Engineering MIL-53(Al) flexibility by controlling the amino tags at molecular level

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Experimental part

Synthesis of pure and ‘mixed’ Al-MIL-53

Al-MIL-53, Al-MIL-53-NH₂ and the four mixed ligand Al-MIL-53 were prepared and purified by a modified synthesis introduced by Stock et al. Solutions containing 1.931 g (8 mmol) of aluminium chloride hexahydrate (Al(Cl)₃·6·H₂O, Sigma-Aldrich, 99%), 8 mmol of benzene-1,4-dicarboxylate (bdc) and 2-aminobenzene-1,4-dicarboxylate (abdc) (Sigma-Aldrich, 98%) in different molar ratio (0, 11.1, 20, 50, 66.7 and 100% of abdc) and 30 ml deionised H₂O was introduced in a 48 ml Teflon-liner. The mixtures were placed in autoclaves and heated to 150°C for 9 h. After cooling the products were separated from water by centrifugation at 4000 rpm for 5 min. In order to remove incorporated abdc and bdc, the as-synthesized products were placed in autoclaves with 30 ml of anhydrous DMF (Sigma Aldrich, 99.8%) and heat at 150°C for 24 h. Then the solvent was substituted by fresh DMF and the solvothermal treatment was repeated twice. Afterwards the DMF was removed by a dichloromethane soxhlet-extraction for 20 h. Finally, solids were dried at 100°C for 9 h at reduced pressure to obtain activated, fine powdered Al-MIL-53 (A), Al-MIL-53-11.1%NH₂ (B), Al-MIL-53-20%NH₂ (C), Al-MIL-53-50%NH₂ (D), Al-MIL-53-66.7%NH₂ (E) and Al-MIL-53-NH₂ (F).

Characterization methods

Powder X-ray diffraction

Powder X-ray diffraction patterns were recorded using a Bruker D-5005 diffractometer and Panalytical X’Pert Pro MPD (Bragg–Brentano geometry, graphite monochromator, Cu Kα radiation).

NMR measurements

All NMR spectra were recorded with the same automated procedure for routine analysis on a Bruker Avance 250 spectrometer operating at 250 MHz for ^1H. Spectra are calibrated using the deuterium signals of DMSO. Due to their high chemical stability, Al-MIL-53 derivate samples were digested in HF/ DMSO-d₆.

CO₂ sorption analysis

CO₂ adsorption/desorption isotherms were measured on a BELSORP-HP at 30°C. The samples were outgassed under vacuum (~ 10-4 mbar) at 150°C for 12 h before beginning the measurements.
**N$_2$-physisorption**

Nitrogen physisorption isotherms were measured at –196 °C using a Micromeretics 2020 apparatus. Prior to the measurement, the samples were activated in vacuum at 150°C for 24 hours. Specific surface areas were calculated using the BET equation ($p/p_o = 0.05-0.2$).

**SEM measurements**

FESEM (Field Emission Scanning Electron Microscopy) on mixed ligand Al-MIL-53 were carried out with a Stereoscan 260 SEM.

**Drift measurement**

Drift spectrum was measured at 20°C using Thermo Scientific Nicolet 8700 FT-IR spectrometer, equipped with a MCT detector. Prior to the measurement, the sample was activated at 100°C for 5 hour.

**Results :**

**XRD patterns**

![XRD patterns](image)

**Fig. S1.** Powder X-ray diffraction of the mixed ligand Al-MIL-53: Al-MIL-53 (A), Al-MIL-53-11.1%NH$_2$ (B), Al-MIL-53-20%NH$_2$ (C), Al-MIL-53-50%NH$_2$ (D), Al-MIL-53-66.7%NH$_2$ (E) and Al-MIL-53-NH$_2$ (F).
Table S1. Crystal data for A, B, C and D samples at 440°C. The crystalline unit cell is orthorombic with space group Imma (no. 74)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Al-MIL-53 0%</th>
<th>Al-MIL-53 11.1%</th>
<th>Al-MIL-53 20%</th>
<th>Al-MIL-53 50%</th>
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<tbody>
<tr>
<td>a [Å]</td>
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<td>6,634</td>
<td>6,634</td>
<td>6,617</td>
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<td>b [Å]</td>
<td>16,6178</td>
<td>16,785</td>
<td>16,819</td>
<td>16,615</td>
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<tr>
<td>c [Å]</td>
<td>12,8604</td>
<td>12,802</td>
<td>12,771</td>
<td>13,044</td>
</tr>
<tr>
<td>V [Å³]</td>
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<td>1425,5</td>
<td>1424,87</td>
<td>1434,1</td>
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Fig. S2. 1H NMR spectra of digested mixed ligand Al-MIL-53: Al-MIL-53 (A), Al-MIL-53-11.1%NH₂ (B), Al-MIL-53-20%NH₂ (C), Al-MIL-53-50%NH₂ (D), Al-MIL-53-66.7%NH₂ (E) and Al-MIL-53-NH₂ (F).
Fig. S3. SEM picture of mixed ligand Al-MIL-53: Al-MIL-53 (A), Al-MIL-53-11.1%NH$_2$ (B), Al-MIL-53-20%NH$_2$ (C), Al-MIL-53-50%NH$_2$ (D), Al-MIL-53-66.7%NH$_2$ (E) and Al-MIL-53-NH$_2$ (F).

Fig. S4 Temperature dependent PXRD: np monoclinic (black line), lp orthorhombic (green line), mixture of np and lp (red line), and collapse of the structure (blue line)

Al-MIL-53 (A)
Fig. S5. Nitrogen adsorption/desorption isotherms at 77.4 K of mixed ligand Al-MIL-53: Al-MIL-53 (A-green line), Al-MIL-53-11.1%NH₂ (B-red line), Al-MIL-53-20%NH₂ (C-purple line), Al-MIL-53-50%NH₂ (D-orange line), Al-MIL-53-66.7%NH₂ (E-black line) and Al-MIL-53-NH₂ (F-turquoise blue line).
**Fig. S6.** CO2 Physisorption isotherms at 303K of mixed ligand Al-MIL-53: Al-MIL-53 (A-green line), Al-MIL-53-11.1%NH2 (B-red line), Al-MIL-53-20%NH2 (C-purple line), Al-MIL-53-50%NH2 (D-orange line), Al-MIL-53-66.7%NH2 (E-black line) and Al-MIL-53-NH2 (F-turquoise blue line).

**Fig. S7.** Drift spectrum of Al-MIL-53-NH2 (F) after one hour desorption at 100°C.

The bands at 3500 and 3390 cm\(^{-1}\) correspond to the symmetric and asymmetric stretching of the primary amine. The doublet at 3660 and 3700 cm\(^{-1}\) is due to the bridging OH in the chains of trans corner-sharing AlO\(_4\)(OH)\(_2\) octahedra\(^1\). The broad signals between 3100 and 2500 cm\(^{-1}\) are due to the hydroxyl group in the presence of NH\(_2\) group. Large signals between 1600 and 1300 cm\(^{-1}\) are carboxylic acid function. The C=O band of free acid and DMF are not observed\(^2\).
Fig. S8. 13C MAS NMR spectrum of Al-MIL-53-NH2
The 13C spectrum of the Al-MIL-53-NH2 exhibits five broad signals between 149.5 and 115.4 ppm due to the C atoms of the phenyl ring and one signal at 174.9 ppm which match with the carboxylate groups. No signals attributable to DMF molecules are observed and the whole spectrum is consistent with the Al-MIL-53-NH2 it one described in the literature².
Fittings to thermodynamic isotherm
(see energy values in Table S4)

Al-MIL-53-0\%NH$_2$ (A)

![Graph of CO$_2$ uptake vs. pressure for Al-MIL-53-0\%NH$_2$ at 303 K]

Al-MIL-53-11.1\%NH$_2$ (B)

![Graph of CO$_2$ uptake vs. pressure for Al-MIL-53-11.1\%NH$_2$ at 303 K]

Al-MIL-53-20\%NH$_2$ (C)

![Graph of CO$_2$ uptake vs. pressure for Al-MIL-53-20\%NH$_2$ at 303 K]
Al-MIL-53-50%NH$_2$ (D)

Al-MIL-53-67%NH$_2$ (E)
Al-MIL-53-100%NH₂ (F)

Thermodynamic isotherm models

Methods can be found elsewhere: Llorens, J; Pera-Titus, M, J. of Colloid Int. Sci., (2009) vol. 331(2), 302-311;

\[
\begin{align*}
\text{Adsorption:} & \quad \frac{\Psi}{RT} = \int_0^1 Z^{-1} \delta \theta = \frac{G_{\text{adh}}^\omega}{1 + \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} + \frac{\lambda_3 \lambda_4}{\lambda_3 + \lambda_4}} \\
\text{Desorption:} & \quad \frac{\Psi}{RT} = \int_0^1 Z^{-1} \delta \theta = \frac{G_{\text{adh}}^\omega}{1 + \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} + \frac{\lambda_3 \lambda_4}{\lambda_3 + \lambda_4}}
\end{align*}
\]
with \( \lambda_i = k_i Z^\infty \) \( \left( \frac{Z}{Z_i} \right)^n \) \( i=1,4 \)

**Other definitions**

\[
\Delta G^o = \left\{ \frac{G_{ads}^o - G_{des}^o}{RT} \right\} \\
\Delta G_{ads-des}^o = \Delta G^o - \left\{ \frac{-\Psi^o}{RT_{ads}} - \frac{-\Psi^o}{RT_{des}} \right\}_n
\]

**Table S2. Adsorption curves**

<table>
<thead>
<tr>
<th>%NH₂</th>
<th>G°</th>
<th>First zone</th>
<th></th>
<th>Second zone</th>
<th></th>
<th>Third zone</th>
<th></th>
<th>Fourth zone</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>m₁ Z₁</td>
<td>m₂ Z₂</td>
<td>m₃ Z₃</td>
<td>m₄ Z₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>2.91</td>
<td>22 ± 1 0.194 ± 0.001</td>
<td>1.07 ± 0.05</td>
<td>0.300 ± 0.003</td>
<td>44 ± 11</td>
<td>0.448 ± 0.001</td>
<td>7 ± 1</td>
<td>0.394 ± 0.001</td>
<td>51 ± 0.02</td>
</tr>
<tr>
<td>11.1</td>
<td>2.77</td>
<td>19 ± 1 0.176 ± 0.001</td>
<td>1.46 ± 0.03</td>
<td>0.23 ± 0.07</td>
<td>65 ± 13</td>
<td>0.52 ± 0.03</td>
<td>5.8 ± 0.4</td>
<td>0.44 ± 0.01</td>
<td>88 ± 0.01</td>
</tr>
<tr>
<td>20</td>
<td>2.69</td>
<td>19 ± 1 0.174 ± 0.001</td>
<td>0.86 ± 0.02</td>
<td>0.27 ± 0.09</td>
<td>24 ± 3</td>
<td>0.520 ± 0.004</td>
<td>4.3 ± 0.6</td>
<td>0.38 ± 0.03</td>
<td>90 ± 0.01</td>
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<tr>
<td>50</td>
<td>2.54</td>
<td>16 ± 1 0.161 ± 0.001</td>
<td>0.65 ± 0.03</td>
<td>0.286 ± 0.005</td>
<td>28 ± 4</td>
<td>0.600 ± 0.004</td>
<td>6.2 ± 0.3</td>
<td>0.50 ± 0.01</td>
<td>110 ± 0.01</td>
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<tr>
<td>66.7</td>
<td>2.44</td>
<td>19 ± 1 0.164 ± 0.001</td>
<td>0.69 ± 0.02</td>
<td>0.327 ± 0.004</td>
<td>39 ± 11</td>
<td>0.604 ± 0.004</td>
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<td>0.58 ± 0.01</td>
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<td>100</td>
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<td>-</td>
<td>7.9 ± 0.2</td>
<td>0.88 ± 0.006</td>
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**Table S3. Desorption curves**

<table>
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<th>%NH₂</th>
<th>G°</th>
<th>First zone</th>
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<th>Third zone</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>m₁ Z₁</td>
<td>m₂ Z₂</td>
<td>m₃ Z₃</td>
<td>m₄ Z₄</td>
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<tr>
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<td>3.29</td>
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<td>2.5 ± 0.2</td>
<td>0.274 ± 0.006</td>
<td>43 ± 20</td>
<td>0.34 ± 0.02</td>
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<td>0.325 ± 0.003</td>
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<td>11.1</td>
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<td>2.6 ± 0.2</td>
<td>0.255 ± 0.005</td>
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<tr>
<td>20</td>
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<td>26 ± 4 0.152 ± 0.001</td>
<td>1.9 ± 0.2</td>
<td>0.279 ± 0.009</td>
<td>54 ± 5</td>
<td>0.37 ± 0.04</td>
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<td>0.3 ± 0.1</td>
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<tr>
<td>50</td>
<td>3.23</td>
<td>18 ± 3 0.154 ± 0.002</td>
<td>1.8 ± 0.1</td>
<td>0.289 ± 0.006</td>
<td>59 ± 6</td>
<td>0.39 ± 0.03</td>
<td>3.2 ± 0.1</td>
<td>0.258 ± 0.006</td>
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<tr>
<td>66.7</td>
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<td>27 ± 14 0.151 ± 0.006</td>
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<td>2.6 ± 0.1</td>
<td>0.21 ± 0.01</td>
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**Table S4. List of relevant energies and breathing pressures**

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<th>%NH₂</th>
<th>ΔG° (kJ/mol)</th>
<th>First transition (lp→np)</th>
<th>Second transition (np→lp)</th>
<th>P Г₁ (kPa)</th>
<th>P Г₂ (kJ/mol)</th>
<th>P Г₂ (kJ/mol)</th>
<th>P Г₂ (kJ/mol)</th>
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<td>-0.1</td>
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* Data measured from the fittings to the thermodynamic isotherm
† Phase transition energies estimated according to Coudert et al., J. Am. Chem. Soc. 130 (2008) 14294 using Tóth isotherms for describing the adsorption behaviour of the np and lp phases.