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Chemical Modification of a Bridging Ligand Inside a Metal–Organic Framework while Maintaining the 3D Structure

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A new metal–organic framework (MOF) with amino groups situated inside the pores has been synthesized. This MOF has been modified by post-synthesis with two different functionalities. The crystal structures of the two functionalized MOFs clearly demonstrate that it is possible to transform the cavities of a MOF without modifying its original 3D structure. These unprecedented results open up tremendous possibilities in the field of MOF chemistry because many potential applications in the fields of catalysis, material science or nanochemistry can be envisaged when applying the reported synthetic pathway.

Introduction

The generation of metal–organic frameworks (MOFs) enables the tailoring of novel solids with regular, controllable porosity from the micropore to the nanopore scale. These materials may display remarkable functionalities that are potentially exploitable for a number of applications, such as gas storage and gas separation,[1,2] nonlinear optics,[3] ion exchange[4] and even catalysis.[5] Since the discovery of this new family of nanoporous, zeolite-type materials[5] and the concept of so-called 'reticular design',[6] already thousands of different types of MOFs are known.[1,7] Thus, the design and controlled construction of such crystalline host materials are now commonly achieved.[8] The next and very important challenge to be addressed in this topical field of material science consists of conceiving and preparing MOFs with *functionalized* pores,[9] especially for applications in catalysis.[7,10] Herein we report the controlled synthesis of a 3D metal–organic framework with amino functional groups oriented inside the pores, as evidenced by X-ray single-crystal analysis. These amino groups undergo conversion by way of diffusion of an organic functionality into the framework, which results in modified cavities. This synthetic approach allows the post-synthesis functionalization of the pores, in contrast to the currently proposed in situ strategy,[10] which is based on a functionalization through the use of different building blocks to create the material. Contrary to the old approach, the present method does not require the preparation of specific, intricate building blocks for the generation of each targeted functional MOF. Indeed, the same porous compound can be easily and purposely modified by its subsequent reaction (through the amine functions) with a variety of different organic molecules.

Results and Discussion

The reaction of gadolinium(III) nitrate with 2-amino-1,4-benzene dicarboxylic acid (N-H_2BDC) in dimethylformamide (dmf) at 120 °C produces the 3D coordination network $\{[Gd_2(\text{N-BDC})_3(\text{dmf})_4]\}_n$ (MOF-LIC-1), whose building unit is depicted in Figures 1A and S1. Details for the structure solution and refinement are summarized in Table S1 and the theoretical and experimental X-ray powder diffraction patterns are shown in Figure S2. The Gd^{III} ions are coordinated to seven oxygen atoms belonging to five different N-BDC ligands and two dmf molecules and exhibit a tricapped trigonal-prismatic geometry; the capping atoms are O2, O7 and O6_d (Figure S3). Each Gd^{III} ion is connected to another metal centre through four bridging carboxylato moieties of four distinct N-BDC ligands, thus generating a dinuclear core (Figures 1A, S1 and S3A) that acts as the node of the 3D inorganic–organic framework. Each dinuclear unit is surrounded by two O,O′-, two μ-O,O′- and two μ-O,O,O′-carboxylato donor groups (Figure S4) of six N-BDC ligands, which are depicted respectively in red, blue and green in Figure 1A. The dinu-

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clear Gd core (node) together with its six coordinated N-BDC ligands (organic linkers), schematized in Figure 1B, represent the building block of the 3D architecture. Eight digadolinium blocks are required to form a cube, as illustrated in Figure 1C and Figure 2. The infinite associations of these cubes produce an octahedral network,[11] which is characterized by porous channels (Figure 1D). In a manner similar to that in the compound IRMOF-3 reported by Yaghi and co-workers,[12] the 2-amino substituent of the N-BDC ligand does not coordinate to the dinuclear Gd_2O_7 cluster (see MOF-LIC-1 in Figure 2). As very recently pointed out by Cohen and co-workers,[9] these amine groups may therefore be modified by reaction with an appropriate organic molecule. The amino groups in MOF-LIC-1 occupy two crystallographic positions with occupancy factors of 0.5 (see Figures 1A, 2 and S1).

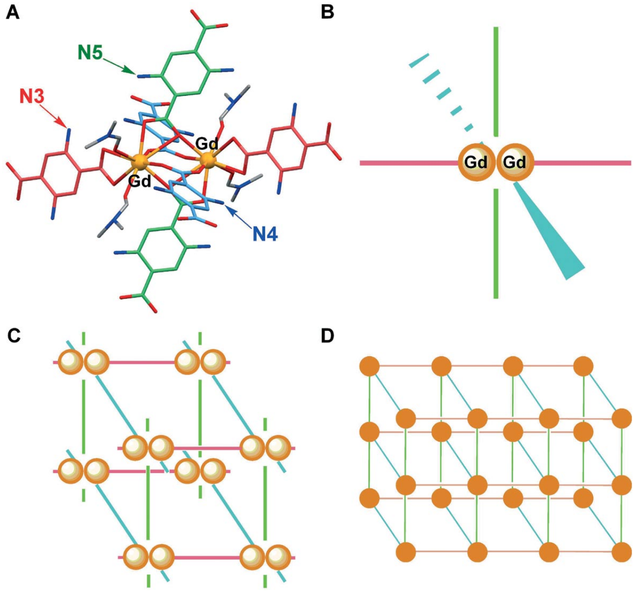


Figure 1. A: Illustration of the dinuclear complex showing the three different types of N-BDC ligands (the red ligands contain the amino groups N3, the blue ligands the amino groups N4, and the green ligands the amino groups N5); B: schematic representation of the dinuclear building block; C: cube generated from 8 building blocks; D: octahedral network of MOF-LIC-1.

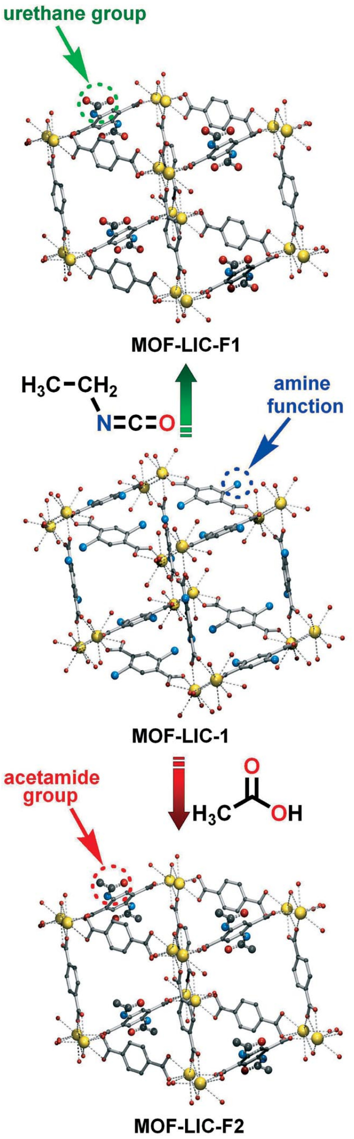
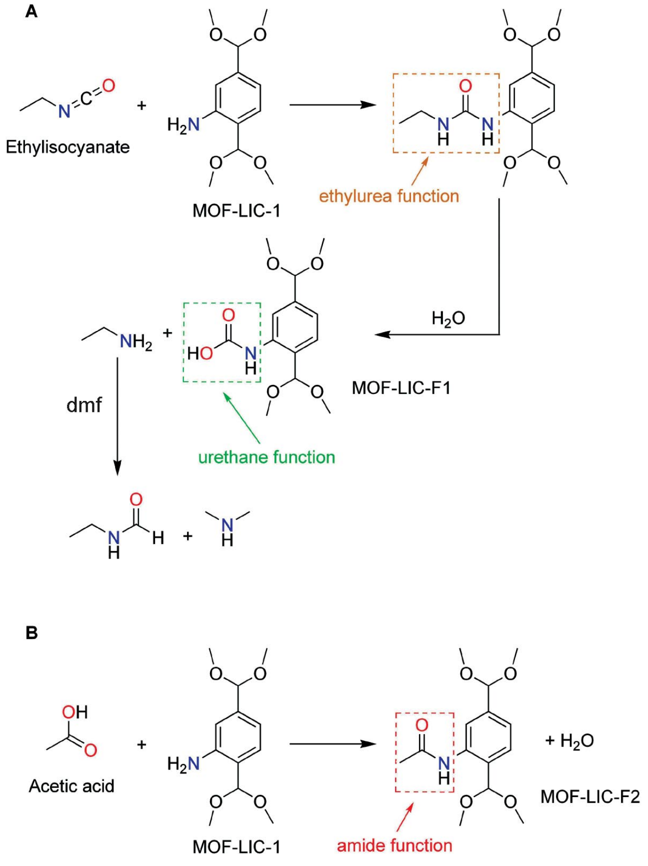


Figure 2. Representations of the cubic building blocks of the three different MOFs prepared. MOF-LIC-F1 and MOF-LIC-F2 are obtained by reaction of MOF-LIC-1 with ethylisocyanate and acetic acid, respectively.

The reaction of ethylisocyanate with single crystals of MOF-LIC-1 (Scheme 1A) for 1 h at 120 °C leads to a slight colour change of the material, from yellow to yellow–orange, while the material remains crystalline. The X-ray diffraction analysis of a modified single-crystal (MOF-LIC-F1) reveals that the amine groups have been converted to urethane functions (MOF-LIC-F1; Figure 2). The nitrogen atom of the bis(O,O′-carboxylato) N-BDC ligand (blue ligand in Figure 1A) of the original MOF-LIC-1 material is partially transformed into a –NH–CO–OH group. It thus appears that the expected ethylurea function (Scheme 1A) has been hydrolyzed by atmospheric water to a urethane group. As evidenced in Scheme 1, the hydrolysis of the initially formed urea groups leads to the formation of ethylamine. Indeed, the generation of ethylamine is confirmed in the crystal structure of the modified MOF-LIC-F1, in which a molecule of ethylformamide (O8′–C16′–N5′–C17′–C18′) is now coordinated to Gd1 (Figure S5). Ethylformamide obviously results from the transamination of dmf with ethylamine. The driving force of this reaction is the release of dimethylamine, which is sterically more hindered than ethylformamide (ethylformamide is linear, whereas dimethylformamide is branched) and has a lower boiling point than ethylamine [b.p. (Me_2NH) = 7 °C; b.p. ($EtNH_2$) = 17 °C].

It has to be noted that not all amine substituents of the bis(O,O′-carboxylato) N-BDC ligand (blue ligand in Figure 1A) are functionalized. The other amine groups (from the red and green ligands in Figure 1A) have remained unchanged. A closer look at the X-ray structure of MOF-LIC-1 clearly indicates that the three types of amine substituents (corresponding to the different N-BDC ligands classified



Scheme 1. A: Reaction of MOF-LIC-1 with ethylisocyanate; B: reaction of MOF-LIC-1 with acetic acid.

by their binding modes; Figures 1A and S4) have distinct individual accessibilities. The amine function of the bis(μ-O,O′-carboxylato) N-BDC ligand (red ligand in Figure 1A) strongly interacts with one methyl group of a dmf molecule (C14···N3 distance 2.970 Å; Figure S6A). The amine substituent of the bis(μ-O,O,O′-carboxylato) N-BDC ligand (green ligand in Figure 1A) is also in close contact with a dmf methyl group (C15···N5 distance 3.214 Å; Figure S6C). In contrast, the nitrogen atom N4 (blue ligand in Figure 1A) is separated from the dmf methyl groups by distances that are greater than 4.1 Å (Figure S6B). Consequently N4 is available to potential functionalization, in contrast to N3 and N5, as is displayed in the X-ray structure of modified MOF-LIC-F1 (Figure 2). Each crystallographic position of the nitrogen atom N4 is partly changed to a urethane group (the occupancy factor of each urethane function is 0.2), which results in a conversion of 40% to the functionalized amine.

Post-synthetic transformation of the amino functionality in MOF-LIC-1 has also been undertaken with acetic acid (Scheme 1B). The X-ray structure of the resulting modified MOF-LIC-F2 is depicted in Figure 2. As expected, the original N4 atom is now partly substituted by an acetyl group. The amidic function observed in the crystal structure of modified MOF-LIC-F2 (Figure 2) arises from the condensation reaction between the amine and acetic acid. Once again, only the amine groups N4 are subjected to chemical modification. In this case, 50% of each crystallographic position is transformed into an amide group. It has to be mentioned here that MOF-LIC-1 is more degraded in the presence of acetic acid than in ethylisocyanate. If the reaction is carried out for more than one hour, the material (MOF-LIC-F2) gradually loses its crystallinity (this is not observed with MOF-LIC-F1).

Conclusions

In summary, a new metal–organic framework, MOF-LIC-1, has been synthesized and, for the first time, structurally characterized by X-ray diffraction before and after post-synthetic chemical modification. MOF-LIC-1 displays an octahedral network containing infinite porous channels. These channels present –NH_2 groups that can be covalently functionalized. The reaction of MOF-LIC-1 with ethylisocyanate and acetic acid generates two new MOFs whose porous channels have been modified. The first crystallographic proof of post-synthetic modification has been obtained, which clearly strengthens this synthetic approach as a powerful, simple and versatile method to prepare custom-made functional MOFs in a straightforward manner. For example, the covalent integration of specific ligands inside the pores of MOFs may ultimately allow the design and synthesis of MOF-based heterogeneous catalysts.

Experimental Section

Preparation of MOF-LIC-1: Gadolinium(III) nitrate hexahydrate (601 mg, 1.33 mmol) dissolved in dmf (10 mL) was added to a solution of the ligand N-H_2BDC (361 mg, 2.00 mmol) in dmf (20 mL) in a glass tube (Corning Pyrex culture tube, diameter 20 mm, height 220 mm). The tube was sealed and the contents well mixed. The tube was placed in an oven at 120 °C for 20 h, which resulted in the formation of light-yellow single-crystals in good yield (563 mg, 74%). $C_{36}H_{43}Gd_2N_7O_{16}$ (1144.26): calcd. C 37.79, N 8.57, H 3.79; found C 37.58, N 8.45, H 3.67. The crystals were analyzed by single-crystal X-ray diffraction (Figure 1) and by X-ray powder diffraction (Figure S2).

Preparation of Modified MOF-LIC-F1 and MOF-LIC-F2: Both modified MOFs were prepared in the following manner. Single-crystals (about 10 mg) of MOF-LIC-1 were introduced in a test tube (diameter 7 mm, height 60 mm) and wetted with dmf (not dried). This tube was then placed in a glass tube (Corning Pyrex culture tube, diameter 13 mm, height 100 mm) containing a few drops of the reactant used to functionalize the cavities of MOF-LIC-1 (ethylisocyanate for MOF-LIC-F1 and acetic acid for MOF-LIC-F2). The tube was sealed and placed in the oven at 120 °C for 1 h to allow a gas phase/solid phase reaction between the organic reactant (ethylisocyanate, b.p. = 60 °C; acetic acid, b.p. = 118 °C) and the crystals (MOF-LIC-1). After 1 h, slightly darkened crystals (some of them remained as single-crystals that were suitable for X-ray diffraction analysis) were obtained.

MOF-LIC-F1: $C_{36.2}H_{43}Gd_2N_7O_{16.4}$ {corresponding to [Gd_2(N-BDC)$_{2.8}$(N-BDC$_{modified}$)$_{0.2}$(dmf)$_4$]} (1153.07): calcd. C 37.71, N 8.50, H 3.76; found C 37.38, N 8.37, H 4.53. The X-ray single-crystal structure and the XRPD pattern of MOF-LIC-F1 are depicted in Figures 2 and S7, respectively.

MOF-LIC-F2: $C_{42.5}H_{57.5}Gd_2N_9O_{18.25}$ {corresponding to [Gd_2(N-BDC)$_{2.75}$(N-BDC$_{modified}$)$_{0.25}$(dmf)$_4$](dmf)$_2$} (1300.96): calcd. C 39.24, N 9.69, H 4.45; found C 38.81, N 7.53, H 4.92. The low percentage for N is most likely due to partial degradation of the material upon reaction with acetic acid. After a reaction time of 1 h, most of the single crystals lost their transparency (they became opaque), which was not the case when the reaction was performed with ethylisocyanate (see above). The X-ray single-crystal structure and the XRPD pattern of MOF-LIC-F2 are depicted in Figures 2 and S8, respectively. In both cases (MOF-LIC-F1 and MOF-LIC-F2), the XRPD spectra clearly show that the bulk materials remain crystalline.

Structural Determination: Measurements on single crystals of MOF-LIC-1 and MOF-LIC-F2 were performed by using silicon-(111) monochromated synchrotron radiation ($\lambda = 0.8457$ Å for MOF-LIC-1 and $\lambda = 0.7848$ for MOF-LIC-F2) and a Bruker APEXII CCD area-detector diffractometer, with standard procedures and programs for Station 16.2 of Daresbury SRS. Data were collected on a Bruker APEXII diffractometer with the APEX2 software. X-ray diffraction (XRD) data for MOF-LIC-F1 were recorded on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). DENZO-SMN was used for data integration, and SCALEPACK corrected data for Lorentz-polarization effects.[13] In all three cases, the crystals were mounted onto the diffractometer at low temperature under nitrogen at ca. 150 K. The structures were solved by direct methods and refined over F^2 with the SHELXTL package.[14,15] CCDC-666828, -666829, -666830 contain the supplementary crystallographic data for MOF-LIC-1, MOF-LIC-F1 and MOF-LIC-F2, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk. X-ray powder diffraction (XRPD) data for MOF-LIC-1, MOF-LIC-F1 and MOF-LIC-F2 were obtained by using a Phillips Xpert pro equipped with a X′celerator, with Cu-K_α-radiation ($\lambda \approx 1.5408$ Å), in 2θ range 10–60°. The diffraction patterns were recorded at room temperature.

Supporting Information (see footnote on the first page of this article): Single-crystal and powder diffraction data for MOF-LIC-1, MOF-LIC-F1 and MOF-LIC-F2, selected bond lengths and angles for MOF-LIC-1, and illustrative schematic representations of the structural features characterising MOF-LIC-1, MOF-LIC-F1 and MOF-LIC-F2 are presented.

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