Soft synthesis of isocyanate-functionalised metal-organic frameworks.

Soft synthesis of isocyanate-functionalised Metal Organic Frameworks

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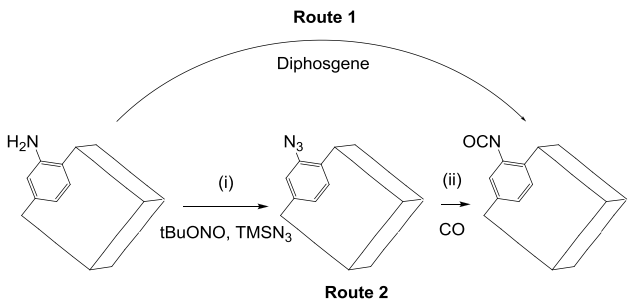
We have developed an original synthetic pathway for the conversion of MIL-68(In)-NH_2 metal-organic framework into its corresponding isocyanate (-NCO) derivate. This two-step soft post-modification technique leads to highly porous isostructural materials.

Metal-Organic Frameworks (MOFs) are the latest generation of porous crystalline materials.[1-3] Their organic-inorganic hybrid nature allows their cavities to be modified by post-synthetic methods[4-7] in order to tune their hydrophilicity/hydrophobicity[8] or acidity/basicity.[9] Even if this characteristic is not a prerogative of MOFs, in this case the versatility and scope of the reactions are decidedly wider than for zeolites and mesoporous silicates. The functionalisation of MOFs by post-synthetic methods (PSM) is an emerging, efficient approach to tuning the properties of porous coordination polymers at the molecular scale.[9-13] Many post-functionalisation approaches have been developed for MOFs; they range from simple condensation reactions to more complex methods involving protection/deprotection steps.[14-18]

MOFs constructed from 2-aminoterephthalate are excellent starting precursors for post-synthetic functionalisation: this is due to the affordability of this linker and because one can employ the same synthesis conditions as for their unfunctionalised counterparts.[19-21] Unfortunately, the weak nucleophilicity of aromatic amines limits their application. On the contrary, strongly electrophilic groups such as isocyanates have been shown to be highly versatile in this respect, allowing the introduction of various carbamate and urea functional groups.[22] The direct synthesis of MOFs possessing such functional groups is difficult, however, so in general these groups are introduced by post-synthetic means. Interestingly, it is possible to transform amino into isocyanate groups in MOFs, but the present method requires the use of diphosgene (route 1 in Scheme 1). In fact, the treatment of MIL-53(Al)-NH_2 (MIL: Materials from Institut Lavoisier, Al(OH)(2-amino-1,4-benzenedicarboxylate)) leads to the corresponding MIL-53(Al)-NCO.[22, 23]This method cannot, however, be applied to most MOFs, because the diphosgene treatment involves HCl formation, which in turn leads to the solubilisation of the solid.

The protection-deprotection approach is a general concept that allows this limitation to be circumvented. Very recently, Kitagawa[24] and Cohen[25] reported the first light-driven deprotection of MOFs in order to reveal "dormant" reactive functionalities.[18] In particular, Sato et al.[24] have shown that azide groups in MOFs can be transformed into nitrene species upon photoactivation.[24-26] Nitrenes in the triplet spin state are very reactive species that can easily react with gas molecules, solvents and organic compounds.[27, 28] In fact, in the presence of CO and upon UV irradiation, the transformation of MOF-N_3 to MOF-NCO has been reported,[24] in analogy to what was reported previously for matrix-isolated aryl azides in cryogenic conditions.[29-31] The possibility of converting azide into isocyanate has also been reported for the reaction of these species with metal carbonyls[32-37] or through the Curtius rearrangement of acyl azide groups. Unfortunately, the azide to isocyanate conversion was performed over a very long reaction time with a requirement for continuous cooling with liquid nitrogen in order to transform the inert singlet-state azide group into the reactive triplet species. Moreover, a very low amount of isocyanate was obtained after 12 h.[24]



Scheme 1. Possible synthetic routes to MOF with pendent isocyanate groups

The present study concerns an original procedure for synthesising MOF-NCO from a MOF based on 2-amino-1,4-BDC (BDC: 1,4-

benzenedicarboxylate) by a two-step soft post-modification technique (route 2 in Scheme 1). This new method combines two reactions already reported in the literature that here are juxtaposed for the first time. This combination makes it possible to exploit the advantages of both the amino and isocyanate precursors in order to derive new MOFs. As a proof of concept, this study deals with the post-modification of In(OH)(2-amino-1,4-BDC), hereafter denoted MIL-68(In)-NH_2.[38, 39] This material has been chosen because, despite its good stability in air, it easily hydrolyses in water, making the diphosgene treatment unsuitable for MIL-68. This method can be applied to other MOF structures with varying degrees of functionalisation: these results and the properties of the MOFs that can be obtained by exploiting the rich reactivity of isocyanate groups will be described elsewhere.[40] The first step involves the conversion of MIL-68(In)-NH_2 into the corresponding azide compound MIL-68(In)-N_3 by following a post-synthetic method reported previously.[38, 41] In the second step, MIL-68(In)-N_3 is thermally activated in the presence of CO to form MIL-68(In)-NCO. Due to the high reactivity of the aryl nitrenes, it is important that these groups are sufficiently widely spaced within the material for reactions between them to be prevented.[42] For this reason, an $–NH_2$ diluted structure was considered as a starting material. This material was synthesised using an 80:20 ratio of BDC and BDC-NH_2 (MIXMOF-MIL-68(In)-20%NH_2). The preservation of the ligand ratio in the synthesised material and its homogeneity were demonstrated previously.[43, 44] The integration of the aromatic proton signals of BDC-NH_2 (7, 7.35 and 7.75 ppm) in ^{1}H-NMR (Figure 2a) accordingly indicated that the 18.22% of the total linkers of this material are BDC-NH_2.
MIL-68(In) materials are MOFs constituted of wires of $InO_4(OH)_2$ octahedra linked by BDC-based linkers, giving rise to a Kagomé structure characterised by two families of 1D pores of hexagonal (17.8 Å, nucleus-nucleus distances) and triangular shape (7.8 Å). MIXMOF-MIL-68(In)-20%NH_2 was (i) treated with tBuONO and $TMSN_3$ in THF overnight at room temperature to produce the corresponding azide intermediates; (ii) dried in air and activated under ultra-high vacuum at 90°C overnight in order to remove all the solvent and water molecules; and (iii) reacted three times with an excess of CO (300 mbar) at 120°C for 48 h (total reaction time).

The crystallinity and surface area of each sample were verified by X-ray powder diffraction (XRPD) and nitrogen adsorption and compared with theoretical values (Table S1 and Figure S2). The transformation of $–N_3$ into –NCO was followed by Fourier transform infrared (FTIR) and ^{1}H-NMR spectroscopies.

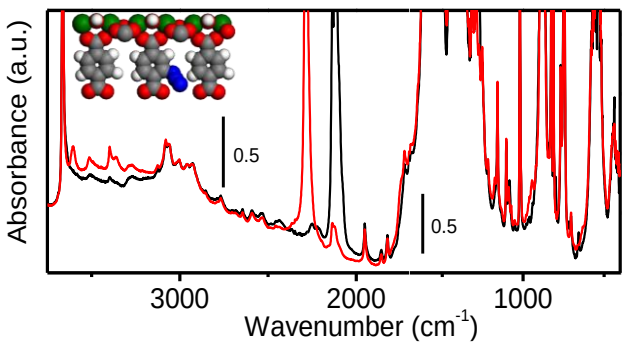


Fig. 1. FTIR spectra of MIXMOF-MIL-68(In)-N_3 degassed at 90°C overnight (black curve) and after reaction with 300 mbar of CO at 120°C for 48 hours (red curve). In the pictorial scheme of the MOF walls, the atoms are represented as spheres with the colour code: red (oxygen), grey (carbon), white (hydrogen), blue (nitrogen) and green (indium).

The IR spectra of MIXMOF-MIL-68(In)-N_3 samples before and after reaction with CO are reported in Figure 1a (black and red curve, respectively). The spectrum of activated MIXMOF-MIL-68(In)-N_3 was characterised by a sharp IR absorption at 3662 cm^{-1} associated with the structural isolated hydroxyls, an intense band at 2118 cm^{-1} due to the stretching of azide groups and a complex set of signals below 1790 cm^{-1} mainly associated with framework modes. The negligible intensity of signals at 3506 and 3393 cm^{-1} assigned to N-H stretching was an indication of the total amino-to-azide transformation that was also confirmed by ^{1}H-NMR (see below). After the reaction with CO, the only significant change in the IR spectrum (red curve) was the consumption of -N_3 and the growth of a strong band at 2285 cm^{-1} characteristic of the –NCO group.[24] The transformation of $–N_3$ species into –NCO is confirmed by the sequence of spectra in Figure S6, in which an isosbestic point is visible at about 2230 cm^{-1}. An estimation of the degree of conversion was difficult to be achieved by FTIR because of the high extinction coefficient of both azide and isocyanate groups.
The full conversion of azide into isocyanate groups was confirmed by ^{1}H-NMR.

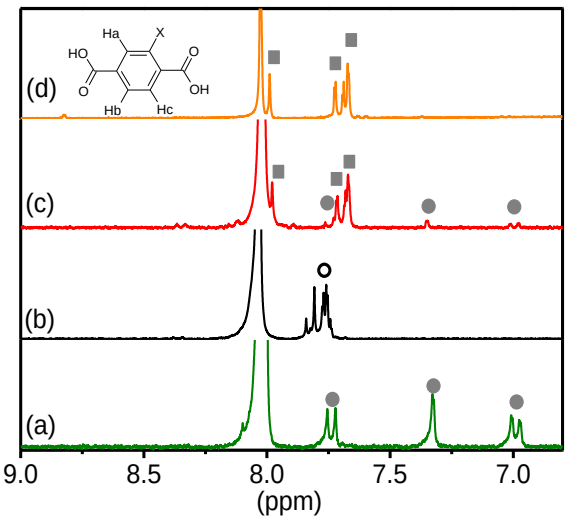


Fig. 2. ^{1}H-NMR spectra of MIXMOF-MIL-68(In)-NH_2 (a), MIXMOF-MIL-68(In)-N_3 (b) and MIXMOF-MIL-68(In)-NCO (c). The spectrum of MIXMOF-MIL-53(Al)-NCO obtained via diphosgene treatment is also reported for comparison (d). Before measurements all samples were digested in HF/DMSO-d_6.[22] Filled circles refer to amino signals, empty circles to azide species and filled squares to isocyanate groups.

^{1}H-NMR was used to follow the modification of the ligand substitution due to the strong shift of its aromatic protons and to quantify the degree of conversion of azide into isocyanate groups. The spectra are reported in Figure 2.

A singlet at 8.02 ppm corresponds to the aromatic protons of pure terephthalic acid. The spectrum of MIXMOF-MIL-68(In)-NH_2 (green curve) exhibits two doublets (7 ppm, H_b, and 7.75 ppm, H_c) and a singlet (7.35 ppm, H_a, filled circles) that are not present after the transformation of amino into azide groups (black curve).The MIXMOF-MIL-68(In)-N_3 spectrum is characterised by a broad signal around 7.75 ppm (empty circle). The spectrum of MIXMOF-MIL-68(In)-NCO (red curve) shows two doublets at 7.6 (H_b) and 8 ppm (H_c) and a singlet at 7.6 ppm (H_a) (squares). These signals can be associated with the formation of isocyanates as seen for the spectrum obtained for MIXMOF-MIL-53(Al)-NCO (80:20 ratio between BDC and BDC-NH_2, orange curve) following the diphosgene route.[22] In the isocyanate-modified materials (red and orange curves) the signals related to amino groups (filled circles) are observed due to side reactions. Their weak intensity confirms the very low concentration of these species, in agreement with FTIR results.

XRPD measurements indicated that the reaction with CO did not affect the MIXMOF-MIL-68(In) pattern (Figure S2). These findings were further confirmed by nitrogen adsorption measurements that demonstrate that the MOF pore structure is not modified after the reaction with CO (Figure S1 and Table S1).

In conclusion, this new two-step synthesis extends the possibility of post-functionalisation with isocyanate groups to a higher number of MOFs than was achievable with the diphosgene route, with these MOFs representing intermediates for the design of diverse sophisticated and functional porous MOFs. Moreover, the thermal activation of $-N_3$ groups in MOF materials, by avoiding the use of solvents, offers the possibility of further extending the nitrene chemistry.[29-31]

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Notes and references

† Electronic Supplementary Information (ESI) available: [Experimental procedures, XRPD and nitrogen adsorption measurements, MIL-68(In) structure, thermal gravimetric analysis of MIXMOF-MIL-68(In)-N_3, IR spectra obtained for different reaction temperatures and times of CO/MIL-68(In)-N_3.].

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