Delamination and Photochemical Modification of a Novel Two-Dimensional Zr-based MOF

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Metal-organic frameworks (MOFs) are currently one of the most intensely researched class of materials.[1] Zr-based MOFs usually exhibits high thermal and chemical stability which are interesting properties for industrial applications. Post-synthesic modifications allow further adaptation of MOFs for application. It is usually performed on specific functionalities on the linkers like amino, alkyne, azide or halide groups or by click chemistry.[2,3] Here, we present a novel two-dimensional Zr-based metal-organic framework which offers the possibility for postsynthetic photochemical modification at the linker molecule benzophenone-4,4'-dicarboxylic acid (H_2*bzpdc*).[4] The new Zr-*bzpdc*-MOF crystallizes in the orthorhombic system as crystals with rhombic shape; a crystal structure model shows that the Zr-*bzpdc*-MOF is built up from 2D layers (figure 1).

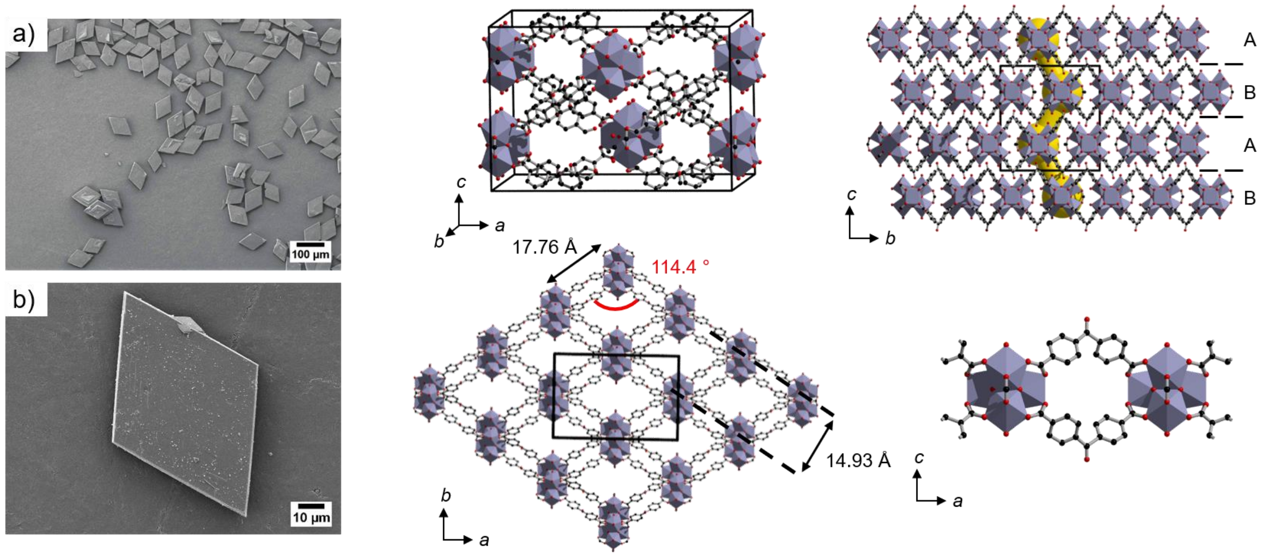

Figure 1. Left: SEM images of Zr-*bzpdc*-MOF crystals with rhombic shape. Center: Crystal structure model of the Zr-*bzpdc*-MOF with unit cell. Top right: stacking of the two-dimensional layers and the shape of a pore along the *c* axis (yellow channel); bottom right: connection between two IBUs.

Single crystals of the Zr-*bzpdc*-MOF were modified postsynthetically based on the intrinsic photochemical reactivity of the benzophenone moiety with C–H bond containing molecules.[5] In this way, the surface properties of the MOF crystals (e.g. dispersibility in different solvents) can be changed drastically. We carried out photochemical reactions with a hydrophilic polymer and a hydrophobic alkane as model reactions. Zr-*bzpdc*-MOF crystals were dispersed in the solvents and irradiated under inert conditions resulting in yellowish products indicating a successful reaction (figure 2).

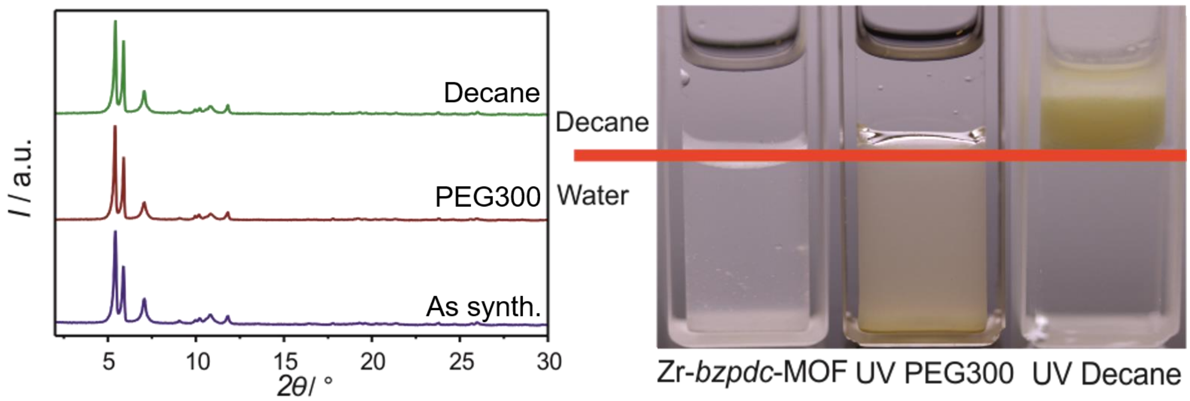

Figure 2. Left: PXRD pattern of postsynthetically modified samples of Zr-*bzpdc*-MOF; right: Zr-*bzpdc*-MOF and its postsynthetically modified derivatives exposed to a water/decane two-phase system.

The photochemical reaction does not result in any changes in the PXRD patterns, showing that the MOF is basically stable under the reaction conditions and also does not undergo any structural transformations during postsynthetic treatment (figure 2 left). The most obvious result is the fact that the dispersibility in different solvents changed drastically after postsynthetic modification (figure 2 right). The MOF itself as well as the modified sample with PEG show hydrophilic characteristics. However, the sample modified with decane is hydrophobic which also indicates a successful postsynthetic modification. An extensive characterization of the Zr-*bzpdc*-MOF and its post-synthetic derivatives are given in ref 4.

Based on the 2D layered structure, the Zr-*bzpdc*-MOF also offers the possibility of delamination which leads to thin sheets of the material of only few nanometer thickness, as shown by SEM, TEM and AFM investigations (figure 3).

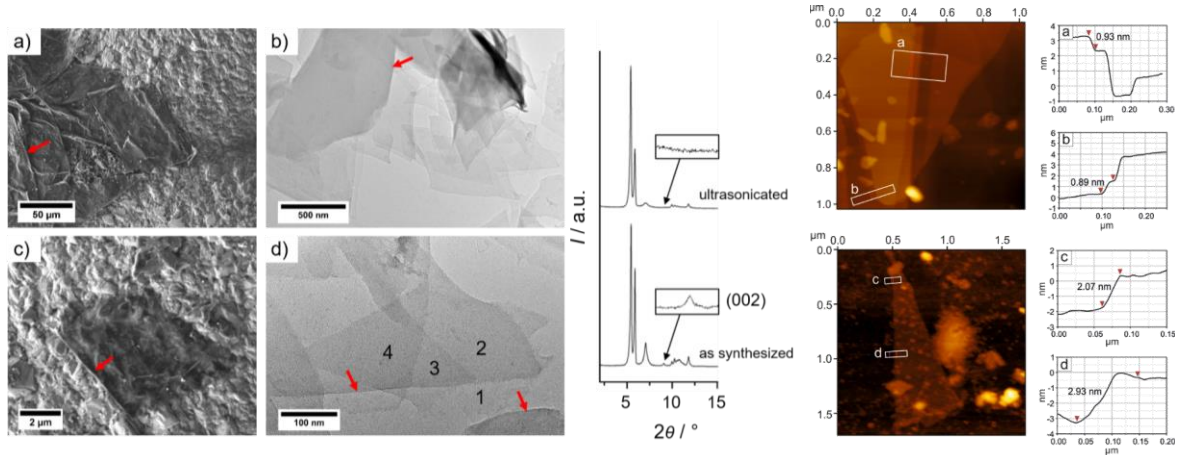

Figure 3. Left: SEM (a,c) and TEM images (b,d) of delaminated sheets of the Zr-*bzpdc*-MOF. Middle: PXRD patterns of Zr-*bzpdc*-MOF before (as-synthesized) and after delamination (ultrasonicated); insets show the region of the 002 reflection. Right: AFM investigations of thin particles of Zr-*bzpdc*-MOF with stepped facets at the edges (top) and for an isolated sheet (bottom); height determinations are provided for two different facets.

The thicknesses of the sheets and facets were determined via AFM investigations (figure 3). The delaminated Zr-*bzpdc*-MOF sheets have thicknesses of 2-10 nm. Thicker particles exhibit facets with heights of about 0.9 nm, which is in agreement with the thickness of an individual layer as observed in the crystal structure of the Zr-*bzpdc*-MOF.

Delamination and adaptation of the surface chemistry open up novel ways for shaping MOFs, e.g. for the incorporation into polymer composites, and pave the way for various applications.

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