Evaluation of amine-incorporated porous polymer networks (PPNs) as sorbents for post-combustion CO_2 capture

NETL Kick-Off Meeting

Hong-Cai "Joe" Zhou
Department of Chemistry
Texas A&M University

Outline

- Background
- Project Objectives
- Technical approach
  - Build amine-PPNs from anchors
  - Directly assemble amine-PPNs materials with alkyl amine groups
- Project progress
- Budget
- Risks

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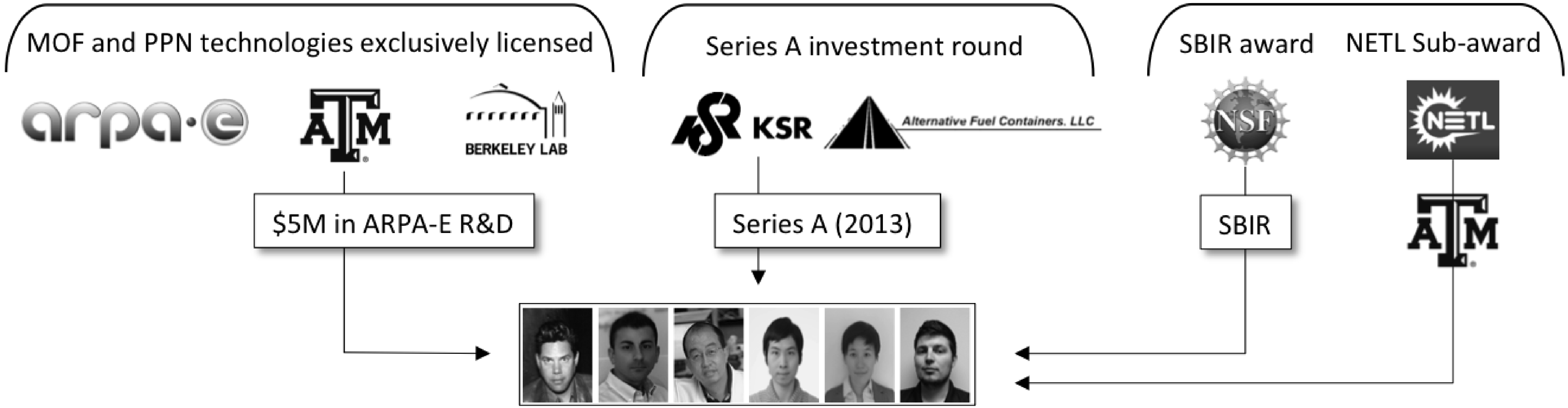
Team Background-Dr. Zhou

- PhD from Texas A&M University 2000 under F.A. Cotton
- Post-doctoral fellow in the Holm lab at Harvard University 2000-2002
- Associate/Assistant Professor at Miami University 2002-2008
- Moved to TAMU in 2008 currently a Robert A. Welch Chair in Chemistry
- Previously led successful carbon capture grants with ARPA-e IMPACCT program for post-combustion capture and the Office of Naval Research for carbon capture from air
- Currently the Zhou group (37 total) has 26 graduate students, three post doctorial fellows, two visiting scholars, and four undergraduate researchers
- 200 publications, 19,533 citations, *h*-index of 66, and 5 patents

Team Background – *framergy*, Inc.



- An office space, a wet chemistry - materials synthesis laboratory and a materials testing laboratory located in the technology incubator space of Texas A&M University
- Availability for expansion to accommodate the project team (Chemical Technician, Engineering Technician) and required testing instrumentation

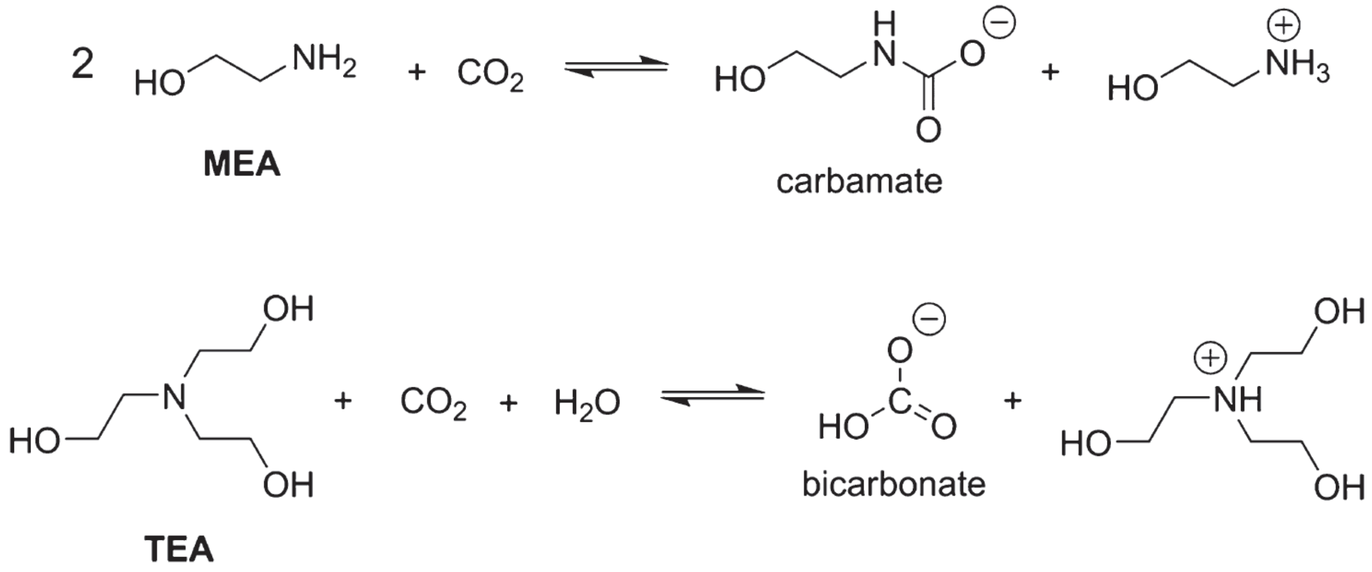
Team Background – Ray Ozdemir

- 12 Years of Technology and Product Development Experience
- Synthesis and Characterization of High Capacity CO_2 Adsorbents
  - Synthesized and tested interior surface modified mesoporous adsorbents for selective capture of CO_2 from flue gas streams
  - This work was funded under a performance based U.S. DOE SBIR contract
  - Successfully converted Phase I to Phase II (DOE Grant Contract No: DE-FG02-06ER84549)
- Inventor of a New Contactor Material for the Selective Capture of CO_2 from Atmosphere
  - This work was funded by U.S. DOD for the purpose of capturing atmospheric CO_2 as a feedstock for generating liquid hydrocarbon fuels (DOD Grant Contract No: W911QX-10-C-0070)

Project Organization

Project Team	Prof. Hong-Cai 'Joe' Zhou Texas A&M University Principal Investigator	Lanfang Zhou Texas A&M University Materials Synthesis Lead Xuan Wang, Yujia Sun, Sai Che, Qi Wang, Xinyu Yang Texas A&M University Graduate Research Assistants	Zachary Perry Texas A&M University Project Coordinator Carrie R Frederiksen Texas A&M University Report on Project Spending	Mr. O.K. 'Ray' Ozdemir *framergy*, Inc. Co-Principal Investigator	TBD *framergy*, Inc. Chemical Technician	TBD *framergy*, Inc. Eng. Technician
Year 1 Role	• Project Oversight • Technical and Administrative Point of Contact (POC)	• New Materials Synthesis and Characterization • Molecular Simulation • Lab Scale Testing and Screening	• Coordinate Technical Progress • Report on Project Spending • Report on Resource Management	• Sorbent Synthesis Optimization – Projected Cost Analysis • *framergy* POC		
Year 2 Role	• Project Oversight • Technical and Administrative Point of Contact	• New Materials Synthesis and Characterization • Molecular Simulation • Lab Scale Testing and Screening	• Coordinate Technical Progress • Report on Project Spending • Report on Resource Management	• Technical and Administrative Oversight • Sorbent Optimization – Cost Analysis • *framergy* POC	• Assist Initial Sorbent Scale-up • Assist Attrition and Mechanical Hardness Tests	• Assist Initial Fixed Bed Testing
Year 3 Role	• Project Oversight • Technical and Administrative Point of Contact	• New Materials Synthesis and Characterization • Molecular Simulation • Lab Scale Testing and Screening	• Coordinate Technical Progress • Report on Project Spending • Report on Resource Management	• Technical and Administrative Oversight • Technology EH&S Assessment • *framergy* POC	• Sorbent Production	• Optimal Fixed Bed Testing

Aqueous Alkanolamine Absorbents



Traditional “wet scrubbing” methods:

- High regeneration cost
- Fouling of the equipment
- Solvent boil-off

Long, J. R. *et al Chem. Rev.* **2012,** *112* (2), 724-781.

Basic Adsorptive-Separation Mechanisms

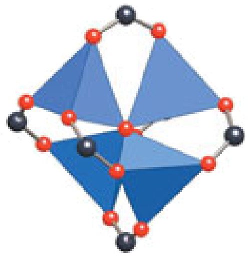
- **Size and/or shape exclusion**
- **Thermodynamic equilibrium effect ---**adsorbate-surface and/or adsorbate packing interactions
- **Kinetic effect ---**different diffusing rates
- **Quantum sieving effect---**the quantum effect

Table 4 Physical parameters of selected gas and vapor adsorbates[20,31,33,34]

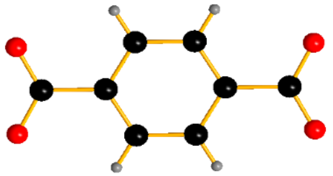
Adsorbate	Normal BP/K	Liquid V_{mol} at NBP/cm^3 mol^{-1}	T_c/K	V_c/cm^3 mol^{-1}	P_c/bar	Kinetic diameter/Å	Polarizability $\times 10^{25}$/cm^3	Dipole moment $\times 10^{18}$/esu cm	Quadruple moment $\times 10^{26}$/esu cm^2
He	4.30	32.54	5.19	57.30	2.27	2.551	2.04956	0	0.0
Ne	27.07	16.76	44.40	41.70	27.60	2.82	3.956	0	0.0
Ar	87.27	28.7	150.86	74.57	48.98	3.542	16.411	0	0.0
Kr	119.74	34.63	209.40	91.20	55.00	3.655	24.844	0	0.0
Xe	165.01	42.91	289.74	118.00	58.40	4.047	40.44	0	0.0
H_2	20.27	28.5	32.98	64.20	12.93	2.827–2.89	8.042	0	0.662
D_2	23.65	24.81	38.35	60.20	16.65	2.827–2.89	7.954	0	—
N_2	77.35	34.7	126.20	90.10	33.98	3.64–3.80	17.403	0	1.52
O_2	90.17	27.85	154.58	73.37	50.43	3.467	15.812	0	0.39
Cl_2	239.12	45.36	417.00	124.00	77.00	4.217	46.1	0	—
Br_2	331.90	51.51	584.10	135.00	103.00	4.296	70.2	0	—
CO	81.66	35.5	132.85	93.10	34.94	3.690	19.5	0.1098	2.50
CO_2	216.55	37.4	304.12	94.07	73.74	3.3	29.11	0	4.30

Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38,* 1477-1504.
Long, J. R. *et al Chem. Rev.* **2012,** *112* (2), 724-781.

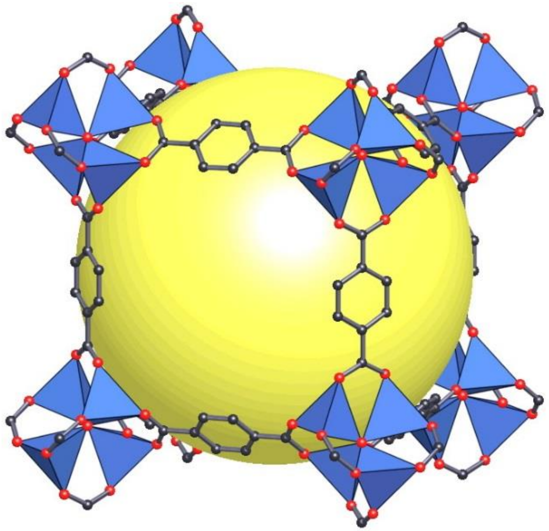
Metal-Organic Frameworks (MOFs)



Inorganic clusters



Organic linkers



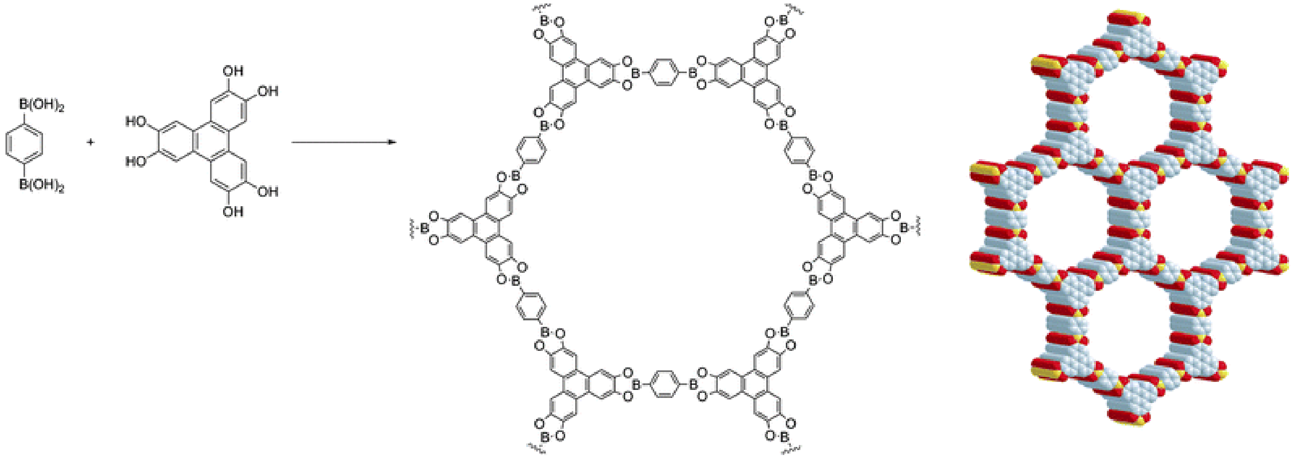
MOF-5

- Crystalline inorganic-organic hybrid porous materials
- Properties:
  - ✓Defined crystalline structure
  - ✓Permanent porosity
  - ✓Extremely high surface area
  - ✓Tunable pore size and shape
  - ✓Adjustable functionalization

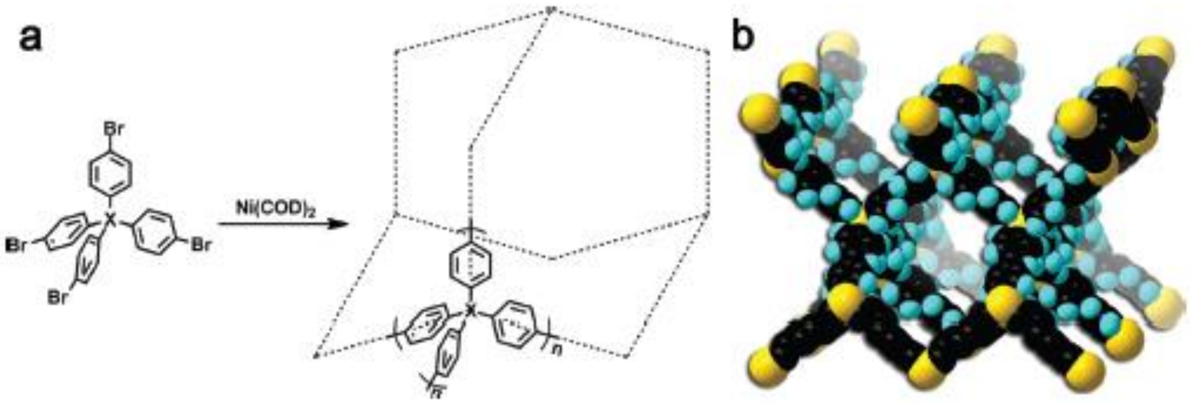
Zhou, H.-C.; Long, J. R.; Yaghi, O. M., *Chem. Rev.* **2012,** *112*, 673.
Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J., *Nature* **2003,** *423*, 705.

Porous Polymer Networks (PPNs)

- **Networks connected by covalent bonds**
  - ✓Boronic acid condensation
  - ✓Schiff-base reaction
  - ✓Yamamoto coupling
- **Properties:**
  - ✓High surface area
  - ✓Extremely low density
  - ✓High thermal and chemical stability



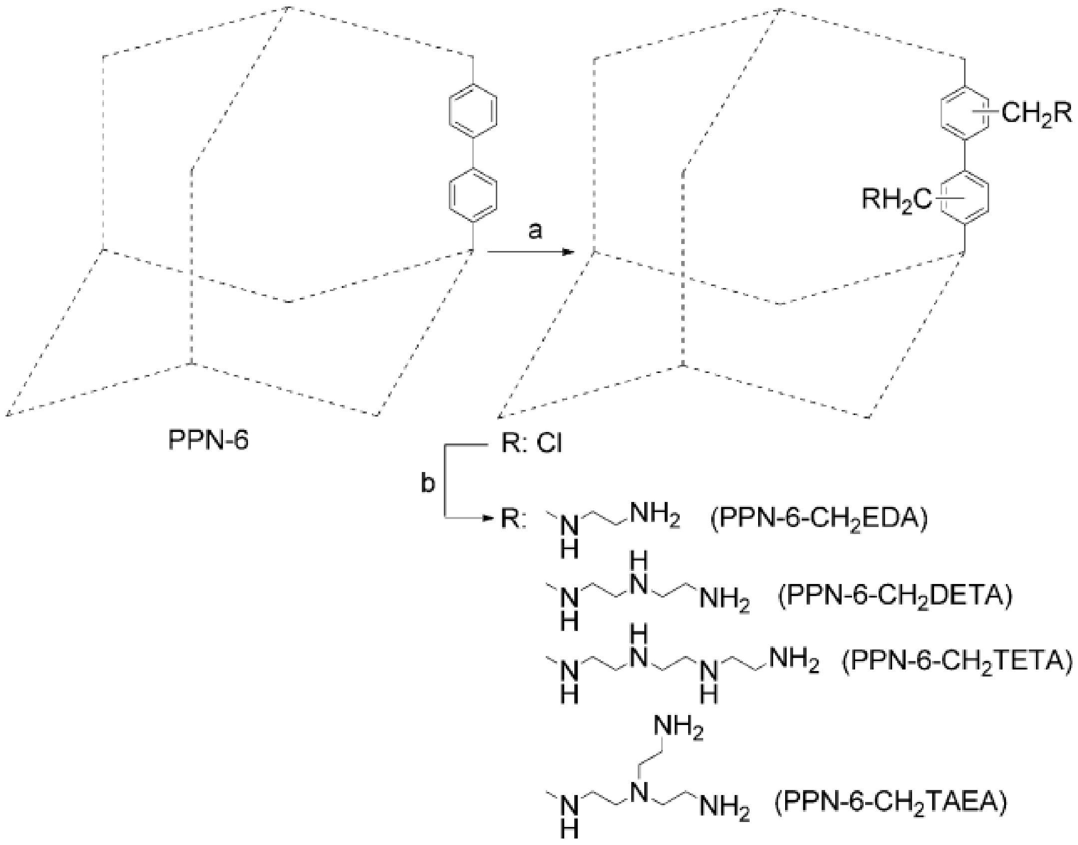
COF-5

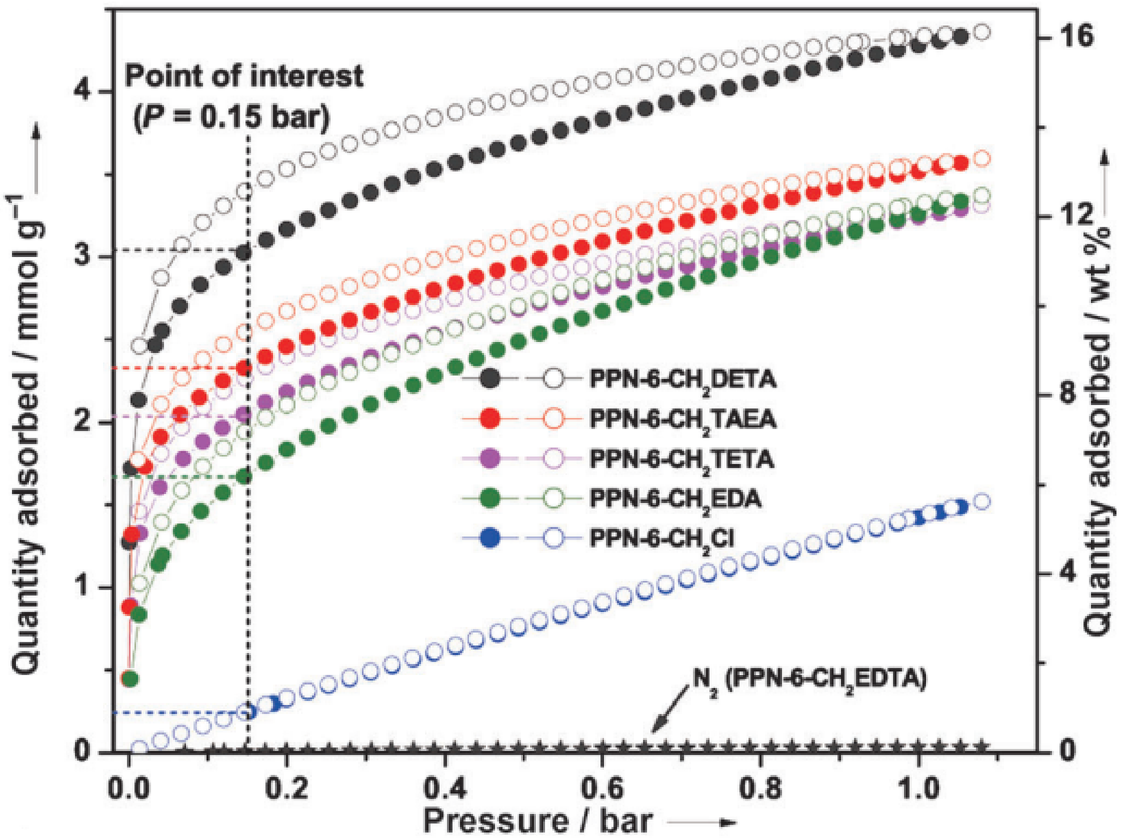


PPN-6

Zhou, H.-C. *et al*, *Adv. Mater.* **2011,** *23*, 3723; Yaghi, O. M. *et al*, *Science* **2005,** *310*, 1166.

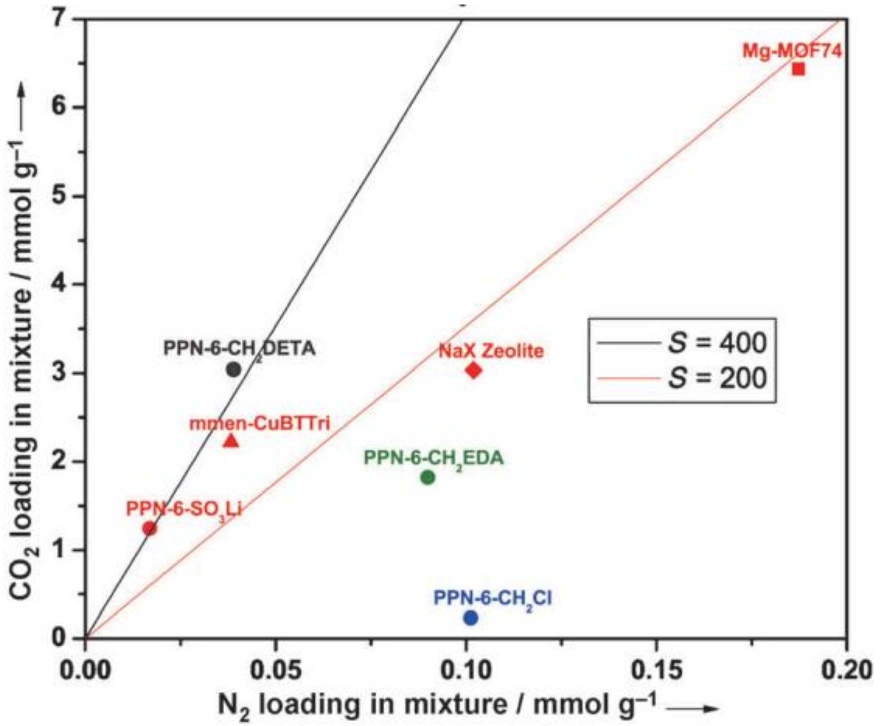
Amine-tethered PPN-6

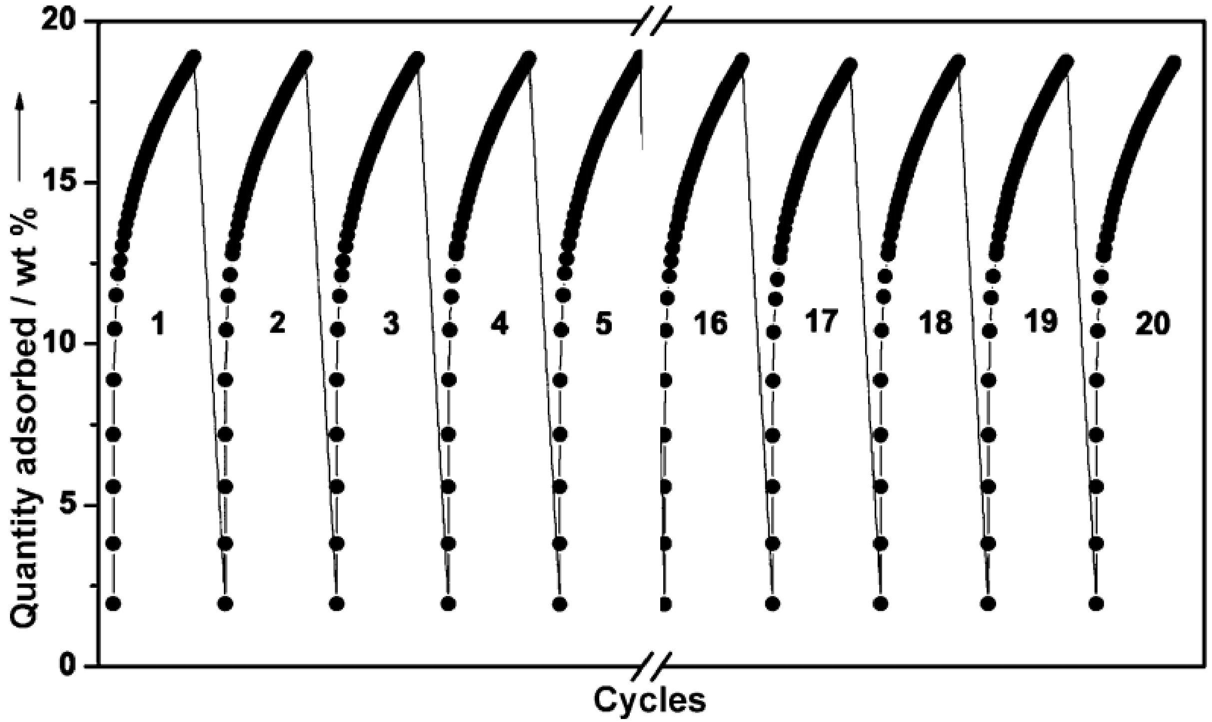




Zhou, H.-C. *et al*, *Angew. Chem. Int. Ed.* **2012,** *51*, 7480.

Amine-tethered PPN-6

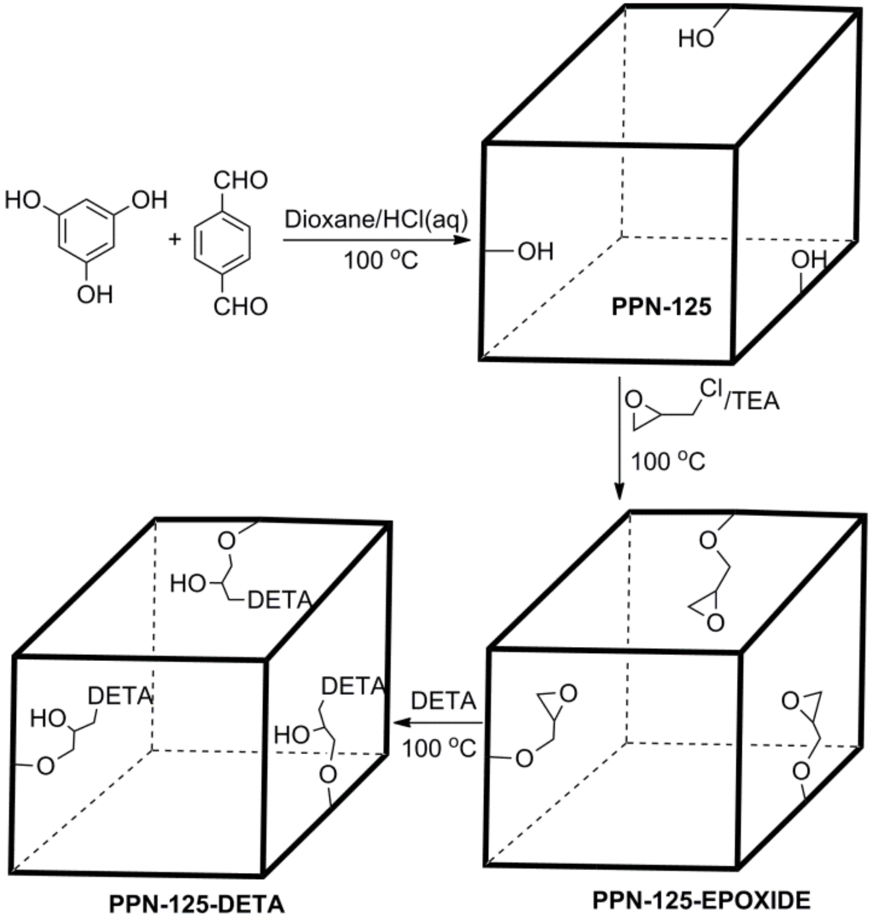


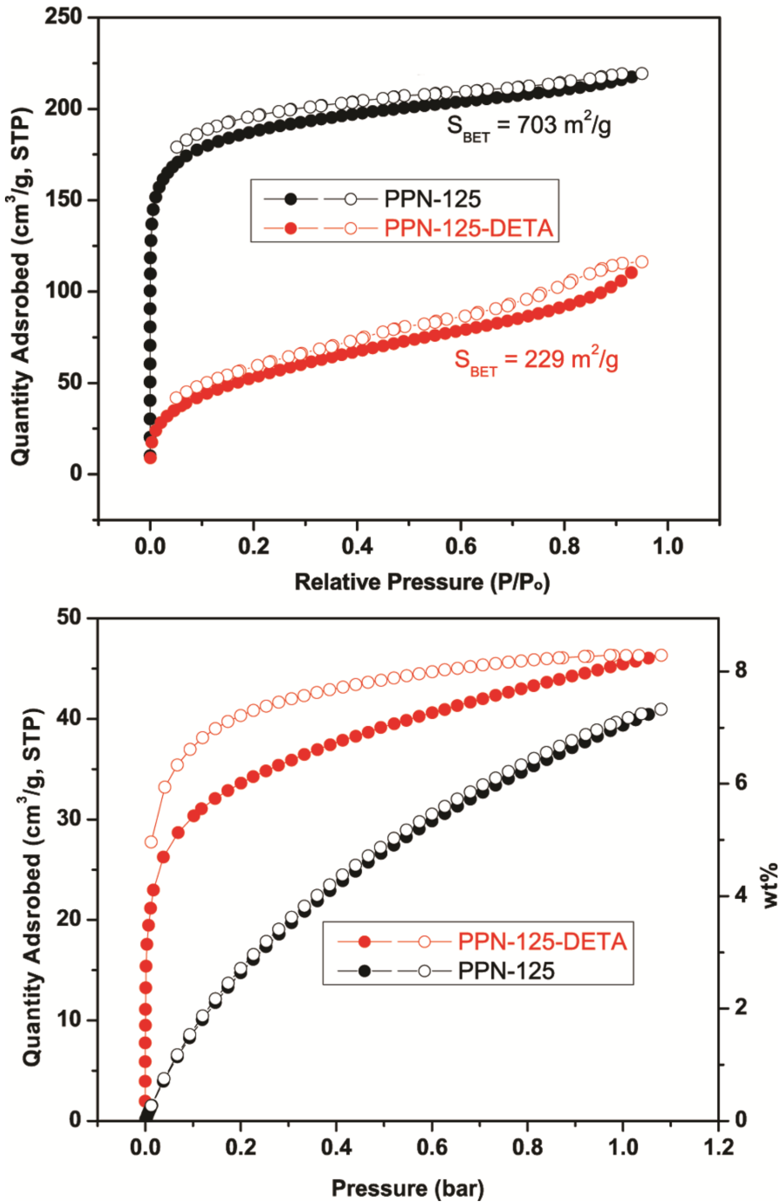


- Dramatic increases in CO_2 uptake capacities at low pressures and exceptionally high CO_2/N_2 adsorption selectivity
- Expensive bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$) are required
- Purely serves as a support for amine chains, decreasing volumetric CO_2 uptake

Zhou, H.-C. *et al*, *Angew. Chem. Int. Ed.* **2012,** *51*, 7480.

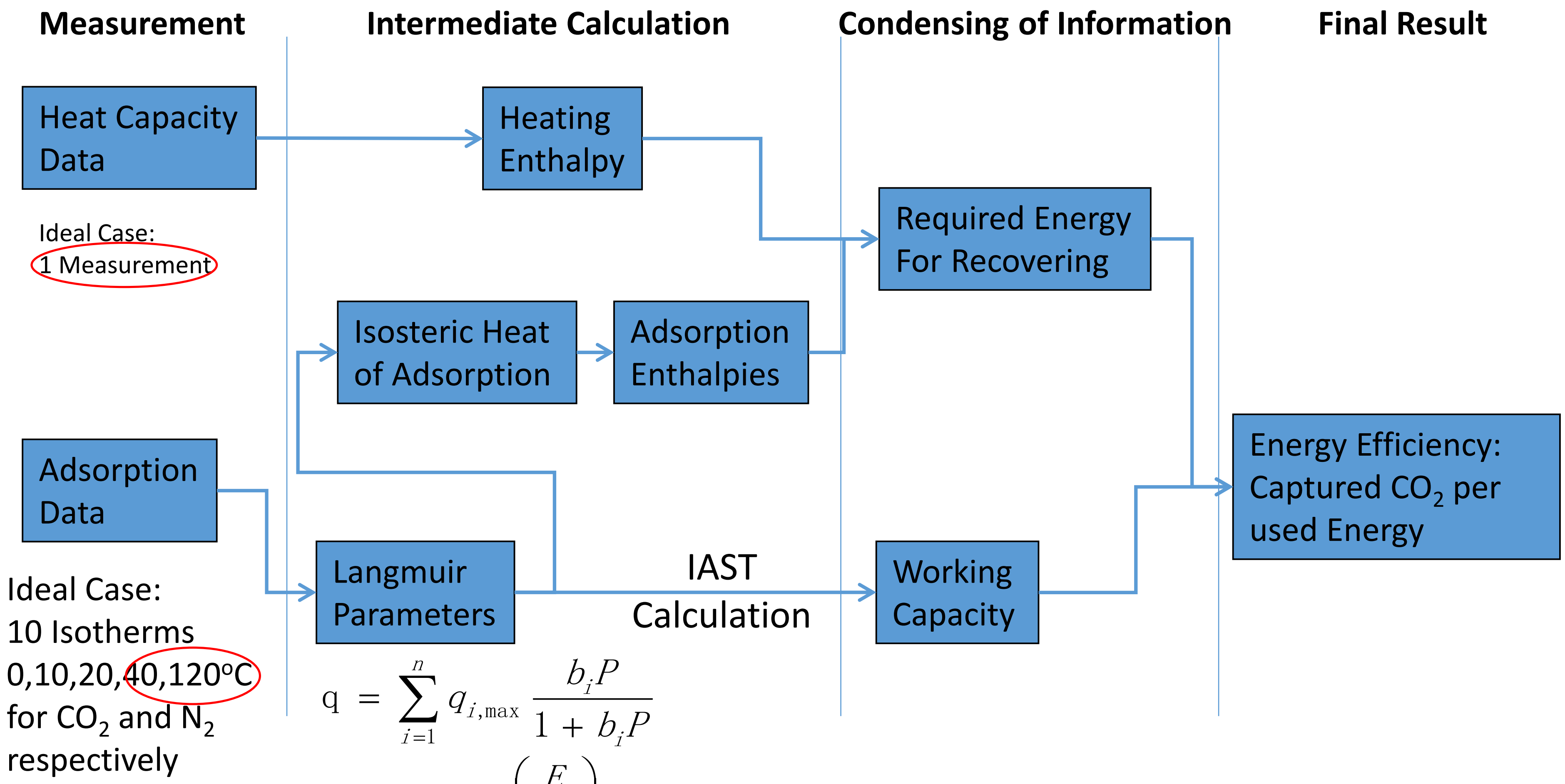
PPN-125





Zhou, H.-C. *et al*, *ChemSusChem* **2015,** *8* (3), 433-438.

High-throughput Energy Model



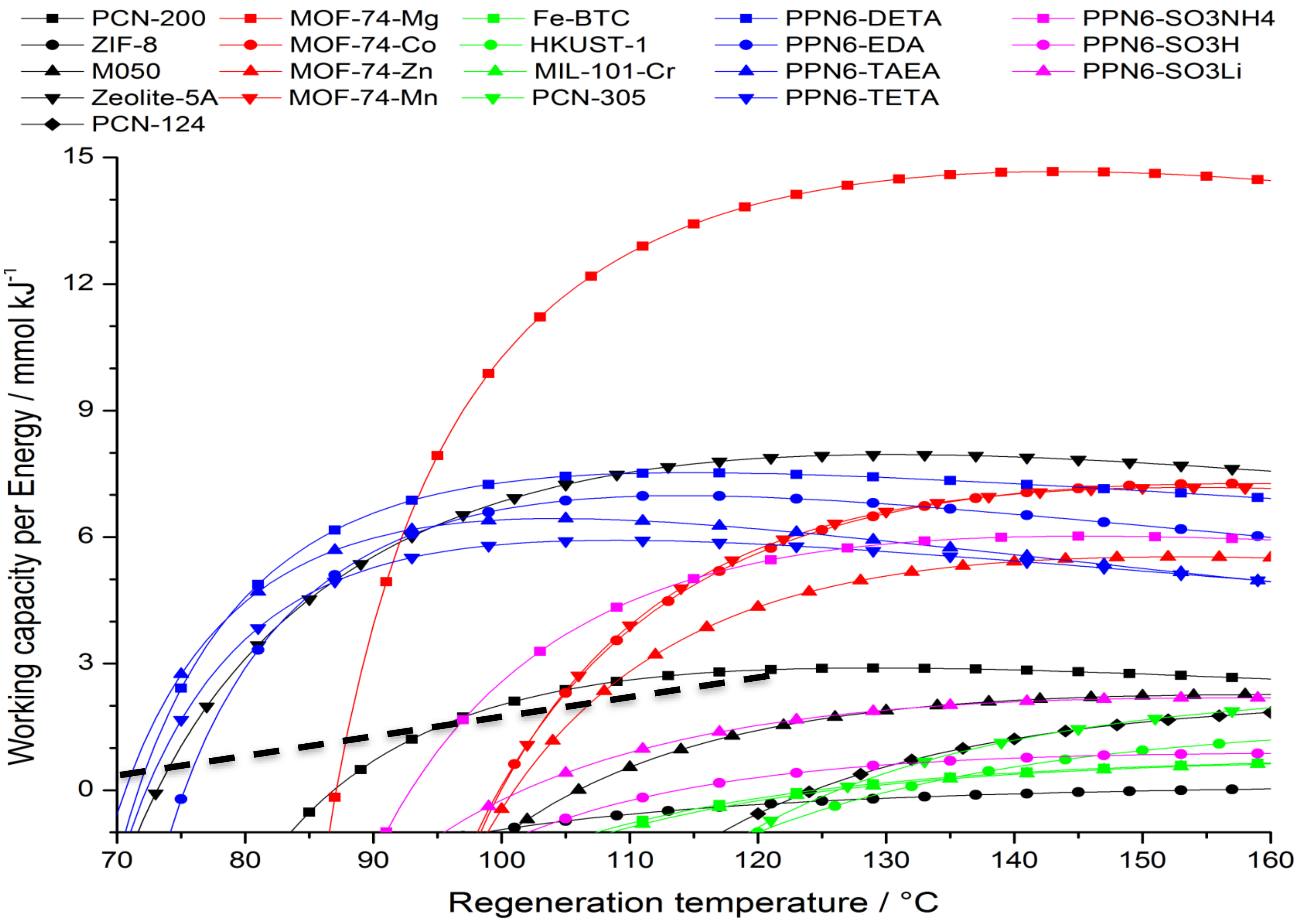
$$q = \sum_{i=1}^{n} q_{i,\max} \frac{b_i P}{1 + b_i P}$$

$$b_i = b_{i,0} \exp\left(\frac{E}{RT}\right)$$

Zhou, H.-C. *et al*, Manuscript Submitted.

Sculley, P. J.; Verdegaal, W. M.; Lu, W.; Wriedt, M.; Zhou, H.-C., *Adv. Mater.*, **2013**, *25*, 3957-3961.

Energy Efficiency



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Project Objectives

- Global objective:

"The overall objective of the proposed work is to demonstrate the feasibility of the Recipient's (Texas A&M University) amine-incorporated porous polymer networks (aPPNs) as sorbents for post-combustion carbon dioxide (CO_2) capture while demonstrating significant progress toward achievement of the overall fossil energy performance goals of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches."

Success Criteria

Decision Point	Basis for Decision/Success Criteria
Completion of Budget Period 1	Successful completion of all work proposed in Budget Period 1
	Novel aPPN sorbent formulation retains a CO_2 adsorption capacity of at least 0.1 kg/kg after 30 cycles via TGA or physisorption testing
	Produce ~50 grams of at least the two top-performing aPPN sorbent formulations
Completion of Budget Period 2	Produce ~200 grams of at least the two top-performing aPPN sorbent formulations (≥0.1 kg/kg working capacity) for initial fixed-bed cycling tests
	Top-performing aPPN sorbent formulation retains a CO_2 working capacity of at least 0.1 kg/kg after 30 cycles during automated fixed-bed testing
Completion of Budget Period 3	Produce at least 1 kilogram of the top-performing aPPN sorbent formulation (≥0.12 kg/kg working capacity) for optimal fixed-bed cycling tests
	Optimal aPPN sorbent formulation retains a CO_2 working capacity of at least >0.12 kg/kg after 50 cycles in the presence of moisture and sulfur dioxide and <10% parasitic energy loss due to regeneration
	Results of the initial technical and economic feasibility study show significant progress toward achievement of the overall fossil energy performance goals of 90% CO_2 capture rate with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches

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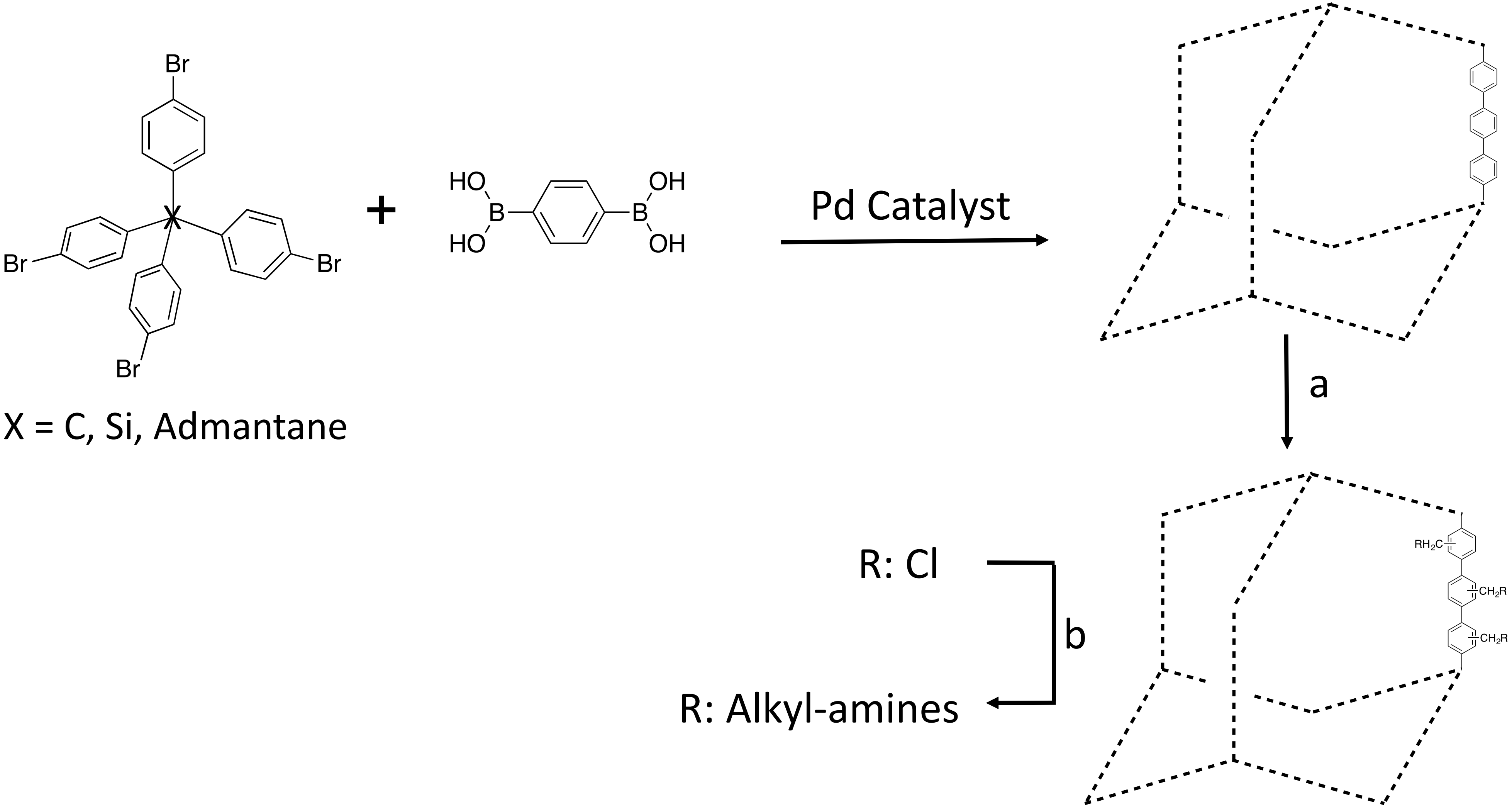
Material Development

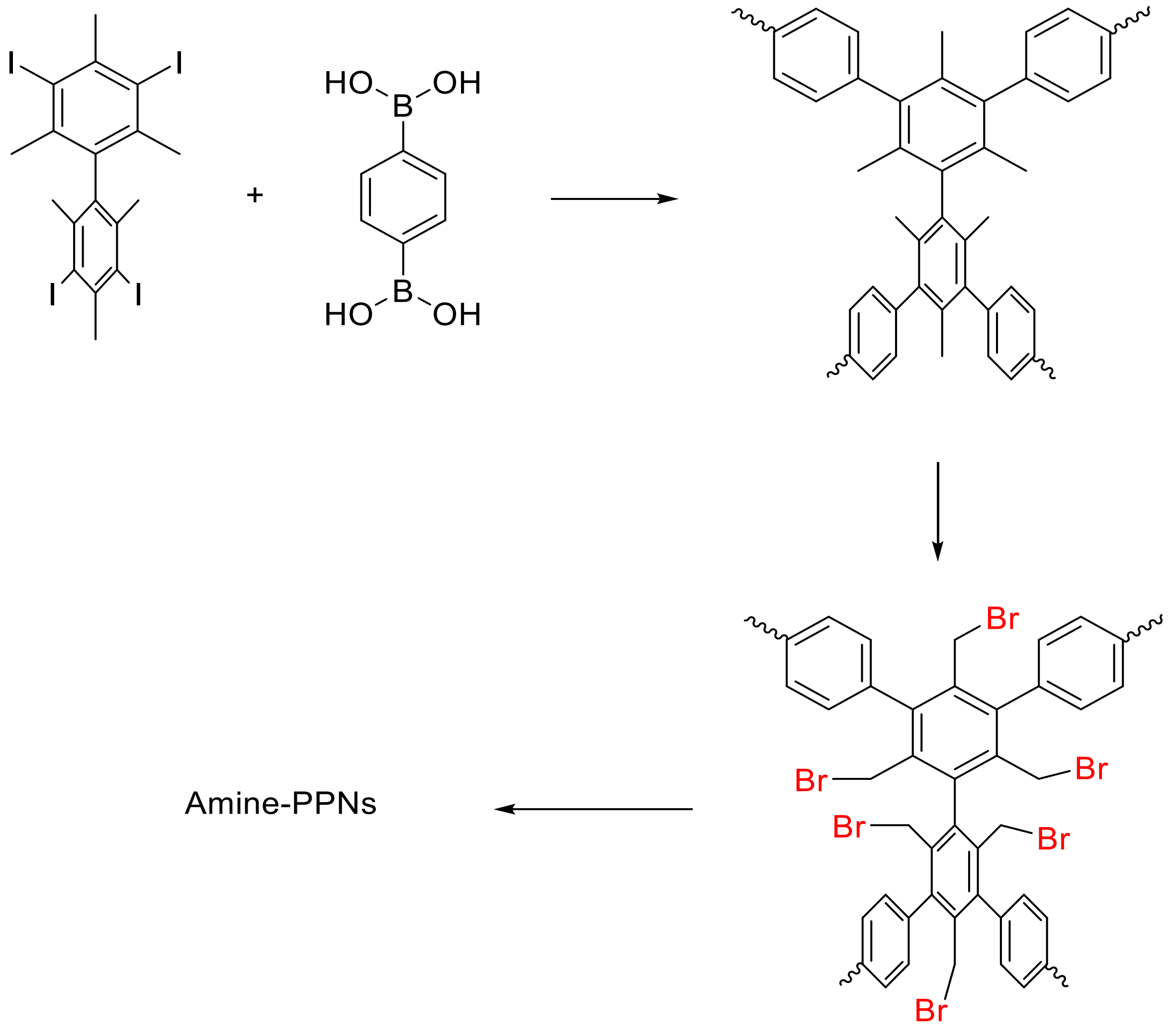
- Multiple reaction pathways are being investigated
  - Sequential assembly and amine incorporation
  - Nitrogen incorporation then activation
  - Direct amine incorporation

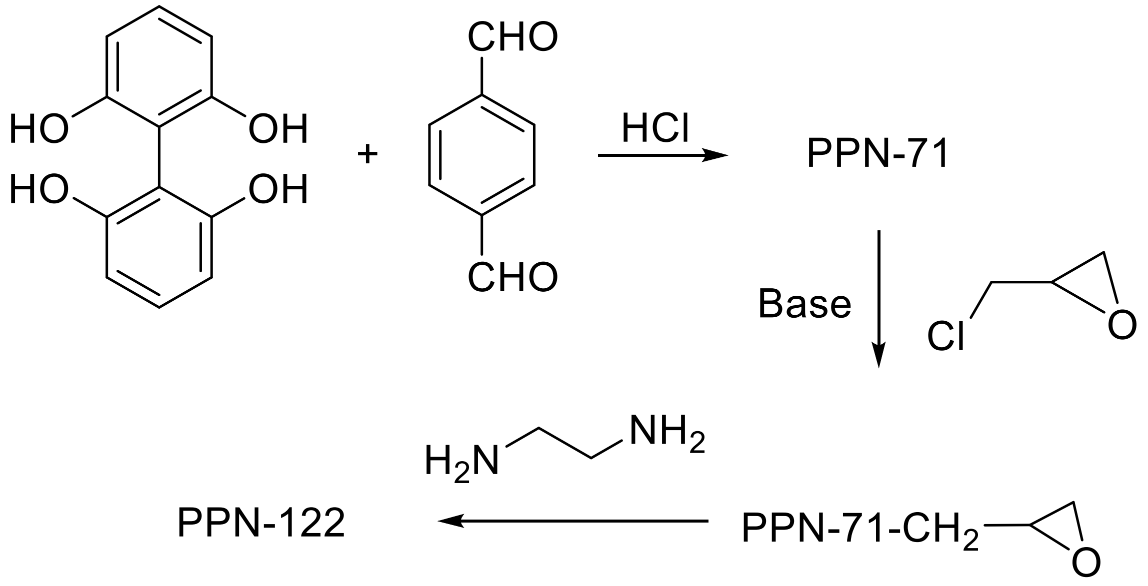
- Metrics for evaluation:
  - CO_2 Uptake
  - Scalability
  - Stability
  - Cost

Proposed Amine-PPNs: 1

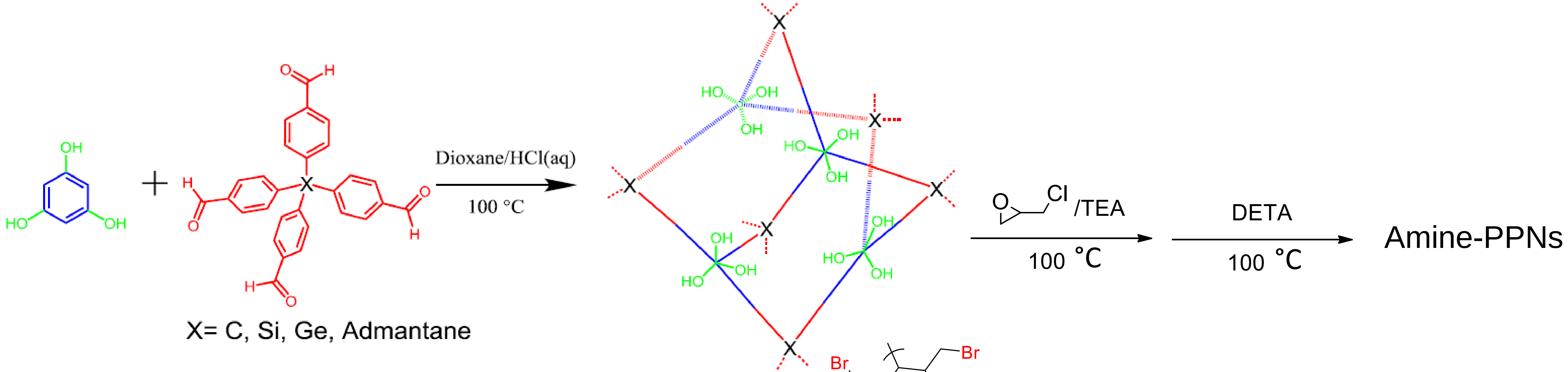


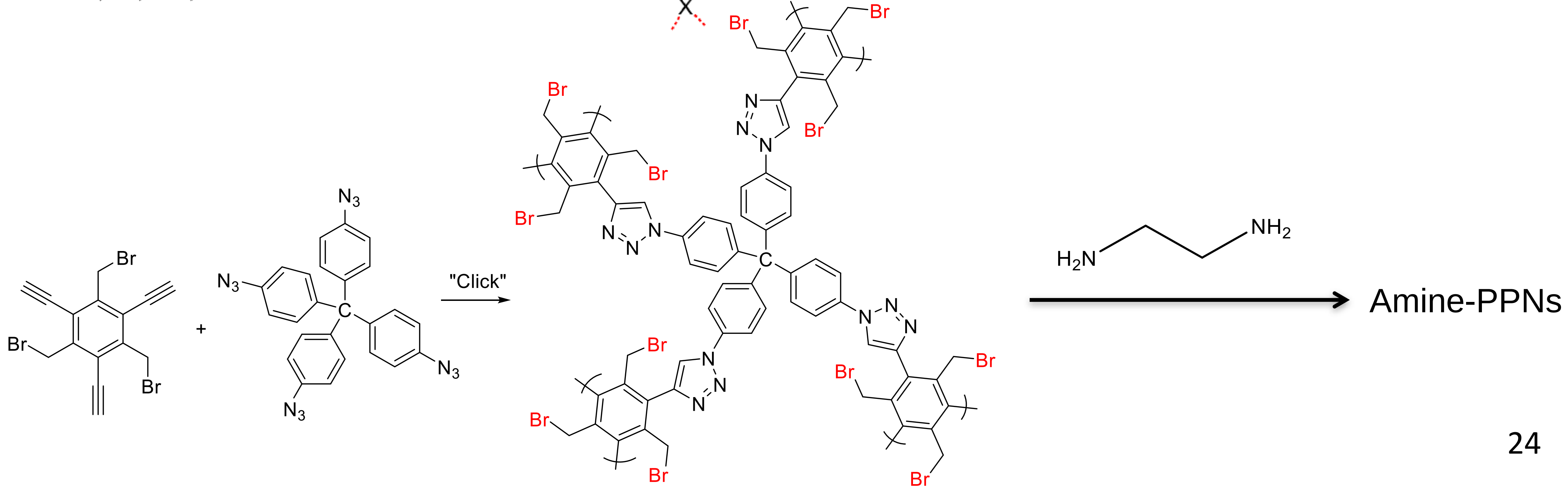
Proposed Amine-PPNs: 2-3



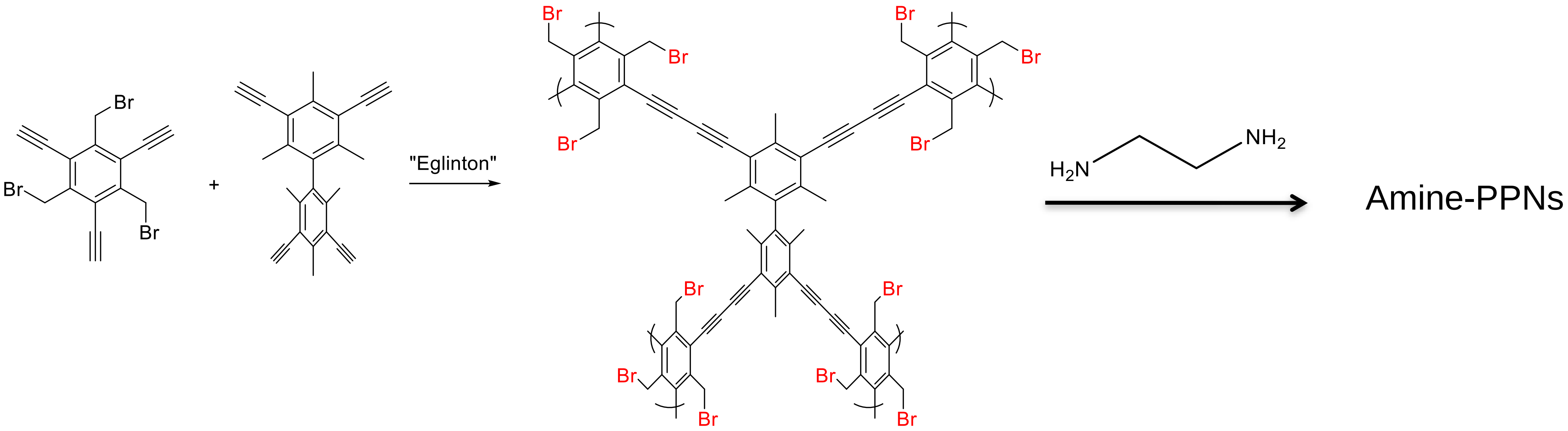


Proposed Amine-PPNs: 4-5





Proposed Amine-PPNs: 6



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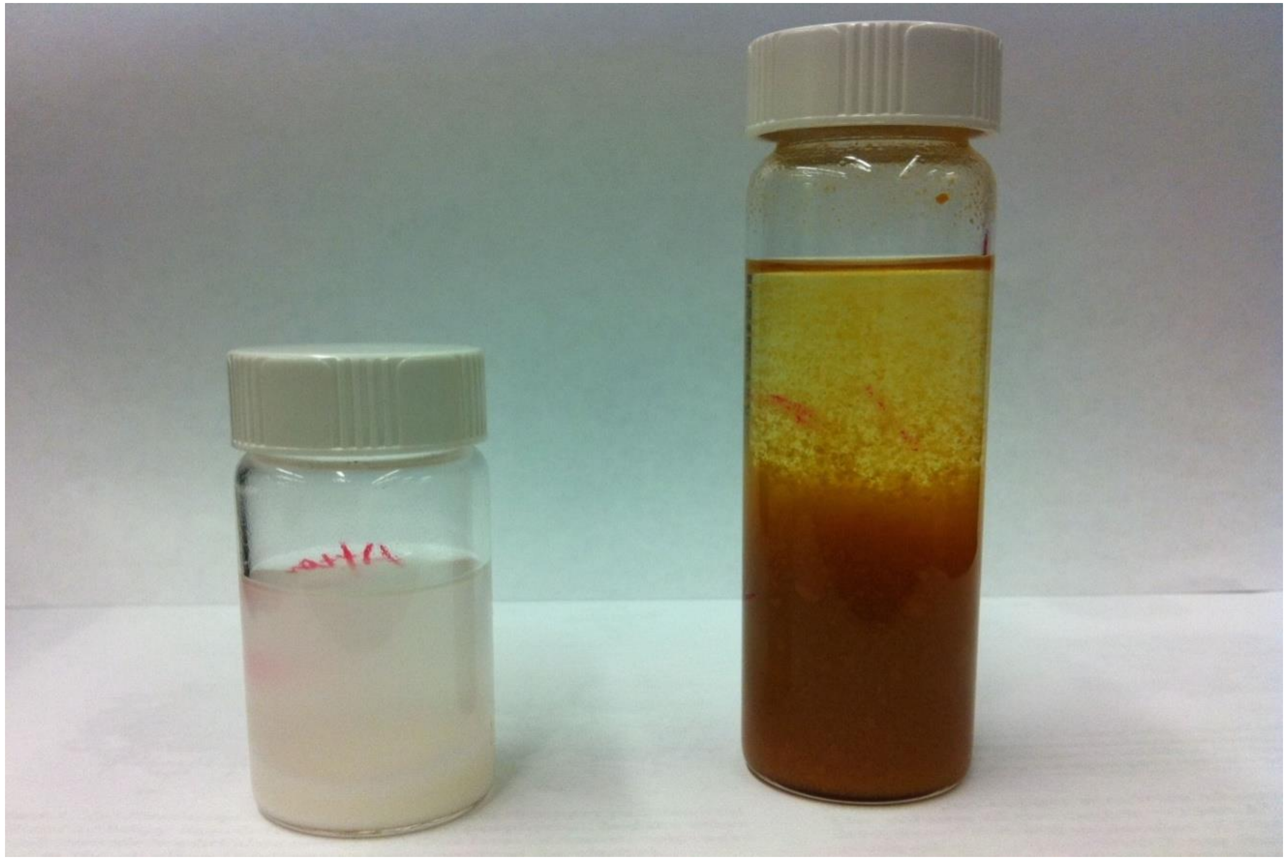
Directly Assemble Amine-PPNs

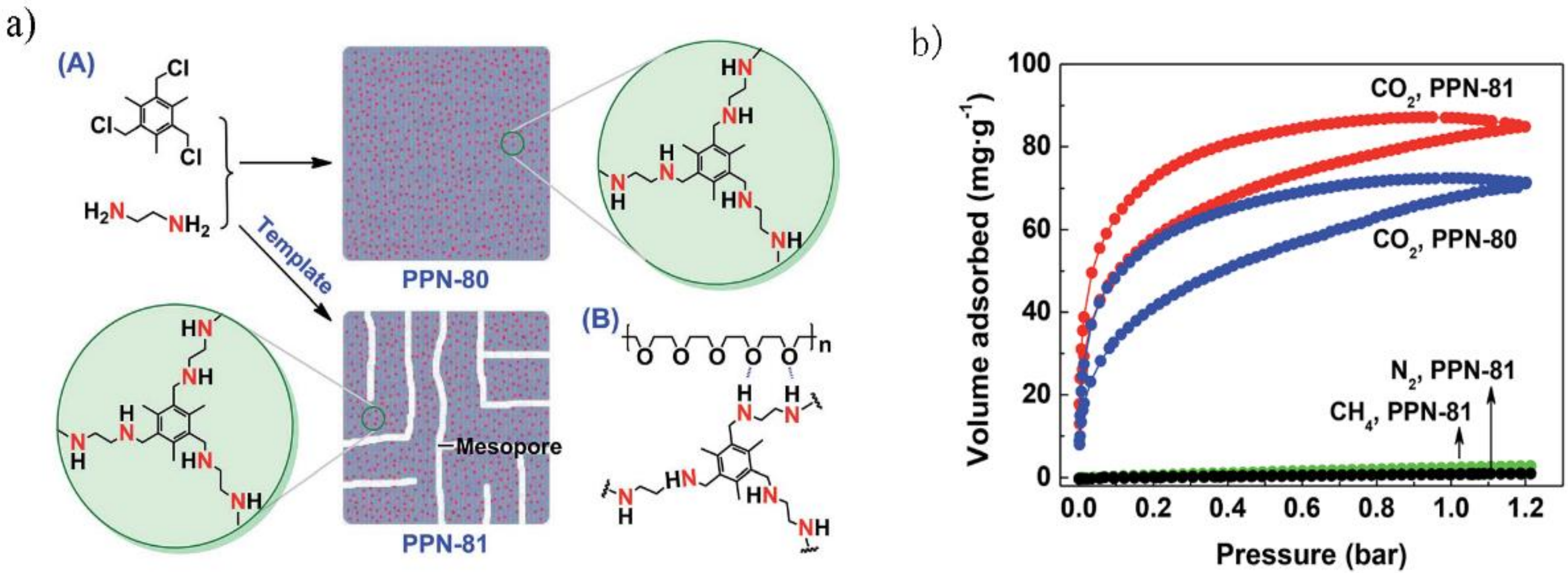
Resist to oxidation



Secondary amine–framework PPN
-stable toward oxygen

Primary amine containing PPN
- oxidized

Amine-tethered PPN-80

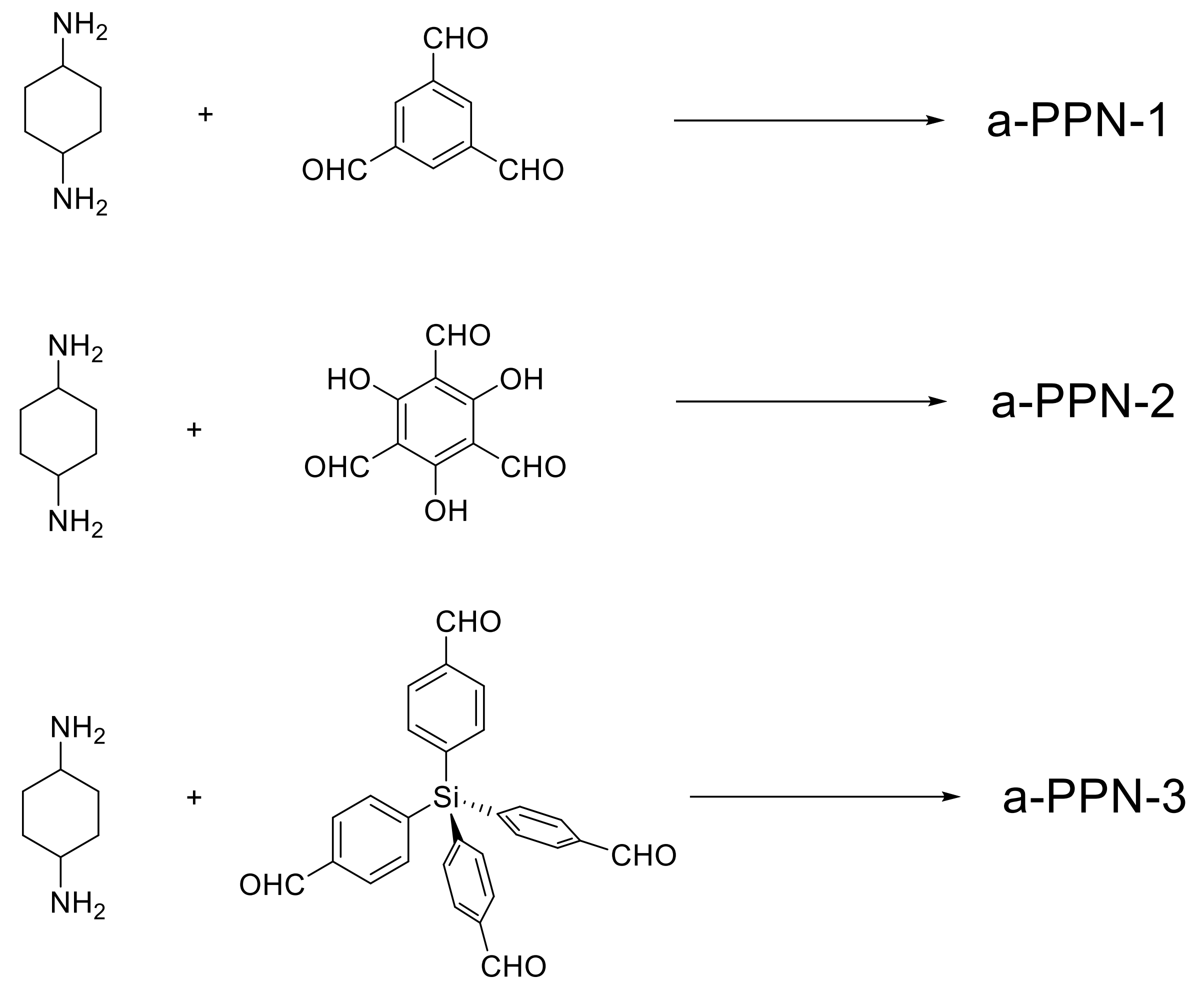


- Commercially available alkyl amine as starting materials
- Facile synthesis, catalyst-free, High density of secondary amines
- Limited crystallinity, amorphous

Zhou, H.-C. et al, *J. Mater. Chem.*,**2015,** *3*, 3252-3256.

Directly assemble a-PPNs

- Schiff base reaction is utilized to synthesize high crystalline amine-functionalized PPNs (a-PPNs)
- Postsynthetic functionalization:
  - ✓ Reduction
  - ✓ Tautomerism



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Project Progress-Budget Period 1 Milestones

MS	Task	Milestone Description	Planned Completion	Verification Method
c	2	Complete synthesis of least 5 novel aPPN sorbent formulations at small-scale (~100 milligrams)	1/31/2016	Results reported in the quarterly report
d	3.0	Complete synthesis of two Gen 0 materials (PPN-6-DETA and MOF-74-Mg) for standardization of measurements	1/31/2016	Results reported in the quarterly report
e	3.1	Complete initial CO_2 adsorption testing with at least five aPPN sorbent formulations and generate CO_2 loading isotherms	3/31/2016	Results reported in the quarterly report
f	2	Complete synthesis of 5 or more additional aPPN sorbents (~100 mg)	5/31/2016	Results reported in the quarterly report
g	3.2	Complete initial aPPN sorbent physical property characterization (heat capacity, heat of reaction, density, particle size, etc.)	6/30/2016	Results reported in the quarterly report
h	3.3	Complete initial TGA testing with the top-performing aPPN sorbents (>0.08 kg/kg CO_2 capacity) in the presence of moisture	6/30/2016	Results reported in the quarterly report
i	3.3	Complete initial thermal and chemical stability (H_2O, SO_2) studies via TGA cycling and small breakthrough	8/30/2016	Results reported in the quarterly report
j	2	Sorbent Synthesis Optimization – Projected Cost Analysis	8/30/2016	Results reported in the quarterly report
k	2	Produce ~50 grams of at least the two top-performing aPPN sorbent formulations	9/30/2016	Results reported in the quarterly report

Project Progress-Budget Period 2 Milestones

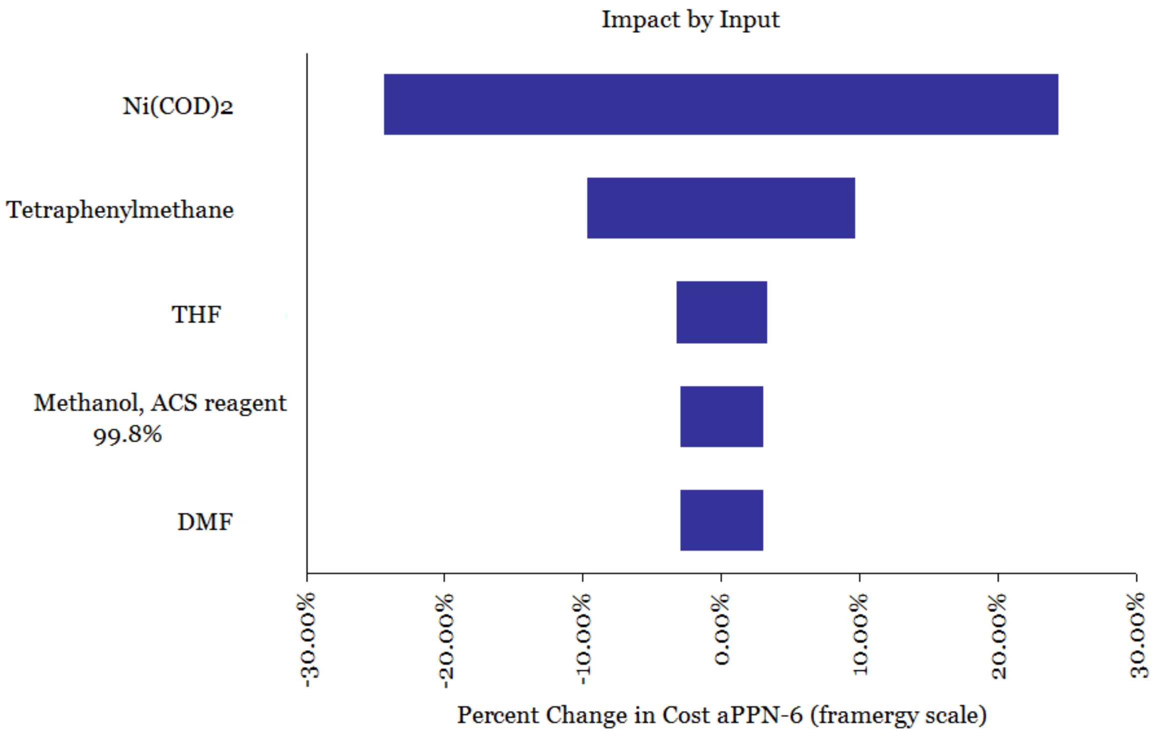
MS	Task	Milestone Description	Planned Completion	Verification Method
l	6.0	Complete acquisition and installation of the temperature-controlled, fixed-bed test unit coupled with a mass spectrometer	1/31/2017	Description and photos provided in the quarterly report
m	4.0	Identify synthesis conditions (temperature, reaction time, monomer ratios, etc.) that yield optimal aPPN sorbent performance and cost	3/31/2017	Results reported in the quarterly report
n	5.0	Finalize scale-up procedure for top-performing aPPN sorbent formulations and prepare laboratory facilities	3/31/2017	Results reported in the quarterly report
o	5.0	Produce ~200 grams of at least the two top-performing aPPN sorbent formulations (≥0.1 kg/kg working capacity) for initial fixed-bed cycling tests	7/31/2017	Results reported in the quarterly report
p	6.0	Complete initial fixed-bed cycling tests with the scaled-up aPPN sorbent formulations and maintain at least ≥0.1 kg/kg working capacity	9/30/2017	Results reported in the quarterly report
q	7.0	Complete attrition and mechanical hardness testing of the top-performing aPPN sorbent formulations	6/30/2017	Results reported in the quarterly report

Project Progress-Budget Period 3 Milestones

MS	Task	Milestone description	Planned Completion	Verification Method
r	8	Produce at least 1 kilogram of the top-performing aPPN sorbent formulation (≥0.12 kg/kg working capacity) for optimal fixed-bed cycling tests	3/31/2018	Results reported in the quarterly report
s	9	Complete optimal fixed-bed cycling tests with the top-performing aPPN sorbent formulation and maintain at least ≥0.12 kg/kg working capacity in the presence of moisture and sulfur dioxide	7/31/2018	Results reported in the quarterly report
t	10	Complete initial technical and economic feasibility study	9/30/2018	Results reported in Final Report

Subcontracted Cost Analysis and Testing Tasks

- Sensitivity Analysis



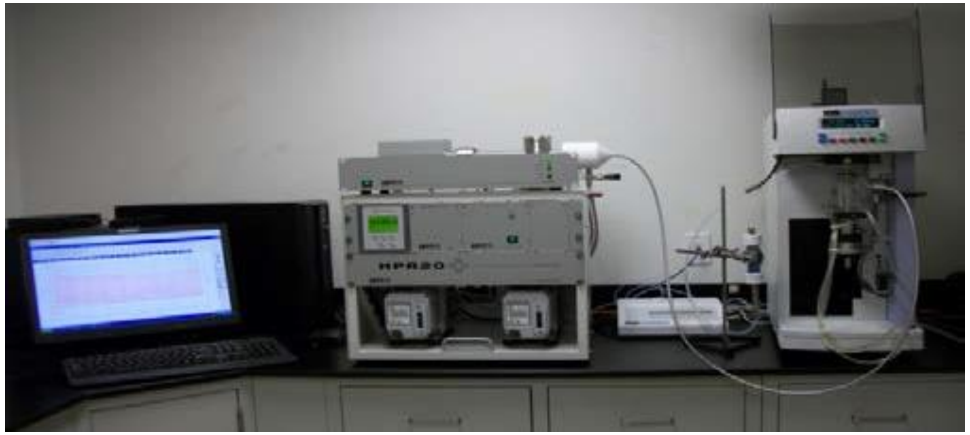
Preliminary data: Tornado diagram generated for sensitivity analysis – cost of aPPN is mostly impacted by the changes in the Ni $(COD)_2$ reagent cost

- Mechanical Hardness Testing
  - As per ASTM D4179 and D6175
  - Crush strength – resistance of a solid sorbent to compression: Evaluate the mechanical failure modes of the developed sorbent material (different than loss of activity)

- Attrition in Fluidized Bed
  - As per ASTM D-5757-95
  - Attrition of powdered sorbents in fluidized beds
  - Air Jet Attrition (AJI) will be reported

Subcontracted Testing Tasks (*cont.*)

- Tasks 6. Initial Fixed Bed Testing
  - ACES, LLC Instrument acquisition & training
  - Generate breakthrough data
  - Variable CO_2/N_2 (v/v) rates
  - Variable flow rates
  - Gas Analysis: Hiden Analytical HPR20 gas analysis system
- Task 9. Optimal Fixed Bed Testing
  - ACES, LLC Instrument acquisition & training
  - Cyclic testing of sorbents under simulated flue gas conditions



Technical Risks

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)
Adequate sorbent working capacity	Moderate	High
Sorbent handling and attrition	Low	Moderate
Uniform process temperature control	Low	Moderate
Process energy demand	Moderate	Moderate
Relating fixed-bed performance/desired sorbent attributes to fluidized bed performance/desired sorbent attributes	Moderate	Moderate
Difficulty controlling particle size distribution	Moderate	Moderate
Diffusion limitations and slow adsorption kinetics due to increased amine density	Moderate	High
High sorbent costs due to high cost of reagents	Moderate	High
High sorbent costs due to high cost of synthesis and wash solvents	Moderate	High
Resource Risks:		
Timely acquisition of the fixed-bed test unit and required ancillary support	Low	High
framergy™ is a start-up company with relatively few employees	Moderate	Moderate
framergy™ is a start-up company and relatively small (infrastructure and laboratory and office space) compared to TAMU	Moderate	Moderate

Acknowledgement

NETL