

# Impact of tailored chemical and textural properties on the performance of nanoporous borazine-linked polymers in small gas uptake and selective binding

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**Abstract** Six borazine-linked polymers (BLPs) have been synthesized through the thermolysis reaction of *p*-phenylenediamine, 1,3,5-tris-(4-aminophenyl)benzene, benzidine, or tetra-(4-aminophenyl)methane with boron tribromide or boron trichloride. Each product exists as an amorphous polymer whose chemical connectivity was confirmed by FT-IR and elemental analysis while thermogravimetric analysis revealed moderate thermal stabilities up to about 200 °C under nitrogen atmosphere. All BLPs possess high surface areas with chlorinated BLPs exhibiting higher values than brominated BLPs (1,174–1,569 vs. 503–849 m<sup>2</sup>/g, respectively). Gas storage capabilities were investigated as well. BLPs possess good hydrogen uptakes (0.68–1.75 wt% at 77 K) and zero-coverage isosteric heat of adsorption,  $Q_{st}$ , (7.06–7.65 kJ/mol) as calculated by the virial method. The uptakes and heat of adsorption for carbon dioxide (51–141 mg/g at 273 K with  $Q_{st}$ : 22.2–31.7 kJ/mol) are also attractive. BLPs do not, however, appear to exhibit significant methane storage

capacities (1.9–15.2 mg/g at 273 K with  $Q_{st}$ : 17.1–21.7 kJ/mol). Accordingly, CO<sub>2</sub>/CH<sub>4</sub> selectivity studies were performed using the ideal adsorbed solution theory and further supported by initial slope calculations. The results indicate that BLP-1(Br) and BLP-2(Br) exhibit very high CO<sub>2</sub>/CH<sub>4</sub> selectivities 23 and 26, respectively, which make them attractive for small gas separation applications.

**Keywords** Borazine-linked polymers · Gas separation · Carbon dioxide capture · Hydrogen storage · Nanoporous polymers · Ideal adsorbed solution theory · Natural gas purification

## Introduction

In the pursuit of the realization of alternative energy sources, hydrogen and methane have emerged as attractive subjects as a result of their clean and sometimes renewable designations (Schlapbach and Züttel 2001). Carbon dioxide contamination, however, poses as a significant obstacle since its presence can hinder the efficiency of using hydrogen or methane as an energy source (Ma and Zhou 2010); therefore, separating CO<sub>2</sub> from more energetically useful gases has also become an interest in the scientific community. The sequestration of carbon dioxide, a greenhouse gas, from flue gas can have an environmental effect as well. Among the promising ways to address

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these concerns is the application of highly porous organic polymers whose high surface areas bring about a wide range of potential applications including gas storage and separation (McKeown and Budd 2010). Within this class of materials are covalent-organic frameworks (COFs) which can be tailored to possess exceptional porosities, very low densities, and pore metrics that span the micro- and meso-porous ranges (Côté et al. 2007; El-Kaderi et al. 2007; Côté et al. 2007; Tilford et al. 2006; Wan et al. 2008; 2009; Hunt et al. 2008; Uribe-Romo et al. 2009; Kuhn et al. 2008a, b; Spitler and Dichtel 2010; Tilford et al. 2008; Han et al. 2008; Furukawa and Yaghi 2009). In the absence of reversible synthetic conditions, covalently linked polymers lack long range ordering and tend to be amorphous (Weber et al. 2008; Farha et al. 2009; Jiang et al. 2008; Ben et al. 2009). Nevertheless, such polymers can be designed to possess well-defined cavities through the use of building blocks that dictate the spatial growth of the polymer and can still exhibit very high surface areas. One potential building block for covalently linked polymers is borazine which is structurally similar to the boroxine units found in COFs prepared by boronic acid self-condensation reactions (Anand et al. 2008). Although borazine has been previously used for the fabrication of BN-based ceramics or in organic optoelectronics (Salles et al. 2009; Duperrier et al. 2007; Sham et al. 2005; Wakamiya et al. 2005; Yamaguchi and Wakamiya 2006), its use for the preparation of porous polymers for gas storage and selectivity had been undeveloped until recently. (Reich et al. 2011; Jackson et al. 2011).

Herein we report on the synthesis of two new BLPs and examine the performance of six different polymers featuring selected organic linkers and halide functionalized pores in small gas storage and separation studies. The results presented in this study indicate that halide pore decoration can lead to enhanced CO<sub>2</sub> uptakes and binding affinities.

## Experimental

### Materials and methods

Tetra-(4-aminophenyl)methane was synthesized according to previously reported procedures (Bao et al. 2006; Plietzsch et al. 2009). All other starting materials were obtained from Thermo Fisher

Scientific Inc. and used without further purification. Preparations of BLP-1(Br), BLP-1(Cl), BLP-2(Br), and BLP-2(Cl) were performed based on previously reported procedures (Reich et al. 2011). Dichloromethane and dichloroethane were distilled from calcium hydride, and toluene was distilled from sodium. All products were handled under a nitrogen atmosphere using glovebox and Schlenk line techniques. FT-IR spectra were obtained as KBr pellets using a Nicolet Nexus 670 FT-IR spectrometer. Representative solid-state nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on a Bruker DSX-300 spectrometer using a Bruker magic angle spinning (MAS) probe with 4 mm (OD) 80  $\mu$ L volume zirconia rotors with Kel-F drive caps. SEM samples were prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The samples were then gold coated using an EMS (Electron Microscopy Sciences) 550 $\times$  Sputter Coater at  $1 \times 10^{-1}$  mbar of pressure in a nitrogen atmosphere for 120 s while maintaining 20 mA of current. Samples were analyzed on a Zeiss EVO XVP Scanning Electron Microscope using the SEI detector with accelerating voltages ranging from 10 to 20 kV. Thermogravimetric analysis was obtained using a TA Instruments TGA Q5000 analyzer with 50  $\mu$ L platinum pans to assess the thermal stability of each borazine-linked polymer. Experiments were run at a ramp rate of 5 K/min under a nitrogen atmosphere. Nitrogen sorption experiments were run using a Quantachrome Autosorb 1-C analyzer at 77 K, and pore size distributions (PSD) were calculated using Non-Local Density Functional Theory (NLDFT) on the adsorption branch with a cylindrical pore model.

### Synthetic aspects

#### *Synthesis of BLP-10(Br)*

Benzidine (0.30 g, 1.63 mmol) was dissolved in 60 mL of dry dichloromethane under a nitrogen atmosphere and cooled to  $-78$  °C. While stirring, 5.0 mL of 1 M boron trichloride (5.0 mmol) in dichloromethane was added. After 30 min of stirring, all of the dichloromethane was removed under reduced pressure and replaced with 60 mL of dry toluene. The mixture was refluxed overnight and taken into a glovebox. The white solid was filtered over a

medium glass frit and rinsed with dry dichloromethane. The product was soaked in dry dichloromethane for 24 h at which point the solvent was decanted, and fresh, dry dichloromethane was replenished. Decantation and addition of fresh solvent was repeated once more. The solid was filtered over a medium glass frit then activated at 80 °C under reduced pressure ( $1.0 \times 10^{-5}$  bar) for 18 h to afford BLP-10(Br) (0.51 g, 87 %) as a white solid. Anal. Calcd. for  $C_{36}H_{24}B_6N_6Br_6$ : C, 39.85; H, 2.23; N, 7.75. Found: C, 40.97; H, 2.66; N, 7.32.

#### Synthesis of BLP-12(Cl)

In a fashion similar to the preparation of BLP-10(Br), tetra-(4-aminophenyl)methane (0.15 g, 0.39 mmol) was dissolved in 180 mL of dry dichloroethane under a nitrogen atmosphere. While stirring, 5.0 mL of 1 M boron trichloride (5.0 mmol) in hexane was added dropwise. After 2 h of stirring, all of the dichloroethane was removed under reduced pressure and replaced with 60 mL of dry toluene. The mixture was refluxed overnight and taken into a glovebox. The white solid was filtered over a medium glass frit and rinsed with dry dichloromethane. The product was soaked in dry dichloromethane for 24 h at which point the solvent was decanted, and fresh, dry dichloromethane was replenished. Decantation and addition of fresh solvent was repeated once more. The solid was filtered off then activated at 80 °C under reduced pressure ( $1.0 \times 10^{-5}$  bar) for 18 h to afford BLP-12(Cl) (0.16 g, 73 %) as a white solid. Anal. Calcd. for  $C_{75}H_{48}B_{12}N_{12}Cl_{12}$ : C, 53.86; H, 2.89; N, 10.05. Found: C, 51.52; H, 3.39; N, 9.20.

## Results and discussion

The synthetic strategy for the preparation of the first BLPs; BLP-1 and BLP-2 were reported recently and involved treatment of arylamines with the corresponding boron trihalide followed by thermolysis in toluene under refluxing conditions for 18 h (Fig. 1). We have extended this approach to prepare two new polymers; BLP-10(Br) and BLP-12(Cl) in good yields as described in the synthetic section. The chemical composition and structural aspects of these polymers were investigated by spectral and analytical methods while porosity was examined by  $N_2$  porosity

measurements (Supplementary Material). Unlike COFs, all BLPs are amorphous which precluded their investigation by XRD technique, and scanning electron microscopy (SEM) images showed that these polymers exist as irregular particles of  $\sim 0.2 \mu\text{m}$  in size. Worth mentioning is that gas storage in porous materials is independent of particle size or size distribution and rather is a function of pore size and chemical nature. The latter properties are discussed in this study by porosity measurements and microelemental analysis as we have demonstrated recently (Reich et al. 2012). To establish the chemical connectivity and geometry of the boron sites, we collected FT-IR spectra and carried out solid-state  $^{11}\text{B}$  multiple quantum magic angle spinning (MQMAS) NMR experiments. FT-IR spectra show significant depletion of the stretching and bending bands of amine protons around 3,420 and 1,610  $\text{cm}^{-1}$ , respectively, and the formation of new bands  $\sim 1487$ , 1406, and 819  $\text{cm}^{-1}$  which are characteristic of the  $B_3N_3$  ring (Jäschke and Jansen 2006). We have selected a representative material for  $^{11}\text{B}$  and  $^{13}\text{C}$  NMR experiments, BLP-1(Cl). The data, which are very sensitive to the boron magnetic and chemical environments, revealed one signal for BLP-1(Cl) at 30 ppm with a quadrupole coupling constant,  $Q_{cc}$ , of 2.39 MHz (Nöth and Wrackmeyer 1978). This signal falls in the reported range for tri-coordinated boron atoms in borazines, which usually appear at  $\sim 25$ –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) (Nöth and Wrackmeyer 1978). The data collected from these spectral experiments in conjunction with elemental analysis results, which are very sensitive due to the high mass of the halide atoms, clearly illustrate the formation of the borazine building block for each of these polymers.

Both BLP-10(Br) and BLP-12(Cl) are amorphous as evidenced by powder-XRD studies. To assess the thermal stability of the BLPs, thermogravimetric analysis was conducted under a flow of nitrogen. TGA traces show a major weight loss around 200 and 450 °C, the former which may result from halogen evolution due to boron-halide decomposition and the latter from framework collapse as observed for previous halogen decorated BLPs (Reich et al. 2011). The low thermal stability of halogenated BLPs

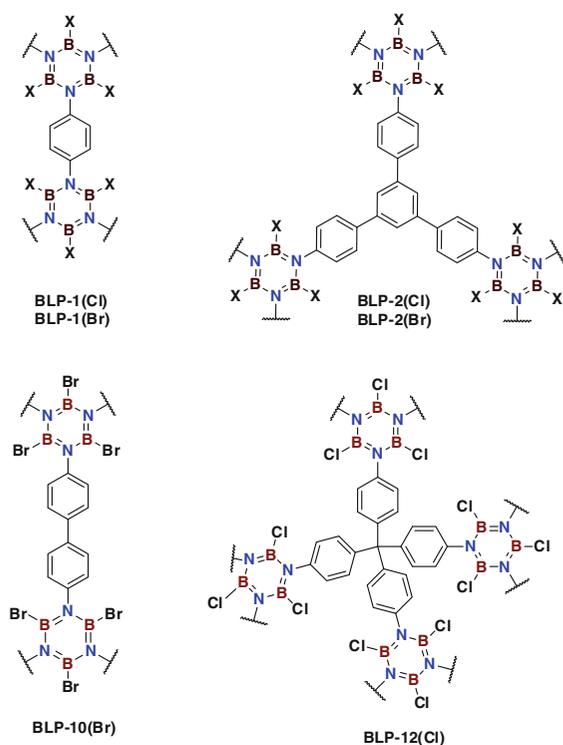
can limit their use in gas storage and separation applications. The halogen substituents on the borazine ring play significant role in tuning the electronic and physical nature of the pores and their limited thermal stability impedes the purification processes of BLPs.

#### Porosity measurements and gas storage studies

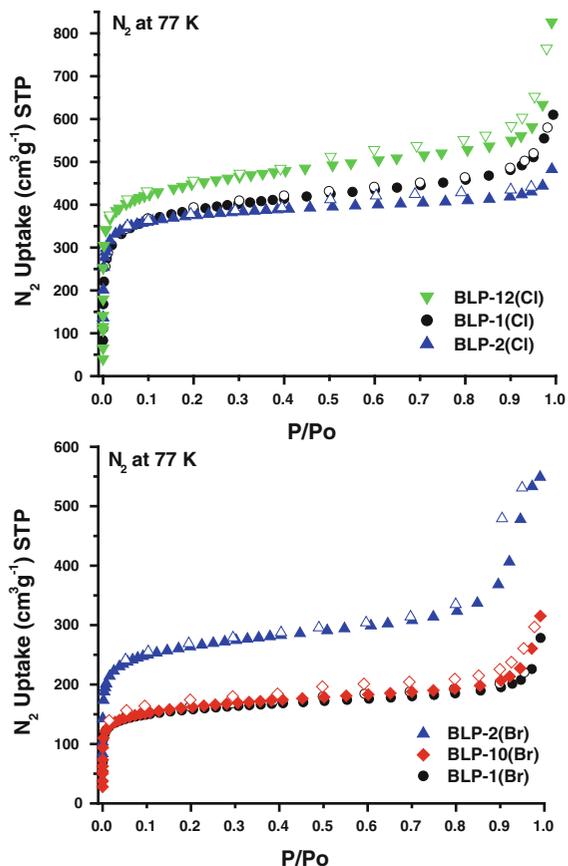
To investigate the permanent porosity of BLPs, we carried out  $N_2$  sorption experiments at 77 K and 0–1 bar on activated samples. The activation process involved guest molecule exchange with anhydrous dichloromethane followed by filtration then degassing at 110 °C/150 mTorr for 18 h prior to data collection. The  $N_2$  uptakes (Fig. 2) display Type I isotherms with a sharp increase in the  $P/P_0 = 0-0.1$  range which is indicative of their microporous nature, while the final rise at  $P/P_0 = 0.9-1.0$  is due to nitrogen condensation in macro- and meso-porous interparticulate cavities. Additionally, a 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-

12(Cl): 1569, BLP-1(Cl): 1364, and BLP-2(Cl): 1,174  $m^2/g$  than the Br-decorated polymers BLP-2(Br): 849, BLP-10(Br): 520, and BLP-1(Br): 503  $m^2/g$ . This trend in surface area might be surprising as BLP-2(Cl) should exhibit higher surface area than BLP-1(Cl). However, these polymers do not conform to such expectations hence their amorphous nature. Quite possibly the faces of the benzene rings in BLP-1(Cl) are more exposed than in BLP-2(Cl) resulting in an altered surface area trend, another possibility would be polymer network entanglement that increases density and reduces pore volume as well as surface area. In regards to pore volume in BLPs, the calculated results at  $P/P_0$  of 0.9 showed halide dependence as each of the chlorinated polymers yielded higher pore volumes than their brominated counterparts. This finding is consistent with the smaller atomic size of chlorine when compared to bromine. Pore size distribution (PSD) was calculated using NLDFT and found to be centered about 1.1 nm for BLP-10(Br) and BLP-12(Cl) and centered about 1.3 nm for the other four polymers. These values are in line with 2D COFs such as CTF-1 (Kuhn et al. 2008a, b) ( $SA_{BET} = 791 m^2/g$ ; PSD = 1.2 nm) and COF-1 (Côté et al. 2007) ( $SA_{BET} = 711 m^2/g$ ; PSD = 0.90 nm).

Since hydrogen represents an attractive source of energy with its renewable and clean aspects particularly in automotive applications, numerous studies have been reported recently on hydrogen storage capabilities (Schlapbach and Züttel 2001). Physisorbed hydrogen storage, which takes advantage of high surface area materials, MOFs, COFs, and organic polymers among others, is very promising because of the rapid uptake and release of hydrogen (Germain et al. 2009). Theoretical studies, however, highlight the weak interactions between hydrogen molecules and pore walls which lead to required use at low temperatures and elevated pressure conditions. Therefore, the ongoing quest for new materials with enhanced storage properties remains a great challenge and is tangibly beyond the targets set by the US Department of Energy for 2015 (5.5 wt% hydrogen and 0.040 kg hydrogen/L). Additionally,  $CO_2$  and  $CH_4$  have garnered increased interest. Carbon dioxide gas exists as an impurity in both flue gases and methane-dominated natural gases, which can be used as a fuel or in the production of hydrogen. Advancements in this area can lead to higher purity energetic gas in a more economically-friendly manner as well as



**Fig. 1** Halogen-decorated BLPs used in this study prepared via thermolysis of arylamine-boron trihalides



**Fig. 2** Nitrogen uptake isotherms for chlorinated (*top*) and brominated (*bottom*) BLPs; adsorption (*filled*) and desorption (*empty*) at 77 K and 0–1 bar

a reduction in atmospheric greenhouse gases. Along these lines, gas selectivity and separation remain at the forefront among the scientific community. Of

particular interest is in the selectivity and separation of CO<sub>2</sub> from gases like N<sub>2</sub> and CH<sub>4</sub> for the aforementioned environmental and economical reasons. Among the promising methods of addressing this issue is through the use of highly porous organic polymers.

Owing to the scientific interest in gas storage, selectivity, and separation as well as the high surface area for all BLPs, we initiated enhanced investigation by analyzing their performance in the storage of H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>. Hydrogen isotherms were performed at 77 and 87 K whereas CO<sub>2</sub> and CH<sub>4</sub> isotherms were performed at 273 and 298 K. The combined isotherms for all polymers are displayed for H<sub>2</sub> at 77 K (Fig. 3a), CO<sub>2</sub> at 273 K (Fig. 4a), and CH<sub>4</sub> at 273 K (Fig. 5a). All isotherms are fully reversible illustrating the facile gaseous release typical for organic polymers that make them energetically attractive for gas storage applications.

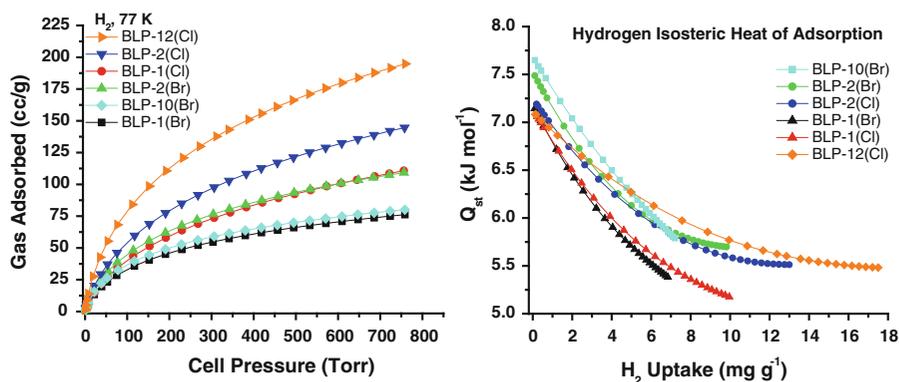
The order with which BLPs store CO<sub>2</sub> at 273 K is in much the same fashion as in the case of H<sub>2</sub>. The CO<sub>2</sub> values listed in Table 1 were generally, but not universally, higher for BLPs of higher surface area, and again the extent of halogen decoration seems to have a modest impact on the final uptake at the above-mentioned conditions and range between 51–141 and 27–78 mg/g at 273 and 298 K, respectively. Additionally just like for H<sub>2</sub>, the type of halogen incorporated into the polymer also seems to have an impact as the chlorinated BLPs exhibited higher carbon dioxide uptake than brominated BLPs in all cases. This observation is most likely the result of the differences in the spatiality and electronegativity between chlorine and bromine. These uptakes are comparable to the values reported for COFs (Belof et al. 2007), ZIFs

**Table 1** Porous properties of BLPs

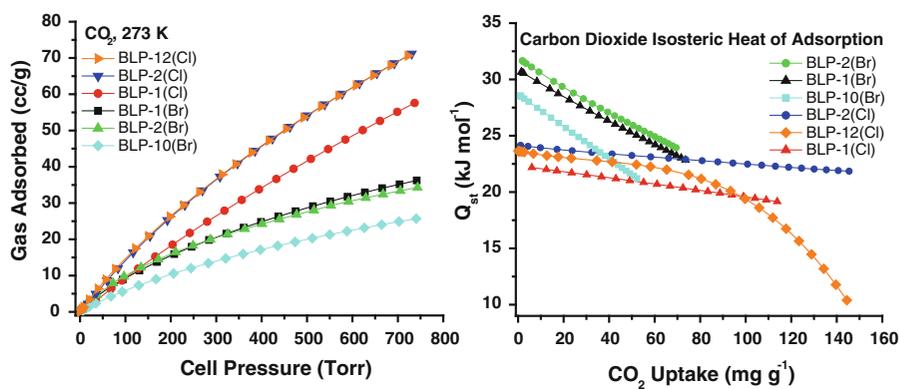
Polymer	SA <sub>Lang</sub> (m <sup>2</sup> /g) <sup>a</sup>	SA <sub>BET</sub> (m <sup>2</sup> /g) <sup>a</sup>	P <sub>vol</sub> (cm <sup>3</sup> /g) <sup>b</sup>	PSD (nm) <sup>c</sup>	H <sub>2</sub> , 77 K (wt%)	CO <sub>2</sub> , 273 K (mg/g)	CH <sub>4</sub> , 273 K (mg/g)
BLP-1(Cl)	1,828	1,364	0.746	1.33	1.00	114	4.1
BLP-1(Br)	730	503	0.303	1.27	0.68	72	1.9
BLP-2(Cl)	1,699	1,174	0.649	1.27	1.30	141	11.1
BLP-2(Br)	1,221	849	0.571	1.27	0.98	68	2.6
BLP-10(Br)	755	520	0.321	1.06	0.72	51	4.8
BLP-12(Cl)	2,091	1,569	0.853	1.13	1.75	140	15.2

<sup>a</sup> Calculated by the Langmuir and BET methods  
<sup>b</sup> Calculated from nitrogen adsorption at P/P<sub>o</sub> = 0.9  
<sup>c</sup> Calculated from NLDFT

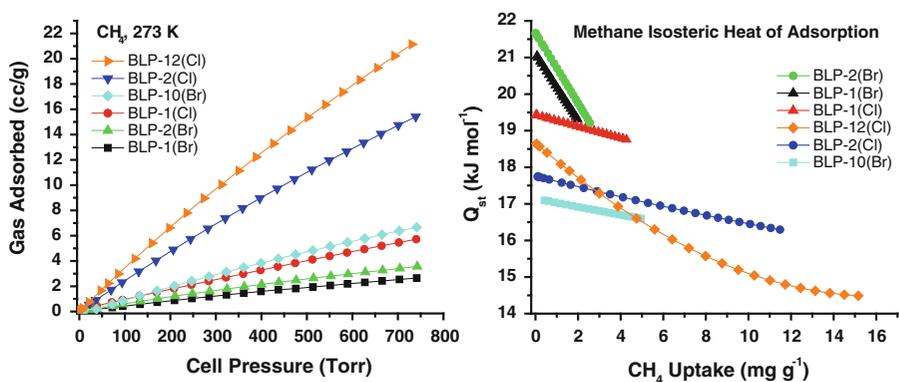
**Fig. 3** Hydrogen uptake isotherms at 77 K and 0–1 bar and their respective  $Q_{st}$  curves.  $Q_{st}$  values were calculated in conjunction with data taken at 87 K (Supporting information)



**Fig. 4** Carbon dioxide uptake isotherms at 273 K and 0–1 bar and their respective  $Q_{st}$  curves.  $Q_{st}$  values were calculated in conjunction with data taken at 298 K (Supporting information)



**Fig. 5** Methane uptake isotherms at 273 K and 0–1 bar and their respective  $Q_{st}$  curves.  $Q_{st}$  values were calculated in conjunction with data taken at 298 K (Supporting information)



(Phan et al. 2010), diimide polymers (Farha et al. 2009), or imine-lined organic cages (Tozawa et al. 2009) but are less than that of benzimidazole-linked polymers (BILPs) (Rabbani and El-Kaderi 2011; Rabbani et al. 2012) and CO<sub>2</sub>-selective MOFs (An et al. 2010; Vaidhyathan et al. 2009, 2010; Caskey et al. 2008). The CH<sub>4</sub> uptakes, which are also reported in Table 1 and are in the range of 1.9–15.2 mg/g at

273 K and 1.0–9.4 mg/g at 298 K, show that BLPs generally do not store appreciable quantities of the gas. The values are particularly meager when compared to MOFs, COFs, commercially available carbons (Menon and Komarneni 1998), and porous coordinated networks (PCNs) (Ma et al. 2008) which can store CH<sub>4</sub> at over 250 mg/g at room temperature. Nevertheless, the meager methane uptakes exhibited

by BLPs bring about intriguing characteristics for selectivity particularly when examining the differences between their methane and carbon dioxide uptakes as is discussed later.

From the H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> isotherms, isosteric heat of adsorption,  $Q_{st}$ , was calculated using the virial method (Rowell and Yaghi 2006) to determine the interaction of H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> with each polymer (Figs. 3b, 4b, 5b, respectively). The zero-coverage values for each gas are shown in Table 2. The hydrogen isosteric heat of adsorption at zero coverage range from 7.06 to 7.65 kJ/mol. Although these values are slightly lower than what has been reported for the benzimidazole-linked polymers (7.9–8.2 kJ/mol) and BPL carbon (8.0 kJ/mol), they compare well to many other organic polymers such as porous polymer networks (PPNs, 5.5–7.6 kJ/mol) (Lu et al. 2010), POFs (5.8–8.3) (Pandey et al. 2010; Katsoulidis and Kanatzidis 2011), COFs (3.9–7.0 kJ/mol) (Furukawa and Yaghi 2009), and PAF-1 (4.6 kJ/mol) (Ben et al. 2009). As polymer coverage increases, these values only drop down to 5.2–5.8 kJ/mol at 1 bar-worth of uptake, which illustrates BLPs' potential in high pressure storage. For CO<sub>2</sub>, the zero-coverage  $Q_{st}$  values in the range 22.2–31.7 kJ/mol, particularly on the high end, are comparable to BILPs, CO<sub>2</sub>-selective MOFs and ZTFs which feature amine functionality that enhances CO<sub>2</sub> affinity. These values typically drop off in a near-linear fashion with the exception of BLP-12(Cl) which exhibits a progressively steepening drop off in affinity beginning around 80 mg/g of coverage. The CH<sub>4</sub> values for BLPs at zero coverage (17.1–21.7 kJ/mol) are higher than COFs (8–19 kJ/mol) (Furukawa and Yaghi 2009) and BILPs (13.2–16.6 kJ/mol) (Rabbani and El-Kaderi 2011) and is comparable to BPL carbon (20 kJ/mol) (Furukawa and Yaghi 2009).

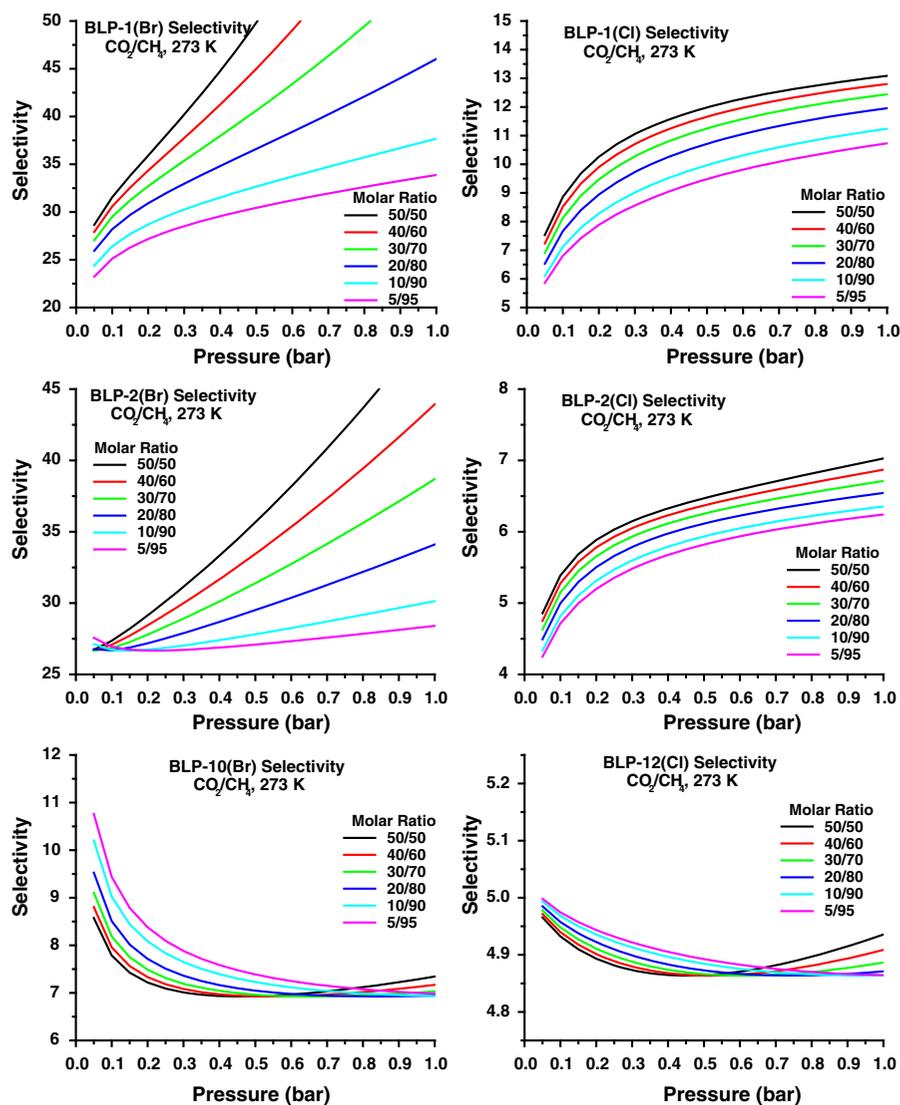
### Gas selectivity studies

The differences in the initial slopes of carbon dioxide and methane as well as their overall uptakes suggest that BLPs should exhibit selective behavior for carbon dioxide over methane. Along these lines, we set out to investigate the CO<sub>2</sub>/CH<sub>4</sub> selectivity of BLPs. These selectivities were calculated at 273 K by the ideal adsorbed solution theory (IAST) (Myers and Prausnitz 1965; Herm et al. 2011) which utilizes data taken from pure component isotherms to assess theoretical gas mixtures. The resulting graphs plot selectivity either as

a function of pressure for specific molar ratios (Fig. 6) or as a function of molar ratio for specific pressures (Supporting information). BLP-1(Cl), BLP-2(Cl), BLP-10(Br), and BLP-12(Cl) do not exhibit high levels of CO<sub>2</sub>/CH<sub>4</sub> selectivity. Their values do not exceed 13 at 1 bar for even the most favorable of molar ratios which puts them in line with diimide polymers (Farha et al. 2009) and PPNs (Lu et al. 2010). In the cases of BLP-2(Cl) and BLP-12(Cl), for example, both polymers store good amounts of CO<sub>2</sub>; however, they both also store much higher levels of CH<sub>4</sub> than the other BLPs. Nevertheless, BLP-1(Br) and BLP-2(Br) both exhibit significant CO<sub>2</sub>/CH<sub>4</sub> selectivity. For a 5/95 mixture of CO<sub>2</sub> and CH<sub>4</sub>, BLP-2(Br)'s selectivity at low pressure is over 26 which exceeds the selectivity for ZIFs (Phan et al. 2010) and activated carbons (Cavenati et al. 2004) and is comparable to PIMs (Budd et al. 2005), TZPIMs (Du et al. 2011), and the more selective MOFs (Murthi and Snurr 2004). With increasing bulk phase ratios of CO<sub>2</sub>, this selectivity at higher pressures in BLP-2(Br) increases further. Additionally, the shape of the curve suggests that with increasing pressure, the selectivity would continue to increase as well. BLP-1(Br) also exhibits good CO<sub>2</sub>/CH<sub>4</sub> selectivity between 23 and 28 at low pressure for all molar ratios. Additionally, these values increase as the pressure approaches 1 bar in a similar fashion to BLP-2(Br), and like BLP-2(Br), the shape of the curve suggests that the selectivity would increase with increasing pressure for all molar ratios. The dramatic increase in selectivity for BLP-1(Br) and BLP-2(Br) results from methane uptake approaching saturation quicker than the carbon dioxide uptake. Interestingly, the CO<sub>2</sub> uptakes for BLP-1(Cl), BLP-2(Cl), and BLP-12(Cl) exceed that of BLP-1(Br) and BLP-2(Br); however, the latter group's low CH<sub>4</sub> uptakes compensate for any CO<sub>2</sub>-based disadvantage.

**Table 2** Zero-coverage isosteric heats of adsorption ( $Q_{st}$ ) of H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> for BLPs

Polymer	H <sub>2</sub> (kJ/mol)	CO <sub>2</sub> (kJ/mol)	CH <sub>4</sub> (kJ/mol)
BLP-1(Cl)	7.06	22.2	19.4
BLP-1(Br)	7.14	30.7	21.0
BLP-2(Cl)	7.19	24.1	17.7
BLP-2(Br)	7.49	31.7	21.7
BLP-10(Br)	7.65	28.6	17.1
BLP-12(Cl)	7.08	23.6	18.6



**Fig. 6** IAST-calculated  $\text{CO}_2/\text{CH}_4$  selectivity of BLPs at 273 K

As reported in previous investigations (Murthi and Snurr 2004), the validity of selectivity calculations based on the IAST method is subject to the ideality of the polymer. Consequently, we sought to confirm these selectivity values by the initial slopes of the isotherms for BLP-1(Br) and BLP-2(Br). The resulting selectivities for  $\text{CO}_2/\text{CH}_4$  (BLP-1(Br): 26; BLP-2(Br): 22) are in good agreement with the IAST values at low pressure despite the polymer's amorphous nature. These findings are consistent with the narrow pore size distributions (Supplementary material), which suggest a limitation on the heterogeneity of the pores. Additionally, gas uptake measurements were successfully

reproduced from samples prepared in two different batches for each polymer to further confirm the uptake and selectivity values reported in this study.

## Conclusion

In conclusion, we have investigated several borazine-linked polymers through the simple synthetic avenue of the thermolysis of arylamines with boron trihalides. The resultant polymers exhibit high surface areas making them attractive for use in gas sorption and separation that can be tuned in a facile manner through

the dutiful incorporation of different halogens and aryl building blocks. The gas storage studies suggest that BLPs have good levels of H<sub>2</sub> and CO<sub>2</sub> gas storage capabilities with high isosteric heats of adsorption. BLPs also perform well in CO<sub>2</sub>/CH<sub>4</sub> selectivity studies making them attractive for both gas storage and separation applications.

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