sub>/N<sub>2</sub> adsorption selectivities (*S*<sub>LAST</sub> = 327 at 25 °C) reported to date.<sup>[7]</sup> Despite its large isosteric heat of CO<sub>2</sub> 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.<sup>[6a,8]</sup>

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<sup>[9]</sup> (PPN stands for porous polymer networks), which has an exceptionally high surface area and an extremely robust all-carbon scaffold

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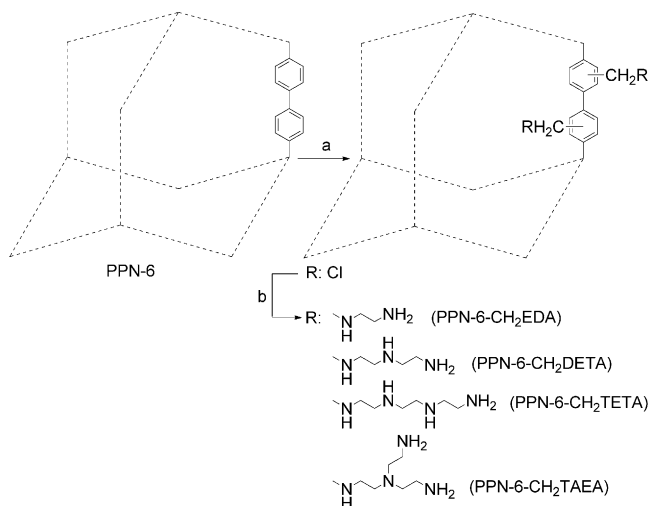
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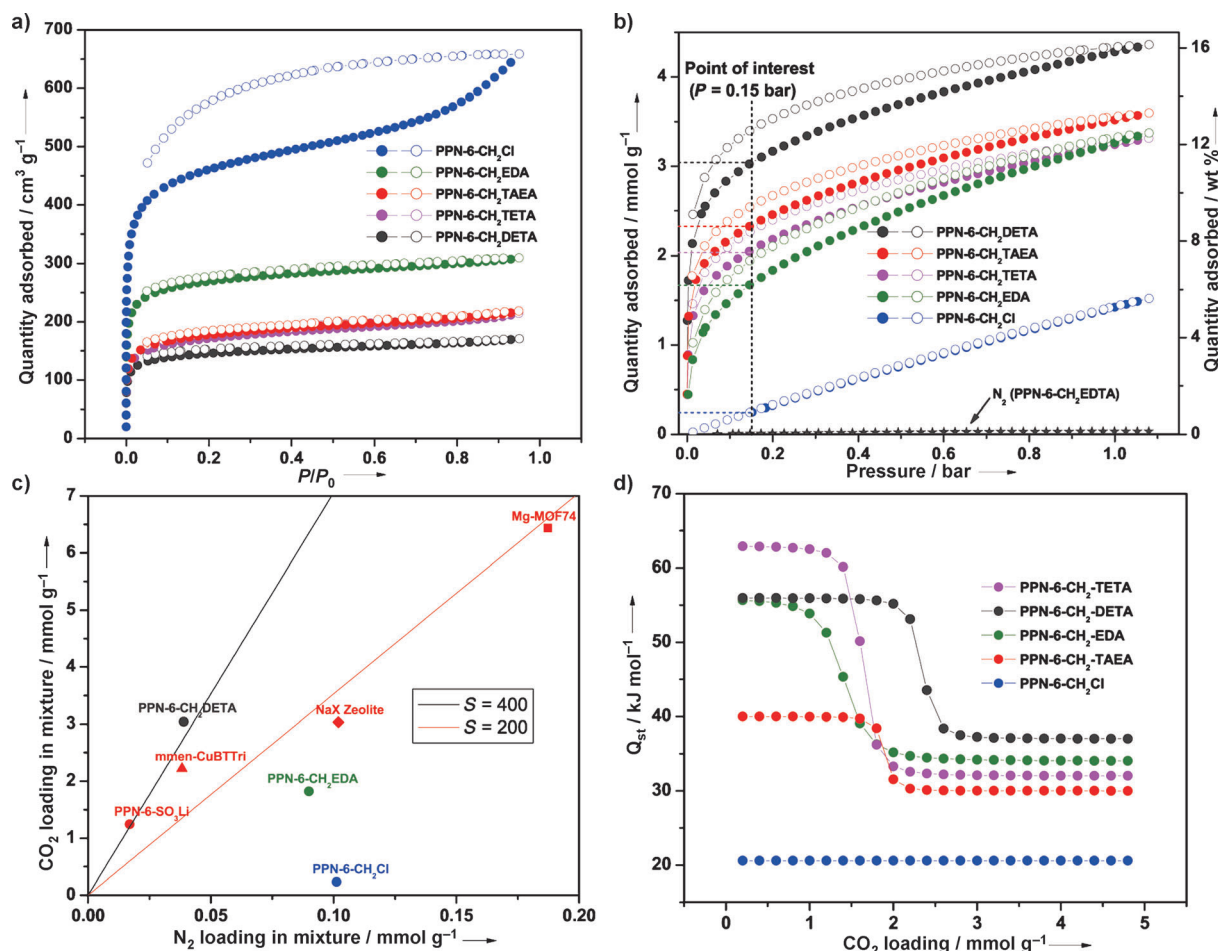
based on biphenyl rings, is ideal for the introduction of CO<sub>2</sub>-philic groups under harsh reaction conditions. PPN-6 (also known as PAF-1, first reported by Ben et al.<sup>[8a]</sup>) was synthesized by using a modified Yamamoto homocoupling polymerization procedure.<sup>[10]</sup> It has a Brunauer–Emmett–Teller (BET) surface area as high as 4023 m<sup>2</sup> g<sup>-1</sup>, and takes up 1.3 mmol g<sup>-1</sup> (5.4 wt %) CO<sub>2</sub> at 295 K and 1 bar. The polyamine-tethered PPNs (Scheme 1, and see Experimental Section) show dramatic increases in CO<sub>2</sub>-uptake capacities at low pressures, and exceptionally high CO<sub>2</sub>/N<sub>2</sub> 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 m<sup>2</sup> g<sup>-1</sup> for PPN-6-CH<sub>2</sub>Cl, PPN-6-CH<sub>2</sub>EDA, PPN-6-CH<sub>2</sub>TAEA, PPN-6-CH<sub>2</sub>TETA, and PPN-6-CH<sub>2</sub>DETA respectively. Notably, the huge adsorption/desorption hysteresis in PPN-6-CH<sub>2</sub>Cl 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) CH<sub>3</sub>COOH/HCl/H<sub>3</sub>PO<sub>4</sub>/HCHO, 90 °C, 3 days; b) amine, 90 °C, 3 days.



**Figure 1.** a) N<sub>2</sub> adsorption (●) and desorption (○) isotherms at 77 K. b) CO<sub>2</sub> adsorption (●) and desorption (○) isotherms, as well as PPN-6-CH<sub>2</sub>DETA N<sub>2</sub> adsorption, at 295 K. c) The component loadings of N<sub>2</sub> and CO<sub>2</sub> calculated by IAST with bulk gas-phase partial pressures of 85 kPa and 15 kPa for N<sub>2</sub> and CO<sub>2</sub>, respectively, with PPN-6-CH<sub>2</sub>DETA, PPN-6-CH<sub>2</sub>EDA, PPN-6-CH<sub>2</sub>Cl, PPN-6-SO<sub>3</sub>Li,<sup>[9]</sup> NaX zeolite,<sup>[9]</sup> MgMOF-74,<sup>[10]</sup> mmen-CuBTtri.<sup>[7]</sup> Loadings for calculated selectivities of 200 and 400 are shown as a guide. d) Isothermic heats of adsorption  $Q_{st}$  for the adsorption of CO<sub>2</sub>, calculated using the dual-site Langmuir isotherm fits.

tion). The chlorine content of 14.42 % in PPN-6-CH<sub>2</sub>Cl was reduced to only trace amounts in the polyamine-tethered PPNs. PPN-6-CH<sub>2</sub>DETA 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 CO<sub>2</sub> adsorption characteristics at 295 K and low pressures (Figure 1b). The trend of improvement in CO<sub>2</sub> adsorption in terms of tethered polyamine groups was DETA > TAEA > TETA > EDA. Although PPN-6-CH<sub>2</sub>DETA has the lowest surface area, it exhibits the highest CO<sub>2</sub>-uptake capacity of all the polyamine-tethered PPNs. This finding indicates that the CO<sub>2</sub>-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.<sup>[8f]</sup> At 295 K and 1 bar, PPN-6-CH<sub>2</sub>DETA exhibits exceptionally high CO<sub>2</sub> uptake (4.3 mmol g<sup>-1</sup>, 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,<sup>[8f,9]</sup> including top-performing N-containing ones, such as N-TC-EMC<sup>[11]</sup> (4.0 mmol g<sup>-1</sup>), BILP-4<sup>[12]</sup> (3.6 mmol g<sup>-1</sup>), and MFB-600<sup>[13]</sup> (2.25 mmol g<sup>-1</sup>).

Coal-fired power plants emit flue gas that contains approximately 15 % CO<sub>2</sub> at total pressures of around 1 bar; thus, CO<sub>2</sub>-uptake capacity at about 0.15 bar (partial pressure of CO<sub>2</sub> in flue gas) is more relevant to realistic post-combustion applications. At 295 K and 0.15 bar, PPN-6-CH<sub>2</sub>Cl only takes up 0.25 mmol g<sup>-1</sup> CO<sub>2</sub> (1.1 wt %), whereas PPN-6-CH<sub>2</sub>DETA takes up 3.0 mmol g<sup>-1</sup> of CO<sub>2</sub> (11.8 wt %). This latter value is comparable to other top-performing materials, such as mmen-CuBTTr<sup>[7]</sup> (9.5 wt % at 298 K) and MgMOF-74<sup>[14]</sup> (22.0 wt % at 293 K), but PPN-CH<sub>2</sub>DETA 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<sup>-1</sup> for PPN-6-CH<sub>2</sub>Cl to 37.5 g L<sup>-1</sup> for PPN-6-CH<sub>2</sub>DETA at 295 K and 0.15 bar (the tap densities were measured to be 0.12 and 0.28 g cm<sup>-3</sup> for PPN-6-CH<sub>2</sub>Cl and PPN-6-CH<sub>2</sub>DETA, respectively; see Table S6 and Figure S2 in the Supporting Information).

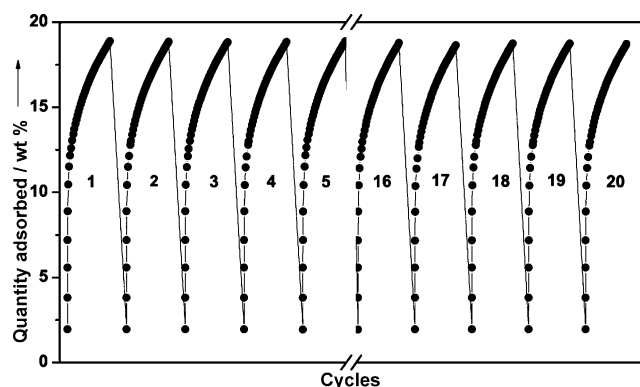
At 295 K, the polyamine-tethered PPNs adsorb less N<sub>2</sub> than PPN-6-CH<sub>2</sub>Cl (see Figure S3 in the Supporting Information). PPN-6-CH<sub>2</sub>DETA is especially interesting, with an uptake of less than 0.1 wt % N<sub>2</sub> at 1.0 bar, approximately one third of that of PPN-6-CH<sub>2</sub>Cl. It is possible that the added polar sites in the former may enhance N<sub>2</sub> adsorption, but that this is totally offset by the significant loss of surface area. Conversely, the CO<sub>2</sub> uptake is significantly enhanced because the strong interactions play a more significant role.

To evaluate the CO<sub>2</sub>/N<sub>2</sub> 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<sup>[15]</sup> 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 N<sub>2</sub> and CO<sub>2</sub> for PPN-6-CH<sub>2</sub>Cl, PPN-6-CH<sub>2</sub>EDA, PPN-6-CH<sub>2</sub>DETA, PPN-6-SO<sub>3</sub>Li, MgMOF-74, NaX zeolite, and mmen-CuBTTr calculated by IAST with bulk phase equilibrium partial pressures of 85 kPa (N<sub>2</sub>) and 15 kPa (CO<sub>2</sub>). Two factors that define a material for efficient separation of CO<sub>2</sub> are a high CO<sub>2</sub> loading and a high selectivity over N<sub>2</sub>. Figure 1c clearly shows both factors, and highlights the high loading on PPN-6-CH<sub>2</sub>DETA and its exceptional selectivity of CO<sub>2</sub> over N<sub>2</sub> (the better the material, the closer to the top left corner of the graph). We note that CO<sub>2</sub> loading is highest for MgMOF-74; however, PPN-6-CH<sub>2</sub>DETA has a much lower N<sub>2</sub> uptake than MgMOF-74, thereby leading to an unprecedented selectivity compared to any reported material (see Table S7 in the Supporting Information). The poor N<sub>2</sub> adsorption with PPN-6-CH<sub>2</sub>DETA can be attributed to low porosity (pore volumes are 0.573 and 0.264 cm<sup>3</sup> g<sup>-1</sup> for MgMOF-74<sup>[14]</sup> and PPN-6-CH<sub>2</sub>DETA, respectively).

To better understand the adsorption properties, the isosteric heats of adsorption ( $Q_{st}$ ) were calculated from dual-site Langmuir fits of the CO<sub>2</sub> 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-CH<sub>2</sub>DETA retains its strong CO<sub>2</sub> interactions to a relatively high CO<sub>2</sub> loading (ca. 2.0 mmol g<sup>-1</sup>), which is consistent with its large CO<sub>2</sub>-uptake capacity. The temperatures of flue-gas streams emitted from power plants, however, are much higher than 295 K. To be practically useful for CO<sub>2</sub> capture under realistic flue-gas conditions, the preservation of high isosteric heats of adsorption is essential for solid adsorbents so as to maintain high CO<sub>2</sub>-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 CO<sub>2</sub>-uptake capacity of PPN-6-CH<sub>2</sub>DETA 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 CO<sub>2</sub> capacities at low partial pressures; however, concerns about material regeneration are often raised. To test the cyclability of PPN-6-CH<sub>2</sub>DETA we simulated temperature and vacuum swings with an ASAP2020 analyzer, by saturating with CO<sub>2</sub> 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-CH<sub>2</sub>DETA shows higher energy demands for regeneration, possibly because of the large percentage of primary amines in PPN-6-CH<sub>2</sub>DETA as opposed to only secondary amines in mmen-CuBTTr—primary amines have been shown to form stronger bonds with CO<sub>2</sub>. 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<sup>-1</sup>) necessitate heating the solutions containing about 70 % water



**Figure 2.** Twenty cycles of CO<sub>2</sub> 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<sup>-1</sup> K<sup>-1</sup>).

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 CO<sub>2</sub> capacity, high selectivity, and low regeneration costs are the criteria by which new adsorbents for post-combustion CO<sub>2</sub> 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 CO<sub>2</sub>-uptake capacity but much lowered N<sub>2</sub>-uptake capacity at low pressures. PPN-6-CH<sub>2</sub>DETA exhibits an exceptionally high binding affinity and the largest selectivity for CO<sub>2</sub> 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 CO<sub>2</sub> 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)<sub>2</sub>]; 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-CH<sub>2</sub>Cl:** A resealable flask was charged with PPN-6 (200 mg), paraformaldehyde (1.0 g), glacial AcOH (6.0 mL), H<sub>3</sub>PO<sub>4</sub> (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-CH<sub>2</sub>Cl as a brown powder in quantitative yield.

**General procedure for the introduction of polyamine groups (with the synthesis of PPN-6-CH<sub>2</sub>DETA as an example):** A resealable

flask was charged with PPN-6-CH<sub>2</sub>Cl (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-CH<sub>2</sub>DETA as a brown powder in quantitative yield.

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