First Direct Imaging of Giant Pores of the Metal−Organic Framework MIL-101

O. I. Lebedev,[†] F. Millange,*[,‡] C. Serre,[‡]
G. Van Tendeloo,[†] and G. Férey[‡,§]

University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium, and Institut Lavoisier, UMR 8637, Université de Versailles St-Quentin-en-Yvelines, 45 Avenue des Etats-Unis F-78035, Versailles Cedex, France

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The subject of this study is a chromium(III) terephthalate (1,4-benzene dicarboxylate, 1,4-BDC). It was obtained by the combination of targeted chemistry[1] and global optimization simulations of crystal structures.[2] Its cubic structure ($a \sim 89$ Å) exhibits several unprecedented features: a mesoporous zeotype architecture [related to mobil thirty-nine (MTN) topology],[3] a giant cell volume (702 000 Å^3), a hierarchy of extra-large pore sizes (ø ∼ 29−34 Å, cage volumes ≈ 12 700 and 20 600 Å^3), and a record sorption capacity ($S_{\text{Langmuir}} \sim 5900 \pm 300$ m^2·g^{-1}). The structure of MIL-101 is built up from a corner-sharing of so-called supertetrahedra (ST).[4] Each ST is made from the linkage of inorganic trimers and 1,4-BDC anions (Figure 1a,b). The four vertexes of the ST are occupied by the trimers while the organic linkers are located at the six edges of the ST (Figure 1c). The connection of the ST ensures a three-dimensional network of "corner-sharing" ST with an augmented MTN zeotype architecture (Figure 1d) and provides a new example of our concept of scale chemistry.[5] The ST are microporous (∼8.6 Å free aperture for the windows) while the resulting framework delimits two types of mesoporous cages filled with free water molecules. These two cages, which are present in a 2:1 ratio, are delimited by 20 and 28 ST with an internal *free* diameter of ∼29 and 34 Å, respectively. To the best of our knowledge, these values are the highest ever obtained in the field of metal−organic frameworks (MOFs). The smallest cages exhibit pentagonal windows with a free opening of ∼12.0 Å while the larger cages possess both pentagonal and larger hexagonal windows of a ∼14.5 × 16.0 Å free aperture (see Supporting Information).

Transmission electron microscopy (TEM) of porous solids has only been applied when these solids possess an inorganic skeleton.[6−8] The present study on the above MOF is, therefore, a precept study. MIL-101 is extremely sensitive to the electron beam and, in usual conditions, the structure collapses after a few minutes. To minimize changes of the structure, a minimum electron dose and a minimum flux are used for electron diffraction (ED) or high-resolution electron microscopy (HREM) measurements. For the latter, the magnification is kept as low as possible. Another problem is the insulating character of the materials, leading to charging of the crystals and drift and vibrations in the image. To image the pore configuration, the HREM images were taken at relatively large under-focus conditions. Under these conditions the contrast is determined by the focus and the "projected charge density" approximation of Cowley and Moodie is valid.[9] Tunnels will then show up as bright dots, and dense matter will be dark.[10]

ED patterns of MIL-101 are shown in Figure 2. The diffraction patterns can be completely indexed in the $Fd\bar{3}m$ space group using the unit cell parameters determined from X-ray powder diffraction ($a \sim 89$ Å). The reflections obey the following conditions (hkl, $h + k$, $h + l$, $k + l = 2n$; $h00$, $h = 4n$; hhl, $h + l = 2n$; $0kl$, $k + l = 4n$, k, $l = 2n$), imposed by the $Fd\bar{3}m$ space group. All reflections are very sharp and illustrate the perfection of the MIL-101 crystals. The dimensions of the MIL-101 crystals range from 100 nm up to about 1 μm. The cubic symmetry of the MIL-101 is also reflected in the shape of the crystals (see Supporting Information). In TEM the morphology aspect is complemented by extra crystallographic information. The crystals are clearly facetted, and often crosslike dark contrast lines (Bragg fringes) divide the facetted surface according to the projected symmetry along the electron beam. The shape and the aspect ratio of the projected crystal dimensions also

* To whom correspondence should be addressed. E-mail: millange@chimie.uvsq.fr.
[†] University of Antwerp.
[‡] Université de Versailles St-Quentin-en-Yvelines.
[§] Present address: Institut Universitaire de France (Versailles), F-78035 Versailles Cedex, France.

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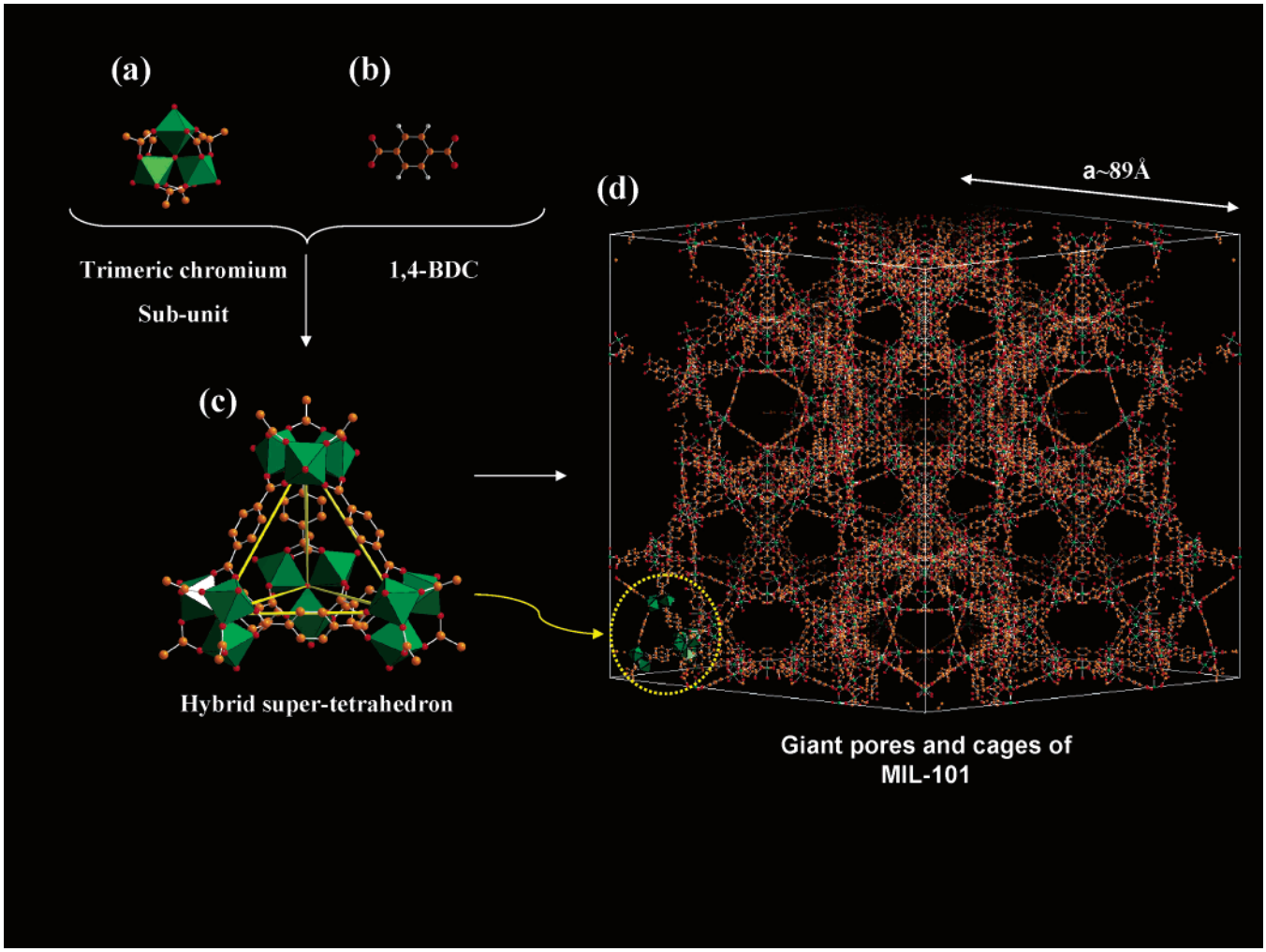

Figure 1. (a) Inorganic trimer; (b) 1,4-BDC; (c) ST made from the linkage of inorganic trimers and 1,4-BDC; (d) schematic view of the MIL-101 structure.

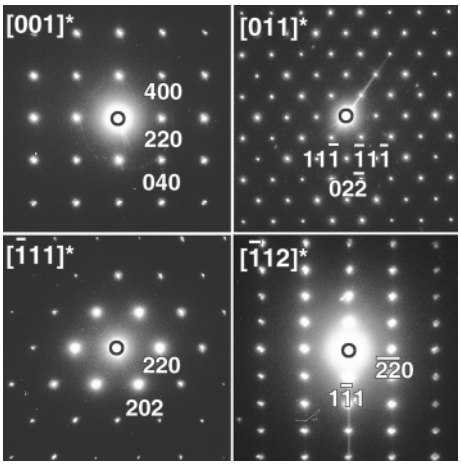

Figure 2. ED patterns of the MIL-101 structure along the main crystallographical zone axis indexed with respect to the *Fd*$\bar{3}$*m* space group.

reflect the cubic symmetry. Low-magnification TEM images of MIL-101 nanocrystals along [001], [111], and [112] are shown in Figure 3. The [001] oriented nanocrystal demonstrates square facets divided by diagonal Bragg fringes into four quadrants. The arms of the cross are directed along [100] and [010]. The hexagonal shaped particle obviously corresponds to a [111] oriented cubic crystal, that is, viewed along the threefold axis of the octahedron. The Bragg fringes, directed along the ⟨110⟩ directions, draw a perfect sixfold star. A view along [112] allows the exact three-dimensionalshape of the crystal to be reconstructed unambiguously. On the basis of the observed TEM images along different directions, we deduce that the cubic MIL-101 crystals grow as nanocrystals with a nearly perfect octahedral shape. The individual crystals can also be imaged under high-resolution conditions along different zone axes, in this way showing a perfect image of the pore distribution within the crystals. Figure 4 shows the HREM images of MIL-101 along two major directions [111] and [011]. The [111] HREM image (Figure 4a) shows a perfect hexagonal packing of bright dots of size approximately 15 Å in diameter. Imaging the structure along the [011] direction is more difficult because of a more pronounced electron charging with the electron beam along this particular direction. As a result, most [011] HREM images are blurry (Figure 4b), but the main features are easily recognized. HREM image simulations based on the structure

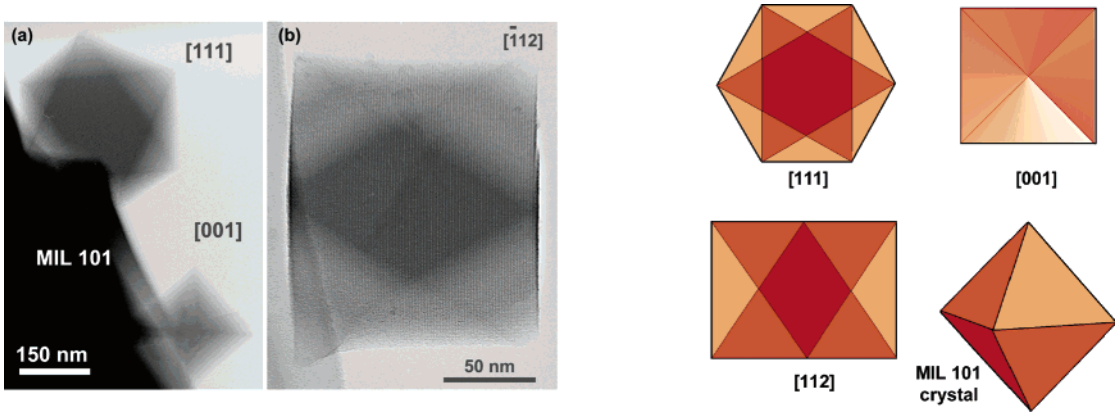

Figure 3. TEM images of the MIL-101 nanocrystals differently oriented toward the incident electron beam: (a) close to [111] and [011] and (b) close to [112]. Schematic representation of the TEM images of the nanocrystal and a reconstructed three-dimensional shape of the crystal. The MIL-101 crystal has cubo-octahedral shape.

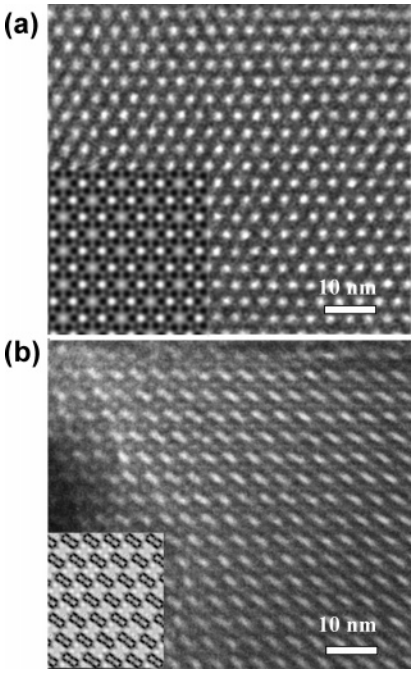

Figure 4. HREM images of the MIL-101 structure along the two main zone axes (a) [111] and (b) [011]. The calculated images based on the cubic $Fd\bar{3}m$ structure along corresponding directions are given as insets (scale bar = 10 nm).

model deduced from X-ray diffraction with the $Fd\bar{3}m$ symmetry have been performed for different defocus and thickness values and confirm our interpretation that the bright dots do correspond to the tunnels. The calculated images along [111] and [011] for a defocus value of 250 nm and a thickness of 100 nm are given as insets in Figure 4a,b. The simulation is in good agreement with the experimental image, although the fine details are not observed in the experimental HREM image because of the strong drift due to the charging and the minimum exposure time.

The experimental methods are as follows. The synthesis of MIL-101 consists of the hydrothermal reaction of H_2BDC (166 mg, 1 mmol) with $Cr(NO_3)_3{\cdot}9H_2O$ (400 mg, 1 mmol), fluorhydric acid (1 mmol), and 4.8 mL of H_2O (265 mmol) for 8 h at 220 °C, producing a pure and highly crystallized green powder of the chromium terephthalate with formula $Cr_3F(H_2O)_2O[(O_2C)-C_6H_4-(CO_2)]_3{\cdot}nH_2O$ ($n \sim 25$), based on chemical analysis.

Supporting Information Available: Figure showing the pentagonal window, hexagonal window, and two types of mesoporous cages filled with free water molecules and SEM images of the MIL-101 (PDF) and crystallographic structure information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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