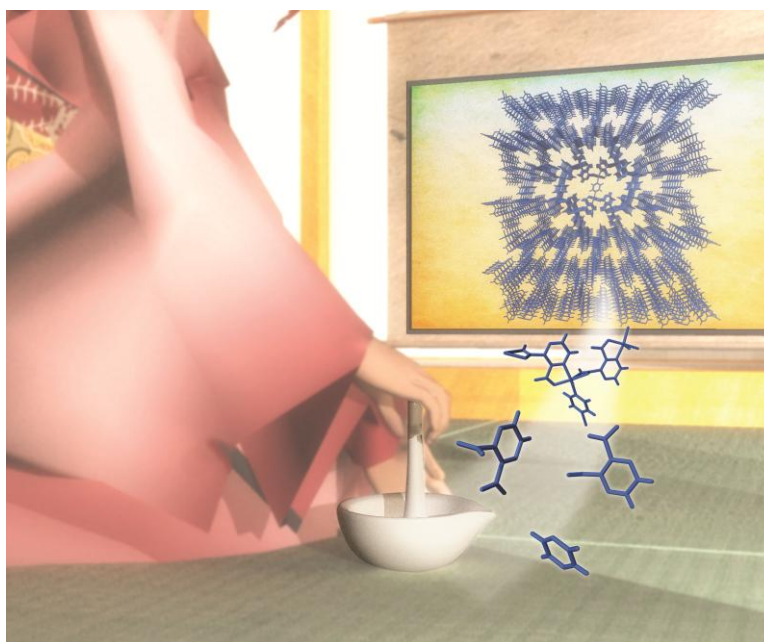This article is published as part of the *Dalton Transactions* themed issue entitled:

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COMMUNICATION

Highly oriented surface-growth and covalent dye labeling of mesoporous metal–organic frameworks†

Florian M. Hinterholzinger,[a] Stefan Wuttke,[a] Pascal Roy,[b] Thomas Preuße,[b] Andreas Schaate,[c] Peter Behrens,[c] Adelheid Godt[b] and Thomas Bein*[a]

Mesoporous amino-functionalized metal–organic framework thin films with the UiO-68 topology were grown in a highly oriented fashion on two different self-assembled monolayers on gold. The oriented MOF films were covalently modified with the fluorescent dye Rhodamine B inside the pore system, as demonstrated with size-selective fluorescence quenching studies. Our study suggests that mesoporous metal–organic frameworks are promising hosts for the covalent attachment of numerous functional moieties in a molecularly designed crystalline environment.

Metal–organic frameworks (MOFs) are a class of porous materials synthesized in a building-block fashion from metal ion or metal cluster nodes interconnected by organic molecules. These porous solids can be used for several applications such as gas storage, separation, catalysis, drug delivery or as chemical sensors due to their exceptional porosity and structural diversity.[1–4] The diffusional access of guest molecules to the interior of the MOF structures can be facilitated by presenting them as thin films. The key principle for the fabrication of MOF chemosensors is the incorporation of a recognition-transduction mode.[5,6] This can be achieved by implementing organic functional groups, *e.g.* –NH$_2$ or –OH groups, in order to functionalize the internal pore surface of the MOF. These groups are intended to act as anchoring points for the covalent attachment of a receptor and/or transducer by using post-synthetic modification (PSM).[7,8] One significant challenge in this area is the development of large-pore MOFs with adequate chemical and thermal stability, whose internal surface can be appropriately functionalized.[9]

Based on our previous results on the substrate-directed oriented growth of various MOF films,[10–12] we report here the highly oriented growth of the mesoporous and functionalized MOF UiO-68–NH$_2$ on SAM-modified gold substrates. UiO-68–NH$_2$ is a zirconium-based MOF with 2′-amino-4,4″-dicarboxy-1,1′:4′,1″-terphenyl as the linker.[13] UiO-68–NH$_2$ exhibits the desired stability as well as mesopores of 2.7 nm with accessible large windows of 1.0 nm for the incorporation of sterically demanding molecules. This is demonstrated by the post-synthetic covalent modification of UiO-68–NH$_2$ films with a dye molecule, that is, Rhodamine B isothiocyanate (Scheme 1). Finally, selective quenching experiments provide evidence for the successful attachment of the dye to the internal surface of the oriented functionalized MOF thin film and the accessibility of the interior for guest molecules.

In order to achieve the preferred crystallographic orientation of UiO-68–NH$_2$ crystals, Au (111) substrates were modified with both 11-mercapto-1-undecanephosphonate (MUP) SAMs (denoted as MOF film (a), Fig. 1, top/middle) and 16-mercapto-hexadecanoic acid (MHDA) SAMs (denoted as MOF film (b), Fig. 1, bottom) that either exhibit terminal phosphonate groups or carboxyl groups, respectively. The idea to include SAMs with terminal phosphonate groups was inspired by results obtained with zincophosphate frameworks.[14] The modified gold substrates were subsequently immersed in a saturated UiO-68–NH$_2$ crystallization solution. After several days at room temperature, crystal layers with perfect crystallographic orientation grew on the monolayers. In Fig. 1 the XRD patterns of both the as-prepared and the post-synthetically dye-labeled UiO-68–NH$_2$ thin films are presented.

By comparing the simulated powder pattern of bulk UiO-68–NH$_2$ with the diffraction patterns of the thin films (Fig. 1), the structure-directed orientation of the UiO-68–NH$_2$ crystals layers along the [111] direction is clearly apparent. The crystal orientation is additionally confirmed by reflections of higher order lattice planes. Note that the highly oriented crystal morphology was even observed for the films that were post-synthetically modified with a dye solution, proving the chemical stability of the MOF structure. Moreover, the diffraction patterns of UiO-68–NH$_2$ thin films prepared on both phosphonate-terminated SAMs (MOF film (a), Fig. 1, top) and on carboxyl-terminated SAMs (MOF film (b), Fig. 1, bottom) exclusively show the reflections corresponding to (111) as well as to higher order lattice planes of the MOF.

The immersion times for UiO-68–NH$_2$ film growth were varied between 5–30 days. It was found that an immersion time

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†Electronic supplementary information (ESI) available: Including additional information derived from X-ray diffraction, SEM and fluorescence microscopy data of UiO-68-NH$_2$ thin films. See DOI: 10.1039/c2dt12265k
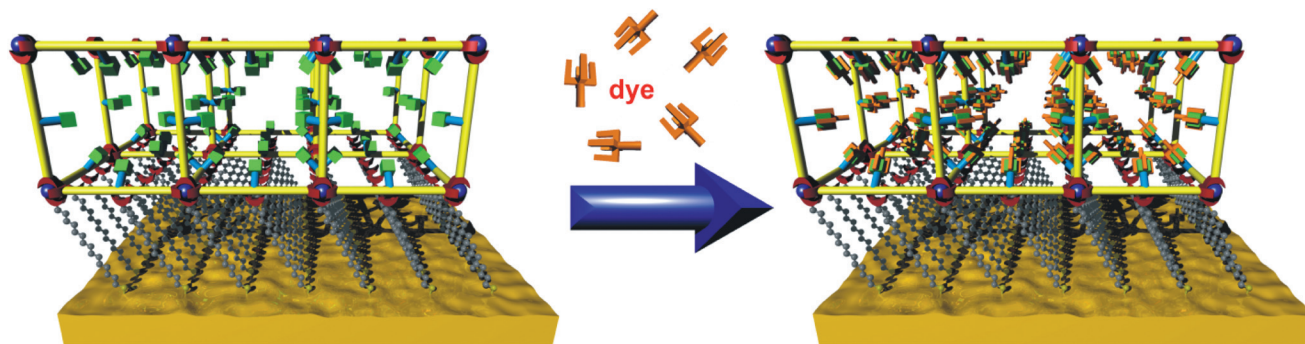
Scheme 1 Schematic representation of oriented and functionalized MOF crystals grown on SAM-modified gold substrates (left) followed by the post-synthetic modification of the MOF thin film with dye molecules (right).
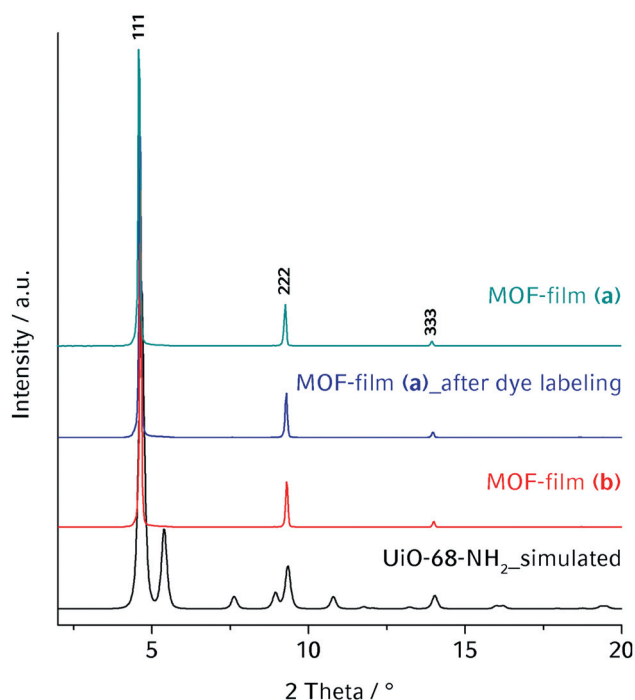

Fig. 1 X-ray diffraction patterns (background corrected) of highly oriented UiO-68–NH₂ thin films grown on self-assembled monolayers of 11-mercapto-1-undecanephosphonate (MUP, MOF film (a), top/middle) and 16-mercaptohexadecanoic acid (MHDA, MOF film (b), bottom) on gold substrates. The as-prepared and dye-labeled films are compared to simulated data.

Fig. 2 Scanning electron micrographs showing the highly oriented growth of UiO-68–NH₂ crystals along the preferred [111] orientation. MOF film (b) was synthesized by immersing the 16-mercaptohexadecanoic acid SAM-modified substrates in the crystallization solution for 20 days at room temperature followed by a second growth step of 10 days in a freshly prepared crystallization solution. The SEM images are depicted at different magnifications (see scale bars).

of 7 days was sufficient to result in the surface growth of UiO-68–NH₂ crystals in a highly oriented fashion (see the ESI, Fig. S3 and S4†). With the intention to achieve a dense coverage of the gold surface, immersion times were extended to 30 days (as in the case for the dye-labeled MOF thin film (a), Fig. 1, top). Furthermore, a secondary crystal growth was carried out by additionally immersing the MOF film in a freshly prepared crystallization solution (MOF film (b), Fig. 1, bottom). It was observed that both approaches, the extended immersion time as well as the secondary growth in a fresh crystallization solution, result in a somewhat higher surface coverage with UiO-68–NH₂ crystals (see the ESI, Fig. S4†).
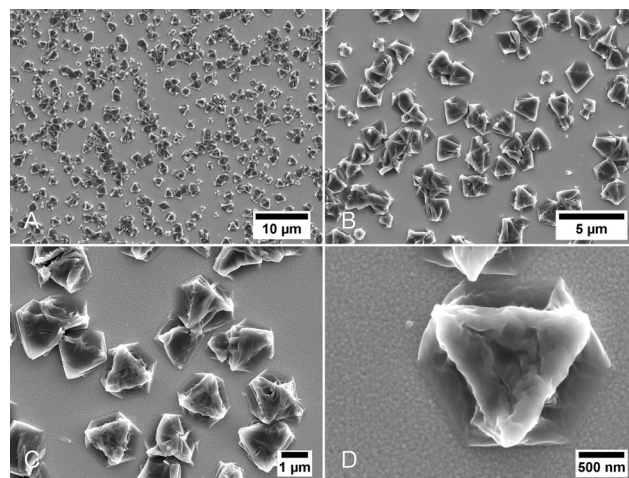
The oriented surface growth of the UiO-68–NH₂ crystals is also reflected in the SEM pictures shown in Fig. 2.

The SEM images show a UiO-68–NH₂ crystal population that is attached to MHDA-SAM functionalized gold substrates. The presented surface coverage was obtained by performing the secondary growth step as mentioned above. Micrometer-sized octahedra are displayed in Fig. 2. The preferred orientation along the [111] direction is clearly shown by the presence of the triangular (111) faces of the UiO-68–NH₂ octahedra, which is in excellent agreement with the 111 reflection intensity deduced from the XRD results (Fig. 1).

The ability to grow mesoporous amino-functionalized MOF thin films provides the basis for post-synthetic modification (PSM) reactions and thus for the incorporation of functionality into the scaffold. PSM reactions on bulk samples are being intensively studied,[7,15,16] whereas post-synthetic modifications of MOF thin films are still very rare.[17] This is due to the limited number of addressable MOF candidates meeting the
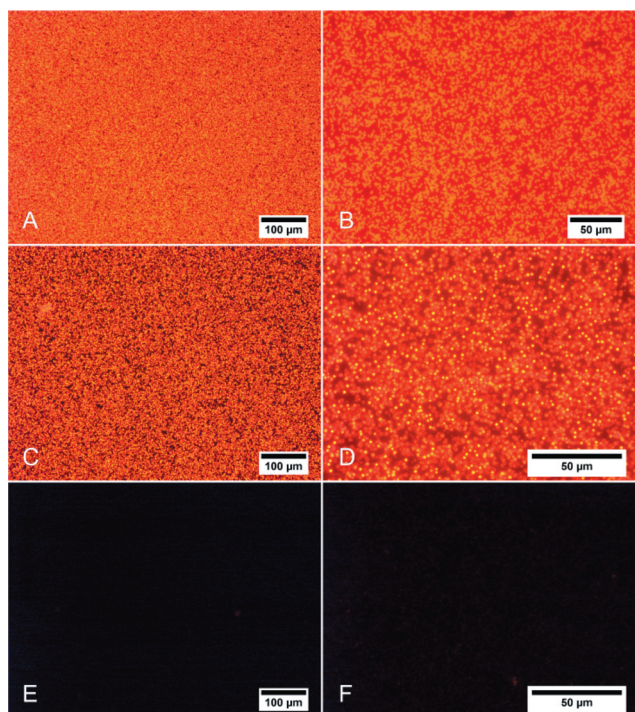
Fig. 3 Fluorescence microscopy images demonstrating the post-synthetic labeling of oriented UiO-68–NH$_2$ thin films (A + B, MOF film (a)) with Rhodamine B as well as the results of fluorescence quenching experiments using a colloidal AuNP solution (C + D, MOF film (b)) and diquat dibromide monohydrate (E + F, MOF film (a)). The fluorescence images are shown at different magnifications (see scale bars).

requirements (functional group, chemical stability and accessible large pores) for post-synthetic modifications. We emphasize that the highly oriented UiO-68–NH$_2$ thin films described here feature all the desired properties, a chemically addressable amino group and large pores of 2.7 nm diameter that are accessible through the large windows of 1.0 nm diameter. Thus, the UiO-68–NH$_2$ thin films were modified using the fluorescent dye Rhodamine B isothiocyanate. The films were immersed in an ethanolic Rhodamine B isothiocyanate solution for 5 h at room temperature to achieve covalent coupling (see the ESI†).

In Fig. 3 (A+B, MOF film (a)) the fluorescence images of UiO-68–NH$_2$ thin films after dye labeling are depicted. Bright red fluorescence due to the covalently bound Rhodamine B is observed. In order to provide evidence for the successful dye labeling of the interior of the MOF crystals, two different quenching experiments were carried out. Gold nanoparticles (AuNPs) with an average diameter of 5 nm were used as a colloidal suspension for quenching experiments of dye molecules bound to the external surface of UiO-68–NH$_2$ crystal layers.[18] Clearly, the red fluorescence is mostly retained after exposure to the AuNPs (Fig. 3, C+D, MOF film (b)) indicating that dye labeling mainly occurred within the mesopores of UiO-68–NH$_2$. To support this interpretation as well as to prove the accessibility of the dye modified pores, diquat dibromide monohydrate with a kinetic diameter of about 0.7 nm was chosen for quenching the fluorescence of Rhodamine B.[19] Near complete fluorescence

quenching of the dye-labeled UiO-68–NH$_2$ thin films was achieved as indicated in Fig. 3 (E+F, MOF film (a)) . This observation demonstrates complete molecular access into the mesopore system of the crystal layer.

Conclusions

In summary, highly oriented UiO-68–NH$_2$ thin films were obtained by room temperature growth on two different types of self-assembled monolayers. It was shown for the first time that MOF thin films could be grown in a highly oriented fashion on phosphonate termini of an organic monolayer. Moreover, the post-synthetic pore modification of UiO-68–NH$_2$ thin films with a fluorescent dye was achieved and confirmed by quenching experiments with differently sized quenching agents. The concept of oriented crystal growth on SAM-modified gold substrates could successfully be extended to functionalized and mesoporous MOF structures. We anticipate that mesoporous UiO-68–NH$_2$ thin films will offer a versatile platform for precisely designing various host–guest interactions within a stable pore system featuring a well-defined molecular framework.

Acknowledgements

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