

Supporting Information

Optimizing Post-synthetic Metal Incorporation in Mixed-Linker MOFs: Insights from metalation studies on UiO-67 containing different linker ratios

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General Methods

Materials

Solvents and commercially acquired chemicals were reagent grade and used as received without further purification. $ZrCl_4$ (99,99%), biphenyl-4,4'-dicarboxylic acid (bpdc) (97%), 2,2'-bipyridine-5,5'-dicarboxylic acid (BPY) (97%), benzoic acid (>99.5%), NaOD (40 wt % in D_2O , 99.5 atom %), and deuterium oxide (99.9 atom %) were purchased from Sigma-Aldrich. Ethanol (abs) and *N,N*-Dimethylformamide (DMF) ($\geq 99.7\%$) were purchased from VWR, DMF was degassed with Ar and dried using an Inert PureSolv MD solvent purification system. Deionized water was used in synthetic procedures. P-type (boron doped) silicon wafers were purchased from Sievert Wafer and cut into approximately 0.7 x 1.5 cm substrate slides.

Synthesis of mixed linker UiO-67-BPY@Si

P-type (boron doped) single-side polished <100> Si wafers were cut to approximately 0.7 x 1.5 cm sized substrate slides, cleaned with ethanol at 75 °C for 15 minutes, and air-dried. A precursor solution was prepared, adapted from a previously reported procedure for the growth of UiO-67-bpy single crystals.¹ For the synthesis of mixed-linker MOFs, the total linker concentration was kept constant, but varying ratios of the two different linkers were used (Table S1): A mixture of 2,2'-bipyridine-5,5'-dicarboxylic acid (BPY, Table S1) and biphenyl-4,4'-dicarboxylic acid (bpdc, Table S1), benzoic acid (1.85 g, 15.2 mmol), and 15 mL anhydrous DMF were sonicated inside a 20 mL vial for 10 minutes. $ZrCl_4$ (87.4 mg, 0.38 mmol) was added, and the mixture was sonicated for further 10 minutes before 24 μ L water was added. After sonicating the final mixture for another 10 minutes, 2 mL of the mixture was added to a 4 mL vial containing the silicon-slide. The vials were sealed with caps with septa before being placed on a sand bath inside a 120 °C preheated oven. After 5 days the vials were removed, the solution decanted, and the slides were gently washed with anhydrous DMF. Prior to analysis the solvent was exchanged to acetone, for easier sample drying under vacuum. Due to the water sensitivity of UiO-67-BPY air exposure of the samples was minimized.^{2, 3}

| Determined BPY % | Initial feeding BPY % | mg | mmol | Bpdc % | mg | mmol |
|------------------|-----------------------|------|------|--------|------|------|
| 100 | 100 | 45.8 | 0.19 | 0 | 0 | 0 |
| 50 | 50 | 22.9 | 0.09 | 50 | 22.7 | 0.09 |
| 30 | 25 | 11.5 | 0.05 | 75 | 34.1 | 0.14 |
| 15 | 10 | 4.6 | 0.02 | 90 | 40.9 | 0.17 |

Table S1: BPY and bpdc amounts in mg and mmol for the synthesis of mixed-linker UiO-67-BPY featuring different ratios of linker. The final BPY ratios determined by NMR slightly differed from the initially used feeding values during the synthesis.

The synthesized crystals were approximately 5-10 μ m thick, 10-20 μ m wide and highly oriented along the <111> axis. This was demonstrated by SEM imaging as well as by the XRD patterns which show almost exclusively the <111> reflection.

Post-synthetic metalation with $NiCl_2$

A 4 mM metal solution was prepared from $NiCl_2$ (13 mg, 0.1 mmol) in 25 mL anhydrous DMF. Freshly synthesized UiO-67-BPY@Si samples were taken directly from the synthesis vial (no solvent exchange or drying), rinsed with DMF and placed into fresh vials containing 3 mL $NiCl_2$ solution. The vials were capped and placed in a preheated block heater at 100 °C for the

specific duration of the metalation experiment. After the set time, the solutions were decanted and the samples were heated in fresh DMF for one hour to remove uncoordinated NiCl₂ from the MOF pores. The samples were rinsed with DMF and transferred to clean 20 mL vials and washed three more times at room temperature for several hours before being stored in DMF. Prior to analysis the solvent was exchanged to acetone, for easier sample drying under vacuum. Due to the water sensitivity of UiO-67-BPY air exposure of the samples was minimized.^{2, 3} XRD measurements (Figure S1) confirmed retention of the UiO-67 structure.

¹H NMR spectroscopy

¹H NMR spectra were measured using a JEOL 400 MHz spectrometer. The chemical shifts given in ppm are internally referenced to the residual solvent signal.

Powder X-ray diffraction

Powder X-ray diffraction patterns (PXRD) were obtained using a Siemens D5000 diffractometer (Cu K α , $\lambda = 0.154 \text{ \AA}$, 18 nm) at 45 kV and 40 mA, using a step size of 0.02°.

Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained using a Zeiss 1550 Schottky field-emission scanning electron microscope equipped with an InLens detector at 2 kV acceleration voltage. The MOF bearing Si slides were anchored to conductive carbon tape on a sample holder disk. For improved image quality, charging effects were prevented by sputter-coating the samples with an approximately 5-10 nm thick Au/Pd layer prior to imaging.

RBS setup

The μ -RBS measurements were carried out at the Tandem Laboratory of Uppsala University.⁴ A beam of He²⁺ ions, accelerated to 5 MeV kinetic energy by the 5 MV 15SDH-2 Tandem Pelletron accelerator, was focused to a spot of approximately 3-4 μm (FWHM) and raster-scanned over the individual MOF crystals by the scanning nuclear microprobe end-station.⁵ The energy of backscattered ions was detected, as a function of their position of origin, by means of an annular-type solid state particle detector with a mean detection angle of $\Theta = 168^\circ$. The primary beam energy allowed us to obtain depth-profiles of the MOFs down to several micrometers depth from the surface.

Curve fitting

The recorded μ -RBS spectra were processed by the SIMNRA simulation software, v7.03.⁶ Our RBS model, described in detail in reference 7, considers true element depth gradients as a consequence of the diffusion process during metalation, as well as virtual gradients as a consequence of the truncated octahedral crystal shape.⁷ For modelling the MOF composition, nominal atomic concentrations according to the BPY linker percentage were used as input parameters. The Ni and Cl surface concentrations and their depth gradients were treated as free parameters in the fitting routine and returned back after optimization of the RBS spectrum fits.

Calculations and extraction of diffusion parameters and diffusion depth

The elemental depth gradients were considered to be a consequence of purely Fickian diffusion, assuming an unlimited (constant concentration) surface source of NiCl_2 . They were therefore supposed to have the form of $c(x,t) = c_0 \cdot \text{erfc}\left(\frac{x}{\sqrt{2Dt}}\right)$, where c_0 is the surface concentration, x is the depth and L is the characteristic diffusion length. The characteristic diffusion length, where the concentration drops to $\approx 1/2 c_0$, can be expressed as $L = (\pi \cdot t)^{1/2}$, where t is the elapsed (metalation) time and D is the diffusion coefficient.

Experiments

Post metalation X-ray diffraction

X-ray diffraction was used to confirm the retention of structure and crystallinity during PSM (Figure S1). The spectra show the retention of the characteristic UiO-67 $\langle 111 \rangle$ reflection, confirming the crystallinity of the metalated materials.

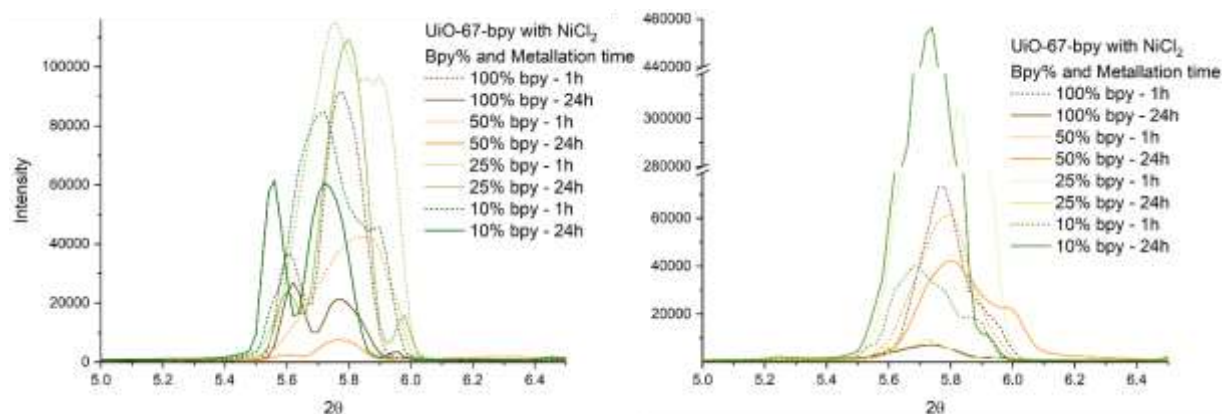


Figure S1: XRD spectra of UiO-67-BPY single crystals, containing different percentages of BPY, and post synthetically metalated with NiCl_2 for 1 or 24 hours.

Depending of the sample orientation relative to the XRD beam, the reflection sometimes splits into two peaks. The relative ratios of the two peaks change when the sample is rotated, and even collapses into one peak at certain geometrical conditions. Apart from the shown $\langle 111 \rangle$ reflection, only the $\langle 222 \rangle$ reflection was observed in the spectrum.

SEM

SEM imaging helped confirm the structural integrity of the MOF crystals post metalation and post RBS measurements. Figure S2 shows images of UiO-67-BPY single crystals from each experiment presented in figure 6.

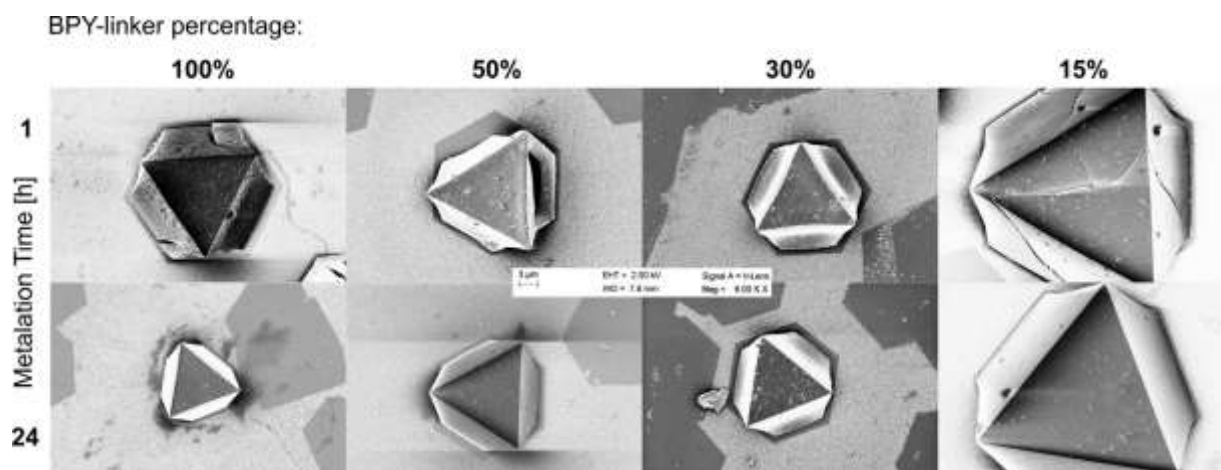


Figure S2: SEM images of UiO-67-BPY single crystals containing different BPY percentages, taken after post-synthetic metalation and RBS measurements.

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