Selective Porous Polymer Networks Supported on Hollow Fiber Superstructures for Direct Air Capture of CO_2

UCFER Annual Meeting

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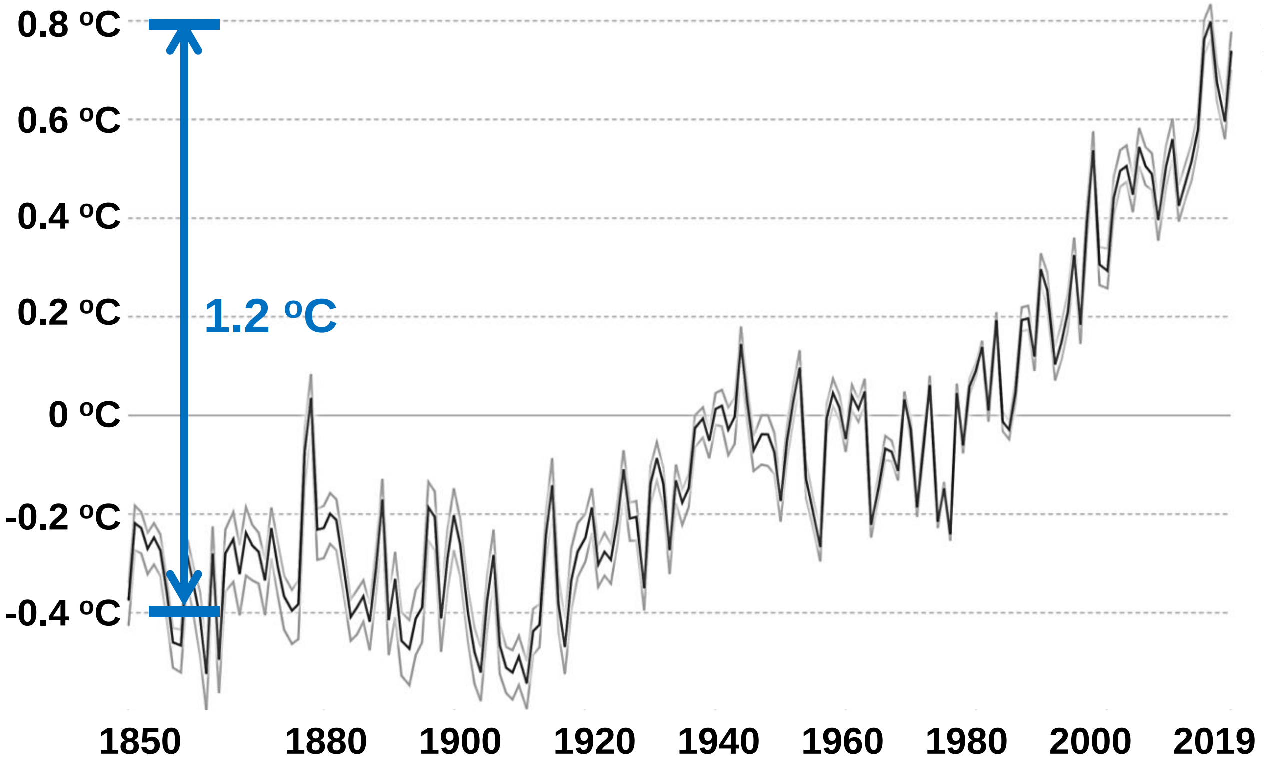
Content

- Background
- Porous polymer network (PPN) candidates
- PPN modifications
- Collaboration with NETL
- Summary
- Acknowledgement

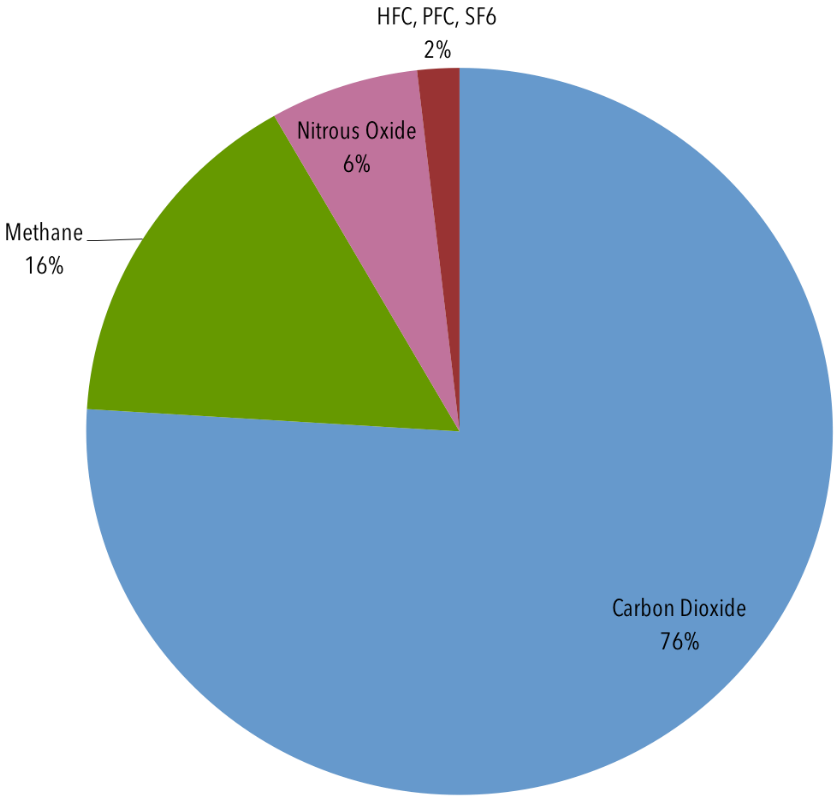
▪ Background

➢ Global average temperature



Roughly 1.2 ºC increase

➢ Green house gases

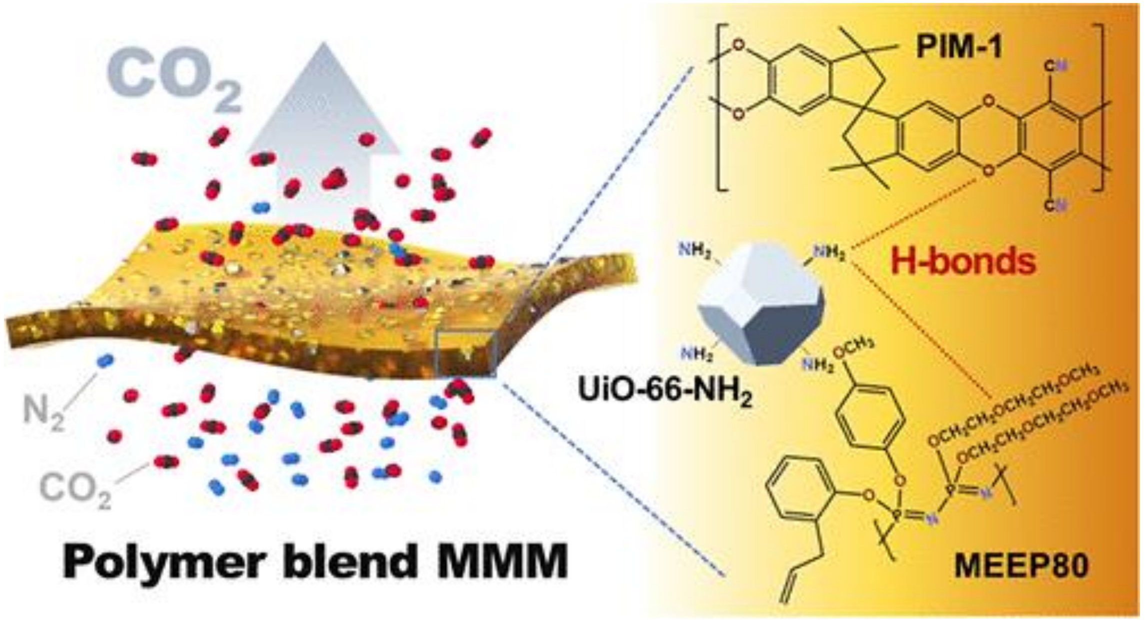


CO_2, dominant green house gas

CO_2 and greenhouse gas emissions. www.ourworldindata.org/ (accessed September 26, 2021)

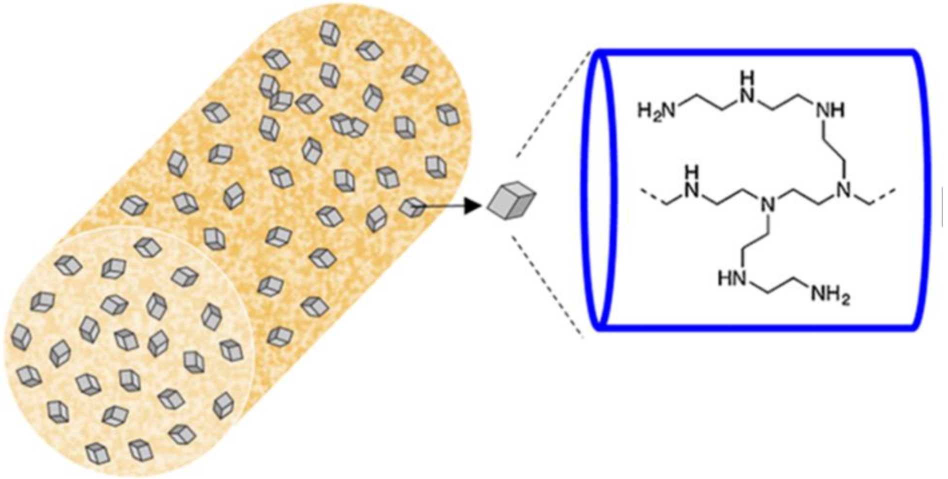
Methods for Carbon Capture

Post-combustion CO_2 separation



Mixed matrix membrane (MMM)

Direct air capture (DAC)

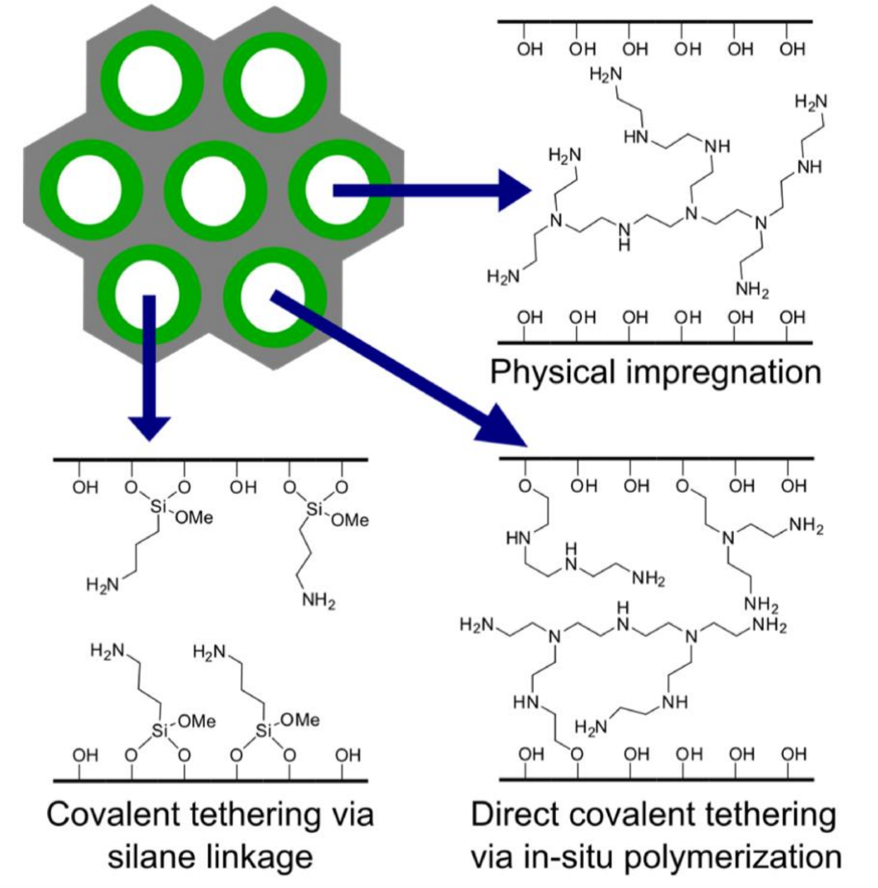


Amine-functionalized cellulose acetate silica fiber sorbents

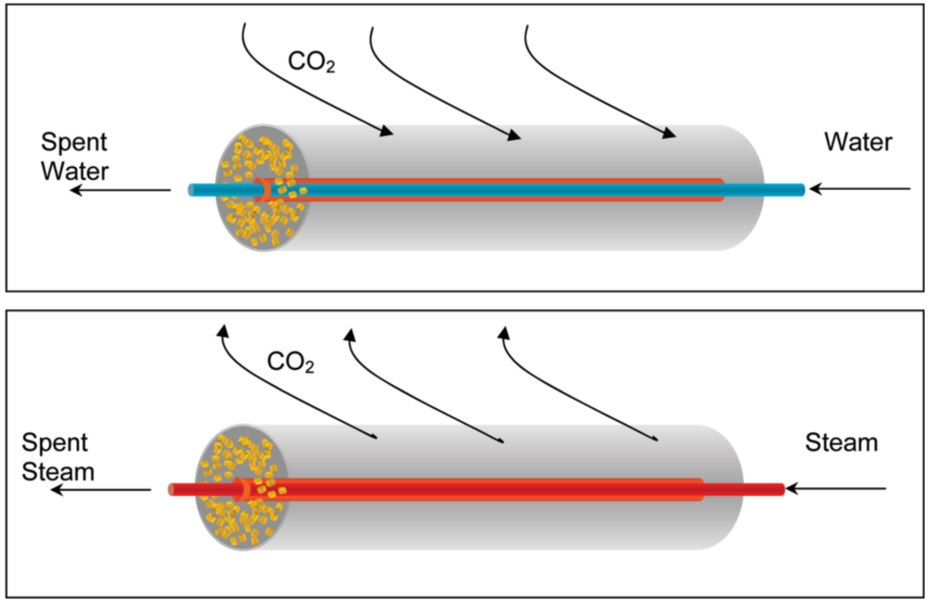
Shouliang Yi, Ali K. Sekizkardes, Nathaniel L. Rosi, et al., *ACS Materials Lett.*, **2020**, *2*, 821
Ryan P. Lively, et al., *ACS Sustainable Chem. Eng.*, **2019**, *7*, 5264

▪ Challenges in DAC and Solutions

- ➢ **Low concentration, 400 ppm**
- ➢ **Sorption and regeneration**



Amine functionalization

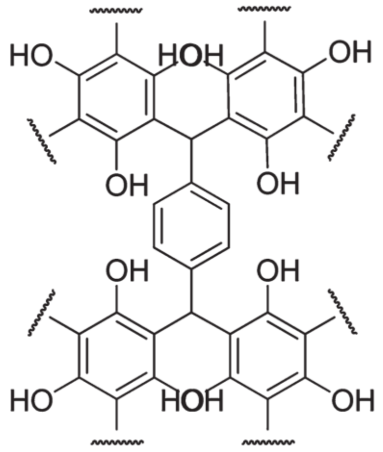


Rapid temperature swing adsorption (RTSA)

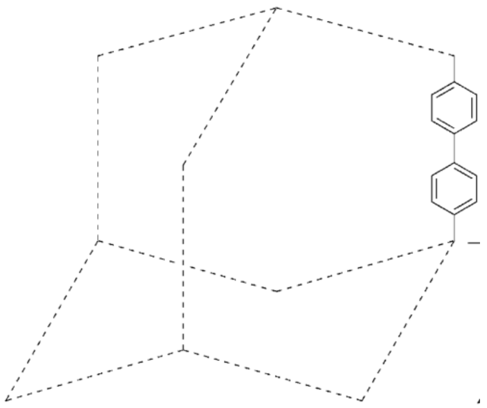
Stephanie A. Didas, Georgia Institute of Technology: **2014**
Ryan P. Lively, et al., *ACS Sustainable Chem. Eng.*, **2019**, *7*, 5264

▪ Porous Polymer Networks-Based Hollow Fibers for DAC

➢ Porous polymer networks (PPNs)



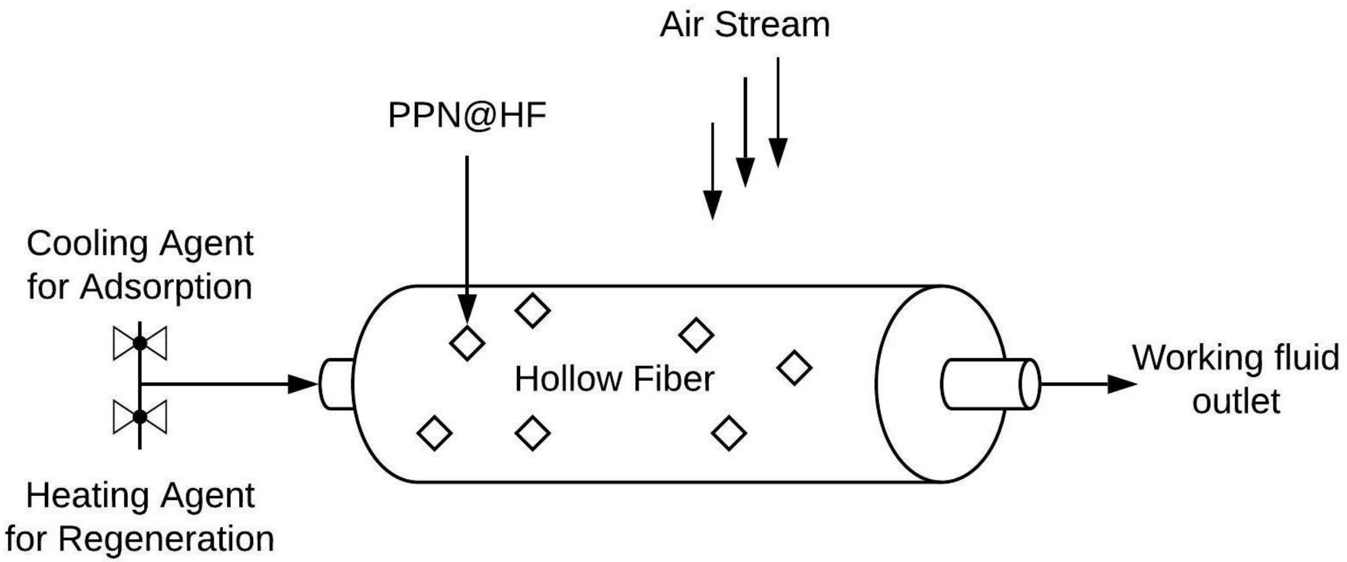
PPN-125



PPN-6

Porous, stable, functionalizable, CO_2 adsorption and selectivity

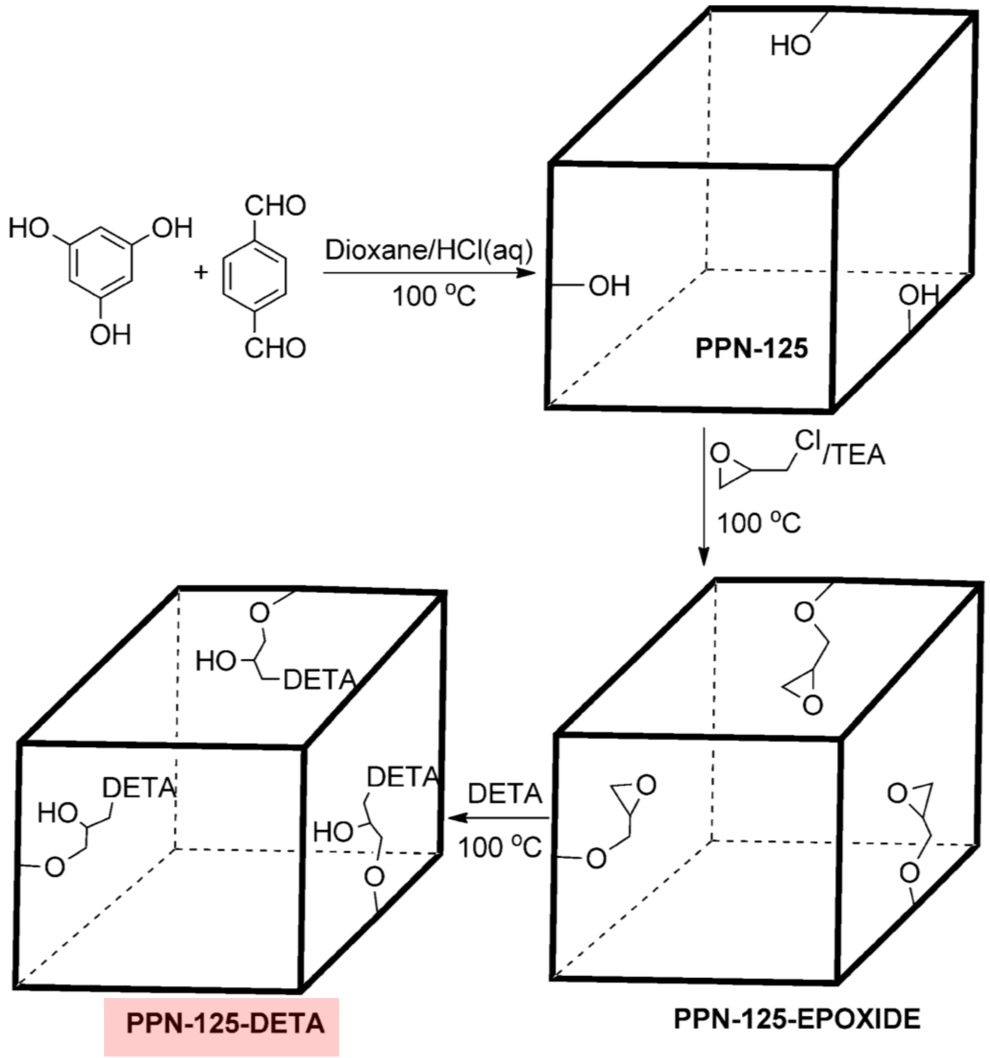
➢ The proposed idea

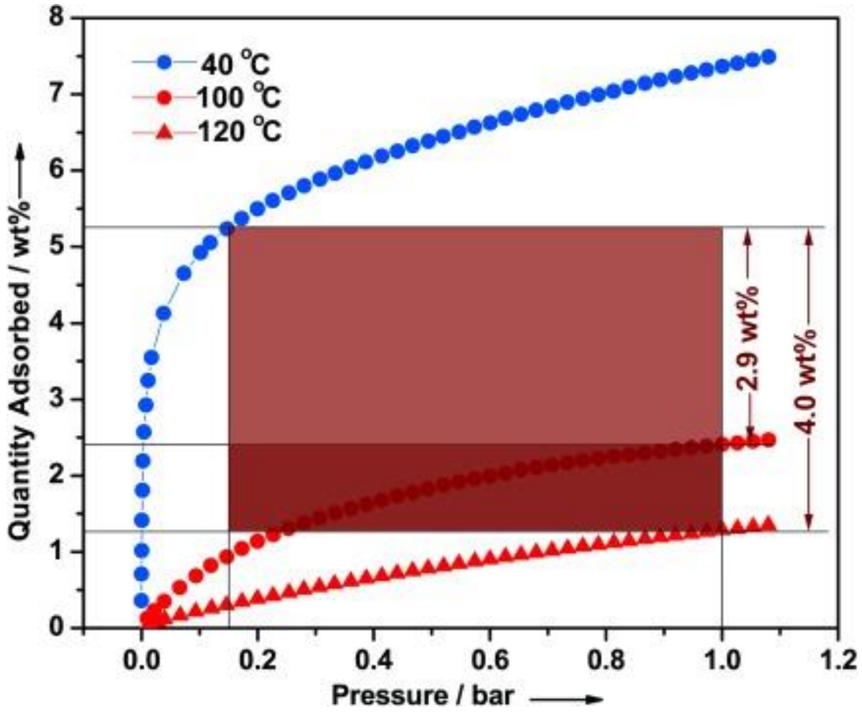


PPN sorbent + RTSA method

Mercouri G. Kanatzidis, et al., *Chem. Mater.*, **2011**, *23*, 1818
Hong-Cai Zhou, et al., *Angew. Chem. Int. Ed.*, **2012**, *51*, 7480

▪ PPN Candidates – PPN-125-DETA (diethylenetriamine)

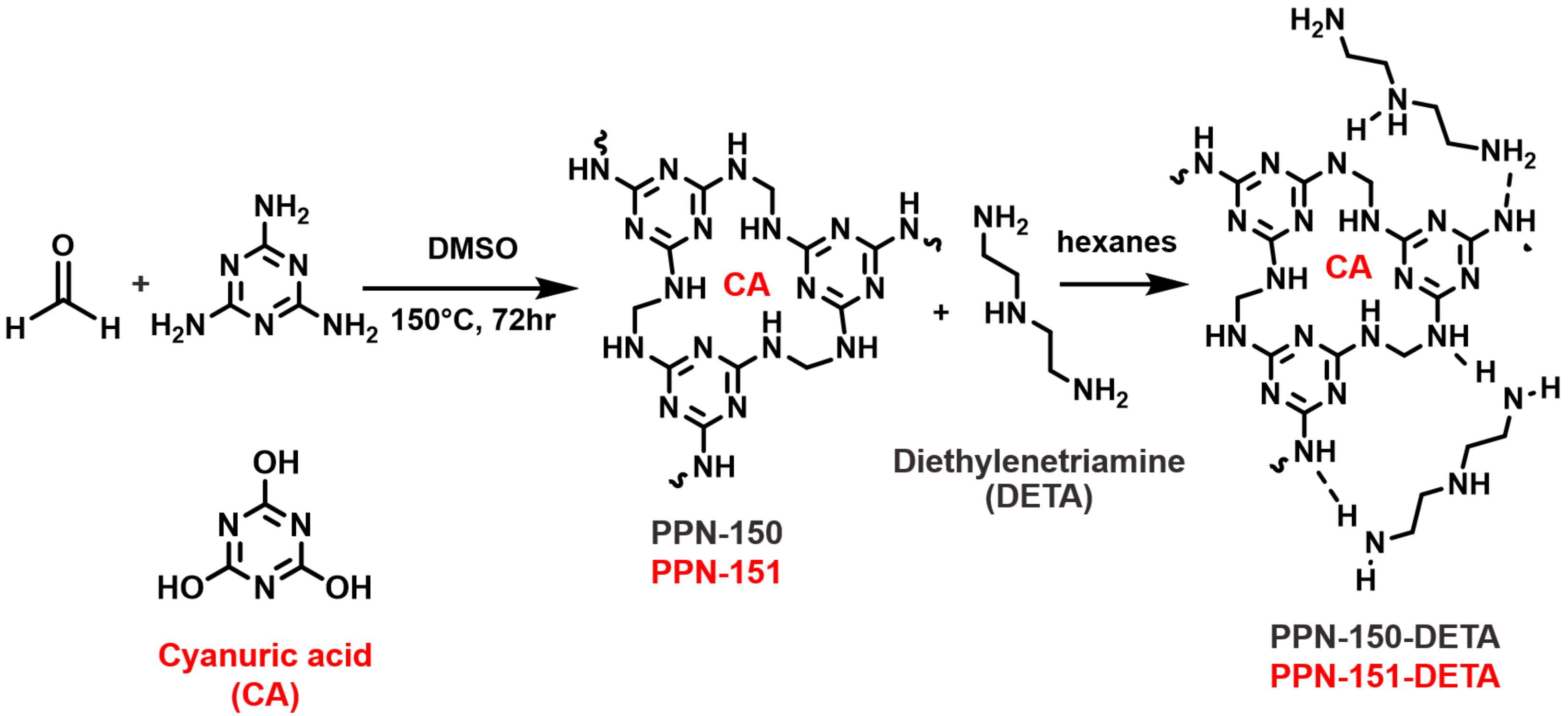


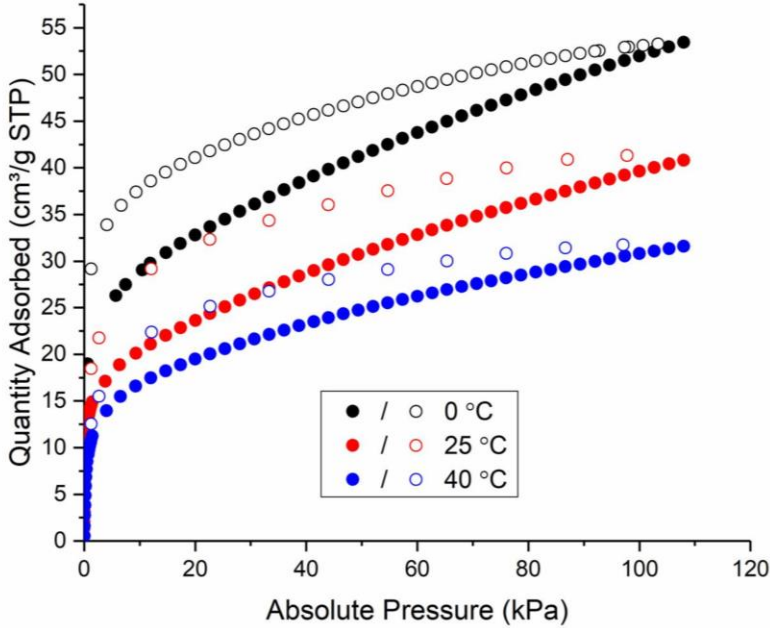


Working capacity: 1.0 mmolg^{-1} (4.0 wt%)
(comparable to monoethanolamine (**MEA**) solutions)
Low cost, controllable pore size

Hongcai Zhou, et al., *ChemSusChem*, **2015**, *8*, 433

▪ PPN Candidates – PPN-150 Series





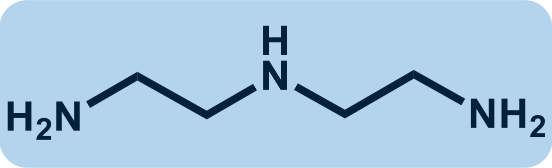
CO_2 adsorption of PPN-151-DETA

Working capacity: 5 wt% (dry), 18 wt% (wet)
Regenerative energy: 82.8 kJ/mol CO_2 (MEA, 185 kJ/mol CO_2)
Low cost, large scale preparation

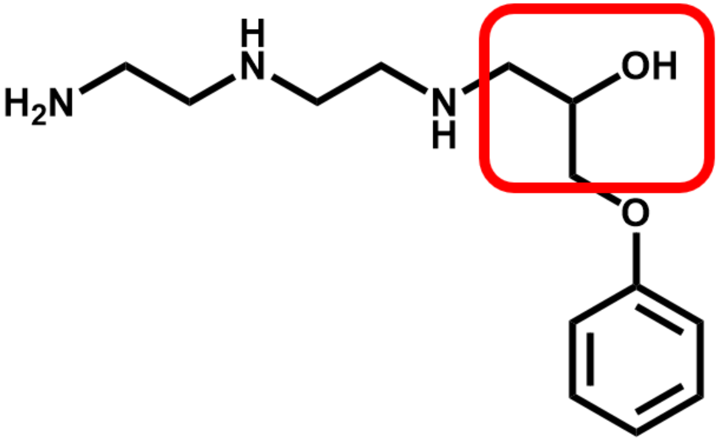
Hongcai Zhou, et al., *Adv. Sustain. Syst.*, **2019**, *3*, 1900051

▪ Modifications of PPNs

Diethylenetriamine (DETA):

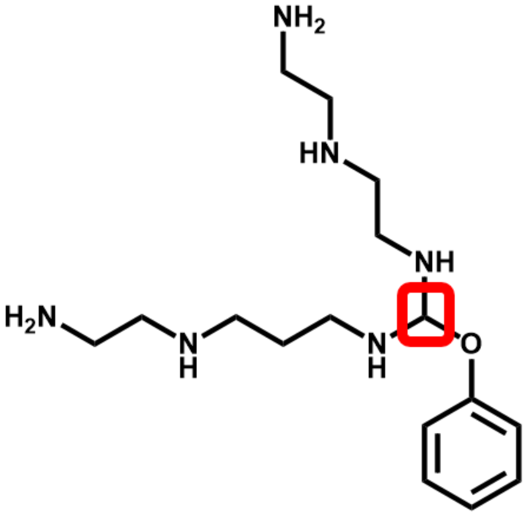


41% N mass/additional masses



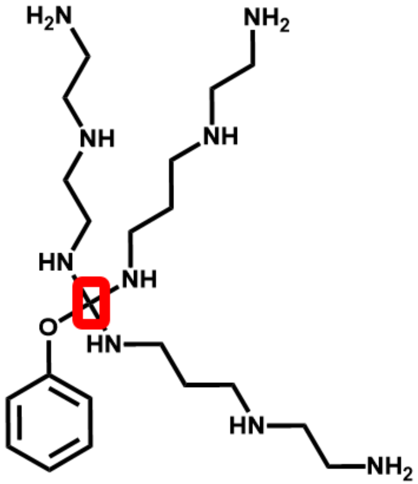
$C_7O_1N_3H_{18}$-3N

26% N mass/additional masses



$C_9N_6H_{25}$-6N

39% N mass/additional masses



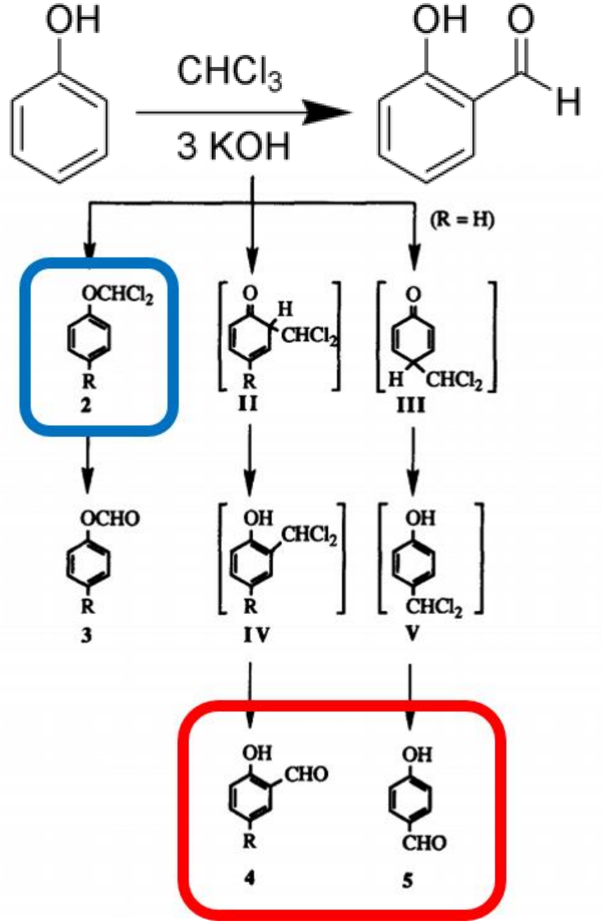
$C_{13}N_9H_{36}$-6N

40% N mass/additional masses

Much higher (2-3X) amine density!

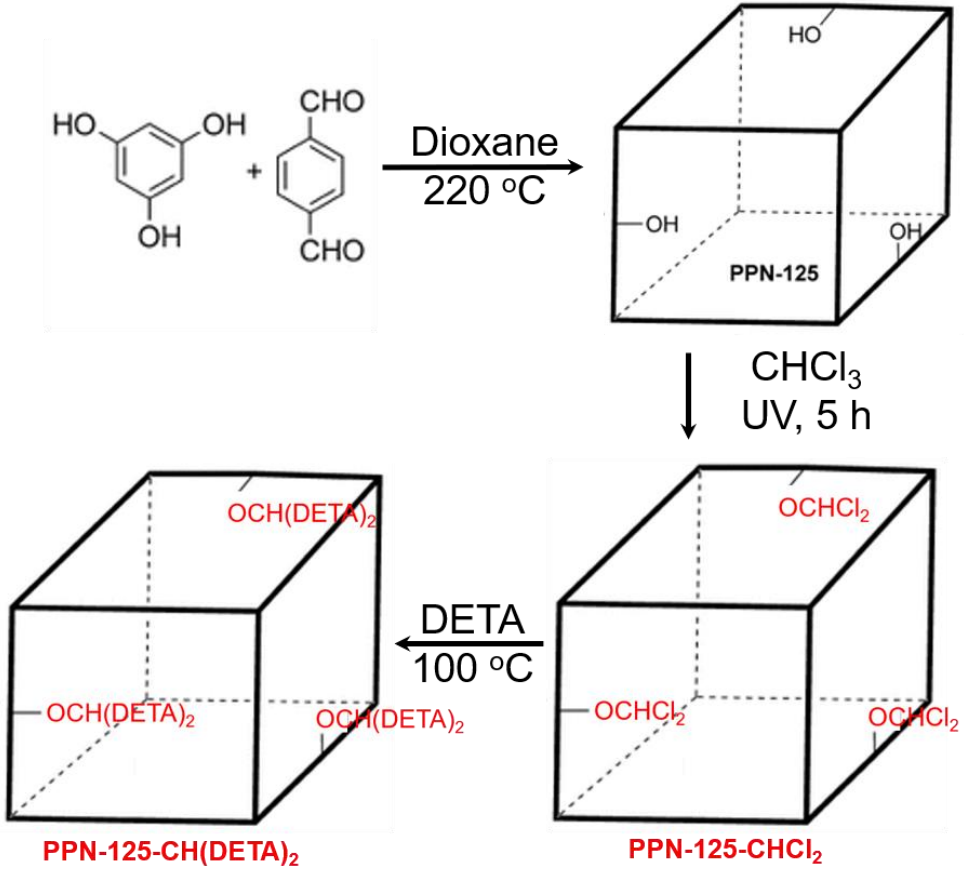
Modifications of PPNs

Reimer-Tiemann reaction



Product 2 can be the dominant

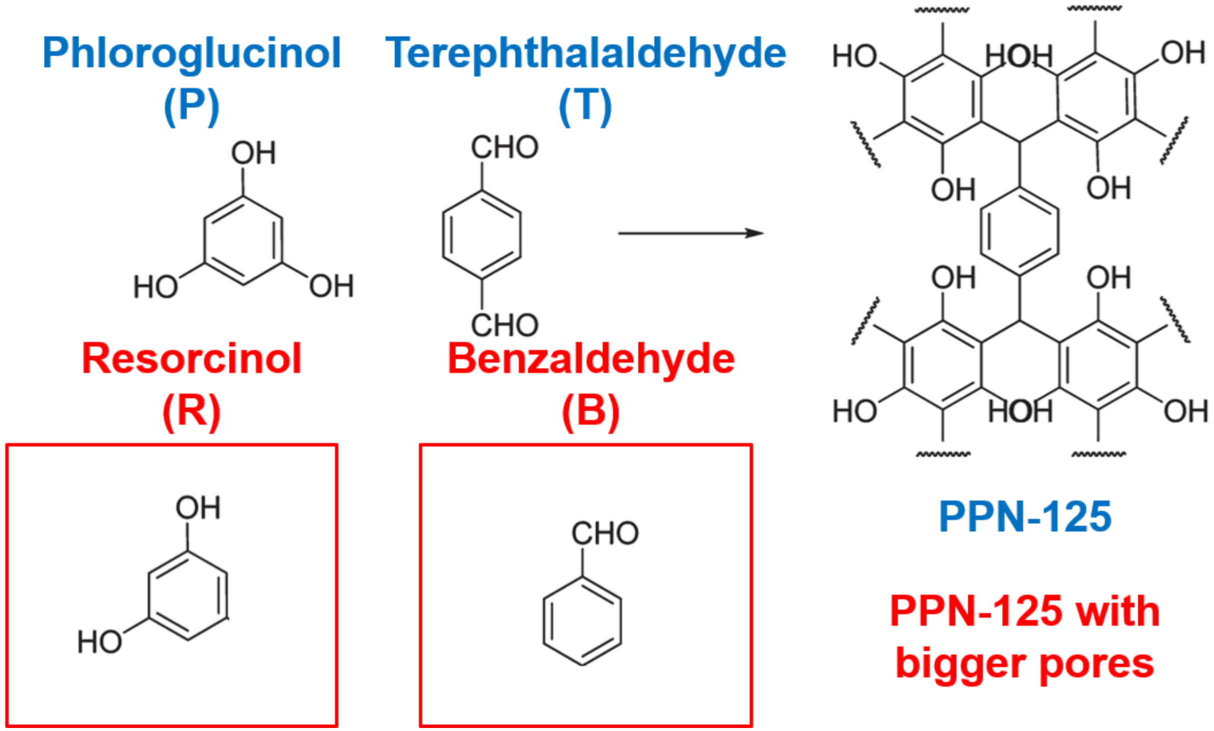
PPN-125 modification



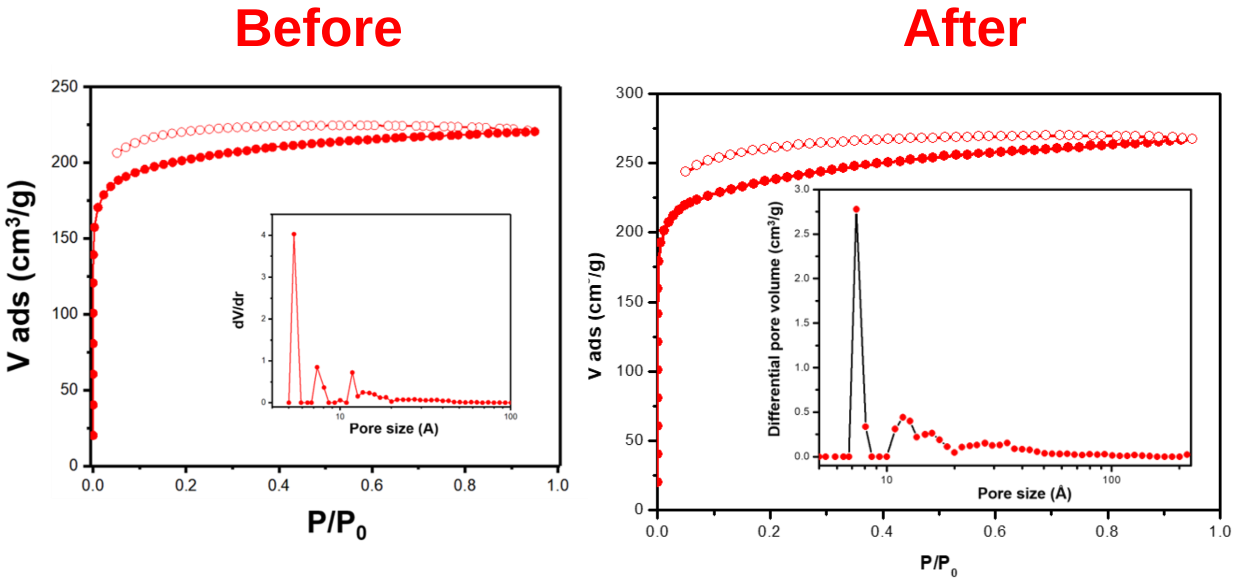
Pore blockage ➡ Enlarge pores

Rosa Tormos, et al., *Tetrahedron*, **1995**, 51, 5825

▪ Enlarge the Pore Size – Method 1



PPN-125 with bigger pores



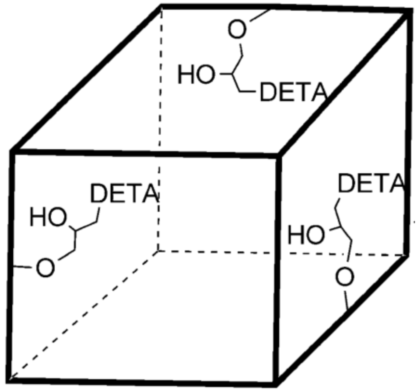
Surface area: 750 m^2/g
Pore size: 5.5 Å

BET surface area: 910 m^2/g
Pore size: 8 Å

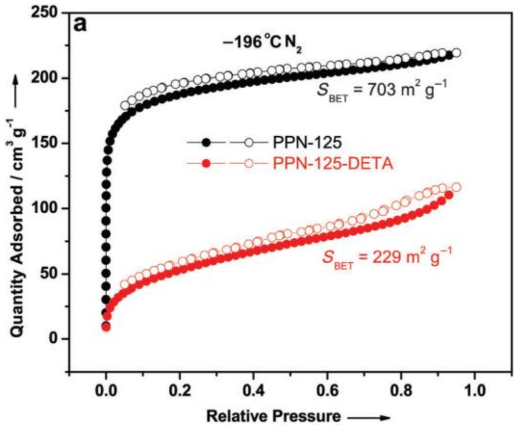
Blend monomers with less branches

▪ Enlarge the Pore Size – Method 2

➢ **Long side chain effect**

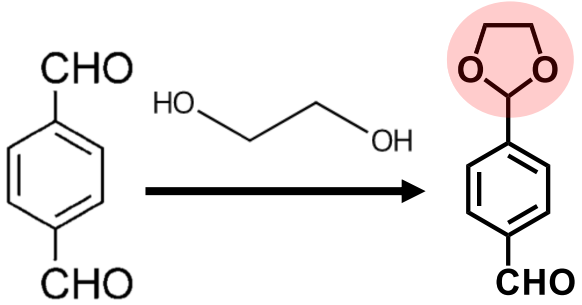


PPN-125-DETA

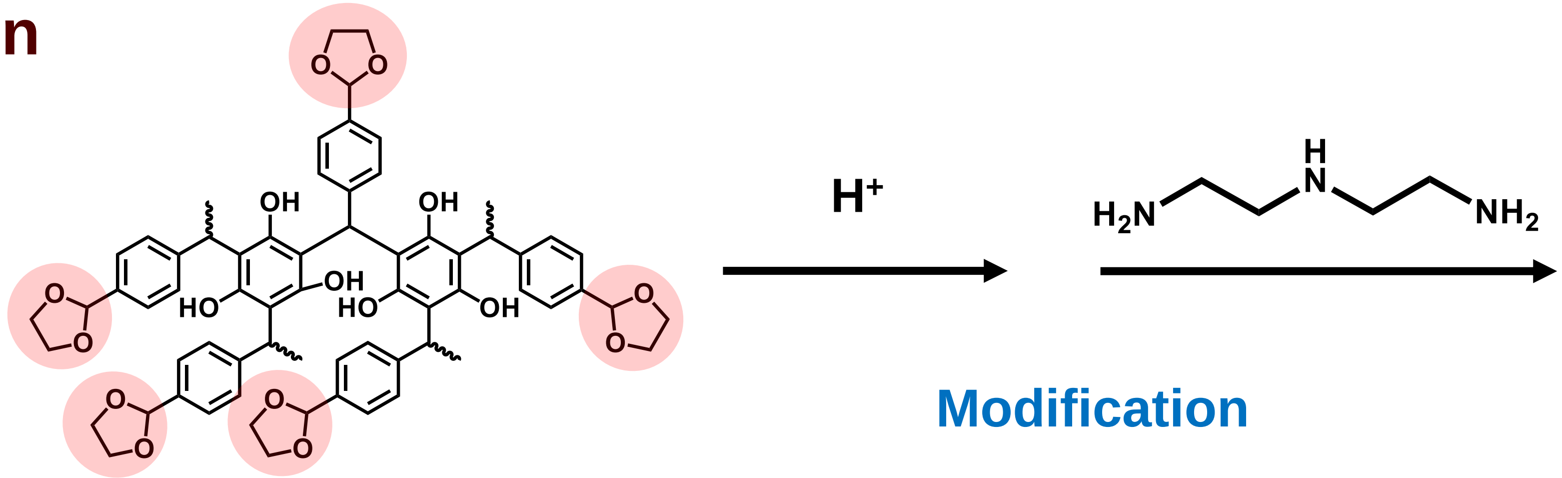


Surface area drop

➢ **Aldehyde group protection**



Protection



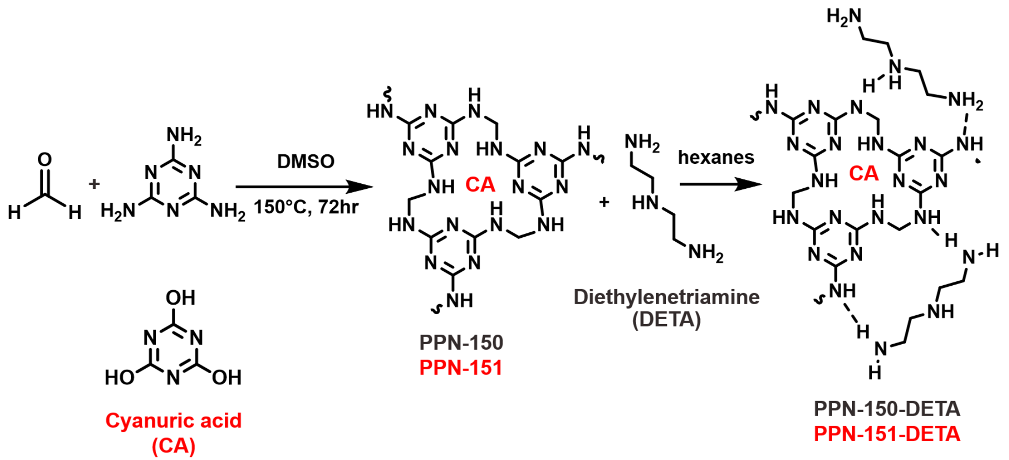
Modification

Directly connect to DETA to reduce the long side chain

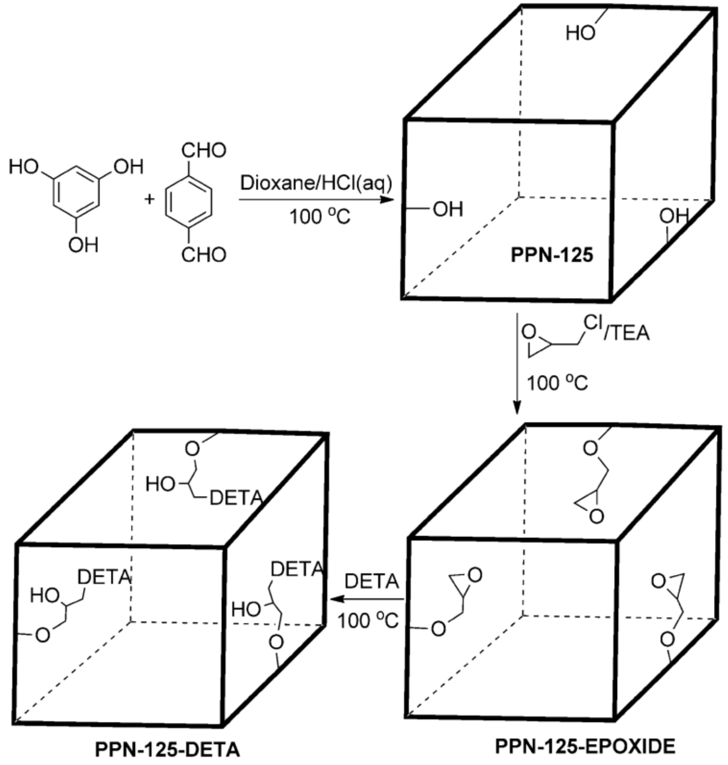
▪ Collaboration with NETL



Drs. David Hopkinson | Ali Sekizkardes | Shouliang Yi



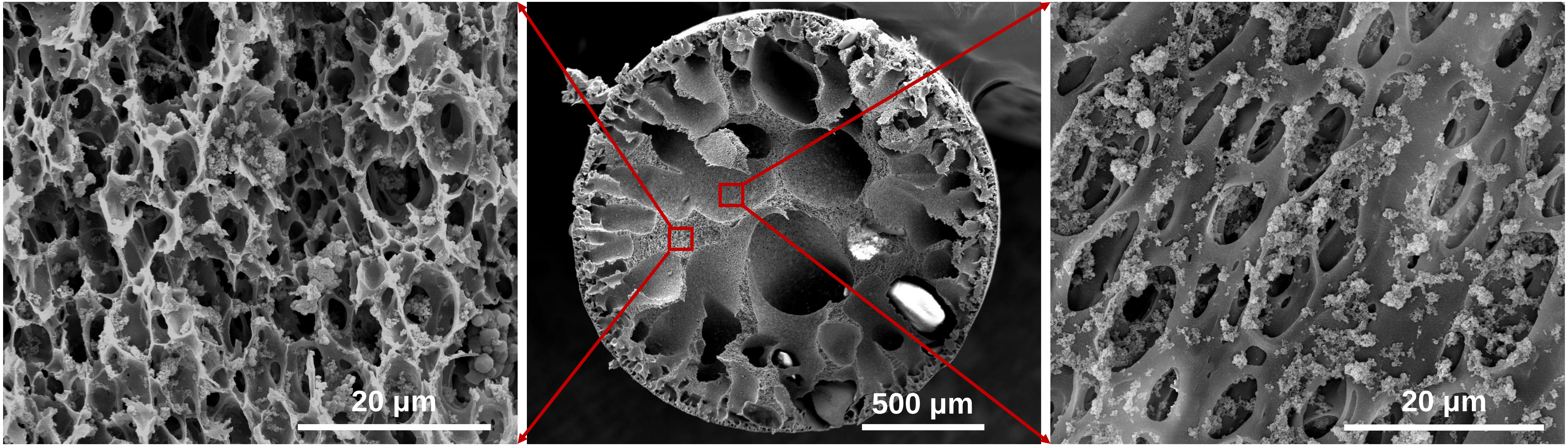
10 g PPN-151-DETA
5 g PPN-151



10 g PPN-125-DETA

Hongcai Zhou, et al., *ChemSusChem*, **2015**, *8*, 433
Hongcai Zhou, et al., *Adv. Sustain. Syst.*, **2019**, *3*, 1900051

▪ Preliminary Results



50 wt% PPN-151-DETA@cellulose acetate (CA)

- Highly porous for carbon capture
- Durable and robust

SEM image taken by Dr. Shouliang Yi

Future Plan

- **Smaller size of PPN powders for better results**

- **90 wt% PPN@polymer matrix**

- Reason: high compatibility between PPN and polymer matrix
- Amazingly high loading ratio
- Up to 90% CO_2 uptake of PPN's powder form
- Much better than silica-based or MOF-based sorbents due to their relatively low loading capability in matrices

Summary

- Hollow fiber supported PPN sorbents for DAC
- PPN candidates selection
- PPN modification and pore size adjustment
- Collaboration with NETL
- Preliminary result collection
- Promising high loading ratio and CO_2 uptake

Acknowledgements

Dr. Ali Sekizkardes Dr. David Hopkinson

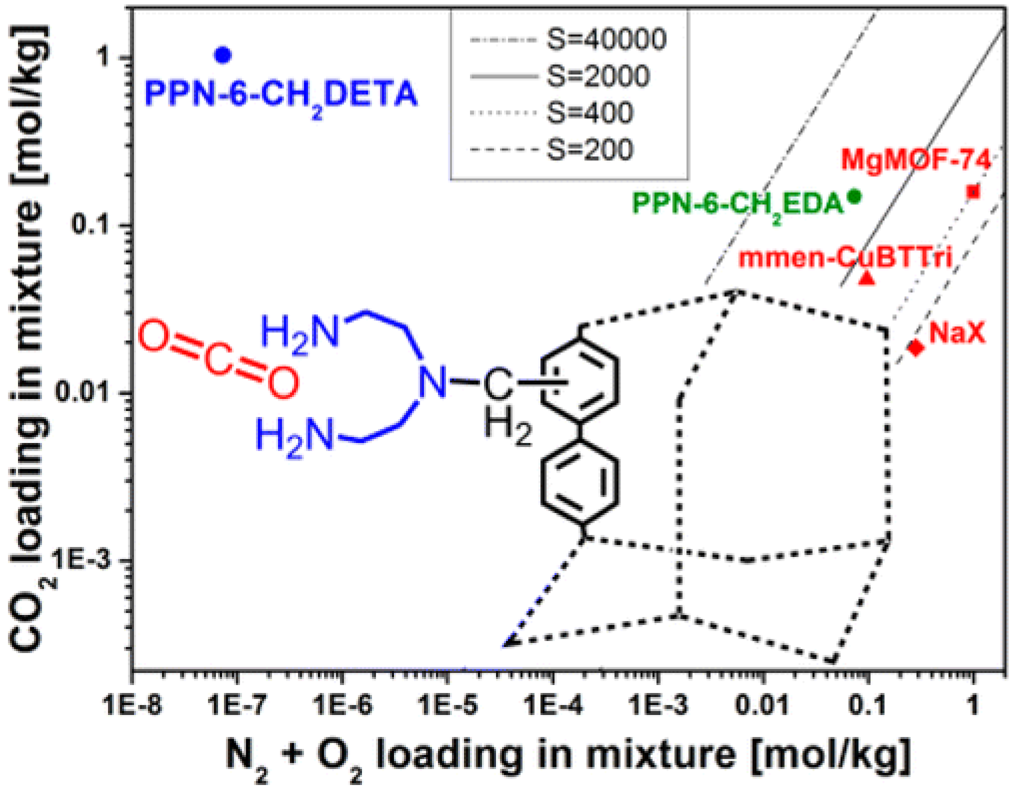
Dr. Shouliang Yi Dr. David Lang

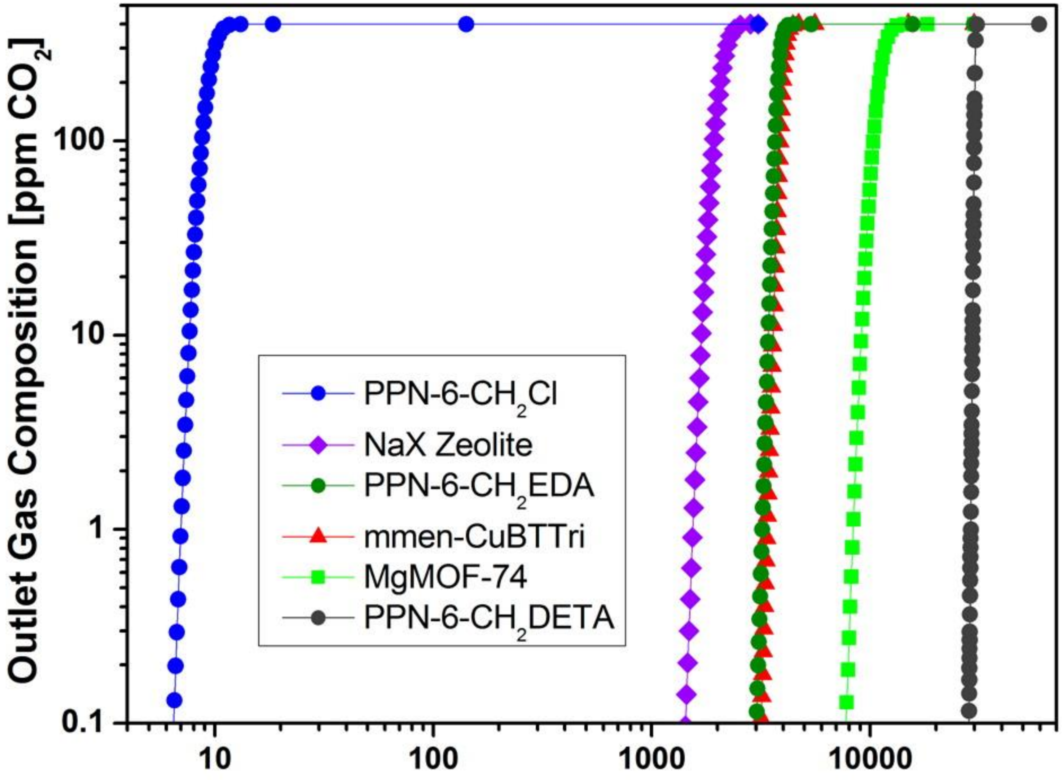
Dr. Benjamin Wilhite & Naveen Mishra (Chemical Engineering)

Fan Chen & Peiyu Cai (Chemistry, Zhou group)

Thank you! Questions?

- **PPN-6-CH2-DETA**





Simulated using ideal adsorption solution theory (IAST) with ultradilute CO_2 400 ppm

Strength: microporous, ultra-high selectivity, high CO_2 loading efficiency (1.04 mol/kg)

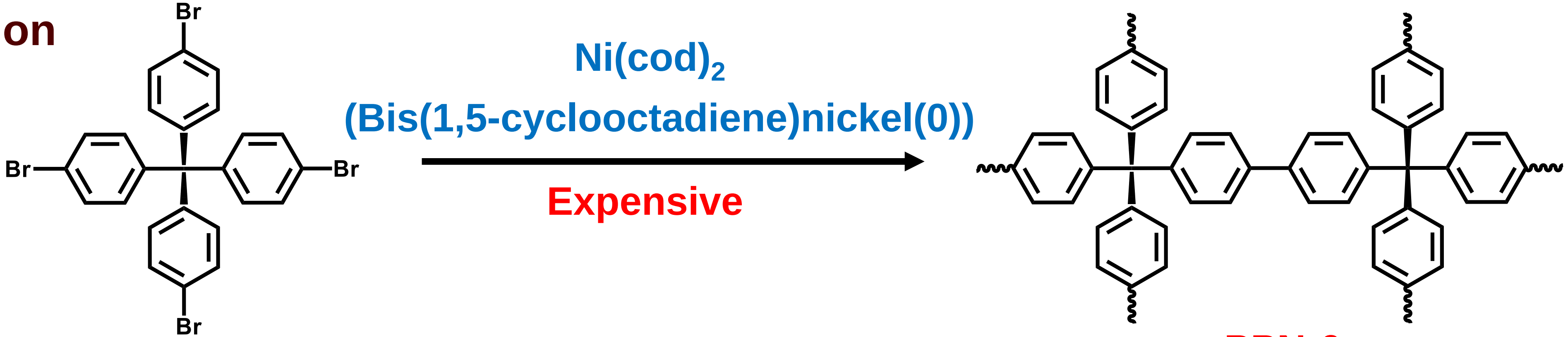
Defect: expensive

Methods to synthesize PPN-6 at low cost is wanted

Hongcai Zhou, et al., *J. Phys. Chem. C*, **2013**, 117, 4057

▪ Efforts on Synthesis of PPN-6’

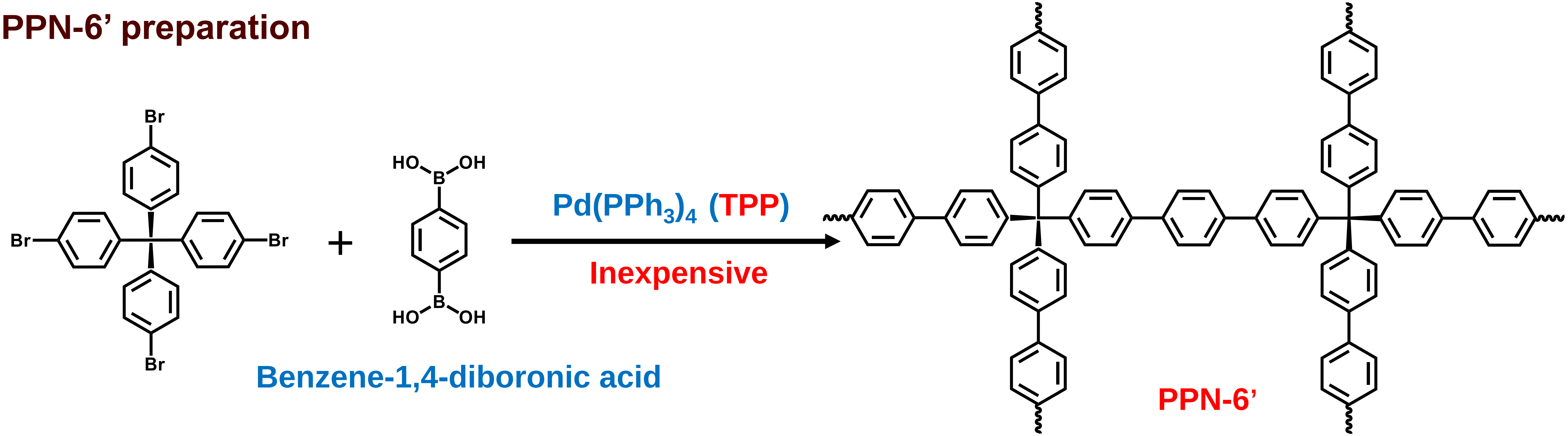
➢ PPN-6 preparation



Tetrakis(4-bromophenyl)methane (TBM)

PPN-6

➢ PPN-6’ preparation

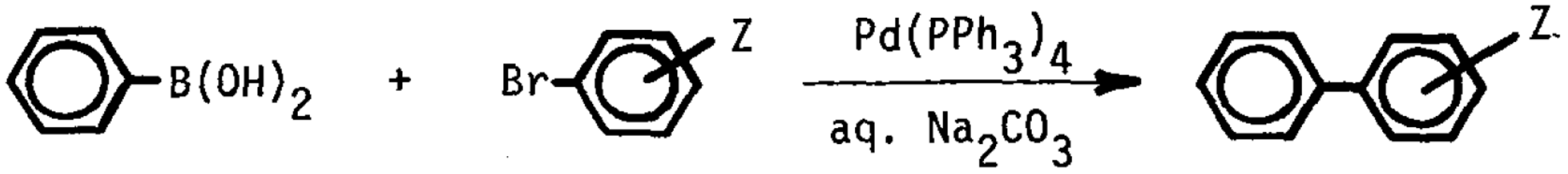


Benzene-1,4-diboronic acid

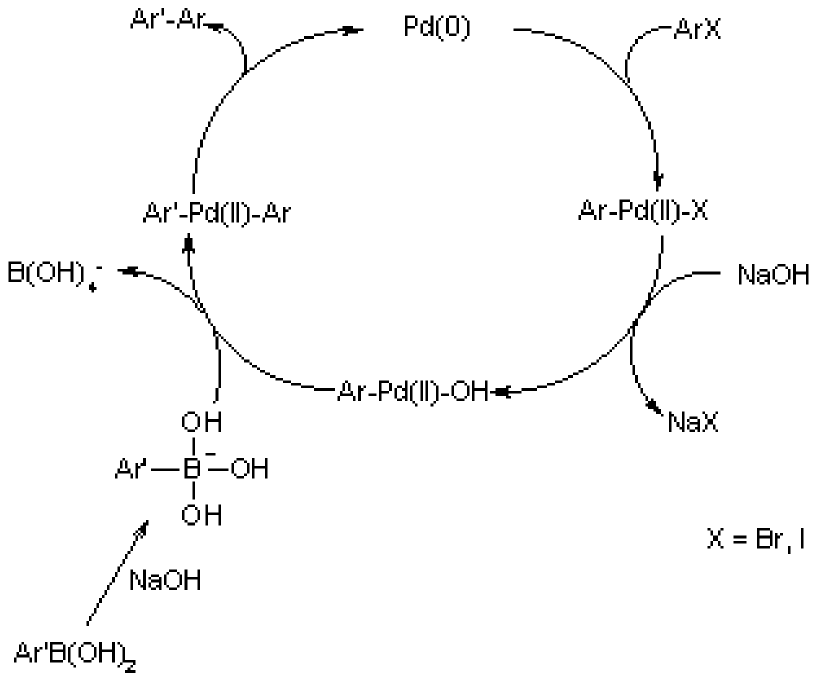
PPN-6’

▪ Reaction Mechanism & Preparation Process

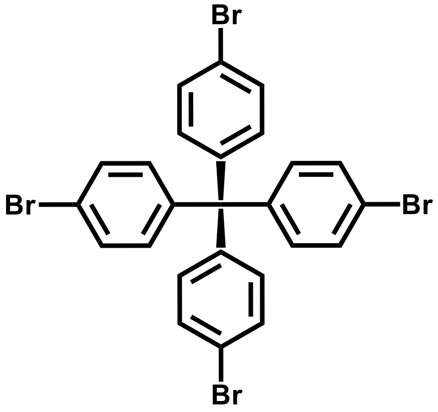
➢ Suzuki-Miyaura coupling reaction mechanism



Suzuki, A., et al., *Synth, Commun.*, **1981**, *11*, 513



➢ Preparation process & results



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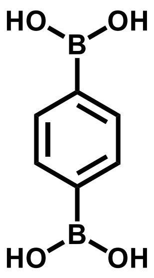


$Pd(PPh_3)_4$

50 ml p-dioxane
(oxygen & water free)
1 g Na_2CO_3
120 °C, 7 days

100 mg

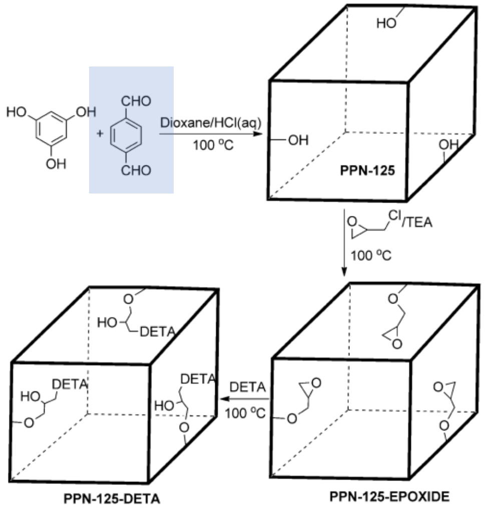
300 mg

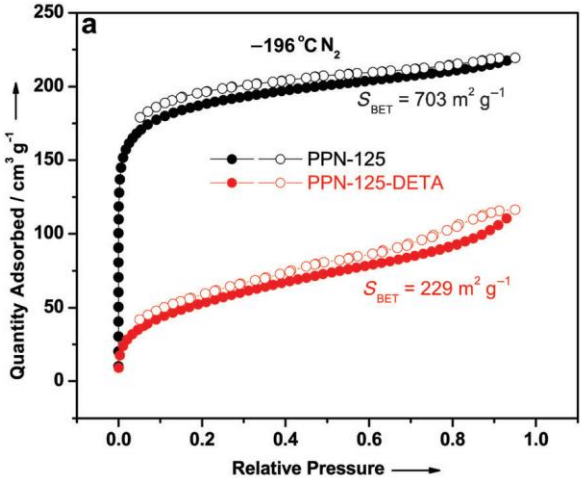
Only soluble species were generated
Oligomers but not PPNs

Unsuccessful

▪ Plans for More Attempts on PPN-125

➢ Surface area drop after modification

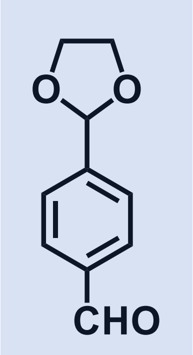


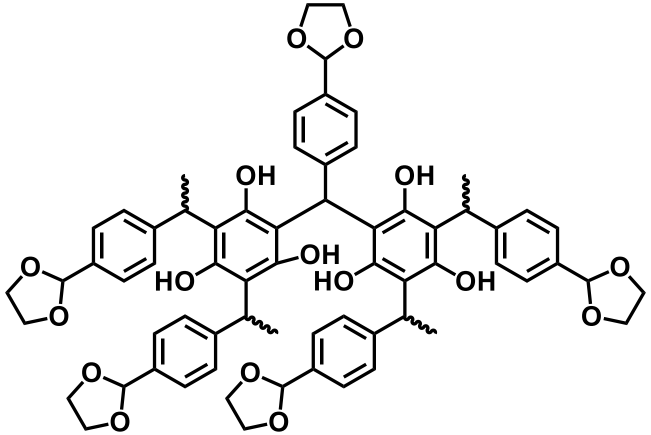


Long side chain brings the surface area down

Add amines with short side chains

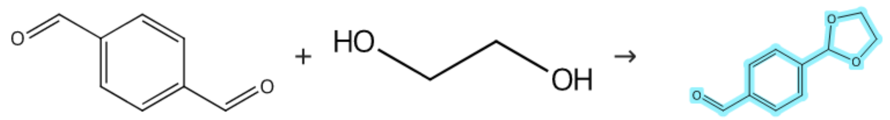
➢ Plan-1



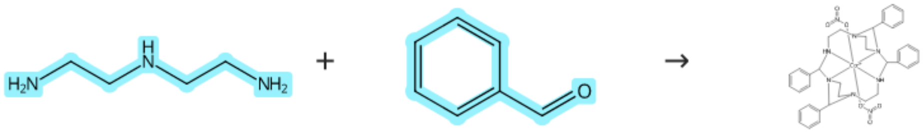


Partially protect aldehyde groups

Excess aldehyde group for amine



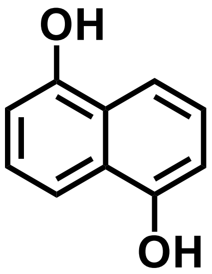
Protect reaction



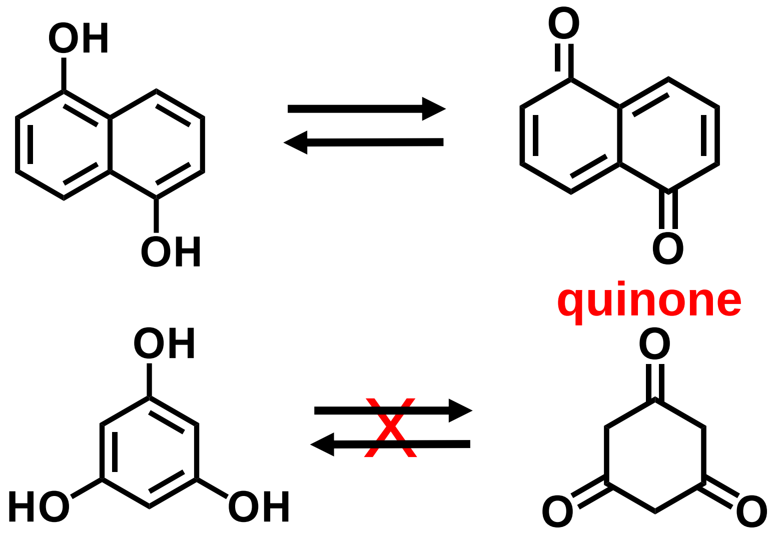
Modification reaction

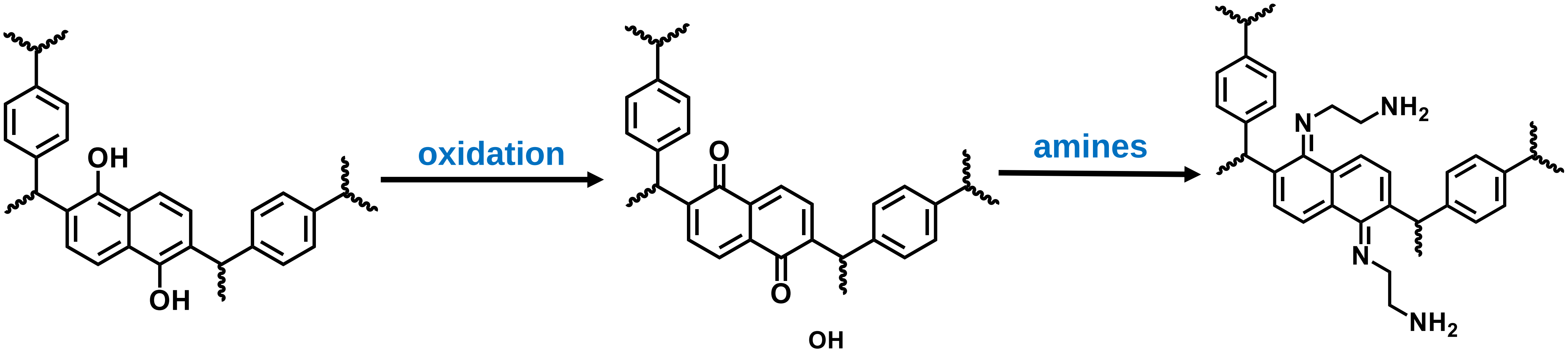
▪ Plans for More Attempts on PPN-125

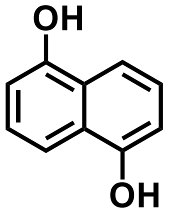
➢ Plan-2

Blend  into PPN-125 synthesis?

1,5-dihydroxy naphthalene

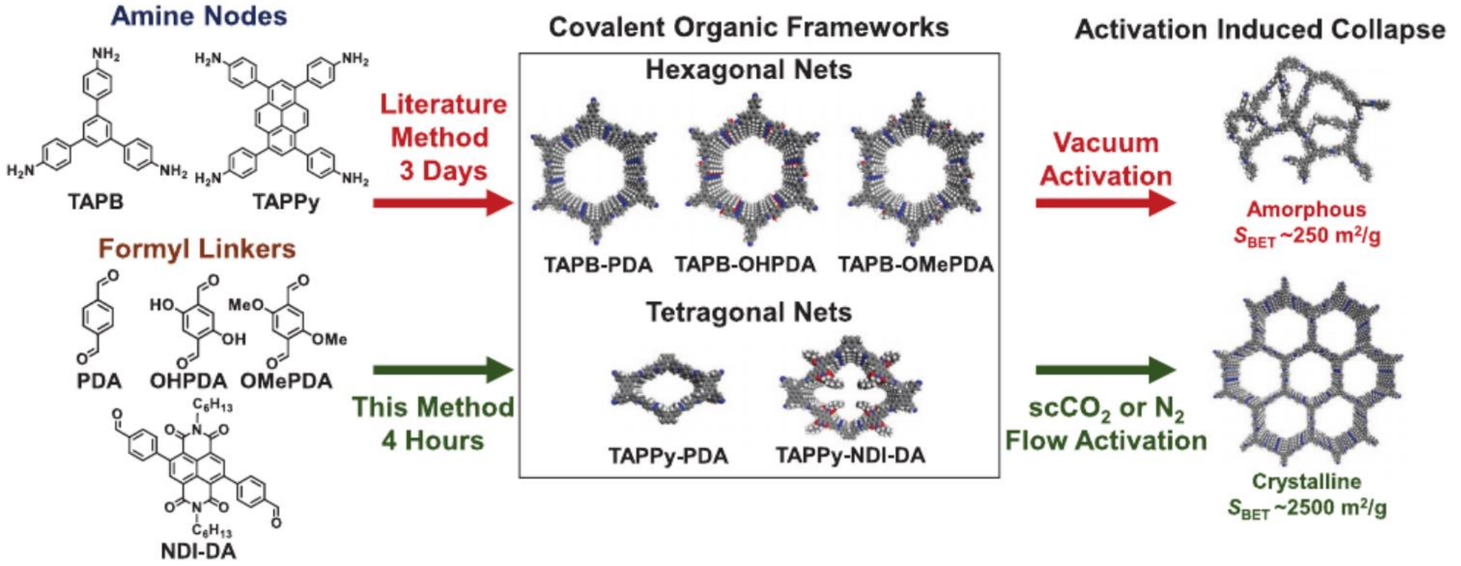


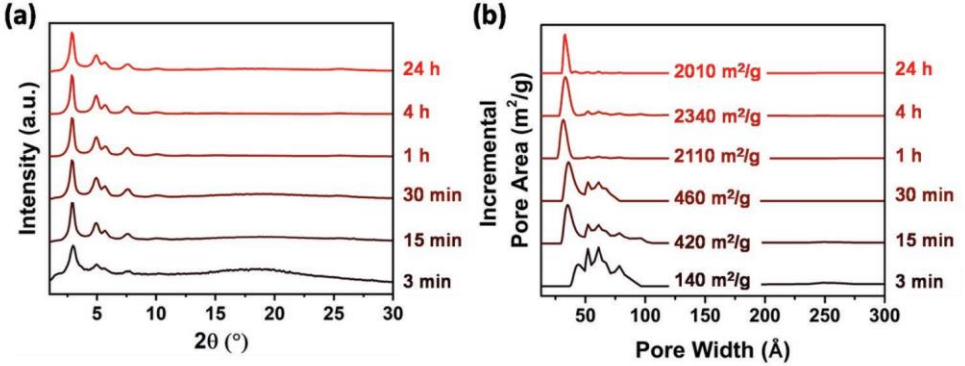


Take the advantage of the oxidation ability of  to generate ketone groups for amines

▪ Consideration of materials with much larger surface areas

➢ COFs with high BET surfaces





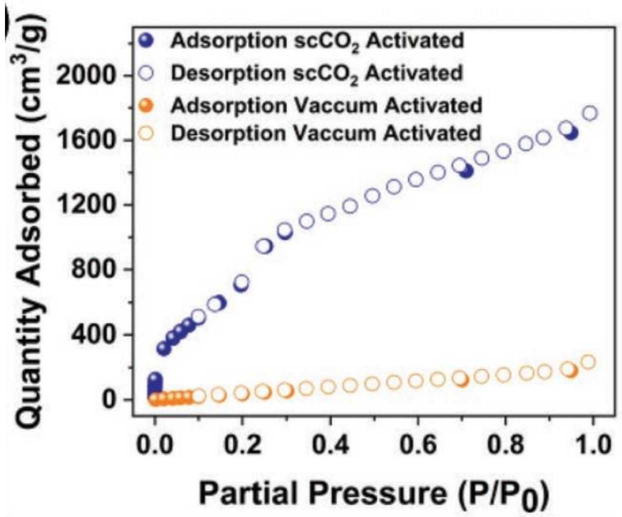
TAPB-PDA COF

Rapid synthesis

Large surface area

Experimental Section

General COF Synthesis Method: Amine and aldehyde monomers were weighed in the amounts listed in **Table 1** below, and combined in a 4 mL vial. To this, an amount of 4:1 (v/v) 1,4-dioxane:mesitylene was added according to Table 1. The monomers were sonicated for several minutes, then the monomer solution was preheated to 70 °C using an aluminum heating block. Once the monomer solution reached 70 °C, an amount of 10.5 M aqueous acetic acid was added according to Table 1. The reaction proceeded for 4 h (with the exception of timed reactions referenced in Figure 1), then the material was filtered and rinsed thoroughly with methanol. Care is taken during filtration to not allow the solid to dry



Future plan:

- ➢ **Pre-design amine attached PDA**
- ➢ **Post-modification on OH/OMePDA part**

William R. Dichetel, Seth R. Marder, et al., *Adv. Mater.*, **2020**, *32*, 1905776