

Localized Conversion of Metal-Organic Frameworks into Polymer Gels via Light-Induced Click Chemistry

Sophia Schmitt, Stéphane Diring, Peter G. Weidler, Salma Begum, Stefan Heißler, Susumu Kitagawa, Christof Wöll, Shuhei Furukawa, Manuel Tsotsalas

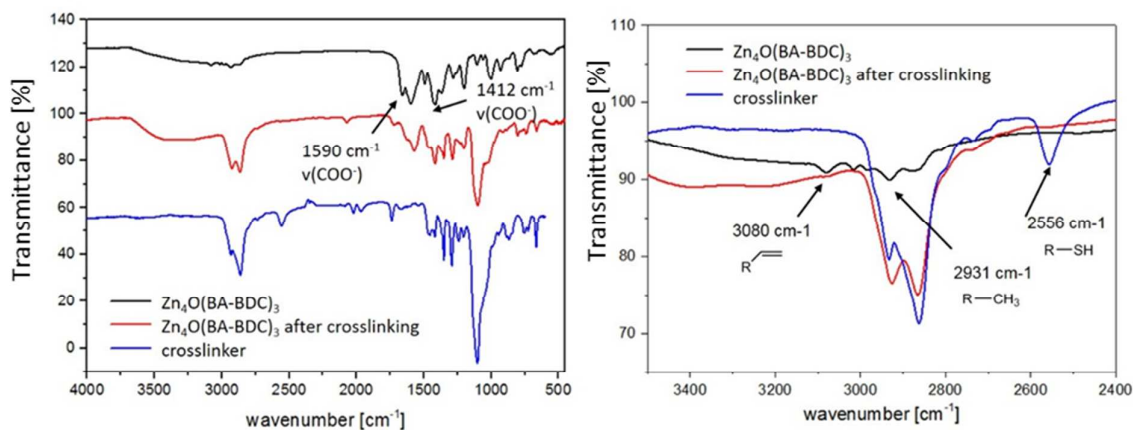


Figure S1: IR spectra of the different steps of the GEL conversion using the $\text{Zn}_4\text{O}(\text{BA-BDC})_3$ single crystals.

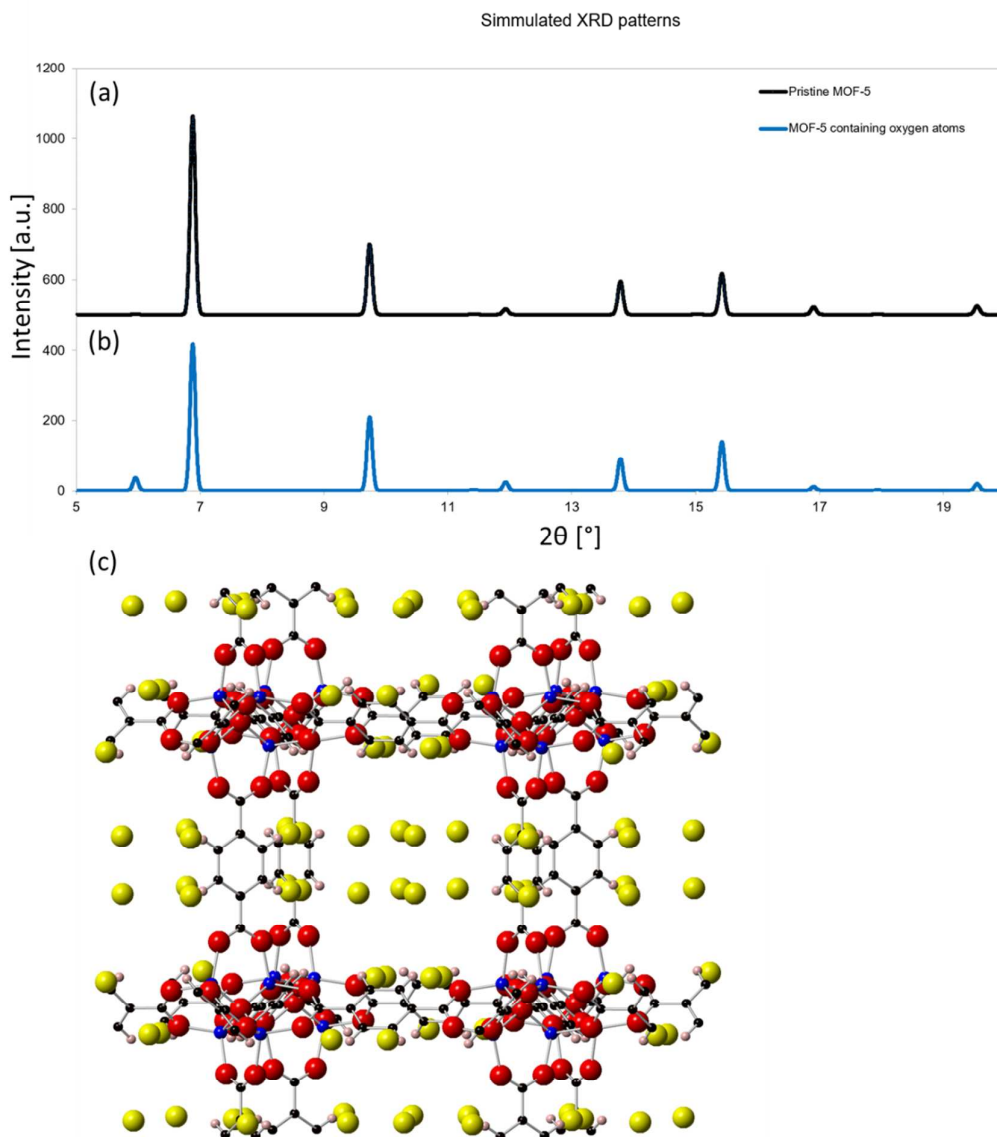


Figure S2: Simulated XRD patterns of (a) pristine MOF-5 and (b) “oxygen loaded” MOF 5.

(c) Shows the unit cell of an “oxygen loaded” MOF-5 with the additional oxygen atoms representing possible positions of the oxygen atoms corresponding to the tetrathiol PETMA crosslinker in yellow.

Based on the observation of significant intensity changes particularly for the (111) peak in the XRD data, simulations based on the MOF-5 structure (cif-file) were carried out with the program suit CrystalMaker and CrystalDiffra.

These changes are most likely due to the incorporation of an alien molecule into the pores, thus changing the structure factor, especially for the (111). A promising starting point is the middle of the unit cell of MOF-5.

By loading O-atoms into the pore at various positions around the mid-point and changing the occupancy, the calculated intensities of the diffractogram for each of these position and occupancies, resulted in the model presented in the manuscript.

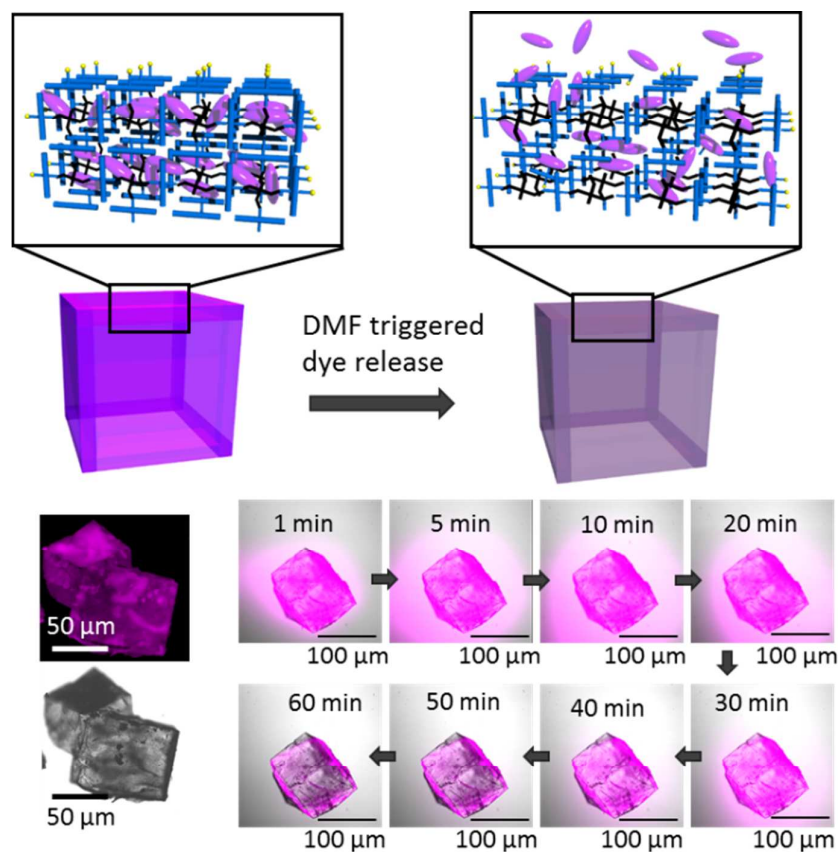


Figure S3: Rhodamine loaded gel particles showing dye release triggered by their immersion and swelling in DMF.

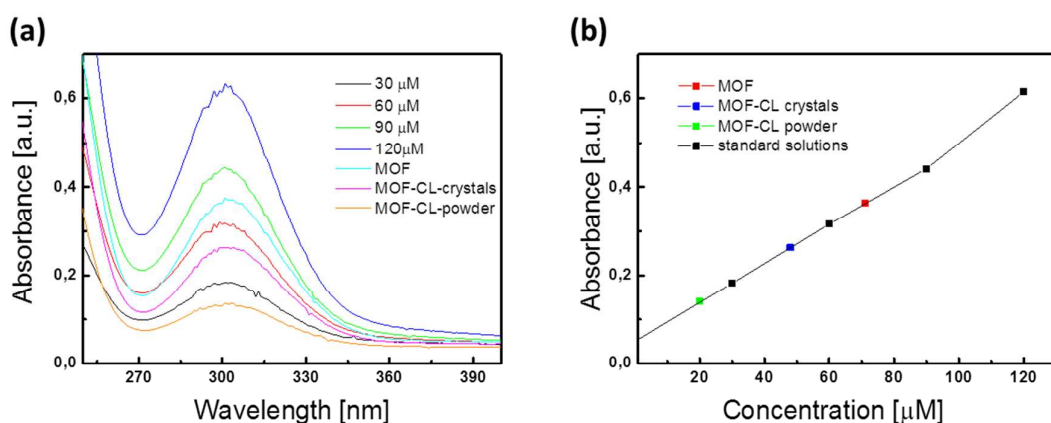


Figure S4: UV-Vis spectroscopic determination of the amount of linker released during the EDTA treatment.

To determine the amount of linker released from the MOF and MOF-CL (cross-linked MOF) analogue during the EDTA treatment UV-Vis spectroscopy was used.

For the experiment first a calibration with different linker concentrations (30 μM , 60 μM , 90 μM and 120 μM) was performed. Afterwards the amount of released linker during the EDTA step was

determined for an equal amount of MOF and MOF-CL sample. For each case, 5mg of sample was dissolved in 1 mL of EDTA solution and volume was made up to 45 mL by adding water. The stock sample solutions were 4 times diluted for keeping the absorbance measurement in calibration limits. The linker concentration (for diluted samples) detected in the MOF case is equivalent to 71 μM and in the case of MOF-CL decreased to 48 μM . The results suggest a cross-linking degree for the single crystals of about 33%. However, as mentioned in the manuscript that the formed GEL crystals are hollow, which most likely is due to the limited penetration depth of the light used to initiate the thiol-ene reaction. In addition, we performed a control experiment by grinding the same amount of MOF crystals and crosslinking afterwards. The linker concentration of this “MOF-CL powder” sample showed significantly lower absorbance at 20 μM . For the “powder MOF-CL” sample the experiments suggest a crosslinking degree of about 72%.

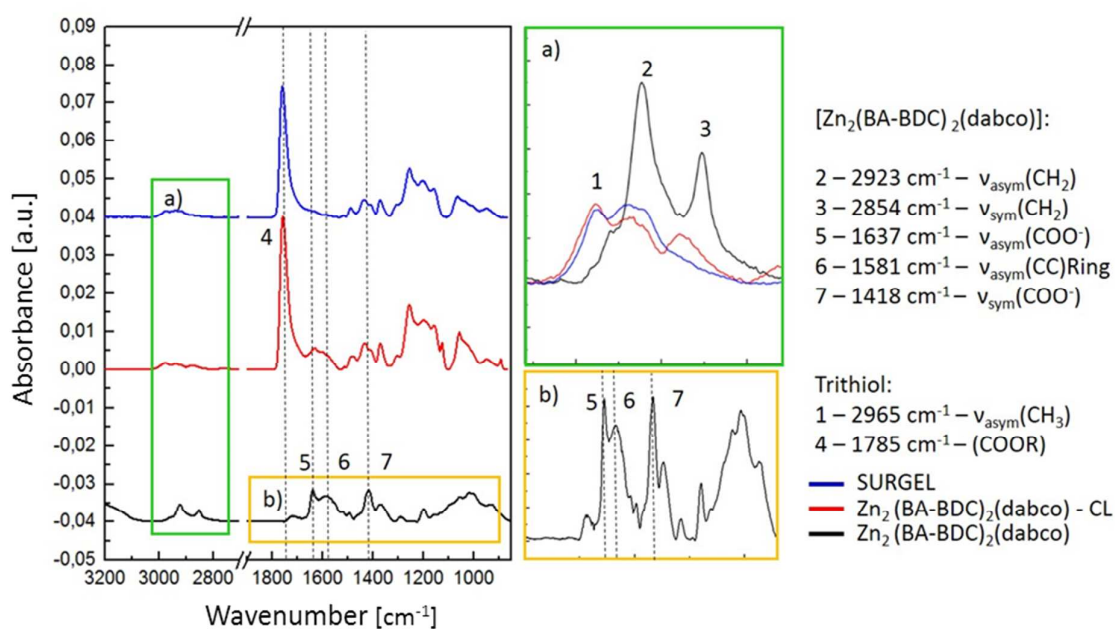


Figure S5. IRRA spectroscopy after the different steps of the SURGEL conversion.

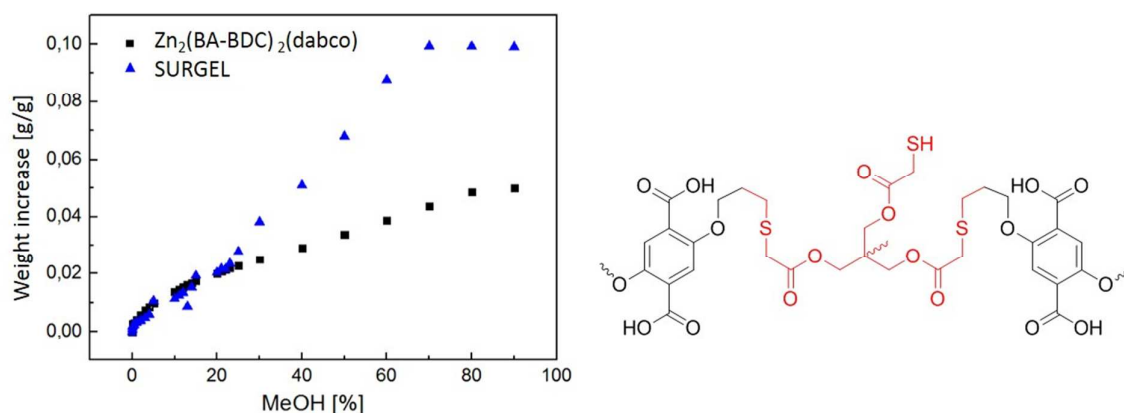


Figure S6: Methanol adsorption isotherms of the $\text{Zn}_2(\text{BA-BDC})_2(\text{dabco})$ SURMOF (black) and the SURGEL (blue).

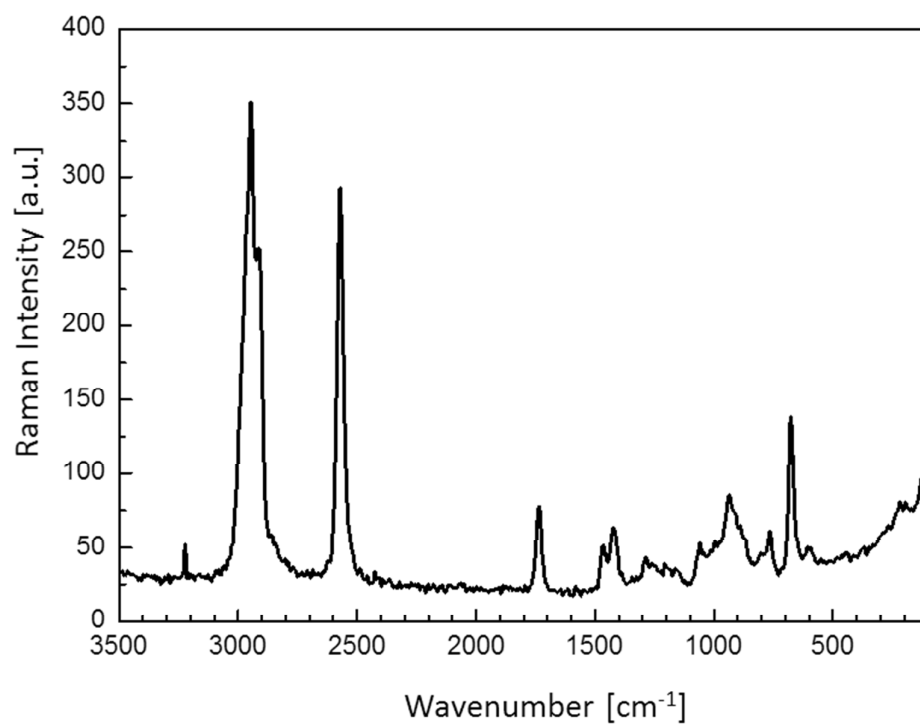


Figure S7: Raman spectrum of the tetrathiol PETMA crosslinker.