Synthesis and post-synthetic modification of MIL-101(Cr)-NH$_2$ via a tandem diazonisation process†


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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.\(^3,^4\)

The chromium(III) MOF [Cr$_3$(O,F,OH)(H$_2$O)$_2$(bdc)$_2$]$_n$H$_2$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\(^5\) 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\(^6\) and sulfoxy acid\(^10\) 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 \textit{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.\(^6\)

The iron and aluminium compounds, MIL-101(M)-NH$_2$ (M = Fe, Al), have been prepared by the direct reaction of iron(III)\(^11\) and aluminium(III)\(^12\) 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,\(^13\) whereas Stock and co-workers had previously prepared this material by post-synthetic modification involving nitration of MIL-101(Cr) followed by reduction.\(^5\)

We were able to synthesise MIL-101(Cr)-NH$_2$ hydrothermally from a suitable reagent mixture molar ratio $[\text{1.25Cr(NO$_2$)$_3$} \cdot \text{H$_2$O} : 1.26 \text{H}_2\text{bdc-NH$_2$} : 389\text{H}_2\text{O}]$ 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.\(^13\) Analysis of the TEM images revealed that our samples of MIL-101(Cr)-NH$_2$ have an average particle size of $16 \pm 4$ 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).\(^14\) 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,\(^5\) 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)\(^15\) 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$^{-1}$.\(^15\)
are diazonium chloride, MIL-101(Cr)-N$_2$Cl$^-$, was not isolated, but used in situ, whereas the tetrafluoroborate salt, MIL-101(Cr)-N$_2$BF$_4^-$, was digested in alkaline solution (NaOD/D$_2$O) and characterised by $^1$H NMR spectroscopy.

The PXRD patterns for the modified materials are similar to those for MIL-101(Cr)-NH$_2$-I, confirming that diazotisation followed by substitution or coupling does not alter the framework structure (Figure S3). The linker modification reactions were followed by $^1$H NMR spectroscopy of the digested product in alkaline solution (NaOD/D$_2$O). In the case of MIL-101(Cr)-I (Figure S6), there are three $^1$H resonances, two doublets and a singlet, in the aromatic region of the $^1$H NMR spectrum which is in line with the spectrum observed for H$_2$bdc-I. These resonances appear at different chemical shifts from the resonances observed in the spectra of H$_2$bdc-NH$_2$ and H$_2$bdc-N$_2$F$^-$ for MIL-101(Cr)-F, the $^1$H 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 H$_2$bdc-NH$_2$ and H$_2$bdc 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 $^{19}$F NMR spectrum of digested MIL-101(Cr)-I contains a doublet of doublets at $\delta$ ~122 ppm for H$_2$bdc-F, plus two other signals that can be attributed to tetrafluoroborate ($\delta$ ~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 $^1$H 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 functional groups and the weaker peaks from the ortho-azo functional groups. These features are in line with those observed for H$_2$bdc-N=C$_6$H$_4$OH when synthesised from H$_2$bdc-NH$_2$ using the previously reported method. 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=C$_6$H$_4$OH$^-$] (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 group in the compound, whereas the absorption peak at 329 nm observed in MIL-101(Cr)-NH$_2$ 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, $^1$H 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. Samples of MIL-101(Cr)-azo were irradiated at either 365 nm or

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**Scheme 1. Tandem post-synthetic modification of MIL-101(Cr)-NH$_2$:**

1. NaNO$_2$, HCl(aq);
2. NaNO$_2$, HBF$_4$ (aq);
3. C$_2$H$_5$OH (aq), Na$_2$CO$_3$;
4. KI (aq); 5. $100 ^\circ$C.

Scheme 1 also shows the potential of this approach by preparing synthetic modification of arenediazonium salt was prepared in situ by suspending MIL-101(Cr)-azo to an acidic aqueous solution following by slow addition of NaNO$_2$ 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 fluorinated functionalised material, MIL-101(Cr)-NH$_2$ was treated with Na$_2$CO$_3$ and HBF$_4$ 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 Na$_2$CO$_3$. 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
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CO₂ sorption properties of the functionalised MIL-101(Cr) materials were studied at 273 K (Figure S10 and Table 2). MIL-101(Cr)-NH₃ 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), and may be attributed to the stronger interaction of the amino group with CO₂ than with N₂. MIL-101(Cr)-F and MIL-101(Cr)-azo show decreased CO₂ capacities over MIL-101(Cr)-NH₃. 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 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, 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.

In conclusion, we have prepared MIL-101(Cr)-NH₃ 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.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental details, including the synthesis of MIL-101(Cr)-NH₃, post-synthetically modified MIL-101(Cr) materials and the azo dye prepared with HBr-dc-N₂H₅ and PXRD, SEM, UV-visible, ATR-IR, TGA. H NMR, CO₂ sorption and CO₂ sorption data. See DOI: 10.1039/b000000x/