

## *Electronic Supplementary Information*

### **Targeted Synthesis of a Porous Borazine-Linked Covalent Organic Framework**

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**Materials and Methods Section S1: Full synthetic procedures for the preparation of BLP-2(H) and starting materials.**

**General Synthetic Procedures:** All starting materials and solvents, unless otherwise noted, were obtained from the Aldrich Chemical Co. and used without further purification. Dichloromethane was dried over CaH<sub>2</sub>. Toluene and mesitylene were dried over sodium. The isolation and handling of all products were performed under an inert atmosphere of nitrogen using either glove box or Schlenk line techniques. 1,3,5-*tris*(*p*-aminophenyl)benzene was synthesized using methods reported in literature.<sup>1</sup>

**Synthesis of 1,3,5-*Tris*(*p*-aminophenyl)benzene-borane** (C<sub>6</sub>H<sub>3</sub>(PhNH<sub>2</sub>·BH<sub>3</sub>)<sub>3</sub>). A 100 ml Schlenk flask was charged with 100 mg (0.285 mmol) of 1,3,5-*tris*(*p*-aminophenyl)benzene and 80 ml of anhydrous dichloromethane. The solution was cooled -78 °C in an acetone/dry ice bath and treated with 2.5 ml (2.5 mmol) of 1M borane-dimethylsulfide drop-wise. The clear solution was allowed to warm to room temperature while stirring overnight. On the following day, a white suspension had formed. The solid white product was filtered and rinsed several times with dichloromethane. FT-IR:  $\nu$  (cm<sup>-1</sup>) = 3424 (br, s), 2922 (m), 1619 (s), 1510 (s), 1455 (w), 1267 (w), 1177 (w), 1247 (m), 1092 (m), 1020 (m), 825 (m); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.82 (d, J<sub>HH</sub> = 2.4, CH), 7.28 (d, J<sub>HH</sub> = 8.7, CH), 7.75 (s, CH), 7.314 (s, NH<sub>2</sub>), 1.59 (q, BH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, *d*<sub>6</sub> DMSO)  $\delta$  123.35, 124.82, 128.30, 138.06, 141.80, 143.78.

*Further characterization by Mass Spectrometry and elemental analysis were unsuccessful due to the instability of the amine-borane adduct in the absence of solvents and due to polymerization upon heating under elemental analysis testing conditions.*

**Synthesis of BLP-2(H).** Pyrex tubes were charged with 30 mg of dry 1,3,5-*Tris*(*p*-aminophenyl)benzene-borane and 2 ml of a mesitylene:toluene (1:4; vol:vol) solution. The tubes were then sonicated for 30 min before they were flash-frozen, evacuated and sealed. The reaction tubes were slowly heated (0.1 °C/min) in an oven to 120 °C for 48 hrs to afford a fluffy white polymer which was isolated by filtration over a medium glass frit and washed with anhydrous dichloromethane. The product was immersed in anhydrous dichloromethane (20 ml) for 24 h, during which the activation solvent was decanted and freshly replenished twice. Anal. Calcd. for (C<sub>8</sub>H<sub>6</sub>BN): C, 75.56%; H, 4.76%; N, 11.02%. Found: C, 72.96%; H, 5.19%; N, 9.34%

**Caution:** *This polymerization process releases hydrogen, and therefore any scale-up procedures should take into consideration the flammability and generated pressure of the released hydrogen.*

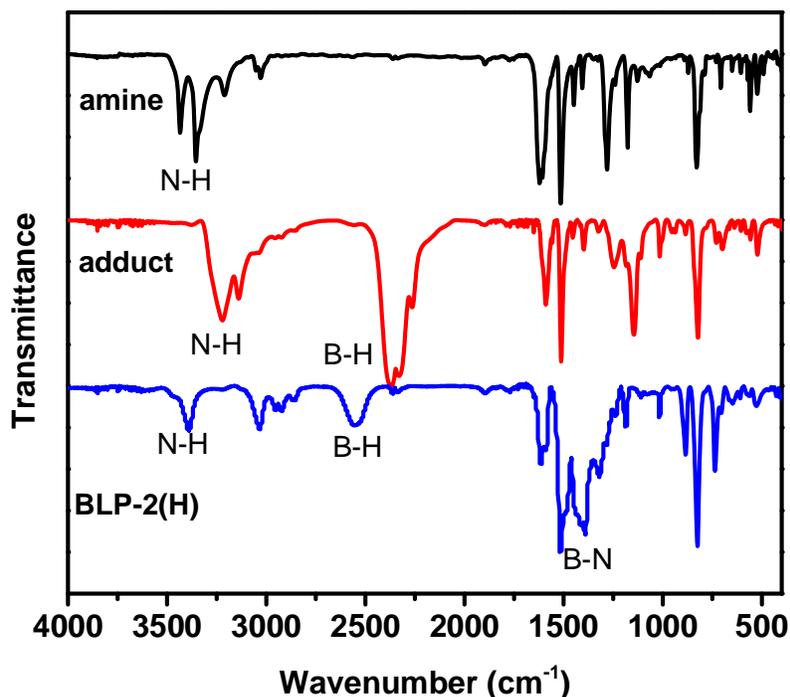
\* Organoboron compounds typically give lowered carbon values in elemental microanalysis due to the formation of non-combustible boron carbide byproducts. The higher hydrogen content may arise from trapped hydrocarbon solvents (toluene/mesitylene) and/or exposure to moisture during analysis; this observation is consistent with most of the reported 2D and 3D COFs.<sup>2</sup>

**Activation of BLP-2(H) for gas adsorption measurements.** Inside a glove-box, about 150 mg of an as-prepared sample of BLP-2(H) was loaded into an Autosorb cell then heated to 120 °C under dynamic vacuum (1.0 x 10<sup>-5</sup> torr) for 16 h. The sample was back-filled with nitrogen to exclude adsorption of moisture prior to N<sub>2</sub> adsorption measurements.

**Materials and Methods Section S2: FT-IR Spectroscopy of BLP-2(H) and Starting Materials.**

FT-IR data was used to verify that the products were being produced. By observing the loss of certain stretches expected for dehydrocoupling reactions combined with the appearance of borazine-characteristic peaks, the formation of the expected products can be confirmed. FT-IR spectra of BLP-2(H) and starting materials were obtained as KBr pellets using Nicolet - Nexus 670 spectrometer. The bands at 3300-3500  $\text{cm}^{-1}$  that correspond to the N-H stretching of amine/amine-borane adducts are significantly reduced after polymerization, however, the remaining weak signals are due to N-H stretches from unreacted  $-\text{NH}_2$  on the surface of the polymer's particles and incompletely reacted groups at defects in the material. The aromatic C-H stretching was observed around 2800-3100  $\text{cm}^{-1}$ . Borane B-H peaks in adducts were observed at approximately 2400  $\text{cm}^{-1}$  while a slight shift to about 2550  $\text{cm}^{-1}$  occurs after the formation of the borazine ring during polymerization. The strong stretch appearing at 1400  $\text{cm}^{-1}$  also supports the formation of the B-N bonds of the borazine ring.

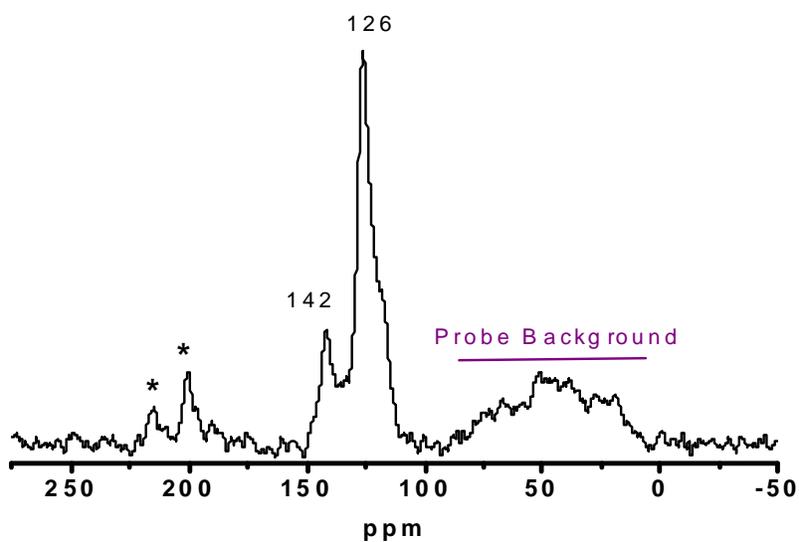
**Figure S1:** FT-IR spectrum of 1,3,5-*tris*(*p*-aminophenyl)benzene, 1,3,5-*tris*(*p*-aminophenyl)benzene-borane, and BLP-2(H)



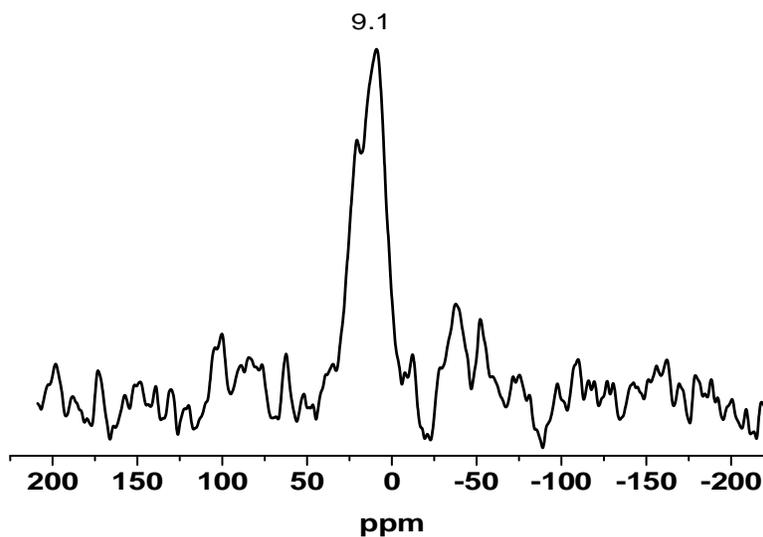
**Materials and Methods Section S3: Solid-State  $^{11}\text{B}$  and  $^{13}\text{C}$  Cross-Polarization Magic Angle Spinning (CPMAS) Nuclear Magnetic Resonance**

$^{11}\text{B}$  MAS NMR data were collected with a 45 degree  $^{11}\text{B}$  pulse length and a recycle delay of two seconds. High-power H-1 decoupling was employed during acquisition only. Samples were spun at the magic angle at about 7 kHz. Chemical shifts are referenced to external neat boron trifluoroetherate. Solid-state NMR spectra were recorded at ambient temperature on a 360-1 instrument by Spectral Data Services, Inc., Champaign, IL. Asterisks represent spinning side bands.

**Figure S2:** Solid state  $^{13}\text{C}$  NMR for BLP-2(H)



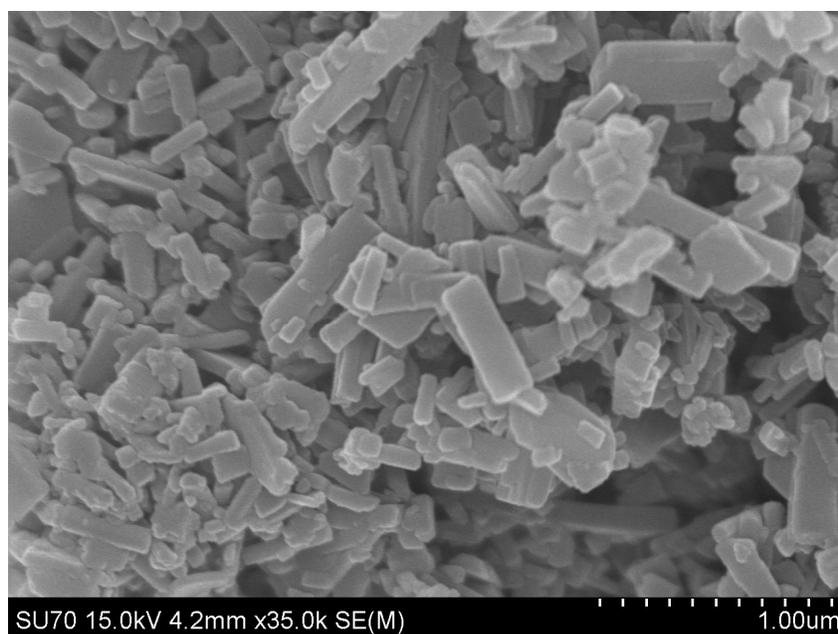
**Figure S3:** Solid state  $^{11}\text{B}$  NMR for BLP-2(H)



**Materials and Methods Section S4: Scanning Electron Microscopy Imaging (SEM) for BLP-2(H).**

In order to determine the purity of products, SEM was used to scan for the morphology present in the sample. A sample of the BLP-2(H) material was subjected to scrutiny under the SEM microscope. Only one type of morphology was found to exist, confirming the purity of the material produced. Samples were prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The sample was then platinum-coated using a Denton Vacuum V TSC HP Cold Sputtering Platform at  $1 \times 10^{-4}$  mbar of pressure in a nitrogen atmosphere for 120 seconds. Samples were analyzed on a Hitachi SU-70 Scanning Electron Microscope using an accelerating voltage of 15 kV.

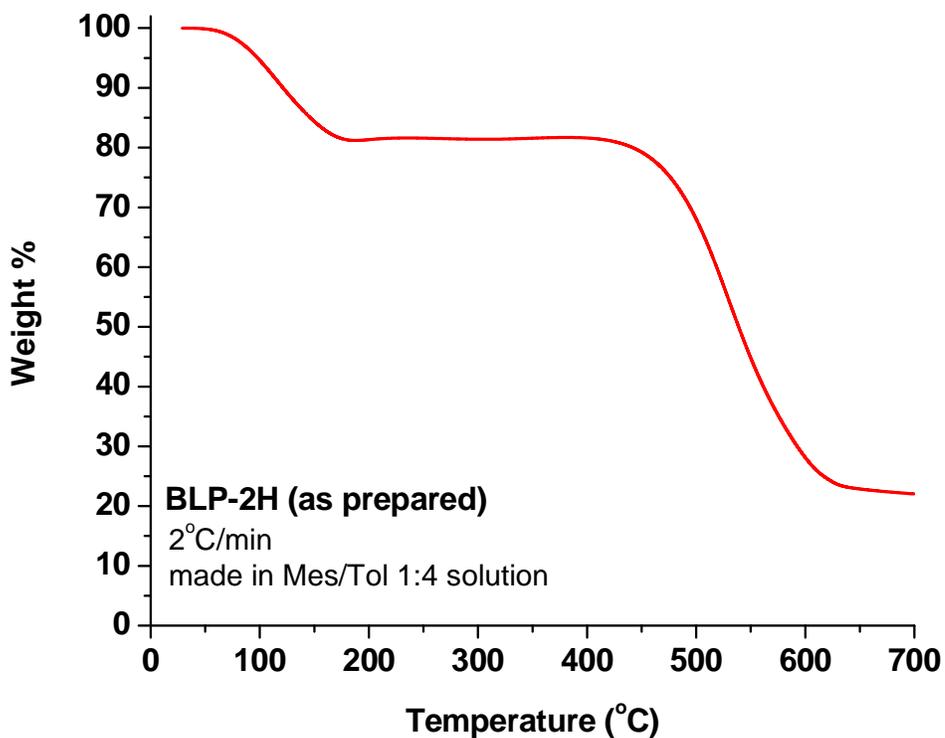
**Figure S4:** SEM image of BLP-2(H) revealing a spherical morphology.



**Materials and Methods Section S5: Thermogravimetric Analysis**

BLP-2(H) was analyzed by TGA to determine the thermal stability of the material produced as well as confirm that all guests have been removed. The sample was run on a TA Instruments Q-5000 series thermal gravimetric analyzer with samples held in platinum pans under an atmosphere of nitrogen.

**Figure S5:** TGA trace for an as prepared sample of BLP-2(H).



**Materials and Methods Section S6: Argon and Hydrogen Adsorption Measurements for BLP-2(H).**

Argon experiment was run using a Quantachrome Autosorb 1-C analyzer at 87 K. Pore Size Distribution (PSD) was calculated using Non-Local Density Functional Theory (NLDFT) on the adsorption branch with a cylindrical pore model. Hydrogen sorption experiments were run on the same Quantachrome Autosorb 1-C analyzer at both 77 K and 87 K. Ultrahigh purity helium (99.999%) was used to calibrate the free volume in the sample cell before each measurement. For H<sub>2</sub> uptake measurement, hydrogen with purity of 99.999% was used (from Airgas Inc. Radnor, PA).

Using the data taken at 77 K and 87 K, the isosteric heat of adsorption for each polymer was calculated according to previous reports<sup>3</sup> by solving the virial-type expression:

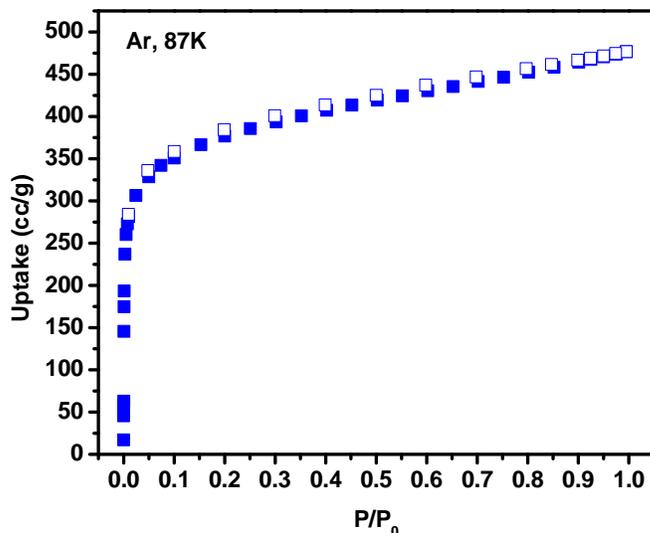
$$\ln P = \ln N + (1/T) \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i$$

where P is pressure in torr, T is temperature in Kelvin, and N is the mmol of gas adsorbed per gram of sample. The values for  $m$  and  $n$  were varied such that  $m \geq n$  and resulted in the best fit as determined by the sum of the squares of the errors. The values for  $a_0, a_1, \dots, a_m$  were used in the calculation for the isosteric heat of adsorption,  $Q_{st}$ :

$$Q_{st} = -R \sum_{i=0}^m a_i N^i$$

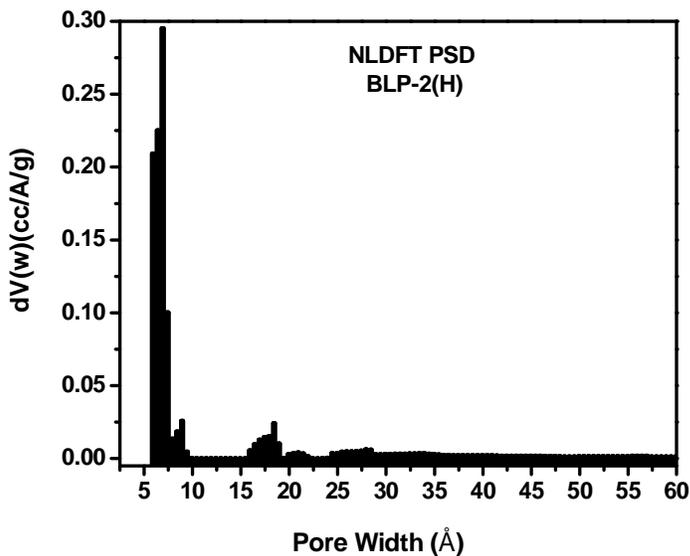
The calculated values were plotted as they relate to surface coverage, and the isosteric heat of adsorption values at the point of zero-coverage were highlighted in the text.

**Figure S6:** Ar adsorption isotherm for BLP-2(H) measured at 87 K. The filled squares are adsorption points and the empty squares are desorption points.

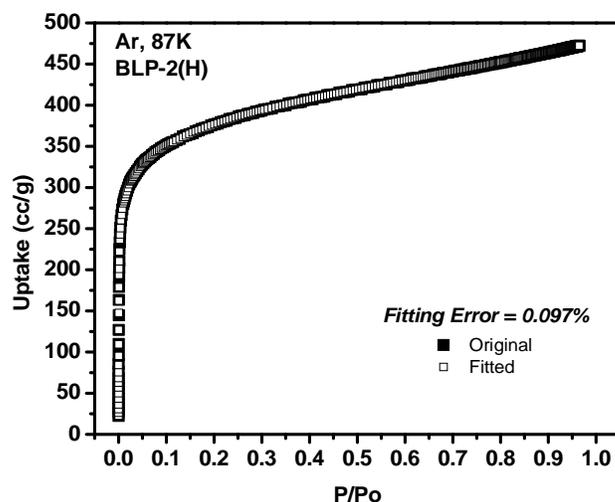


Pore Size Distribution (PSD) was calculated using Non-Local Density Functional Theory (NLDFT) on the adsorption branch with a cylindrical/sphere pore model on the argon experiment.

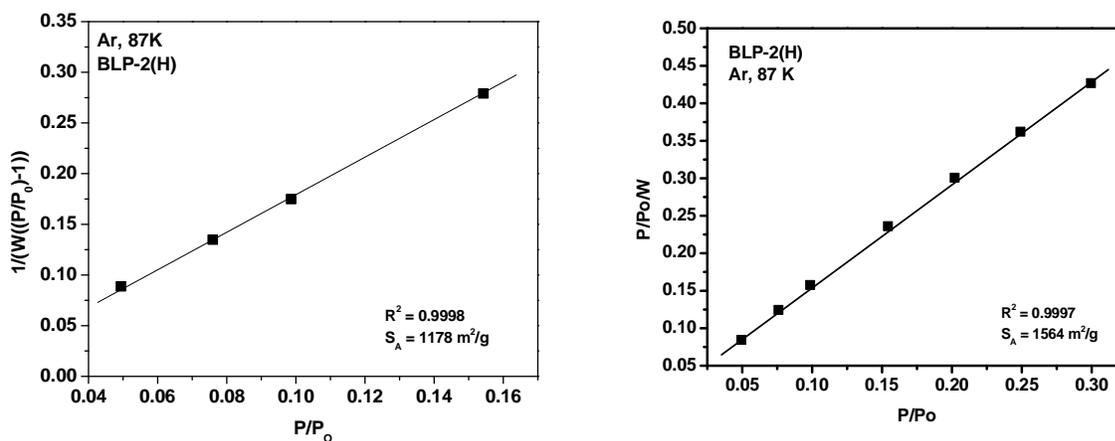
**Figure S7:** NLDFT Pore Size Distribution for BLP-2(H)



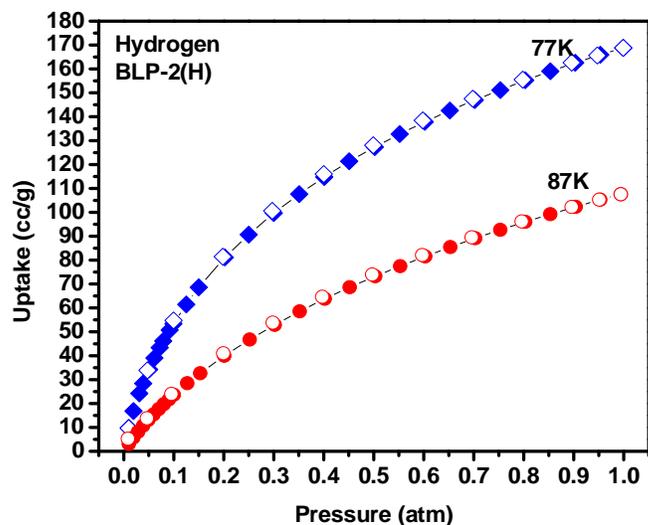
**Figure S8:** Experimental Ar adsorption isotherm for BLP-2(H) measured at 87 K is shown as filled squares. The calculated NLDFT isotherm is overlaid as open squares. Note that a fitting error of < 1 % indicates the validity of using this method for assessing the porosity of BLP-2(H).



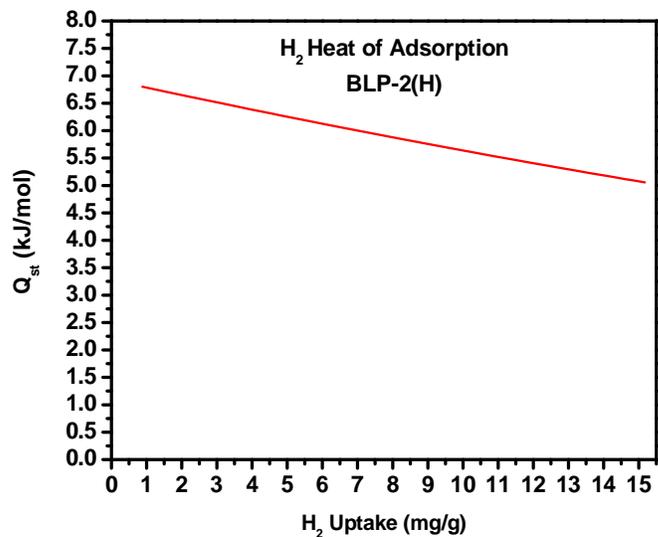
**Figure S9:** BET plot for BLP-2 (H) calculated from the Ar adsorption isotherm at 87 K. The model was applied from P/P<sub>o</sub>= 0.05-0.15. The correlation factor is indicated. Langmuir plot for BLP-2(H) calculated from the Ar adsorption isotherm at 87 K. The model was applied from P/P<sub>o</sub>= 0.05-0.30. The correlation factor is indicated.



**Figure S10:** Hydrogen adsorption isotherm for BLP-2(H) measured at 87 K (red circles) and 77 K (blue diamonds). The filled shapes are adsorption points and the empty shapes are desorption points.

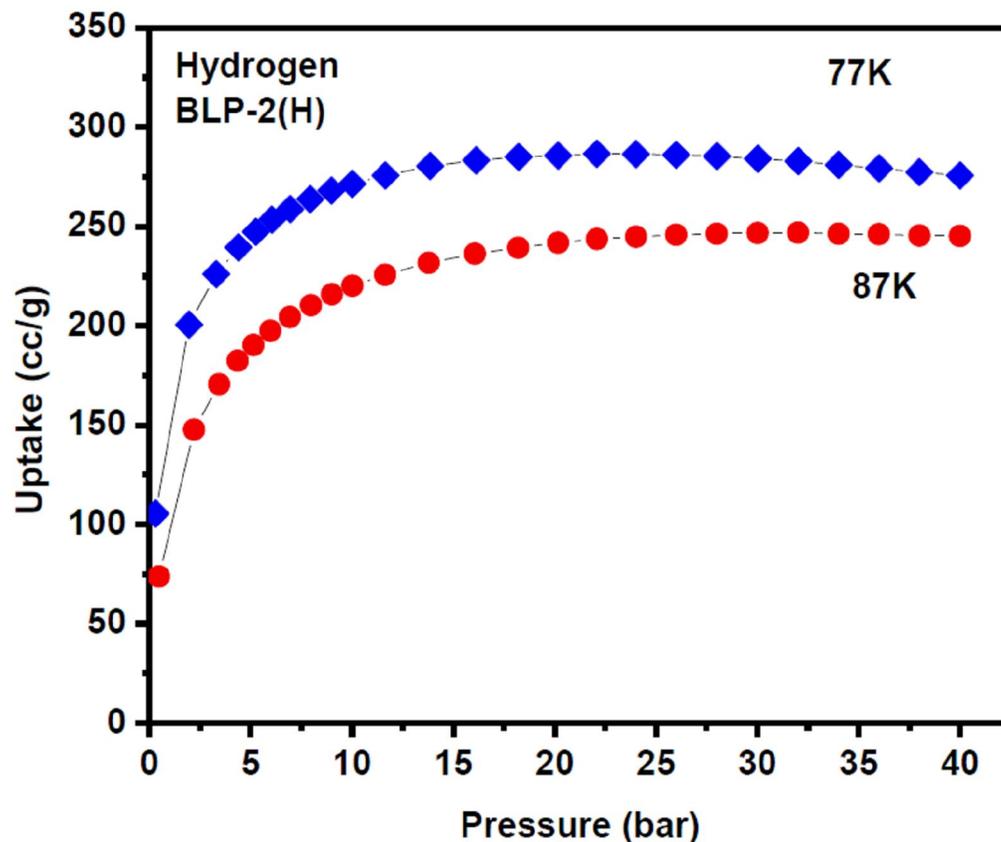


**Figure S11:** Hydrogen isosteric heat of adsorption ( $Q_{st}$ ) for BLP-2(H).



High pressure hydrogen sorption isotherms were run using a VTI HPVA-100 volumetric analyzer at 77 and 87 K. Ambient and analysis free space measurements were performed prior to data collection utilizing ultra-high purity helium to establish the appropriate cold zone compensation factors. The skeletal density of the material was found in the course of analysis for appropriate density correction factorization.

**Figure S12:** High pressure hydrogen adsorption isotherm for BLP-2(H) measured at 87 K (red circles) and 77 K (blue diamonds).



### **Materials and Methods Section S7: BLP-2(H) Structural Models**

Models were generated using *Materials Studio Version 4.3*<sup>4</sup> utilizing the Forcite module. BLP-2(H) was created using a derivative form of the boron nitride topology with a space group of *P-6m2* for an eclipsed conformation and with a graphite topology of space group *P6<sub>3</sub>/mmc* for a staggered conformation. Vertex positions were obtained from the Reticular Chemistry Structure Resource (<http://rcsr.anu.edu.au>).<sup>5</sup> The vertices were replaced by benzene or borazine (B<sub>3</sub>N<sub>3</sub>) rings with the nitrogen atoms pointing along the means of extension. The midpoint of each extension was replaced by a benzene ring. The structure's energy was then minimized using Geometry Optimization and Universal Forcefield procedures. The positions of atoms in the unit cell were determined using *CrystalMaker for Windows Version 1.4.5* and are shown as fractional atomic coordinates in Tables S1-S2.

**Table S1:** Fractional atomic coordinates for BLP-2(H) eclipsed conformation calculated from *Materials Studio* modeling.

<b>BLP-2(H) (Eclipsed)</b>			
P-6m2 a = b = 15.2905 Å ; c = 3.4579 Å $\alpha = \beta = 90^\circ ; \gamma = 120^\circ$			
Atom	x	Y	Z
B1	0.4404	0.7203	0.0000
C1	0.5617	0.2808	0.0000
C2	0.6126	0.2252	0.0000
C3	0.5523	0.6044	0.0000
C4	0.6049	0.5515	0.0000
C5	0.5549	0.4451	0.0000
C6	0.4451	0.5549	0.0000
H1	0.5272	0.7636	0.0000
H2	0.4019	0.3143	0.0000
H3	0.3151	0.3999	0.0000
H4	0.7591	0.5182	0.0000
N1	0.3890	0.7780	0.0000

**Table S2:** Fractional atomic coordinates for BLP-2(H) staggered conformation calculated from *Materials Studio* modeling.

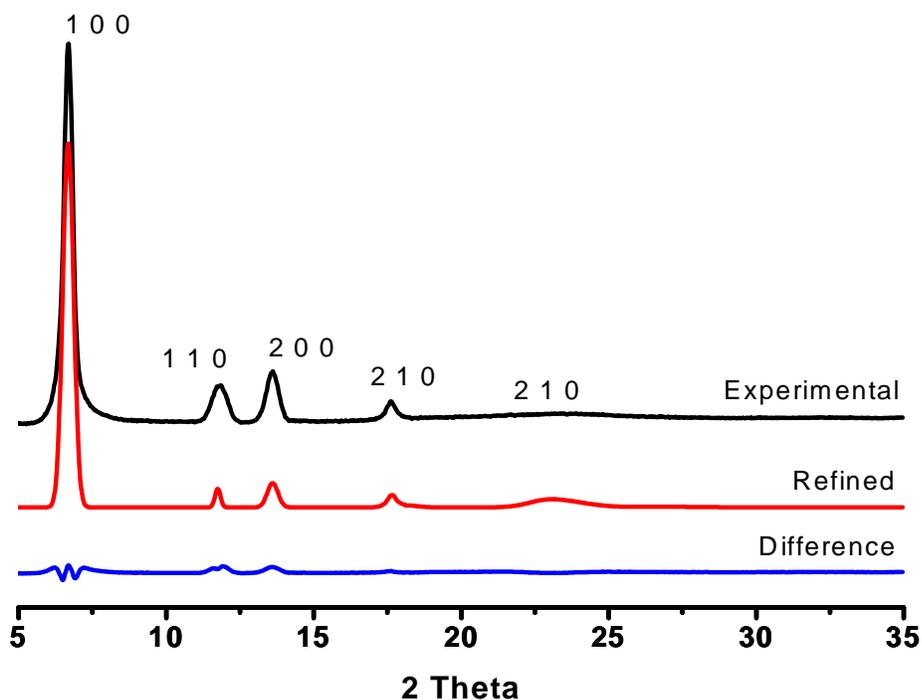
<b>BLP-2(H) (Staggered)</b>			
P6 <sub>3</sub> /mmc a = b = 15.2197 Å ; c = 7.0593 Å $\alpha = \beta = 90^\circ ; \gamma = 120^\circ$			
Atom	x	y	Z
B1	0.3869	0.6131	0.2500
C1	0.0541	0.1081	0.2500
C2	0.1117	0.2234	0.2500
C3	0.2220	0.4441	0.2500
C4	0.1047	0.0524	0.2500
C5	0.2190	0.2800	0.2500
C6	0.2712	0.3860	0.2500
H1	0.4303	0.5697	0.2500
H2	0.0921	0.1842	0.7500
H3	0.5805	0.6484	0.2500
H4	0.7529	0.7324	0.2500
N1	0.2781	0.5563	0.2500

### **Materials and Methods Section S8: Powder X-ray Diffraction Analysis of BLP-2(H)**

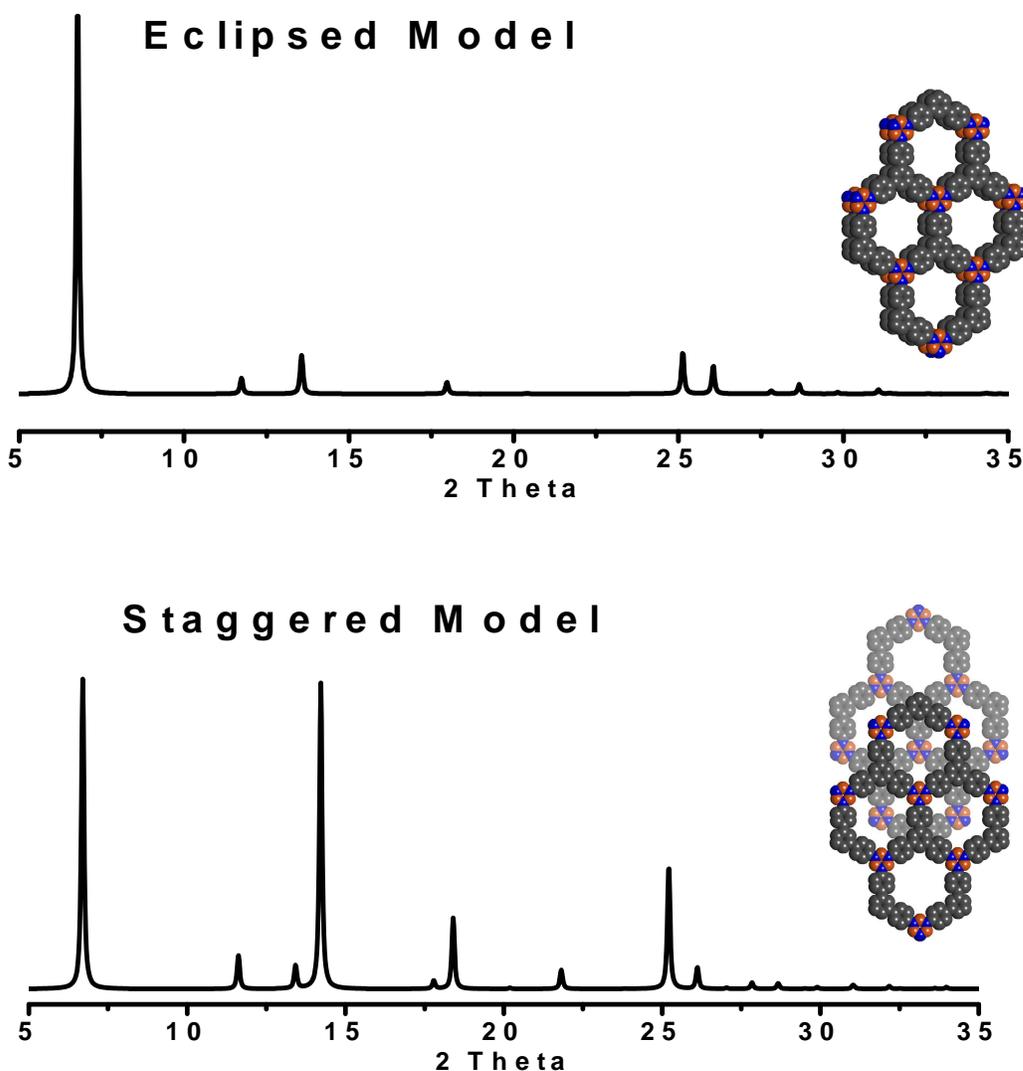
Powder X-ray diffraction data of BLP-2(H) were collected on a Panalytical X'pert Pro Multipurpose Diffractometer (MPD). Samples were mounted on a zero background sample holder measured in transmission mode using Cu K $\alpha$  radiation with a  $2\theta$  range of 5-35°.

The powder XRD data was subjected to refinement by the Rietveld method utilizing the GSAS and EXP-GUI software packages with a general least squares fit. The background was simulated using a 12-order polynomial. Refinement produced a PXRD curve with lattice parameters of  $a = b = 14.79 \text{ \AA}$  and  $c = 3.82 \text{ \AA}$ . The  $wRp$  and  $Rp$  values converged to 0.0265 and 0.0156 respectively.

**Figure 13.** PXRD pattern of BLP-2(H) with the experimental pattern in black, the Rietveld refined profile in red, and the difference plot in blue.



**Figure S14:** PXRD pattern of BLP-12(H) (top) compared to calculated pattern for the eclipsed (middle) and the staggered arrangements (bottom). Note the pattern from the eclipsed model more closely resembles the pattern of BLP-2(H).



## References

1. C. Bao, R. Lu, M. Jin, P. Xue, C. Tan, T. Xu, G. Liu, Y. Zhao, *Chem. Eur. J.* 2006, **12**, 3287.
2. a) A. P. Côte, A. A. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger, O. M. Yaghi, *Science* 2005, **310**, 1166. b) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Côte, R. E. Taylor, M. O’Keeffe, O. M. Yaghi, *Science* 2007, **316**, 268; c) A. P. Côte, H. M. El-Kaderi, H. Furukawa, J. R. Hunt, O. M. Yaghi, *J. Am. Chem. Soc.* 2007, **129**, 12914;
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