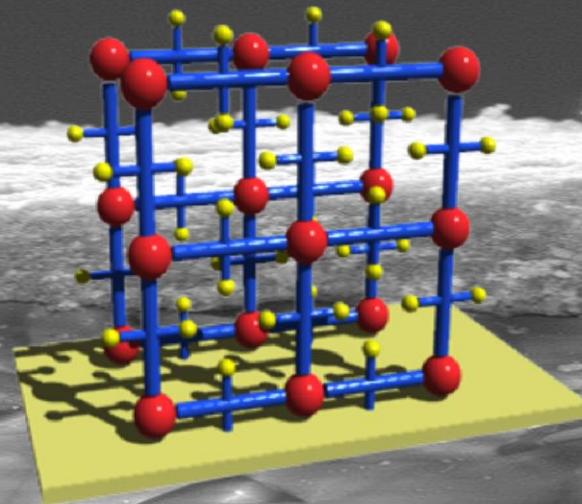


Selbstorganisierende, hochkristalline Dünnschichten als innovative Materialplattform mit hohem Anwendungspotential

H. Gliemann

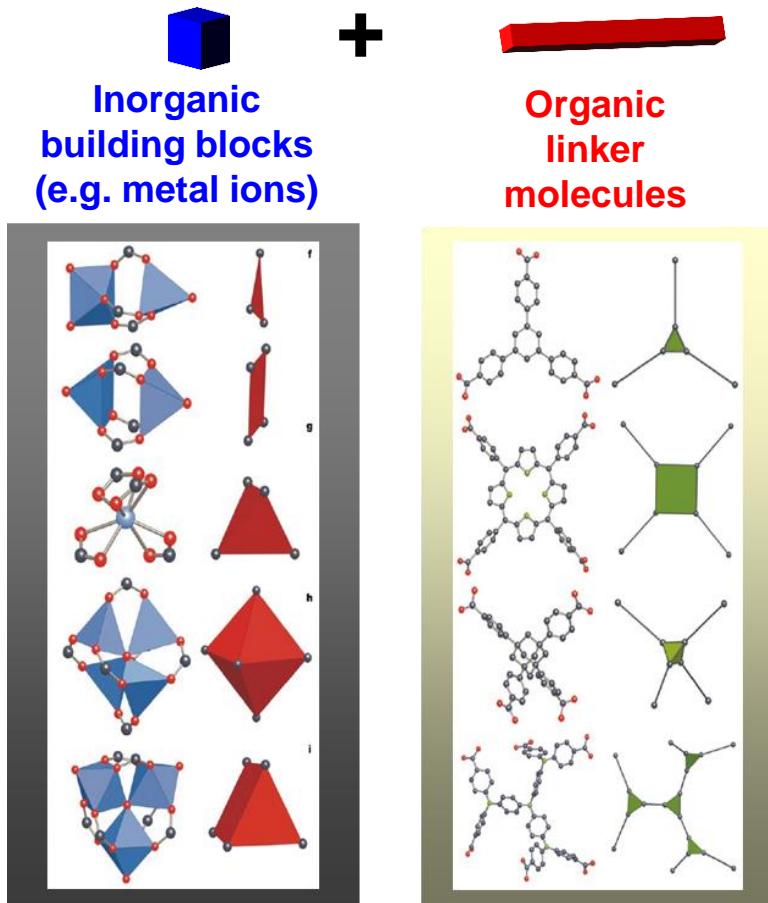
Institut für Funktionelle Grenzflächen (IFG), Karlsruher Institut für Technologie (KIT)
hartmut.gliemann@kit.edu



- **Introduction of Metal-Organic Frameworks (MOFs)**
- **Surface-Anchored Metal-Organic Frameworks (SURMOFs)**
 - Principle of layer-by-layer preparation
 - Characterization
 - Automated preparation techniques
- **Examples of Application**
 - Sensor technology
 - Energy harvesting
 - Catalysis
 - Biology
- **Conclusion**

Metal-Organic Frameworks (MOFs)

Yaghi, O. M., et al., *Nature* (1995) 378, 703



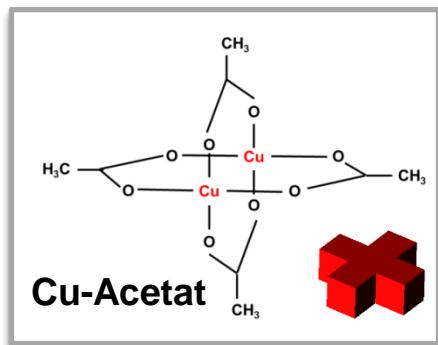
Control of...

- Pore size
- Pore properties

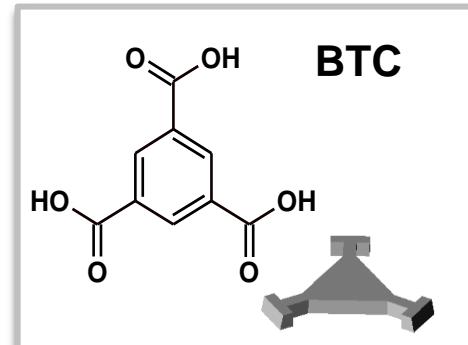
More than 70,000 different structures known meanwhile!

Metal-Organic Frameworks (MOFs)

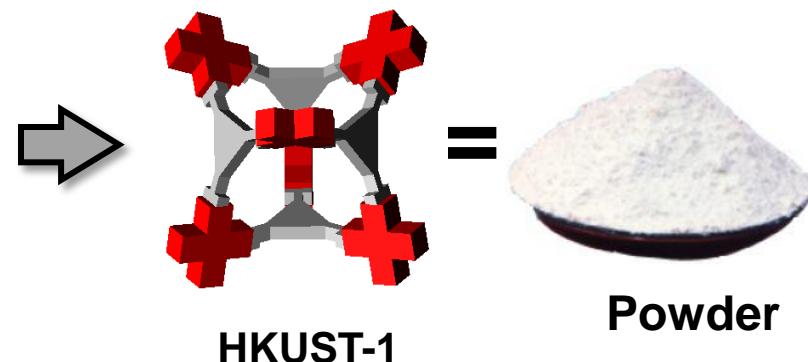
Inorganic building block



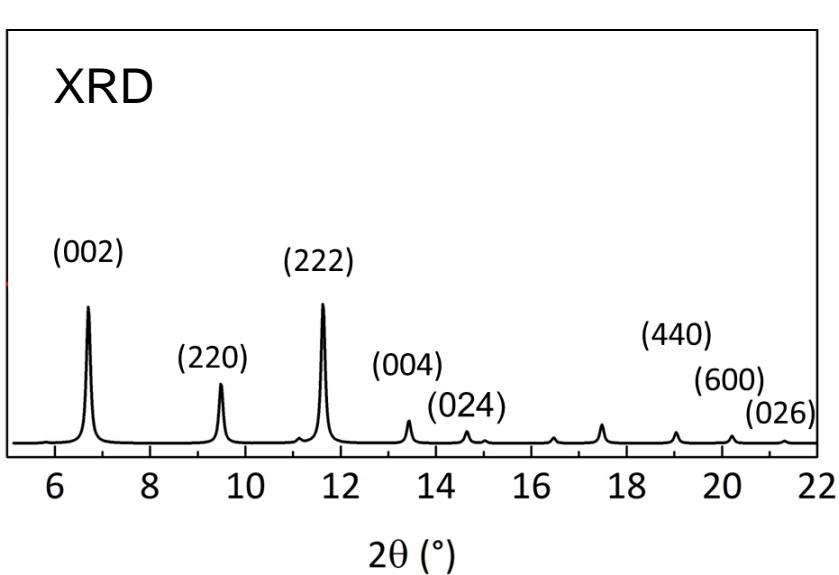
Organic linker



Example



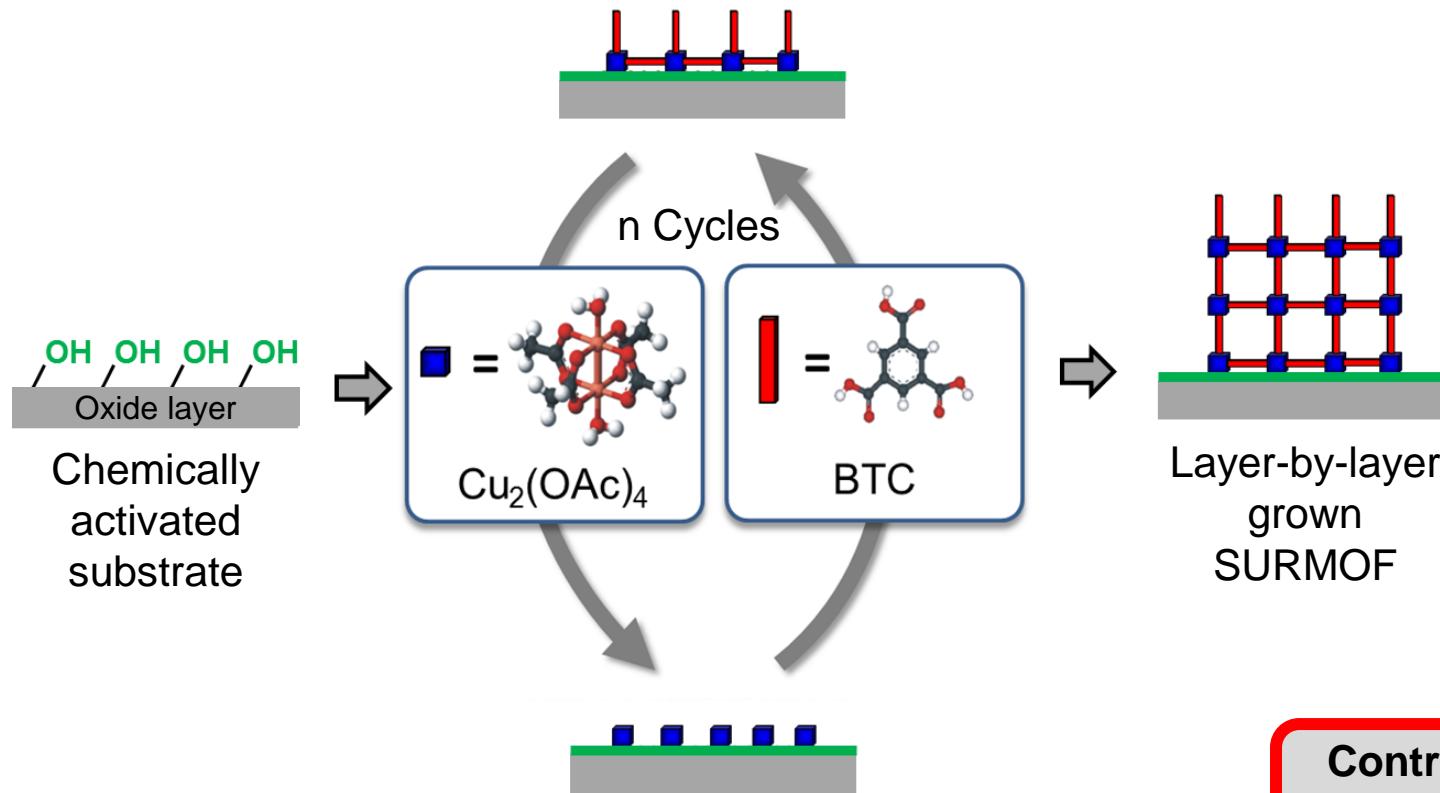
Intensity (a.u.)



Chui, S. S. Y., et al., *Science* (1999) 283, 1148.

How to get MOFs
on a substrate?

Preparation of Surface-Anchored Metal-Organic Frameworks (SURMOFs) by Layer-by-Layer Process

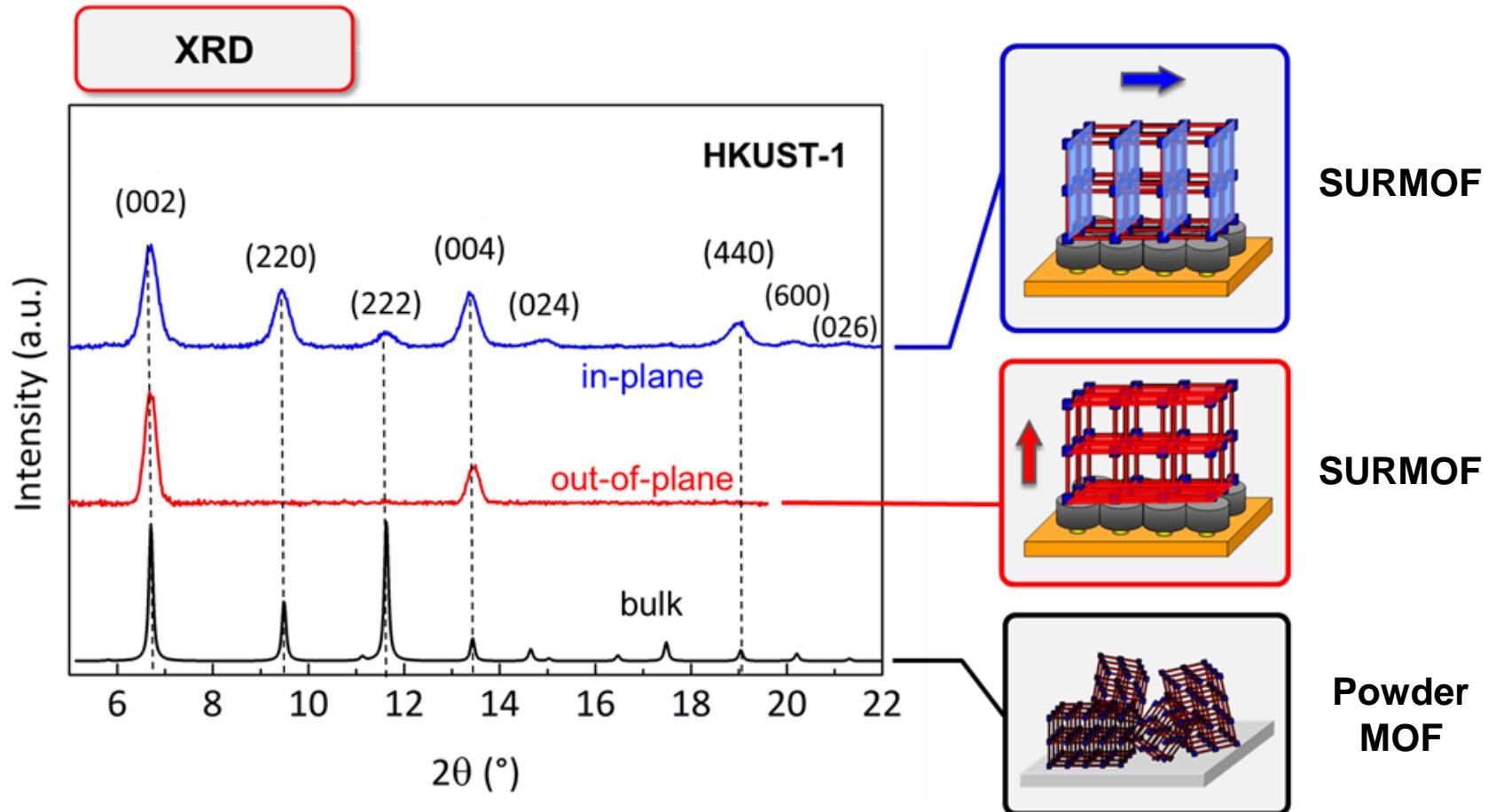


Shekhah, Wang, Zacher, Fischer, Wöll, *J. Am. Chem. Soc.*, **129** (2007) 15118

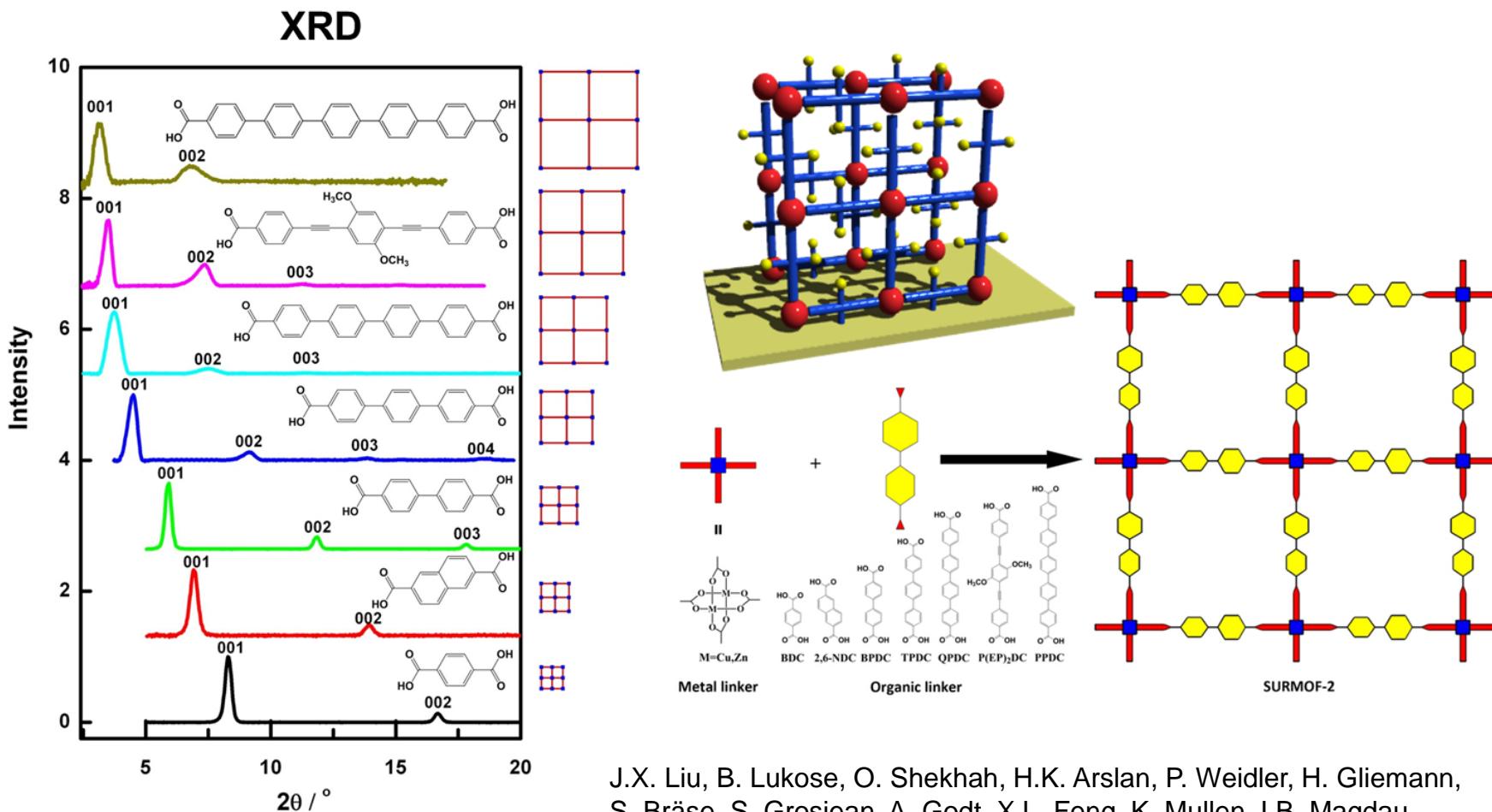
Shekhah, Wang, Paradinas, Ocal, Schüpbach, Terfort, Zacher, Fischer, Wöll, *Nat. Mat.* **8** (2009) 481

- Control of**
- Pore size
 - Pore properties
 - Thickness
 - Orientation

Oriented Growth of SURMOFs Produced by Layer-by-Layer Process

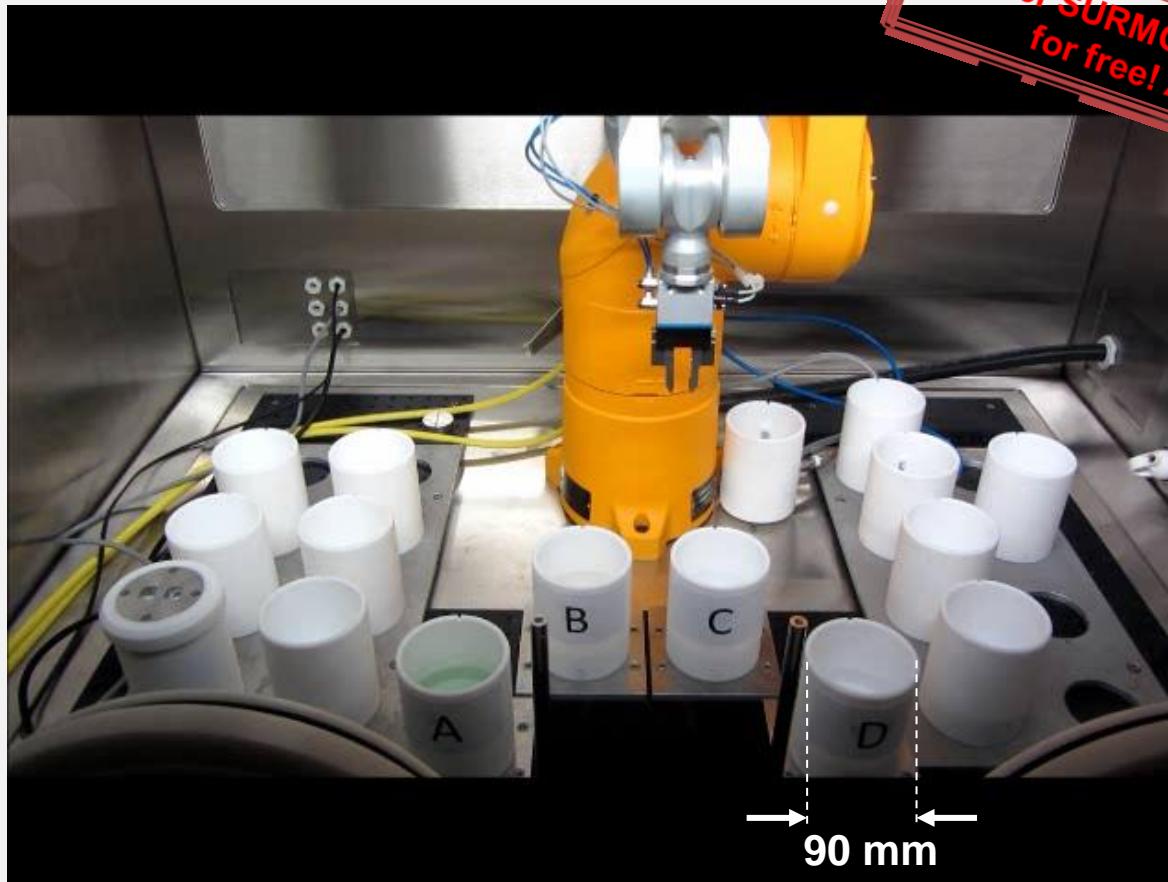


Pore Size Control by Variation of Linker Molecules



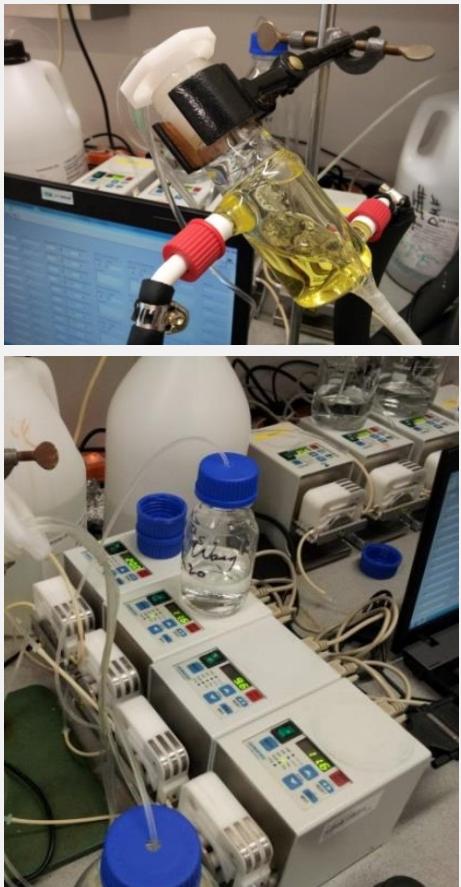
J.X. Liu, B. Lukose, O. Shekhah, H.K. Arslan, P. Weidler, H. Gliemann, S. Bräse, S. Grosjean, A. Godt, X.L. Feng, K. Mullen, I.B. Magdau, T. Heine, C. Wöll, *Scientific Reports* **2**, (2012), 921

Preparation of SURMOFs by Robot-Supported Dipping Layer-by-Layer Process

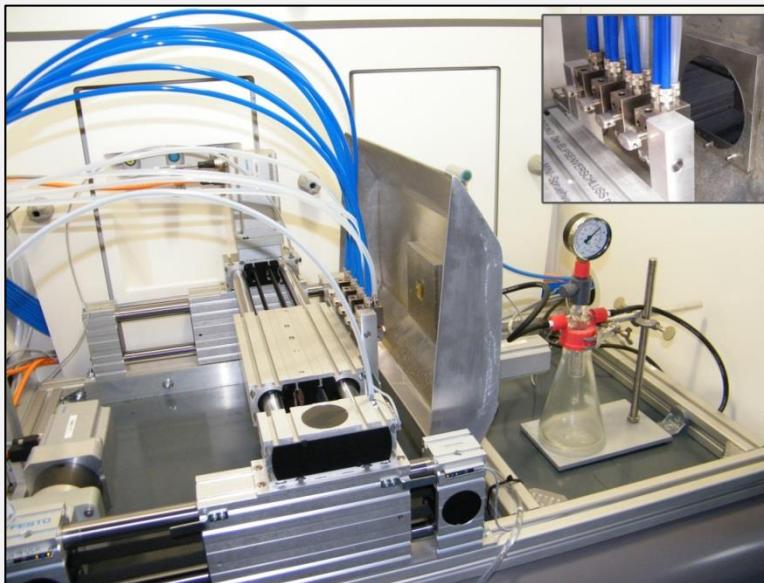


Preparation of SURMOFs by Other Automated Layer-by-Layer Techniques

Immersion technique



Spray technique



Spin coater



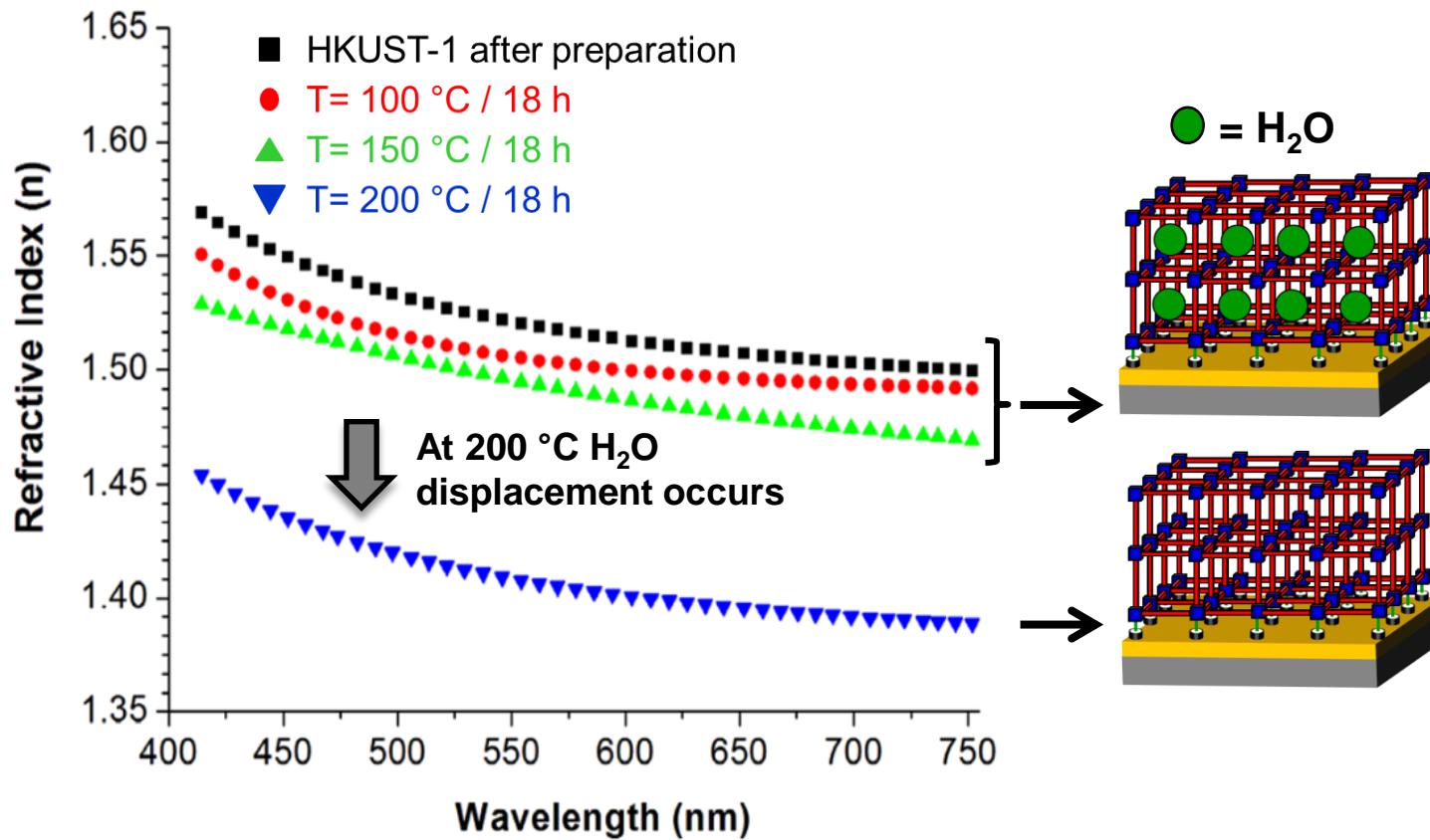
Different SURMOFs can be produced in an optimal way by using different preparation techniques

Shekhah, Wang, Zacher, Fischer, Wöll, *J. Am. Chem. Soc.*, **129** (2007), 15118

Arslan, Shekhah, Wohlgemuth, Franzreb, Fischer, Wöll, *Adv. Funct. Mat.* **21** (2011), 4228

Examples of Application: Optical Sensors

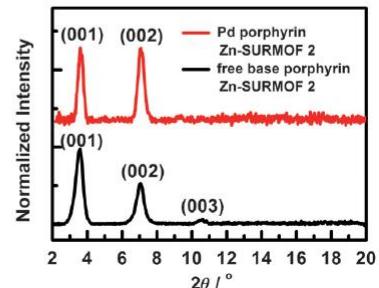
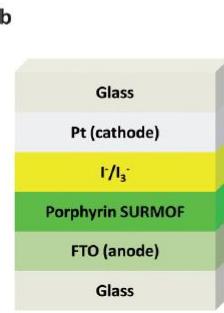
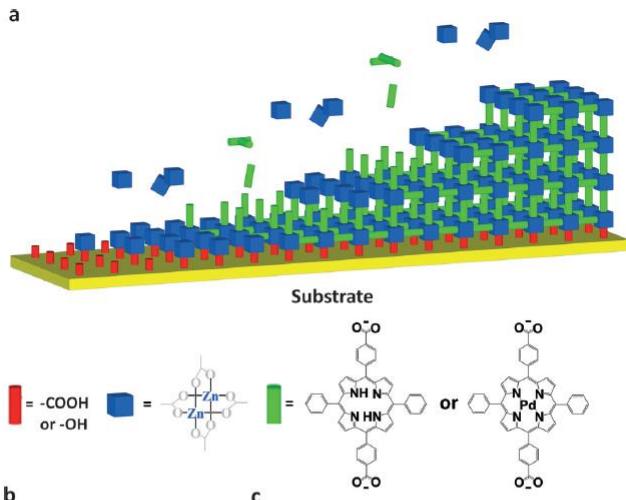
Change of refractive index of HKUST-1 SURMOF as a function of loading with molecules



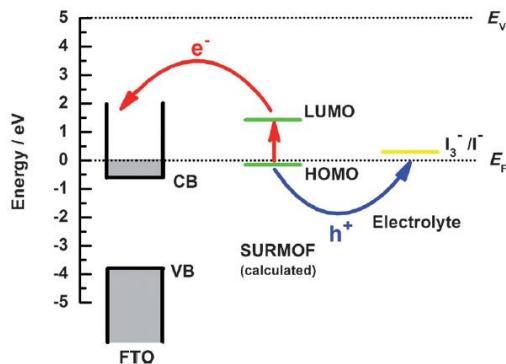
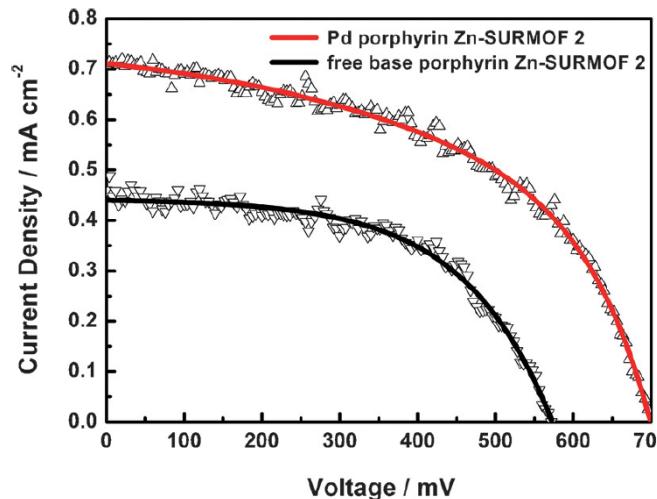
E. Redel, Z. Wang, S. Walheim, J.X. Liu, H. Gliemann, C. Wöll, *Appl. Phys. Lett.* **103** (2013), 091903

Examples of Application: Energy Harvesting

SURMOF-based solar cell



Components of the porphyrin based SURMOF (a), the setup of the solar cell (b), and the XRD data of the SURMOF (c).



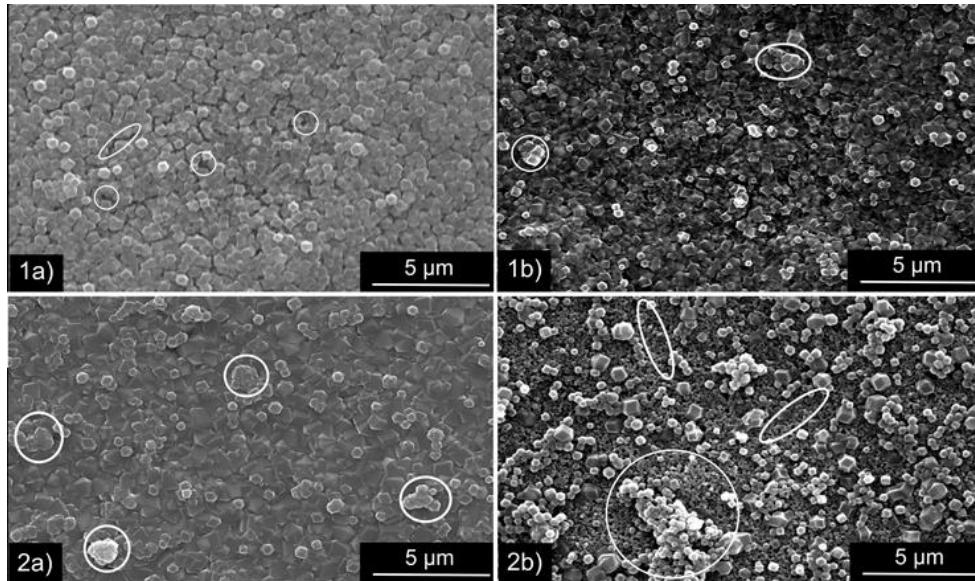
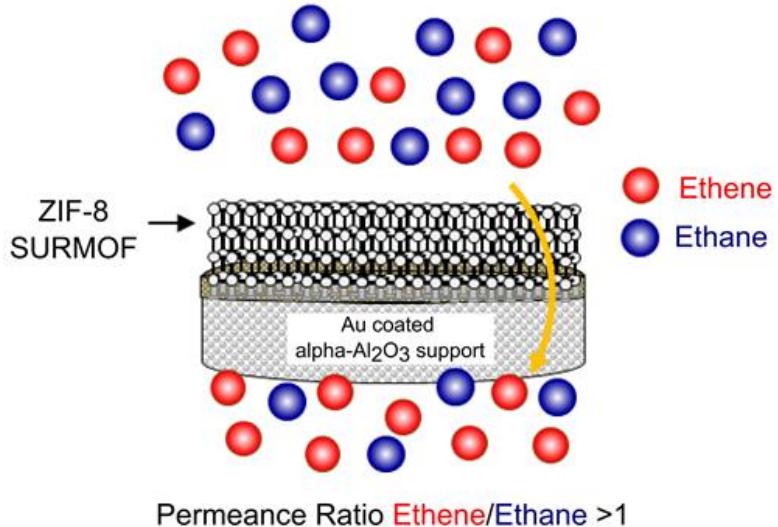
I/V characteristics for freebase porphyrin (black) and Pd porphyrin (red) Zn-SURMOF 2 based photovoltaic devices. Illumination: AM 1.5 G simulated solar light (100 mWcm^{-2}); liquid electrolyte: (I/I_3^-) ; active area: 0.25 cm^2 .

Schematic description of photon absorption and excitons separation process in the porphyrin SURMOF-based photovoltaic device.

J. Liu, W. Zhou, J. Liu, I. Howard, G. Kilibarda, S. Schlabach, D. Coupry, M. Addicoat, S. Yoneda, Y. Tsutsui, T. Sakurai, S. Seki, Z. Wang, P. Lindemann, E. Redel, Th. Heine, C. Wöll, *Angew. Chem. Int. Ed.* **54** (2015), 7441

Examples of Application: Catalysis

Separation of catalytically produced gases



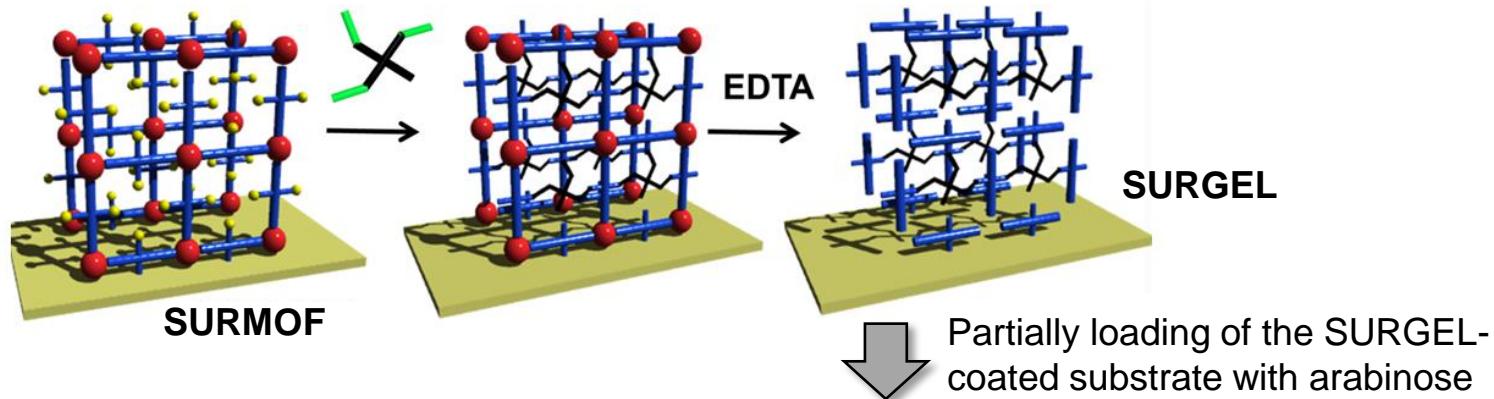
SEM images of ZIF-8 SURMOF growth on: 1a) α -Al₂O₃ + Au support for 150 cycles, 1b) α -Al₂O₃ + Au support for 200 cycles, 2a) α -Al₂O₃ support for 150 cycles, 2b) α -Al₂O₃ support for 200 cycles

	Pressure	Ethane Permeance	Ethene Permeance	Ethene/Ethane Permeance Ratio
	bar	10^{-7} mol m ⁻² s ⁻¹ Pa ⁻¹	10^{-7} mol m ⁻² s ⁻¹ Pa ⁻¹	
Sample 1	1,213	0,136	0,164	1,21
Sample 2	1,213	0,164	0,283	1,72

E.P. Valadez Sánchez, H. Gliemann, K. Haas-Santo, C. Wöll, R. Dittmeyer*, *Chem. Ing. Tech.* **88** (2016) 1798

Examples of Application: Biology

SURGELs as SURMOF-based biocompatible porous materials



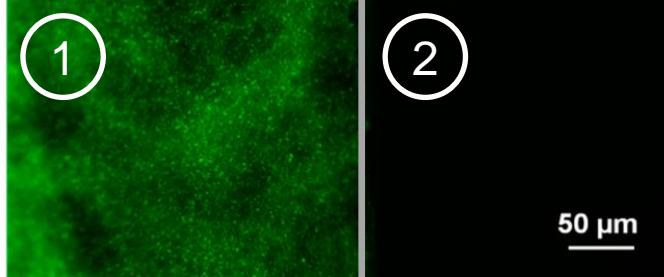
Fluorescence microscope image

■ *P. putida* pJN::GFP bacteria after arabinose metabolism

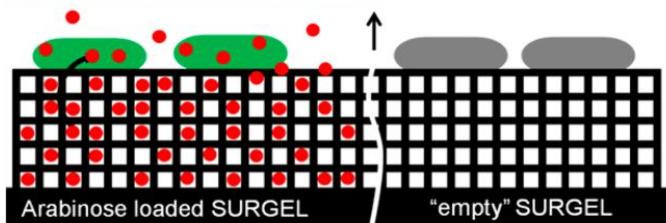
■ *P. putida* pJN::GFP bacteria

● Arabinose

Area 1:
During arabinose metabolism, bacteria attached to the substrate express the green fluorescent protein (GFP)



Area 2:
No GFP expression by bacteria attached to the substrate



M. Tsotsalas, J.X Liu, B. Tettmann, S. Grosjean, A. Shahnas, Z.B. Wang, C. Azucena, M. Addicoat, T. Heine, J. Lahann, J. Overhage, S. Bräse, H. Gliemann, C. Wöll,
J. Am. Chem. Soc. **136** (2014), 8

Conclusion

