Electronic Supplementary Information

High CO₂ Uptake and Selectivity by Triptycene-Derived Benzimidazole-Linked Polymers

Mohammad Gulam Rabbani, Thomas E. Reich, Refaie M. Kassab, Karl T. Jackson, Hani M. El-Kaderi*

Department of Chemistry, Virginia Commonwealth University,
1001 W. Main Street, Richmond, Virginia 23284-2006

*To whom correspondence should be addressed. E-Mail: helkaderi@vcu.edu

Table of Contents

Section S1  Synthetic Procedures  2
Section S2  Thermogravimetric Analysis  15
Section S3  Scanning Electron Microscopy Imaging (SEM)  16
Section S4  XRD-pattern for BILPs  17
Section S5  FT-IR Spectroscopy of Starting Materials and BILPs  18-19
Section S6  ¹³C Nuclear Magnetic Resonance Studies for BILPs  20
Section S7  Low Pressure (0 – 1.0 bar) Gas Adsorption Measurements for BILPs  21
**Section S1: Synthetic Procedures**

**General Synthetic Procedures**

All starting materials and solvents, unless otherwise noted, were obtained from the Aldrich Chemical Co. and used without further purification. The air sensitive samples and reactions were handled under an inert atmosphere of nitrogen using either glovebox or Schlenk line techniques. Elemental microanalyses were performed at the Midwest Microlab, LLC. $^{13}$C cross-polarization magic angle spinning (CP-MAS) NMR measurements were recorded by Spectral Data Services, Inc.
Scheme S1: Synthetic routes for 2,3,6,7,14,15-hexaaminotriptycene

Previous routes: Route-1 in reference 1
Route-2 in reference 2
Scheme 2: Synthesis of 2,3,6,7,14,15-hexaaminotriptycene (HATT) (Route-3, this work)

2,3,6,7,14,15-Hexabromotriptycene (2). This compound was synthesized according to a published method. Recrystallization from hot chloroform yielded a white solid (4.0 g, 69%). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 5.23 (s, 2H), 7.62 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) 144.2, 129.3, 122.0, 51.3.

N$_2$N$_3$N$_6$N$_7$N$_{14}$N$_{15}$-Hexakis(diphenylmethylene)triptycene-2,3,6,7,14,15-hexaamine (3): Tris(dibenzylideneacetone)dipalladium(0) (614 mg, 0.67 mmol) and rac-BINAP (840 mg, 1.36 mmol) were charged in a 250 mL Schlenk flask under nitrogen atmosphere and 70 mL of anhydrous toluene was added. The solution was then stirred at 110 °C for 30 min under N$_2$ atmosphere then cooled to room temperature. To the resultant solution was added benzophenone imine (3.60 mL, 21.4 mmol), 2 (2.00 g, 2.75 mmol), sodium tert-butoxide (2.06 g, 21.4 mmol), and the mixture was stirred at 110 °C overnight. The resultant solution was cooled to room temperature, diluted with CH$_2$Cl$_2$ then filtered through a filter paper (Whatman®, 55 mm ø) and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on silica gel with AcOEt/hexane (1:4) as the eluent. The second fraction was collected and evaporated to dryness to give an orange solid. Recrystallization of this solid from EtOAc/EtOH afforded 3 as a yellowish-orange crystalline solid (3.06 g, 84%). $^1$H
NMR (300 MHz, CDCl₃) δ (ppm) 7.62 (d, j = 6.0 Hz, 12H, o–Ph CH), 7.23-7.40 (m, 24H, m–Ph CH (12H), p–Ph CH (6H+6H)), 7.13 (t, j = 9.0 Hz, 12H, m–Ph CH), 6.60 (d, j = 6.0 Hz, 12H, o–Ph CH), 6.35 (s, 6H, triptycene aromatic CH), 4.36 (s, 2H, triptycene aliphatic CH). 13C NMR (75 MHz, CDCl₃) δ (ppm) 166.9, 141.0, 140.9, 137.5, 137.1, 130.2, 129.8, 129.4, 128.7, 128.0, 117.2, 52.7. TOF MS ES+ m/z for C₉₈H₆₈N₆: [M + H]⁺ found 1330.48, calcd 1330.56. IR (KBr pellet): ν (cm⁻¹) 3418 (br), 3081 (w), 3055 (s), 2955 (w), 2928 (vw), 2869 (vw), 1954 (vw), 1891 (vw), 1812 (vw), 1769 (vw), 1623 (s, br), 1597 (sh), 1575 (m), 1491 (m), 1458 (m), 1445 (s), 1395 (w), 1316 (s), 1287 (s), 1180 (m), 1133 (m), 1075 (m), 1043 (m), 1028 (m), 1001 (w), 957 (s), 912 (m), 889 (w), 846 (w), 784 (s), 694 (vs). Anal. Calcd. for C₉₈H₆₈N₆: C, 88.52; H, 5.15; N, 6.32. Found: C, 88.27; H, 5.28; N, 6.25%.

2,3,6,7,14,15-Hexaaminotriptycene (HATT): 2.0 M aqueous HCl solution (1.7 mL, 3.4 mmol) was added to a THF solution (22 mL) of 3 (500 mg, 0.38 mmol) and the mixture was stirred at room temperature for 0.5 h. The precipitate was isolated by filtration, washed with THF and hexane, and dried under vacuum to give the hexaammoniumtriptycene hexachloride salt (4) as an off-white solid (216 mg, 95%). 1H NMR (300 MHz, DMSO-d₆) δ (ppm) 6.99 (s, 6H, triptycene aromatic CH), 5.26 (s, 2H, triptycene aliphatic CH). 1H NMR (300 MHz, D₂O) δ (ppm) 7.23 (s, 6H, triptycene aromatic CH), 5.52 (s, 2H, triptycene aliphatic CH). 13C NMR (75 MHz, D₂O) δ (ppm) 142.9, 124.6, 118.5, 50.6. TOF MS ES+ m/z for C₂₀H₂₂N₆Cl₆.0.5THF: [M + H]⁺ found 345.18, calcd 345.18. Anal. calcd for C₂₀H₂₆N₆Cl₆.05THF: C, 44.10; H, 5.05; N, 14.02. Found: C, 43.92; H, 5.04; N, 13.45%.

The neutralization of 4 was carried out by stirring a suspension of 4 (88.0 mg, 0.15 mmol) in THF (4 mL) with 1.0 M aqueous NaOH solution (1.0 mL, 1.0 mmol). The resulting solid was filtered, washed with THF and hexane, and dried under vacuum to give HATT as an off-white solid (~60 mg). 1H NMR (300 MHz, DMSO-d₆) δ (ppm) 6.44 (s, 6H, triptycene aromatic CH), 4.50 (s, 2H, triptycene aliphatic CH), 4.01 (s, 12H, NH₂). 13C NMR (75 MHz, DMSO-d₆) δ (ppm) 137.6, 130.6, 111.4, 51.9. TOF MS
ES+ m/z for C\textsubscript{20}H\textsubscript{20}N\textsubscript{6}: [M + H]\textsuperscript{+} found 345.00, calcd 345.18; [M + Na]\textsuperscript{+} found 366.97, calcd 367.16.

IR (KBr pellet): ν (cm\textsuperscript{-1}) 3380 (sh), 3325 (s), 3211 (sh), 3004 (vw), 2945 (w), 2870 (vw), 2683 (vw), 1633 (s), 1589 (s), 1479 (vs), 1442 (w), 1332 (m), 1298 (m), 1196 (w), 1049 (w), 881 (m), 747 (m), 611 (s). Anal. calcd for C\textsubscript{20}H\textsubscript{20}N\textsubscript{6}.1.8NaCl: C, 53.43; H, 4.48; N, 18.69. Found: C, 53.50; H, 4.80; N, 17.47%.

Note: **HATT** is air sensitive and changes color to light pink upon exposure to air (presumably due to amine oxidation) and therefore we used its HCl-slat form (4) in subsequent polymerization steps.
Synthesis of benzimidazole-linked polymers (BILPs)

Synthesis of BILP-3: A 100 mL Schlenk flask was charged with 4 (87 mg, 0.15 mmol), 30 mL of anhydrous DMF, and a stir-bar. The resultant solution was cooled to ca. -30 °C and treated drop-wise with a solution of Tetrakis(4-formylphenyl)methane, TFPM (50 mg, 0.12 mmol) in anhydrous DMF (15 mL). The temperature was maintained around -30 °C for 6 hours during which a yellowish brown solid formed then the resultant slurry solution was left to warm to room temperature overnight. The flask containing the reaction mixture was flushed with air for 10 minutes and capped tightly. The reaction mixture was then transferred to a static oven and heated gradually to 130 °C (0.5 °C/min) and kept for 3 days to afford a fluffy yellow polymer (see image insert). The solid was isolated by filtration over a medium glass frit and subsequently washed with DMF, acetone, water, 0.5M HCl, 0.5M NaOH, water, and acetone. 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 at 120 °C under vacuum (150 mTorr) to give BILP-3 as a fluffy
yellow solid (70 mg, 75%). Anal. Calcd. for C_{167}H_{92}N_{24}.24H_{2}O: C, 69.96%; H, 4.92%; N, 11.92%. Found: C, 69.21%; H, 4.69%; N, 9.96%.

**Synthesis of BILP-6:** In a fashion similar to the preparation of BILP-3, a 100 mL Schlenk flask was charged with 4 (90 mg, 0.16 mmol), 30 mL of anhydrous DMF, and a stir-bar. The resultant solution was cooled to ca. -30 ºC then treated drop-wise with a solution of terephthalaldehyde (32 mg, 0.24 mmol) in anhydrous DMF (15 mL). The temperature was maintained around -30 ºC for 6 hours during which a yellowish brown solid product formed then the resultant slurry solution was left to warm to room temperature overnight. The flask containing the reaction mixture was flushed with air for 10 minutes and capped tightly. The reaction mixture was then transferred to a static oven and heated gradually to 130 ºC (0.5 ºC/min) and kept for 3 days to afford a fluffy yellow polymer which was isolated by filtration over a medium glass frit and subsequently washed with DMF, acetone, water, 0.5M HCl, 0.5M NaOH, water, and acetone. The product was then immersed in acetone/CH_{2}Cl_{2} (1:1 v/v) for one day, during which the activation solvent was decanted and freshly replenished twice. After filtration, the product was dried at 120 ºC under vacuum (150 mTorr) to afford BILP-6 as a yellow fluffy solid (60 mg, yield 77%). Anal. Calcd. for C_{64}H_{34}N_{12}.12H_{2}O: C, 64.75%; H, 4.92%; N, 14.16%. Found: C, 65.15%; H, 3.77%; N, 12.87.
$^1$H NMR for 2,3,6,7,14,15-Hexabromotriptycene (2) in CDCl$_3$:

\[ \text{Compound Structure} \]

$^{13}$C NMR for 2,3,6,7,14,15-Hexabromotriptycene (2) in CDCl$_3$:

\[ \text{Compound Structure} \]
$^1$H NMR for N$_2$N$_3$N$_6$N$_7$N$_{14}$N$_{15}$-hexakis(diphenylmethylene)triptycene-2,3,6,7,14,15-hexaamine (3) in CDCl$_3$: 

Electronic Supplementary Material (ESI) for Chemical Communications 
This journal is © The Royal Society of Chemistry 2011
for N²,N³,N⁶,N⁷,N¹⁴,N¹⁵-Hexakis(diphenylmethylene)triptycene-2,3,6,7,14,15-hexaamine (3) in CDCl₃:
$^1$H NMR for 2,3,6,7,14,15-Hexaammoniumtriptycene salt (4) in DMSO-$d_6$ (A) and D$_2$O (B).

$^{13}$C NMR for 2,3,6,7,14,15-Hexaammoniumtriptycene salt (4) in D$_2$O.
$^1$H NMR for 2,3,6,7,14,15-Hexaaminotriptycene (HATT) DMSO-$d_6$:

![$^1$H NMR spectrum for HATT DMSO-$d_6$.]

$^{13}$C NMR for 2,3,6,7,14,15-Hexaaminotriptycene (HATT) DMSO-$d_6$:

![$^{13}$C NMR spectrum for HATT DMSO-$d_6$.]
$^{13}$C NMR for Tetraphenylmethane (TPM) in CDCl$_3$:

![13C NMR for Tetraphenylmethane (TPM) in CDCl$_3$](image)

$^{13}$C NMR for Tetrakis(4-formylphenyl)methane (TFPM) in CDCl$_3$:

![13C NMR for Tetrakis(4-formylphenyl)methane (TFPM) in CDCl$_3$](image)
**Supplementary Section S2: Thermogravimetric Analysis**

TGA studies were performed on TA Instruments Q-5000IR series thermal gravimetric analyzer with samples held in 50 μL platinum pans under air. A 5 °C/min ramp rate was used.

**Figure S1**: TGA traces of BILP-3 and BILP-6
**Section S3: Scanning Electron Microscopy Imaging (SEM) for BILPs**

SEM was used to determine phase purity and morphology of BILPs. Each sample was prepared by dispersing the material onto a sticky carbon surface attached to a flat aluminum sample holder. The sample was then coated with platinum at $1 \times 10^{-4}$ mbar of pressure in a nitrogen atmosphere for 120 seconds before imaging. Images were taken on a Hitachi SU-70 Scanning Electron Microscope.

**Figure S2:** SEM image of BILPs revealing spherical morphology for BILP-3 (left) and platelet morphology for BILP-6 (right).
**Section S4: XRD-pattern for BILPs**

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.

**Figure S3**: XRD-pattern for BILPs. Intense peak at 2θ is due to the surface characteristics of sample holder. The broad peak at around 2θ = 15 indicates the amorphous characteristics of BILPs.
Section S5: FT-IR Spectroscopy of Starting Materials and BILPs

FT-IR spectra of starting materials and synthesized BILPs were obtained as KBr pellets using Nicolet - Nexus 670 spectrometer. Assignment and analysis of infrared absorption bands of starting materials and BILPs are presented in this section. The data and its discussion pertaining to the IR spectral relationships between these compounds are offered as support for the formation of the covalently linked extended solids.

Figure S4: FT-IR spectra (2000-4000 cm⁻¹) of starting materials and BILPs: The 2736 and 2831 cm⁻¹ bands in TFPM (2756 and 2806 cm⁻¹ bands in TPAL) due to C-H stretching of O=C-H almost disappeared in BILPs. The aromatic C-H stretching was observed around 2800-3100 cm⁻¹ in BILPs. Benzimidazole NH peaks were observed at 3415 (free N-H), 3210 (hydrogen bonded N-H).8a-c
Figure S5: FT-IR spectra (400-2000 cm\(^{-1}\)) of starting materials and BILPs: The presence of band at around 1700 cm\(^{-1}\) due to C=O stretching in BILPs indicates the residual terminal aldehyde functional group in polymers. There is considerable depletion of the absorption bands for C-N stretching at 1298 and 1332 cm\(^{-1}\) and appeared to be shifted to 1320, 1356 cm\(^{-1}\) upon benzimidazole ring formation (spectra for HATT and BILPs). Intense new bands also appeared at 1437 and 1492 cm\(^{-1}\) which have been assigned to skeleton vibration of benzimidazole ring.\(^{8c-d}\) The broad band at around 1610 cm\(^{-1}\) presumably due to the mixing of C=C and C=N stretching.
**Section S6: **$^{13}$C Nuclear Magnetic Resonance Studies for BILPs

**Figure S6:** Solid state $^{13}$C CP-MAS NMR spectrum of BILP-3 and BILP-6.

![Solid state $^{13}$C CP-MAS NMR spectrum of BILP-3 and BILP-6.](image)

**Table S1.** Assignments of the $^{13}$C CP-MAS NMR peaks.

<table>
<thead>
<tr>
<th>Peaks (ppm)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>BILP-3</td>
<td>BILP-6</td>
</tr>
<tr>
<td>55</td>
<td>54</td>
</tr>
<tr>
<td>64</td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>106</td>
</tr>
<tr>
<td>114</td>
<td>113</td>
</tr>
<tr>
<td>129 (broad)</td>
<td>128 (broad)</td>
</tr>
<tr>
<td>140, 141</td>
<td>139, 141</td>
</tr>
<tr>
<td>146</td>
<td></td>
</tr>
<tr>
<td>152</td>
<td>151</td>
</tr>
</tbody>
</table>
Section S7: Low Pressure (0 –1 bar) Gas Adsorption Measurements for BILP-3 and BILP-6

Sorption experiments were run using a Quantachrome Autosorb 1-C analyzer. Nitrogen isotherms were collected at 77 K, 273 K and 298 K. Ar isotherm was collected at 87 K. Hydrogen isotherms were collected at 77 K and 87 K. Carbon dioxide and methane isotherms were collected at 273 and 298 K. Pore Size Distributions (PSDs) were calculated using Non-Local Density Functional Theory (NLDFT) on the adsorption branch with a cylindrical pore model.

In order to calculate the isosteric heat of adsorption ($Q_{st}$) for CO$_2$, H$_2$ and CH$_4$ for each polymer, the sorption data measured at temperatures $T_1$ and $T_2$, were fitted by the virial equation:

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

where $P$ is pressure in torr, $T$ is temperature in Kelvin, $N$ is the mmol of gas adsorbed per gram of polymer sample, $a_i$ and $b_i$ are temperature independent empirical parameters, and $m$ and $n$ determine the number of terms required to adequately describe the isotherm. The isosteric heat of adsorption ($Q_{st}$) was then estimated as function of uptake:

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

Where $R$ is the universal gas constant (8.314 J K$^{-1}$ Mol$^{-1}$).
**Figure S7:** N$_2$ adsorption isotherms for BILP-3 (red circles) and BILP-6 (blue circles) measured at 77 K. The filled circles are adsorption points and the empty circles are desorption points.
**Figure S8:** Experimental N\textsubscript{2} adsorption isotherms (filled circles) for BILP-3 and BILP-6 measured at 77 K. The calculated NLDFT isotherm is overlaid as open circle. Note that a fitting error of < 1 % indicates the validity of using this method for assessing the porosity of BILPs. The fitting error is indicated.
**Figure S9**: BET plots for BILP-3 and BILP-6 calculated from the N$_2$ adsorption isotherm at 77 K. The model was applied from P/P$_o$= 0.05-0.15. The correlation factor is indicated. ($W =$ Weight of gas absorbed at a relative pressure P/P$_0$).
Figure S10: Ar adsorption isotherm for BILP-3 (red circles) and BILP-6 (blue circles) measured at 87 K. The filled circles are adsorption points and the empty circles are desorption points.
**Figure S11:** The Pore Size Distribution of BILPs was calculated from the Ar adsorption isotherm by the Non-Local Density Functional Theory (NLDFT) method using a cylindrical pore model.

Pore Width (Mode) = 7.2 Å (BILP-3)

Pore Volume = 0.65 cc/g at P/P₀ = 0.95 (BILP-3)

Pore Width (Mode) = 6.8 Å (BILP-6)

Pore Volume = 0.66 cc/g at P/P₀ = 0.95 (BILP-6)
**Figure S12:** Experimental Ar adsorption isotherm (filled circles) for BILP-3 and BILP-6 measured at 87 K. The calculated NLDFT isotherm is overlaid as open circle. Note that a fitting error of < 1 % indicates the validity of using this method for assessing the porosity of BILPs. The fitting error is indicated.
Figure S13: BET plots for BILP-3 and BILP-6 calculated from the Ar adsorption isotherm at 87 K. The model was applied from $P/P_0 = 0.05$-$0.15$. The correlation factor is indicated. ($W =$ Weight of gas absorbed at a relative pressure $P/P_0$).
**Figure S14:** Gas uptake isotherms for BILP-3 (red) and BILP-6 (blue); adsorption (filled) and desorption (empty). CO$_2$ at 273 K (circles) and 298 K (diamonds); H$_2$ at 77 K (circles) and 87 K (diamonds); and CH$_4$ at 273 K (circles) and 298 K (diamonds).
Figure S15: Virial analysis of CO₂ adsorption data for BILP-3 (A) and BILP-6 (B) (green circles: 77 K, blue squares: 87 K) and their isosteric heat of adsorption (Qₜ₈) (C). For A: a₀ = -3438.7378, a₁ = 60.800894, a₂ = 1.24798869, b₀ = 16.36531934. For B: a₀ = -3417.597, a₁ = 121.207669, a₂ = -5.7030854, b₀ = 15.94163175.
Figure S16: Virial analysis of H₂ adsorption data for BILP-3 (A) and BILP-6 (B) (green circles: 77 K, blue squares: 87 K) and their isosteric heat of adsorption (Qₑ) (C). For A: a₀ = -966.238391962527, a₁ = 43.1140385, a₂ = -0.7930763, b₀ = 13.69146502, b₁ = -0.151528247. For B: a₀ = -992.46481, a₁ = 36.9966574, a₂ = -0.5918349, b₀ = 13.46194292, b₁ = -0.060455728.
Figure S17: Virial analysis of CH₄ adsorption data for BILP-3 (A) and BILP-6 (B) (green circles: 273 K, blue squares: 298 K) and their isosteric heat of adsorption (Qₑ) (C). For A: $a_0 = -1999.5669$, $a_1 = 7.49332546$, $a_2 = 124.717619$, $b_0 = 13.36444454$, $b_1 = -0.530722545$. For B: $a_0 = -1588.1599$, $a_1 = -37.796925$, $a_2 = 66.3572525$, $b_0 = 11.57903001$. 
Figure S18: Pure component isotherm data for CO$_2$, CH$_4$ and N$_2$ measured for BILP-3 and BILP-6 at 273 and 298 K.
**Figure S19:** Adsorption selectivity of CO$_2$ over N$_2$ and CH$_4$ for BILPs from initial slope calculations. CO$_2$ (black), CH$_4$ (red) and N$_2$ (blue) isotherms collected at 273 K and 298 K.

- **BILP-3 (273 K):**
  - CO$_2$: $y = 18.22492x + 8.68207E-4$
  - CH$_4$: $y = 2.24393x - 9.94755E-4$
  - N$_2$: $y = 0.30941x - 6.84723E-5$

- **BILP-3 (298 K):**
  - CO$_2$: $y = 6.56208x - 0.00223$
  - CH$_4$: $y = 1.21432x - 0.00194$
  - N$_2$: $y = 0.21293x + 7.38819E-5$

- **BILP-6 (273 K):**
  - CO$_2$: $y = 22.48727x + 0.00243$
  - CH$_4$: $y = 2.67801x + 0.00151$
  - N$_2$: $y = 0.35941x - 6.72204E-5$

- **BILP-6 (298 K):**
  - CO$_2$: $y = 8.90335x - 0.00223$
  - CH$_4$: $y = 1.66949x - 0.00194$
  - N$_2$: $y = 0.22931x + 1.79201E-4$
References