IV.H.3 SISGR: Design and Synthesis of Chemically and Electronically Tunable Nanoporous Organic Polymers for Use in Hydrogen Storage Applications

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Objectives

- Design and synthesis of new classes of low density nanoporous organic polymers that are linked by strong covalent bonds and composed of chemically and electronically tunable building blocks.
- Use gas sorption experiments to investigate porosity and determine hydrogen storage at variable temperature and pressure ranges.
- Investigate the impact of pore functionalization on hydrogen storage and binding affinity and predict gas binding sites by computational studies.

Technical Barriers

This project addresses the following technical barriers for on-board hydrogen storage:

- Gravimetric and volumetric storage
- Fueling/defueling rates
- Chemical stability of sorbents

Abstract

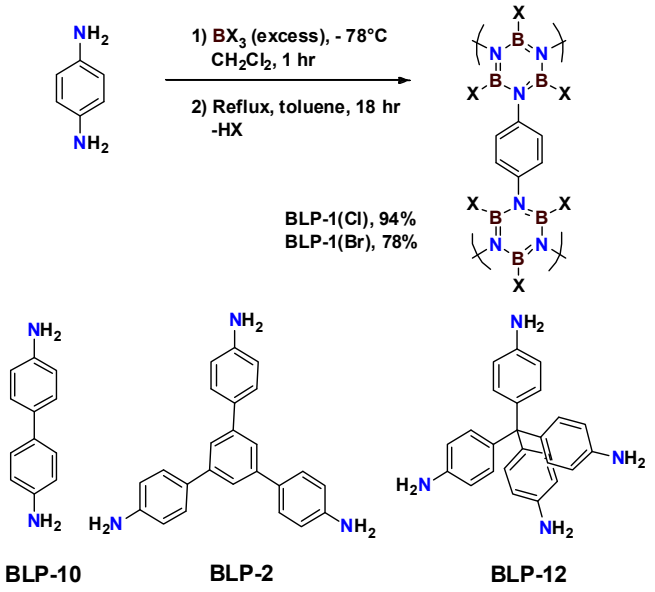
The designed synthesis of two novel classes of porous organic polymers, borazine-linked polymers (BLPs) and benzimidazole-linked-polymers (BILPs), that are composed of chemically and electronically tunable building blocks have been performed and their use in hydrogen and other small gas storage has been investigated. Highly porous BLPs were prepared by employing thermal decomposition of amine-borane or amine-borontrihalide adducts in non-polar solvent mixtures. The textural properties and hydrogen storage capacity of these polymers were carried out using conventional low- and high-pressure gas sorption experiments. Additionally, porous BILPs featuring high imidazole linkage density were synthesized and tested for hydrogen storage. Among the most attractive properties of this class of polymers are their chemical and physical stabilities, amphoteric pore walls, and their high gas storage capabilities. BLPs can store up to 4.25 wt% of hydrogen at 77 K and 40 bar whereas BILPs can store 2.3 wt% of hydrogen at 77 K and only 1 bar. Both types of these purely organic polymers exhibit relatively moderate hydrogen isosteric heats of adsorption (6.0 to 8.3 kJ mol^{-1}). An advantageous feature of these polymers is their functionalizable channels/pores that alter their affinity for small gases.

Progress Report

This project is aimed at the synthesis and characterization of two new classes of porous organic polymers: BLPs and BILPs. In these polymers the resulting chemical connectivity between building units can potentially lead to structures analogous to those of covalent-organic frameworks (COFs) linked by B-O bonds [1,2], BLPs and BILPs feature functionalized pore walls and moderate surface areas. One significant motivation for pursuing isolated B_3N_3 rings in porous materials was the potential of the borazine rings to undergo hydrogenation by molecular dihydrogen in the presence of a catalyst. Thereby BLPs would store hydrogen by both chemical (B-H and N-H) and physical (physisorption within the pores) means.

Borazine-Linked Polymers (BLPs)

We have described for the first time the incorporation of borazine units bearing three different B-substituents (H, Cl, Br) as building blocks for the construction of porous networks to assess the impact of pore decoration on hydrogen storage and selective gas binding. In halogen-decorated BLPs, treatment of arylamines with the corresponding boron trihalide followed by thermolysis in toluene under refluxing conditions produced the desired polymer (Scheme 1). We have extended this approach to prepare seven polymers in good yields using various amine building units. The chemical composition and structural aspects of these polymers were investigated by spectral (Fourier transform infrared, ^{11}B and



SCHEME 1. Representativesynthesisforhalogen-decoratedBLPs

^{13}C solid-state nuclear magnetic resonance, scanning electron microscopy) and analytical methods (elemental analysis) while porosity was examined by N_2 porosity measurements. Unlike COFs, all BLPs are amorphous which precluded their investigation by X-ray diffraction techniques. From their porosity measurements, halogen-decorated BLPs exhibit moderate surface areas and relatively high gas uptakes in comparison to porous organic polymers (Table 1). The highest gas uptake was reported for BLP-12(Cl) which has the highest surface area and pore volume values; it stores 1.75 wt% of hydrogen with an isosteric heat of adsorption of 7.08 kJ/mol which is considerably somewhat higher than those reported for two-dimensional and three-dimensional COFs as a result of the narrower halogen decorated pores.

We have expanded the field of BLPs by the synthesis of halogen-free polymers following the same thermolysis approach described above to produce several borazine-rich polymers with very high surface areas. All BLPs were isolated as white powders in good yields and subjected to a battery of characterization methods: powder X-ray diffraction, scanning electron microscopy, thermogravimetric analysis, Fourier transform infrared, and Ar porosity measurements. Halogen-free BLPs are thermally stable up to ~420°C and were subjected to hydrogen storage experiments under low- and high-pressure conditions. Our studies indicate that halogen-free BLPs can store significant amounts of hydrogen under high pressure settings as in the case of BLP-12(H) which stores 4.25 wt% at 77 K and 40 bar.

Benzimidazole-Linked-Polymers (BILPs)

In addition to our work on BLPs, we have developed a simple synthetic route for several organic polymers by using condensation reactions between a variety of aryl-o-diamine and aryl-aldehyde building units to form BILPs. BILPs have remarkable chemical and thermal stabilities and considerable H_2 uptakes as well as high CO_2 selectivity over N_2 and CH_4. The notable enhanced CO_2 capture and selectivity of BILPs compared to other purely organic or organic-inorganic hybrid materials such as MOFs, for example, were attributed to their subnano pore dimensions and imidazole-functionalized pore walls that facilitate selective CO_2 capture and storage. Similarly, these textural properties of BILPs resulted in high H_2 uptakes and binding affinities at low pressure and cryogenic conditions as shown in Figure 1 and summarized in Table 2.

All BILPs exhibit excellent chemical stability that allow for their handling and purification under ambient conditions. They remain intact upon washing with a 2M aqueous solution of HCl or NaOH. BILPs also exhibit high thermal stability according to thermogravimetric analysis which showed decomposition only after ~420°C. Porosity and gas storage measurements (Table 2) reveal that BILPs are some of the most attractive purely organic materials for gas storage applications. BILPs with high surface area in particular exhibit noteworthy hydrogen storage capabilities (1.9-2.3 wt% at 77 K and 1 bar). In addition, these polymers in general can store significant amounts of CO_2 (up to

TABLE 1. Porous properties and H_2 uptakes of BLPs. SA_{Lang}: calculated by the Langmuir method. P_{vol}: calculated from nitrogen adsorption at P/P_o = 0.9. PSD: calculated using non-local density functional theory (NLDFT).

Polymer	SA_{Lang} ($m^2 g^{-1}$)	P_{vol} ($cm^3 g^{-1}$)	PSD (nm)	H_2, 77 K (wt%)	H_2 Q_{st} (kJ mol^{-1})
BLP-1(Cl)	1,828	0.746	1.33	1.00	7.06
BLP-1(Br)	730	0.303	1.27	0.68	7.14
BLP-2(Cl)	1,699	0.649	1.27	1.30	7.19
BLP-2(Br)	1,221	0.571	1.27	0.98	7.49
BLP-12(Cl)	2,091	0.853	1.13	1.75	7.08
BLP-1(H)	1,360	0.69	1.27	1.33; (3.97, 40 bar)	6.8
BLP-2(H)	1,178	0.59	1.13	1.43; (2.48, 40 bar)	6.8
BLP-12(H)	2,866	1.08	1.27	1.93; (4.25, 40 bar)	6.0

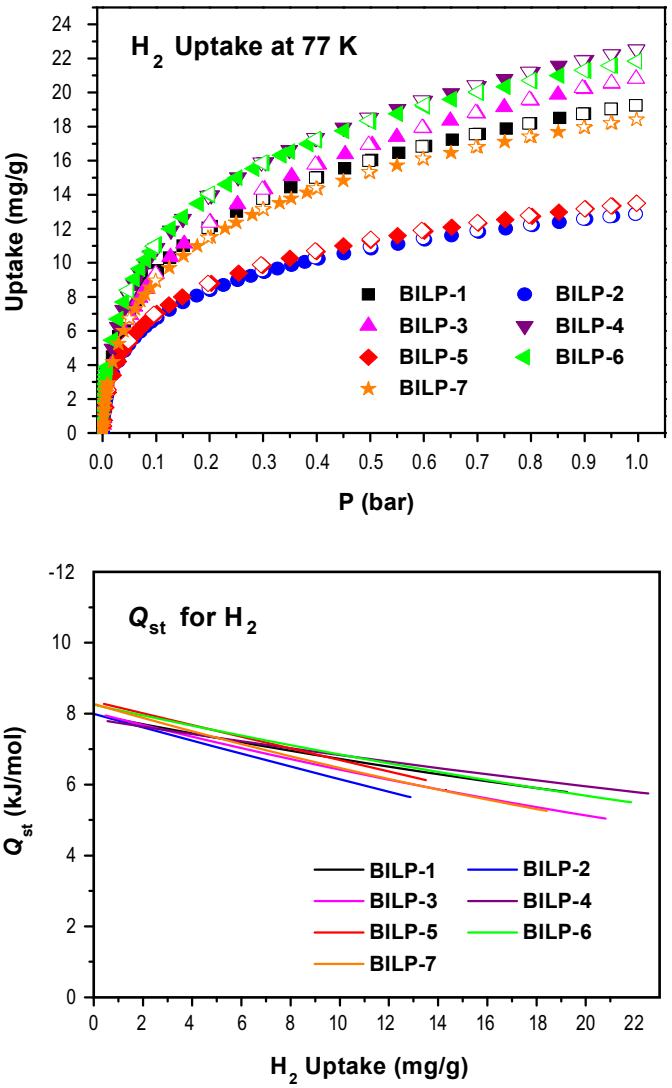


FIGURE 1. Hydrogen uptake isotherms and isosteric heats of adsorption for H_2. Adsorption (filled) and desorption (empty).

5.3 mmol g^{-1} at 273 K and 1 bar) with very high selectivities. The presence of amphoteric building units in the pore walls of BILPs can allow for post-synthesis modification with light metal ions (Li^+, Na^+, etc.) for enhanced hydrogen storage capacities which will be addressed in future work.

Future Directions

Our future research goals will focus on developing new synthetic methods to enhance the crystallinity and porosity of BLPs and BILPs to attain higher hydrogen storage capacities in these polymers especially under elevated pressure conditions. Additionally, pore surface modification by post-synthesis processes or by the use of pre-functionalized building blocks will also be explored to enhanced H_2 isosteric heat of adsorption. Future studies will also address the potential of borazine-rich BLPs in chemical hydrogen storage.

References

1. El-Kaderi, H.M.; Hunt, J.R.; Mendoza-Cortés, J.L.; Côté, A.P.; Taylor, R.E.; O'Keeffe, M.;Yaghi, O.M. *Science* **2007**, *316*, 268-272.

2. Côté, A.P.; El-Kaderi, H.M., Furukawa, H.; Hunt, J.R.; Yaghi, O.M. *J. Am. Chem. Soc.* **2007**, *129*, 12914-12915.

Publications and patents acknowledging the grant or contract

1. "Synthesis and Characterization of Porous Benzimidazole-Linked Polymers and Their Performance in Small Gas Storage and Selective Uptake," Rabbani, M.G.; El-Kaderi, H. M. *Chem. Mater.* **2012** (DOI: http://dx.doi.org/10.1021/cm300407h).

2. "High CO_2 uptake and selectivity by triptycene-derived benzimidazole-linked polymers," Rabbani, M.G.; Reich, T.E.; Jackson, K.T.; Kassab, R.M.; El-Kaderi, H. M. *Chem. Commun.* **2012**, *48*, 1411.

TABLE 2. H_2 Storage Capacity for BILPs

	Surface Area (m^2 g^{-1})[a]		Pore Size[b]	Pore Volume[c]	H_2 uptake at 1 bar (wt%)		Q_{st} for H_2
polymer	BET	Langmuir	nm	cm^3 g^{-1}	77 K	87 K	kJ mol^{-1}
BILP-1	1,172	1,563	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	1,306	1,715	7.2	0.65	2.1	1.5	8.0
BILP-4	1,135	1,486	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	1,261	1,654	6.2	0.66	2.2	1.6	8.2
BILP-7	1,122	1,489	6.8	0.74	1.8	1.4	8.3

[a]Surface area was calculated from Ar isotherm. [b]Pore size distribution was calculated by NLDFT. [c]Pore volume was calculated at P/P_o = 0.95. BET = Brunauer-Emmett-Teller

3. "Impact of tailored chemical and textural properties on the performance of nanoporous borazine-linked polymers in small gas uptake and selective binding," Reich, T.E.; El-Kaderi, H.M. *J. Nanopart. Re.* **2012** (submitted)

4. "Synthesis of highly porous borazine-linked polymers and their application to H_2, CO_2, and CH_4 storage," Jackson, K.T.; Rabbani, M.G.; Reich, T.E.; El-Kaderi, H.M. *Polym. Chem*. **2011**, *2*, 2775.

5. "Design, Synthesis, and Characterization of Halogen-Decorated Porous Borazine-Linked Polymers and their performance in hydrogen storage application," Reich, T.E, Jackson, K.T.; Li, S.; Jena. P.; El-Kaderi, H.M. *J. Mater. Chem*., **2011**, *21*, 10629.

6. "Template-Free Synthesis of a Highly Porous Benzimidazole-Linked Polymer for CO_2 Capture and H_2 Storage," Rabbani, M.G.; El-Kaderi, H.M. *Chem. Mater.*, **2011**, *23*, 1650.

7. "Nickel-Catalyzed Synthesis of Soft Nanoporous Organic Frameworks and Their Potential Use in Gas Storage Applications" Kassab, R.M.; Jackson, K.T.; El-Kaderi, O.M.; El-Kaderi, H.M. *Res. Chem. Intermed*. **2011**, *7*, 747.

8. "Synthesis and Characterization of Highly Porous Borazine-Linked Polymers via Dehydrogenation/Dehydrocoupling of Borane-Amine Adducts and their Applications to Gas Storage," Jackson, K.T. Virginia Commonwealth University, Richmond, VA, December **2011**, Ph.D. thesis.

9. "Designed Synthesis and Characterization of Halogenated Borazine-Linked Polymers and their Application to Gas Storage," Reich, T.E. Virginia Commonwealth University, Richmond, VA, December **2011**. PhD. thesis.

10. "Highly Porous Benzimidazole-Linked Polymers for Use in Gas storage and Separation Applications," Rabbani, M.G.; El-Kaderi, H.M. Provisional Patent (Issued on Jan 14th, **2011** by Virginia Commonwealth University).