Virginia Commonwealth University

SISGR: Design and Synthesis of Chemically and Electronically Tunable Nanoporous Organic Polymers for Use in Hydrogen Storage Applications

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Richmond VA, USA

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Project ID#: BES004

Overview

Time Line

- Start date: Sept. 15th, 2009
- End date: Sept. 14th, 2012
- 85% complete

Barriers

- Low H_2 Binding Affinity
- Low Gravimetric and Volumetric Capacity
- Low Chemical Stability

Budget

- Total Project Funding:
  - DOE BES: 570 K
  - Funding received in 2012: 190 K

Collaborating Partner

Prof. Puru Jena

Department of Physics

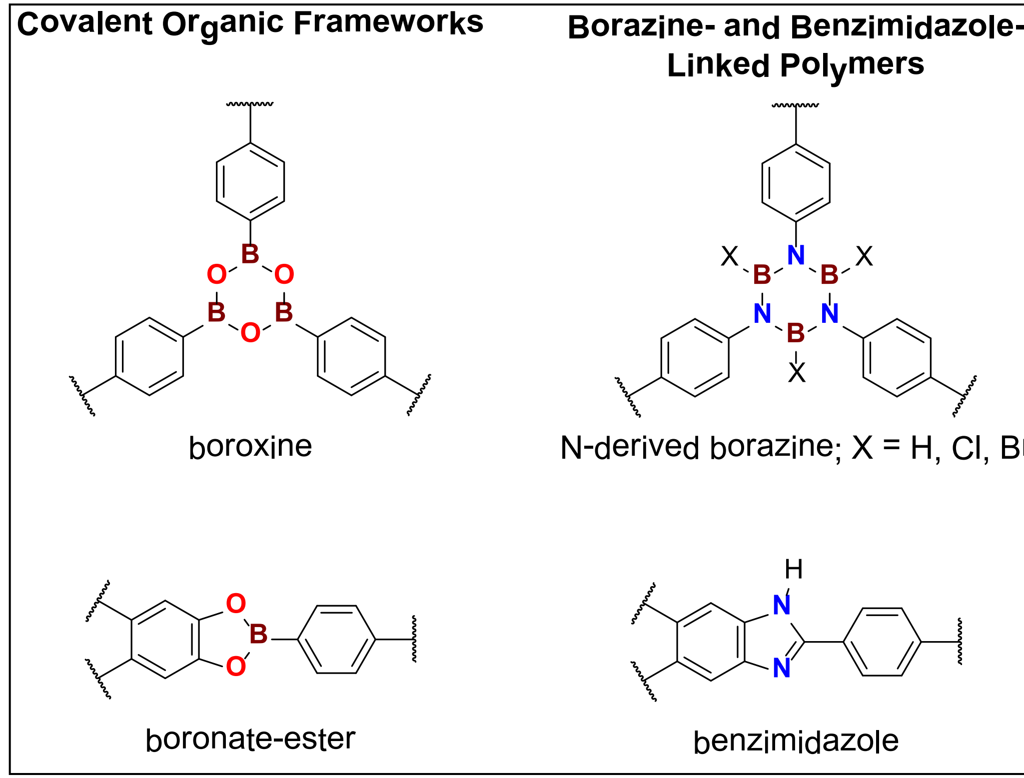
VCU

Objectives

- Design new low density and highly porous organic polymers
- Develop new synthetic routes for pore functionalization
- Incorporate polarizable building units into polymers
- Enhance hydrogen storage by a simultaneous physisorption and chemisorption approach
- Develop physicochemically stable polymers to allow for post-synthesis modification
- Evaluate hydrogen storage capacity under low and high pressure settings

Approach: Pore Functionalization of Porous Polymers

- Replace boroxine by borazine rings
- Use substituents on boron to decorate pores
- Replace boronate-ester connectivity with imidazole
- Create amphoteric sites for gas interaction
- Probe gas binding sites using DFT studies

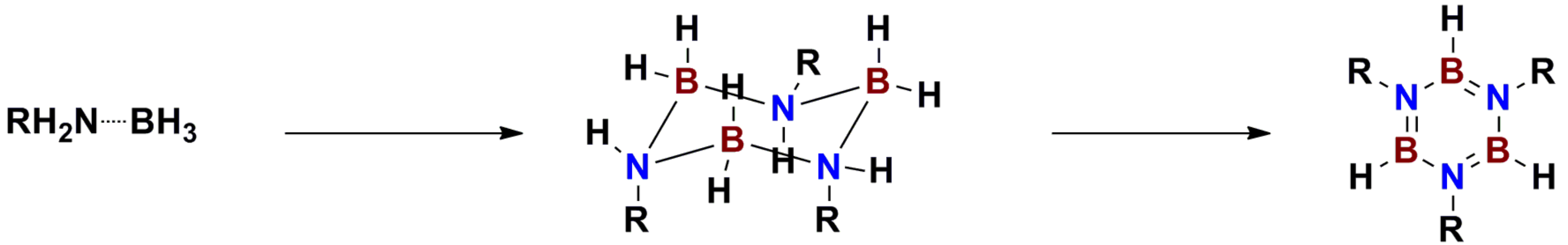


Science **2005**, 310, 1166
Science **2007** 316, 268

Polym. Chem. **2011**, 2, 2775
J. Mater. Chem. **2011**, 21, 10629
Chem. Mater., **2011**, *23*, 1650
Chem. Commun. **2012**, *48*, 1141
Chem. Mater., **2012** (ASAP)

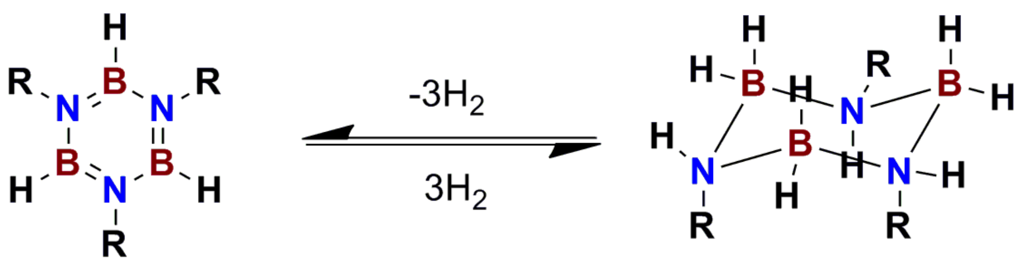
Chemical Hydrogen Storage by Molecular Borazine

Borazine formation from Amine-Borane Adduct (AB)

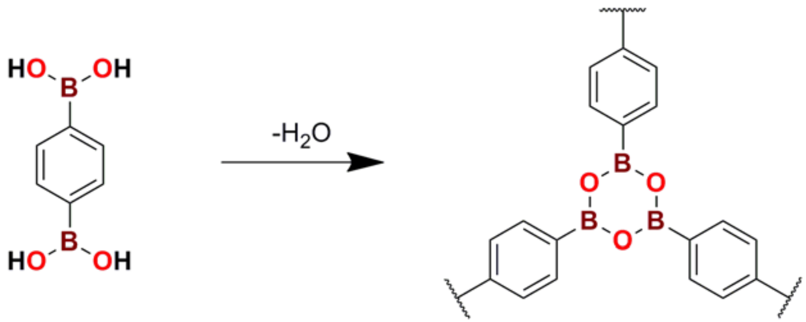


Amine-Borane Borazane Borazine

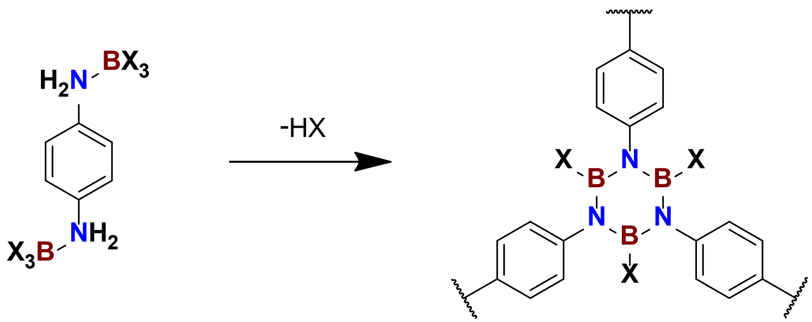
Reversible hydrogenation of borazine to borazane



Synthetic Routes for Pore-Decorated BLPs

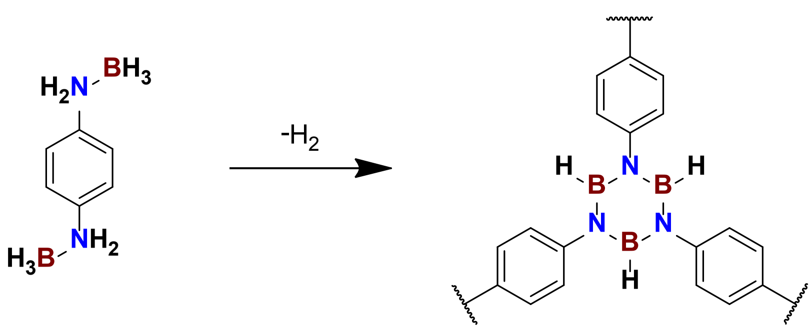


Cote, A. P. et al, *Science* **2005**, 310, 1166



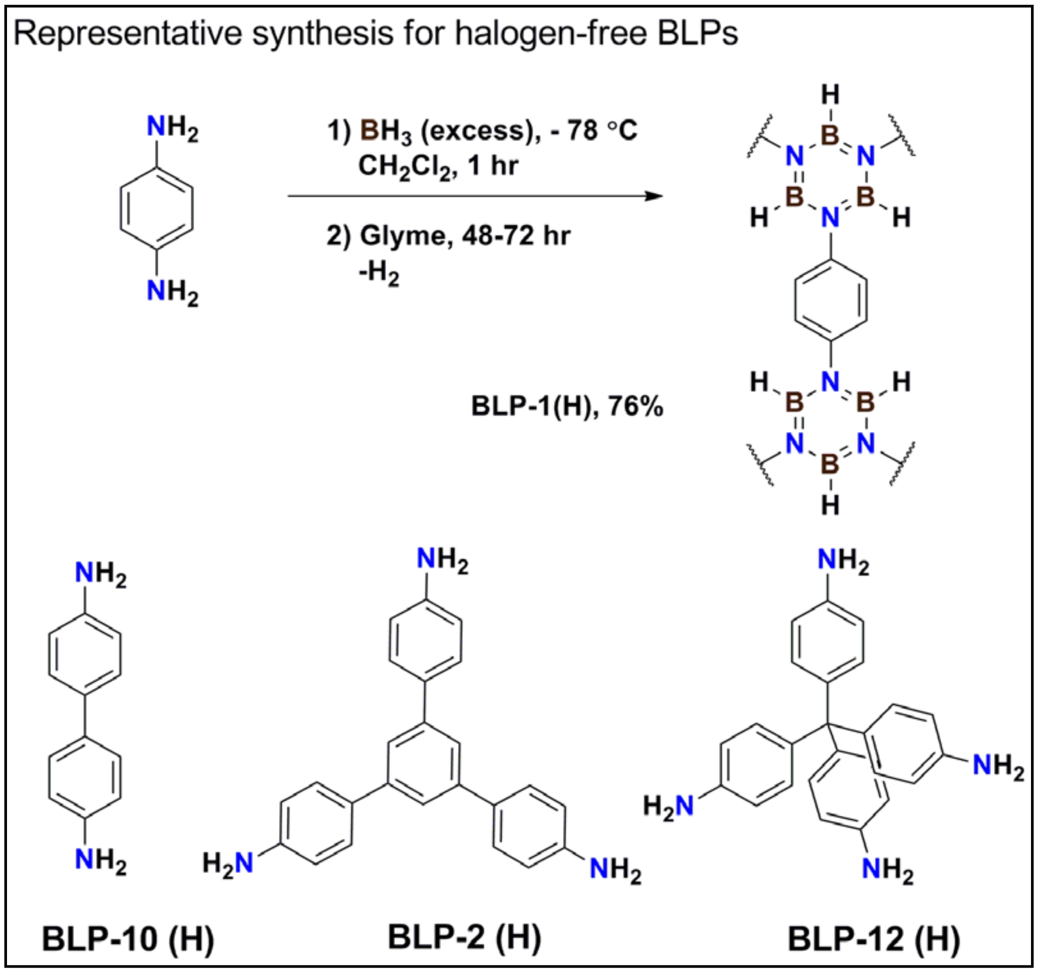
X=Cl or Br

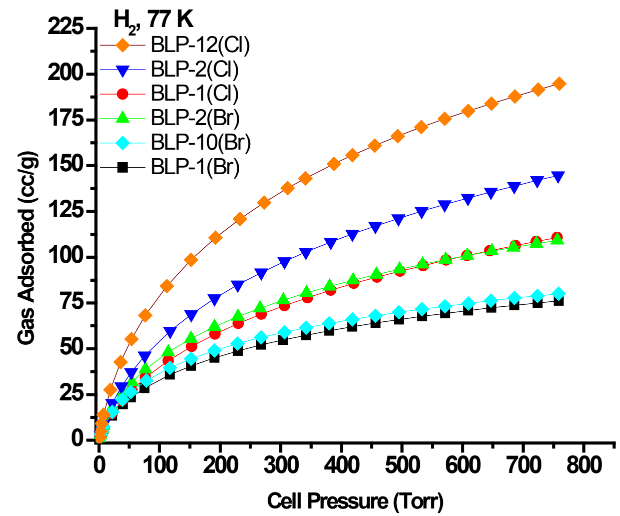
Reich, T. R. et al, *J. Mater. Chem.* **2011**, 21, 10629

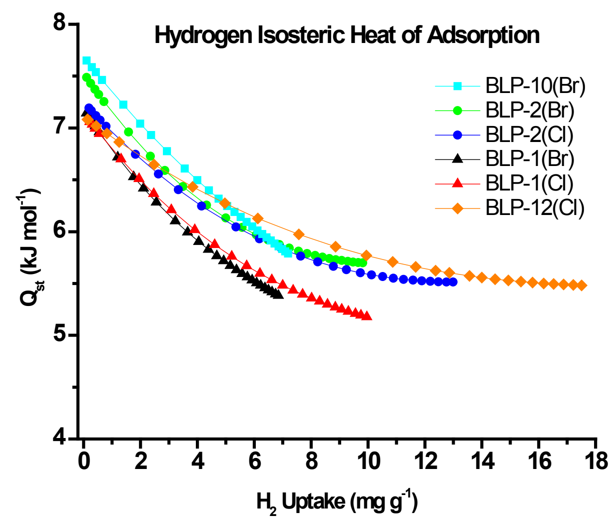


Jackson, K. T. et al. *Polym. Chem.* **2011**, 2, 2775

Synthetic Route for Pore-Decorated BLPs





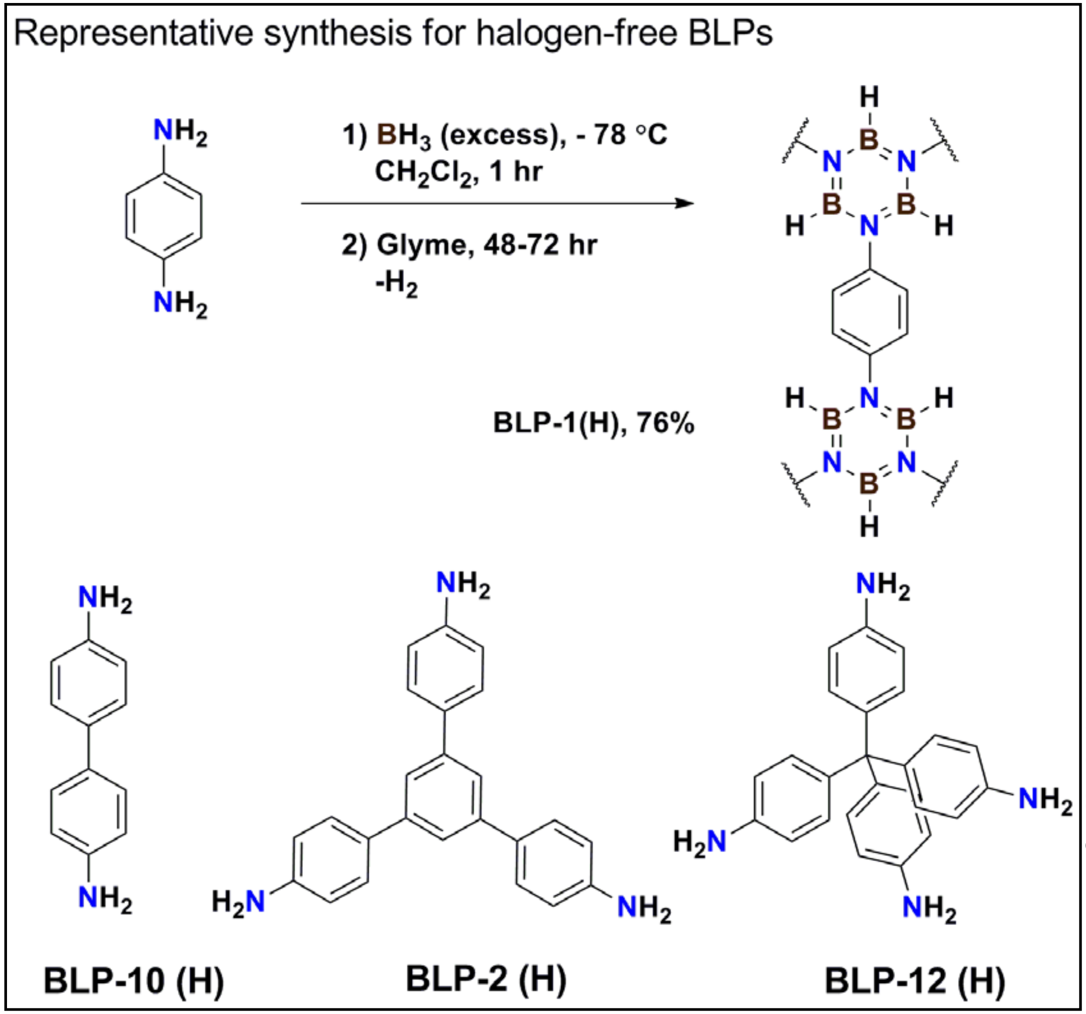


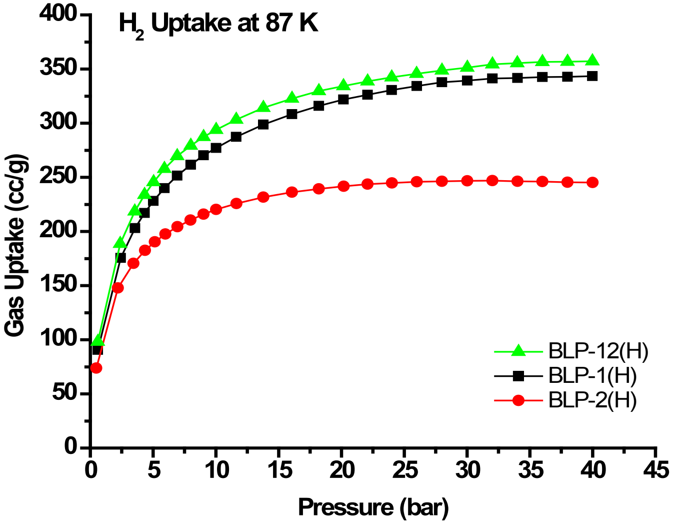
Hydrogen Storage by Halogen-Decorated BLPs

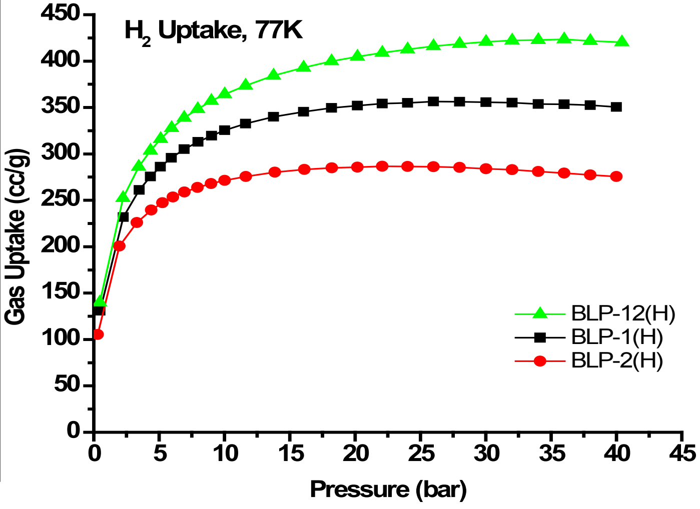
Polymer	SA_{Lang} (m^2/g)	P_{vol} (cm^3/g)	PSD (nm)	H_2, 77 K , 1 bar (wt%)	Q_{st} (kJ/mol)
BLP-1(Cl)	1828	0.746	1.33	1.00	7.06
BLP-1(Br)	730	0.303	1.27	0.68	7.14
BLP-2(Cl)	1699	0.649	1.27	1.30	7.19
BLP-2(Br)	1221	0.571	1.27	0.98	7.49
BLP-10(Br)	755	0.321	1.06	0.72	7.65
BLP-12(Cl)	2091	0.853	1.13	1.75	7.08

J. Mater. Chem. **2011**, 21, 10629

Hydrogen Storage at High Pressure





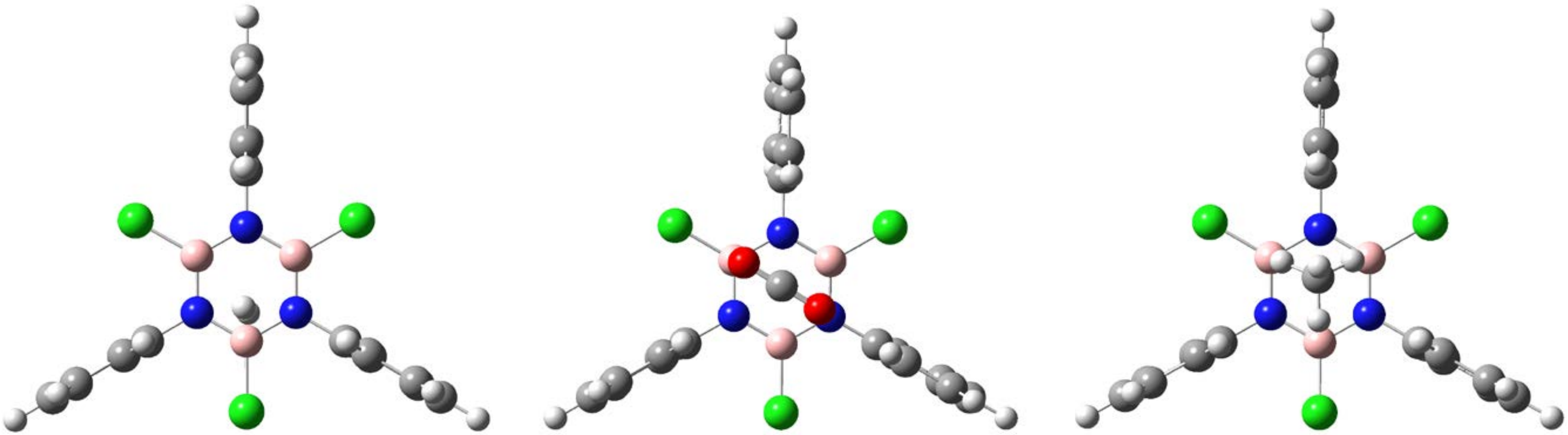


Hydrogen Storage by Halogen-Free BLPs

	SA_{BET} (m^2/g)	$V_{p,}$ (cm^3/g)	H_2 Qst (kJ/mol)	H_2 Uptake (cm^3/g), 1 bar
BLP-1(H)	1360	0.69	6.8	148
BLP-12(H)	2240	1.08	6.8	215
COF-1	750	0.30	6.2	135
COF-6	750	0.32	7.0	140
COF-102	3620	1.55	3.9	138
COF-103	3530	1.54	4.4	142

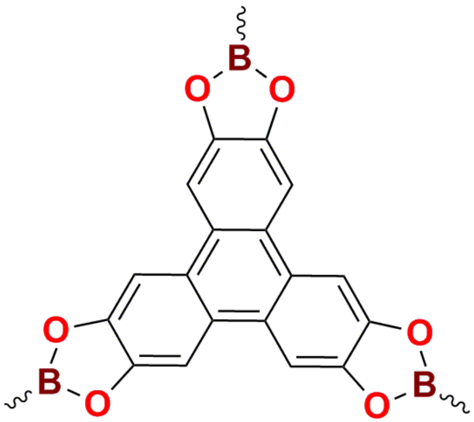
Polym. Chem. **2011**, 2, 2775

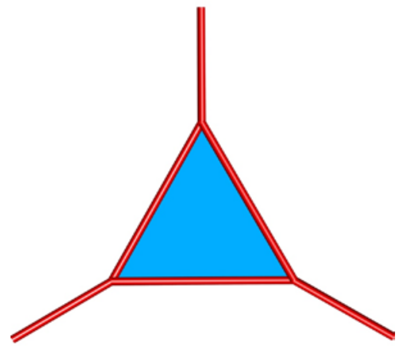
Small Gas Binding Site and Affinity: DFT Studies

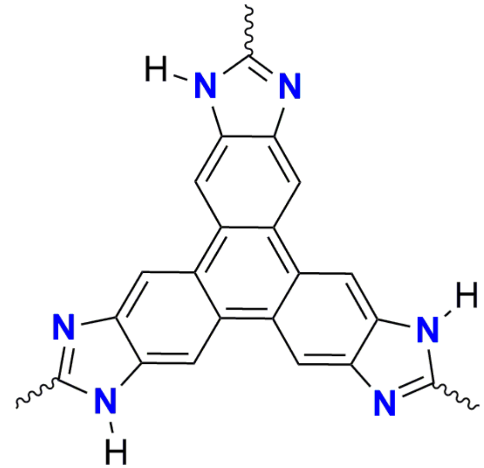


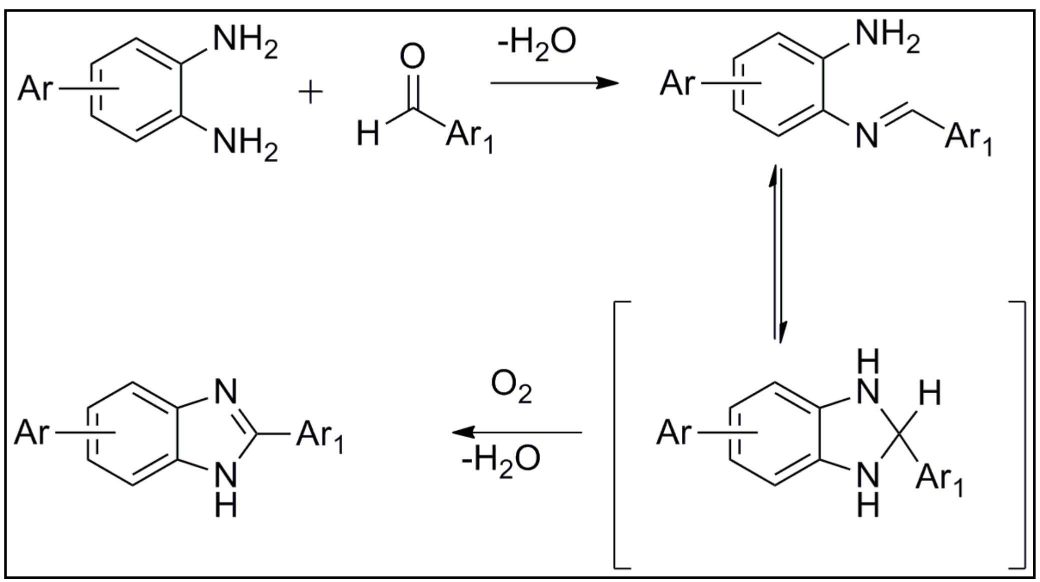
Clusters	Expt (kJ/mol)	B3LYP/6-311+G* (kJ/mol)	M06/6-311+G* (kJ/mol)	SVWN/6-311+G* (kJ/mol)
CB-H_2	7.46	-2.33	9.05	10.39
CB-CO_2	28.28	--	15.46	25.95
CB-CH_4	20.2	-0.22	20.22	20.30

Benzimidazole-Linked Polymers (BILPs)





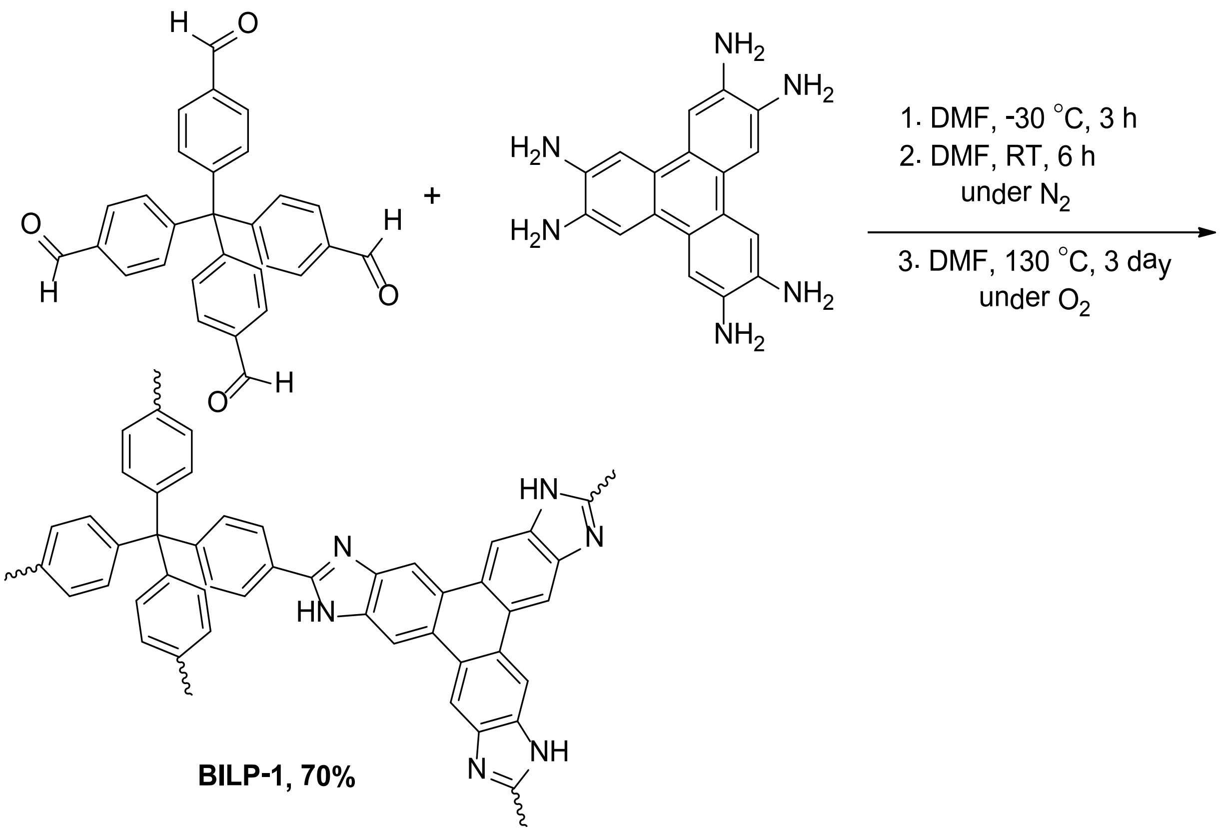


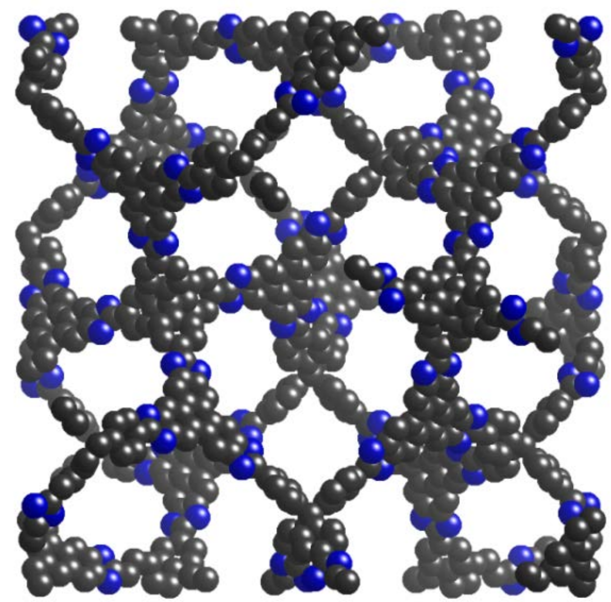


Macromolecules **1983**, *16*, 128–136

- High thermal and chemical stability
- Versatile synthetic routes
- Amphoteric nature
- Multiple binding sites

Template-Free Synthesis of BILPs

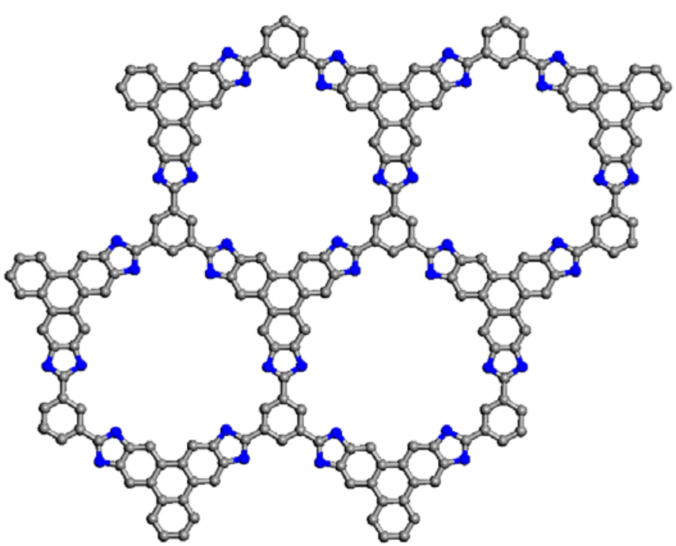


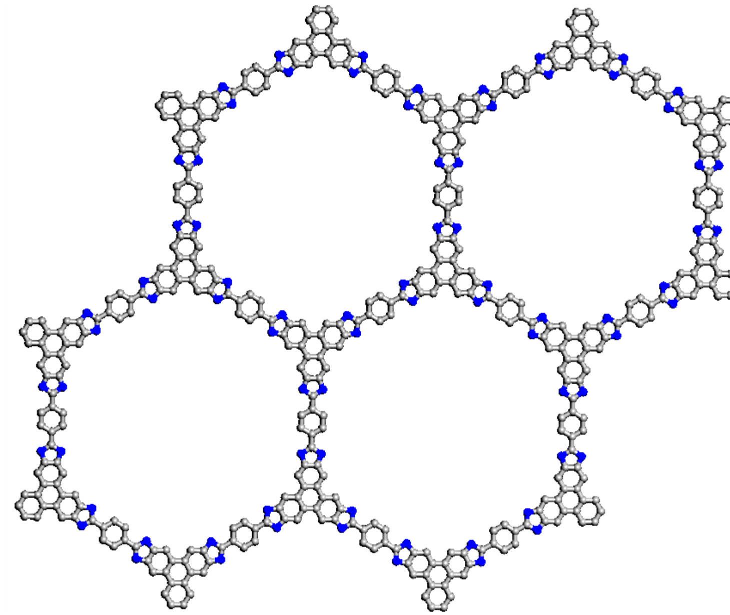


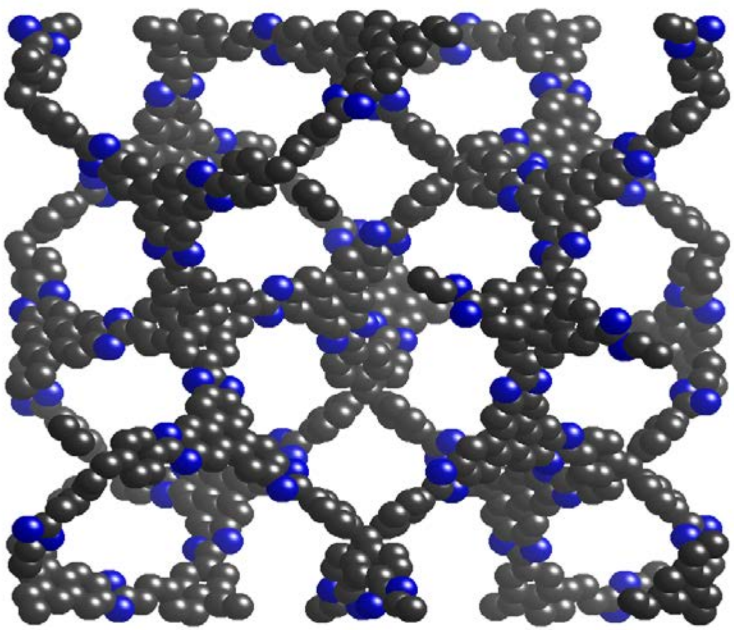
SA_{BET} = 1172 m^2 g^{-1}

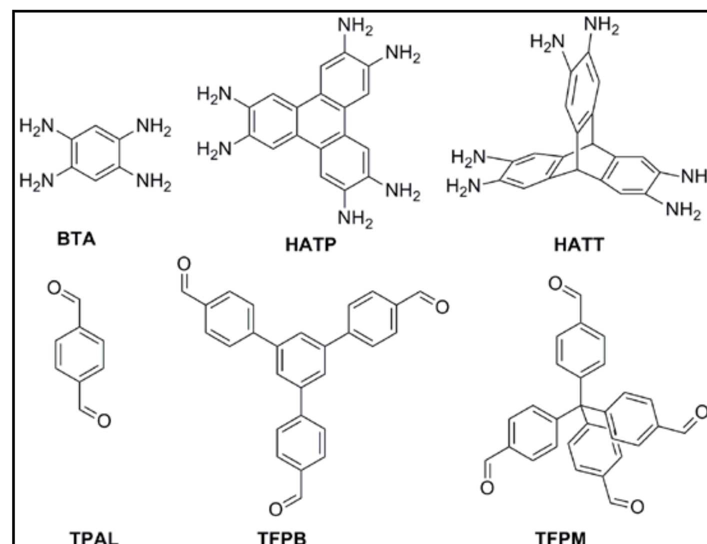
Rabbani, M. G.; El-Kaderi, H. M. *Chem. Mater.,* **2011,** *23*, 1650–1653

Predicted Network Topologies

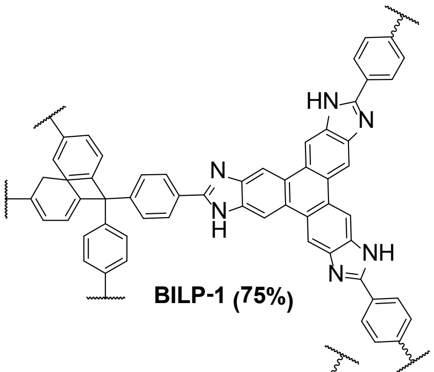




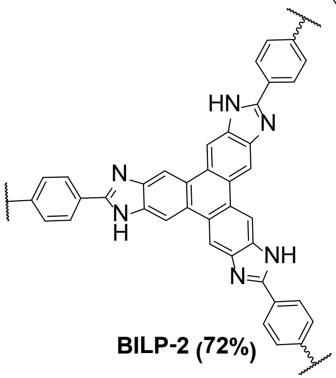




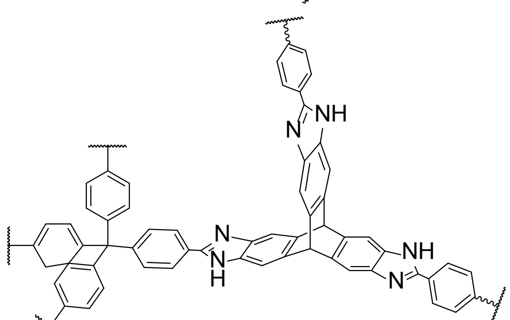
Benzimidazole-Linked Polymers



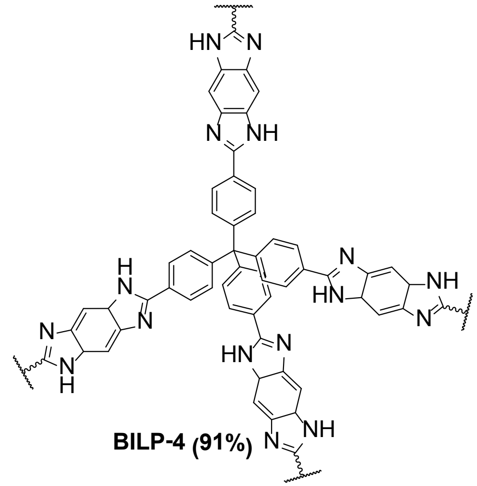
BILP-1 (75%)



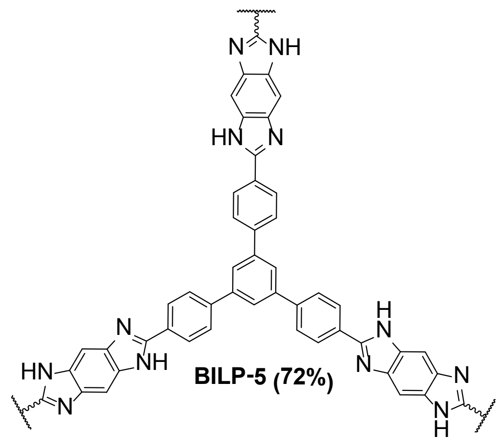
BILP-2 (72%)



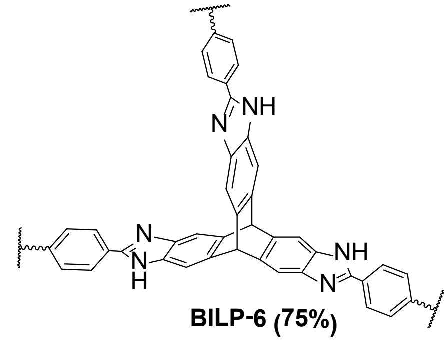
BILP-3 (77%)



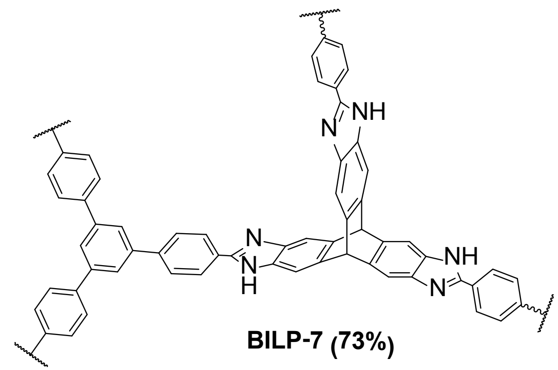
BILP-4 (91%)



BILP-5 (72%)



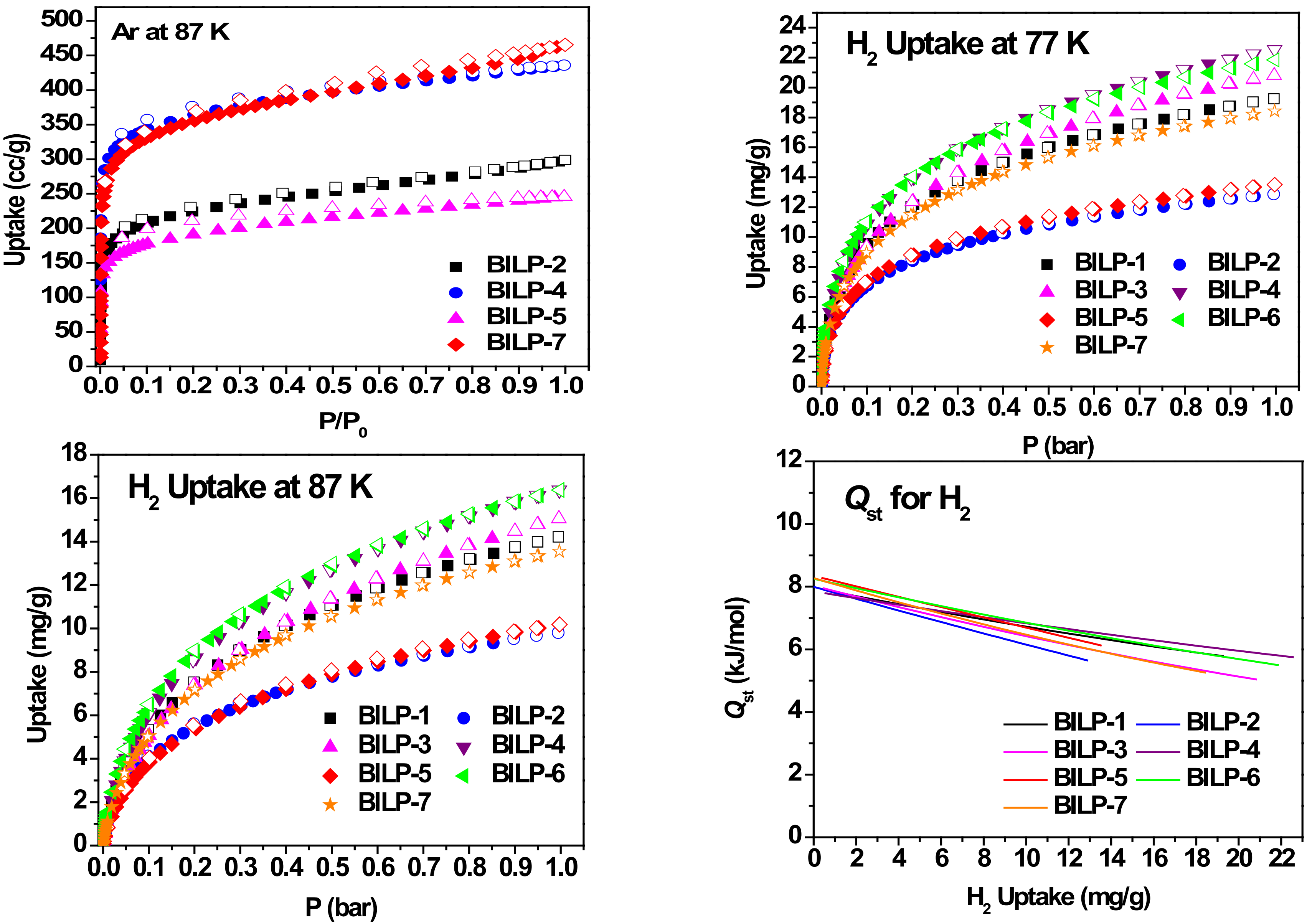
BILP-6 (75%)



BILP-7 (73%)

Rabbani, M. G.; El-Kaderi, H. M. *Chem. Mater.*, **2012** (ASAP)

Hydrogen Storage at Low Pressure

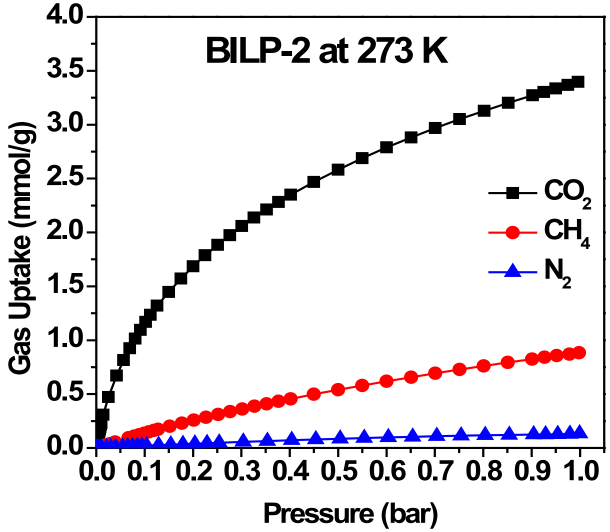


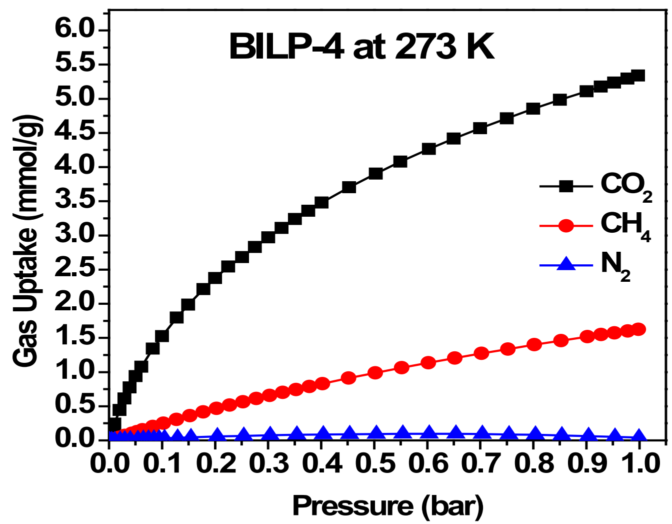
Hydrogen Storage at Low Pressure

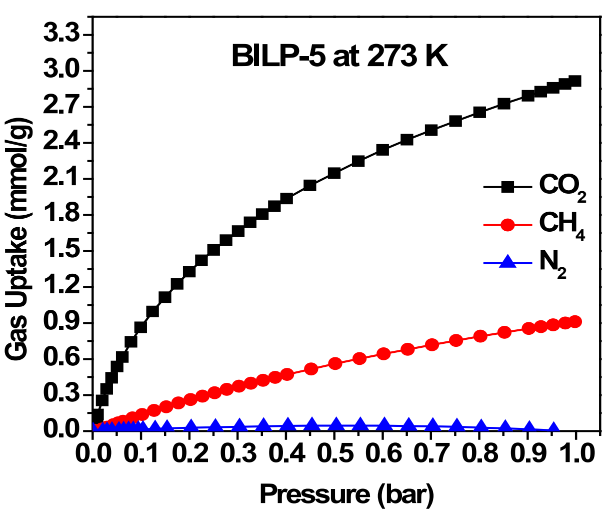
Polymer	SA ($m^2\ g^{-1}$) BET	SA ($m^2\ g^{-1}$) Langmuir	Pore Size Å	Pore Volume $cm^3\ g^{-1}$	H_2 uptake (wt. %) 77 K	H_2 uptake (wt. %) 87 K	Q_{st} kJ mol^{-1}
BILP-1	1172	1563	6.8	0.70	1.9	1.4	7.9
BILP-2	708	942	6.8	0.49	1.3	1.0	8.0
BILP-3	1306	1715	7.2	0.65	2.1	1.5	8.0
BILP-4	1135	1486	6.8	0.65	2.3	1.6	7.8
BILP-5	599	799	6.8	0.36	1.4	1.0	8.3
BILP-6	1261	1654	6.2	0.66	2.2	1.6	8.2
BILP-7	1122	1489	6.8	0.74	1.8	1.4	8.3

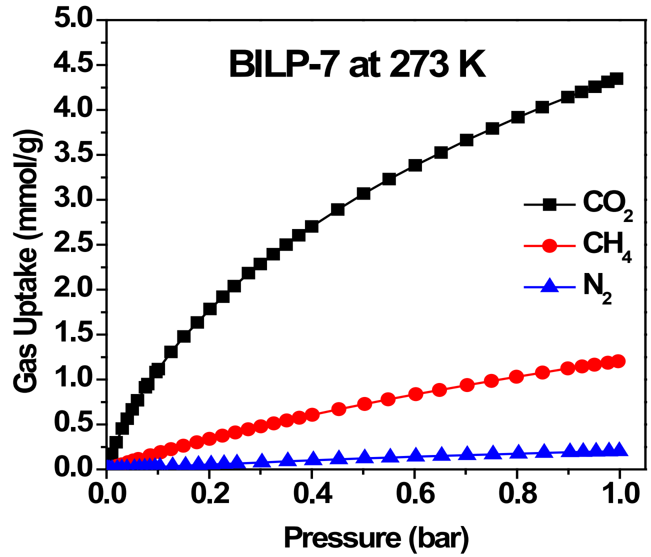
- H_2 uptakes are among the highest by porous organic polymers
- High H_2 binding affinities and narrow pore size distribution (6.2-7.2 Å)
- Higher pore volume and surface area would be required to enhance uptake under high pressure settings

Other Related Applications: CO_2 Capture









Accomplishments

- Developed new methods to design low density highly porous and B-rich organic polymers
- Polymers have high thermal and chemical stability
- BLPs can store 4.25 wt.% of hydrogen at 40 bar / 77 K
- Computational studies indicated that H_2 molecules interact with boron sites with ~10 kJ mol^{-1}
- Pore functionalization is instrumental in gas storage and separation applications
- BILPs can store up to 2.4 wt.% at 1 bar / 77 K
- The amphoteric nature of imidazoles is expected to facilitate metal nanocluster impregnation
- Other potential applications include heterogeneous catalysis, hydrogen purification, and CO_2 capture

Proposed Future Work

- Develop novel methods to crystallize and enhance the porosity of halogen-free BLPs
- Develop borazine-rich polymers and investigate their use in chemical and physical hydrogen storage
- Use metal-doped BLPs and assess their potential in hydrogen spill-over studies
- Use post-synthesis modification to enhance hydrogen storage in benzimidazole-linked polymers
- Develop new synthetic routes to enahce BILPs' porosity by controlling the kinetics of C-N bond formation.
- Increase nitrogen content in BILPs' backbone

Summary

- **Relevance:** Developed novel polymers to address the DOE 2015 on-board hydrogen storage targets (volumetric density: 40 g L^{-1}; gravimetric density: 5.5 wt%)
- **Approach:** Developed porous borazine and imidazole rich polymers that facilitate strong dihydrogen binding and are capable of storing hydrogen by chemical means
- **Collaboration:** Used computational studies (Prof. Jena, Physics Department at VCU) to determine the hydrogen-borazine interaction sites and predicted the binding affinity of hydrogen
- **Technical accomplishments and progress:** Developed two novel classes of porous organic polymers with tunable chemical and electronic properties that can store up to 4.25 wt. % at 40 bar / 77 K.
- **Proposed future research:**
  - Develop new methods for metal cluster impregnation / metal ion decoration for chemical hydrogen storage
  - Develop new synthetic strategies to enhance porosity and crystallinity