Evaluation of amine-incorporated porous polymer networks (aPPNs) as sorbents for post combustion CO2 capture

DOE AWARD NUMBER: DE-FE0026472

PI: Joe Zhou Texas A&M

Sub-Award: framergy

Zac Perry

Outline

- Objectives and Budget
- Background
- Four Synthetic Approaches to Novel PPNs
  - PPN-200
  - PPN-60
  - aPPNs
  - Acid Catalyzed Trimerization
- Synergy with Framergy
- BP2 Goals

Project Objectives

- To improve and optimize sorbent and process technologies so that, by the end of the 36-month effort, a scalable highly-robust and highly-efficient sorbent can be delivered and validated through lab-scale testing in a fixed-bed carbon capture/sorbent regeneration system
- The cost of the advanced sorbents will be reduced to a point where it will be economically feasible to scale-up and use the sorbents in commercial carbon capture processes
- The ideal sorbents for post-combustion CO_2 capture at project's end will demonstrate 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.

Project Organization Chart

TEXAS A&M UNIVERSITY

framergy™

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

Resource Loaded Schedule

					Budget Period 1				Budget Period 2				Budget Period 3			
Task	Mileston	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
1.0- Program Management and Planning	a, b	9/30/2015	9/30/2018	$ 187,853												
1.1-Project Management Plan		9/30/2015	9/30/2018													
1.2-Briefings and Reports		9/30/2015	9/30/2018													
2.0-Sorbent Synthesis and Optimization	c, f, J, k	9/30/2015	9/30/2016	$ 352,156												
3.0-Initial Sorbent Testing	d	9/30/2016	9/30/2016	$ 286,656												
3.1-Physisorption Tests	e	9/30/2015	6/30/2016													
3.2-Physical Property Characterization	g	1/30/2015	6/30/2016													
3.3-Initial TGA Tests	h	1/30/2016	6/31/16													
3.4-Initial Degredation Studies	i	3/30/2016	9/30/2016													
4.0-Sorbent Optimization	m	9/30/2016	9/30/2017	$ 202,042												
5.0-Initial Sorbent Scale-up	n, o	1/30/2017	6/31/2017	$ 191,585												
6.0-Initial Fixed Bed Testing	l, p	9/30/2016	9/30/2017	$ 65,000												
7.0-Attrition and Mechanical Hardness Tests	q	1/30/2017	6/30/2017	$ 34,300												
8.0-Sorbent Production	r	9/30/2017	6/30/2018	$ 221,330												
9.0-Optimal Fixed Bed Testing	s	1/30/2018	9/30/2018	$ 186,694												
10.0-Technology Assessment	t	3/30/2017	9/30/2018	$ 80,000												
			Total	$ 1,807,616												

Project Budget

	Budget Period 1 10/01/15-09/30/16		Budget Period 2 10/01/16-09/30/17		Budget Period 3 10/01/17-09/30/18		Total Project	
	Federal Share	**Cost Share**	**Federal Share**	**Cost Share**	**Federal Share**	**Cost Share**	**Federal Share**	**Cost Share**
Texas A&M University	$542,953	$140,286	$ 377,316	$94,329	$ 291,736	$72,943	$ 1,212,005	$303,011
framergyTM	$18,189	$0	$63,199	$20,701	$152,692	$33,271	$234,080	$58,519
Total	$561,144	$140,286	$ 440,514	$115,030	$ 444,428	$106,214	$ 1,446,086	$361,530
Cost Share	80.0%	20.0%	80.0%	20.0%	80.0%	20.0%	80.0%	20.0%

BP1 Milestone Log

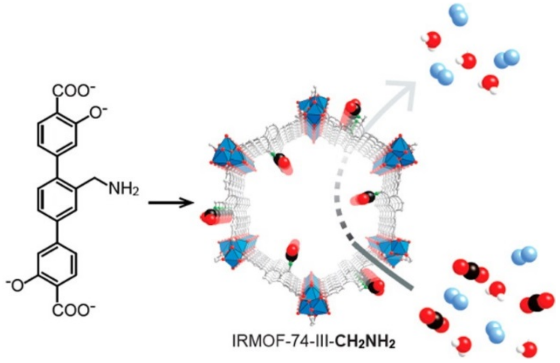
ID	Task	Milestone Description	Planned Completion	Actual Completion	Percentage Complete	Verification Method
a	1	Updated Project Management Plan	10/31/2015	10/31/2015	100%	Project Management Plan file
b	1	Kick-off Meeting	12/31/2015	12/31/2015	100%	Presentation file
c	2	Complete synthesis of least 5 novel aPPN sorbent formulations at small-scale (~100 milligrams)	1/31/2016	1/31/2016	100%	Results reported in the quarterly report
d	3.0	Complete synthesis of two Gen 0 materials (PPN-125-DETA and MOF-74-Mg) for standardization of measurements	1/31/2016	1/31/2016	100%	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	3/31/2016	100%	Results reported in the quarterly report
f	2	Complete synthesis of 5 or more additional aPPN sorbents (~100 mg)	5/31/2016	5/31/2016	100%	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	8/30/2016*	30%	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	8/30/2016*	50%	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	8/30/2016*		Results reported in the quarterly report
j	2	Sorbent Synthesis Optimization – Projected Cost Analysis	8/30/2016	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	9/30/2016*		Results reported in the quarterly report

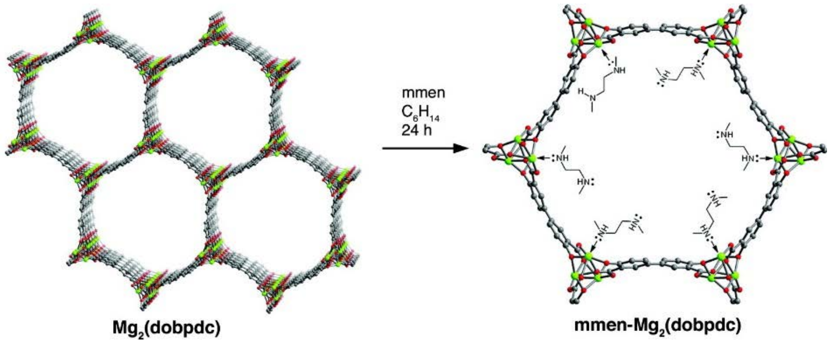
BP1 Success Criteria

Decision Point	Basis for Decision/Success Criteria	Status
Completion of Budget Period 1	Successful completion of all work proposed in Budget Period 1	On Track
	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	Amine functionalized PPN-200 has the CO_2 uptake of 0.09 kg/kg at 0.15 bar and 298K and 11.3 kg/kg at 1 bar and 298K. We are working on the condition optimization to reach a higher CO_2 uptake and performing cycling experiments.
	Produce ~50 grams of at least the two top-performing aPPN sorbent formulations	We are currently working towards scale-up and expect completion by the end of BP1.
	Submission and approval of a Continuation Application in accordance with the terms and conditions of the award. The Continuation Application should include a detailed budget and budget justification for budget revisions or budget items not previously justified, including quotes and budget justification for service contractors and major equipment items	The BP2 Continuation Application was submitted on July 12, 2016

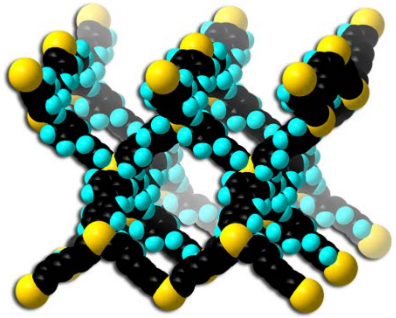
Amine-decorated Porous Materials

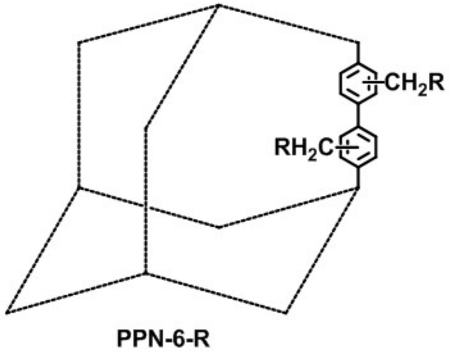
- Metal-Organic Frameworks (MOFs)

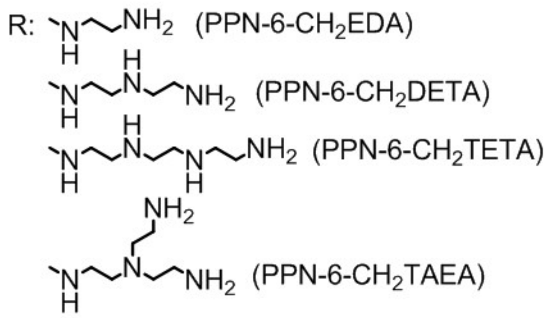




- Porous Polymer Networks (PPNs)

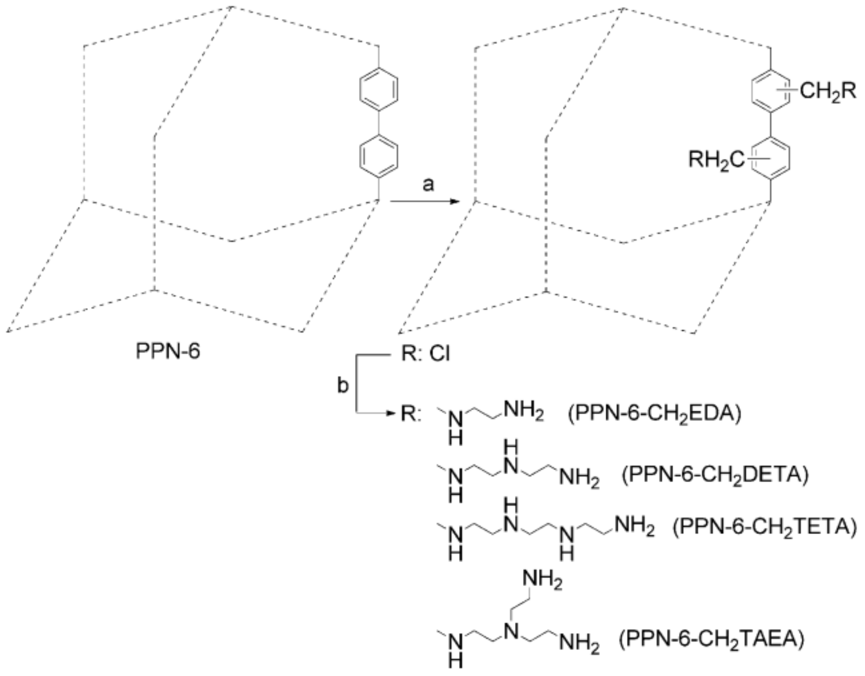


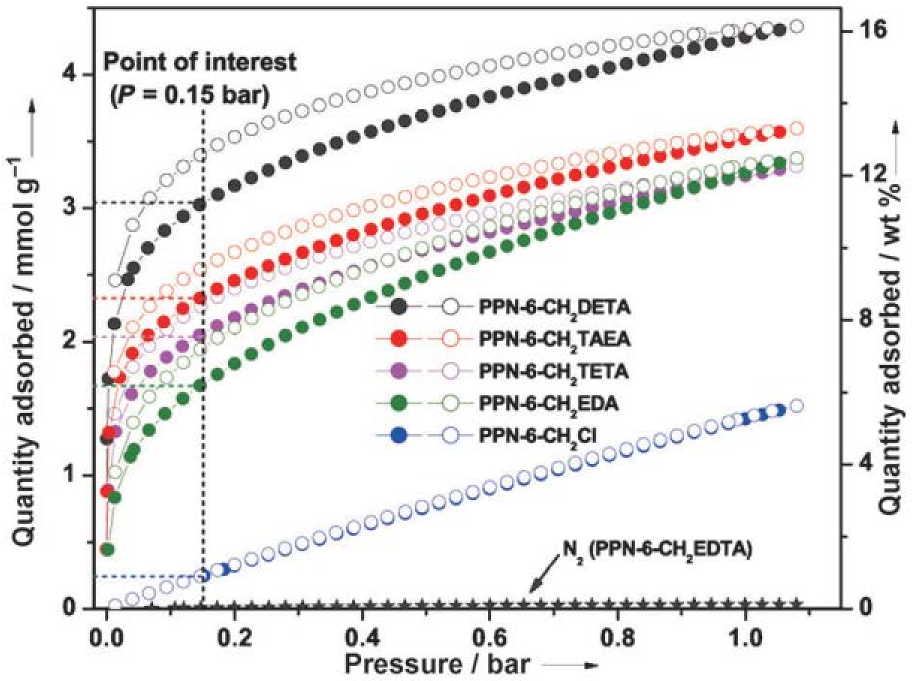




A. M. Fracaroli, H. Furukawa, M. Suzuki, M. Dodd, S. Okajima, F. Gándara, J. A. Reimer, O. M. Yaghi, *J. Am. Chem. Soc.*, **2014**, *136*, 8863-8866.
McDonald, T. M.; Long, J. R., *Nature* **2015,** *519* (7543), 303-308.
Lu, W.; Sculley, J. P.; Yuan, D.; Krishna, R.; Wei, Z.; Zhou, H.-C., *Angew. Chem. 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)$_2$) is required
- Purely serves as a support for amine chains, decreasing volumetric CO_2 uptake

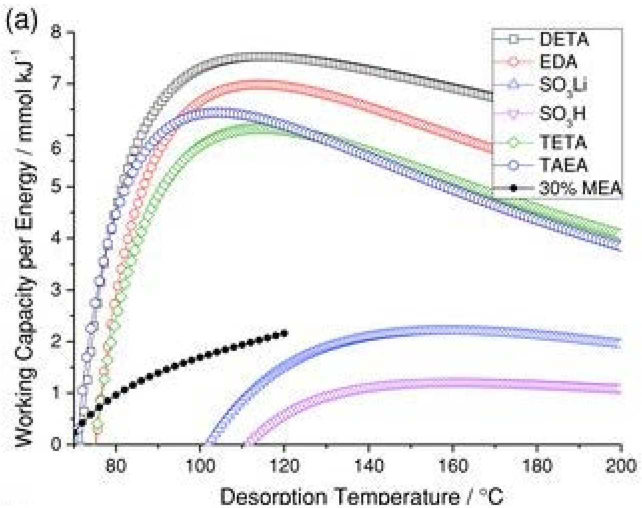
Lu, W.; Sculley, J. P.; Yuan, D.; Krishna, R.; Wei, Z.; Zhou, H.-C., *Angew. Chem. Int. Ed.* **2012,** *51*, 7480.

Calculating the Benefits of PPNs

- Low Heat Capacities
- Reduced Energy costs

Table S2. IAST selectivity and Purity for each compound.

	$-SO_3Li$	$-SO_3H$	–EDA	–DETA	–TETA	–TAEA
N_2 loading	0.058	0.09	1.09E-06	1.45E-09	2.99E-08	2.75E-09
CO_2 IAST	1.317	0.908	1.616	2.967	1.984	2.264
CO_2 pure	1.361	0.954	1.616	2.967	1.984	2.264
IAST selectivity	129.25	57.09	8.39E+06	2.05E+09	3.76E+08	8.22E+08
Purity	95.78%	90.98%	100.00%	100.00%	100.00%	100.00%



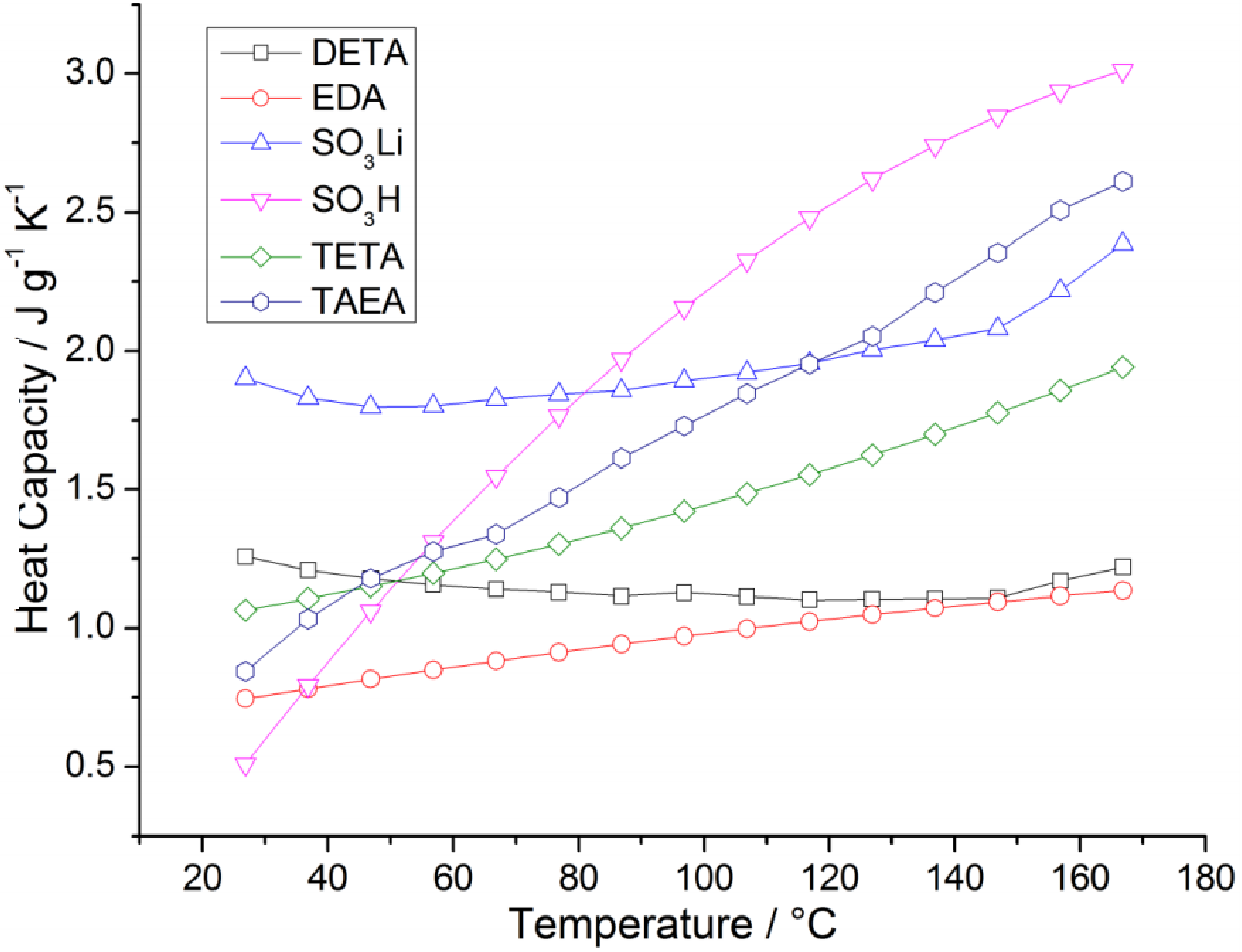


Figure S10. Heat capacity of PPNs as a function of temperature.

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

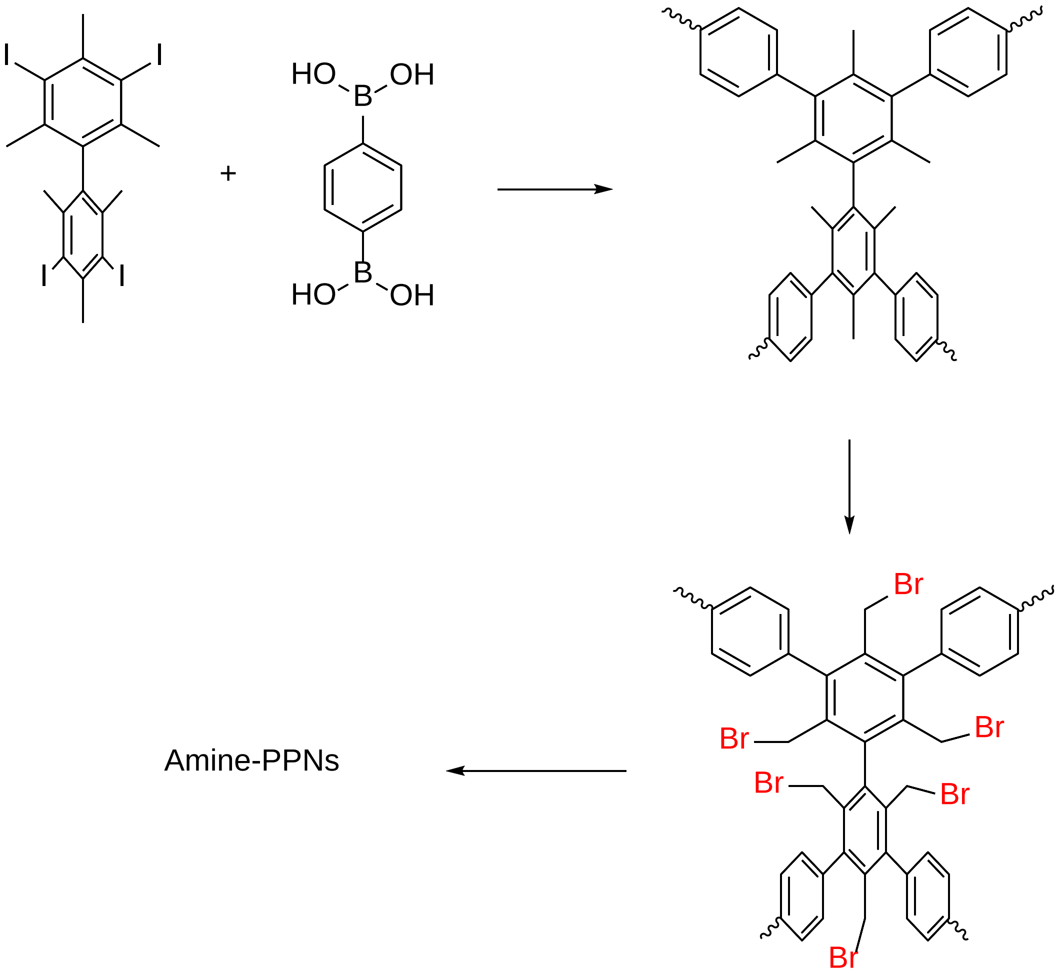
N_2 and CO_2 Uptake of New PPN Materials

Temperature (298 K)

Sorbent	N_2 uptake (cm^3 g^{-1})	Pore Volume (cm^3 g^{-1})	CO_2 Uptake (kg/kg)	
			0.15 bar	1 bar
a-PPN-1	415	0.2099	0.018	0.128
a-PPN-1R	210	0.2555	0.080	0.125
a-PPN-2R	210	0.1336	0.033	0.113
PPN-60	365	0.4270	-	-
PPN-60-DETA	118	0.0343	0.055	0.090
PPN-60-TAEA	23	0.0332	0.064	0.102
PPN-200	450	0.4812	-	-
PPN-200-DETA	-	-	0.081	0.131
PPN-200-TETA	-	-	0.090	0.113
PPN-200-TAEA	-	-	0.089	0.126
PPN-300	230	-	-	-
PPN-300-DETA	-	-	0.043	0.090

PPN-200 *via* Cross-Coupling, Post-Synthetic Amine Tethering

- Post-synthetic modification via PPN-200-Br to yield amine tethered PPN materials

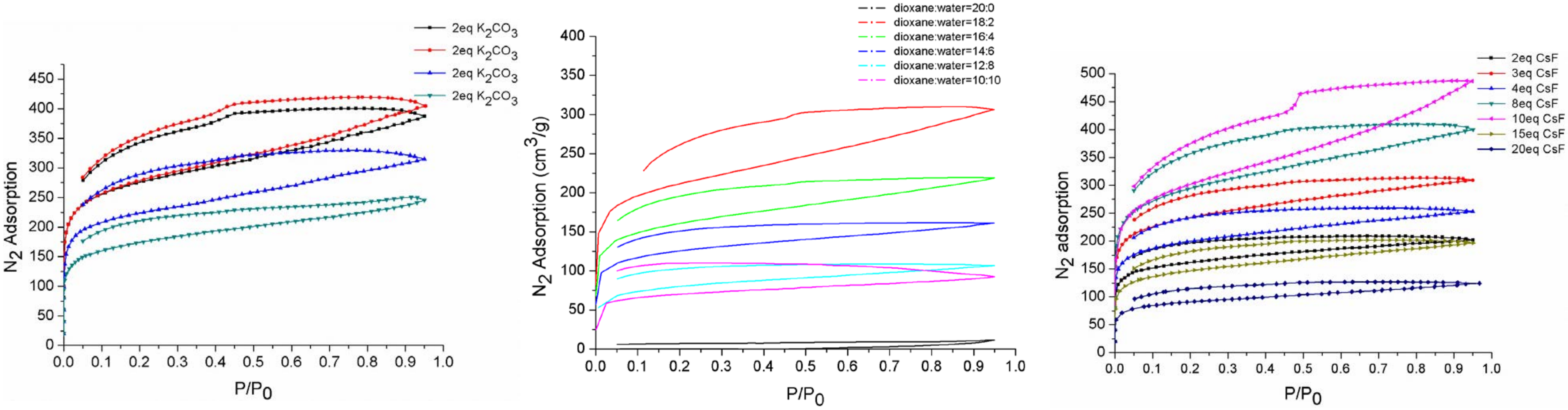


PPN-200

PPN-200Br

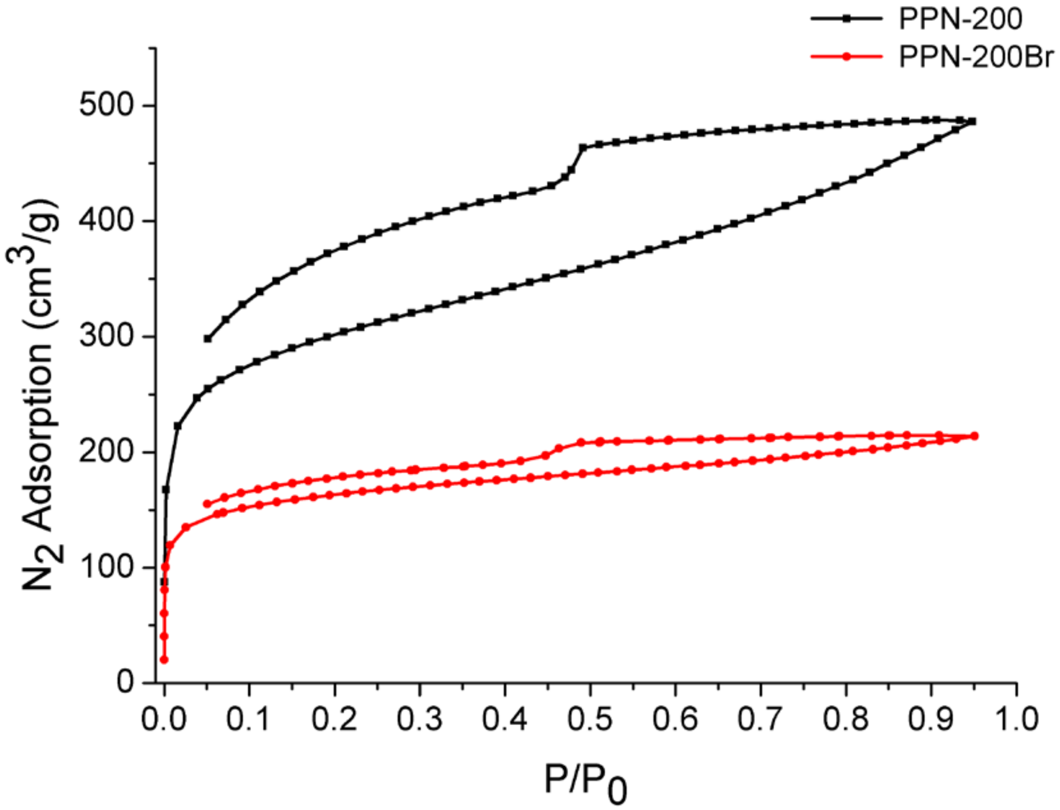
PPN-200EDA
PPN-200DETA
PPN-200TETA
PPN-200TAEA

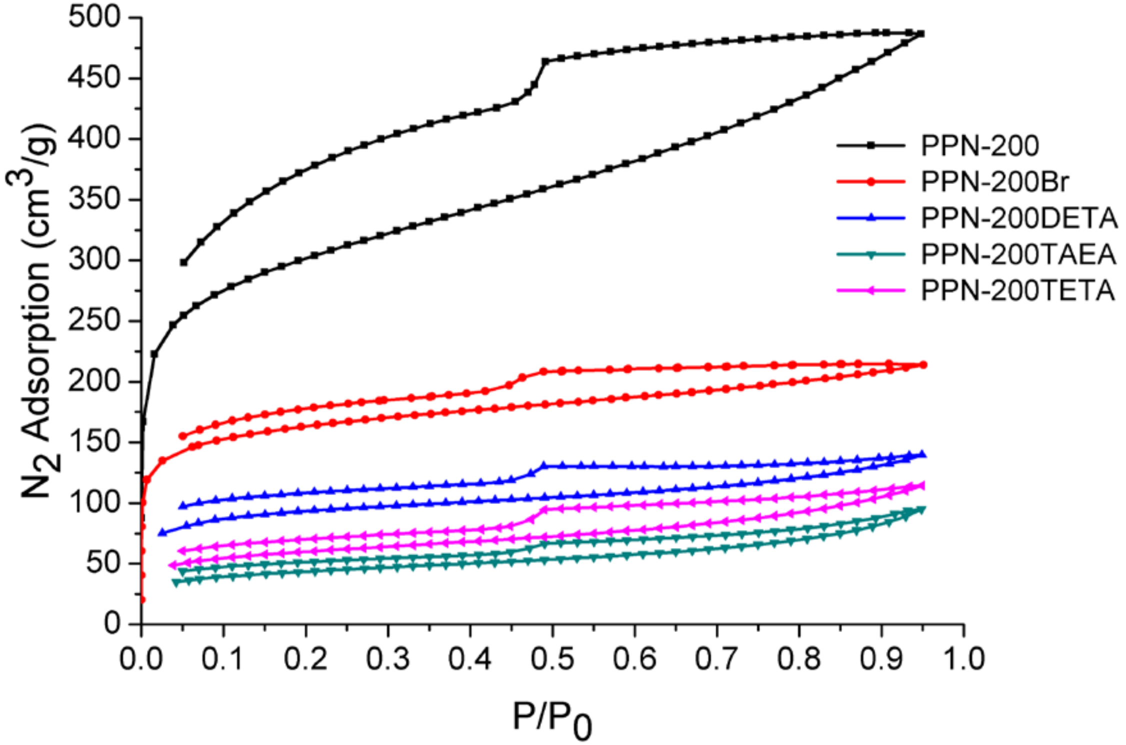
Optimization of PPN-200 Synthesis



- Optimizing the synthetic conditions for cross-coupling reaction by variation of reagent and solvent conditions

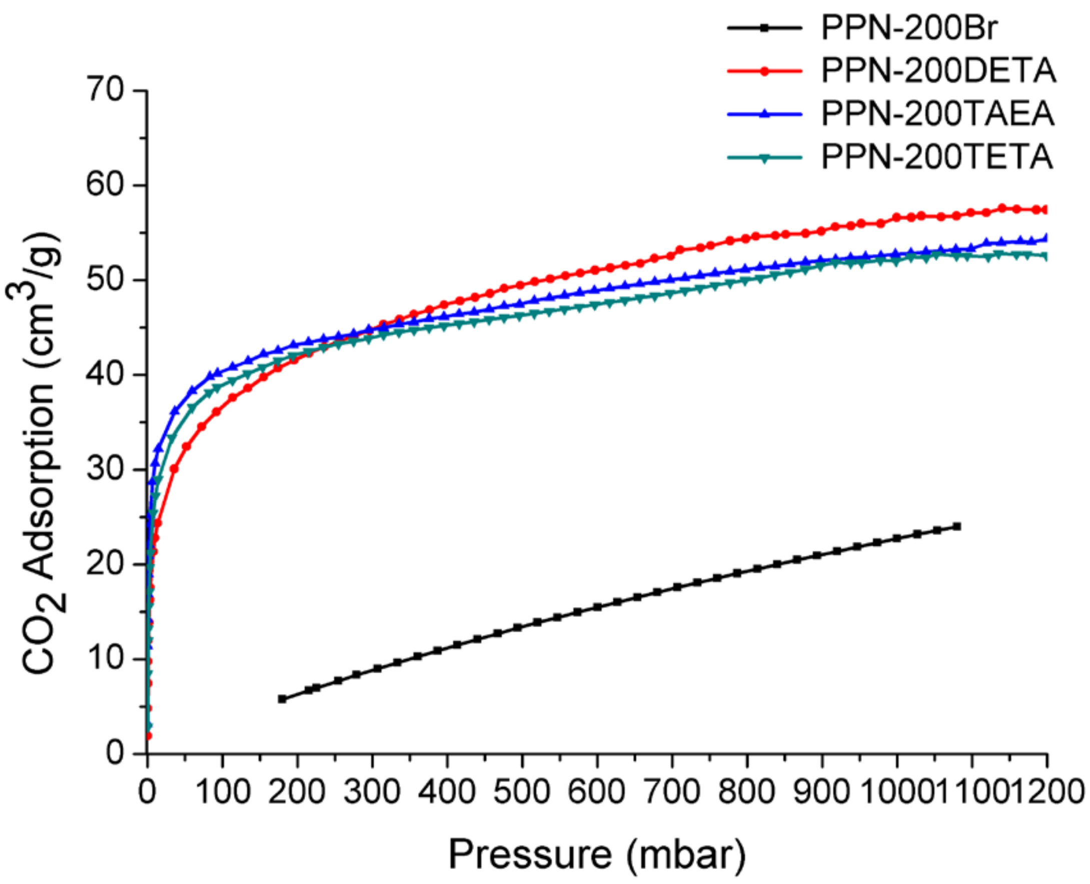
Post Synthetic Functionalization of PPN-200





- 28% conversion of methyl to bromomethyl
- Optimizing the bromination conditions to maximize the conversion

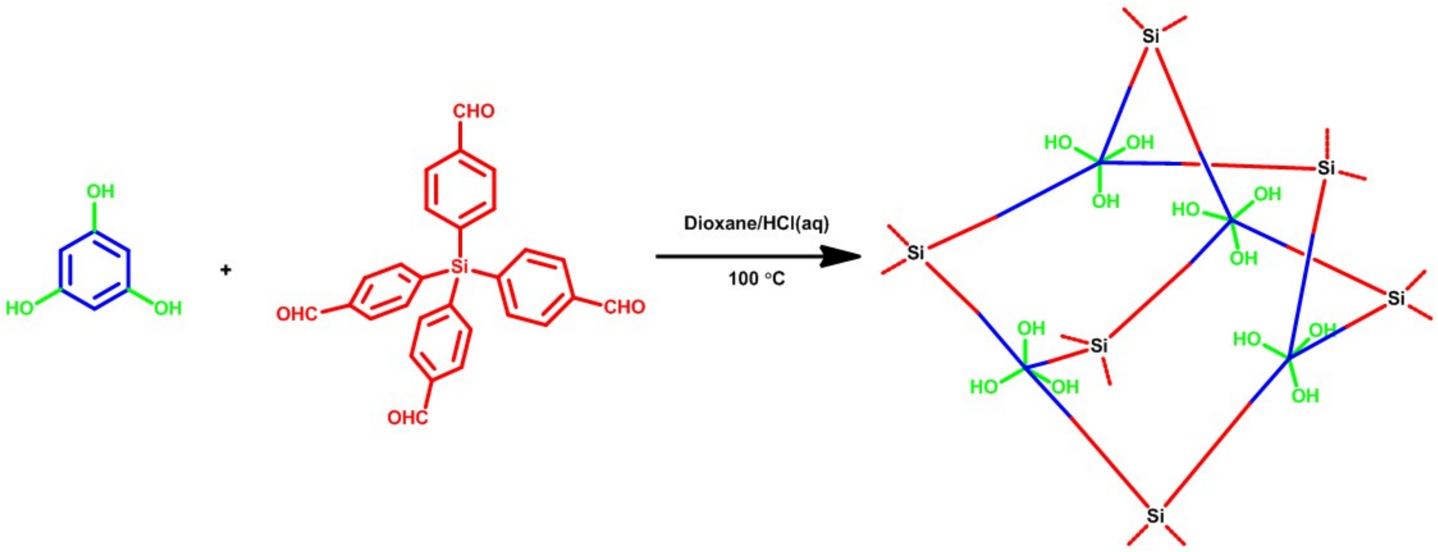
Amine Appended PPN-200 Series



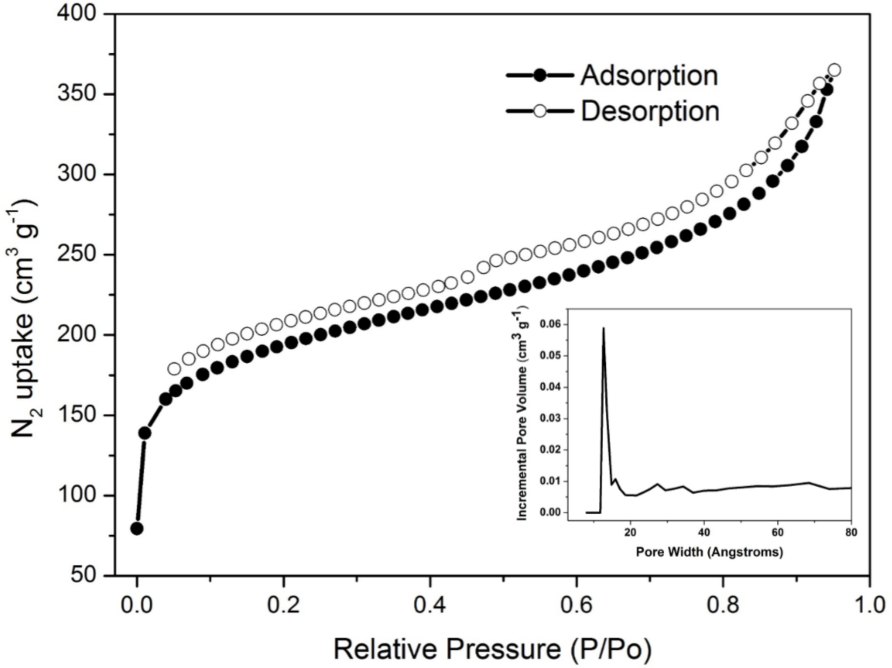
BP1 Target Capacity	0.1 kg/kg
PPN-200DETA	0.081 kg/kg
PPN-200TAEA	0.090 kg/kg
PPN-200TETA	0.089 kg/kg

298 K, 0.15 bar

PPN-60 *via* Hetero-coupling of Tetrahedral Monomers



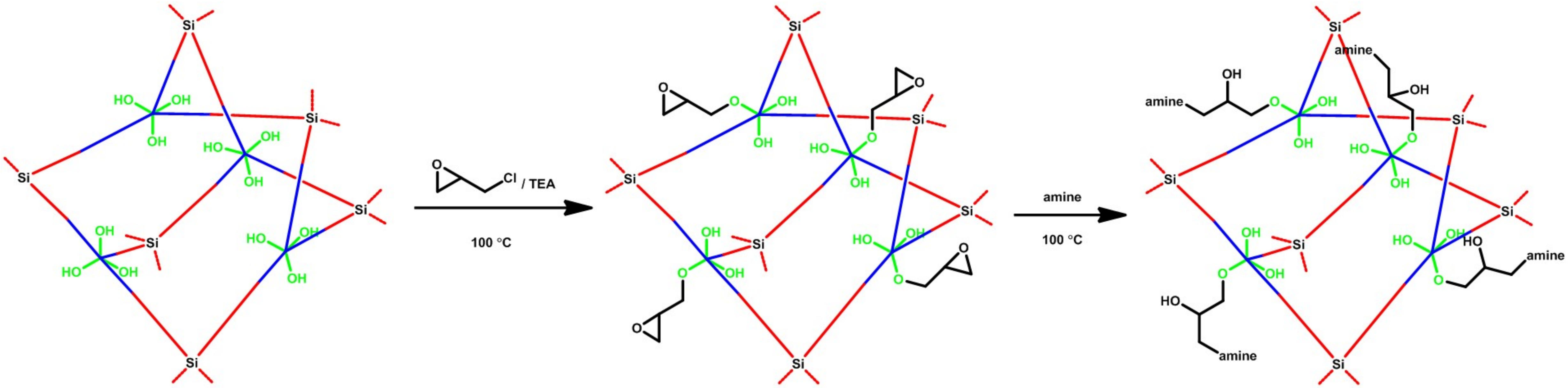
PPN-60



- Further functionalization of PPN-60 post-synthetically

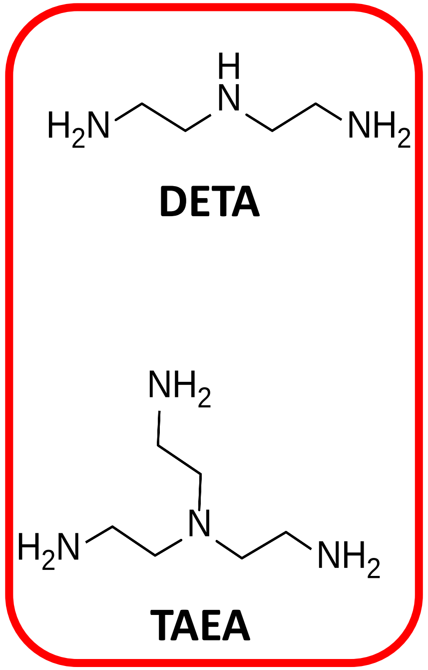
N_2 uptake of 365 cm^3 g^{-1} at 1 bar, 77K
BET surface area of 601 m^2 g^{-1}

Post-Synthetic Functionalization of PPN-60

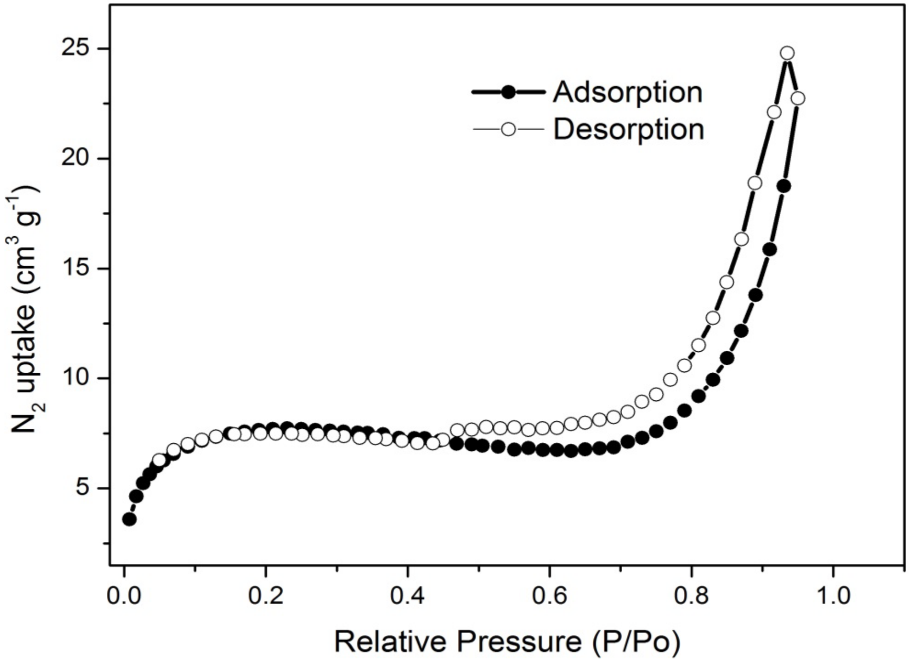


PPN-60 **PPN-60-epoxide** **PPN-60-amine**

N_2 Uptake of PPN-60-DETA and PPN-60-TAEA

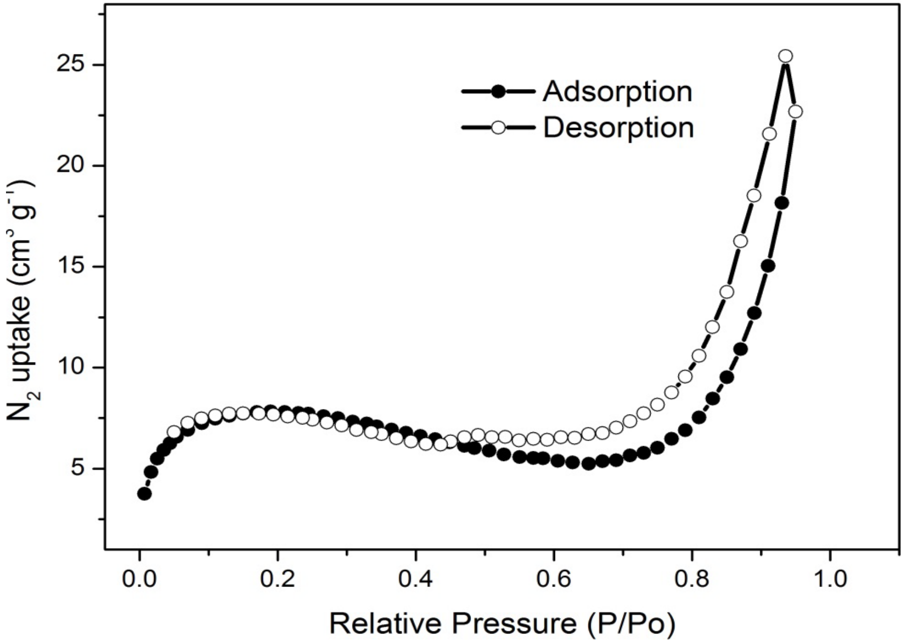


PPN-60-DETA



N_2 uptake of 23 cm^3 g^{-1} at 1 bar, 77K

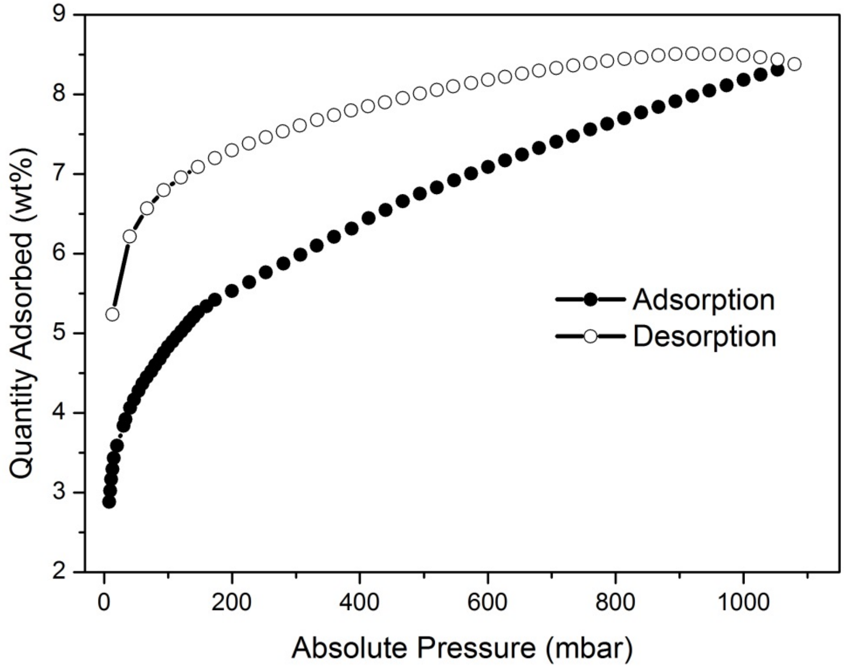
PPN-60-TAEA



N_2 uptake of 23 cm^3 g^{-1} at 1 bar, 77K

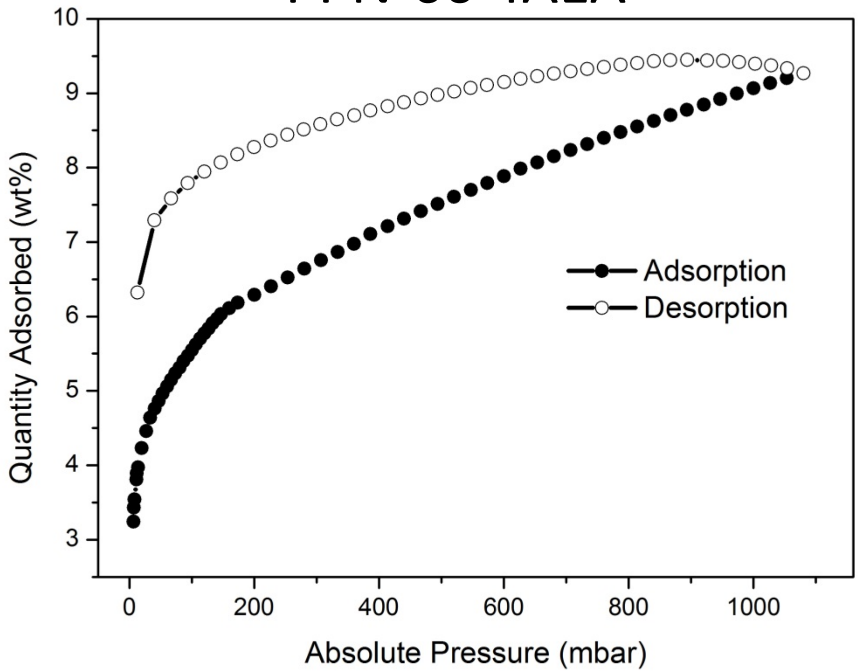
CO_2 Uptake of PPN-60-DETA and PPN-60-TAEA

PPN-60-DETA



CO_2 uptake of **0.055 kg/kg** (0.15 bar) and **0.090 kg/kg** (1 bar) at 298 K

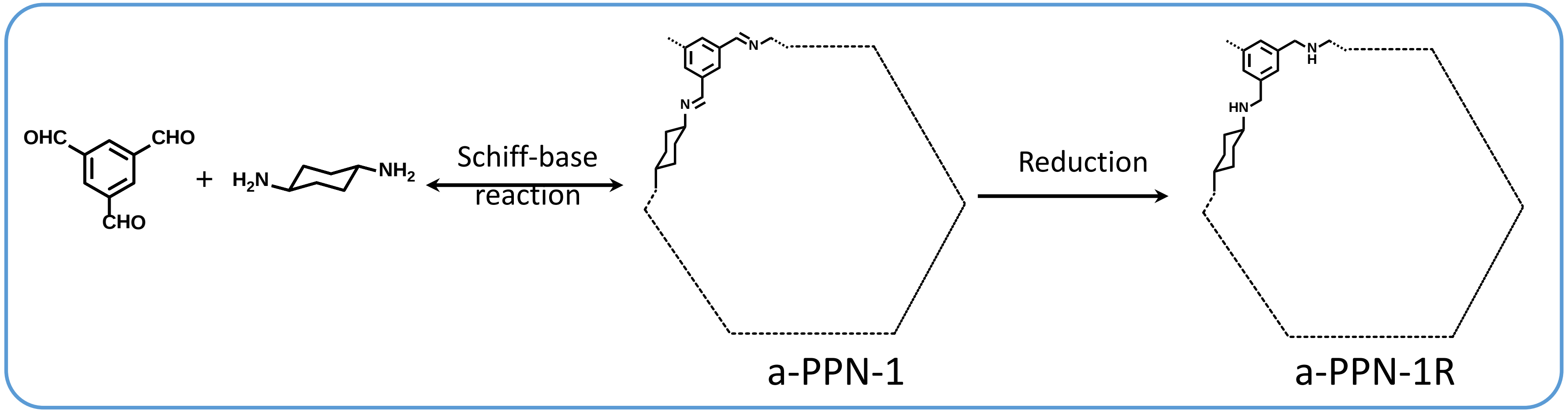
PPN-60-TAEA

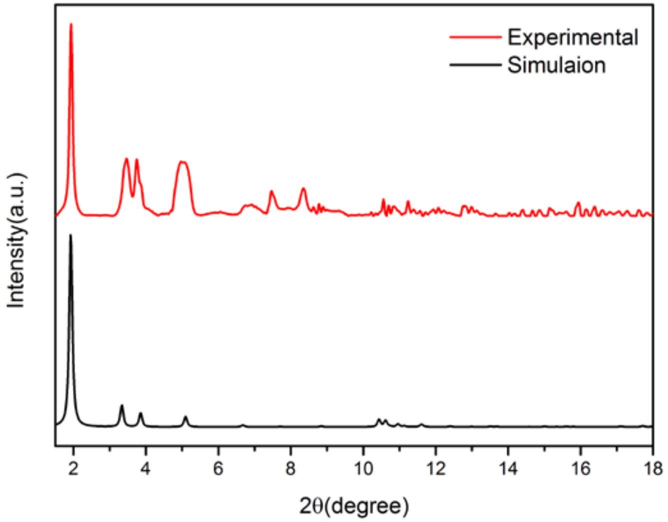


CO_2 uptake of **0.064 kg/kg** (0.15 bar) and **0.102 kg/kg** (1 bar) at 298 K

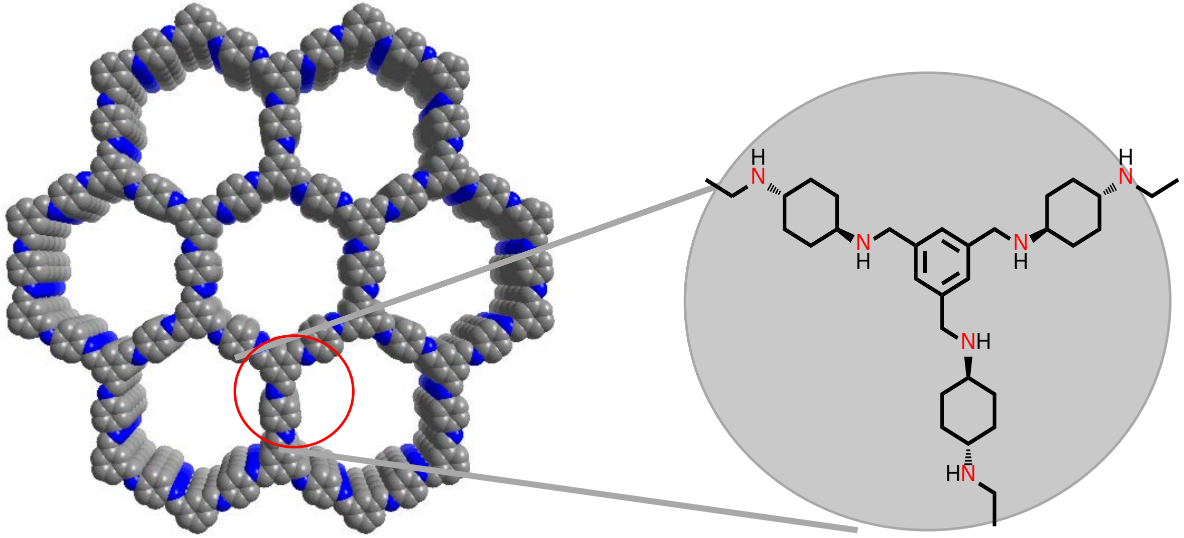
Crystalline a-PPNs Formed *via* Schiff-base Reactions

Post-synthetic reduction of a-PPN-1 to a-PPN-1R



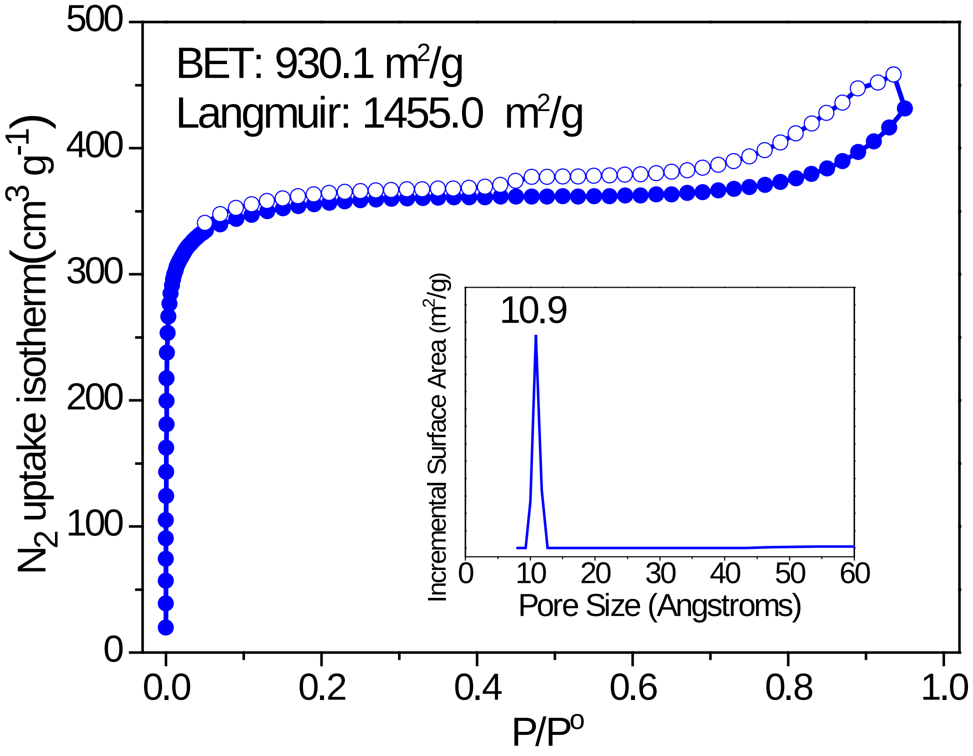


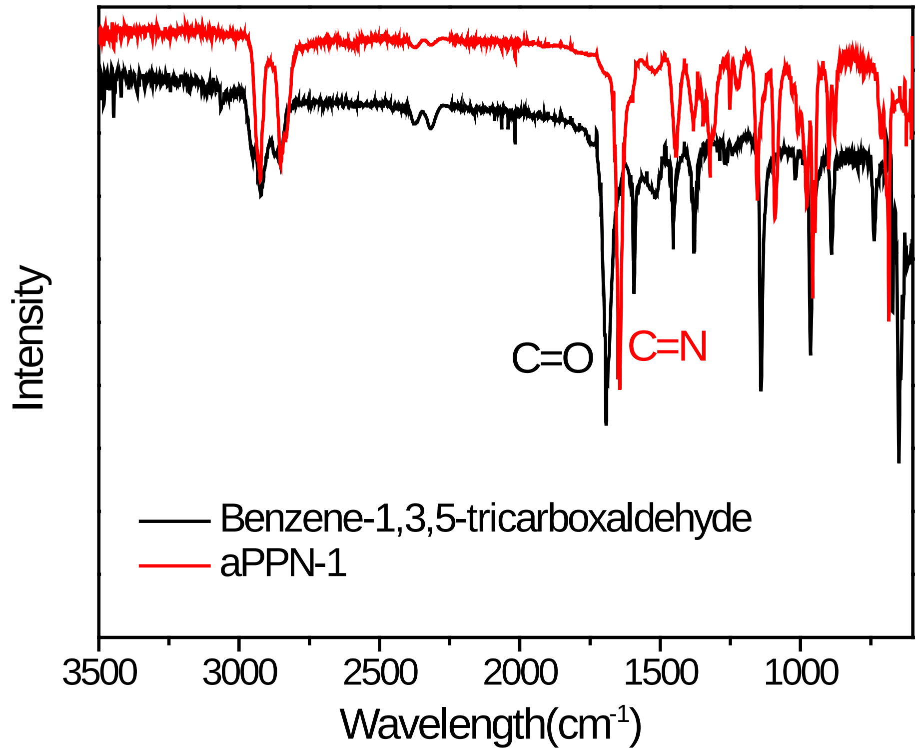
Synchrotron PXRD



Simulated structure

Analysis of a-PPN-1

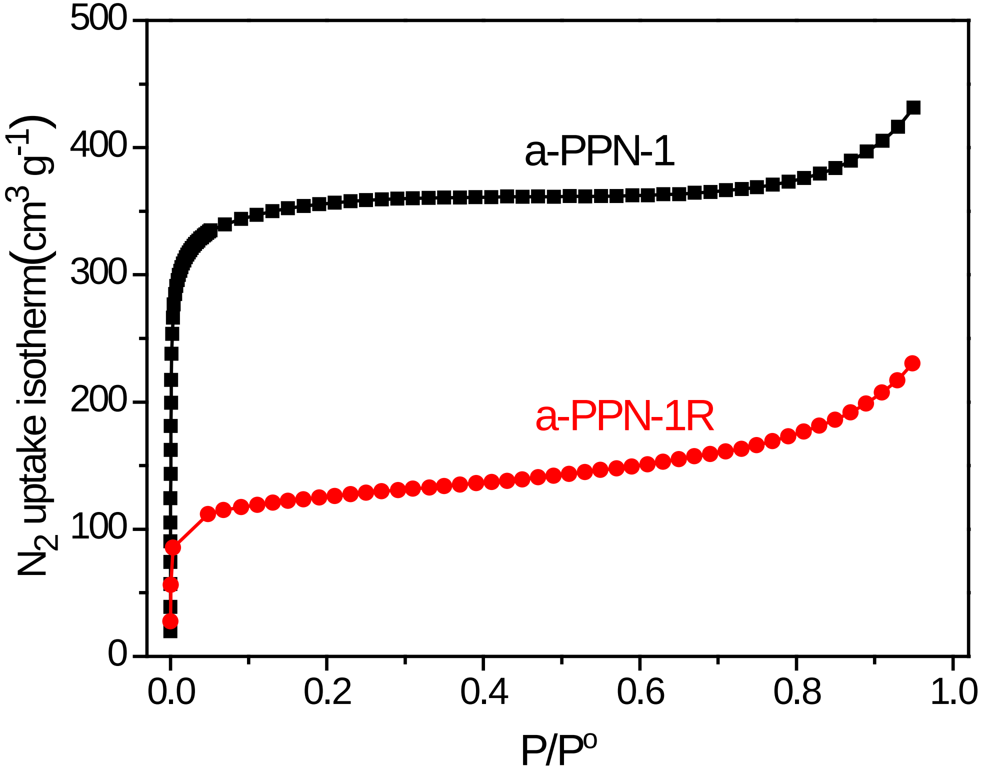




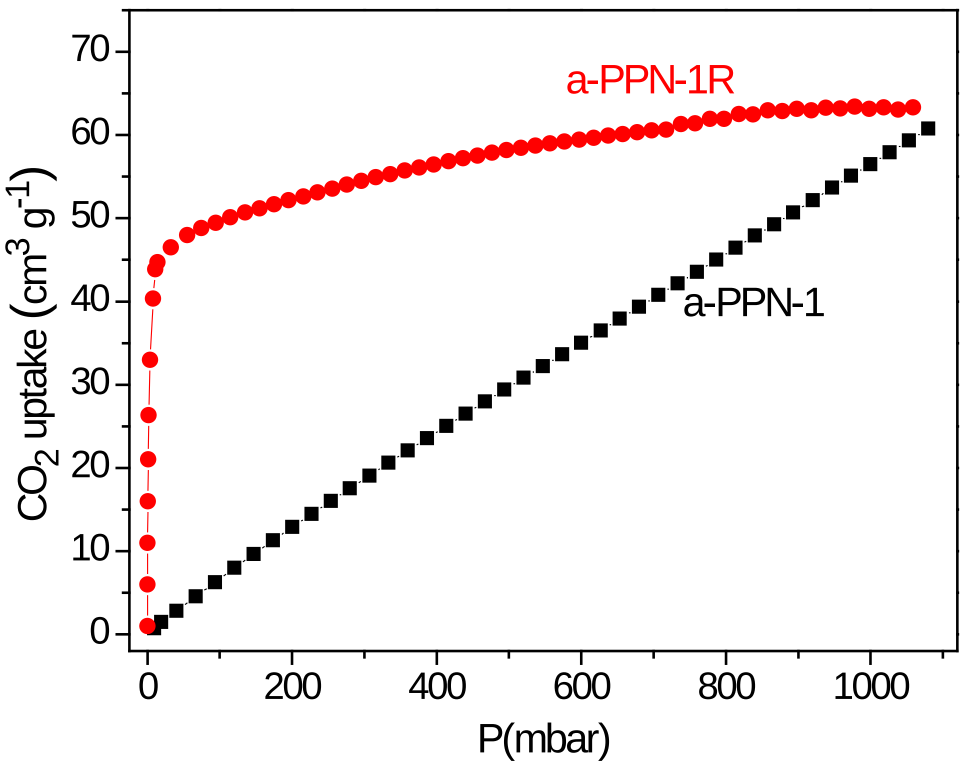
- N_2 uptake at 77K
- Pore size distribution pictured inset

- Appeared: Imine C=N stretching: 1644 cm^{-1}
- Disappeared: Aldehyde C=O stretching 1692 cm^{-1}

Analysis of a-PPN-1R



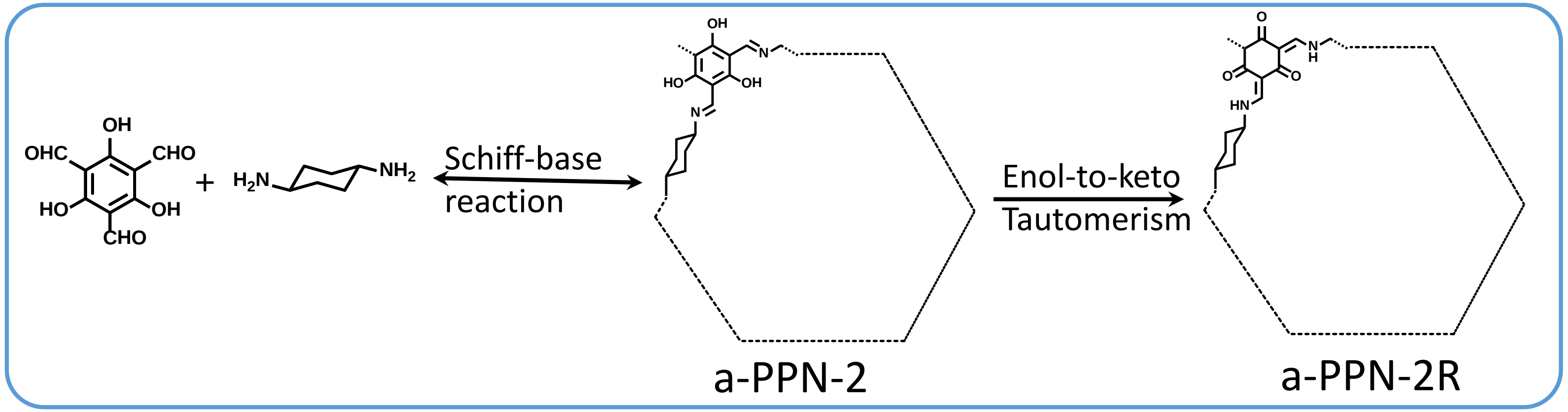
N_2 uptake isotherm at 77K

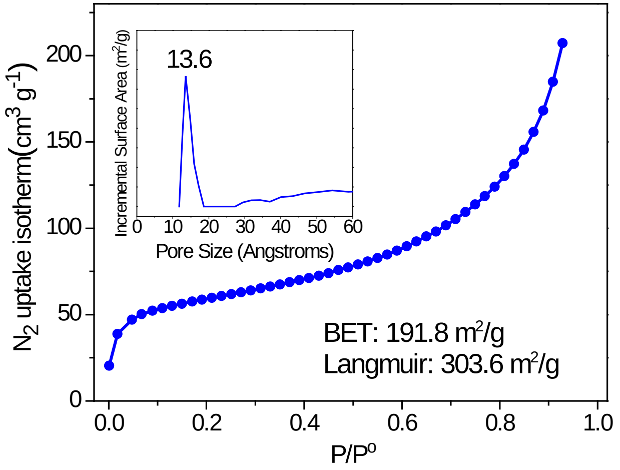


CO_2 uptake: 0.1 kg/kg at 0 °C and 0.15 bar

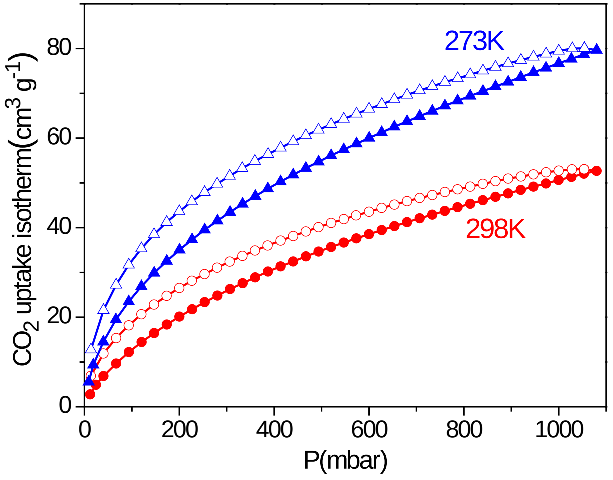
Crystalline a-PPNs (Cont.)

- Direct synthesis



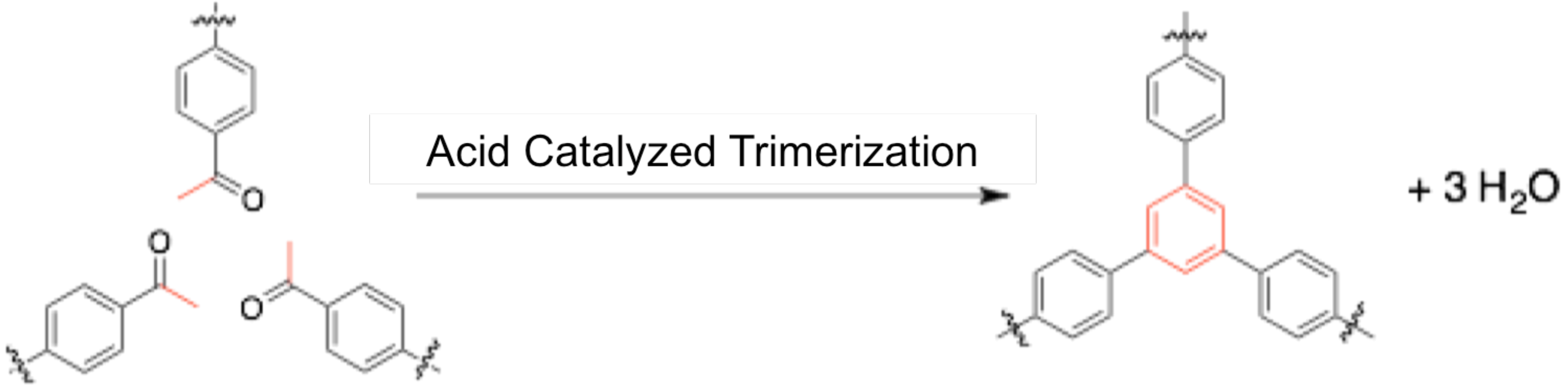


N_2 uptake at 77K
Pore size distribution inset



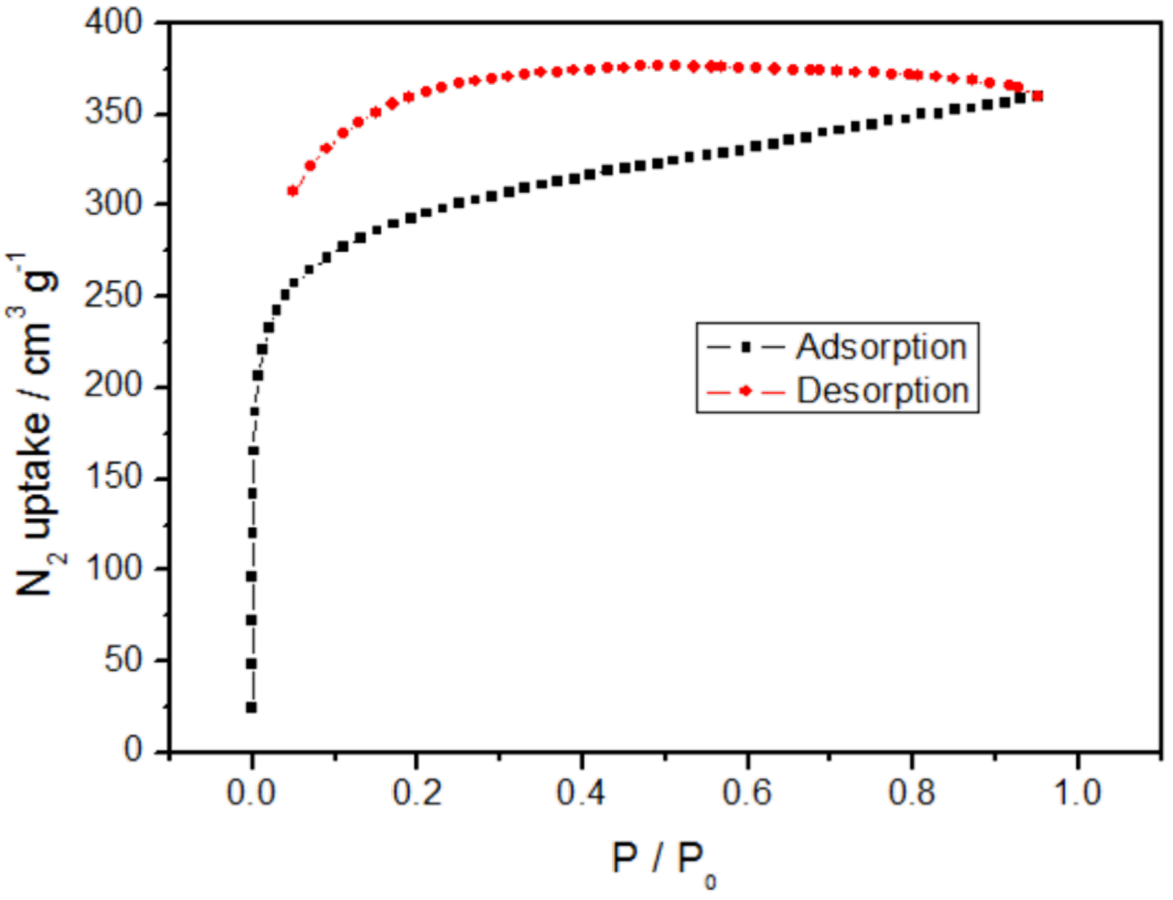
CO_2 uptake at 273K and 298K

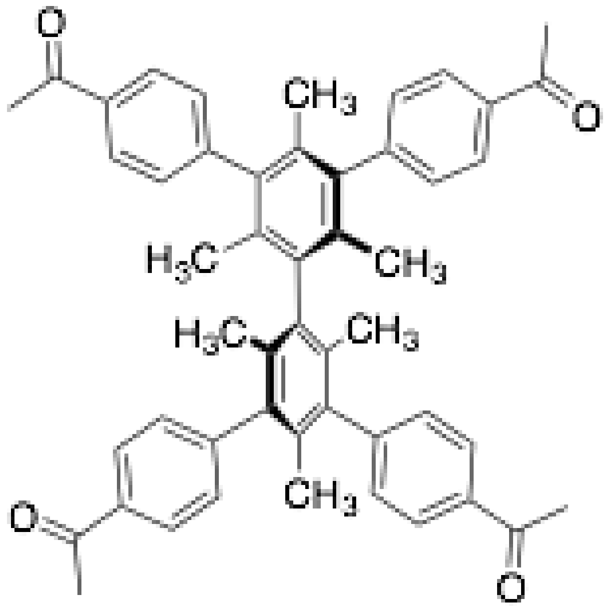
Cyclotrimeriztion of Acetyl Groups



- Novel trimerization route, cheap at industrial scale

Preliminary N_2 Uptake of Trimerized Monomer

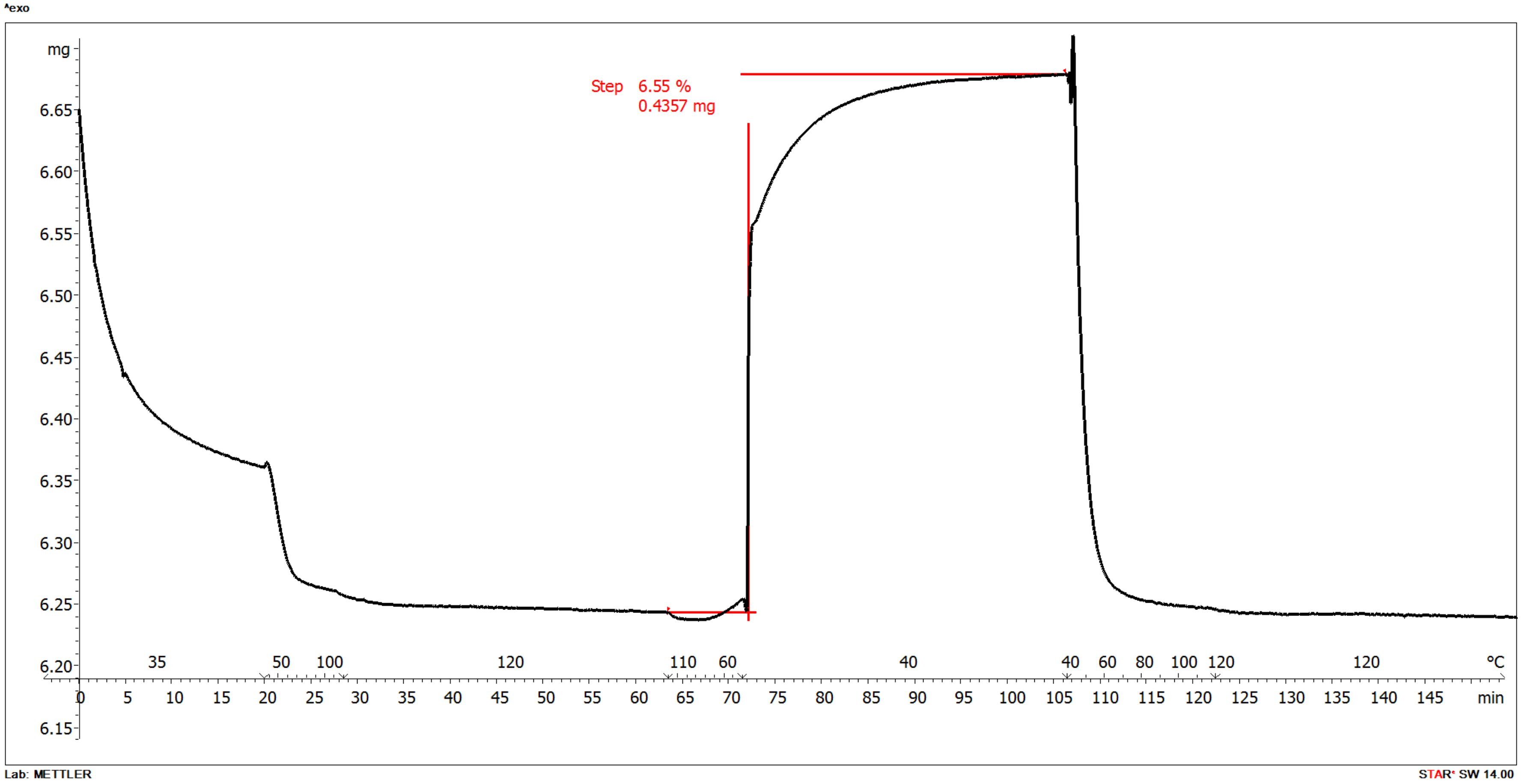




BET surface area: 1000 m^2/g

TGA Experiments

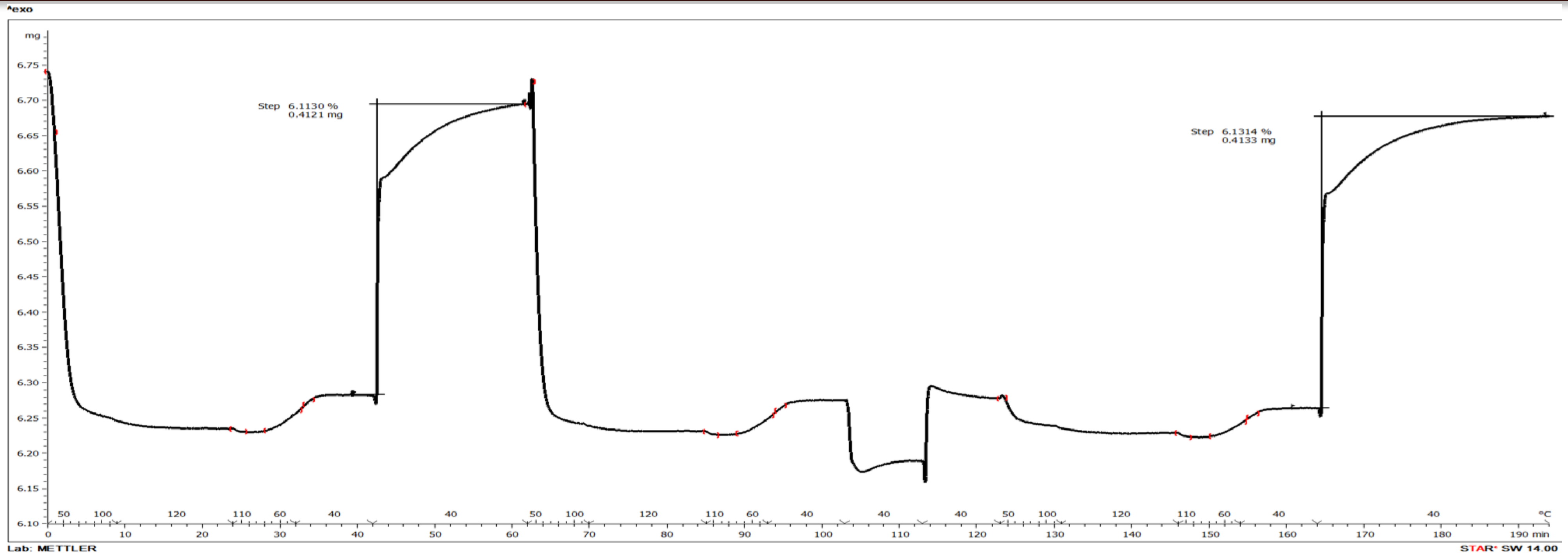
- Initial difficulties with TGA/MS
  - Have been resolved
- Testing at 40 °C
  - Humidification studies next
  - Breakthrough is better suited
- Checking reactivation methods
  - Pressure vs. Temperature swing



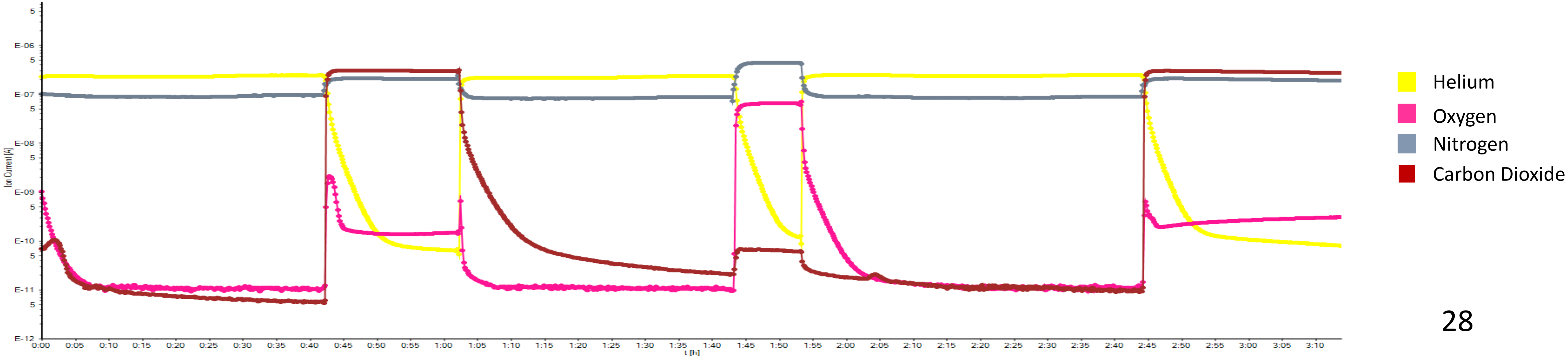
TGA of PCN-200 TAEA after 1 month air under CO2 gas stream @ 40 C

TGA Experiments-Air Exposure

TGA



MS



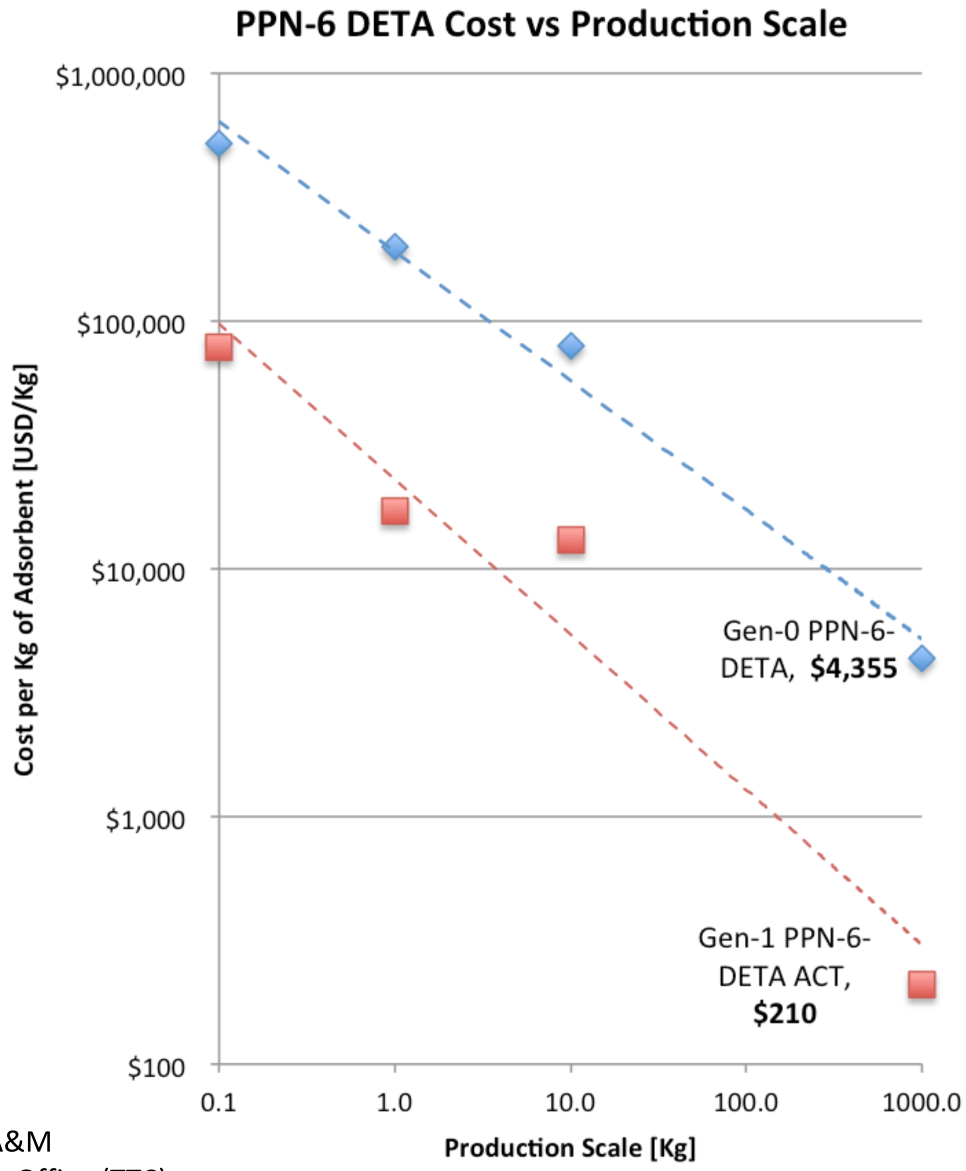
framergy's Role in BP1 - NETL

- Gen-0 Material (PPN-6-DETA) Cost Analysis
  - Identification of high impact cost components through sensitivity analysis
  - Monte-Carlo simulation (Palisade @Risk Decision Tools Suite) based optimization via variation of cost components, volatility, make-or-buy decision analysis
  - Material cost projections based on quantity demanded

- Gen-1 Material (PPN-6-DETA *via* Acid Catalyzed Trimerization) Cost Analysis

- Gen-2 Material (PPN-200-Br) Cost Analysis

Cost Analysis of PPN-6-DETA



Novel, Acid Catalyzed Trimerization (ACT) Route*:

x20 Cost Reduction

(*) **Invention Disclosure** has been submitted to Texas A&M University's Technology Transfer and Commercialization Office (TTC)

BP2 Success Criteria

- Successful completion of all work proposed in 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
- Submission and approval of a Continuation Application in accordance with the terms and conditions of the award. The Continuation Application should include a detailed budget and budget justification for budget revisions or budget items not previously justified, including quotes and budget justification for service contractors and major equipment items

Acknowledgement and Disclaimer

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