Direct covalent post-synthetic chemical modification of Cr-MIL-101 using nitrating acid†

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For the first time, functionality has been covalently introduced into the Cr-MIL-101 network by post-synthetic modification of the terephthalate linker molecule through nitration. The nitro group was reduced and the amino group was reacted with ethyl isocyanate to yield the corresponding urea derivative.

Metal–organic frameworks (MOFs) have gained widespread attraction due to their striking physical and chemical properties such as pore size distribution, surface properties and chemical functionality. They exhibit large, regular and accessible pores, thus, so far, no successful synthesis of the amino-derivative of Cr-MIL-101 could be obtained.

Cr-MIL-101 was initially synthesized starting from Cr(NO3)3·9H2O and terephthalic acid via hydrothermal reaction according to the literature.16 Cr-MIL-101–NO2 was synthesized by nitration of Cr-MIL-101 using nitric acid (HNO3 conc. and H2SO4 conc.) for five hours under ice cooling (named Cr-MIL-101–NO2(1)).† The direct synthesis of Cr-MIL-101–NO2 is achieved by a hydrothermal reaction of CrCl3 and nitrotetraphthalic (H2BDC–NO2) acid (molar ratio CrCl3 : H2BDC–NO2 : H2O = 1.6 : 1 : 278) at 180 °C for 96 hours (named Cr-MIL-101–NO2(2)). In both cases several activation steps using water and ethanol in a microwave oven at 150 °C for 1 h were performed. Subsequently, the nitro groups were reduced to amino groups using SnCl2·2H2O and ethanol for 6 h at 70 °C to yield Cr-MIL-101–NH2 (Fig. 1). Noteworthy, an amorphous Sn-containing product is observed in Cr-MIL-101–NH2 by EDX measurements, which is removed through dissolution using concentrated hydrochloric acid followed by a treatment with H2O and EtOH.

X-Ray powder diffraction (XRPD) measurements were employed to identify and to prove the stability of the Cr-MIL-101 compounds (Fig. 2). Sorption measurements were performed to demonstrate permanent porosity (Fig. 3).

To prove the successful formation of the covalent functionalized compounds, infrared spectroscopy (IR) and solution Nuclear Magnetic Resonance (NMR) spectroscopy were performed.

Some of us reported the compound MIL-101 (MIL = Matériaux de l’Institut Lavoisier).16 Cr-MIL-101, [Cr3F(H2O)2–(μ3-O)(O2CC6H4CO2)3]·nH2O, is outstanding due to its high thermal and chemical stability and its large apparent surface area. It forms a zeotypic MTN network and exhibits two large accessible mesoporous cages accessible through microporous windows and is therefore an interesting candidate for post-synthetic modification reactions.4 Since Cr-MIL-101 is synthesized under hydrothermal conditions above 200 °C, the use of aminotetraphthalic acid leads to its decomposition and thus, so far, no successful synthesis of the amino-derivative of Cr-MIL-101 could be obtained.

Here we report the first post-synthetic modification of a MOF by electrophilic aromatic substitution, i.e. the nitration of Cr-MIL-101 to Cr-MIL-101–NO2 using nitric acid and the subsequent reduction to the amino functionalized Cr-MIL-101–NH2. Furthermore, we present the direct synthesis of Cr-MIL-101–NO2 under hydrothermal conditions.

Metal–organic frameworks (MOFs) have gained widespread attention due to their striking physical and chemical properties such as pore size distribution, surface properties and chemical functionality. They exhibit large, regular and accessible pores, which are connected by organic linkers.5 With the choice of the linker molecules the pore size, the chemical functionality and physical properties can be varied.6

A very promising method to introduce functionality is the post-synthetic modification of MOFs.7 This can be achieved via coordination of a functionalized ligand (e.g. amines) to unsaturated metal sites or by ligand substitution.8 Another well-established method is the covalent modification of functional groups attached to the linker molecule.9 This has been previously shown by introducing functionalized ligands, mainly containing –NH2 groups.10,11 Especially the amino group is suitable for further modification reactions. Other reactions that have been reported are nucleophilic addition of isocyanates to yield the urea derivatives or condensation reactions with phosgene/thio-phosgene to yield the isocyanates/ithiocyanoates.12 Other post-synthetic functionalization reactions starting from aldehyde,13 hydroxyl14 or azide groups15 have been reported, which include the reduction of aldehyde groups and the formation of imines.

Although some amino-functionalized MOFs can be obtained directly by replacing the unfunctionalized by the corresponding functionalized linker, i.e. terephthalic acid by aminoterephthalic acid, this is not always easily accomplished. Especially for compounds that are synthesized at high temperatures some functional groups cannot be incorporated since the starting material decomposes during the synthesis.

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While the crystallinity is barely changed during the harsh synthesis conditions using nitrat ing acid, the specific surface area decreases from $S_{BET}$ 2600 m$^2$/g$_0$1 for Cr-MIL-101 to 1425 m$^2$/g$_0$1 for Cr-MIL-101–NO$_2$(1) (Fig. 3). This value corresponds well with the specific surface area of the directly synthesized Cr-MIL-101–NO$_2$(2).

After reduction of the nitro groups, the change in the relative reflection intensities in the XRPD patterns (Fig. 2) is in agreement with a partial pore filling of the dense amorphous Sn-containing product. This is also demonstrated by N$_2$-sorption experiments where specific surface areas of 1307 and 1053 m$^2$/g$_0$1 for Cr-MIL-101–NH$_2$(1)as and Cr-MIL-101–NH$_2$(2)as are observed. XRPD measurements of the activated Cr-MIL-101–NH$_2$ samples exhibit the expected relative intensities and the specific surface areas increase to 2306 and 2313 m$^2$/g$_0$1 for Cr-MIL-101–NH$_2$(1) and Cr-MIL-101–NH$_2$(2).

The successful linker modification can be followed by IR spectroscopy. After nitration the characteristic stretching vibration of the nitro group is observed at 1533 cm$^{-1}$ (Fig. S1, top, ESI†). Additionally, the C–N stretching vibration appears at 1165 cm$^{-1}$. After the reduction the signal of the NO$_2$ stretching vibration is no longer present. The characteristic amine vibrations can be observed by IR spectroscopy as well. At 3494 cm$^{-1}$ and 3378 cm$^{-1}$ the asymmetric and symmetric N–H-stretching vibrations of the amino group (Fig. S2, ESI†) and at 1165 cm$^{-1}$ the C–N stretching vibration are observed (Fig. 4, bottom). After digestion of the Cr-MIL-101 compounds using NaOH, terephthalic acid, aminoterephthalic acid as well as nitroterephthalic acid were observed in proportions depending on the nitration time. While nitration for ten minutes leads to a mixture of nitroterephthalic and terephthalic acids, a reaction time of five hours yields only nitroterephthalic acid (Fig. S3, ESI†). Thus, partial nitration of Cr-MIL-101 is possible. Expanding the nitration time to 48 h, no multiple nitration of the aromatic system was observed. This is due to the $-\text{M}$ and $-\text{I}$ effect of the nitro group which deactivates the system and prevents a second electrophilic substitution reaction. After the subsequent reduction only aminoterephthalic acid was observed (see S4, ESI†). Analogous nitration reactions of Cr-MIL-53 were not successful since they led to the dissolution of the MOF.

To prove the presence and the reactivity of the amino groups Cr-MIL-101–NH$_2$ was reacted with ethyl isocyanate to yield Cr-MIL-101–UR2. In a typical reaction, Cr-MIL-101–NH$_2$ was suspended in acetonitrile, ethyl isocyanate was added and the mixture was allowed to react at 70 °C for five hours under nitrogen atmosphere. To remove by-products and traces of educts the product was washed using acetonitrile, water and ethanol. This post-synthetic functionalization step leads to the urea derivative (Fig. 1), as demonstrated by IR and
NMR-spectroscopy (Fig. 4 and 5). The urea N–H stretching vibration appears at 3322 cm\(^{-1}\), the aliphatic C–H stretching vibration at 2973 cm\(^{-1}\) (Fig. S5, ESIF). A characteristic signal for urea appears at 1690 cm\(^{-1}\) which is due to the C=O stretching vibration. The asymmetric stretching vibration of the urea N–C–N group is observed at 1304 cm\(^{-1}\). At the same time the specific surface area decreases from 2313 m\(^2\) g\(^{-1}\) to 1327 m\(^2\) g\(^{-1}\). \(^{1}\)H and \(^{13}\)C-NMR-spectroscopy give strong evidence on the successful formation of the urea product (Fig. 5 and 6; Fig. S6, ESIF).

All signals in both spectra can be clearly assigned to the compounds containing product Cr-MIL-101–NH\(_2\), which can be precipitated under acidic conditions. After centrifugation and washing with acetone, the yellowish precipitate is dissolved using a half concentrated deuterated sodium hydroxide solution.

In summary, the post-synthetic functionalization of Cr-MIL-101 using nitrating acid has been achieved to obtain the nitro compound Cr-MIL-101–NO\(_2\), which can also be obtained by the direct hydrothermal synthesis of Cr-MIL-101–NO\(_2\) using nitrilic acid. XRPD measurements confirm the integrity of the structure as well as a decrease of the specific surface area. The subsequent reduction of the nitro groups leads to the –NH\(_2\) containing product Cr-MIL-101–NH\(_2\), which upon activation possesses an adequate specific surface area. Finally, the functionalization of Cr-MIL-101–NH\(_2\) with ethyl isocyanate yields the urea derivative Cr-MIL-101–UR2, which indicates that an easy access to a functionalized, highly stable and highly porous MOF has been demonstrated. Cr-MIL-101–NH\(_2\) is therefore the ideal candidate for a large variety of post-synthetic modification reactions.

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Notes and references

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