



MIXED-LIGAND MOF

Synthesis, Characterization and Applications

Summer Student Programme presentation, September 10, 2025

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Under the supervision of Dr. Jose Velazquez Garcia

Metal-Organic Frameworks (MOFs)

- PBU, metallic centre
- Organic ligands for bridging, linkers

Characteristics:

- High porosity
- Enormous internal surface
- Crystalline materials

Applications

- Catalysis
- Selective adsorption
- Gas storage
- Nanomedicine
- Sensors

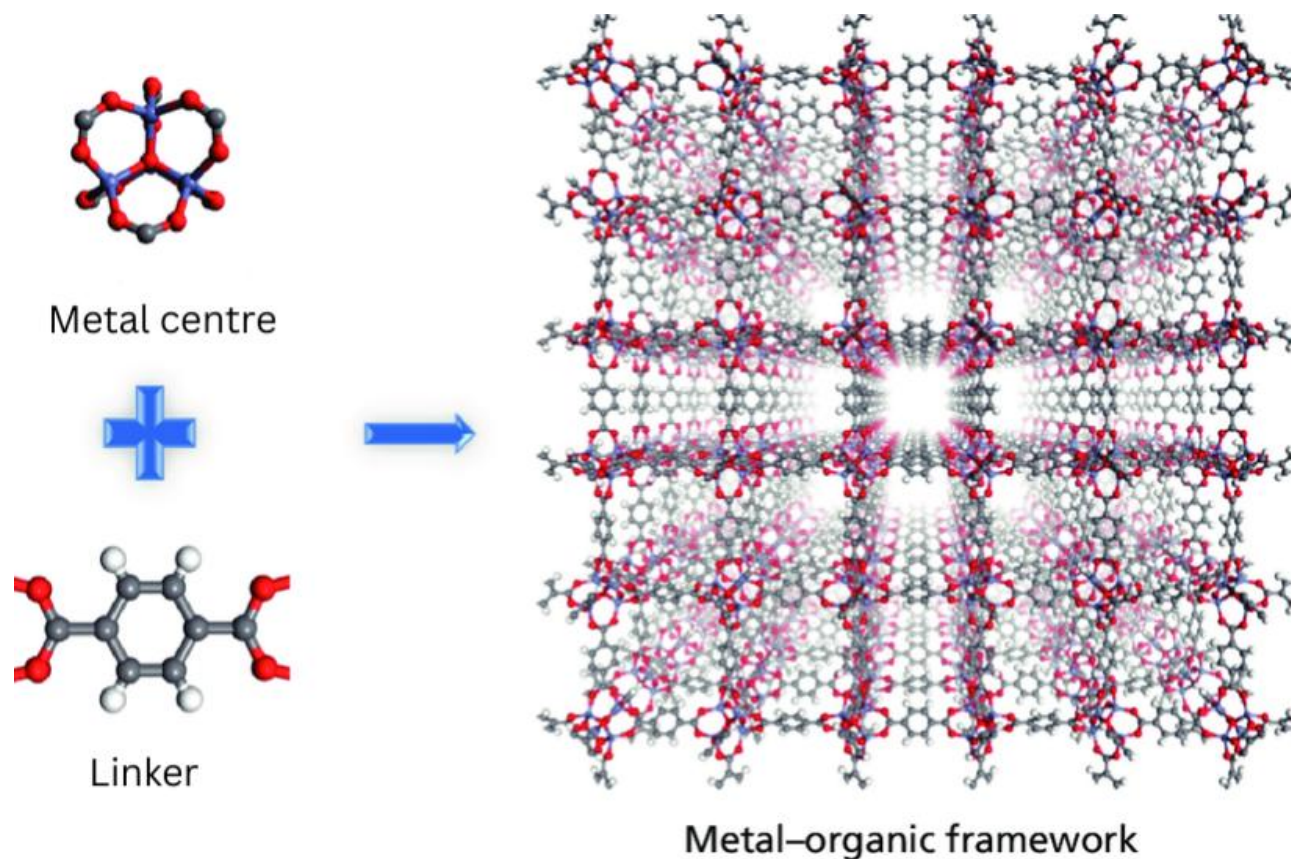


Figure 1: MOF. From atoms and molecules to supramolecular structures, Bell, David. 2018.

Monolith MOF

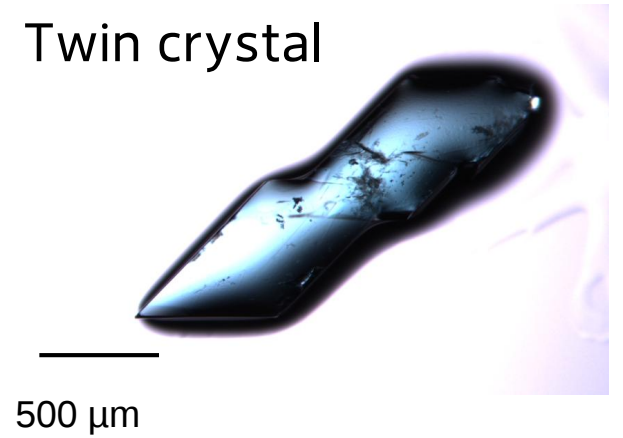
They are continuous macro-size (mm to cm) material that retain the characteristic **porosity of the framework**

Advantages

- Hardness
- High bulk densities
- Easier handling

They are obtained by post-synthesis modification using mechanical methods, but also by direct synthesis through **sol-gel methods** (cf. ZIF-8)

Twin crystal



Monolith



Outline

1. Single-ligand monolith MOF

Sol-gel method for ZIF-8

(already reported, see DOI: 10.1039)



2. Mixed-ligand monolith MOFs

Sol-gel method for Bob

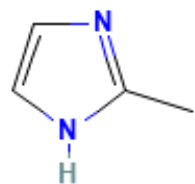


Sol-gel monolith ZIF-8

Synthesis in methanol at room temperature

Zinc nitrate hexahydrate
2-methylimidazole

+ doped with cobalt
ultrasonication



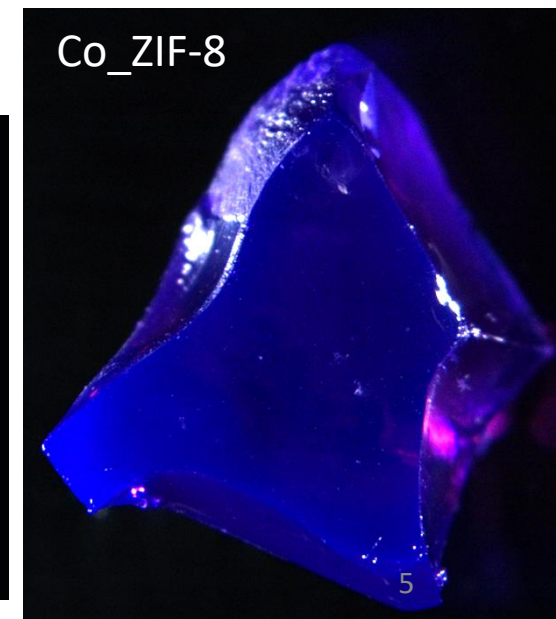
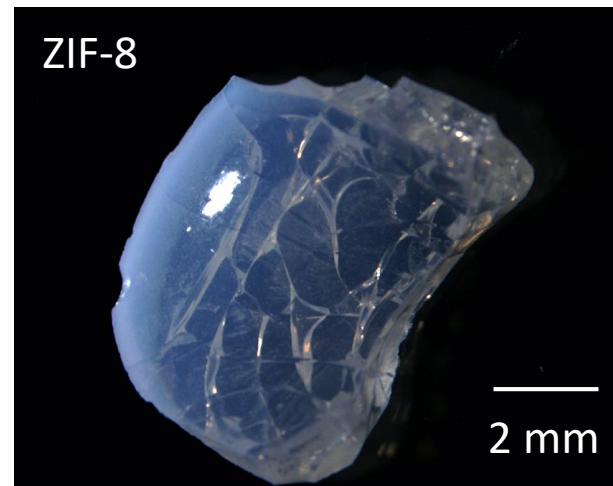
sol-gel

Monoliths: polycrystalline continuous solid

Gel MOFs obtained

centrifugation enables aggregation of the nanoparticles

Air drying

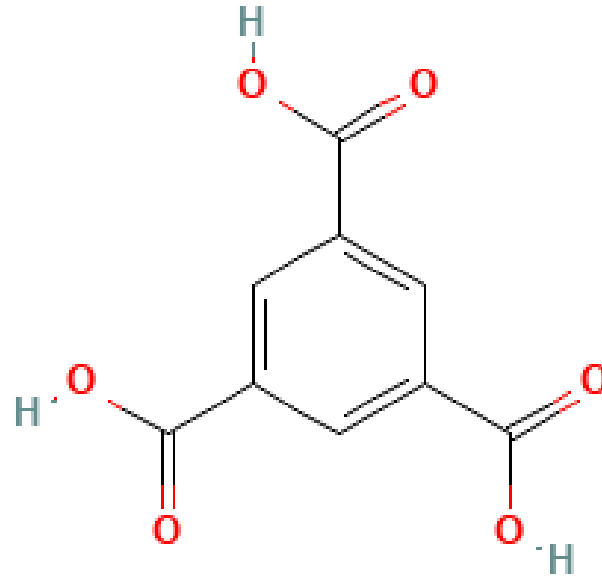


Mixed-ligand MOFs

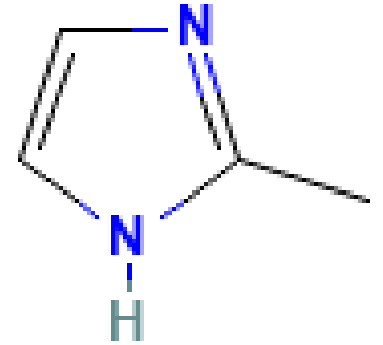
- Metal centre
- Multiple ligands

Advantages:

- Stability enhancement
- Multifunctionality
- Tunable pore structures



Trimesic acid, PubChem



2-methylimidazole, PubChem

Crystal MOF Bob

Metal:

copper nitrate hemi(pentahydrate) or
nickel nitrate hexahydrate

2 organic ligands:
2-methylimidazole
trimesic acid

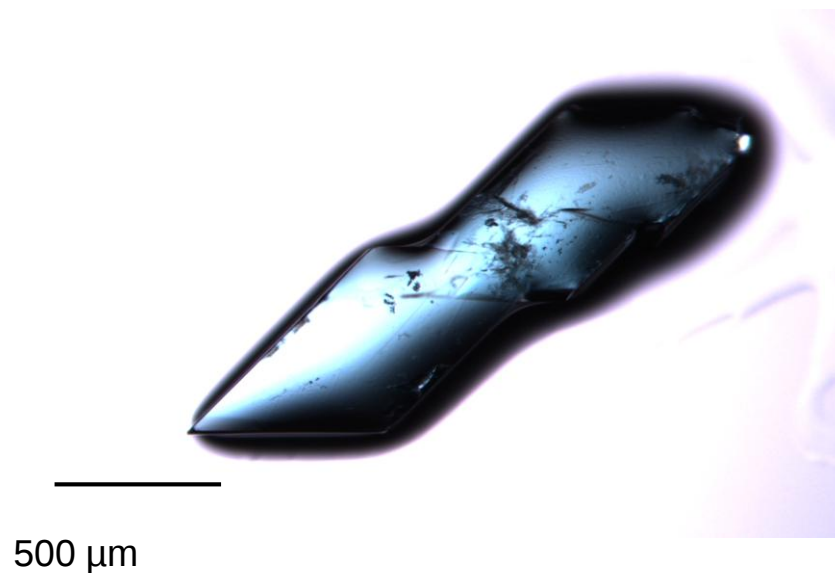
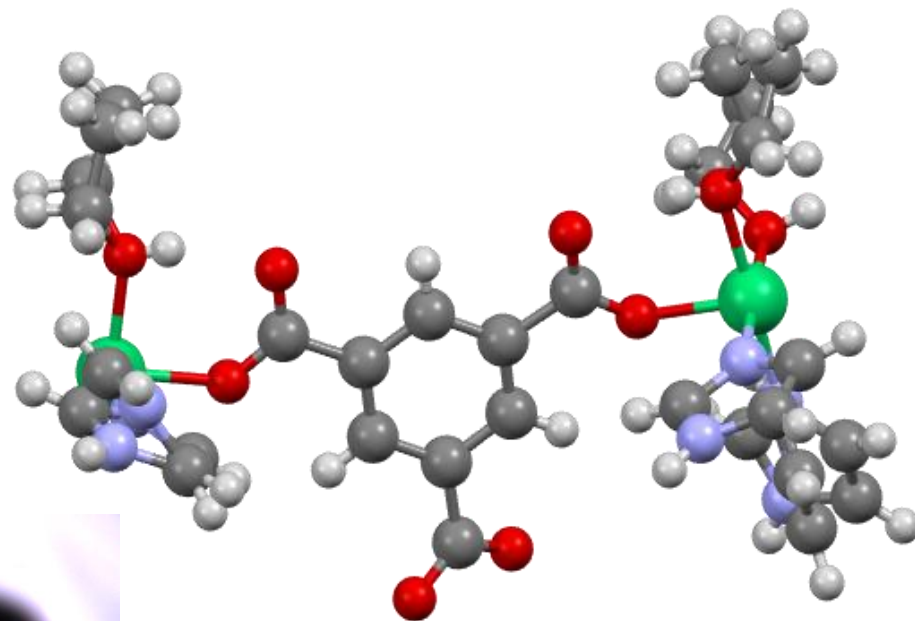


Figure 2: Bob 1 optical image



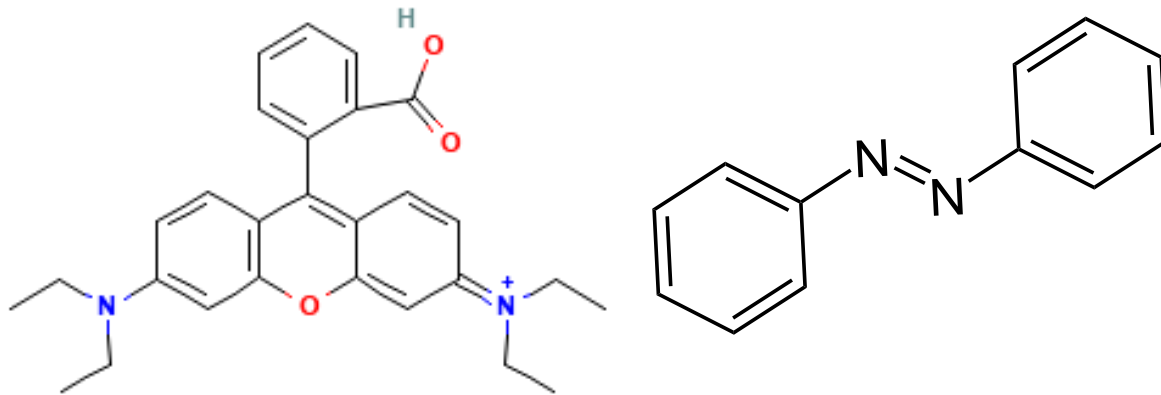
*Figure 3: Asymmetric unit of
Bob 1, edited with Mercury*

Monolith MOF Bob synthesis

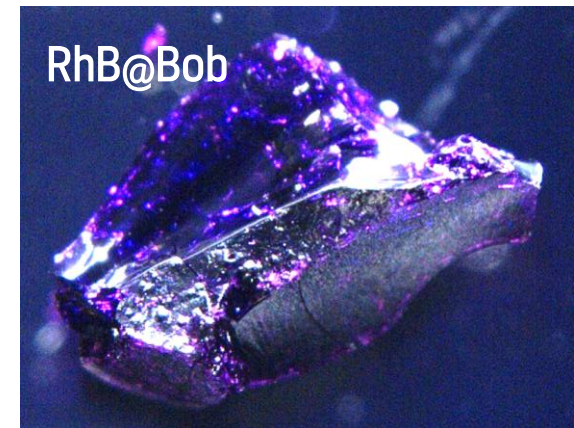
Sol-gel method: we centrifuged the gel to make it compact

Let it air dry

Encapsulation: **rhodamine B (RhB)** and **azobenzene**



Cl^-





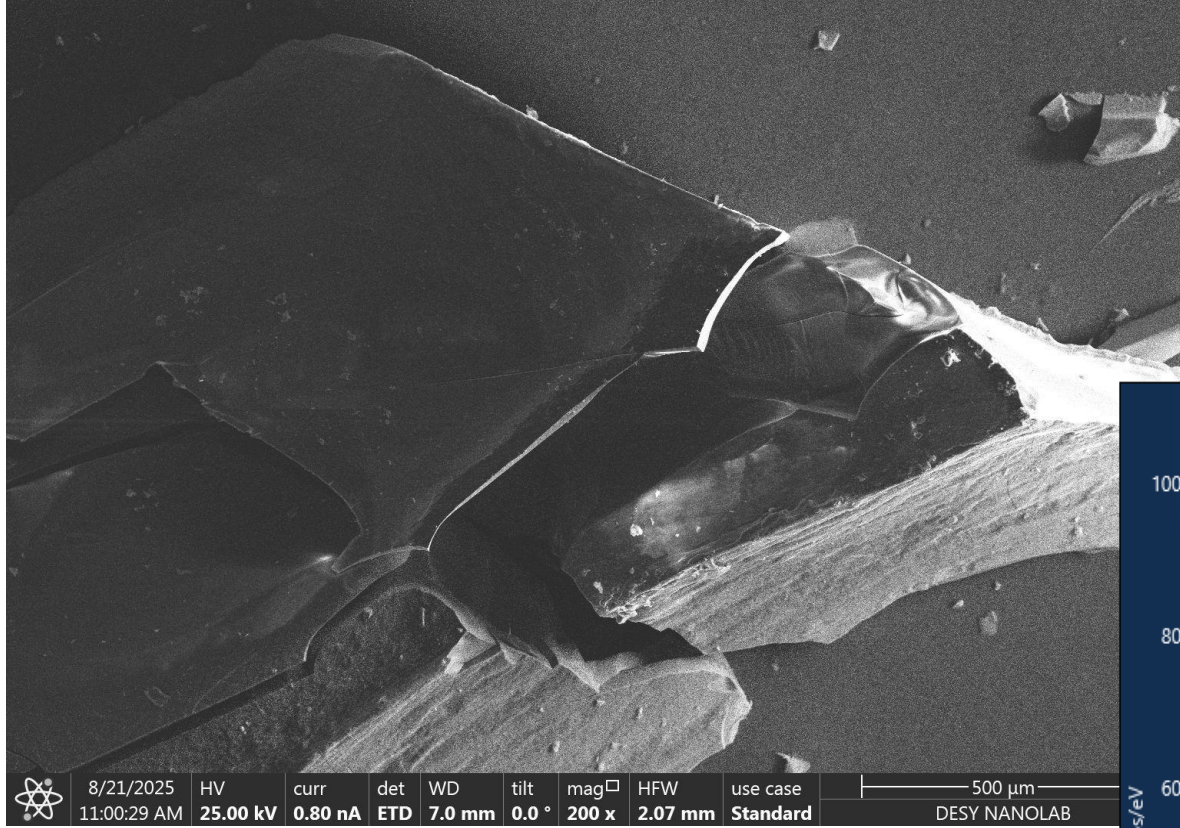
Bob without rhodamine B



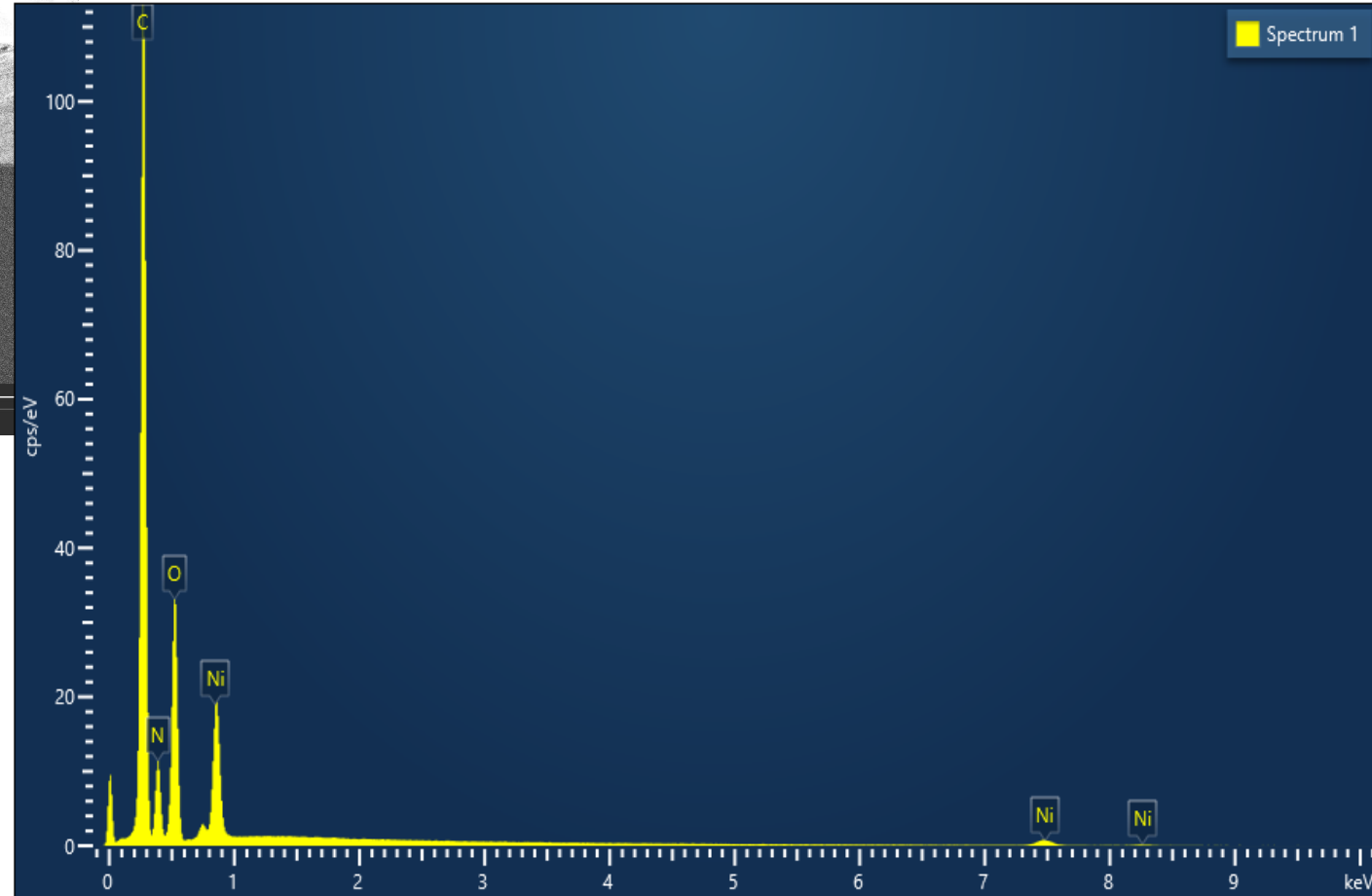
Bob with rhodamine B

2 mm

Bob

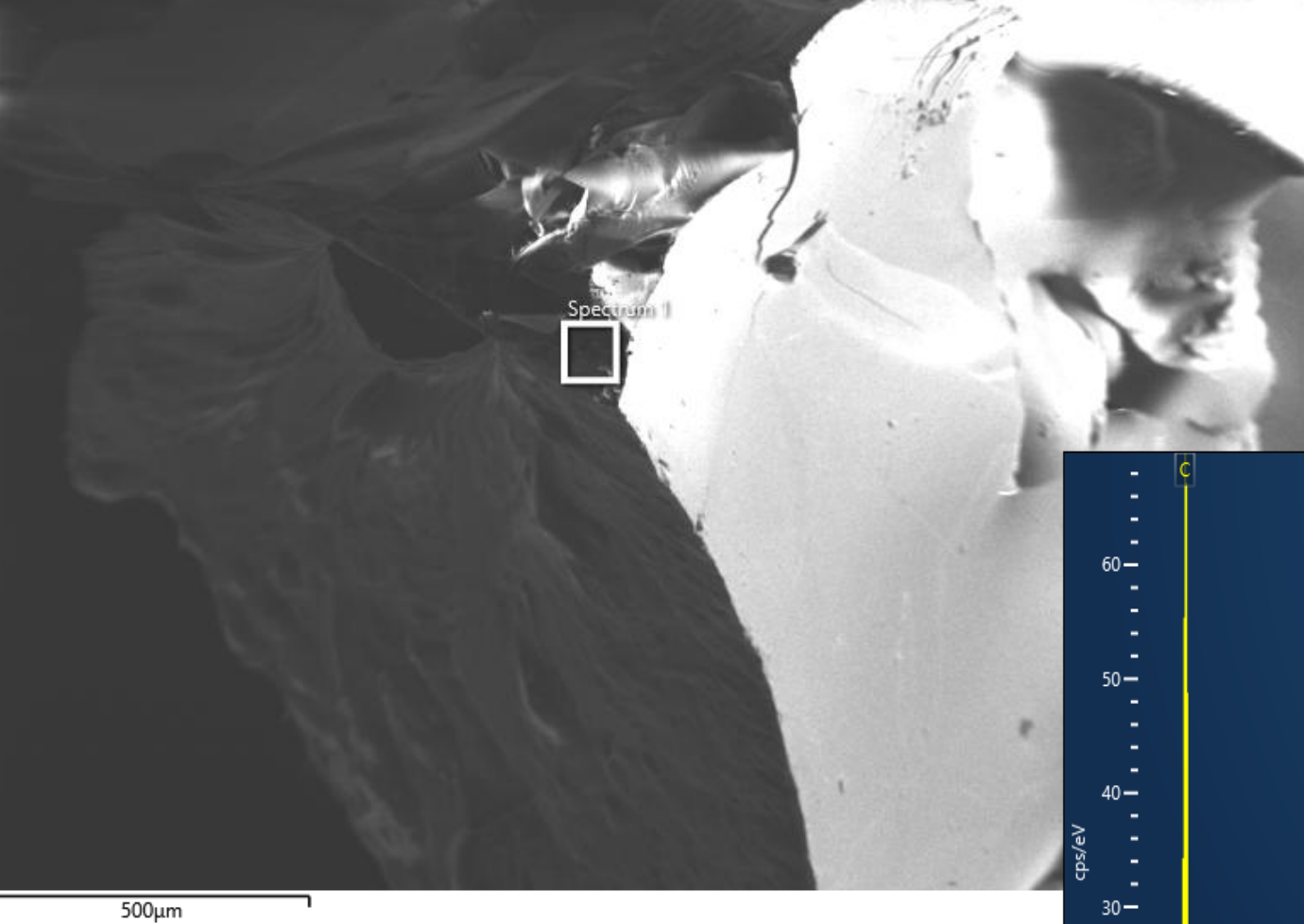


Bob, SEM imaging, DESY Nanolab



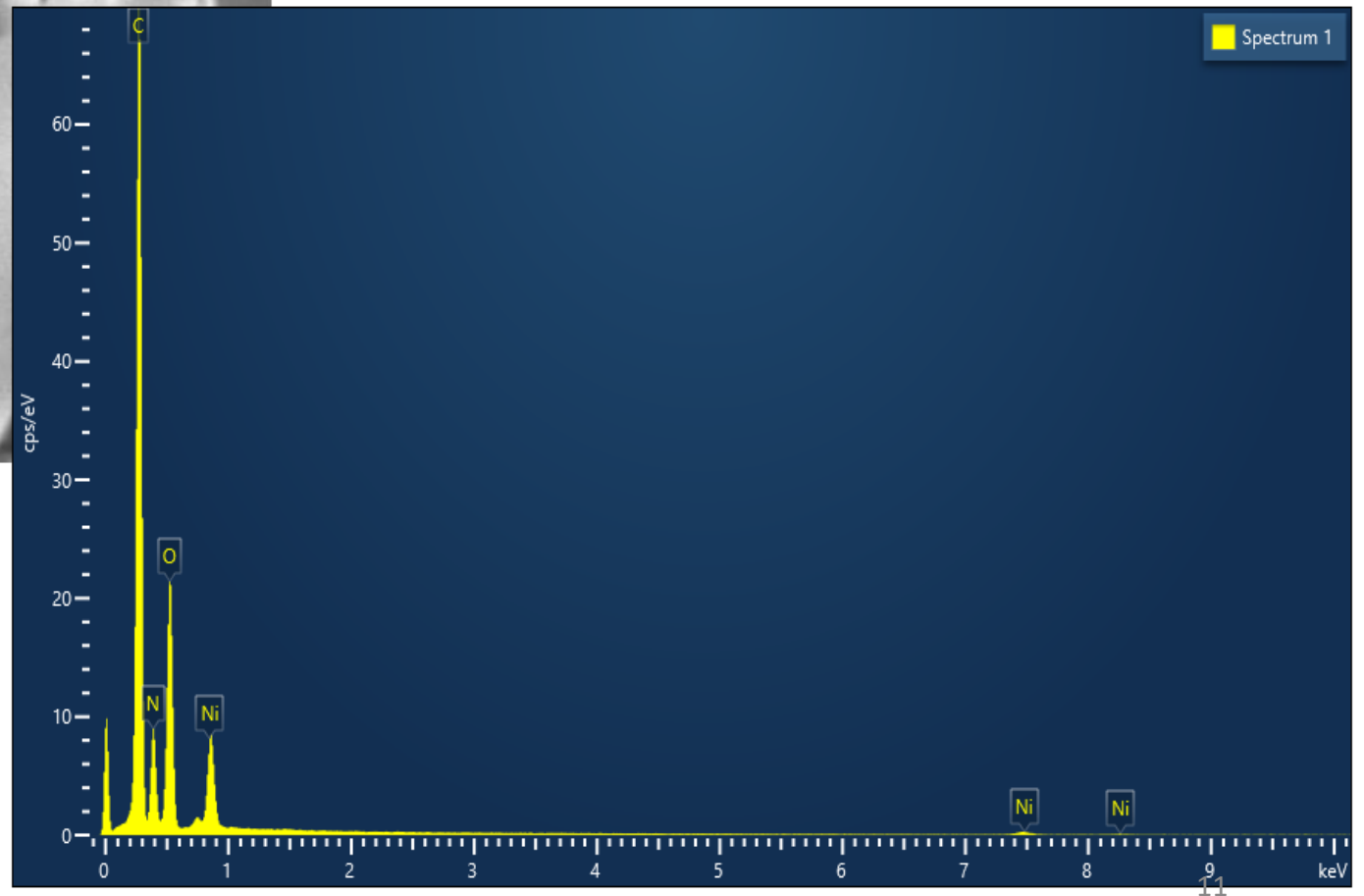
*Bob, EDS
Spectrum,
DESY
Nanolab*

RhB@Bob

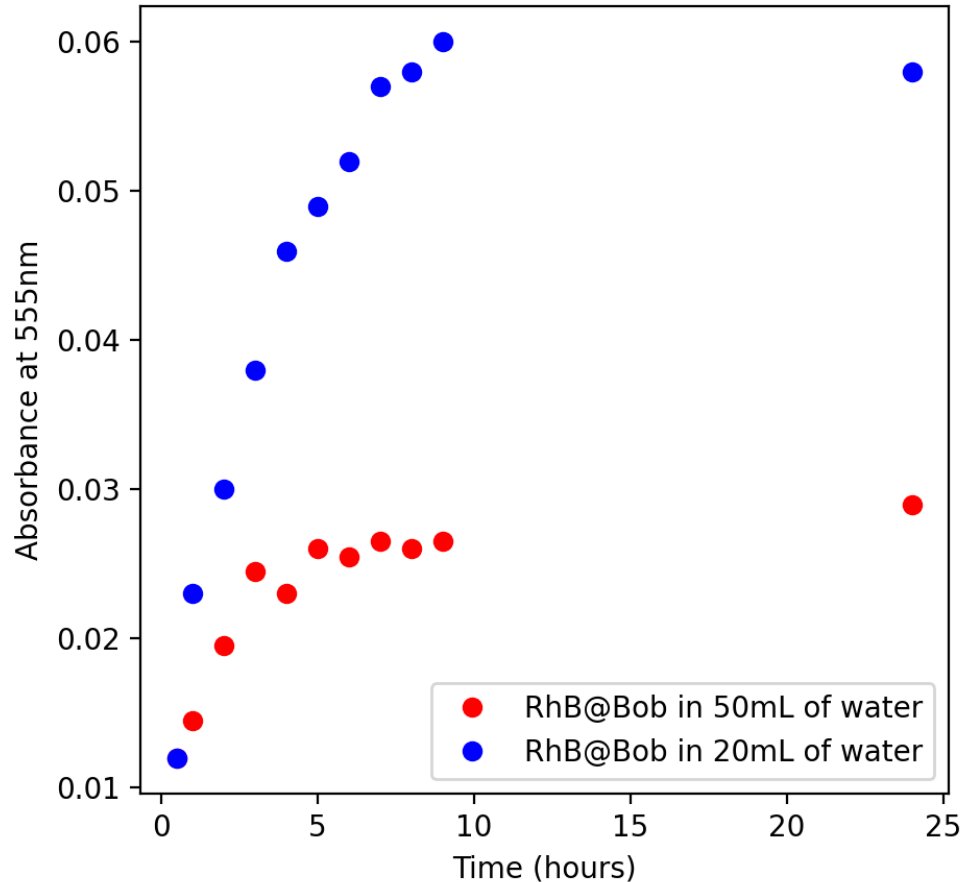


SEM image of RhB@Bob, DESY Nanolab

*EDS spectrum of
RhB@Bob,
DESY Nanolab*



Degradation tests



Degradation of RhB@Bob over time upon immersion in 20mL and 50mL of water. UV-vis measurements. 08.2025

By increasing the volume of water solution, degradation accelerates, from 10 hours in 20mL to reach almost complete degradation to around 6 hours in 50mL

Stable in ethanol

Next step:
water-ethanol mixtures vs kinetics of degradation

Making more sustainable MOFs?

Green MOFs

Reagents and solvents

Synthesis

Ligands

Solvents

Metals

Room
temperature
synthesis

Waste-
based

**Plant or
fungi-
based**

EtOH,
MeOH,
water

Waste-
based

‘Clean’
mining

Lower the
temperature to
room
temperature

changing the
carboxylic acid

Ideas from Rabiee et al. and Rastin et al.

Project Astera 1st experiments

Ligands

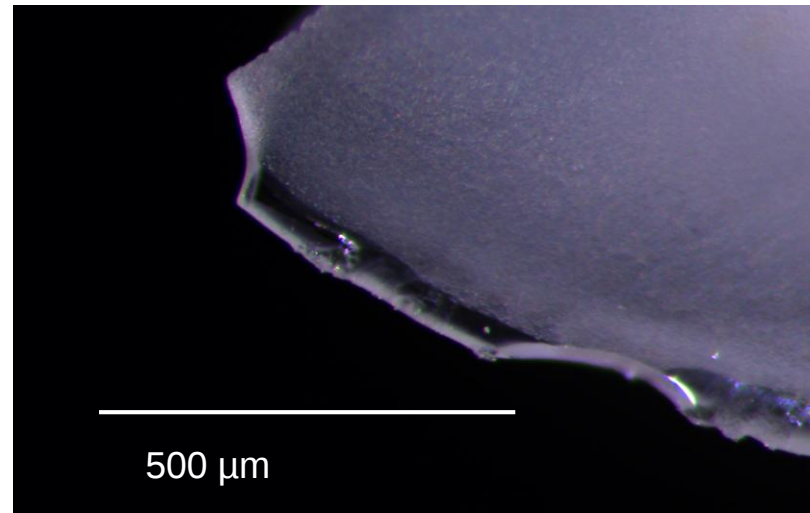
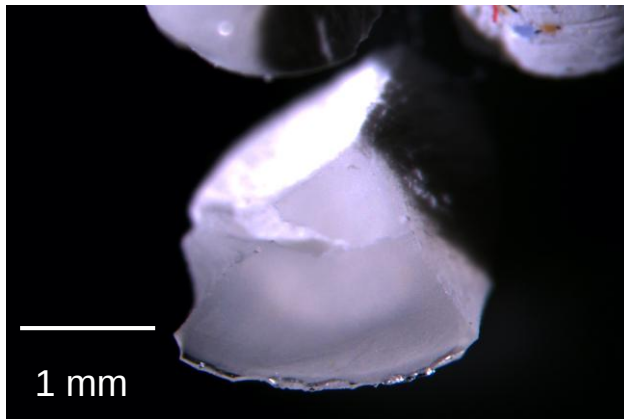
We replace trimesic acid (from oxidation of **petroleum-derived** trimethylbenzene) by **citric acid** (from microbial fermentation)

Metals

Recyclability, abundance, biocompatibility
→ Zinc, Magnesium, Iron

Interim results

Zinc + 2i methylimidazole + citric acid gave gel-like products
→ Centrifugation



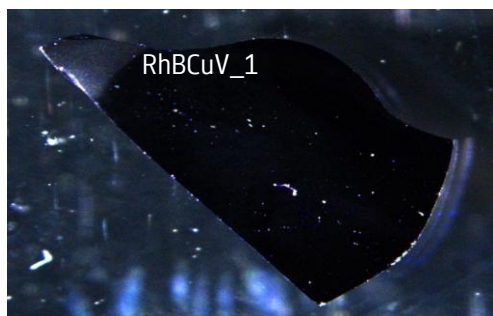
Next steps

- lower the concentration
- Change the carboxylic acid for a **bigger one**
- Try with iron

Conclusion

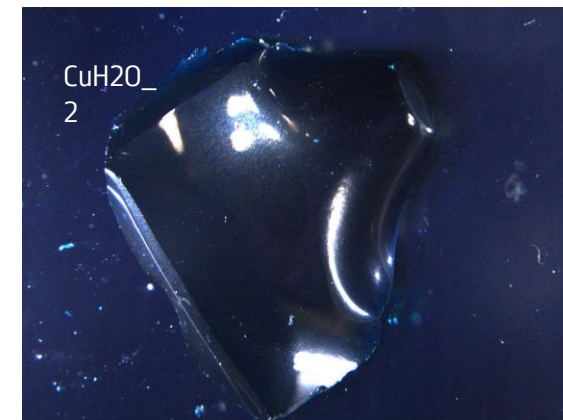
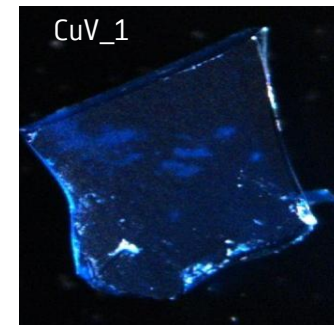
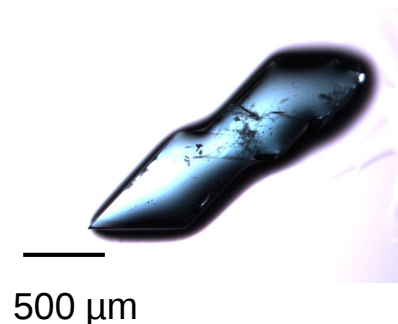
Synthesis

- Monolith ZIF-8
- Monolith Bob



Characterization

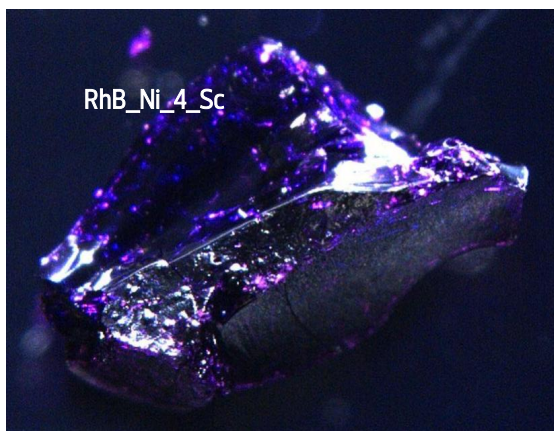
- SEM & EDX
- FTIR



Applications

- SEM & EDX
- UV-vis

Degradation of the framework and slow release of encapsulated small molecule



Acknowledgements

- FS-SCS:
 - Christos Bintas
 - Jose Velazquez
 - Simone Techert
- DESY Summer student programme



**Thank you for your
attention.**



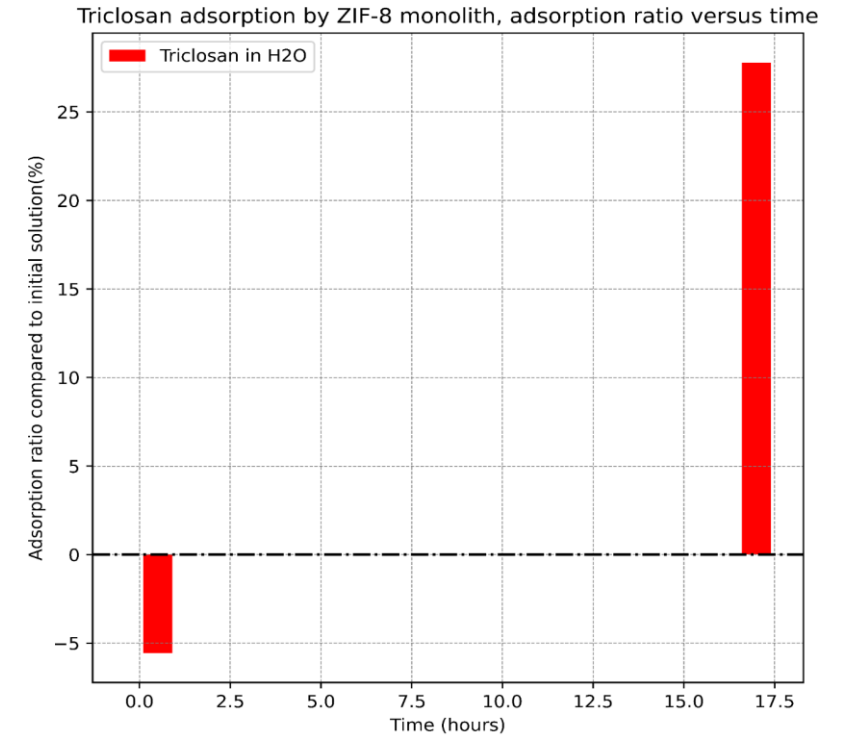
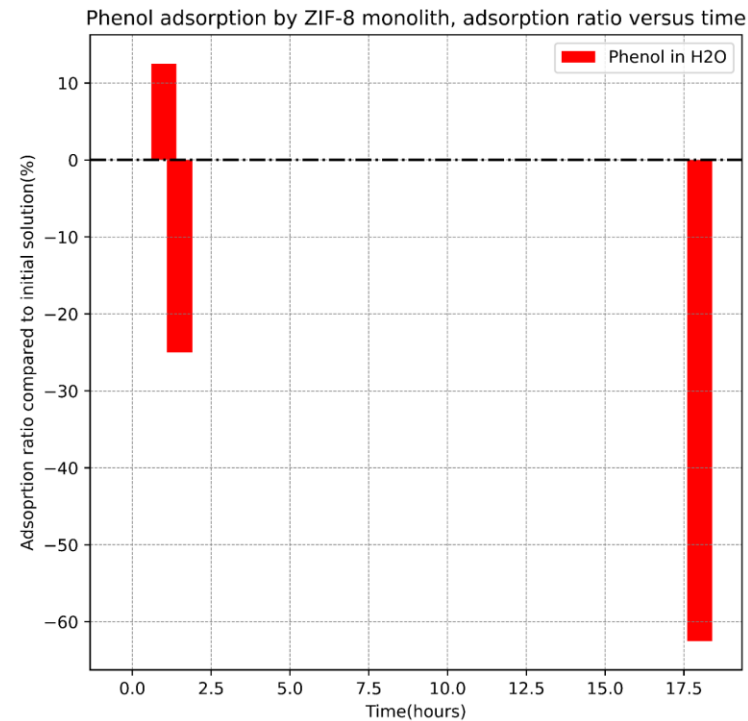
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Adsorption tests in water

ZIF-8
monolith is
not water
resistant



Beer Lambert law: absorbance is proportional to concentration

$$Adsorption_{\%} = \left(1 - \frac{Absorbance(t)}{Absorbance(0)}\right) \cdot 100$$

Triclosan adsorption test to be repeated