A new class of highly porous borazine-linked polymers (BLPs) has been synthesized utilizing arylamines and boron trihalides. BLPs exhibit Brunauer–Emmett–Teller (BET) surface areas in the range of 503 to 1364 m² g⁻¹ and store up to 1.3 wt% of hydrogen with 7.1 kJ mol⁻¹ isosteric heat of adsorption.

The synthesis of highly porous organic polymers with predefined porosity has attracted considerable attention due to their potential in a wide range of applications that encompasses gas storage and separation, conductivity, and catalysis. Among their attractive features are linkage by strong covalent bonds and usual composition of light elements (C, N, B, O) which impart several alluring properties such as low density, high porosity, and physical stability as in the case of microcrystalline covalent-organic frameworks (COFs). In the absence of reversible bond formation processes, covalent polymers lack long range ordering and tend to be amorphous as in the case of polymers of intrinsic microporosity (PIMs), porous aromatic frameworks (PAFs), conjugated microporous polymers (CMPs), porous organic frameworks (POFs), and porous polymer networks (PPNs). Nevertheless, such polymers can be synthetically targeted to allow for well-defined cavities through the use of rigid building blocks that direct growth of the polymer without the aid of templating agents. In addition to customized porosity, some polymerization processes can lead to pore wall functionalization that significantly enhances gas uptake and selectivity as we have demonstrated recently for the benzimidazole-linked polymer, BILP-1. Alternative methods for enhanced gas uptake (i.e. hydrogen) by porous architectures can also be attained by including polarizable building units to improve hydrogen-framework interactions. Along this line, we sought after the inclusion of borazine (B₃N₃) as a functionalized polar building block into porous organic polymers. Borazine is isostructural to the boroxine units found in COFs prepared by boronic acid self-condensation reactions and has been mainly used for the fabrication of BN-based ceramics or in organic optoelectronics. However, up to date, the use of borazine for the preparation of porous polymers for gas storage remains unprecedented.

With these considerations in mind we report herein on the first use of borazine in the construction of highly porous borazine-linked polymers (BLPs) featuring halide decorated cavities for investigation of their impact on porosity and hydrogen uptake under cryogenic conditions. Monomeric halogen-functionalized borazine molecules have been prepared previously by thermal decomposition of arylamines–boron trihalides in aprotic solvents at elevated temperatures. In a similar fashion, treatment of 1,4-phenylenediamine or 1,3,5-tris-(4'-aminophenyl)benzene in dichloromethane at 78 °C with BCl₃ or BBr₃ followed by reflux in toluene afforded BLP-1(Cl), BLP-1(Br), BLP-2(Cl), and BLP-2 (Br), respectively, as white powders in good yields as depicted in Scheme 1 (ESI†). The use of dichloromethane in the first step was essential to dissolve the amine building units which have very poor solubility in toluene at 78 °C while the use of reduced temperature conditions was employed to prevent premature side reactions of the highly reactive boron trihalides with amines. The chemical composition and structural aspects
were investigated by spectral and analytical methods while porosity was examined by nitrogen sorption measurements. The BLPs were isolated by filtration under an inert atmosphere and were washed with dichloromethane and dried at 1 × 10⁻⁵ torr/80 °C for 18 h prior to analytical and spectral characterizations.

All BLPs are amorphous as evidenced by their powder X-ray diffraction (PXRD) studies that were performed on both as-prepared and activated samples. The phase purity and morphology of each polymer were investigated by scanning electron microscopy (SEM) which revealed irregular particles of ~0.2 to 0.3 μm in size (ESI, S†). Furthermore, the micro-elemental analysis on activated BLPs further verified their chemical composition and purity. To establish the chemical connectivity and geometry of the boron sites, we collected FT-IR spectra and carried out solid-state ¹¹B multiple quantum magic angle spinning (MQMAS) NMR experiments. FT-IR spectra show significant depletion of the stretching and bending bands of amine protons around 3420 cm⁻¹ and 1610 cm⁻¹, respectively, and the formation of new bands ~1487, 1406, and 819 cm⁻¹ which are characteristic of the B₂N₃ ring (ESI, S1–S4†). We have selected one representative material for ¹¹B and ¹³C NMR experiments. The data, which are very sensitive to the boron magnetic and chemical environments, revealed one signal at 30 ppm with a quadrupole coupling constant \( Q_{cc} \) of 2.39 MHz (ESI, S5–S7†). This signal falls in the reported range for tri-coordinated boron atoms in borazines, which usually appear at ~25 to 40 ppm, and are in sharp contrast to tetra-coordinated boron which appears upfield (0 to ~45 ppm). In addition, the \( Q_{cc} \) value, which depends on the boron site symmetry, is in agreement with trigonal sites (\( Q_{cc} = 2.8 \) MHz).⁹ This data collected from these spectral experiments in conjunction with elemental analysis results (ESI†) clearly authenticate the formation of the borazine building block for each of these polymers. To assess the thermal stability of the BLPs, thermogravimetric analysis was conducted under a flow of nitrogen. TGA traces show that BLPs remain stable up to about 200 °C where a major weight loss takes place which may result from halogen evolution due to boron-halide bond decomposition (ESI, S9–S12†). Therefore, BLPs are thermally less stable than equivalent organic frameworks or organic polymers which generally remain stable up to ~400 °C.⁶

To investigate the permanent porosity of BLPs, we carried out \( N₂ \) sorption experiments at 77 K on activated samples. The activation process involved guest molecule exchange with anhydrous dichloromethane followed by filtration then degassing at 80 °C/1 × 10⁻⁵ torr for 18 h prior to data collection. The \( N₂ \) uptake (Fig. 1A) displays type I isotherms with a sharp increase in the \( P/P_o \) to 0.1 range which is indicative of their permanent and microporous nature, while the final rise at \( P/P_o = 0.9–1.0 \) is due to nitrogen condensation in macro- and meso-porous interparticulate cavities. A very minor hysteresis for all samples is consistent with their fine powder nature. The Brunauer–Emmett–Teller (BET) surface areas (Table 1) were higher for the Cl-decorated materials BLP-1(Cl): 1364 and BLP-2(Cl): 1174 m² g⁻¹ than the corresponding Br-decorated BLP-2(Br): 849 and BLP-1(Br): 503 m² g⁻¹. Pore size distribution (PSD) was calculated using Non-Local Density Functional Theory (NLDFT) and found to be centered about 1.3 nm (ESI, S14, S18, S22, and S26†). These values are inline with 2D COFs such as CTF-1⁶ (SA⁰ = 791 m² g⁻¹; PSD = 1.2 nm) and COF-1²⁶ (SA⁰ = 711 m² g⁻¹; PSD = 0.9 nm). The irregular trend in surface area values (Table S1†) may arise from solid state packing that can lead to a more accessible surface as indicated by a recent theoretical investigation of 2D COFs.²⁶ The inclusion of Br into the frameworks of BLPs significantly reduces pore volume (Table 1). Despite the structural similarity between borazine building units of BLPs and their boroxine counterparts in COFs, the reactive nature of the boron-halide bonds might promote the formation of cross-linked and hyper-branched polymers. This kind of reactivity in addition to the more robust B–N linkage might be the reasons behind the amorphous nature of all BLPs reported in this study. Additionally, the large halide atoms might sterically preclude the close stacking of 2D sheets typically found in crystalline COFs. This stacking aversion would result in more accessible sheets and explain why BLPs exhibit higher surface areas than their analogous COFs. Nevertheless, estimating porosity and investigating potential solid-state packing for amorphous organic polymers have been established using materials modeling that takes advantage of targeted synthesis where the topology of the system is rationalized based on the geometric shape of employed building units.⁸ Accordingly, we considered two solid-state arrangements for each polymer where the borazine ring participates in the formation of eclipsed and staggered 2D sheets to form hexagonal channels in a fashion that has been thoroughly investigated for 2D COFs. The BLPs’ models were constructed using Materials Studio and their geometry was optimized using Forcite (ESI†).²⁰ Interestingly, all

![Image](316x509 to 543x725)

Fig. 1 Nitrogen uptake isotherms (A); hydrogen isosteric heat of adsorption (B). Hydrogen uptake isotherms at 77 K (C) and 87 K (D); adsorption (filled) and desorption (empty).

Table 1 Porous properties and hydrogen uptake of BLPs

<table>
<thead>
<tr>
<th>Polymer</th>
<th>SA⁰ /m² g⁻¹</th>
<th>( P_{col}^o / cm² g⁻¹ )</th>
<th>PSD / nm</th>
<th>( H_2^o / (wt%) )</th>
<th>( Q_{c} / J mol⁻¹ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLP-1(Cl)</td>
<td>1364/1828</td>
<td>0.746</td>
<td>1.3</td>
<td>1.10</td>
<td>7.1</td>
</tr>
<tr>
<td>BLP-1(Br)</td>
<td>503/730</td>
<td>0.303</td>
<td>1.3</td>
<td>0.68</td>
<td>7.1</td>
</tr>
<tr>
<td>BLP-2(Cl)</td>
<td>1174/1699</td>
<td>0.649</td>
<td>1.3</td>
<td>1.30</td>
<td>7.2</td>
</tr>
<tr>
<td>BLP-2(Br)</td>
<td>849/1221</td>
<td>0.571</td>
<td>1.3</td>
<td>0.98</td>
<td>7.5</td>
</tr>
</tbody>
</table>

\( ^a \) Calculated by BET/Langmuir methods. \( ^b \) Calculated from nitrogen adsorption at \( P/P_o = 0.9 \). \( ^c \) Calculated from NLDFT. \( ^d \) Calculated at 77 K/1 bar. \( ^e \) Calculated from the virial method.
In conclusion, we have prepared four new porous borazine-linked polymers by thermolysis of arylamines–boron trihalides and investigated their porosity and hydrogen uptake under cryogenic conditions. The resultant polymers exhibit high surface areas and feature halide-decorated cavities which should open the door for selective gas uptake and post-synthesis modification studies. The hydrogen sorption experiments indicate that BLPs have moderate low-pressure hydrogen storage capacities and display somewhat higher hydrogen isosteric heat of adsorption; however, higher pressure conditions are required to fully explore the potential of BLPs in hydrogen storage applications. The flexibility in the boron trihalide type and arylamine building units allows for a myriad of possible new BLPs which may lead to enhanced porosity and increased gas storage capacity.

Acknowledgements

We are grateful to the US Department of Energy, Office of Basic Energy Sciences (DE-SC0002576) for generous support of this project. H.M.E. acknowledges support of the Donors of the American Chemical Society Petroleum Research Fund ACS-PRF (48672-G5).

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