

# Hydrogen Storage through Nanostructured Porous Organic Polymers (POPs)

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Project ID  
ST050

# Overview

## Timeline

- Project start: July 2007
- Project end: June 2012
- % complete: 60%

## Budget

- Total project funding: \$2 Million
  - DOE share: \$1.88 Million
  - Contractor share: \$120 K
- Funding received in FY2009
  - \$ 800 K
- Funding for FY2010
  - \$ 500 K

## Barriers

- Barriers addressed
  - A. System Weight and Volume
  - B. System cost
  - C. Efficiency
  - D. Durability/Operability

## Partners

- Interactions/collaborations
  - Argonne National Laboratory (Lead)
  - U of Chicago (Subcontractor)
  - HSCoE Members
    - U of N. Carolina ( $^1\text{H}$  NMR)
    - Air Products (Sample exchange)
    - NREL (Measurement calibration)
    - ORNL (Theory)
  - Non HSCoE Members
    - U of Hawaii (Sample exchange)



# Objective - Relevance

- To design, synthesize, and evaluate nanostructured porous organic polymers (POPs) as new hydrogen storage adsorbents for transportation applications
- To support polymer materials development with modeling/simulation and advanced structural characterizations

## *Potential Advantages of POP H<sub>2</sub> Adsorbent & Their Impact on Technology Barriers*

- **System Weight and Volume** – POPs are light weight and can be converted to high volumetric density by engineering process such as compression, pelletizing, etc.
- **System Cost** – POPs can be scaled-up for industrial production with the existing infrastructure at competitive cost.
- **Efficiency** – POP-H<sub>2</sub> interaction is based on physi-adsorption/desorption principle with minimum parasitic energy consumption.
- **Durability/Operability** – POPs are stable under the temperature and humidity conditions required for hydrogen storage application.



# Approach - Milestones

Month/ Year	Milestones	Status Update
01/10	Complete the design, synthesis, and characterization of first group transition metal-doped polyporphyrin hydrogen adsorbents	<b>Completed.</b> Investigation on Fe doped polyporphyrin found slightly improved $\Delta H_{ads}$ with metal doped system. Finding is published.
03/10	Complete the design and synthesis of a second group of polymers incorporated with non-C main group elements	<b>Completed.</b> A new series of carborane based POPs were prepared with relatively high surface area and porosity.
06/10	Complete the evaluation of compression or pelletizing methods for improvement of volumetric capacity for representative polymers	<b>30% Completed.</b> Investigation on maintaining mechanical property of high surface area POP is underway.
07/10	Complete structural property, hydrogen storage capacity, and heat of adsorption measurement for the second group of polymers incorporated with non-C main group elements	<b>50% completed.</b> Measurement of surface property, H <sub>2</sub> adsorption uptake and isosteric heat of adsorption of carborane based POPs is halfway finished.

**We prepared over 100 POPs and demonstrated great feasibility of incorporating different chemical functionalities in narrowly distributed nanoporous space!**



# Approach - Development Strategy

## New Polymer Exploration (UofC/ANL)

- New POP synthesis through rational design at molecular level
- Molecular structure characterization

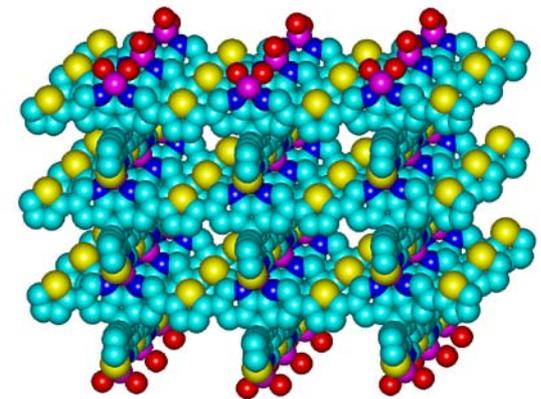
## Characterization & Optimization (ANL)

- H<sub>2</sub> storage capacity measurement
- Surface structure characterization
- Synthesis method improvement

## Modeling & Simulation (ANL/HSCoE)

- H<sub>2</sub>-polymer interaction study via *ab initio*, DFTB & MD methods
- Advanced characterization through NMR, x-ray, etc.

- Prepare high surface area & narrow/adjustable pore size polymers through rational design and synthesis
- Incorporate “metallic” feature into polymer through conductive backbone or metal doping
- Improve polymer-H<sub>2</sub> interaction by incorporating functional groups with hetero (non-C) elements
- Develop fundamental understanding through modeling and advanced characterization



An example of ANL/UofC polymer with conductive backbone incorporated with different elements

# Technical Accomplishment Highlights in FY2010

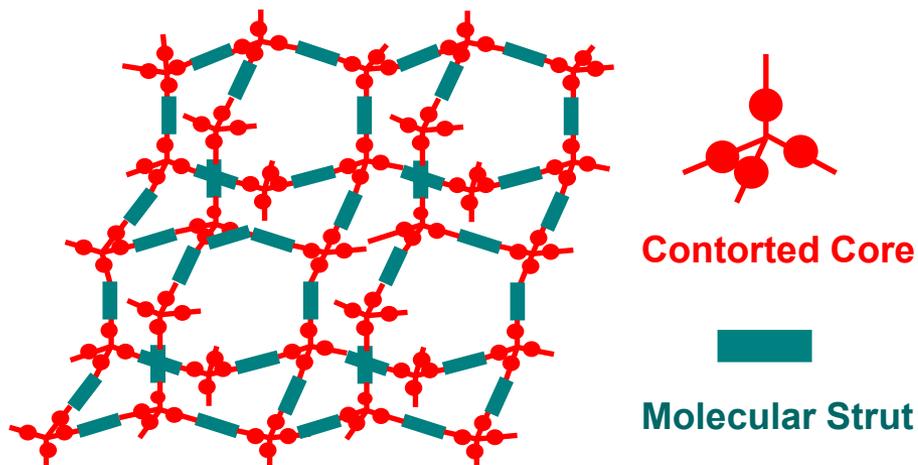
- Successfully designed and synthesized a polyporphyrin based POP (PTTPP) with high BET surface area and narrow pore size distribution. Gravimetric capacities of 5.0% at 77K and 0.6% at ambient temperature were achieved. Atomically dispersed Fe was successfully integrated into PTTPP with marginally improved hydrogen heat of adsorption. The PTTPP system can be used as a platform to investigate H<sub>2</sub>-metal interaction in confined space
- A series of aromatic POPs with similar BET surface areas but variable pore sizes were prepared through facile ethynyl trimerization reaction. H<sub>2</sub> isosteric heat of adsorption up to ~10 kJ/mol was achieved. The H<sub>2</sub> isotherm study also found that the H<sub>2</sub>-POP interaction is more sensitive to chemical environment than pore dimension.
- Several new synthetic methods were developed to incorporate a variety of non-C elements (B, N, etc.) into POPs while maintaining high surface areas and narrow pore diameters. Preliminary experiments demonstrated improved heat of adsorption



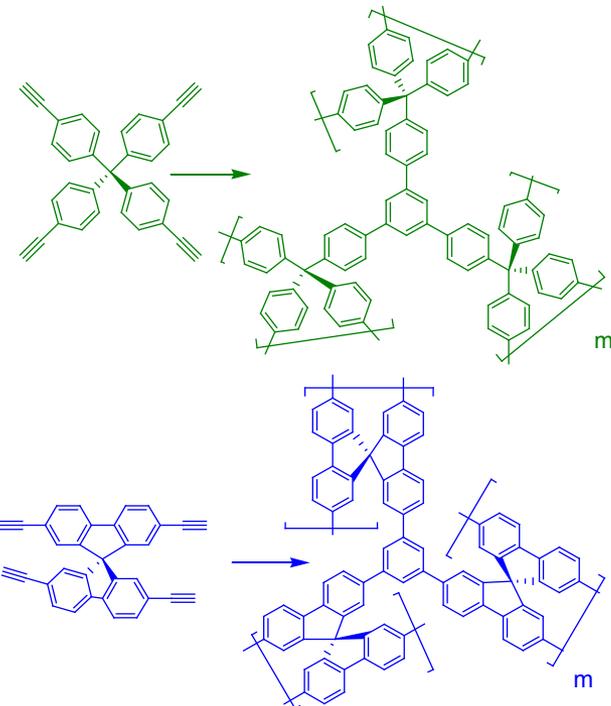
# Technical Accomplishments - Design & Synthesis of POPs

## Creating POPs with contorted cores & variable molecular struts

- High surface area and micropore volume using contorted cores with molecular dimension
- Adjustable pore size via molecular struts of different lengths & crosslinking site densities
- Functionalized surface with different elements & metal exchange sites through monomer design



## Examples of preparing POPs via trimerization of ethynyl groups

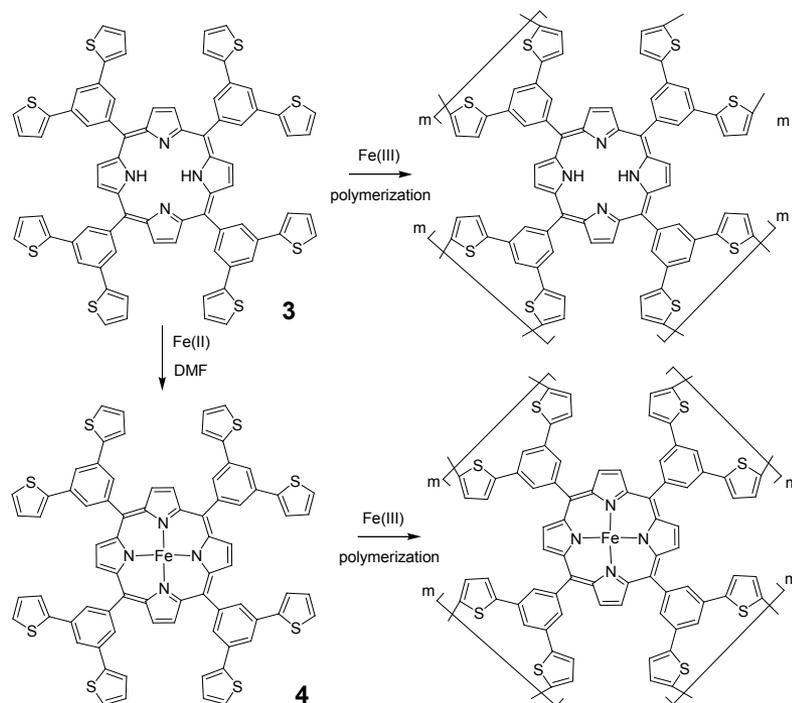
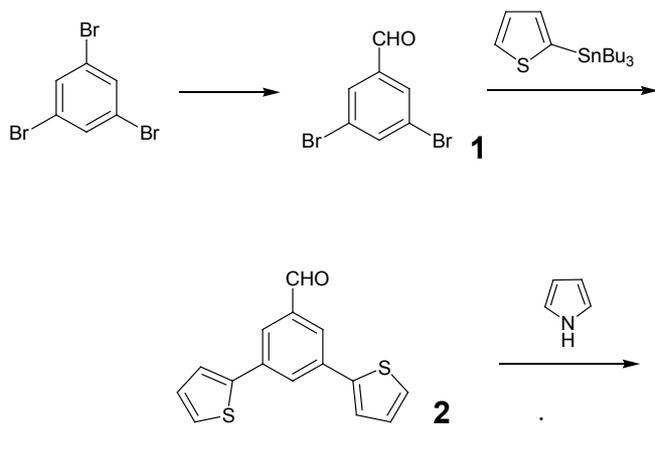


High surface area and microporosity are generated by a broad range of synthetic chemistries, including ethynyl trimerization; oxidative coupling; Friedel Crafts alkylation; condensation of anhydride, amine, hydroxyl, etc.

# Technical Accomplishment 1 - Improving $\Delta H_{ads}$ through POP Doped with Transition Metal

- Unsaturated transition metal/hydrogen interaction could form  $H_2 \cdot TM$  bond, leading to improved heat of adsorption ( $\Delta H_{ads}$ ) without dissociation (Kubas interaction)
- We successfully prepared polyporphyrin with high surface area and narrow pore size distribution with  $N_4$ -macrocyclic ring for metal coordination

## Synthetic Scheme for Preparing Polyporphyrin POPs

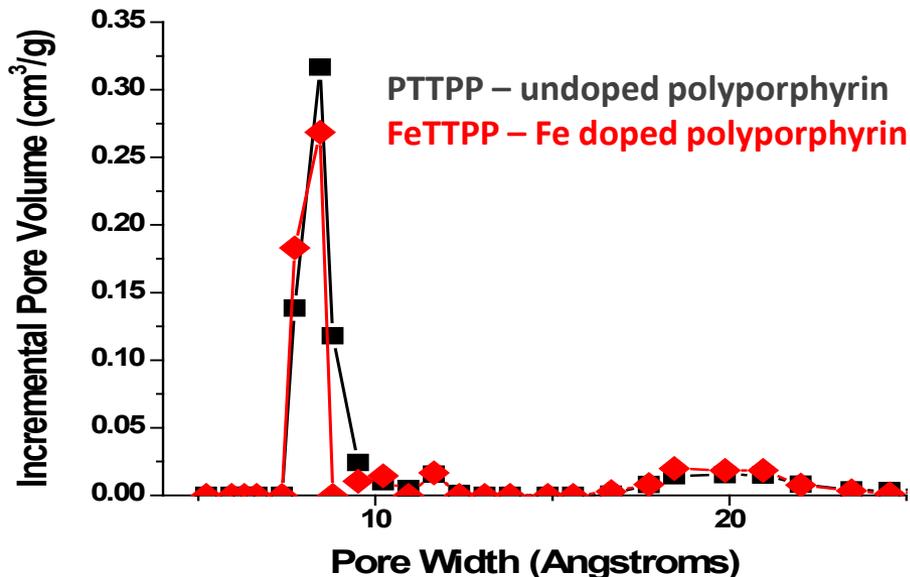
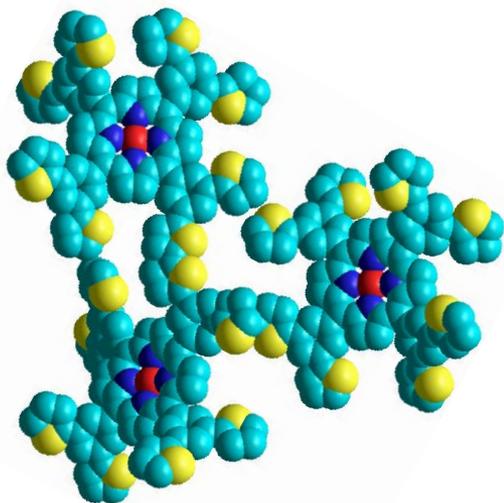


“Nanoporous Polyporphyrin as Adsorbent for Hydrogen Storage” J. Xia, S. Yuan, Z. Wang, S. Kirklin, B. Dorney, D.-J. Liu & L. Yu, *Macromolecules*. **43**, 3325–3330 (2010)

# Technical Accomplishment 1 - Improving $\Delta H_{ads}$ through POP Doped with Transition Metal

Significant surface area and micropore volume are created in 3D polyporphyrin...

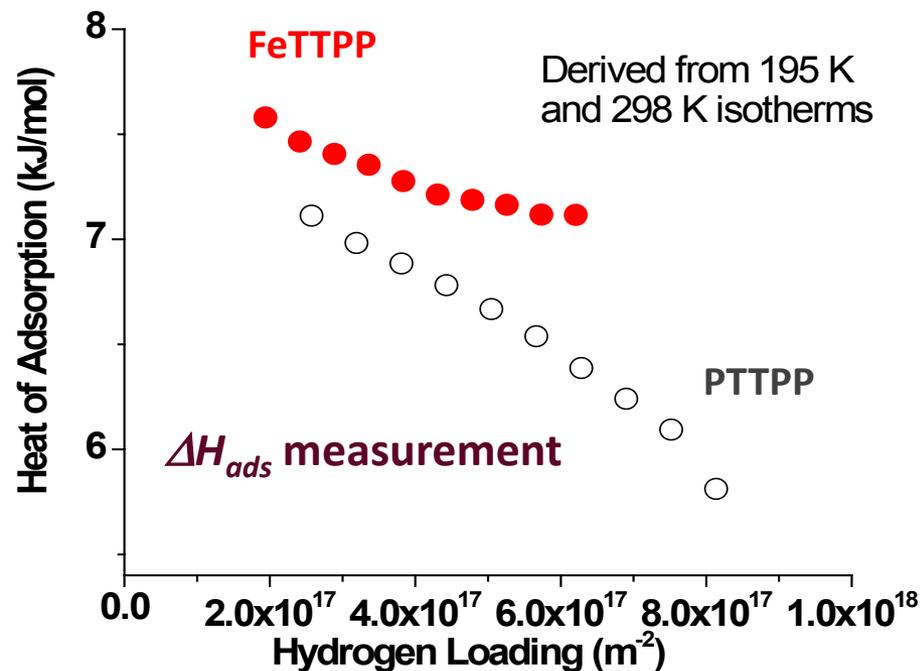
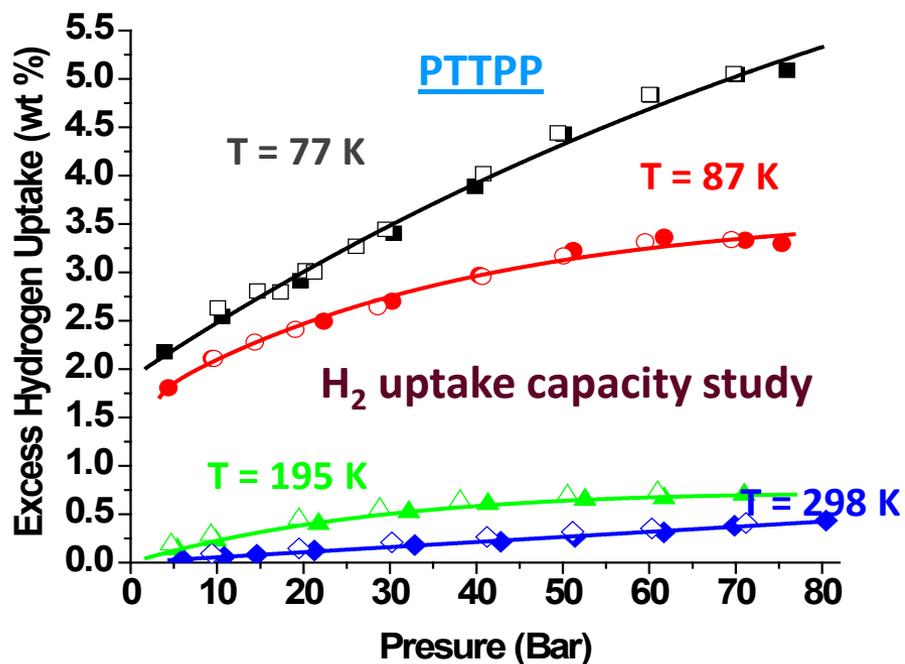
... metal doping leads to slightly reduction of surface area but little change in pore size.



	<i>BET SSA</i> ( $m^2/g$ )	<i>Langmuir</i> <i>SSA</i> ( $m^2/g$ )	<i>Total Pore</i> <i>Vol</i> ( $cm^3/g$ )	<i>Micropore</i> <i>Vol</i> ( $cm^3/g$ )	<i>Pore</i> <i>Diameter</i> ( $nm$ )	<i>Excess H<sub>2</sub></i> <i>Ads. @ 65</i> <i>bar &amp; 77 K</i>
PTTTPP	1522	2030	0.85	0.67	0.85	5.0%
<b>P(FeTTTPP)</b>	<b>1248</b>	<b>1665</b>	<b>0.68</b>	<b>0.54</b>	<b>0.82</b>	<b>4.6%</b>

# Technical Accomplishment 1 - Improving $\Delta H_{ads}$ through POP Doped with Transition Metal

- Fe doped polyporphyrin (FeTPP) shows marginal improvement of  $\Delta H_{ads}$  over undoped sorbent (PTTPP)
- $H_2$  uptake capacity exceeds the values predicted by “Chahine rule” by ~40%, suggesting “hidden” micropores in the polyporphyrins



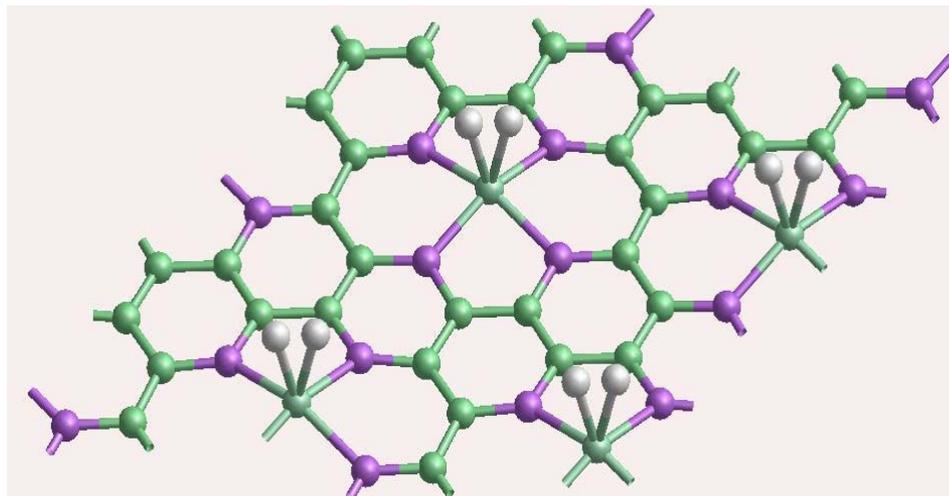
New polyporphyrin based POP can serve platform for exchanging different transition metals for systematic study of H-M interaction!

# Technical Accomplishment 1 - Improving $\Delta H_{ads}$ through POP Doped with Transition Metal

- Computational modeling efforts within HSCoE suggest enhanced  $\Delta H_{ads}$  can be achieved through doping of Ti, V, Ca, Mg, Zn, etc.

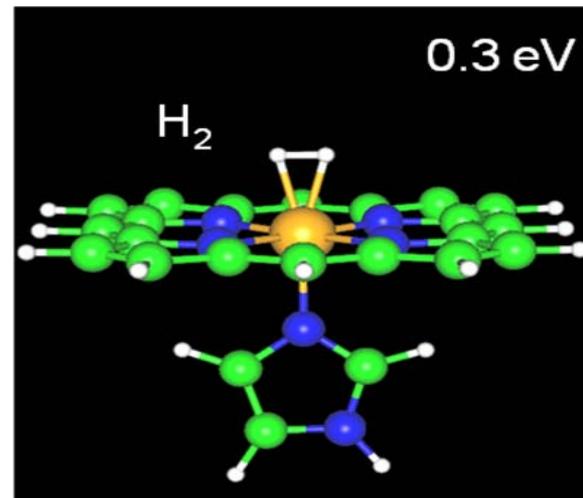
## v7 x v7 Metal-Decorated Graphene Model

*M. Yoon, et.al., HSCoE - ORNL*



## H<sub>2</sub>/HEME Model

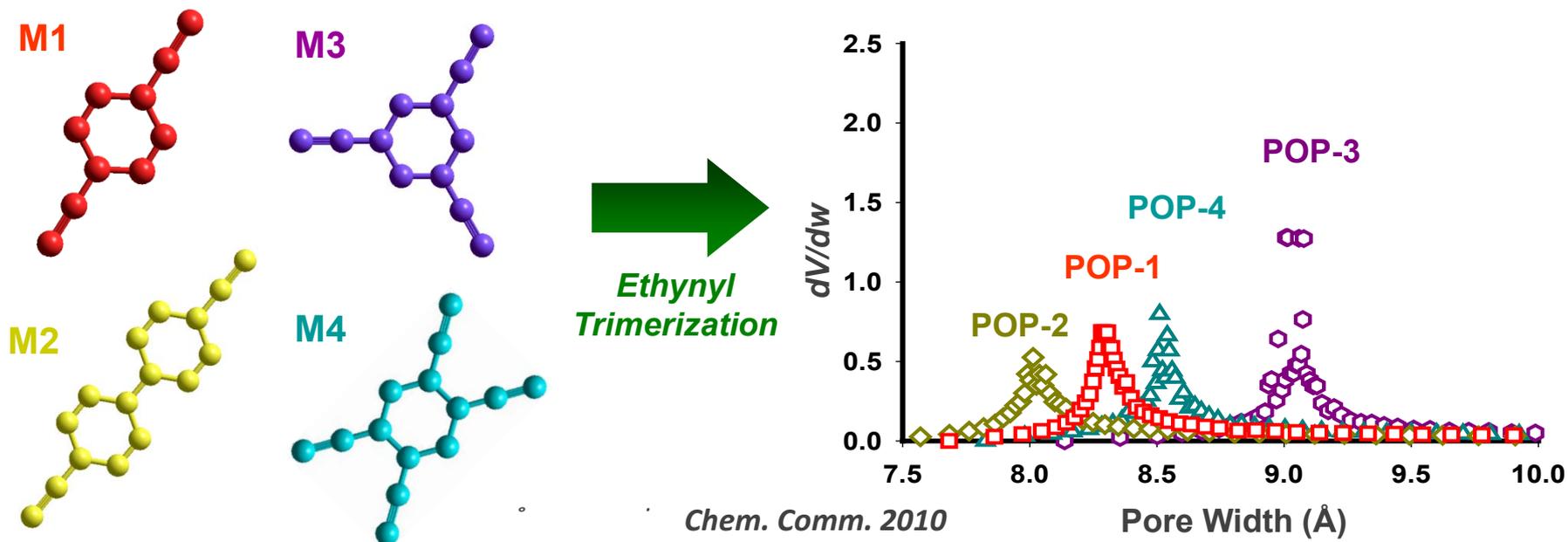
*Kim & Zhang, HSCoE - NREL/RPI*



We are developing new POP synthesis and post-treatment methods for better  $\Delta H_{ads}$  following the theoretical prediction.

# Technical Accomplishment 2 - Optimizing H<sub>2</sub> Sorption through Fine Tuning Nanopore Architecture of POP

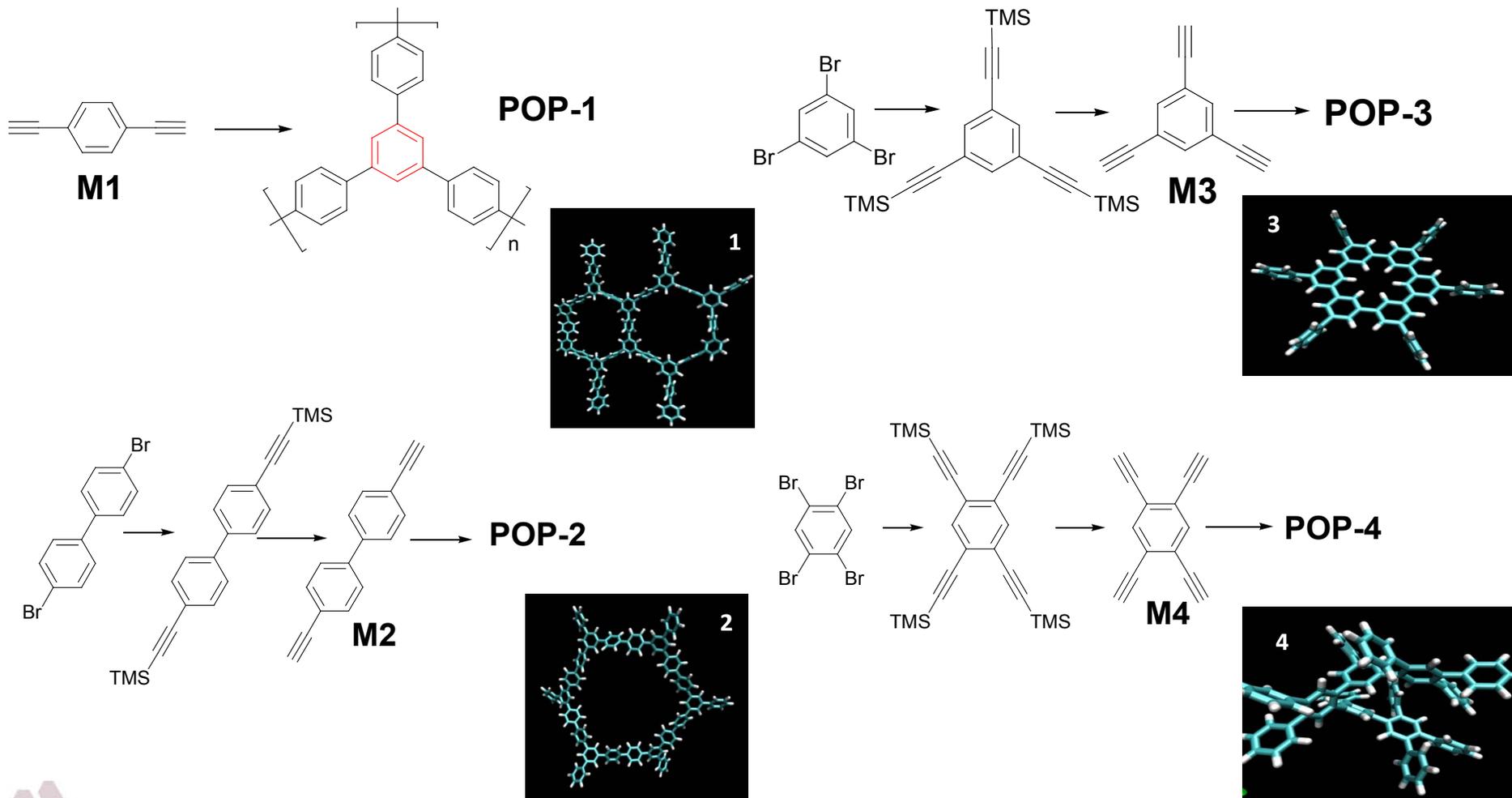
- Theoretical modeling suggests that hydrogen sorption is sensitive to pore size at nanometer range
- We developed a synthetic approach of producing POPs with high BET surface >1000 m<sup>2</sup>/g and tunable pore dimension (0.8 to 0.9 nm) for experimental demonstration



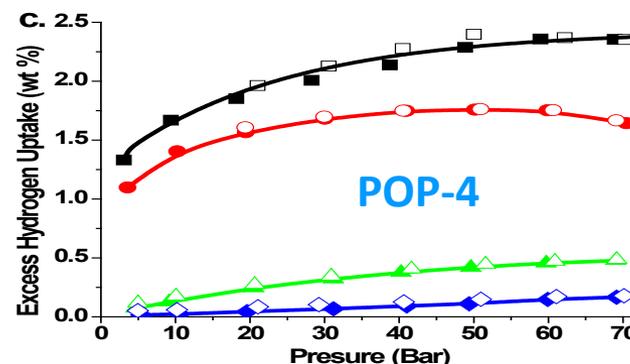
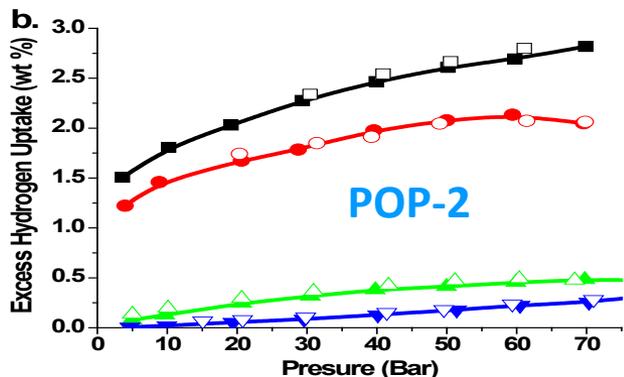
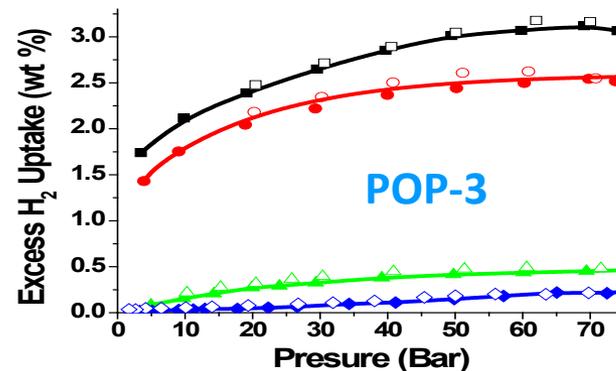
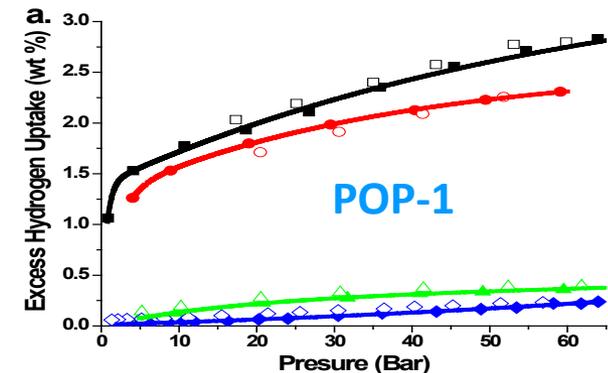
Simple aromatic POPs with similar BET surface areas but variable pore sizes were prepared through facile ethynyl trimerization reaction.

# Technical Accomplishment 2 - Optimizing H<sub>2</sub> Sorption through Fine Tuning Nanopore Architecture of POP

## Trimerization of aromatic monomer functionalized with different number of ethynyl groups



# Technical Accomplishment 2 - Optimizing H<sub>2</sub> Sorption through Fine Tuning Nanopore Architecture of POP



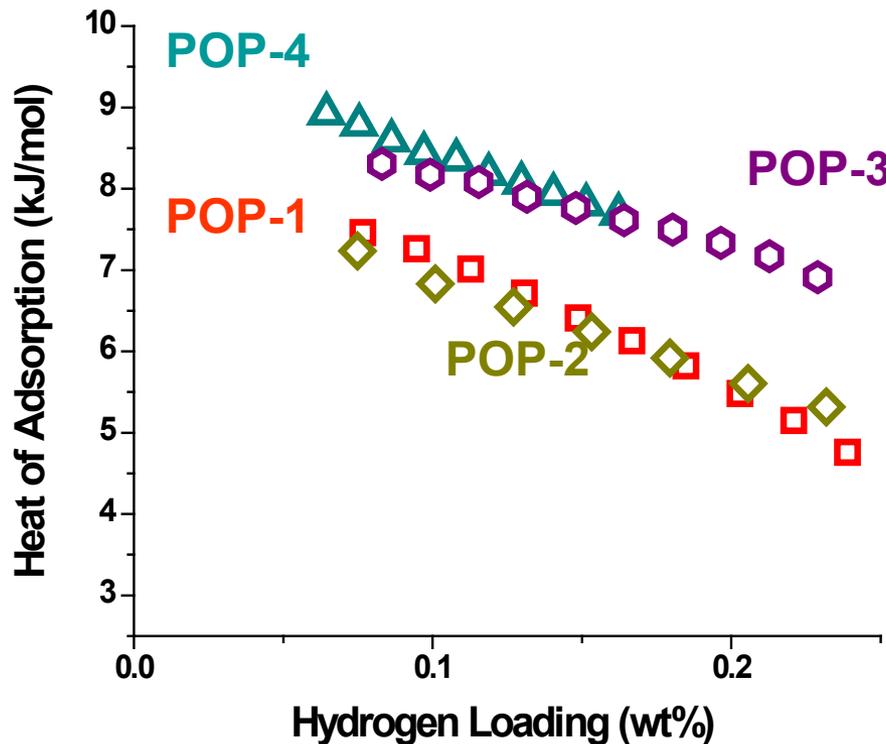
T = 77 K  
 T = 87 K  
 T = 195 K  
 T = 297 K

	BET Surface Area (M <sup>2</sup> /g)	DFT Pore Diameter (nm)	H <sub>2</sub> uptake@ 77 K (wt%)	H <sub>2</sub> uptake@ 87 K (wt%)	H <sub>2</sub> uptake @ 195 K (wt%)	H <sub>2</sub> uptake@ 298 K (wt%)
POP-1	1031	0.772	2.78	2.31	0.36	0.22
POP-2	1013	0.736	2.71	2.14	0.45	0.22
POP-3	1246	0.880	3.07	2.51	0.43	0.20
POP-4	1033	0.810	2.35	1.75	0.46	0.15



# Technical Accomplishment 2 - Optimizing H<sub>2</sub> Sorption through Fine Tuning Nanopore Architecture of POP

Experimental results indicate that  $\Delta H_{ads}$  is more sensitive to  $N_p$  than pore size

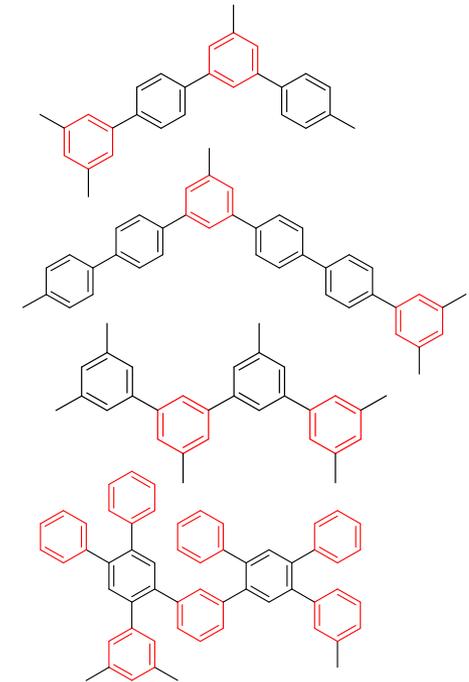


**POP-1**  
 $N_p = 2.5$

**POP-2**  
 $N_p = 2.3$

**POP-3**  
 $N_p = 3.0$

**POP-4**  
 $N_p = 3.5$



$N_p$  = Average # of phenylenes connected benzene in POPs

Our observation suggests that the chemical environment in confined space has higher impact on the H<sub>2</sub>-POP interaction than pore dimension.

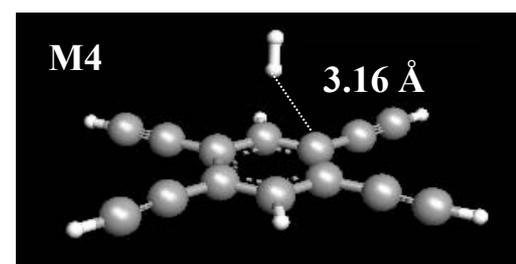
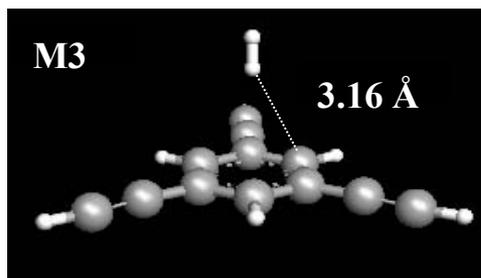
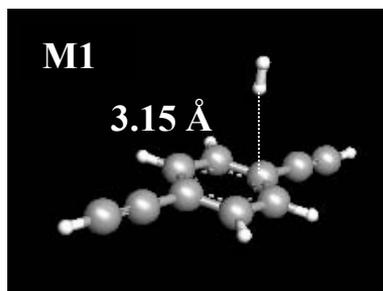
# Technical Accomplishment 2 - Optimizing H<sub>2</sub> Sorption through Fine Tuning Nanopore Architecture of POP

## Comparison of Experimental & Theoretical $\Delta H_{ads}$ (KJ/Mol)

	M1/POP-1 <i>N<sub>p</sub></i> = 2.3	M3/POP-3 <i>N<sub>p</sub></i> = 3	M4/POP-4 <i>N<sub>p</sub></i> = 3.5
Experimental	8.1	9.0	9.7
Single Layer Model	5.1	5.5	6.0
Double Layer Model	10.6	12.6	12.9

- MP2/6-311++G(2d,2p)//MP2/6-31+G\* level of theory.
- Average Binding Energy:  $E = n_2 * E_2 + n_3 * E_3 + n_4 * E_4$  *n<sub>x</sub>* is a fraction of rings with *x* coordination

## Computational simulation of H<sub>2</sub> adsorbed over M1, M3 and M4

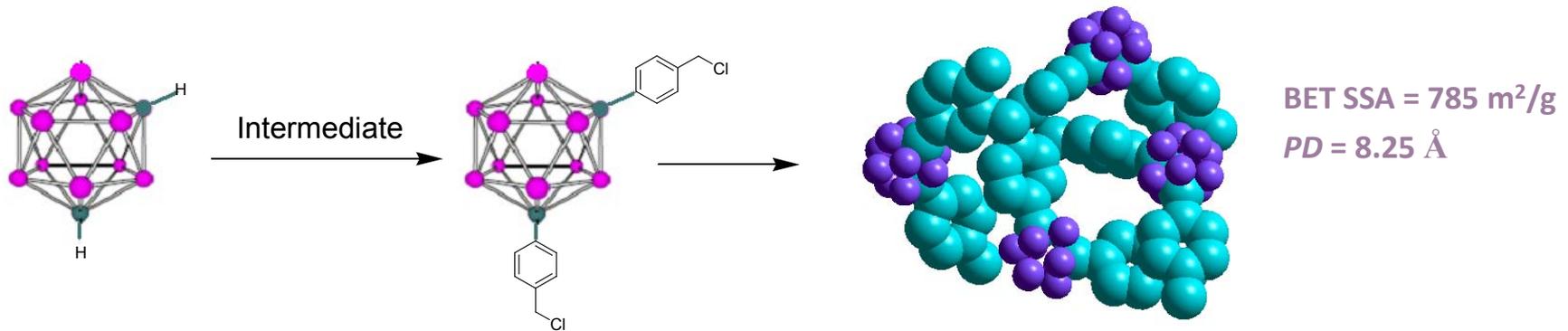


The dependence  $\Delta H_{ads}$  to monomer composition demonstrates the importance of improving hydrogen-POP binding by altering surface chemical composition!

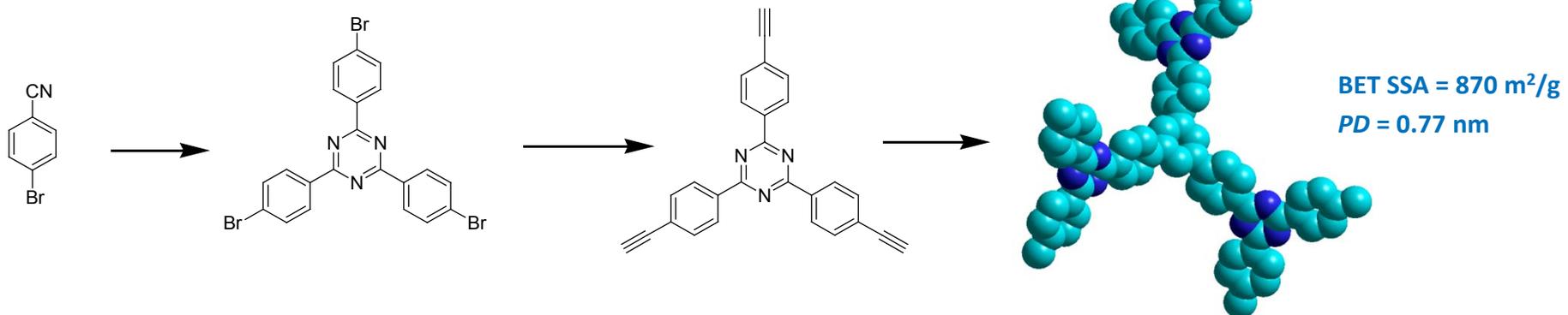
# Technical Accomplishment 3 - Improving H<sub>2</sub>/POP interaction via Other Synthetic & Post-treatment Methods

- Explored and successfully incorporated a variety of non-C elements (B, N, S, O...) into POPs to improve H<sub>2</sub> sorption energy while maintaining high surface areas and narrow pore diameters

## Example of integrating B into high BET surface POP

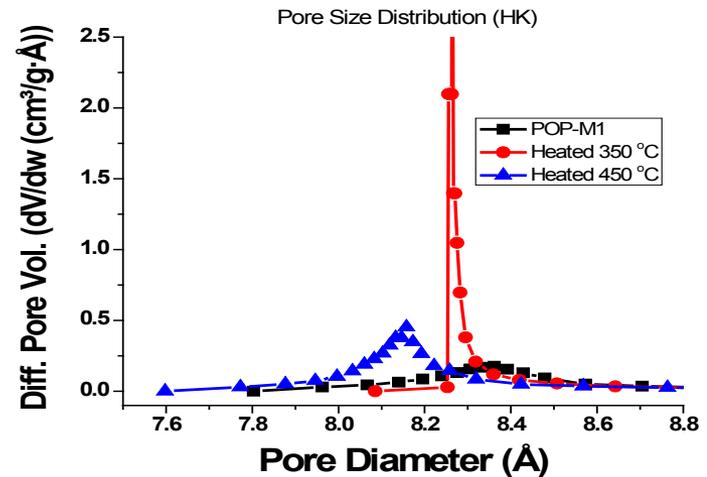
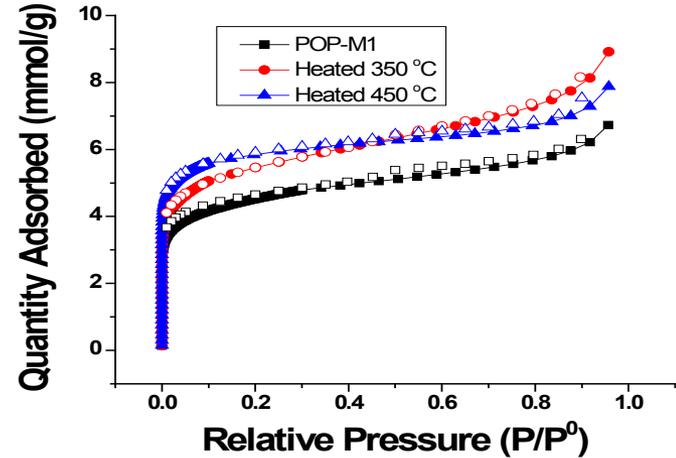
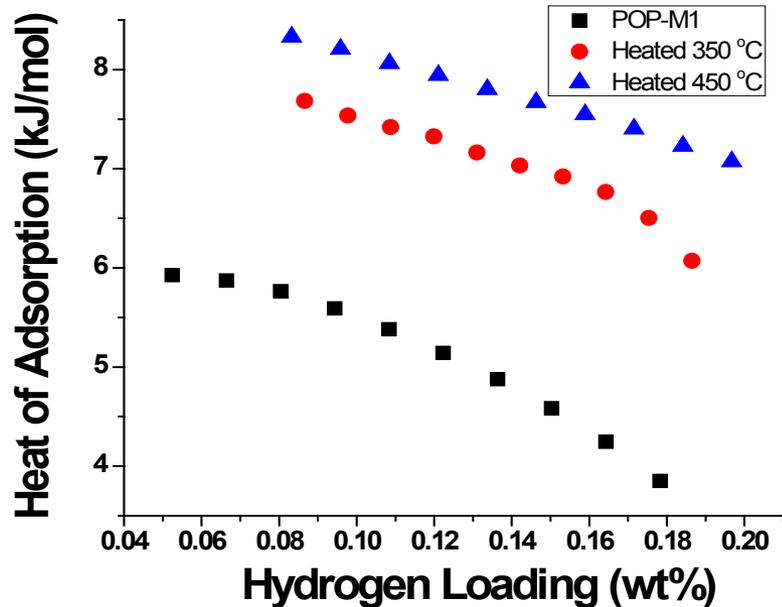
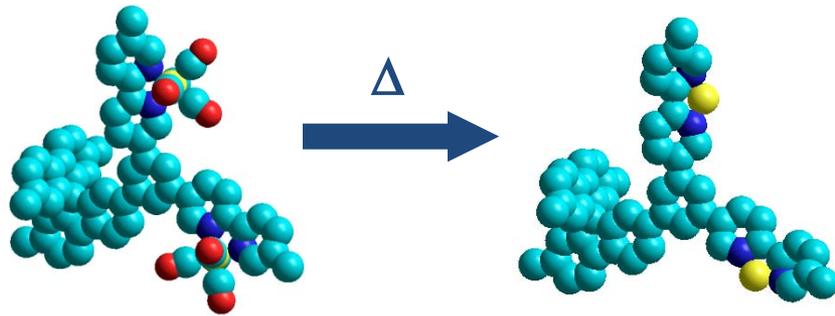


## Example of integrating N into high BET surface POP



# Technical Accomplishment 3 - Improving H<sub>2</sub>/POP interaction via Other Synthetic & Post-treatment Methods

- Thermal activation can be effectively used to expose atomically dispersed metal for improved interaction with hydrogen



# Collaboration

## Partnership within and outside of Hydrogen Sorption Center of Excellence

- Teaming between Argonne National Laboratory (prime) and The University of Chicago (subcontractor)
- Members of DOE HSCoE under the clusters of “Engineered Nanospace” (RC1) and “Substituted Materials” (RC2)
- Collaboration with UNC (HSCoE member) on  $^1\text{H}$  NMR experiment
- Collaboration with NREL (HSCoE member) on measurement validation
- Information exchange with ORNL (HSCoE member) and RPI on computational modeling and simulation
- Benchmark reference sample exchanges with Air Products (HSCoE members)
- Polyaniline sample exchange and analysis with University of Hawaii

## Technology Transfer through HSCoE

- Valuable inputs on our adsorption apparatus test validation
- New ideas and direction, examples include B and metal doped polymers
- Collaboration opportunities in polymer characterization, examples include NMR & neutron studies
- Up-to-date information on new developments in sorption based materials



# Future Work

## FY10

- Complete the design and synthesis of new B doped POP series and the investigation of surface structure as well as hydrogen storage capacity
- Complete the search for synthesis and activation methods for new transition metal doped POPs
- Complete surface property and hydrogen uptake studies on the metal doped POPs to further improve storage capacity/heat of adsorption
- Complete  $^1\text{H}$  NMR study on hydrogen-polymer surface interaction within subnanometer space using pore size tunable POPs (collaboration with UNC group)

**Go/No-go Decision (Draft): To demonstrate one or more POPs with excess gravimetric capacity  $\geq 6\%$  at 77K or  $\Delta H_{ads} \geq 12$  kJ/mol**

## FY11

- Complete further improve surface property, storage capacity and kinetics
- Downselect one or more high capacity POPs for volumetric capacity improvement through compression/pelletizing study
- Prepare final project report

# Summary

- Relevance:** Developing the nanostructured porous organic polymers (POPs) as H<sub>2</sub> storage media to meet DOE performance targets for transportation applications
- Approach:** Rational design and synthesis at the molecular level supported by computational modeling and advanced characterization
- Accomplishments:**
- Over 100 POPs were prepared since project inception with high BET surface (up to 1900 m<sup>2</sup>/g) and narrow pore sizes (7Å to 10Å) achieved.
  - H<sub>2</sub> uptakes up to 5.0% at 77K and 0.6% at RT were achieved.
  - Efforts in metal doping, pore size control and non-C elemental substitution to POPs showed promising passage to further enhance  $\Delta H_{ads}$  and capacity for ambient temperature storage
- Collaboration:** Argonne (prime) and U of Chicago (sub) partnering with HSCoE, information dissemination & experimental collaboration
- Future Work:**
- Continue to incorporate metal and non-C elements to POPs for better hydrogen uptake and heat of adsorption
  - Explore non-conventional activation and doping methods for major improvement in storage capacity and temperature
  - Identify new pathway for next generation POP-adsorbent with the combination in knowledge of rational design, computational modeling and advanced characterization



# Summary Table

## H<sub>2</sub> storage capacities for selected POPs developed by Argonne – U of Chicago Team in FY2010

Sample	Gr. Uptake (77K, 40 bars) (kg H <sub>2</sub> /kg adsorbent+H <sub>2</sub> <sub>ads</sub> )	Vol. Uptake <sup>a</sup> (77K, 40 bars) (kg H <sub>2</sub> /L adsorbent)	Gr. Uptake (RT, 70 bars) (kg H <sub>2</sub> /kg adsorbent+H <sub>2</sub> <sub>ads</sub> )	Vol. Uptake <sup>a</sup> (RT, 70 bars) (kg H <sub>2</sub> /L adsorbent)	$\Delta H_{ads}$ (kJ/mol)
POP-1	2.8	0.024	0.22	0.0019	8.1
POP-2	2.7	0.026	0.22	0.0021	7.9
POP-3	3.1	0.027	0.20	0.0018	9.0
POP-4	2.4	0.021	0.15	0.0013	9.7
PTTPP	5.0	0.019	0.45	0.0017	7.5
P(FeTTTPP)	4.6	0.022	0.30	0.0014	8.0

- a. Volumetric capacity is calculated based on the packing density of polymer powders after compression under medium pressure.

# Additional Slides



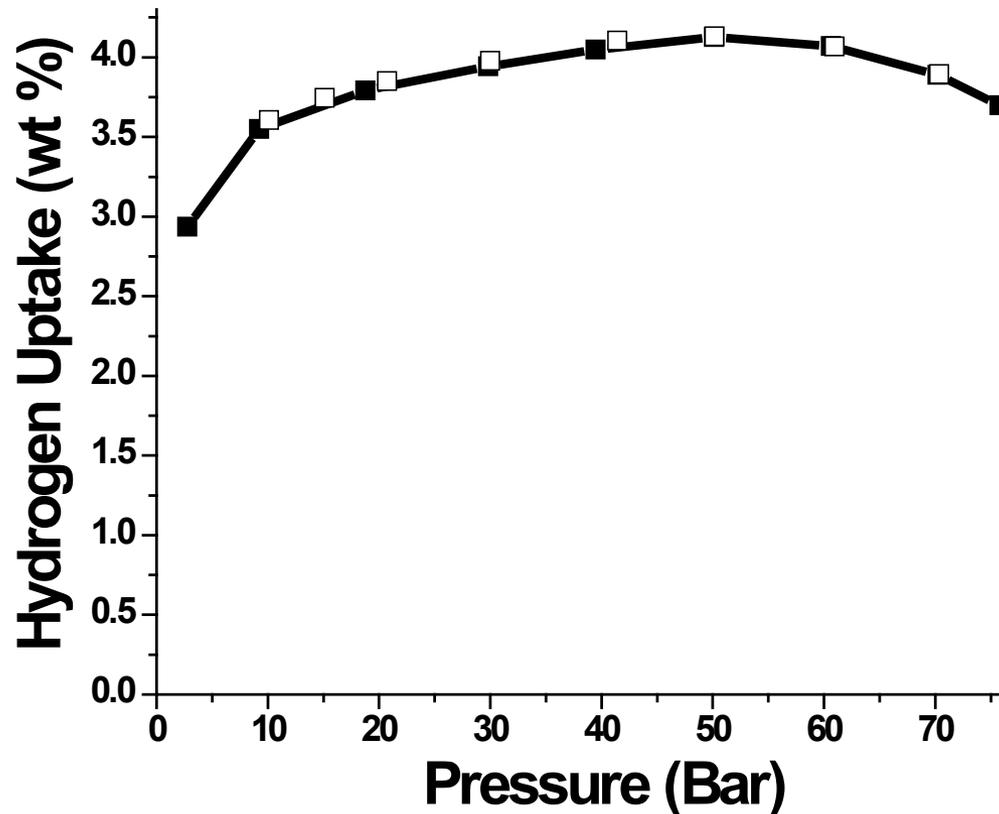
# Supplemental Information - Some Noteworthy Published Reports in Polymeric Hydrogen Storage Materials

- “Targeted Synthesis of a Porous Aromatic Framework with High Stability and Exceptionally High Surface Area” T. Ben, *et. al. Angew. Chem. Int. Ed.* 2009, 48, 9457 –9460.
  - The report demonstrates that very high surface area (Langmuir surface area of 7100 m<sup>2</sup>/g) has been achieved using simple tetraphenyl methane as the contorted core. Corresponding hydrogen adsorption at 48 bar and 77 K was 10.7 wt%
- “Lithium-Doped Conjugated Microporous Polymers for Reversible Hydrogen Storage” An Li, *et. al. Angew. Chem. Int. Ed.* 2010, 49, 1 – 5.
  - Conjugated microporous polymers prepared by polymerizing with 1,3,5-triethynylbenzene, followed by doping with Li. The hydrogen storage amount reaches up to 6.1 wt% at 1 bar and 77 K.

**Both papers are reported by the reputable research institutions in China (one with NIST collaboration) using similar polymer chemistry that we applied. We plan to repeat some of the experiments.**



## Supplemental Information - Our Laboratory Adsorption Isotherm Calibration using Reference Material (AX21)



Hydrogen uptake isotherms over at AX-21 at 77 K, sample weight: 0.3225 g