Synthesis and Characterization of Porous Benzimidazole-Linked Polymers and Their Performance in Small Gas Storage and Selective Uptake

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ABSTRACT: Porous organic polymers containing nitrogen-rich building units are among the most promising materials for selective CO₂ capture and separation which can have a tangible impact on the environment and clean energy applications. Herein we report on the synthesis and characterization of four new porous benzimidazole-linked polymers (BILPs) and evaluate their performance in small gas storage (H₂, CH₄, CO₂) and selective CO₂ binding over N₂ and CH₄. BILPs were synthesized in good yields by the condensation reaction between aryl-aldehyde building blocks. The resulting BILPs exhibit moderate surface area (S BET = 599–1306 m² g⁻¹), high chemical and thermal stability, and remarkable gas uptake and selectivity. The highest selectivity based on initial slope calculations at 273 K was observed for BILP-2: CO₂/N₂ (113) and CO₂/CH₄ (17), while the highest storage capacity was recorded for BILP-4: CO₂ (24 wt % at 273 K and 1 bar) and H₂ (2.3 wt % at 77 K and 1 bar). These selectivities and gas uptakes are among the highest by porous organic polymers known to date which in addition to the remarkable chemical and physical stability of BILPs make this class of material very promising for future use in gas storage and separation applications.

KEYWORDS: carbon dioxide capture, hydrogen storage, gas separation, porous polymers, natural gas purification

1. INTRODUCTION

Recent advances in porous materials design and synthesis have provided purely organic and organic–inorganic hybrid architectures with promising potential in gas storage and separation, catalysis, drug delivery, and sensing. Among this large and diverse library of porous materials are purely organic discrete cage molecules and porous organic networks such as MOFs, for example, were attributed to their subnano pore dimensions and imidazole-functionalized pore walls that allow selective CO₂ capture and storage. These textural properties of BILPs resulted in the highest CO₂ uptake by porous organic materials (5.12 mmol g⁻¹), high CO₂ isosteric heats of adsorption (~28 kJ mol⁻¹), and high CO₂/N₂ selectivity (70). Tailoring materials with such properties is very challenging especially for purely organic discrete molecules. 

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or porous organic networks in which high CO₂ selectivity often compromises its uptake.

Herein we report on the template-free synthesis and characterization of four new BILPs and demonstrate their potential in small gas storage and selective uptake applications. The results from this study indicate that this synthetic approach can lead to new polymers with increased CO₂ storage capacity and selectivity exceeding values reported for previous BILPs.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. All starting materials and solvents, unless otherwise noted, were obtained from Acros Organics and used without further purification. 1,2,4,5-Benzentetramine tetrahydrochloride (BTA), triptycene, and chloroform (stabilized with amylene) were purchased from Aldrich Chemical Co. and used without further purification. Terephthalaldehyde (TPAL) was purchased from Acros Organics. Solvents were dried by distillation from Na (toluene) or Na/benzophenone (THF). Tetrais(4-formylphenyl)methane (TFFP), 2,3,6,7,10,11-hexaaminotriphenylene (HATP) 38 and 2,3,6,7,14,15-hexamino-triphtyene (HATT) 38 were synthesized according to published methods. Air-sensitive samples and reactions were handled under an inert atmosphere of nitrogen using either glovebox or Schlenk line techniques. Chromatographic separations were performed using standard flash column chromatography methods using silica gel (60 Å, 35–70 μm). Elemental microanalyses were performed at the Midwest Microlab, LLC. Liquid 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 CPMAS experiment. All samples were spun at 7.0 kHz. Thermogravimetric analysis (TGA) were carried out using a TA Instruments Q-5000IR thermal gravimetric analyzer with samples held in 50 μL platinum pans under an atmosphere of air (heating rate 5 °C/min). For Scanning Electron Microscopy imaging (SEM), 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 Panalytical X’pert pro multipurpose diffractometer (MPD). 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 a Nicolet-Nexus 670 spectrometer. Porosity and gas sorption experiments were collected using a Quantochrome Autosorb 1-C volumetric analyzer using adsorbates of UHP grade. In a typical experiment, a sample of BILP (~ 60 mg) was loaded into a 9 mm large bulb cell (from Quantochrome) of known weight and then hooked up to the Autosorb 1-C and degassed at 120 °C for 12 h. The degassed sample was refilled with nitrogen, weighed precisely, and then transferred back to the analyzer. The temperatures for adsorption measurements were controlled by using a refrigerated bath of liquid nitrogen (77 K), liquid argon (87 K), or temperature controlled water bath (273 K and 298 K).

2.2. Synthetic Aspects. 2.2. Synthesis of 1,3,5-Tris-(4-formylphenyl)benzene (TFFP). 1,3,5-Tris-(4-bromophenyl)-benzene 39 (1.48 g, 2.73 mmol) was dissolved in dry THF (200 mL) under a N₂ atmosphere for 120 s before imaging. Images were taken on a Hitachi S-4700 scanning electron microscope. The mixture was stirred overnight, while the temperature was allowed to rise to 25 °C. The milky opaque mixture was acidified with aqueous 3 M HCl (46 mL). The organic volatiles were partially removed by evaporation under reduced pressure and extracted with CHCl₃. The organic phase was washed with water, dried over MgSO₄, and filtered. Volatiles were removed under reduced pressure, and the crude light yellow product was further purified by silica gel column using CH₂Cl₂: as eluent to afford colorless crystals in 51% yield (540 mg, 1.38 mmol) upon concentration. 1H NMR (CDCl₃, 300 MHz) δ (ppm) 10.11 (s, 3H), 8.04 (d, J_H_H = 9.0, 6H), 7.91 (s, 3H), 7.88 (d, J_H_H = 9.0, 6H). 13C NMR (CDCl₃, 75 MHz) δ (ppm) 192.0, 146.5, 141.8, 136.0, 130.7, 128.2, 126.7.

Synthesis of BILP-2. A 100 mL Schlenk flask was charged with 90 mg (0.17 mmol) of 3,6,7,10,11-hexaaminotriphenylene (hexahydrochloride salt form) and 30 mL of anhydrous DMF. The solution was cooled to ca. –30 °C, and a solution of terephthalaldehyde (34 mg, 0.25 mmol) in anhydrous DMF (15 mL) was added dropwise. Temperature was maintained around –30 °C until a brown solid product formation completed and then allowed to rise to room temperature and kept for overnight. The flask containing the reaction mixture of brown solids was flushed with air for 10 min and capped. The reaction mixture was then heated in an oven at 130 °C for 3 days to afford a fluffy yellow polymer which was isolated by filtration over a glass frit and subsequently washed with DMF, acetone, water, and acetone in succession. During acid and base treatments, the polymers were soaked for ~5 min. The product was then immersed in acetone/CH₂Cl₂ (1:1, v/v) for one day, during which the activation solvent was decanted and freshly replenished twice. After filtration, the product was dried under vacuum to give BILP-2 (56 mg, yield 72%) as a bright yellow fluffy solid. Anal. Calc. for C₉₀H₆₆N₂₀.H₂O: C, 70.17; H, 4.12%; N, 16.37%. Found: C, 69.42%; H, 4.46%; N, 14.90%.

Synthesis of BILP-4. This polymer was synthesized following the same method described above for BILP-2 using 1,2,4,5-benzentetramine tetrahydrochloride (40 mg, 0.14 mmol) and tetrakis(4-formylphenyl)methane (30 mg, 0.07 mmol). After drying, the final product BILP-4 was obtained as a yellowish brown fluffy solid (40 mg, 91% yield). Anal. Calc. for C₇₂H₄₄N₂₀.H₂O: C, 66.84; H, 4.92%; N, 15.21%. Found: C, 67.04%; H, 4.31%; N, 14.00%.

Synthesis of BILP-5. This polymer was synthesized following the methods mentioned above for BILP-2 using 1,2,4,5-benzentetramine tetrahydrochloride (200 mg, 0.70 mmol) and 1,3,5-(4-formylphenyl)benzene (183 mg, 0.47 mmol). After drying, the final product BILP-5 was obtained as a yellowish brown fluffy solid (180 mg, 72% yield). Anal. Calc. for C₇₄H₄₄N₂₀.H₂O: C, 73.08; H, 4.60%; N, 14.20%. Found: C, 72.67%; H, 4.47%; N, 12.64%.

Synthesis of BILP-7. This polymer was synthesized following the methods mentioned above for BILP-2 using 1,2,4,5,15-hexamino-triphtyene (hexahydrochloride salt form) (100 mg, 0.18 mmol) and 1,3,5-(4-formylphenyl)benzene (69 mg, 0.18 mmol). After drying, the final product BILP-7 was obtained as a yellow fluffy solid (89 mg, 73% yield). Anal. Calc. for C₇₄H₄₄N₂₀.H₂O: C, 77.46; H, 4.43%; N, 11.53%. Found: C, 77.96%; H, 4.79%; N, 10.91%.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of BILPs. The synthesis of all BILPs reported in this study was conducted by using the condensation method we reported recently for BILP-1, BILP-3, and BILP-6. 37,38 This synthetic avenue is based on the condensation reaction between a variety of aryl-o-diamine and aryl-aldehyde building units given in Figure 1. The 2D and 3D building blocks were synthesized according to literature methods as described above in the Materials and Methods section.

In a typical experiment for the preparation of BILPs, a dropwise treatment of a suspension of the amine-containing building units (HCl-salt form) in DMF with a homogeneous solution of the corresponding aldehyde building blocks dissolved in DMF over a period of 3 h at ~30 °C followed by stirring at room temperature for 6 h afforded yellow suspensions that are believed to be imine-linked oligomers. The resulting suspensions were bubbled with oxygen (air) for about
30 min and then heated in a sealed Schlenk flask at 130 °C for 3 days to afford the corresponding BILPs (Figure 2) as yellow powders in good yields after filtration and drying at 120 °C and 1.0 × 10^-5 Torr for 12 h. We have noticed that the slow addition of the aldehyde source and the use of DMF increase initial oligomer solubility and prevent their premature precipitation which enhances pore formation and therefore the overall porosity.41,42 The formation of the imidazole ring proceeds through a rapid formation of imine-linkage followed by cyclization assisted by molecular oxygen.43,44 All resulting polymers exhibit excellent chemical stability that allow for their handling and purification under ambient conditions. The purification of BILPs involved washing with 2 M aqueous HCl and NaOH and subsequently by water and acetone. The use of HCl followed by NaOH was intended to cleave potentially imine-linked materials and to solubilize unreacted amine-containing starting materials, respectively. Subsequent washing with water then acetone and drying under reduced pressure prepared the resulting polymers for spectral, analytical, and porosity studies.

BILPs are insoluble in common organic solvents such as tetrahydrofuran, dimethylformamide, dichloromethane, methanol, and acetone; they also remain intact upon washing with a 2 M aqueous solution of HCl or NaOH which reflects their high chemical stability. Washings with acid or base result in slight color change temporarily; however, further washing with water recovers the yellow color, suggesting protonation or deprotonation of benzimidazole NH under acidic or basic condition. The chemical composition was first determined by microelemental analysis which showed that nitrogen atoms are involved in hydrogen bonding with water molecules as previously reported for BILPs37,38 and the imine-linked COF-300.45 This was further supported by thermogravimetric analysis (TGA) which showed initial weight losses up to around 100 °C followed by decomposition at ∼400 °C (Figure S1).46 Scanning electron microscopy (SEM) of the polymers revealed aggregated particles of variable size. The aggregated morphology differs for different BILPs: BILP-2 has aggregated particles in 0.4−0.6 μm, BILP-4 and BILP-5 possess spherical aggregation in 3−6 μm, and BILP-7 has spherical aggregation (0.3−0.35 μm) to form coral reef-type morphology (Figure 3).

As expected, all BILPs are amorphous as evidenced by powder X-ray diffraction studies (Figure S3). The chemical connectivity and the formation of the imidazole ring were confirmed by FT-IR and solid-state 13C NMR spectroscopy. The FT-IR spectra of BILPs (Figure 4) contain N−H stretching at around 3415 cm⁻¹ (free N−H) and 3215 cm⁻¹ (hydrogen bonded N−H), while new bands appeared at 1612 cm⁻¹ (C=O), and 1495 and 1435 cm⁻¹ which can be assigned to skeleton vibration of the benzimidazole ring.47 The new bands at around 1355 cm⁻¹ can be assigned to C−N stretching for the benzimidazole ring, while the bands at 1637 cm⁻¹ are due to N−H bending. Other bands such as those at ∼2870−3050 cm⁻¹ are due to aromatic C=H stretching, while the bands ∼1700 cm⁻¹ can be ascribed to residual C==O stretching from terminal aldehyde functional groups on the surface of BILPs’ particles.

Figure 1. Molecular building blocks used for the synthesis of BILP-2, BILP-4, BILP-5, and BILP-7.

Figure 2. Schematic representations of the resulting BILP networks formed by condensation reactions. BILP-2 (TPAL/HATP), BILP-4 (BTA/TFPM), BILP-5 (TFPB/BTA), and BILP-7 (BTA/HATT).

Figure 3. Scanning electron microscopy (SEM) images of BILP-2 (A), BILP-4 (B), BILP-5 (C), and BILP-7 (D).
The $^{13}$C CP-MAS NMR spectra of BILPs confirm their successful synthesis with the characteristic peaks (Figure S5 and Table S1 in the Supporting Information). The peaks around 153, 151, 152, and 151 ppm, in BILP-2, BILP-4, BILP-5, and BILP-7, respectively, correspond to N\textsubscript{C}(Ph)N in benzimidazole units. These are consistent with the values observed for isolated benzimidazole rings\textsuperscript{48,49} and our recently reported BILP-1 (151 ppm), BILP-3 (152 ppm), and BILP-6 (151 ppm)\textsuperscript{37,38}. These peaks are in sharp contrast to those reported for imine-linked frameworks that exhibit downfield shifted signals in the range of 158 to 160 ppm\textsuperscript{41,42,45}. Additional signals in the aromatic or aliphatic ranges are consistent with the building units employed for the synthesis of the respective BILPs.

3.2. Porosity Measurements and Gas Storage Studies.

The porosity of BILPs was investigated by argon uptake measurements. Figure 5A shows the argon adsorption and desorption isotherms for the BILPs at 87 K. The isotherms (Type-I) are fully reversible and show a rapid uptake at low pressure (0−0.1 bar) indicating a permanent microporous nature, while the minor hysteresis observed for all materials is consistent with the powdery nature of all BILPs. Applying the Brunauer−Emmett−Teller (BET) model within the pressure range of $P/P_0 = 0.01−0.15$ resulted in apparent surface areas $S_{\text{ABET}}$ of 1135 m$^2$ g$^{-1}$ (BILP-2), 708 m$^2$ g$^{-1}$ (BILP-4), 599 m$^2$ g$^{-1}$ (BILP-5), and 1122 m$^2$ g$^{-1}$ (BILP-7). It has been noticed that the BILPs prepared using 3D building blocks generally possess higher surface areas compared with those prepared using 2D building blocks. This tendency may arise due to favorable π−π stacking in 2D polymers which can also be facilitated by hydrogen bonding between the benzimidazole moieties. Network catenation of purely organic materials can lead to a markedly lower surface area and pore volume as in the case of the imine-linked 3D COF-300 and molecular organic cages. In spite of their amorphous nature, BILPs are considerably porous, and their surface areas are in line with a wide range of porous organic networks such as microporous organic polymers (MOP-A, 4077 m$^2$ g$^{-1}$)\textsuperscript{2a}, PIMs (618−1760 m$^2$ g$^{-1}$)\textsuperscript{47}, cage compounds (1375 m$^2$ g$^{-1}$)\textsuperscript{19}, imine-linked microporous polymer organic frameworks (POFs, 466−1521 m$^2$ g$^{-1}$)\textsuperscript{41}, covalent organic frameworks (COF-300, 1360 m$^2$ g$^{-1}$)\textsuperscript{45}, diimide-based polymers (750−1407 m$^2$ g$^{-1}$)\textsuperscript{50,51a}, functionalized conjugated microporous polymer (CMP) networks (522−1043 m$^2$ g$^{-1}$)\textsuperscript{46} and porous electron-rich covalent organonitridic frameworks (PECONFs, 499−851 m$^2$ g$^{-1}$)\textsuperscript{52}. The potential impact of network interpenetration and cross-linking on the porous nature of BILPs was evident from the pore size distribution (PSD) studies using nonlocal density functional theory (NLDFT). PSD was estimated by fitting the uptake branches of the argon isotherms with NLDFT and found to be centered around 6.8 Å (Figure 5B), while pore volume was calculated from single point measurements ($P/P_0 = 0.95$) and found to be 0.49, 0.65, 0.36, and 0.74 cc g$^{-1}$ for BILP-2, BILP-4, BILP-5, and BILP-7, respectively. The results from PSD studies indicate that the current template-free synthetic strategy used for all BILPs provides very little control over pore metrics, and therefore developing new synthetic avenues would be required to systematically vary pore size.

In addition to Ar porosity measurements, we have also collected N$_2$ isotherms at 77 K (Figure S10). Typically, the use of Ar is preferred especially for studying ultrafine porous materials because Ar has more pore accessibility as a result of its small size. Therefore, the use of Ar can provide more accurate estimates of both pore size distribution and surface area values.

Figure 5. Gas uptake isotherms Ar (A), PSD from NLDFT (B), CO$_2$ (C), $Q_{\text{st}}$ for CO$_2$ (D), $Q_{\text{st}}$ for H$_2$ (F), $Q_{\text{st}}$ for CH$_4$ (G), and $Q_{\text{st}}$ for CH$_4$ (H). Adsorption (filled) and desorption (empty).
reversibly adsorbed by all BILPs reported here. It is worth noting that BILP-4 has the highest CO2 uptake at 235 mg g−1 (273 K/1 bar) which is slightly higher than that of BILP-3 (225 mg g−1) under similar conditions, which is to the best of our knowledge, the highest by porous organic polymers and rivals those of the best performing MOFs.1,2,3

Accordingly, to investigate the impact of these factors on the uptake of small gases such as H2 and CO2 and the preferential CO2 binding over N2 and CH4 we collected H2, CO2, and CH4 isotherms (Figure S5) and calculated their respective isosteric enthalpies of adsorption (Qst) as summarized in Table 1 and compared these results to those of recently reported BILPs. The CO2 isotherms (Figure S5C) are fully reversible and exhibit a steep rise at low pressures. The absence of adsorption-desorption hysteresis indicates that CO2 is reversibly adsorbed by all BILPs reported here. It is worth mentioning that BILP-4 has the highest CO2 uptake at 235 mg g−1 (273 K/1 bar) which is slightly higher than that of BILP-3 (225 mg g−1) under similar conditions, which is to the best of our knowledge, the highest by porous organic polymers and rivals those of the best performing MOFs.1,2,3

The lowest uptake was recorded for BILP-5 (3.3 mmol g−1) which also has the lowest surface area (SA = 599 m2 g−1). The CO2 uptakes exceed those reported for activated carbon and porous organic materials in general. For example, the uptake of BILP-4 (5.3 mmol g−1 at 273 K/1 bar) is higher than those by BPL carbon (3.3 mmol g−1),5 COFs (1.3–3.8 mmol g−1),6 functionalized CMPS (1.6–1.8 mmol g−1),7,8 −OH functionalized POFs (4.2 mmol g−1),9 triptycene-based cage compounds (2.1 mmol g−1),26a and cucurbit[6]uril (2.9 mmol/g).26b They also outperform most of the MOFs (13–15) and ZIFs.8

To determine the binding affinity of BILPs for CO2, we calculated the Qst for CO2 in BILPs using the virial method (Figure S13).5,4 As shown in Figure S5D, the Qst values at zero coverage fall relatively in a very narrow range (26.7–28.8 kJ mol−1) and drop with higher loading. These values are much lower than those reported for organic polymers in general but higher than those of nitrogen-rich networks PECONFs (26–34)11 or PF-1 (34)15 and are comparable to CO2 selective MOFs14,15,56–59 which generally feature −NH2 or −OH functionalized pores. The high CO2 uptake and binding by BILPs is expected to arise from strong interactions of the polarizable CO2 molecules through hydrogen bonding and/or dipole−quadrupole interactions that utilize the protonated and proton-free nitrogen sites of imidazole rings, respectively.1,4,6,6a

The readily reversible sorption/desorption behavior and moderate Qst indicate that CO2 interactions with pore walls are weak enough to allow for material regeneration without applying heat. This is attractive because materials that have high acidic or basic sites usually display high CO2 affinities and require energy input (in the form of heat) to regenerate their active sites as in the case of primary alkanolamine MEA.62

We have also considered BILPs in hydrogen and methane storage studies because both gases are highly attractive candidates for use in automotive applications as a result of their abundance and clean aspect. The hydrogen uptakes for BILPs (1.8–2.3 wt %) at 77 K and 1 bar (Figure S5E) are among the highest values reported for microporous organic polymers.7,29 The Qst for H2 was calculated from adsorption data collected at 77 and 87 K (Figure S14). At zero coverage, the Qst values for BILPs are 7.8–8.3 kJ mol−1 (Figure S5F). The Qst are higher than the values reported for organic polymers such as polyimide networks (5.3–7.0 kJ mol−1),50 COFs (6.0–7.0 kJ mol−1),50a porous aromatic frameworks (PAF-1, 4.6 kJ mol−1),53 porous polymer networks (PPNs, 5.5–7.6 kJ mol−1),60 oligo−OH functionalized POFs (8.3 kJ mol−1)29 and tetrazine-based organic frameworks (TzFs, 7.8–8.2 kJ mol−1).65 Additionally, the H2 uptakes and Qst compete with the best known MOFs for hydrogen storage under similar conditions.10–12 Similarly, we recorded CH4 uptakes at 273 and 298 K up to 1 bar (Figure S5G). Again, both isotherms are completely reversible and exhibit a steep rise at low pressure and then reach maxima of 14–27 mg g−1 at 273 K and 9–19 mg g−1 at 298 K. The Qst for CH4 was calculated by using adsorption data collected at 273 and 298 K. At zero coverage, the Qst is 13.0–18.4 kJ mol−1 (Figure 6, Figure S16).

3.3. Gas Selectivity Studies. Based on our recent studies which demonstrated that BILPs can have good CO2 uptake and selectivity over N2 and CH4, we anticipated the new BILPs prepared in this study to have similar properties. We decided to compare the CO2 uptake and selectivity over N2 and CH4 to evaluate the potential use of BILPs in gas separation applications. The selectivity of BILPs toward CO2 over N2 and CH4 was investigated by collecting gas isotherms at 273 K and 0–1 bar (Figure 6). The initial steep rise in CO2 compared to N2 and CH4 can be attributed due to more favorable interactions of CO2 with the accessible nitrogen sites of imidazole moieties. Noteworthy, at 273 K and 0.15 bar, which is a typical partial pressure of CO2 in flue gas, the CO2 uptake is 1.45 mmol/g, whereas that of N2 is only 0.031 mmol/g for BILP-2. This preferential higher affinity for CO2 by BILPs is very attractive in gas separation applications. One of the common methods to calculate gas adsorption selectivity involves the use of initial slope ratios estimated from Henry’s law constants for single-component adsorption isotherms.1,4,6

This method has been widely applied for organic and inorganic hybrid materials including COFs, MOFs, ZIFs, porous carbons, and cage molecules. In spite of its common use, this method

### Table 1. Gas Uptake and Selectivity (CO2/N2 and CO2/CH4) for BILPs

<table>
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<th>polymer</th>
<th>SA_{BET}/SA_{Lang}</th>
<th>H2 at 1 bar</th>
<th>CO2 at 1 bar</th>
<th>CH4 at 1 bar</th>
<th>N2 at 1 bar</th>
<th>selectivity</th>
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<tr>
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<td>14</td>
<td>7.9</td>
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<td>10</td>
<td>8.0</td>
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<td>16</td>
<td>7.8</td>
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<td>10</td>
<td>8.3</td>
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<tr>
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<td>14</td>
<td>8.3</td>
<td>193</td>
<td>122</td>
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</table>

*Surface area (m2 g−1) was calculated from Ar isotherm. †Gas uptake in mg g−1 and the isosteric enthalpies of adsorption (Qst) in kJ mol−1. Selectivity (mol mol−1) was calculated from initial slope calculations at 273 K and (298 K). Reference 37. Reference 38.

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which employs single-component isotherms cannot give the actual gas selectivity because selectivity factors do not take into consideration other factors such as competition of gas molecules for adsorption sites. However, the selectivity calculations from single-component isotherms are useful and convenient to compare the performance of different porous materials in selective adsorption. Thus, based on initial slope calculations in the pressure range below 0.15 bar (Figure S17), the adsorption selectivity for CO$_2$ over N$_2$ and CH$_4$ was calculated, and the data are provided in Table 1 which also contains results for selectivity studies at 298 K (Figures S16 and S17). The highest selectivity was obtained for BILP-2 (113) and then BILP-5 (95) at 273 K. The exceptionally high selectivity was recorded for BILP-2 (17 at 273 K and 12 at 298 K). The other BILPs have much lower selectivities: 8−10 (273 K) and 5−7 (298 K). The performance of BILP-2 competes with those of diimide-based organic polymers$^{51}$ and most MOFs.$^{16,17}$

Figure 6. Gas sorption capacities for BILP-2, BILP-4, BILP-5, and BILP-7 at 273 K. CO$_2$ (black square), CH$_4$ (red circle), and N$_2$ (blue triangle).

4. CONCLUSION
To conclude we have prepared four new BILPs and investigated their potential in small gas storage and separation. Varying the amine- and aldehyde-containing building blocks afforded polymers with subnanometer pore apertures and moderate surface areas which indicate that the current synthetic approach does not provide precise control over pore metrics. The resulting BILPs are chemically and thermally stable, and the best performing member can exhibit very high CO$_2$ uptake (up to 5.3 mmol g$^{-1}$) and remarkable selectivities based on initial slope calculations: CO$_2$/N$_2$ (113 at 273 K) and CO$_2$/CH$_4$ (17 at 273 K). These results highlight the potential of BILPs in postcombustion CO$_2$ capture and separation. BILPs also can store up to 2.3 wt % of hydrogen at 77 K/1 bar with relatively higher isosteric heats of adsorption (7.8−8.3 kJ mol$^{-1}$) compared to nonfunctionalized organic polymers. We are currently conducting high pressure gas uptake and selectivity studies on BILPs.

ASSOCIATED CONTENT
Supporting Information
Experimental procedures, characterization methods, and gas sorption studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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