Citation for published version:

DOI:
10.1039/c2cc36344e

Publication date:
2012

Document Version
Peer reviewed version

Link to publication

University of Bath

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
The functionalised metal-organic framework MIL-101(Cr)-NH$_2$, containing 2-aminobenzene-1,4-dicarboxylate as the linker, has been synthesised. A new tandem post-synthetic modification strategy involving diazotisation as the first step has been developed and used to introduce halo- and azo-dye-functional groups into the pores.

Metal-organic frameworks (MOFs) are crystalline materials with extended structures that are formed from the self-assembly of metal ions or aggregates with organic bridging ligands. These materials have recently attracted considerable attention due to their high surface areas and the rich diversities in their structures and properties, which has led to potential applications in many areas including gas storage, separations and catalysis. Once synthesised, the physical and chemical properties of MOFs can be further tuned by the incorporation of functional groups on the organic linker or on the unsaturated metal sites in the framework through post-synthetic modification. The chromium(III) MOF [Cr$_3$(OH)(H$_2$O)$_2$(bdc)$_3$]·nH$_2$O, MIL-101(Cr) (bdc = 1,4-benzenedicarboxylate, n ~ 25), first reported by Férey et al., has mesoporous cages together with high chemical/hydrothermal stability. This, in addition to the potential for generation of unsaturated chromium(III) sites in the framework on activation, make MIL-101(Cr) particularly attractive for practical applications. Functionalisation of MIL-101(Cr) has been achieved by grafting ligands such as ethylenediamine onto the unsaturated Cr(III) sites and by encapsulating large molecules or nanoparticles into the mesoporous cages. In addition, direct reaction of MIL-101(Cr) with strong acids has been used to generate analogues containing nitro and sulfoxy acid groups appended to the aromatic rings.

Amine groups are very versatile, and have been introduced into many MOF structures through use of 2-amino-1,4-benzenedicarboxylate (bdc-NH$_2$) as the linker in the MOF synthesis. The amine group on the linker not only helps to improve affinity for particular gases such as CO$_2$, but also provides a platform for developing further functionalised MOFs via post-synthetic modifications. Indeed, a wide range of functionalities have been incorporated into MOFs following reaction with an amine group on the pore wall.

The iron and aluminium compounds, MIL-101(M)-NH$_2$ (M = Fe, Al), have been prepared by the direct reaction of iron(III) and aluminium(III) with H$_2$-bdc-NH$_2$, but until very recently there were no reports of the analogous synthesis of MIL-101(Cr)-NH$_2$. Kong and co-workers reported that this material can be prepared by hydroxide-assisted hydrothermal synthesis, whereas Stock and co-workers had previously prepared this material by post-synthetic modification involving nitration of MIL-101(Cr) followed by reduction.

We were able to synthesise MIL-101(Cr)-NH$_2$ hydrothermally from a suitable reagent mixture molar ratio [1.25Cr(NO$_3$)$_3$·9H$_2$O : 1.26H$_2$-bdc-NH$_2$ : 389H$_2$O] at 130 °C for 24 h. The structure of this material was investigated using powder X-ray diffraction (PXRD). The PXRD pattern is similar to the simulated pattern calculated from the MIL-101(Cr) crystal structure (Figure S1), confirming the formation of an isoreticular MOF. The observation of broad Bragg reflections in the PXRD pattern is a consequence of the small particle sizes, as supported by TEM and SEM images (Figure S2), and consistent with the results of Kong et al. Analysis of the TEM images revealed that our samples of MIL-101(Cr)-NH$_2$ have an average particle size of 16 ± 4 nm.

Figure 1 shows the N$_2$ adsorption-desorption isotherm of MIL-101(Cr)-NH$_2$ at 77 K following evacuation of the sample at 150 °C for 4 h. The nanoMIL-101(Cr)-NH$_2$ exhibited a similar isotherm to that reported for nanoMIL-101(Cr). The two uptake steps near P/P$_0$ = 0.1 and P/P$_0$ = 0.2 reflect the presence of the two kinds of pore in the crystal structure, while the increased nitrogen uptake under high relative pressure and the presence of a hysteresis loop derive from the textural pores created by the aggregated nanoparticles. The pore size distribution curve shows two monodisperse pore sizes with 1.54 and 1.99 nm in MIL-101(Cr)-NH$_2$, which are smaller than those in MIL-101(Cr) (1.71 and 2.22 nm) due to the presence of amino groups projecting into the pores. The broad pore size distribution ranging from 10 nm to 50 nm reflects the existence of textural mesopores in the particle aggregates. MIL-101(Cr)-NH$_2$ has a high specific surface area of 2070 m$^2$ g$^{-1}$ and high total pore volume of 2.26 cm$^3$ g$^{-1}$. 
Scheme 1. Tandem post-synthetic modification of MIL-101(Cr)-NH₂; (i) NaNO₂, HCl (aq); (ii) NaNO₂, HBF₄ (aq); (iii) C₆H₅OH (aq), Na₂CO₃; (iv) KI (aq); (v) 100 °C.

Scheme 1. Tandem post-synthetic modification of MIL-101(Cr)-NH₂; (i) NaNO₂, HCl (aq); (ii) NaNO₂, HBF₄ (aq); (iii) C₆H₅OH (aq), Na₂CO₃; (iv) KI (aq); (v) 100 °C.

which are comparable with those of the previous reported nanoMIL-101(Cr) (2944 m² g⁻¹; 2.57 cm³ g⁻¹).¹⁴ Thermogravimetric analysis (Figure S4) showed that the material is stable up to 250 °C under a N₂ atmosphere.

In addition to its high thermal stability, MIL-101(Cr)-NH₂ is also stable to acids. This property affords the potential for new types of post-synthetic modification, which in turn allows access to new functionalised MOFs. One such process, described in this paper, involves diazotisation. Diazonium salts (RN⁺X⁻), especially those where R is an aryl group, are produced by reaction of primary aromatic amines with sodium nitrite and an aqueous acid. A wide variety of inorganic and organic functional groups can be subsequently incorporated onto an aromatic ring by further reaction of the anilidiazonium salt. This diazotisation route has not previously been reported in MOF chemistry, since the majority of amine-tagged MOFs are not tolerant of the acidic aqueous conditions which are required for the formation of diazenefunctionalised salts. Here we present a new tandem post-synthetic modification strategy involving diazotisation as the first step. We illustrate the potential of this approach by preparing iodo-, fluoro- and aza dye-functionalised MIL-101(Cr) materials (Scheme 1), with the diazonium salt formed in the first step either replaced by iodide or fluoride, or coupled with phenol.

As a first step, an anilidiazonium chloride salt was prepared in situ by suspending MIL-101(Cr)-NH₂ in an acidic aqueous solution followed by slow addition of NaNO₂ and stirring the resulting mixture for 3 h at 0-5 °C. The iodo-functionalised material, MIL-101(Cr)-I, was prepared by adding an aqueous solution of KI into the reaction mixture, which was then stirred for 72 h at room temperature. To prepare the fluoro-functionalised material, MIL-101(Cr)-NH₂ was treated with NaNO₂ and HBF₄ to generate the diazonium tetrafluoroborate salt. This was separated by centrifugation and heated at 100 °C for 18 h to eliminate nitrogen in a Balz-Schiemann reaction, yielding MIL-101(Cr)-F. The aza dye-functionalised MIL-101(Cr) was prepared by adding an aqueous phenol solution to the diazonium chloride, followed by adjustment of the pH to 7.0 by addition of Na₂CO₃. The mixture was stirred for 72 h at room temperature to yield MIL-101(Cr)-azo. The detailed preparation procedures are described in the Supporting Information.

Diazonium chloride, MIL-101(Cr)-N₂Cl, was not isolated, but used in situ, whereas the tetrafluoroborate salt, MIL-101(Cr)-N₂BF₄, was digested in alkaline solution (NaOD/D₂O) and characterised by ¹H NMR spectroscopy.

The PXRD patterns for the modified materials are similar to those for MIL-101(Cr)-NH₂, confirming that diazotisation followed by substitution or coupling does not alter the framework structure (Figure S3). The linker modification reactions were followed by ¹H NMR spectroscopy of the digested product in alkaline solution (NaOD/D₂O). In the case of MIL-101(Cr)-I (Figure S6), there are three ¹H resonances, two doublets and a singlet, in the aromatic region of the ¹H NMR spectrum which is in line with the spectrum observed for H₂bdc-I. These resonances appear at different chemical shifts from the resonances observed in the spectra of H₂bdc-NH₂ and H₂bdc-N₂⁺. For MIL-101(Cr)-F, the ¹H NMR spectrum is second order, but consistent with an ABCX spin system (Figure S7). For both MIL-101(Cr)-I and MIL-101(Cr)-F, only very small amounts (< 5 % total) of H₂bdc-NH₂ and H₂bdc were present in the spectra, implying almost complete diazotisation of the amino groups in the first step, and complete conversion of the diazonium salt into the halo group in the second step. The ¹¹B NMR spectrum of digested MIL-101(Cr)-F contains a doublet of doublets at δ ~122 ppm for H₂bdc-F, plus two other signals that can be attributed to tetrafluoroborate (δ ~151) and a decomposition product.

The negative ion mass spectrum of digested MIL-101(Cr)-I gave a value of m/z 290.9161, consistent with the presence of [Hbdc-I⁻] (m/z 290.9154), whereas the mass spectrum of digested MIL-101(Cr)-F gave a value of m/z 183.0113 (cf. [Hbdc-F⁻], m/z 183.0099).

The digested solution of MIL-101(Cr)-azo showed a more complicated ¹H NMR spectrum than those for the iodo and amino compounds (Figure S8), as expected given the greater number of aromatic protons present. Analysis of the spectrum revealed the presence of two isomers, with the most intensive peaks from the para-azo dye functional groups and the weaker peaks from the ortho-azo dye functional groups. These features are in line with those observed for H₂bdc-N=N-C₆H₅OH when synthesised from H₂bdc-NH₂ using the previously reported method.¹⁵ The negative ion mass spectrum of the digested MIL-101(Cr)-azo gave a value of m/z 285.0522, which is consistent with the presence of [Hbdc-N=N-C₆H₅OH]⁻ (calc. 285.0517). The UV-visible spectrum of MIL-101(Cr)-azo dissolved in base (Figure S5) gave a strong adsorption peak at 400 nm deriving from the N=N-N group in the compound, whereas the absorption peak at 329 nm observed in MIL-101(Cr)-NH₂ was absent. These results show the successful and full formation of aza dye functional groups in MIL-101(Cr)-azo, and demonstrate that the para-isomer is dominant. The pH of the reaction mixture in the synthesis of MIL-101(Cr)-azo has a significant influence on the resulting materials with pH 7 optimum for maximising the para-ortho-ratio (Figure S8). On reducing the pH to 1, ¹H NMR analysis showed that the proportion of the ortho-isomer is increased, with a ratio of ortho-para of 7:3, while some additional unassigned resonances are also present.

Azo compounds can exist as cis and trans isomers, and there is interest in photochemical switching between these forms.¹⁶ Samples of MIL-101(Cr)-azo were irradiated at either 365 nm or...
CO₂ sorption properties of the functionalised MIL-101(Cr) materials were studied at 273 K (Figure S10 and Table 2). MIL-101(Cr)-NH₂ gave a CO₂ capacity of 3.02 mmol g⁻¹ and a selectivity of 25 for CO₂ over N₂ at 1 atm, which is greater than that previously reported for MIL-101(Cr) (selectivity 7),¹⁴ and may be attributed to the stronger interaction of the amino group with CO₂ than with N₂. MIL-101(Cr)-I, MIL-101(Cr)-F and MIL-101(Cr)-azo show decreased CO₂ capacities over MIL-101(Cr)-NH₂. The incorporation of iodo-, fluoro- and azo-groups into MIL-101(Cr) also leads to increases in the selectivity for CO₂ over N₂, with the selectivity between 15 and 21. The selectivities at 0.1 atm are in some cases even greater, with MIL-101(Cr)-F and MIL-101(Cr)-azo showing selectivities at 273 K of 30 and 73 respectively. Hydroxyl groups have previously been shown to enhance CO₂ adsorption,¹⁸ so the high selectivity in MIL-101(Cr)-azo is likely to be a consequence of interactions between the phenol groups and CO₂ molecules. Current work is concentrating on systems in which this is further enhanced.

**Table 2.** CO₂ and N₂ adsorption data for functionalised MIL-101(Cr) materials under 1 atm at 273 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO₂ / mmol g⁻¹</th>
<th>N₂ / mmol g⁻¹</th>
<th>Selectivity</th>
<th>1 atm</th>
<th>0.1 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101(Cr)-NH₂</td>
<td>3.02</td>
<td>0.12</td>
<td>25</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>MIL-101(Cr)-I</td>
<td>1.85</td>
<td>0.12</td>
<td>15</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>MIL-101(Cr)-F</td>
<td>2.24</td>
<td>0.13</td>
<td>19</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>MIL-101(Cr)-azo</td>
<td>1.66</td>
<td>0.08</td>
<td>21</td>
<td>73</td>
<td></td>
</tr>
</tbody>
</table>

[¹⁸] The selectivity was calculated from the single gas isotherms by dividing the CO₂ uptake by that of N₂.

In conclusion, we have prepared MIL-101(Cr)-NH₂ by a direct in situ hydrothermal synthesis route, and developed a new tandem post-synthetic modification route involving diazotisation in the first step, using this to afford access to new functionalised MOFs via substitution or coupling. One of the new modified products, MIL-101(Cr)-azo, shows excellent selectivity for CO₂ sorption at low pressure. This new approach provides a flexible protocol for the preparation of functionalised MIL-101 materials.

The authors thank the EPSRC (EP/H046305/1) for financial support, Diamond Light Source for access to beamline I11 (proposal number EE5764). Dr. Chiu Tang for assistance with the high resolution X-ray diffraction measurements, and Dr. John Lowe for assistance with NMR measurements.

**Notes and references**

*¹ Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK; Tel: 44 1225 386529; E-mail: a.d.burrows@bath.ac.uk
† Electronic Supplementary Information (ESI) available: Full experimental details, including the synthesis of MIL-101(Cr)-NH₂, post-synthetically modified MIL-101(Cr) materials and the azo dye prepared with H₂bdc-NH₂ and PXRD, SEM, UV-visible, ATR-IR, TGA; ¹H NMR, ¹³C NMR, N₂ sorption and CO₂ sorption data. See DOI: 10.1039/b000000x/