Effect of Acid-Catalyzed Formation Rates of Benzimidazole-Linked Polymers on Porosity and Selective CO₂ Capture from Gas Mixtures

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Supporting Information

ABSTRACT: Benzimidazole-linked polymers (BILPs) are emerging candidates for gas storage and separation applications; however, their current synthetic methods offer limited control over textural properties which are vital for their multifaceted use. In this study, we investigate the impact of acid-catalyzed formation rates of the imidazole units on the porosity levels of BILPs and subsequent effects on CO₂ and CH₄ binding affinities and selective uptake of CO₂ over CH₄ and N₂. Treatment of 3,3′-Diaminobenzidine tetrahydrochloride hydrate with 1,2,4,5-tetrakis(4-formylphenyl)benzene and 1,3,5- (4-formylphenyl)-benzene in anhydrous DMF afforded porous BILP-15 (448 m² g⁻¹) and BILP-16 (435 m² g⁻¹), respectively. Alternatively, the same polymers were prepared from the neutral 3,3′-Diaminobenzidine and catalytic amounts of aqueous HCl. The resulting polymers denoted BILP-15(AC) and BILP-16(AC) exhibited optimal surface areas; 862 m² g⁻¹ and 643 m² g⁻¹, respectively, only when 2 equiv of HCl (0.22 M) was used. In contrast, the CO₂ binding affinity (Q₂) dropped from 33.0 to 28.9 kJ mol⁻¹ for BILP-15 and from 32.0 to 31.6 kJ mol⁻¹ for BILP-16. According to initial slope calculations at 273 K/298 K, a notable change in CO₂/N₂ selectivity was observed for BILP-15(AC) (61/50) compared to BILP-15 (83/63). Similarly, ideal adsorbed solution theory (IAST) calculations also show the higher specific surface area of BILP-15(AC) and BILP-16(AC) compromises their CO₂/N₂ selectivity.

1. INTRODUCTION

Acid-catalyzed covalent bond formation plays an important role in organic synthesis. Generally, the rate of bond formation and catalyst (acid) amounts are not crucial for the synthesis of discrete molecules, since they can be isolated and purified from the reaction mixture. However, controlling these parameters during the synthesis of porous organic polymers or frameworks is essential, as they dictate porosity levels and solid-state packing.¹² For example, several classes of porous organic polymers (POPs) were synthesized by acid-catalyzed processes that lead to C—N bond formation as in the case of imine-linked covalent organic frameworks (COFs)³⁻⁵ and polybenzimidazole (PBIs).³⁻¹⁰ In both systems, condensation reactions are facilitated by controlling acid loading and the temperature of the reaction.¹¹,¹² Because water is generated during condensation steps, it can mediate the rate of reversible bond formation as in the case of imine-linked polymers and hence control both porosity and crystalinity of the resulting materials.¹³⁻¹⁵ The role of water in such reactions was clearly outlined for COFs generated from boronic acids in self-condensation reactions or copolymerization with aryl-diols.³ Likewise, the synthesis of PBIs was accomplished by applying acid-catalyzed polycondensation reactions between diamine moieties and aryl-carboxylic acids or aryl-aldehydes and esters in the presence of polyphosphoric acid.¹¹,¹⁶,¹⁷ However, the resulting PBIs have very modest surface area (∼200 m² g⁻¹) due to the lack of controlled polymerization rates.

We have recently investigated the use of BILPs in selective CO₂ capture from gas mixtures containing N₂ and CH₄ as in the case of flue gas and natural gas, respectively. BILPs are very promising because of their high porosity, physiochemical stability, and ability to selectively bind CO₂ over other gases which is mainly due to basic N-functionality within the framework that provides interaction sites for CO₂.⁹,¹⁸ In contrast to alcohol amine-solutions (i.e., MEA) which are volatile, thermally unstable, and toxic, POPs bind CO₂ with moderate affinities and thus enable rapid adsorbent regeneration with a low energy penalty.¹⁹

In this study, we seek to unravel the role of acid concentration and ratio on the textural properties of BILPs. We have synthesized new polymers using our previously reported method, wherein HCl-salts of the amine-containing building units lead to uncontrolled condensation rates and thus surface area. The resulting BILPs were resynthesized using HCl-free amine building units in the presence of diluted acid concentrations and variable acid/amine ratios. The impact of...
the acid on the formation rate and surface area was investigated. The new polymers were characterized using a battery of spectral and analytical techniques, and their selectivity and binding affinity for small gas mixtures were studied and compared to other BILPs. Surprisingly, the acid-controlled synthetic route drastically improved surface area by 47–97%, which can be very useful when high surface area materials are needed for gas storage or separation applications.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. All starting materials and solvents were obtained from Acros Organics, Sigma-Aldrich or Frontier Scientific, unless otherwise noted, and used without further purification. 1,2,4,5-Tetrabromobenzene, 3,3′-diaminobenzidine tetrahydrochloridehydrate (DABA), 3,3′-diaminobenzidine (DAB), 1,4-Dioxane (extra dry over molecular sieves), and ethyl acetate were obtained from Acros Organics. Chloroform (stabilized with anylene) was purchased from Aldrich Company and used without further purification. Tetrahydrofuran (THF) was dried by distillation from Na/benzophenone. BILP-15, tetrakis(4-formylphenyl)benzene (TTFB), and 1,3,5-Tris(4-formylphenyl) benzene (TriFPB) were synthesized according to published methods. All reactions were handled under an inert atmosphere of nitrogen using Schlenk line technique. Elemental microanalyses were performed at the Midwest Microlab, LLC. 1H and 13C NMR spectra were obtained on a Varian Mercury-300 MHz NMR spectrometer (75 MHz carbon frequency). Solid-state 13C cross-polarization magic angle spinning (CP-MAS) NMR spectra for solid samples were taken at Spectral Data Services, Inc. Spectra were obtained using a Tecmag-based NMR spectrometer operating at a H-1 frequency of 363 MHz, using a contact time of 1 ms and a delay of three seconds for the CP-MAS experiment. All samples were spun at 7.0 kHz. For scanning electron microscopy (SEM), imaging samples were prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The samples were then coated with platinum at 1 × 10⁻⁴ mbar of pressure in a nitrogen atmosphere for 120 s before imaging. Images were taken on a Hitachi SU-70 Scanning Electron Microscope. Powder X-ray diffraction data were collected on a Pananalytical X’pert pro multipurpose diffractometer. Samples were mounted on a sample holder and measured using Cu Kα radiation with a 2θ range of 1.5–35. FT–IR spectra were obtained as KBr pellets using Nicolet-Nexus 670 spectrometer. Surface area and gas sorption experiments were collected using a Quantachrome Autosorb IQ2 volumetric analyzer using adsorbates of UHP grade. In a typical experiment, a sample of BILPs (～60 mg) was loaded into a 9 mm large bulb cell (from Quantachrome) of known weight and then hooked up to the Autosorb-IQ2 and degassed at 120 °C/150 mTorr for 12 h. The degassed sample was refilled with nitrogen, weighted precisely, and then transferred back to the analyzer. The temperatures for adsorption measurements were controlled using a refrigerated bath of liquid nitrogen (77 K), liquid argon (87 K), or temperature controlled system (273 and 298 K).

2.2. Synthesis of BILPs. 2.2.1. Synthesis of BILP-16. A 100 mL Schlenk flask was charged with (62 mg, 0.17 mmol) of 3,3′-diaminobenzineditetrachloride hydrate and 30 mL of anhydrous DMF. The solution was cooled to around −30 °C and a solution of 1,2,4,5-tetrakis(4-formylphenyl)benzene (40 mg, 0.10 mmol) in 25 mL anhydrous DMF was added dropwise to the previous charged solution. The temperature was maintained around −30 °C until the formation of a yellowish brown solid product was completed, and then it was allowed to warm up to room temperature overnight. The flask containing the reaction mixture was flushed with air for 15 min and capped tightly. The reaction mixture was heated in an oven at 130 °C (0.5 °C/min) for 3 days to afford BILP-16 as a pale brownish polymer which was isolated by filtration over a medium glass frit. The product was immersed in DMF (20 mL, 18 h) then in acetone (3 × 20 mL, 18 h). The product was dried under vacuum at 120 °C and 1.0 × 10⁻³ Torr for 20 h to afford BILP-16 as a pale green powder solid (100 mg, 75% yield). Anal. Calcd (%) for C₉₀H₅₄N₁₂·6H₂O: C, 76.60; H, 3.83; N, 11.91. Found (%): C, 76.36; H, 4.51; N, 12.42.

2.2.2. Synthesis of BILP-16(AC). BILP-16(AC) was synthesized following the method described above for BILP-16 with a minor modification. A 100 mL Schlenk flask was charged with 0.19 mmol, HCl (1.71 mL, 7.95 mol) and a solution of 3,3′-diaminobenzidine (40 mg, 0.19 mmol) in 25 mL anhydrous DMF was added dropwise to the previous charged solution. The temperature was maintained around −30 °C until the formation of a yellowish brown solid product was completed, and then it was allowed to warm up to room temperature overnight. The flask containing the reaction mixture was flushed with air for 15 min and capped tightly. The reaction mixture was heated in an oven at 130 °C (0.5 °C/min) for 3 days to afford BILP-16(AC) as a pale brownish polymer which was isolated by filtration over a medium glass frit. The product was immersed in DMF (20 mL, 18 h) then in acetone (3 × 20 mL, 18 h). The product was dried under vacuum at 120 °C and 1.0 × 10⁻³ Torr for 20 h to afford BILP-16(AC) as a pale green powder solid (100 mg, 75% yield). Anal. Calcd (%) for C₉₀H₅₄N₁₂·6H₂O: C, 76.60; H, 3.83; N, 11.91. Found (%): C, 76.36; H, 4.51; N, 12.42.

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0.22 M, 0.38 mmol) and anhydrous DMF (30 mL). 1,3,5-(4-
formylphenyl)-benzene (48.5 mg, 0.13 mmol) in DMF was
added dropwise and allowed to react according to the above-
mentioned steps. After purification and activation, BILP-
16(AC) was isolated as a greenish fluffy solid (90 mg, 72%
yield). Anal. Calcd (%) for C_{90}H_{54}N_{12}.6H_{2}O: C, 76.60; H, 3.83;
N, 11.91 Found (%): C, 77.33; H, 4.51; N, 11.79.

2.2.3. Synthesis of BILP-15(AC). BILP-15(AC) was synthe-
sized following the method mentioned above for BILP-16(AC).
A 100 mL Schlenk flask was charged with 3,3′-diamino-
benzidine (40 mg, 0.19 mmol) and HCl (1.71 mL, 0.22 M, 0.38
mmol) and anhydrous DMF (30 mL). 1,2,4,5-Tetrakis(4-
formylphenyl)benzene (46 mg, 0.09 mmol) in DMF was added
and allowed to react according to the above-mentioned steps.
After purification and activation, BILP-15(AC) was isolated as a
greenish fluffy solid (65 mg, 76% yield). Anal. Calcd (%) for
C_{58}H_{34}N_{8}.6H_{2}O: C, 73.26; H, 4.84; N, 11.79. Found (%): C,
72.83; H, 4.28; N, 12.03.

3. RESULTS AND DISCUSSIONS

3.1. Synthesis and Characterization of BILPs. The
synthesis of BILPs reported in this study was carried out by
following the synthetic protocol we developed recently which is
based on condensation coupling reactions between aryl-
aldehyde and aryl-α-diamine (HCl salts) building units in
DMF (Scheme 1). HCl not only catalyzes imidazole ring
formation but also provides amine building units with chemical
stability against oxidation by molecular oxygen. To investigate
the impact of HCl content on the surface area of BILPs we
selected 3,3′-diaminobenzidine (DAB) and its HCl-salt; 3,3′-
Diaminobenzidine tetrahydro-chloridehydrate (DABA), to
construct BILPs from tetrakis(4-formylphenyl)benzene
(TFPB), and 1,3,5-Tris(4-formylphenyl) benzene (TriFPB) as
depicted in Scheme 1. Treatment of DABA with TFPB and
TriFPB afforded BILP-15 and BILP-16, respectively, in good
yields. On the other hand, DAB was treated with TFPB and
TriFPB under acid-controlled conditions to afford BILP-
15(AC) and BILP-16(AC) that display variable surface area
levels as discussed below.

To establish the chemical composition of BILPs and
connectivity between building units of the polymers, we
collected elemental analysis and carried our spectral (FT−IR,
13C−CP-MAS NMR) studies. Microelemental analysis showed
that BILP-15/BILP-15(AC) and BILP-16/BILP-16(AC) have
virtually identical chemical compositions. All polymers exhibit
excellent chemical stability upon treatment with aqueous HCl
and NaOH (4 M) and only start to decompose at ∼400 °C
according to TGA studies (Supporting Information, SI, Figure
S2). The FT-IR spectra confirmed imidazole ring formation
and the consumption of the starting materials. The FT−IR
spectra of BILPs reported in this study were carried out by
Figure 1. Possible rotations around the imidazole rings in rigid BILP-14 and flexible BILP-15 and BILP-16.

Figure 2. FT−IR spectra of BILPs.
aromatic range are consistent with the building units used to construct the polymers. Scanning electron microscopy (SEM) revealed aggregated particles of variable sizes, while the featureless powder XRD patterns (SI Figure S3) are consistent with the expected amorphous nature of BILPs.

3.2. Impact of Acid-Catalyzed Process on Surface Area. Because high surface area and pore volume are among the desired parameters for gas storage applications under high pressure conditions, the use of extended organic struts has been employed to attain exceptionally porous MOFs and POPs. However, when this approach was used for BILPs, as in the case of BILP-15 which was synthesized by condensation reactions between TFPB and DABA, the resultant polymer exhibited lower surface area (448 m$^2$ g$^{-1}$) compared to BILP-14 (1005 m$^2$ g$^{-1}$) which is constructed from shorter building unit (benzene tetraamine). One possible reason would be the somewhat flexible nature of the 3,3′-diaminobenzidine linker core wherein rotation about C–C

Figure 3. SEM images BILP-15, BILP-15(AC), BILP-16, and BILP-16(AC).
Article

The acid protonates the carbonyl group of the aldehyde and catalyzes imine-bond formation followed by molecular oxygen assisted dehydration and cyclization of the imidazole moiety as shown in Scheme 2.12 Because of the reversible nature of the imine bond, which is the first step in network expansion, we sought after controlling the rate of condensation to improve the surface area of BILPs. We have selected DAB, which is acid-free and commercially available. We noted that the surface area of BILP-15 and BILP-16 increased significantly by 92% and 47%, respectively, when the amount of HCl used and its concentration is optimized.

The impact of hydrochloric acid over the surface area of BILP-15 and BILP-16 was studied by scanning the effect of different acid concentrations and mole ratios (with respect to the amine building unit) required for polymer formation. In our first approach, we sought to optimize the acid concentration at constant amount of HCl in order to reveal the effect of water on final porosity. Acid concentration can play an important role as the amount of water present in reaction media might regulate the reversibility of the imine formation by reversing the reaction toward reactants. We postulated that 2 equiv of HCl per DAB is needed as HCl catalyzes only the imine linkage formation step. Therefore, we have kept the HCl amount constant (2 equiv/DAB) and changed the water amount present and compared the final surface area levels to assign optimal HCl concentration. The resulting BET surface areas (Figure 3) reached high values that range from 100 to 643 m² g⁻¹ for BILP-16(AC) as shown in Figure 4A and summarized in Table 1. A gradual increase in surface area at very low acid concentrations (0.05 and 0.16 M) could be related to the enhanced reversible nature of the polycondensation as the water content increases to shift the reaction toward reactants. In contrast, at higher acid concentrations (above 0.22 M), the rate of polymerization increases which leads to “uncontrolled” network growth and much lower surface areas. The optimum surface area of BILP-16(AC) was obtained at 0.22 M (643 m² g⁻¹), which corresponds to an increase by 48% compared to noncatalyzed BILP-16 (435 m² g⁻¹). We have also tried 1:1 (HCl/DAB) mole ratio and different acid concentrations (0.05−2.0 M); the BET surface area was around 120 m² g⁻¹ in all cases (SI Table S1). Moreover, the color of the resulting polymers was black-gray after exposure to air for 2 h. It is assumed that incomplete polymerization processes leave behind unreacted amine sites that undergo oxidation under air.

Table 1. Impact of Variations of [HCl] on the Surface Area of BILP-16(AC) at Ratios of 2:1 for HCl/DAB

<table>
<thead>
<tr>
<th>[HCl] mol L⁻¹</th>
<th>vol° HCl solution (mL)</th>
<th>SA BET (m² g⁻¹)</th>
<th>SA % change b</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>0.19</td>
<td>100</td>
<td>−77.0</td>
</tr>
<tr>
<td>1.23</td>
<td>0.31</td>
<td>150</td>
<td>−66.0</td>
</tr>
<tr>
<td>0.69</td>
<td>0.55</td>
<td>220</td>
<td>−49.0</td>
</tr>
<tr>
<td>0.36</td>
<td>1.05</td>
<td>280</td>
<td>−43.0</td>
</tr>
<tr>
<td>0.29</td>
<td>1.31</td>
<td>450</td>
<td>+3.3</td>
</tr>
<tr>
<td>0.22</td>
<td>1.71</td>
<td>643</td>
<td>+48.0</td>
</tr>
<tr>
<td>0.16</td>
<td>2.31</td>
<td>330</td>
<td>−24.0</td>
</tr>
<tr>
<td>0.05</td>
<td>7.02</td>
<td>152</td>
<td>−65.0</td>
</tr>
</tbody>
</table>

“Volume of HCl solution added is calculated to be 2:1 mol ratio of HCl/DAB where 0.19 mmol DAB is used. bThe percentage change of the surface area BILP-16(AC) polymers compared to the surface area of BILP-16 (435 m² g⁻¹).”

Table 2. Impact of HCl/DBA Mole Ratio on the Surface Area of BILP-16(AC) at a Constant Acid Concentration (0.22 M HCl)

<table>
<thead>
<tr>
<th>HCl/DBA mole ratio</th>
<th>vol° HCl solution (mL)</th>
<th>SA BET (m² g⁻¹)</th>
<th>SA % change b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5:1</td>
<td>0.43</td>
<td>100</td>
<td>−77</td>
</tr>
<tr>
<td>1:1</td>
<td>0.86</td>
<td>120</td>
<td>−72</td>
</tr>
<tr>
<td>2:1</td>
<td>1.73</td>
<td>643</td>
<td>+48</td>
</tr>
<tr>
<td>3:1</td>
<td>2.59</td>
<td>570</td>
<td>+31</td>
</tr>
<tr>
<td>4:1</td>
<td>3.45</td>
<td>500</td>
<td>+15</td>
</tr>
</tbody>
</table>

“Volume of HCl solution added is calculated at different mole ratios of HCl/DBA. HCl concentration is 0.22 M and 0.19 mmol DAB was used for all trials. bThe change percentage of the surface area of BILP-16 (AC) polymers compared to the surface area of BILP-16 (435 m² g⁻¹).”

Figure 4. (A) Surface area of BILP-16(AC) at different [HCl] and 2:1 of HCl/DAB mole ratio and (B) surface area of BILP-16(AC) at different HCl/DAB mole ratios using 0.22 M HCl.
In the second set of experiments, the study was aimed at varying the mole ratio of HCl/DAB at the optimal acid concentration (0.22 M) determined from the above study in order to screen the effect of HCl amount present in the reaction on surface area. The mole ratio of HCl to DAB was varied from 0.5 to 4.0 equiv, whereas the concentration of HCl was kept at 0.22 M for all trials. The optimal surface area was recorded when 2:1 (HCl/DAB) mole ratio was used (Table 2) while a slightly lower surface area was recorded for the higher mole ratios 3:1 and 4:1 as shown in Figure 4B and Table 2. These results suggest that 2 equiv of 0.22 M HCl are needed for optimum surface area while excess acid and water amounts tend to lower surface area. In a similar fashion, we used these synthetic routes to optimize the surface area of BILP-15 (448 m$^2$ g$^{-1}$) to BILP-15(AC) (862 m$^2$ g$^{-1}$); an increase by 92%.

Because porosity is vital for gas storage and separation, we have assessed all polymers in CO$_2$ capture and separation from N$_2$ and CH$_4$. These processes mitigate CO$_2$ emissions and improve the quality of natural gas.

### 3.3. Surface Area Measurements and Gas Storage Studies

The impact of the controlled acid-catalyzed processes on the surface area of BILP-15(AC) and BILP-16(AC) was investigated, and the results were compared to those of BILP-15 and BILP-16. To assess surface areas, argon isotherms were collected at 87 K and 0−1.0 bar (Figure 5A) and used to determine surface area, pore volume, and pore size distribution of all polymers. The rapid Ar uptakes at low pressure ($P/P_0 < 0.1$ bar) are consistent with microporous nature of the polymers, while the hysteresis observed for BILPs is consistent with the flexible nature of the polymers. Pore size distribution (PSD) curves were derived from the Ar adsorption branch by using nonlocal density functional theory (NLDFT) and were

![Graphs](image.png)

**Figure 5.** Gas uptake isotherms Ar (A), PSD (B), CO$_2$ uptake (C), and CH$_4$ uptake (D) Adsorption (filled) and desorption (empty).

<table>
<thead>
<tr>
<th>polymer</th>
<th>SA$^a_{BET}$</th>
<th>CO$_2$ at 1 bar$^b$</th>
<th>CH$_4$ at 1 bar$^b$</th>
<th>N$_2$ at 1 bar$^b$</th>
<th>selectivity$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>273 K</td>
<td>298 K</td>
<td>273 K</td>
<td>298 K</td>
<td>273 K</td>
</tr>
<tr>
<td>BILP-15</td>
<td>448</td>
<td>118.0</td>
<td>80.0</td>
<td>33.0</td>
<td>13.5</td>
</tr>
<tr>
<td>BILP-16</td>
<td>435</td>
<td>118.7</td>
<td>80.7</td>
<td>32.0</td>
<td>13.5</td>
</tr>
<tr>
<td>BILP-15(AC)</td>
<td>862</td>
<td>151.0</td>
<td>101</td>
<td>28.9</td>
<td>16.4</td>
</tr>
<tr>
<td>BILP-16(AC)</td>
<td>643</td>
<td>152.3</td>
<td>102.2</td>
<td>31.6</td>
<td>17.4</td>
</tr>
</tbody>
</table>

$^a$Surface area (m$^2$ g$^{-1}$) was calculated from Ar isotherm. $^b$Gas uptake in mg g$^{-1}$ and the isosteric enthalpies of adsorption ($Q_{st}$) in kJ mol$^{-1}$. $^c$Selectivity (mol mol$^{-1}$) was calculated from initial slope calculations at 273 K and (298 K)
found to be centered around 5.6–7.0 Å as shown in Figure 5B. The random distribution domain of PSD in the range of 5 to 10 Å may arise from the lack of uniform pore growth and network expansion. Pore volume was calculated from single point measurements at $P/P_0 = 0.95$ and found to be 0.27, 0.25, 0.49, and 0.42 cc g$^{-1}$ for BILP-15, BILP-16, BILP-15(AC) and BILP-16(AC), respectively. The overall pore volumes of BILP-15(AC) and BILP-16(AC) improve by 56% and 96%, with respect to the parent polymers. Applying the Brunauer–Emmett–Teller (BET) model within the pressure range of $P/P_0 = 0.05–0.15$ resulted in $S_{\text{BET}}$ of 448 m$^2$ g$^{-1}$ (BILP-15), 862 m$^2$ g$^{-1}$ (BILP-15(AC)), 435 m$^2$ g$^{-1}$ (BILP-16), and 643 m$^2$ g$^{-1}$ (BILP-16(AC)) as shown in Figure S7 (SI). It should be noted that the surface area of BILP-15 and BILP-16 are much lower than those of reported BILPs most likely as a result of flexible nature of the DAB core.

To take advantage of the microporous nature of BILPs and their chemical heterogeneity, preferential binding of small gases has been studied (e.g., N$_2$, CO$_2$, and CH$_4$). Therefore, pure gas uptake isotherms were collected to evaluate gas uptake and selectivity as well as the binding affinity for CO$_2$ and CH$_4$ as summarized in Table 3. At 273 K, all CO$_2$ isotherms (Figure SC) are fully reversible and exhibit a steep rise at low pressure, which is in agreement with the behavior of previously reported BILPs. The uptake by BILP-15 and BILP-16 (∼119 mg g$^{-1}$) is the lowest compared to all reported BILPs (128–235 mg g$^{-1}$). A noticeable increase in the CO$_2$ uptake was recorded for BILP-15(AC) and BILP-16(AC) (∼152 mg g$^{-1}$). The uptake drops to 102 mg g$^{-1}$ at 298 K. On the other hand, CH$_4$ uptakes were in the range of 7.2–17.4 mg g$^{-1}$ (Figure SD). The binding affinities ($Q_d$) of CO$_2$ and CH$_4$ for BILPs were calculated by using the virial method. The $Q_d$ values for CO$_2$ (27.4–33.0 kJ mol$^{-1}$) are within the range reported for BILPs and other nitrogen-rich porous networks. The higher $Q_d$ values observed for BILP-15 and BILP-16 could be attributed to their narrow pores, which provide stronger interactions for CO$_2$ by multi wall interactions.

Similarly, low-pressure CH$_4$ isotherms were collected at 273 and 298 K and used to calculate the $Q_d$ for CH$_4$. At zero coverage, the $Q_d$ values range from 15.7 to 21.7 kJ mol$^{-1}$ (SI Figure S10).

### 3.4. Gas Selectivity Studies

The preferential binding of the herein reported polymers for CO$_2$ over CH$_4$ and N$_2$ was evaluated by using the initial slope calculations and ideal adsorbed solution theory (IAST). Pure gas isotherms for CO$_2$, CH$_4$, and N$_2$ were collected at 273 and 298 K up to 1 bar. The initial slope ratios were estimated from Henry’s law constants from single-component adsorption isotherms collected at the same temperature. Furthermore, the IAST method was applied at 298 K to predict the adsorption selectivity for gas mixtures based on pure components gas isotherms.

The selectivities from IAST were calculated for gas mixture composition of CO$_2$/N$_2$ (10:90) and CO$_2$/CH$_4$ (50:50) at 298 K and were found to be in good agreement with the selectivity values obtained from initial slope calculations as given in Table 3. Accordingly, these calculations were performed to evaluate the impact of the controlled acid-catalyzed synthesis strategy on the selectivity of BILP-15(AC) and BILP-16(AC). From initial slope calculations at 273 K/298 K, notable change in CO$_2$/N$_2$ selectivity values was observed for BILP-15(AC) (61/50) compared to BILP-15 (83/63).

The notable decrease in selectivity can be attributed to the much higher surface area and slightly larger pores of BILP-15(AC) which can be more accessible for nitrogen molecules. In contrast, only a slight change in CO$_2$/N$_2$ selectivity was noted for BILP-16 and BILP-16(AC) because of their similar textural properties (i.e., surface area and pore size). These values indicate that the impact of the controlled acid-catalyzed strategy on the selectivity of BILP-15 is more pronounced compared to BILP-16. The CO$_2$/N$_2$ selectivity values calculated by IAST at 298 K were consistent with initial slope calculations. Moreover, CO$_2$/CH$_4$ selectivity values for all polymers fall in the range of 6 to 10. Both CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivities are within the ranges reported for other BILPs. Our calculations reveal a trade-off between selectivity and CO$_2$ uptake, which is more pronounced for the most porous polymer, BILP-15(AC), reported in this study.

In conclusion, we have synthesized new BILPs and optimized their surface area by controlling polymerization rates using catalytic amounts of HCl. The impact of acid was studied by varying acid concentrations and molar ratios between the acid and aryl-$o$-diamine unit. It was found that using 2 equiv of 0.22 M HCl could catalyze the polymerization process and optimize the surface area of BILPs. According to gas adsorption measurements, the surface area of BILPs prepared under controlled acid concentrations improve significantly; BILP-15(AC) (92%) and BILP-16(AC) (47%), when compared to BILPs prepared by conventional methods. However, the CO$_2$ selectivity and binding affinity of the polymers are compromised.
ASSOCIATED CONTENT
Supporting Information
Synthetic scheme, TGA, PXRD, FTIR, solid state NMR, isotherms collected at 298 K, virial fitting plots, initial slope fitting plots, IAST details, and Langmuir fitting parameters and plots. This material is available free of charge via the Internet at http://pubs.acs.org/.

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REFERENCES
(22) Zou, X.; Ren, H.; Zhu, G. Topology-directed design of porous organic frameworks and their advanced applications. Chem. Commun. 2013, 49 (38), 3925.


