Electronic Supplementary Information (ESI)

A facile synthesis of microporous organic polymers for efficient gas storage and separation

Guoliang Liu,[a,b] Yangxin Wang,[a,b] Chaojun Shen,[a] Zhanfeng Ju[a] and Daqiang Yuan*[a]

[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002 Fujian, People’s Republic of China

[b] University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China

Email: ydq@fjirsm.ac.cn
Experimental Details

1. Synthesis

Trimethyl-1,3,5-benzenetricarboxylate (a). Benzenetricarboxylic acid (10.0 g, 47.5 mmol), methanol (200 mL), and concentrated sulfuric acid (2.5 mL) were mixed and then refluxed for 24 h. The solvent was evaporated, and the residue was dissolved in chloroform (200 mL) and then washed with a saturated solution of potassium carbonate (250 mL). The solvent was removed under reduced pressure to afford a as a white powder (10.91 g, 92%). $^1$H NMR (CDCl$_3$): 8.88 (s, 3H), 4.00 (s, 9H)

1,3,5-Tri(bromomethyl)benzene (C1). A quantity of 1.10 g (29 mmol) of lithium aluminum hydride was added to 80 mL of dry THF. Then, 1.50 g (5.81 mmol) of a in 70 mL of dry THF was added dropwise at room temperature under vigorous stirring and an atmosphere of N$_2$. After the dropwise addition was completed, the mixture was heated to reflux for 24h. The excess of reducing agent was destroyed by slow addition of water, and the solvent was evaporated. Then, 60 mL of a 48% HBr solution and 75 mL of toluene were added and heated to reflux for 24 h. The organic layer was separated, and the aqueous portion was extracted several times with dichloromethane. The organic layers were combined and removed under reduced pressure. The crude material was purified through a short column of silica with petroleum ether. The solvents were evaporated under high vacuum to afford 1.65 g (4.62 mmol, 87% yield) of C1. $^1$H NMR (CDCl$_3$): 7.36 (s, 3H), 4.46 (s, 6H)
1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (C2). To a mixture of mesitylene (6.0 g; 0.05 mol), paraformaldehyde (5.0 g; 0.167 mol), and 25 mL of glacial acetic acid was added 30 mL of a 45 wt% HBr/acetic acid solution rapidly. The mixture was kept for 12 h at 95 °C and then poured into 100 mL of water. The product was filtered off on a G3 glass frit and dried in vacuum to afford 18 g (45 mmol, 91% yield) of C2. \(^1\)H NMR (CDCl\(_3\)): 4.58 (s, 6H), 2.46 (s, 9H)

Synthesis of HCPs

**Synthesis of sample C1M1-Al.** AlCl\(_3\) (anhydrous 500mg, 3.75mmol), 1,3,5-Tris(bromomethyl)benzene (180 mg, 0.5 mmol) and benzene (60 mg, 0.75 mmol) were added to a 100 ml flask, and then 20 ml dry DCM was added to it. The mixture was stirred under nitrogen protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C, 81.56; H, 5.71.

**Synthesis of sample C1M2-Al.** AlCl\(_3\) (anhydrous 500 mg, 3.75mmol), 1,3,5-Tris(bromomethyl)benzene (180 mg, 0.5 mmol) and biphenyl (115 mg,0.75 mmol) were added to a 100 ml flask, and then 20 ml dry DCM was added to it. The mixture was stirred under nitrogen protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C, 88.60; H, 5.50.

**Synthesis of sample C1M3-Al.** AlCl\(_3\) (anhydrous 500mg, 3.75mmol), 1,3,5-Tris(bromomethyl)benzene (180 mg, 0.5 mmol) and 1,3,5-triphenylbenzene (153 mg, 0.5 mmol) were added to a 100 ml flask, and then 20 ml dry DCM was added to it. The mixture were stirred under nitrogen protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C,
Synthesis of sample C2M1-Al. AlCl$_3$ (anhydrous 500 mg, 3.75 mmol), 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (200 mg, 0.5 mmol) and benzene (60 mg, 0.75 mmol) were added to a 100 ml flask, and then 20 ml dry DCM was added to it. The mixture were stirred under nitrogen protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C, 86.20; H, 6.46.

Synthesis of sample C2M2-Al. AlCl$_3$ (anhydrous 500 mg, 3.75 mmol), 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (200 mg, 0.5 mmol) and biphenyl (115 mg, 0.75 mmol) were added to a 100 ml flask, and then 20 ml dry DCM was added to it. The mixture were stirred under nitrogen protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C, 89.40; H, 6.03.

Synthesis of sample C2M3-Al. AlCl$_3$ (anhydrous 500 mg, 3.75 mmol), 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (200 mg, 0.5 mmol) and 1,3,5-triphenylbenzene (153 mg, 0.5 mmol) were added to a 100 ml flask, and then 20 ml dry DCM was added to it. The mixture was stirred under nitrogen protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C, 88.46; H, 5.88.

Synthesis of sample C1M3-Fe. FeCl$_3$ (anhydrous 600 mg, 3.75 mmol), 1,3,5-Tris(bromomethyl)-benzene (180 mg, 0.5 mmol) and 1,3,5-triphenylbenzene (153 mg, 0.5 mmol) were added to a 100 ml flask, and then 20 ml dry DCM was added to it. The mixture was stirred under nitrogen protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C, 86.20; H, 6.46.
protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C, 64.88; H, 3.68.

**Synthesis of sample C2M3-Fe.** FeCl₃ (anhydrous 600 mg, 3.75 mmol), 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene (200 mg, 0.5 mmol) and 1,3,5-triphenylbenzene (153 mg, 0.5 mmol) were added to a 100 ml flask, and then 20 ml dry DCM was added to it. The mixture was stirred under nitrogen protection at 40 °C for 24 h to form the network. The colour of the mixture darkens with time. The resulting precipitate was washed three times with diluted hydrochloric acid, methanol, DCM, acetone, respectively. And then washed with methanol in a Soxhlet for 24 h, and finally dried under reduced pressure at 160 °C for 24 h for further tests. Elemental analysis: C, 70.86; H, 4.58.

**Table S1** The amount of different elements for all materials based on the EDS analysis. “-” represents no detection.

<table>
<thead>
<tr>
<th>Materials</th>
<th>C %</th>
<th>O %</th>
<th>Br %</th>
<th>Al or Fe %</th>
<th>Cl %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1M1-Al</td>
<td>82.47</td>
<td>16.34</td>
<td>0.52</td>
<td>0.09</td>
<td>0.58</td>
</tr>
<tr>
<td>C1M2-Al</td>
<td>89.72</td>
<td>9.81</td>
<td>0.06</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>C1M3-Al</td>
<td>82.14</td>
<td>16.88</td>
<td>0.12</td>
<td>0.35</td>
<td>0.51</td>
</tr>
<tr>
<td>C2M1-Al</td>
<td>82.72</td>
<td>17.24</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C2M2-Al</td>
<td>81.70</td>
<td>17.98</td>
<td>0.06</td>
<td>0.02</td>
<td>0.44</td>
</tr>
<tr>
<td>C2M3-Al</td>
<td>87.10</td>
<td>12.65</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C1M3-Fe</td>
<td>72.64</td>
<td>5.19</td>
<td>20.99</td>
<td>0.02</td>
<td>1.15</td>
</tr>
<tr>
<td>C2M3-Fe</td>
<td>76.51</td>
<td>15.18</td>
<td>7.62</td>
<td>0.01</td>
<td>0.68</td>
</tr>
</tbody>
</table>

**Table S2** Metal elemental analysis based ICP.

<table>
<thead>
<tr>
<th>Materials</th>
<th>C1M1-Al</th>
<th>C1M2-Al</th>
<th>C1M3-Al</th>
<th>C2M1-Al</th>
<th>C2M2-Al</th>
<th>C2M3-Al</th>
<th>C1M3-Fe</th>
<th>C2M3-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al or Fe %</td>
<td>0.262</td>
<td>0.070</td>
<td>0.066</td>
<td>0.0077</td>
<td>0.046</td>
<td>0.014</td>
<td>0.028</td>
<td>0.016</td>
</tr>
</tbody>
</table>

**2. Calculation of the hydrogen isosteric heat of sorption (Qst).**

The H₂ and CO₂ isosteric heat of sorption was calculated as a function of the gas uptake by comparing the adsorption isotherms at different temperatures (H₂: 77 and 87 K, CO₂: 273, 283 and
293 K). The data were modeled with a virial-type expression composed of parameters $a_i$ and $b_i$ (Equation S1), and the heat of adsorption ($Q_{st}$) was then calculated from the fitting parameters using Equation S2, where $p$ is the pressure, $N$ is the amount adsorbed, $T$ is the temperature, $R$ is the universal gas constant, and $m$ and $n$ determine the number of terms required to adequately describe the isotherm.

$$
\ln p = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N_i + \sum_{i=0}^{n} b_i N_i \quad \text{(Equation S1)}
$$

$$
Q_{st} = -R \sum_{i=0}^{m} a_i N_i \quad \text{(Equation S2)}
$$

3. Selectivity calculations based on ideal adsorption solution theory (IAST)

The experimental CO$_2$ and N$_2$ isotherm data at 273 K are first converted from excess loadings to absolute loadings, using information on the pore volumes along with the Peng-Robinson equation of state for estimation of the liquid density inside the pores at the prevailing temperatures and pressures. This conversion to absolute loadings is of vital importance for estimates of component loadings in the mixtures.

For the CO$_2$ and N$_2$ adsorption, there are no discernible isotherm inflections for any of structures and therefore the single-site Langmuir-Freundlich model (Equation S3) was used for fitting the experimental isotherm data.

$$
q = \frac{q_{sat} bp^c}{1 + bp^c} \quad \text{(Equation S3)}
$$

Where $b$ is Langmuir constant (kPa$^{-1}$), $p$ is bulk gas phase pressure of species $i$ (kPa), $q$ is molar loading of species $i$ (mmol g$^{-1}$), $q_{sat}$ is saturation capacity of species $i$ (mmol g$^{-1}$), $c$ is constant.

The adsorption selectivities, $S_{ads}$, for binary mixtures of CO$_2$/N$_2$, defined by Equation S4

$$
S_{ads} = \frac{x_1/x_2}{y_1/y_2} \quad \text{(Equation S4)}
$$

Where $S_{ads}$ is adsorption selectivity, $x_i$ is the mole fractions of component $i$ in the adsorbed phases, $y_i$ is the mole fractions of component $i$ in the bulk phases.

The IAST calculations were carried out for binary mixture containing 15% CO$_2$ ($y_1$) and 85% N$_2$ ($y_2$), which is typical of flue gases. The single-site Langmuir-Freundlich fit parameters for CO$_2$
and N$_2$ are specified in Table S1 for C1M2-Al, C1M3-Al, C2M2-Al and C2M3-Al.

**Table S3.** Single-site Langmuir parameters for adsorption of CO$_2$ and N$_2$. These parameters were determined by fitting adsorption isotherms at 273 K.

<table>
<thead>
<tr>
<th></th>
<th>$q_{sat}$ / mmol g$^{-1}$</th>
<th>b / kPa$^{-1}$</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C1M2-Al</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>8.83619</td>
<td>0.01381</td>
<td>0.82764</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.1613</td>
<td>0.0011</td>
<td>0.9899</td>
</tr>
<tr>
<td><strong>C1M3-Al</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>14.28026</td>
<td>0.00773</td>
<td>0.8589</td>
</tr>
<tr>
<td>N$_2$</td>
<td>4.86074</td>
<td>8.80624E-4</td>
<td>0.9895</td>
</tr>
<tr>
<td><strong>C2M2-Al</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>7.217</td>
<td>0.012</td>
<td>0.821</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.89166</td>
<td>9.9332E-4</td>
<td>0.97795</td>
</tr>
<tr>
<td><strong>C2M3-Al</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>9.16378</td>
<td>0.00961</td>
<td>0.84158</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.96527</td>
<td>0.00108</td>
<td>0.99107</td>
</tr>
</tbody>
</table>
Additional Figures

Fig. S1  EDS analysis of the resulted polymers.
Fig. S2  Thermogravimetric analysis of the polymers under N\(_2\) atmosphere with a heating rate of 10 °C/min

Fig. S3  FT-IR spectra of the polymers.
Fig. S4  X-ray diffraction patterns of the polymers.

Fig. S5  Pore size distribution of the polymers
Fig. S6 SEM images of C1M1-Al at 100 nm resolution.

Fig. S7 SEM images of C1M2-Al at 100 nm resolution.
Fig. S8  SEM images of C1M3-Al at 100 nm resolution.

Fig. S9  SEM images of C2M1-Al at 100 nm resolution.
Fig. S10  SEM images of C2M2-Al at 100 nm resolution.

Fig. S11  SEM images of C2M3-Al at 100 nm resolution.
Fig. S12  SEM images of C1M3-Fe at 100 nm resolution.

Fig. S13  SEM images of C2M3-Fe at 100 nm resolution.
Fig. S14  $V(P_0-P)$ vs. $P/P_0$ for C1M1-AL. Only the range below $P/P_0 = 0.10$ satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.

Fig. S15  $V(P_0-P)$ vs. $P/P_0$ for C1M2-AL. Only the range below $P/P_0 = 0.12$ satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.
**Fig. S16** $V(P_0 - P)$ vs. $P/P_0$ for C1M3-Al. Only the range below $P/P_0 = 0.14$ satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.

**Fig. S17** $V(P_0 - P)$ vs. $P/P_0$ for C1M3-Fe. Only the range below $P/P_0 = 0.14$ satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.
**Fig. S18**  \( V(P_0-P) \) vs. \( P/P_0 \) for C2M1-Al. Only the range below \( P/P_0 = 0.12 \) satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.

**Fig. S19**  \( V(P_0-P) \) vs. \( P/P_0 \) for C2M2-Al. Only the range below \( P/P_0 = 0.14 \) satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.
Fig. S20  \( V(P_0-P) \) vs. \( P/P_0 \) for C2M3-Al. Only the range below \( P/P_0 = 0.14 \) satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.

Fig. S21  \( V(P_0-P) \) vs. \( P/P_0 \) for C2M3-Fe. Only the range below \( P/P_0 = 0.14 \) satisfies the first consistency criterion for applying the BET theory. Inset: Plot of the linear region for the BET equation.