Electronic Supplementary Information

Element-Orgnic Frameworks with high Permanent Porosity

Marcus Rose, a Winfried Böhlmann b, and Stefan Kaske l * a

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S1: Experimental Procedure

EOF-1:
0.5 g (0.77 mmol) tetrakis(4-bromophenyl)silane are placed in a 100 ml three-necked glass flask under argon atmosphere and dissolved in 50 ml of dry tetrahydrofurane (THF). The solution is cooled down to 263 K and 1.23 ml (3.07 mmol, 2.5 M) n-butyllithium are added drop-wise. After stirring the mixture for 10 minutes, 0.17 ml (0.77 mmol) tetraethylorthosilicate (TEOS) are added drop-wise. The mixture is stirred until it reaches room temperature and is then quenched by addition of 40 ml distilled water. The resulting precipitate is removed by centrifugation and washed twice with THF, water and ethanol. The white product is dried at 373 K for a few hours.

EOF-2:
0.78 g (2.5 mmol) 4,4′-dibromobiphenylene are placed in a 100 ml three-necked glass flask under argon atmosphere and dissolved in 50 ml of dry tetrahydrofurane (THF). The solution is cooled down to 263 K and 2.0 ml (5.0 mmol, 2.5 M) n-butyllithium are added drop-wise. After stirring the mixture for 10 minutes, 0.28 ml (1.25 mmol) tetraethylorthosilicate (TEOS) are added drop-wise. The mixture is stirred until it reaches room temperature and is then quenched by addition of 40 ml distilled water. The resulting precipitate is removed by centrifugation and washed twice with THF, water and ethanol. The white product will be dried at 373 K for a few hours.

S2: Used chemicals and analysis equipment

<table>
<thead>
<tr>
<th>chemical product</th>
<th>formula</th>
<th>purity</th>
<th>company</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-dibromobenzene</td>
<td>C₆H₄Br₂</td>
<td>99 %</td>
<td>Acros Organics</td>
</tr>
<tr>
<td>4,4′-dibromobiphenylene</td>
<td>C₁₂H₈Br₂</td>
<td>99 %</td>
<td>Acros Organics</td>
</tr>
<tr>
<td>n-butyl lithium in hexane</td>
<td>CH₃(CH₂)₃Li</td>
<td>2.5 M</td>
<td>Acros Organics</td>
</tr>
<tr>
<td>Silicon tetrachloride</td>
<td>SiCl₄</td>
<td>99 %</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>tetraethylorthosilicate (TEOS)</td>
<td>Si(OC₂H₃)₄</td>
<td>98 %</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>

The tetrahydrofurane for each synthesis was dried under argon atmosphere with potassium.
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**Solid state NMR spectroscopy:**
The solid state NMR measurements were carried out at the department of experimental physics at the University of Leipzig. All samples were measured at the *MSL 500 (BRUKER)* NMR spectrometer with the following parameters:

<table>
<thead>
<tr>
<th></th>
<th><strong>^1H-MAS-NMR</strong></th>
<th><strong>^13C-CP-MAS-NMR</strong></th>
<th><strong>^29Si-MAS-NMR</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>resonance frequency / MHz</td>
<td>500.13</td>
<td>125.75</td>
<td>99.36</td>
</tr>
<tr>
<td>impuls length / μs</td>
<td>5.9</td>
<td>5.9</td>
<td>3</td>
</tr>
<tr>
<td>repeating time / s</td>
<td>10</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>rotation frequency / kHz</td>
<td>12</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>number of scans</td>
<td>32</td>
<td>2048</td>
<td>2000-3000</td>
</tr>
</tbody>
</table>

MAS – magic angle spinning  CP – cross polarization

**IR spectroscopy:**
The IR spectra were measured with the FT-IR-spectrometer *Magna-IR 550 Series II (NICOLET)*. The samples were prepared as a KBr disc.

**Raman spectroscopy:**
The Raman spectra were measured with the FT-Raman-spectrometer *RFS 100 (BRUKER)*.

**DTA/TG (differential thermal analysis/thermal gravimetry):**
The DTA/TG measurements were carried out with the *Simultaneous Thermal Analyzer STA 409 (NETZSCH)*. The samples were heated with 5 K/min to 800 °C in air.

**Physisorption measurements:**
Before all measurements, the samples were activated by heating to 423 K under vacuum for more than five hours. The nitrogen and hydrogen physisorption isotherms were measured at 77 K on the *Autosorb 1-C (QUANTACHROME)*. Water vapor adsorption was measured at 298 K on the *Hydrosorb 1000 (QUANTACHROME)*. The methane storage measurements were carried out at 303 K on the *magnetic suspension balance (RUBOTHERM)*.
S3: $^{13}$C CP MAS NMR spectrum of EOF-1

S4: $^{13}$C CP MAS NMR spectrum of EOF-2
S5: $^{29}$Si MAS NMR spectrum of EOF-1

* spinning sidebands

S6: $^{29}$Si MAS NMR spectrum of EOF-2
S7: IR and Raman spectrum of EOF-1

S8: IR and Raman spectrum of EOF-2
S9: DTA/TG diagram of EOF-1

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S11:  H₂ physisorption isotherm of EOF-1 measured at 77 K

\[ V_{\text{ads}} \text{ [cm}^3\text{g}^{-1}] \]

S12:  H₂ physisorption isotherm of EOF-2 measured at 77 K

\[ V_{\text{ads}} \text{ [cm}^3\text{g}^{-1}] \]
S13: CH$_4$ physisorption isotherm of EOF-1 measured at 303 K

S14: CH$_4$ physisorption isotherm of EOF-2 measured at 303 K