

Supporting Information

Highly Oriented Surface-Growth and Covalent Dye Labeling of Mesoporous Metal-Organic Frameworks

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Methods and Characterization

X-ray diffraction (XRD) measurements were performed using a Bruker D8 diffractometer (Cu-K α 1 = 1.5406 Å; Cu-K α 2 = 1.5444 Å) in *theta-theta* geometry. The films were measured between 5° and 20° *two theta*, with a step-size of 0.05° *two theta* and a scan-speed of 5° min⁻¹.

Scanning electron microscopy (SEM) images were recorded with a JEOL JSM-6500F microscope equipped with an Oxford energy-dispersive X-ray (EDX) analysis system.

Fluorescence microscopy was performed using a Nikon Eclipse Ti-inverted fluorescence microscope.

Characterization of the self-assembled monolayers (SAMs) was performed by reflection absorption infrared (RAIR) spectroscopy, using a Bruker IFS 66v FTIR spectrometer. The sample chamber with a high performance variable angle reflection accessory (A-513) was maintained at 2 mbar during the entire measurement by means of an Edwards rotary-pump. In a typical measurement on gold surfaces, an angle of incidence of 83° to the surface normal was used. A cleaned gold slide was measured as background prior to the measurements.

Experimental section

Chemicals

Zirconium(IV) chloride (99.9 %, *Aldrich*) and benzoic acid (*Aldrich*), 16-mercaptophexadecanoic acid (95 %, *Aldrich*), 11-mercpto-1-undecanol (97 %, *Aldrich*), phosphorus oxide chloride (*Aldrich*) and 2,4,6-trimethylpyridine (*Aldrich*), Rhodamine B isothiocyanate (*Aldrich*), diquat dibromide monohydrate (*Aldrich*), colloidal gold (~ 5 nm, *Aldrich*) as well as solvents are commercially available and were used as received. 2'-Amino-4,4"-dicarboxy-1,1':4',1"-terphenyl ($H_2\text{-}tpdc\text{-}NH_2$) was synthesized according to the literature.¹

Self-assembled monolayers on gold substrates

Microscope glass slides (*Menzel*, 76x26 mm) were cleaned in an ultrasonic bath according to a solvent protocol (acetone, 2-propanol, Hellmanex/H₂O (1:100), H₂O, 2-propanol (Chromasolv)) followed by oxygen plasma cleaning for 30 min. The pre-cleaned microscope glass slides were mounted in a Univex 350 vacuum sputter-coating unit (Oerlikon Leybold Vacuum), and the slides were coated with Ti/Au by electron-beam evaporation under room temperature and ultra high vacuum. The gold substrates were cut in 1 x 1.3 cm pieces and cleaned for 10 min with EtOH and then for 10 min with MeOH in an ultrasonic bath. For the preparation of 11-mercpto-1-undecanephosphonate (MUP) SAMs the cleaned gold slides were immersed in a 1 mM ethanolic solution (6 pieces in

20 mL) of 11-mercaptopropanoic acid at room temperature for 48 h. The phosphorylation of the as-prepared self-assembled organic monolayer was achieved by immersing the gold slides in a mixture (6 pieces in 40 mL) of phosphorus oxide chloride (0.1 M) and 2,4,6-trimethylpyridine (0.1 M) in acetonitrile. For the preparation of carboxyl-terminated SAMs the cleaned gold slides were immersed in a 1 mM ethanolic solution (6 pieces in 20 mL) of 16-mercaptopropanoic acid (16-MHDA) at room temperature for 48 h. Afterwards the SAM-functionalized gold slides were washed repeatedly with ethanol and stored in absolute ethanol until needed.

Preparation of the crystallization solution for the oriented film growth of UiO-68-NH₂

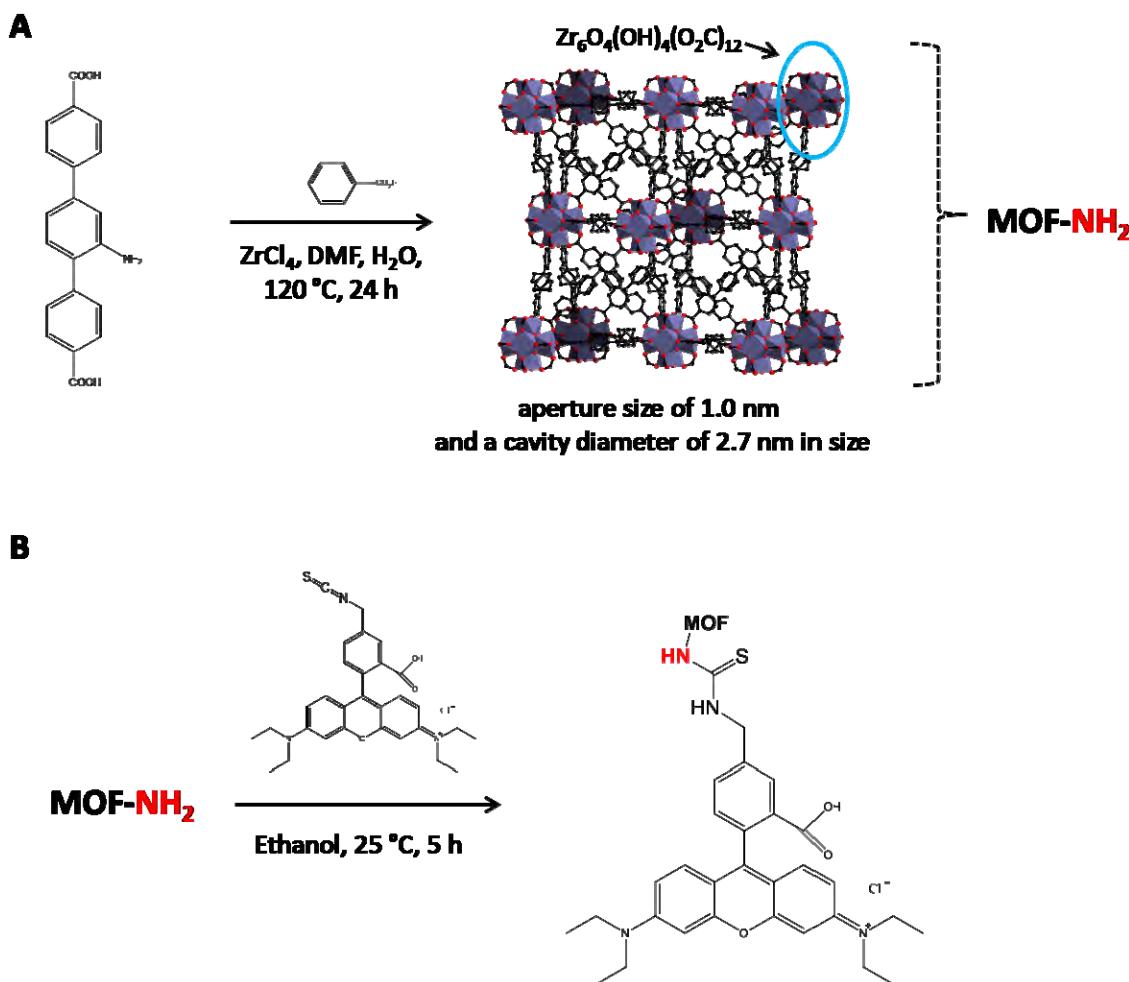
In a 50 mL glass reactor, zirconium(IV) chloride (0.120 g, 0.514 mmol, 1.0 eq.) and benzoic acid (1.88 g, 15.42 mmol, 30 eq.) were dissolved in dimethylformamide (DMF, 20 mL) in an ultrasonic bath. *H₂-tpdc-NH₂* (0.17 g, 0.514 mmol, 1.0 eq.) and water (0.028 mL, 1.54 mmol, 3.0 eq.) were subsequently added to the clear solution. The sealed glass reactor was kept for 24 h in a preheated oven at 120 °C. After cooling the synthesis mixture to room temperature, the bulk material was removed by filtration and the filtrate was used for the growth of thin films.

Oriented film growth of UiO-68-NH₂

The SAM-functionalized gold-slides were placed upside-down in Teflon® supports into the filtered synthesis solution of UiO-68-NH₂ (6 pieces in 20 mL). The growth took place at room temperature in a closed glass reactor. Immersion times were varied between 5-30 d.

Fluorescence dye labeling of UiO-68-NH₂ thin films

For dye labeling experiments, Rhodamine B isothiocyanate (2 mg, 0.003 mmol) was dissolved in absolute ethanol (50 mL). UiO-68-NH₂ thin films were immersed in the ethanolic dye solution for 5 h under stirring. The films were repeatedly washed with ethanol and dried under nitrogen. Note that higher concentrations of the dye solution can result in a loss of crystallinity.



Reaction scheme: Synthesis route for the preparation of UiO-68-NH₂ crystals (**A**) as well as the post-synthetic dye labeling reaction with fluorescein isothiocyanate (**B**).

Quenching experiments of dye labelled UiO-68-NH₂ thin films

Quenching experiments of as-prepared Rhodamine B labeled thin films were carried out either using a monodisperse colloidal gold solution (~ 5 nm; 50 µL/mL) or diquat dibromide monohydrate (0.018 g, 5 mM) which were dissolved in a 1:1 mixture of EtOH/H₂O (10 mL). The dye-labeled films were placed in a beaker which was mounted on a shaker and left in the quencher solution for 24 h.

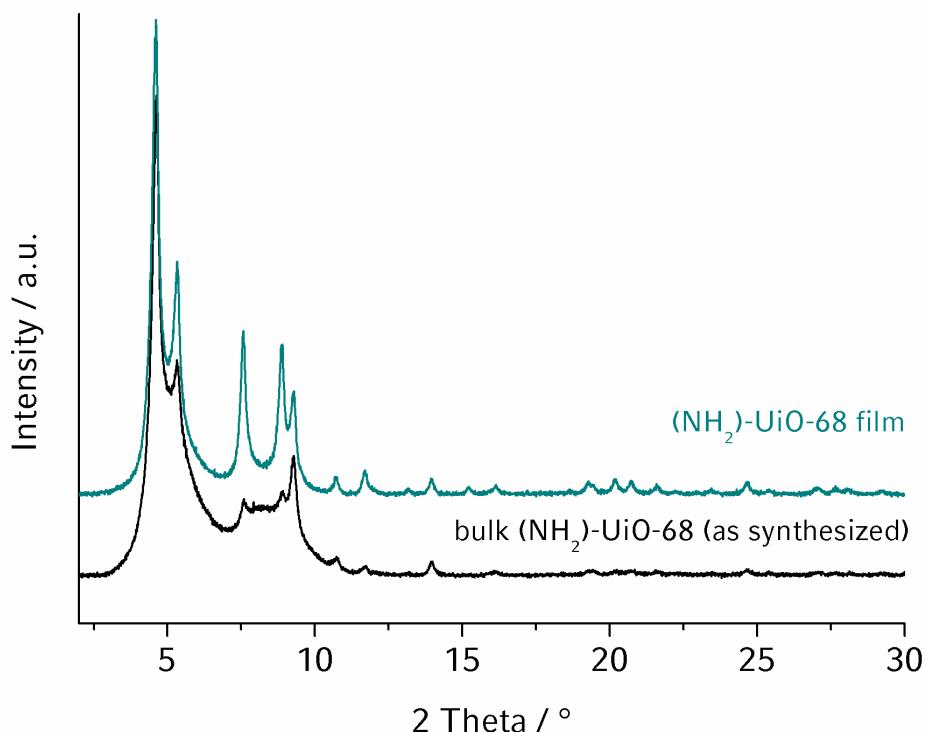


Figure S1: X-ray diffraction pattern (background corrected) of a randomly oriented UiO-68-NH₂ thin film grown on a glass substrate compared to the XRD pattern of as-synthesized bulk UiO-68-NH₂ crystals. The glass substrates were immersed in the crystallization solution for 5 days.

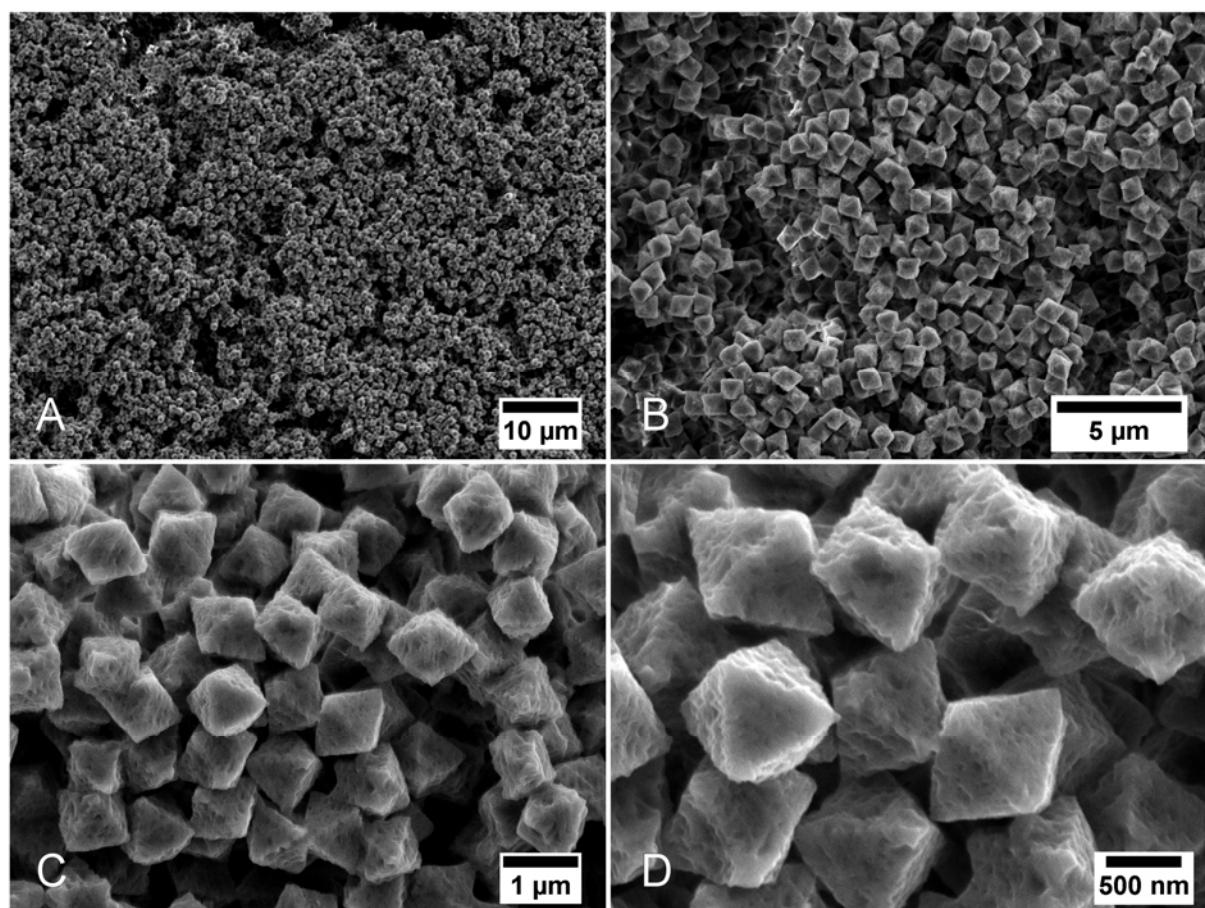


Figure S2: Scanning electron microscopy (SEM) images showing randomly oriented UiO-68-NH₂ crystals attached to the surface of a microscope slide. The SEM micrographs are depicted for different magnifications (**A**: x1.500; **B**: x5.000; **C**: x15.000; **D**: x30.000). The microscope slides were immersed in the crystallization solution for 5 days.

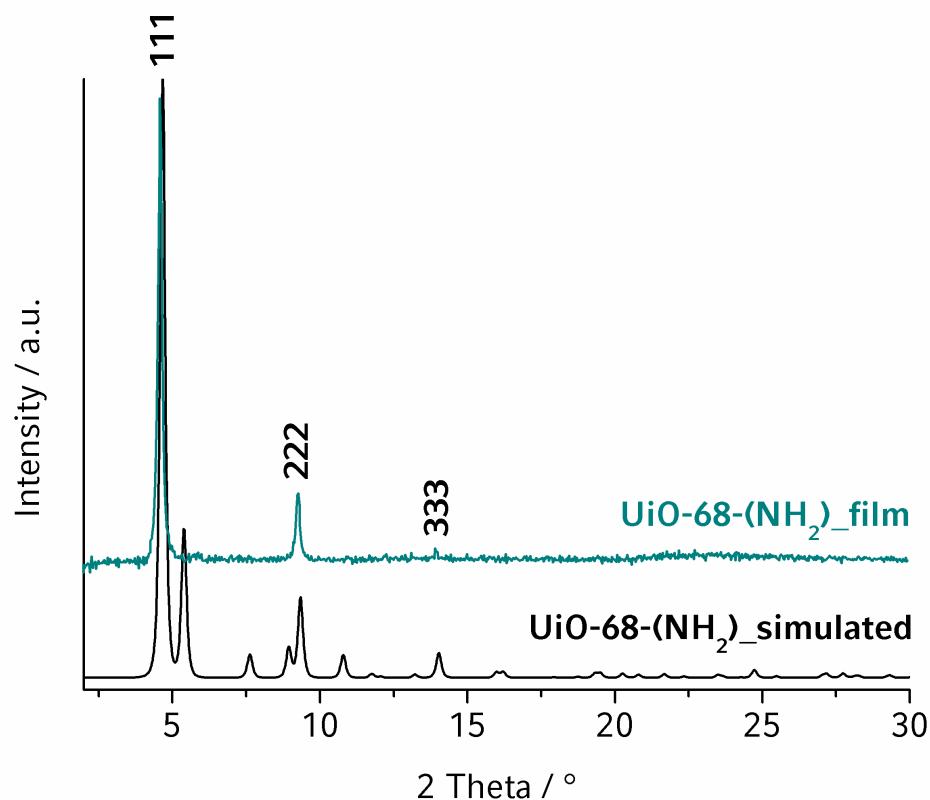


Figure S3: X-ray diffraction pattern (background corrected) of a highly oriented UiO-68-NH₂ thin film grown for 7 d on 11-mercaptopro-1-undecanephosphonate (MUP) SAM functionalized gold substrates compared to simulated data.

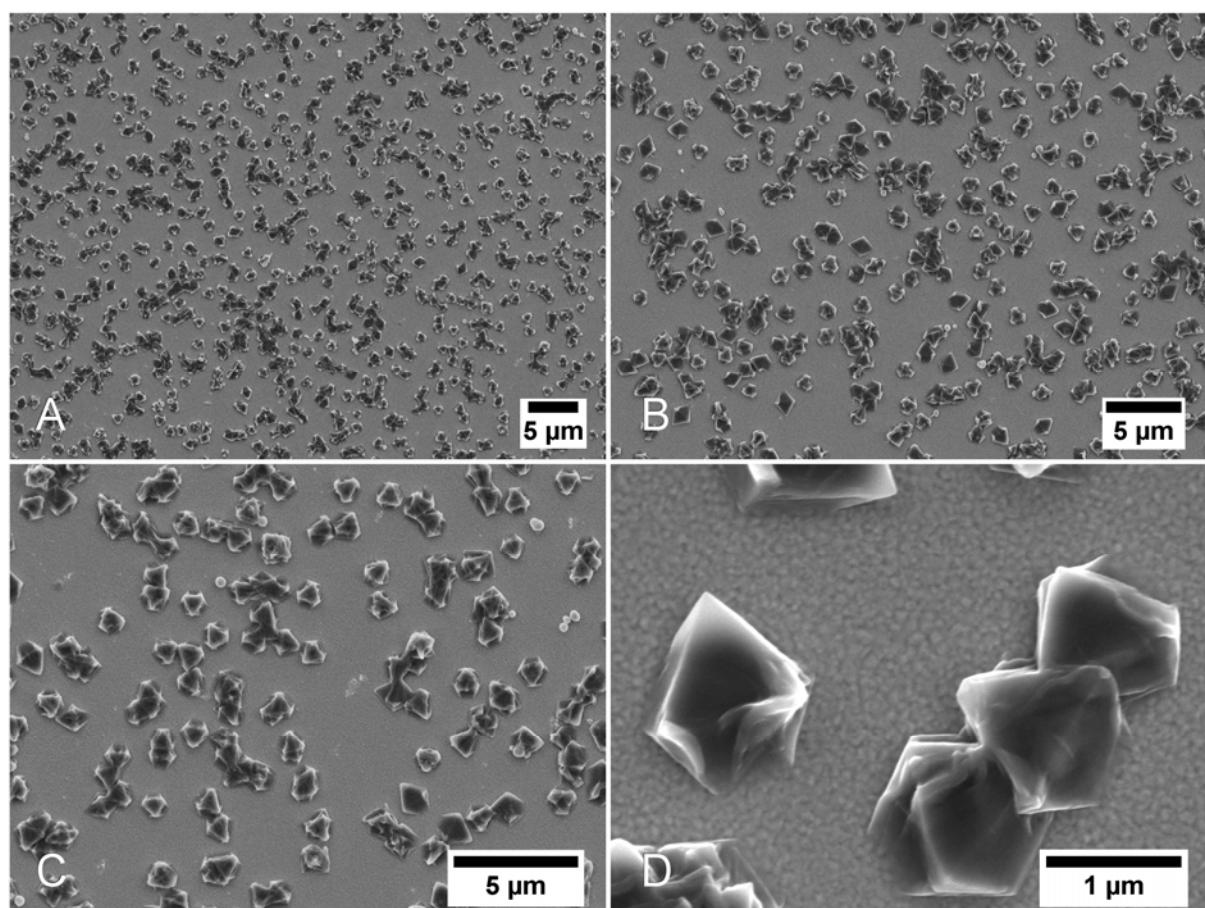


Figure S4: Scanning electron micrographs showing highly oriented growth of UiO-68-NH_2 crystals along the preferred [111] direction on a 16-mercaptopohexadecanoic acid SAM modified gold substrate. The functionalized substrate was immersed in the crystallization solution for 7 days. The SEM micrographs are depicted for different magnifications (**A**: x2.000; **B**: x3.000; **C**: x5.000; **D**: x27.000).

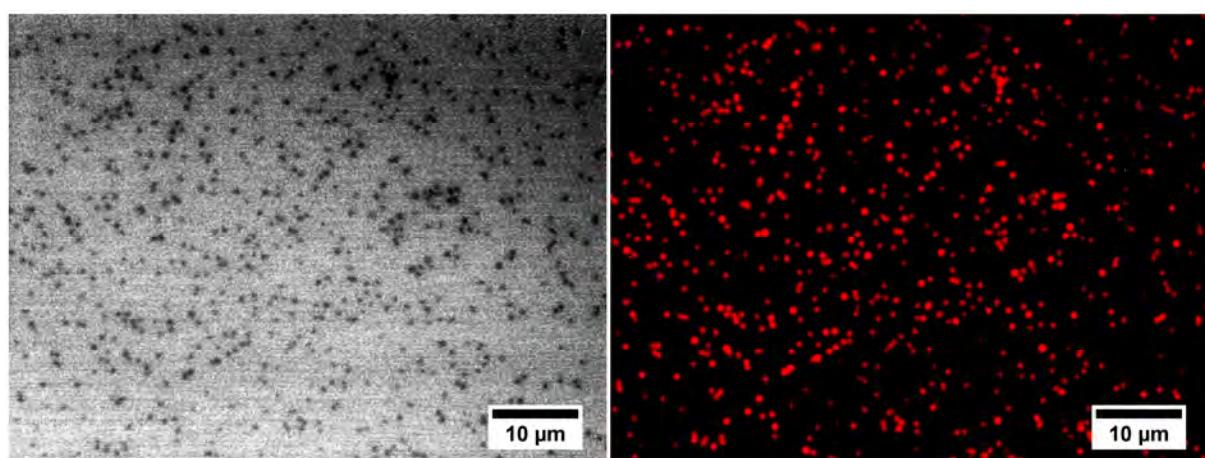


Figure S5: Bright-field image (left) and fluorescence image (right) of a Rhodamine B labelled UiO-68-NH_2 thin film which was immersed in the crystallization solution for 6 days.

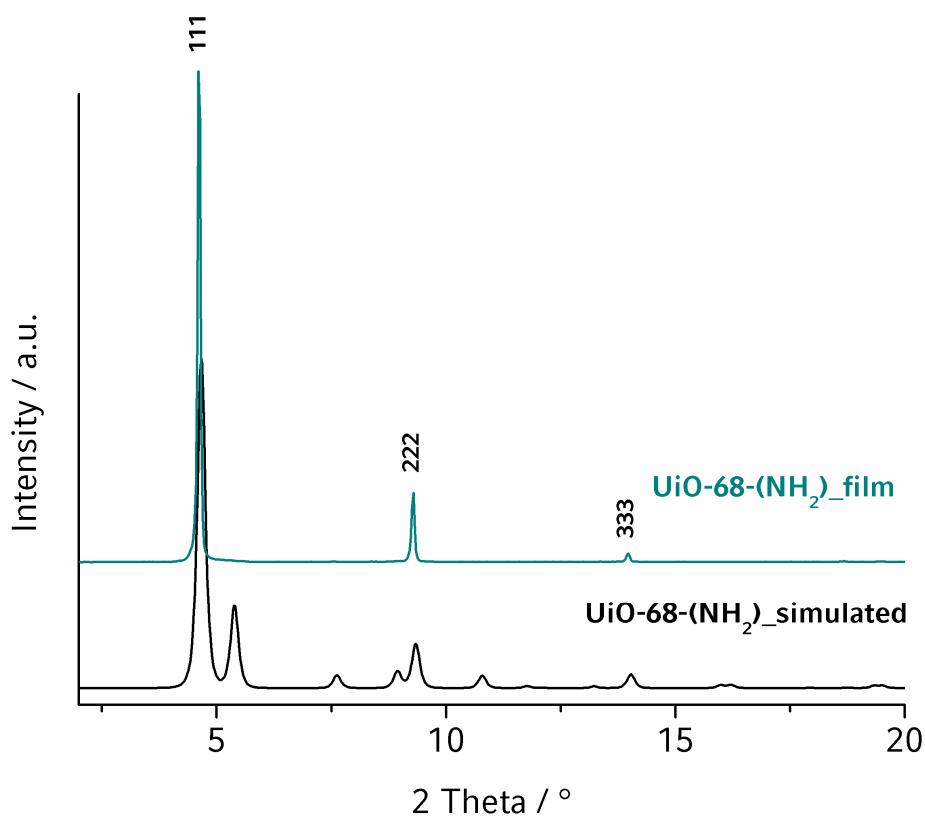


Figure S6: X-ray diffraction pattern (background corrected) of a highly oriented UiO-68-NH₂ thin film grown on 11-mercaptopoundecanephosphonate (MUP) functionalized gold substrates compared to simulated data. The substrate was immersed in the crystallization solution for 30 d.

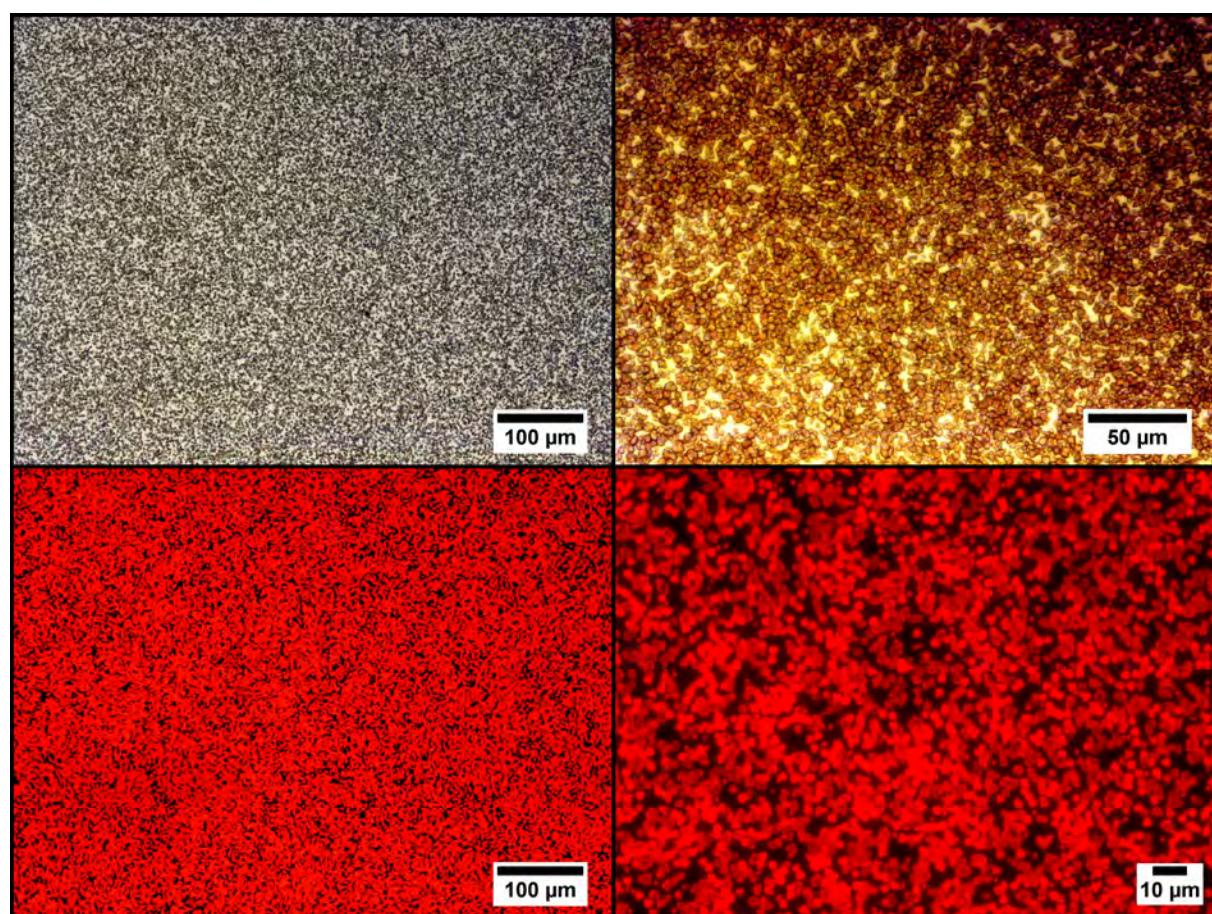


Figure S7: Bright-field (top) and fluorescence images (bottom) of a Rhodamine B labelled UiO-68-NH_2 thin film grown on a 16-mercaptophexadecanoic acid (MHDA) functionalized gold substrate. The films were immersed for 20 days in the filtered mother liquor followed by immersion for 10 days in a freshly prepared crystallization solution.

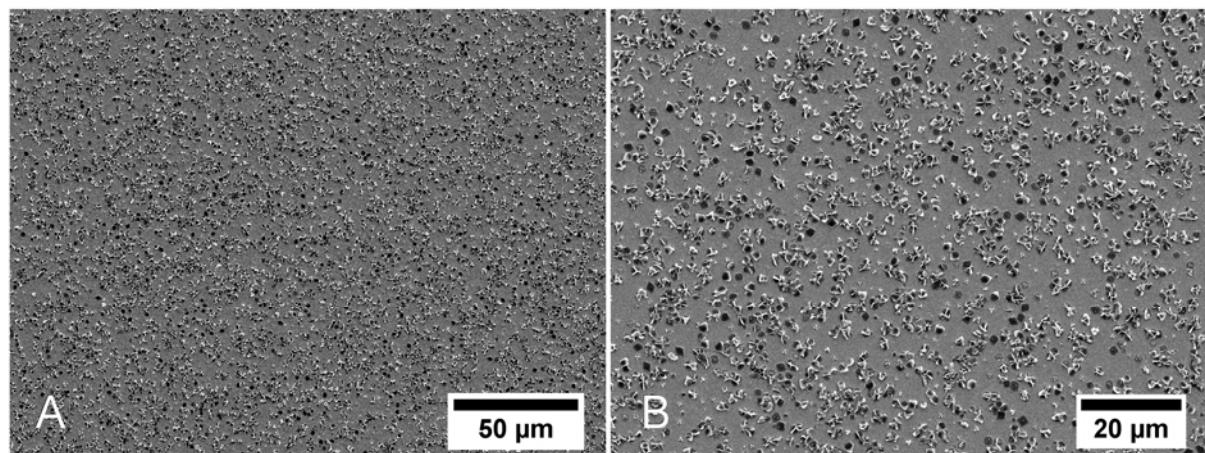


Figure S8: Scanning electron micrographs showing highly oriented growth of MOF-film (**b**) after AuNPs quenching experiments. MOF thin films (**b**) were obtained by immersing the gold substrates for 21 days in the filtered crystallization solution followed by an additional growth step in a freshly prepared mother liquor for 19 days. The SEM micrographs are depicted at different magnifications.

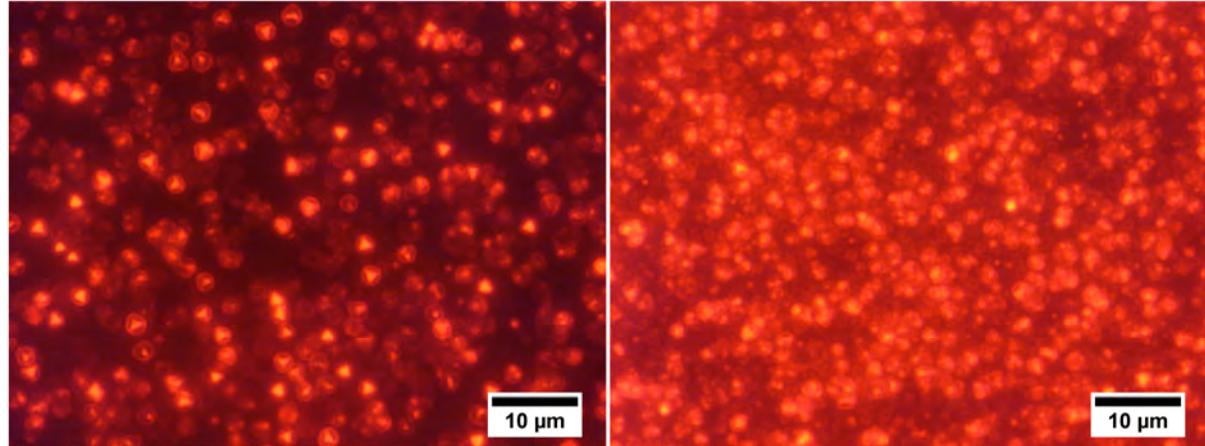


Figure S9: Fluorescence images of MOF-film (**b**) after AuNPs quenching experiments. MOF thin films (**b**) were obtained by immersing the gold substrates for 21 days in the filtered crystallization solution followed by an additional growth step in a freshly prepared mother liquor for 19 days.

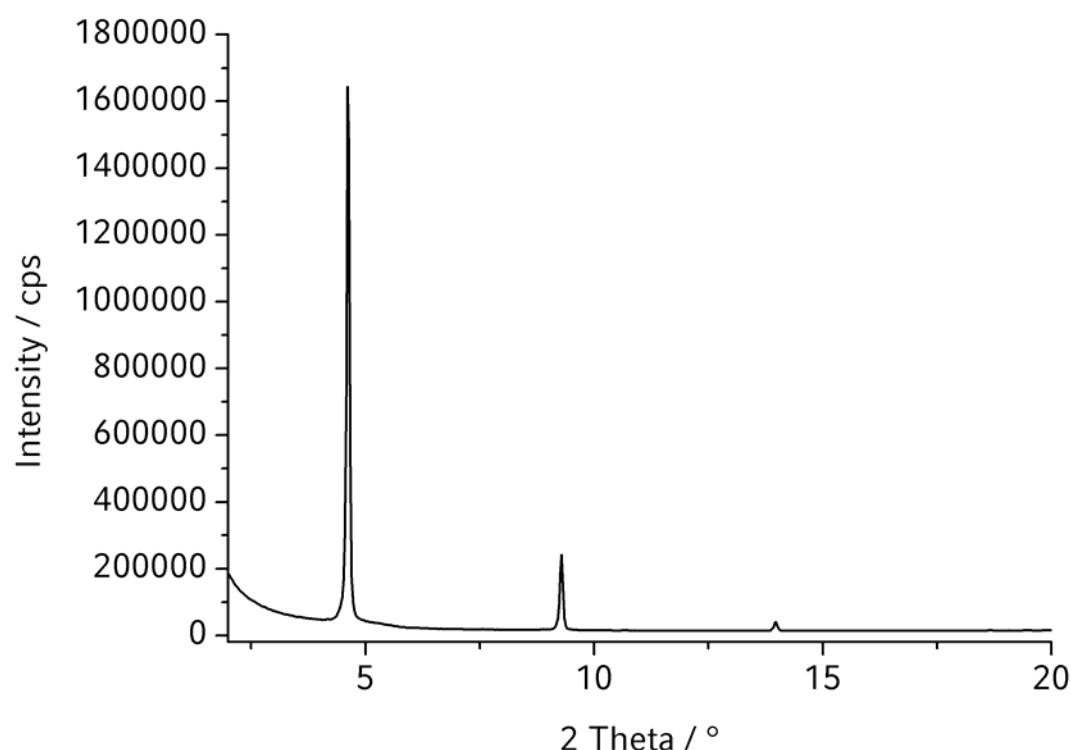


Figure S10: Original X-ray diffraction data of a highly oriented UiO-68-NH₂ thin film (MOF film (**a**)) grown on a 11-mercaptoundecanephosphonate (MUP) SAM functionalized gold substrate for 30 days.

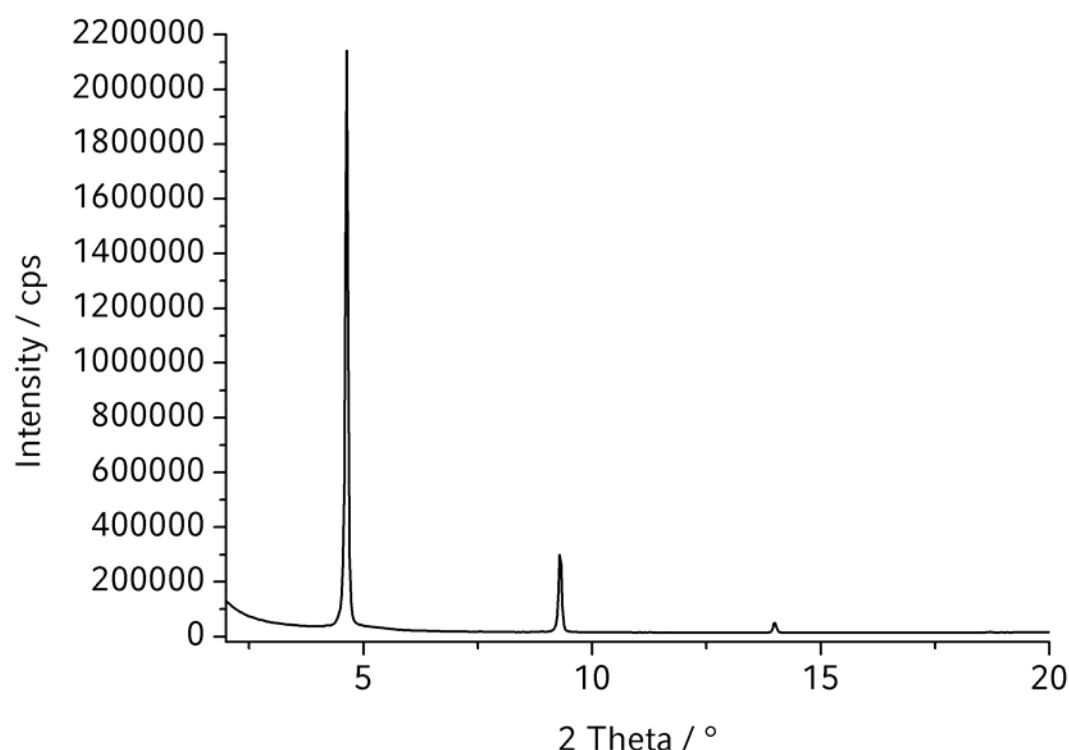


Figure S11: Original X-ray diffraction data of a highly oriented UiO-68-NH₂ thin film (MOF film (**b**)) grown on a 16-mercaptophexadecanoic acid (MHDA) SAM functionalized gold substrate for 21 days followed by an additional growth step in a freshly prepared crystallization solution for 19 days.

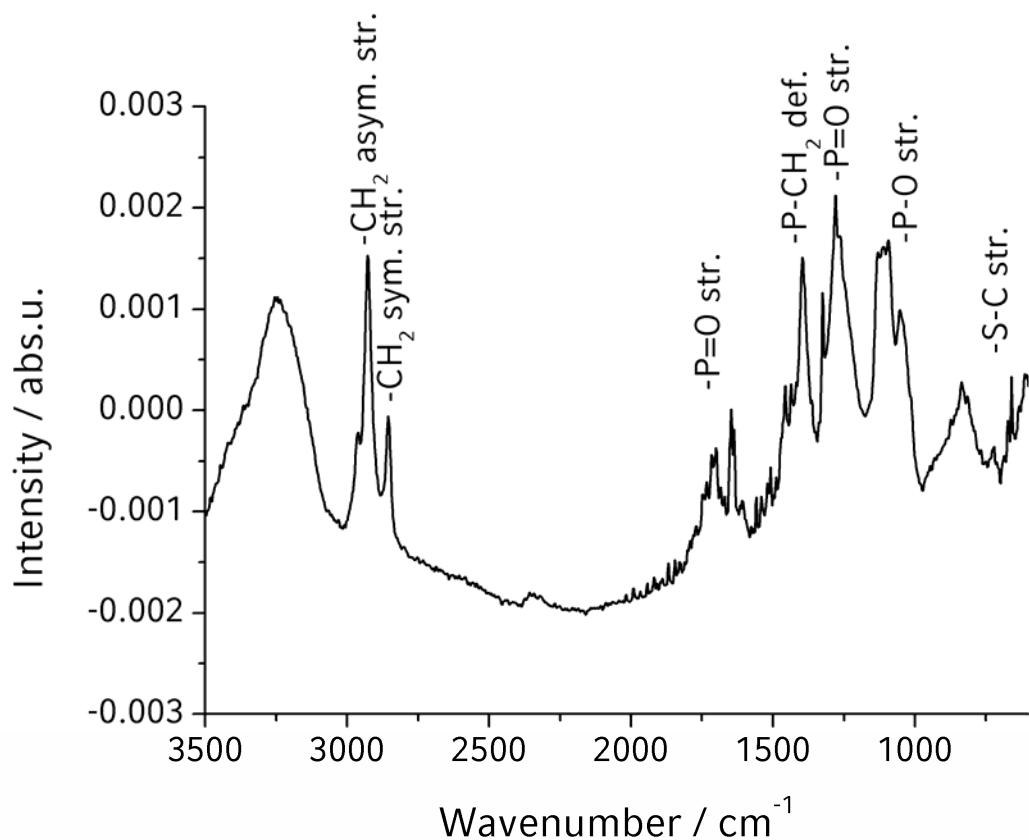


Figure S12: RAIR-spectrum of the 11-mercaptopropanoate self-assembled monolayer on a gold substrate that was immersed in a 1 mM ethanolic solution for 48 h.

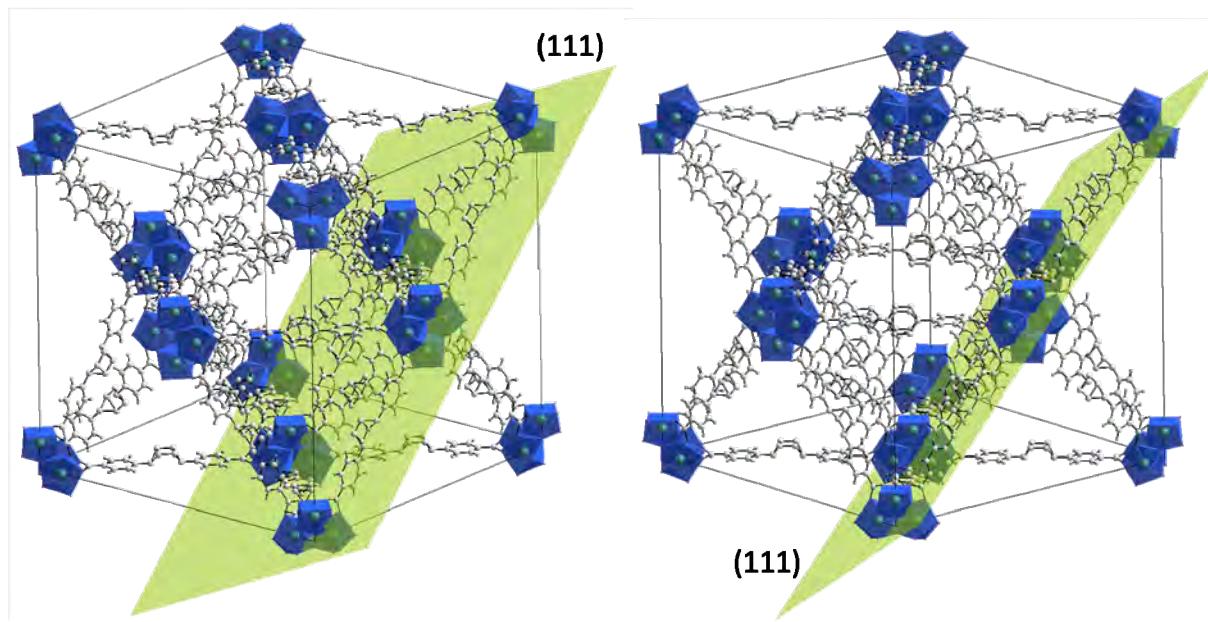


Figure S13: Schematic representation of the unit cell of UiO-68-NH₂ as well as the 111 lattice plane.

References

1. A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, Chemistry – A European Journal, 2011, **17**, 6643-6651.