Synthesis and post-synthetic modification of MIL-101(Cr)-NH₂ via a tandem diazotisation process†


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The functionalised metal-organic framework MIL-101(Cr)-NH₂, 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.\(^3,4\)

The chromium(III) MOF \([\text{Cr}_2\text{O}(\text{F,OH})(\text{H}_2\text{O})(\text{bdc})_3] \cdot n\text{H}_2\text{O}\), MIL-101(Cr) (bdc = 1,4-benzenedicarboxylate, \(n\sim 25\)), first reported by Férey et al.,\(^5\) has mesoporous cages together with high chemical/hydrothermal stability.\(^5\) 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.\(^5\) In addition, direct reaction of MIL-101(Cr) with strong acids has been used to generate analogues containing nitro\(^5\) and sulfoxide acid\(^6\) 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-NH₂) as the linker in the MOF synthesis. The amine group on the linker not only helps to improve affinity for particular gases such as CO₂, 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.\(^5\) The iron and aluminium compounds, MIL-101(M)-NH₂ (M = Fe, Al), have been prepared by the direct reaction of iron(III)\(^1\) and aluminium(III)\(^1\) with H₂bdc-NH₂, but until very recently there were no reports of the analogous synthesis of MIL-101(Cr)-NH₂.\(^6\)

NH₂, Kong and co-workers reported that this material can be prepared by hydroxide-assisted hydrothermal synthesis,\(^1\) whereas Stock and co-workers had previously prepared this material by post-synthetic modification involving nitration of MIL-101(Cr) followed by reduction.\(^8\)

We were able to synthesise MIL-101(Cr)-NH₂ hydrothermally from a suitable reagent mixture molar ratio \([1.25\text{Cr(NO}_3)_2 \cdot 9\text{H}_2\text{O} : 1.26\text{H}_2\text{bdc-NH}_2 : 3.89\text{H}_2\text{O}]\) 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.\(^7\) Analysis of the TEM images revealed that our samples of MIL-101(Cr)-NH₂ have an average particle size of 16 ± 4 nm.

Figure 1 shows the N₂ adsorption-desorption isotherm of MIL-101(Cr)-NH₂ at 77 K following evacuation of the sample at 150 °C for 4 h. The nanoMIL-101(Cr)-NH₂ exhibited a similar isotherm to that reported for nanoMIL-101(Cr).\(^8\) 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)-NH₂, which are smaller than those in MIL-101(Cr) (1.71 and 2.22 nm)\(^1\) 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)-NH₂ has a high specific surface area of 2070 m² g⁻¹ and high total pore volume of 2.26 cm³ g⁻¹.

\[\text{Figure 1. N}_2 \text{adsorption-desorption isotherms (left) and pore size distribution curves (right) of MIL-101(Cr)-NH}_2 \text{ at 77 K.}\]
which are comparable with those of the previously 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 arenediazonium 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
arenediazonium 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 azo 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 arenediazonium 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 azo 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. The
diazonium chloride, MIL-101(Cr)-N₂⁺Cl⁻, was not isolated, but
used in situ, whereas the tetrafluoroborate salt, MIL-101(Cr)-
N₂⁺BF₄⁻, 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 ¹⁹F 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-C₆H₄OH 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-C₆H₄OH]⁻ (calc. 285.0517). The UV-visible spectrum of
MIL-101(Cr)-azo dissolved in base (Figure S5) gave a strong
absorption peak at 400 nm deriving from the -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 azo 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-
to 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

420 nm for 8 h. In both cases, no change in appearance was observed, and the $^1$H NMR spectra of the base-digested product showed no evidence of isomerisation. Similar behaviour was observed for H$_2$bdc-N-$\equiv$N-C$_6$H$_4$OH. This is consistent with a recent report by Velasco and co-workers, which shows that the presence of a phenol ensures rapid (μs to ms) relaxation times for cis-trans isomerisation in azo compounds.

The modified MIL-101(Cr) materials were characterised by N$_2$ sorption at 77 K (Figure S9 and Table 1). MIL-101(Cr)-I and MIL-101(Cr)-F show reduced BET surface areas and total pore volumes from those observed for MIL-101(Cr)-NH$_2$, but the pore size distribution curves are similar. MIL-101(Cr)-azo also showed a decreased BET surface area as well as a decreased pore volume. The larger molecular volume of the azo group compared with the iodo group leads dramatically decreased pore sizes for MIL-101(Cr)-azo.

Table 1. Physicochemical data for functionalised MIL-101(Cr) materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ $^a$ [m$^2$ g$^{-1}$]</th>
<th>$V_{\text{total}}$ $^b$ [m$^3$ g$^{-1}$]</th>
<th>Pore size $^b$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101(Cr)-NH$_2$</td>
<td>2070</td>
<td>2.26</td>
<td>1.54/1.99</td>
</tr>
<tr>
<td>MIL-101(Cr)-I</td>
<td>1431</td>
<td>1.19</td>
<td>1.55/1.97</td>
</tr>
<tr>
<td>MIL-101(Cr)-F</td>
<td>1619</td>
<td>1.26</td>
<td>1.55/1.97</td>
</tr>
<tr>
<td>MIL-101(Cr)-azo</td>
<td>722</td>
<td>0.72</td>
<td>1.10/1.56</td>
</tr>
</tbody>
</table>

$^a$ Specific surface area was calculated using the P/$P_0$ range of 0.05-0.1. $^b$ Total volume was calculated by taking the data at $P/P_0$ 0.99. $^{11}$ Pore size was calculated from BJH mode.

CO$_2$ sorption properties of the functionalised MIL-101(Cr) materials were studied at 273 K (Figure S10 and Table 2). MIL-101(Cr)-NH$_2$ gave a CO$_2$ capacity of 3.02 mmol g$^{-1}$ and a selectivity of 25 for CO$_2$ over N$_2$ at 1 atm, which is greater than that previously reported for MIL-101(Cr) (selectivity 7), and may be attributed to the stronger interaction of the amino group with CO$_2$ than with N$_2$. MIL-101(Cr)-I, MIL-101(Cr)-F and MIL-101(Cr)-azo show decreased CO$_2$ capacities over MIL-101(Cr)-NH$_2$. The incorporation of iodo- and fluor-azos into MIL-101(Cr) also leads to increases in the selectivity for CO$_2$ over N$_2$, 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 CO$_2$ adsorption, so the high selectivity in MIL-101(Cr)-azo is likely to be a consequence of interactions between the phenol groups and CO$_2$ molecules. Current work is concentrating on systems in which this is further enhanced.

Table 2. CO$_2$ and N$_2$ sorption data for functionalised MIL-101(Cr) materials under 1 atm at 273 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO$_2$ / mmol g$^{-1}$</th>
<th>N$_2$ / mmol g$^{-1}$</th>
<th>Selectivity $^d$</th>
<th>1 atm</th>
<th>0.1 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIL-101(Cr)-NH$_2$</td>
<td>3.02</td>
<td>0.12</td>
<td>25</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>MIL-101(Cr)-I</td>
<td>1.85</td>
<td>0.12</td>
<td>15</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>MIL-101(Cr)-F</td>
<td>2.24</td>
<td>0.13</td>
<td>19</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>MIL-101(Cr)-azo</td>
<td>1.66</td>
<td>0.08</td>
<td>21</td>
<td>73</td>
<td>73</td>
</tr>
</tbody>
</table>

$^d$ The selectivity was calculated from the single gas isotherms by dividing the CO$_2$ uptake by that of N$_2$.

In conclusion, we have prepared MIL-101(Cr)-NH$_2$ 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 CO$_2$ sorption at low pressure. This new approach provides a flexible protocol for the preparation of functionalised MIL-101 materials.

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Notes and references

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2. Electronic Supplementary Information (ESI) available: Full experimental details, including the synthesis of MIL-101(Cr)-NH$_2$, post-synthetically modified MIL-101(Cr) materials and the azo dye prepared with H$_2$bdc-NH$_2$, and PXRD, SEM, UV-visible, ATR-IR, TGA, $^1$H NMR, $^{13}$C NMR, N$_2$ sorption and CO$_2$ sorption data. See DOI: 10.1039/b000000x/