Forum 40

Designig of metal-organic frameworks towards water-resistant structures

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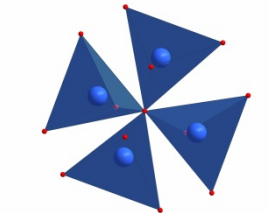
D09 – Department of Inorganic Chemistry and Technology

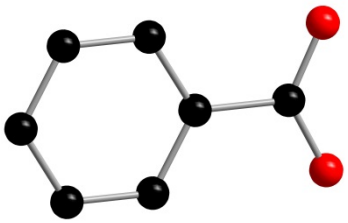
Ljubljana, January 2017

Metal-organic frameworks?

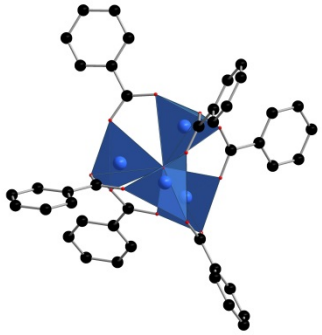
'MOFs are a new class of crystalline materials…'

Structures are composed of metal units and organic ligands



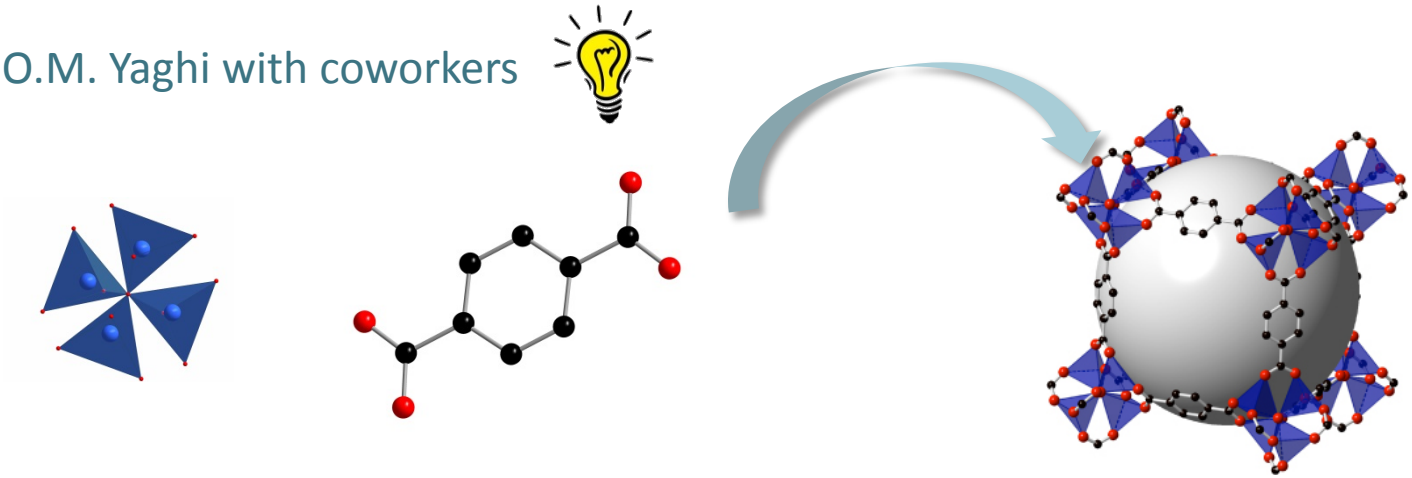


Coordination compounds, complexes



Metal-organic frameworks?

O.M. Yaghi with coworkers



Attractive properties:

- High specific surface areas (< 6000 m^2/g)
- Low densities (> 0.2 g/cm^3)
- High void contribution (up to 90%)

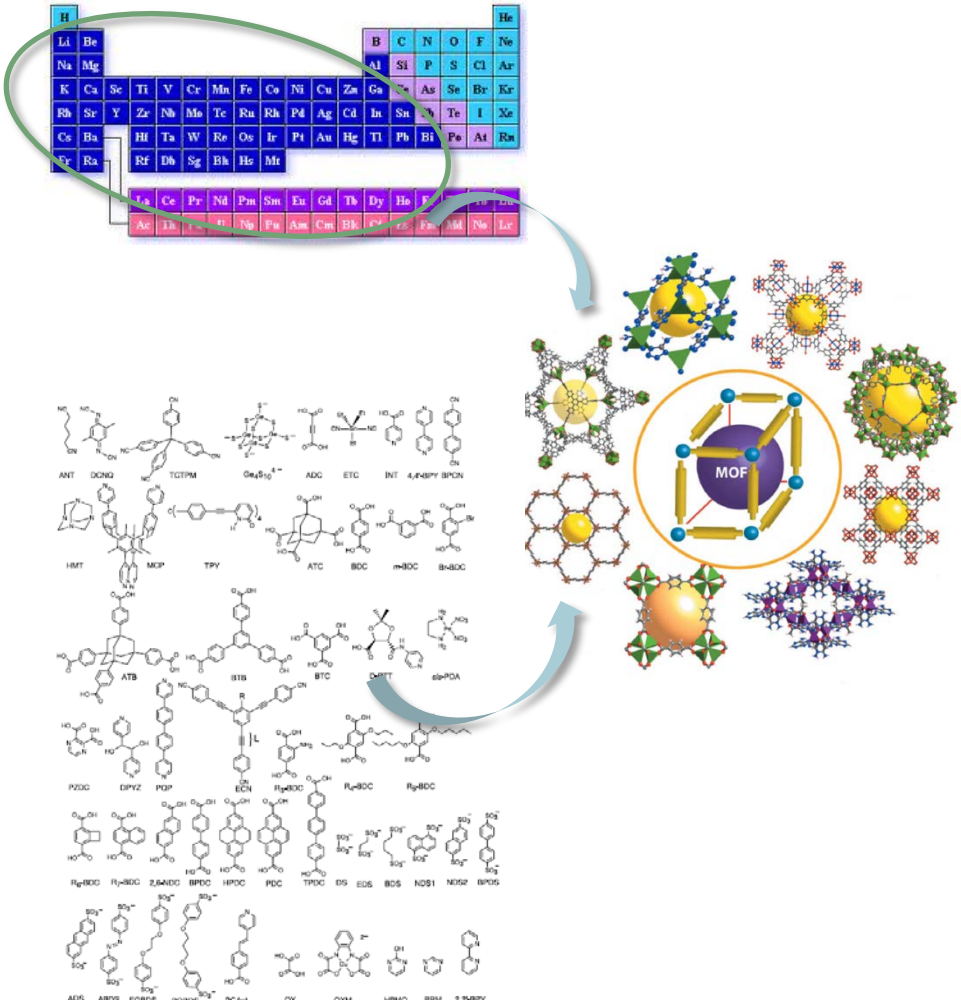
Structural features can be controlled!

Design and synthesis of an exceptionally stable and highly porous metal-organic framework

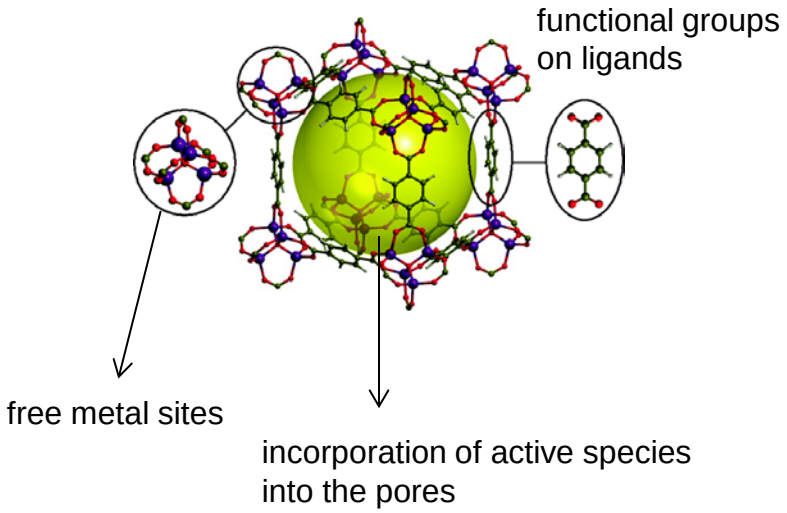
Hailian Li*, Mohamed Eddaoudi†, M. O'Keeffe* & O. M. Yaghi†

*Materials Design and Discovery Group, * Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604, USA*
† Department of Chemistry, University of Michigan, 930 North University, Ann Arbor, Michigan 48109-1055, USA

Control over the MOF topologies



Control over the functionalities



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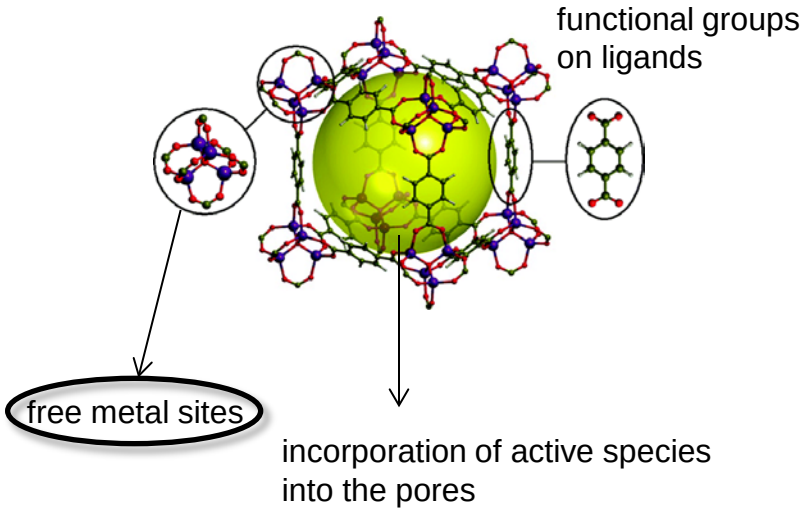
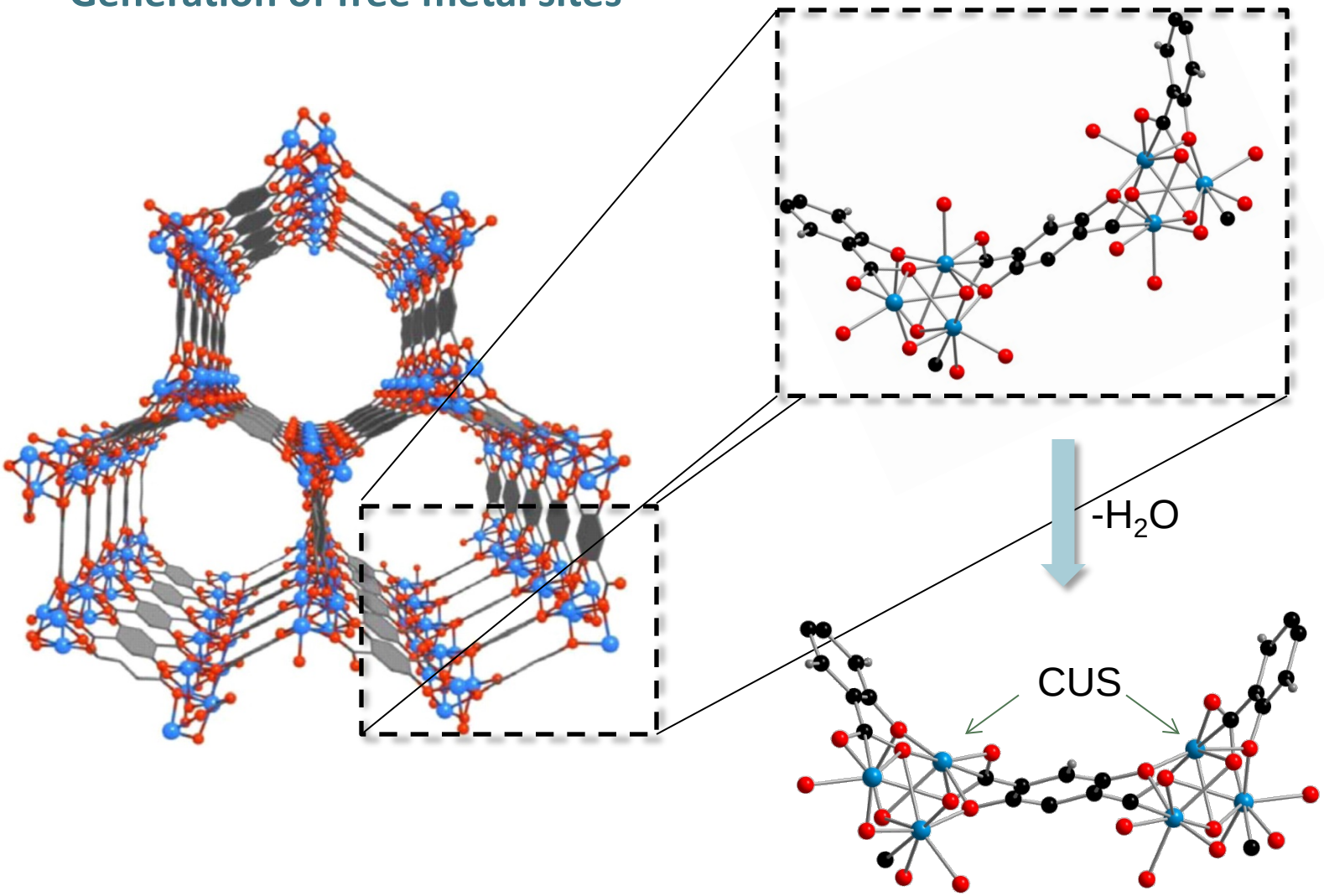
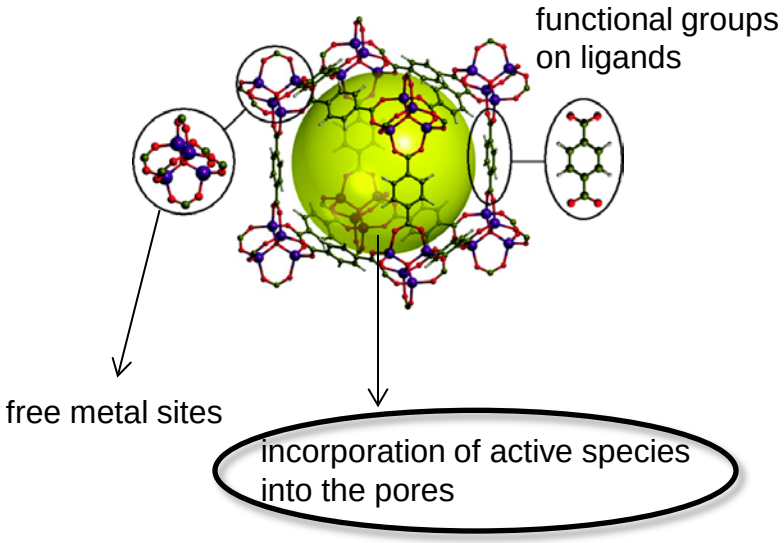
Control over the functionalities



Generation of free metal sites

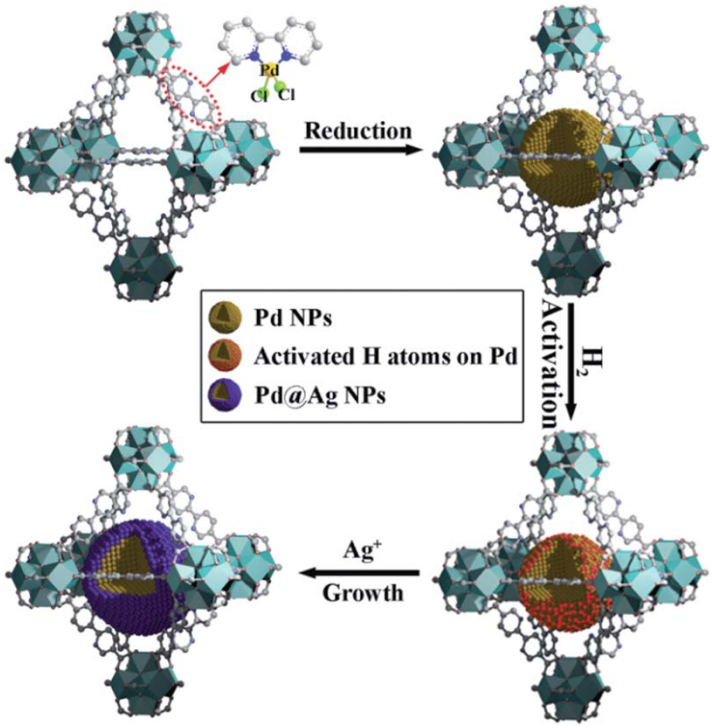


Control over the functionalities



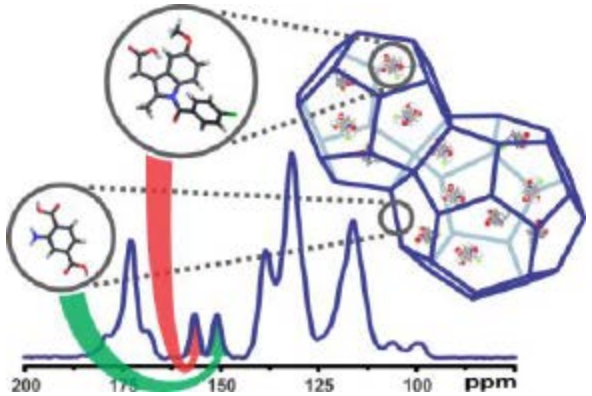
Incorporation of active species

Catalyst carrier



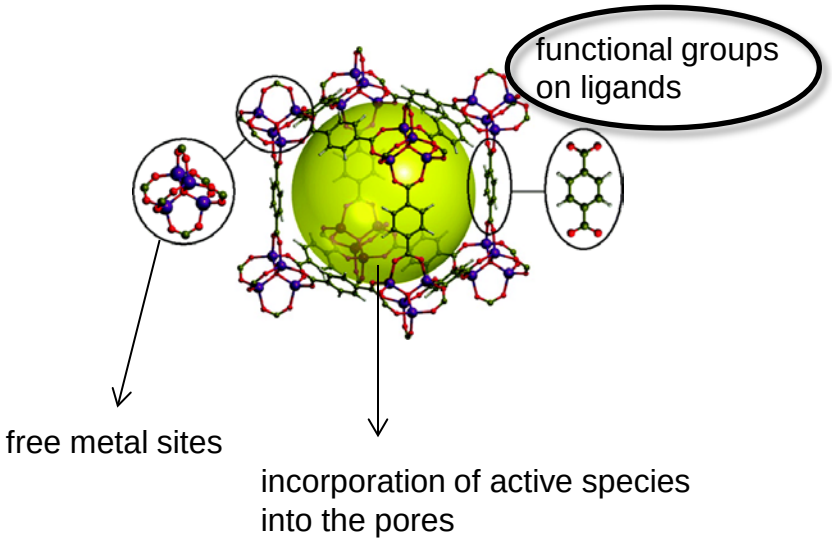
L. Chen et al, *Chem. Sci.* **2016**, *7*, 228

Drug carrier

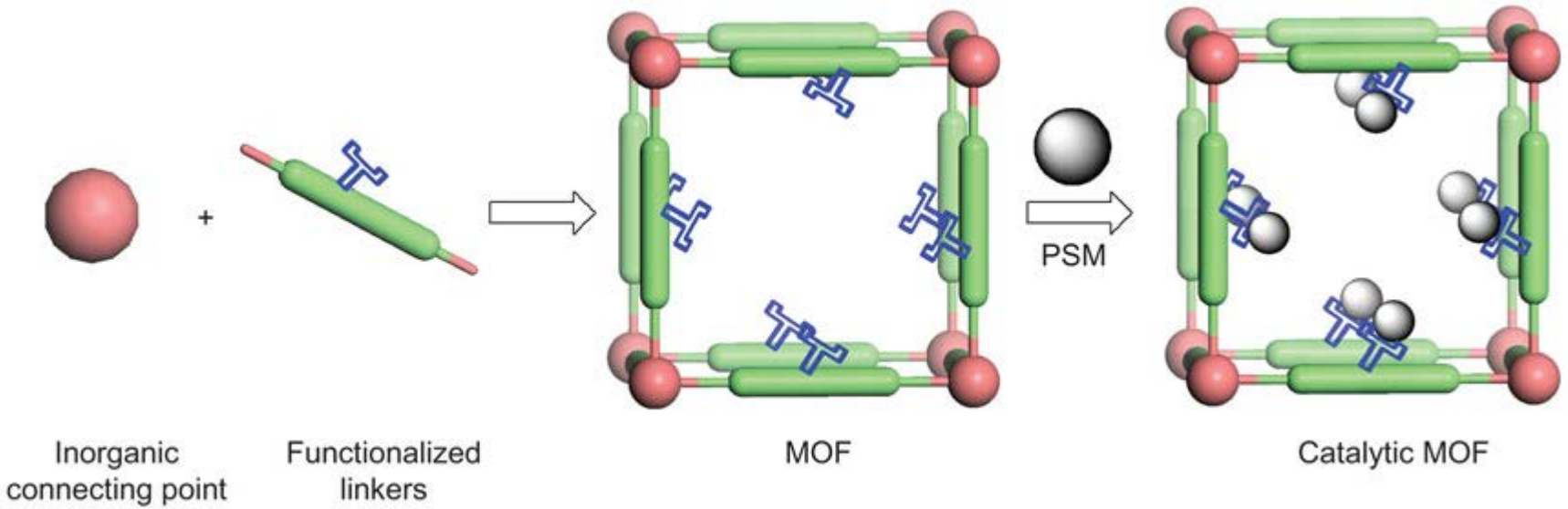


T. Čendak et al, *J.Phys.Chem.C* **2014**, *118*, 6140

Control over the functionalities



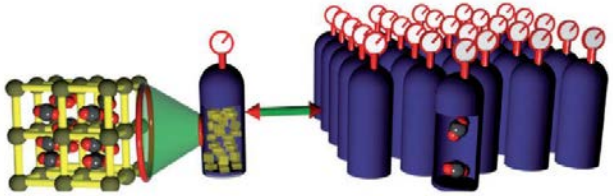
Ligand modification



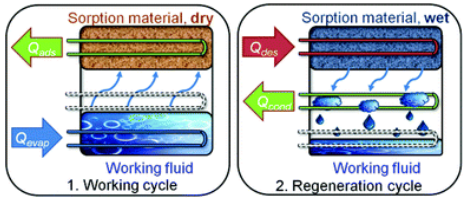
L. Ma et al, *Nature Chem.* **2010**, *2*, 838

Structural diversity and ‘rational design’ opens almost unlimited application opportunities:

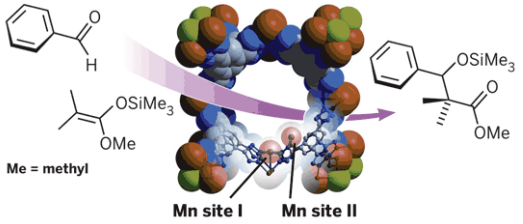
Gas storage and gas separation



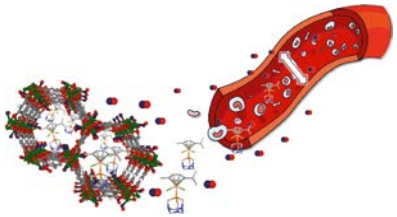
Energy storage



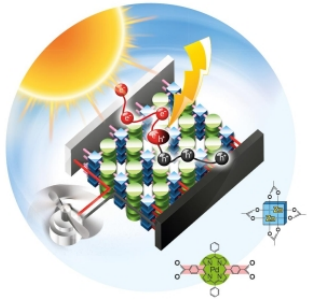
Heterogenous catalysis



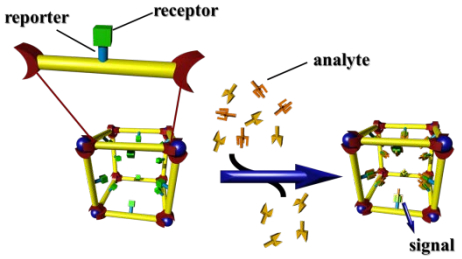
Drug storage and delivery



Photovoltaic



Sensors



...

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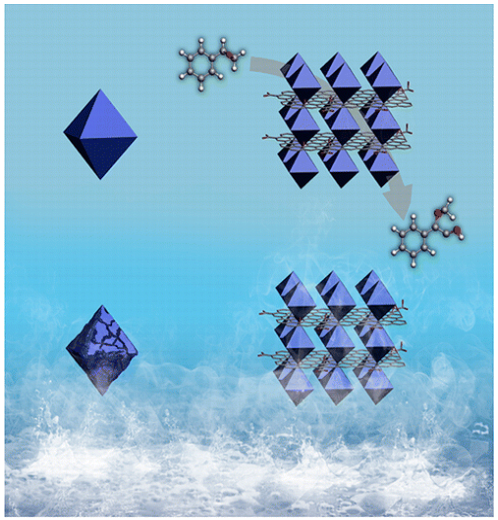
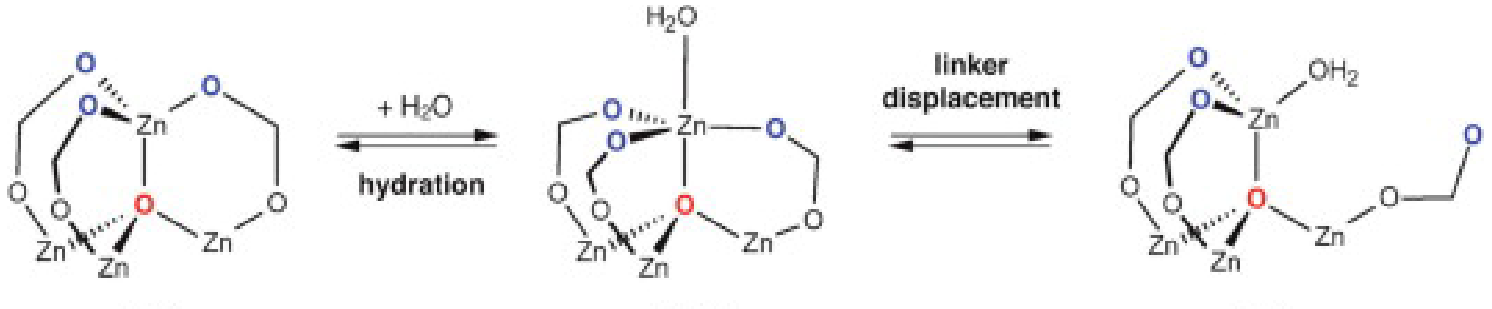
Field of research on MOFs

- Mechanisms of MOF formation
- Structure dynamics upon external stimuli
- MOFs for CO_2 capture and conversion
- Design of MOFs with enhanced hydrostability
- Shaping

MOF‘s applicability can be limited by their sensitivity to moisture



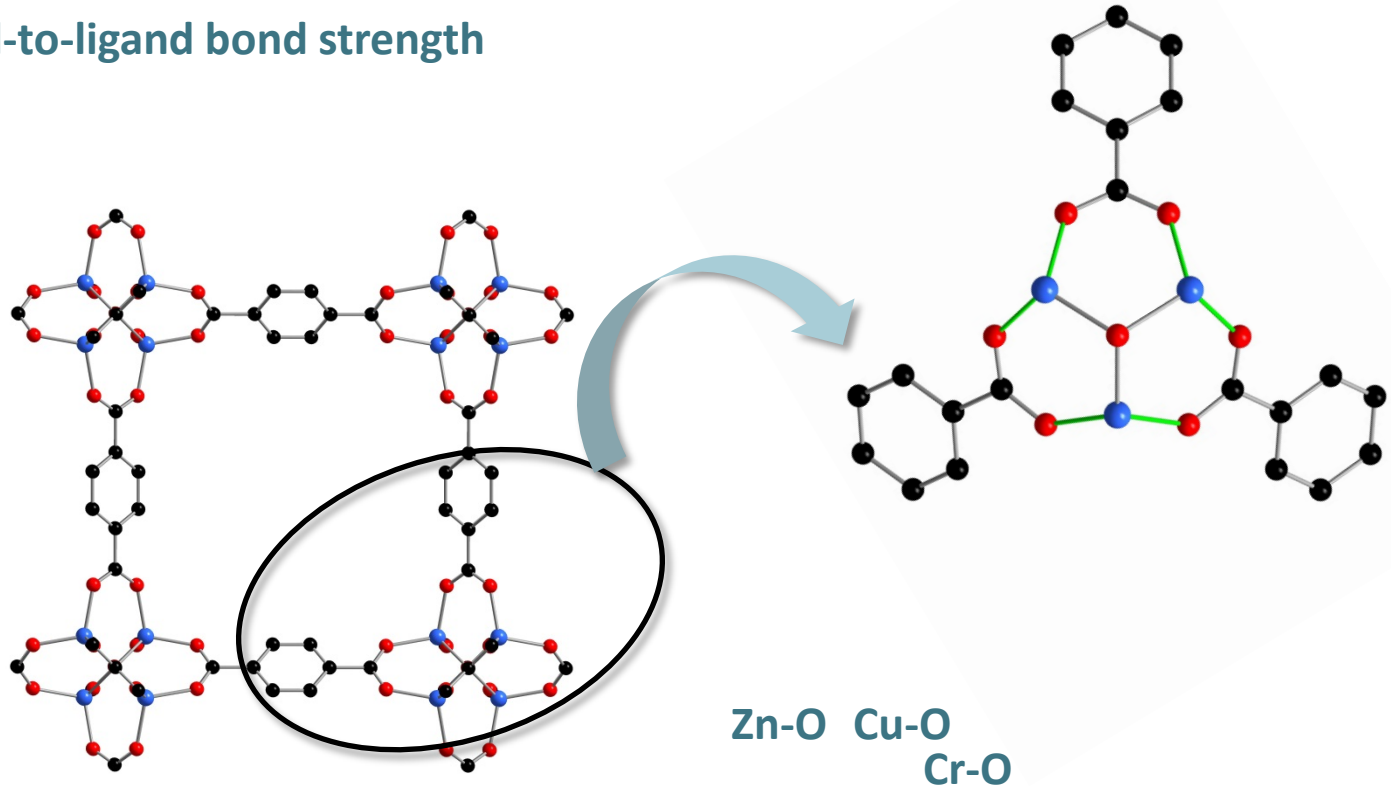


Factors governing hydrostability:

- **Metal-to-ligand bond strength**
- **Basicity of ligand**
- **Coordination number, oxidation number**
- **Metal building unit dimnesionality**

Factors governing hydrostability:

- Metal-to-ligand bond strength



Zn-O Cu-O Cr-O Fe-O

360 kJ/mol 470 kJ/mol

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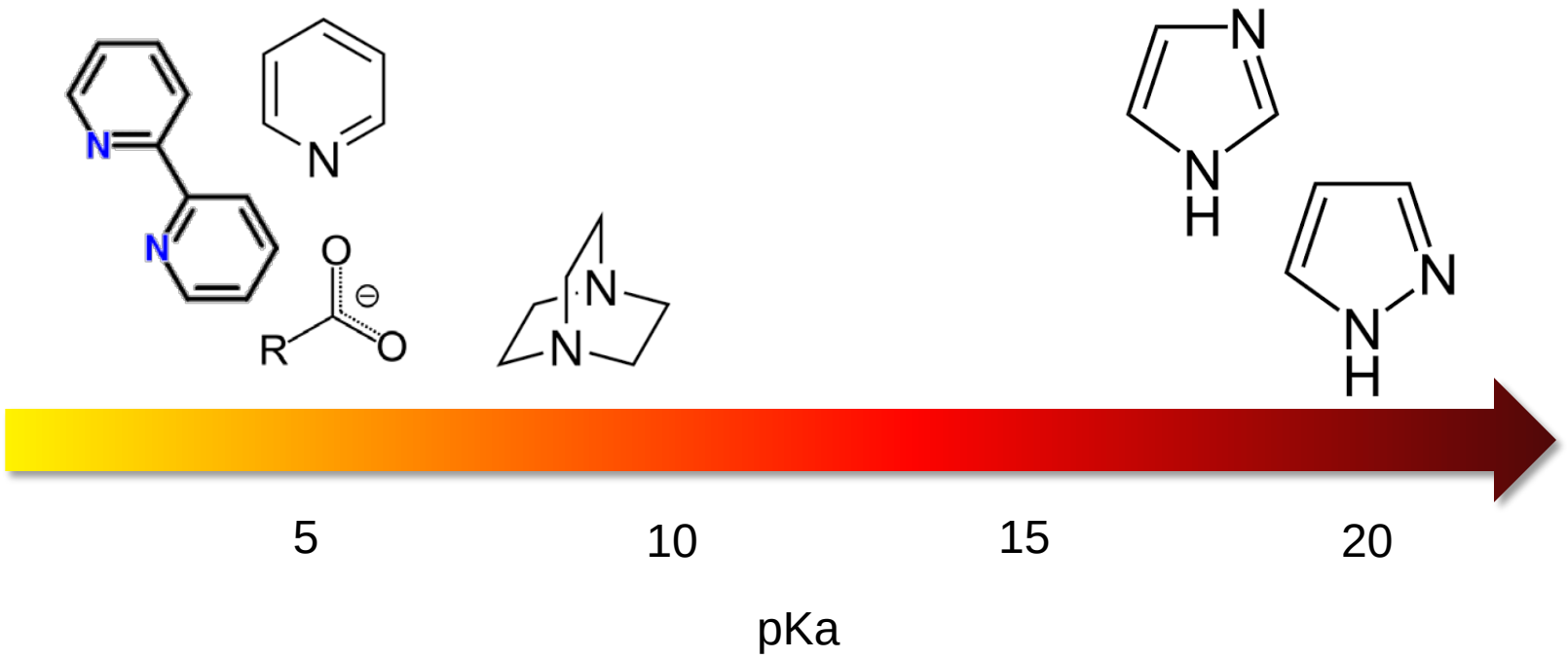
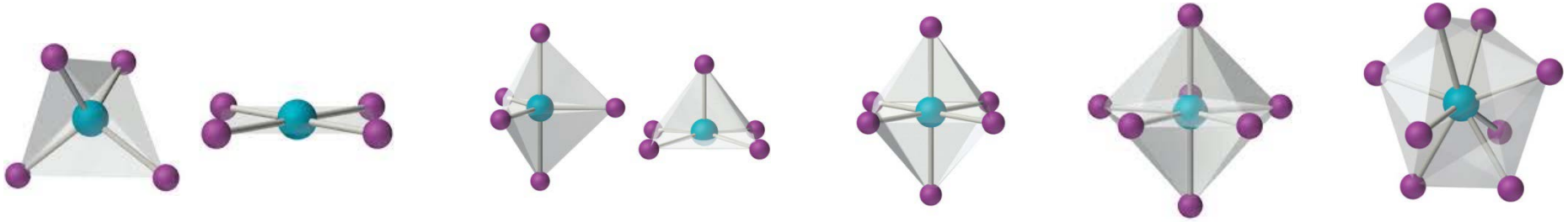
Factors governing hydrostability:

- **Basicity of ligand**



Factors governing hydrostability:

- Coordination number, oxidation number

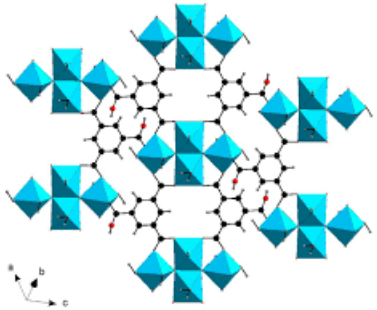


ML_4 ML_5 ML_6 ML_7 ML_8

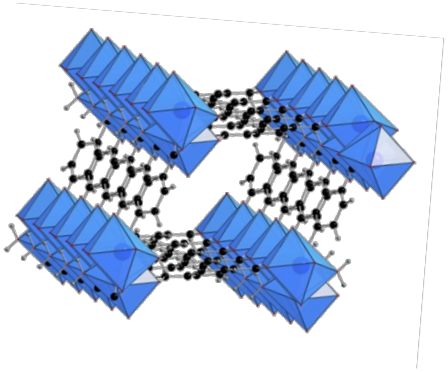
M^{2+} M^{3+} M^{4+}

Factors governing hydrostability:

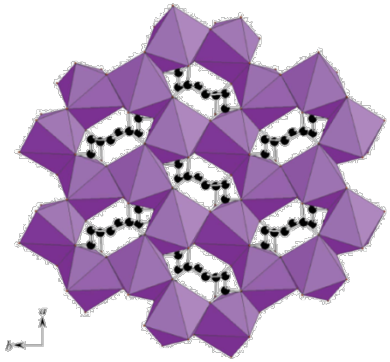
- **Metal building unit dimnesionality**



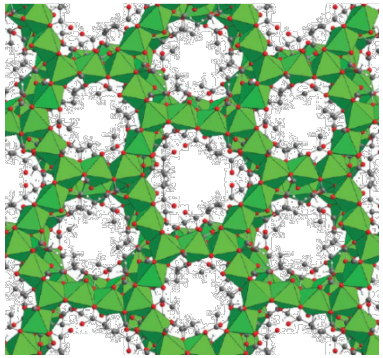
M. Mazaj et al, *Cryst. Growth Design* **2013**, *13*, 3825



M. Mazaj et al, *J.Phys.Chem.C* **2013**, *117*, 7552

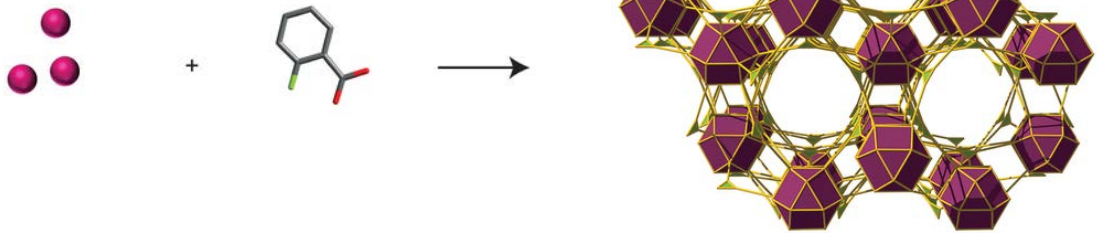


M. Mazaj et al, *Acta Cryst. C* **2012**, *68*, m4



T. Birsa Čelič et al, *ChemSusChem,* **2015**, *8*, 1703

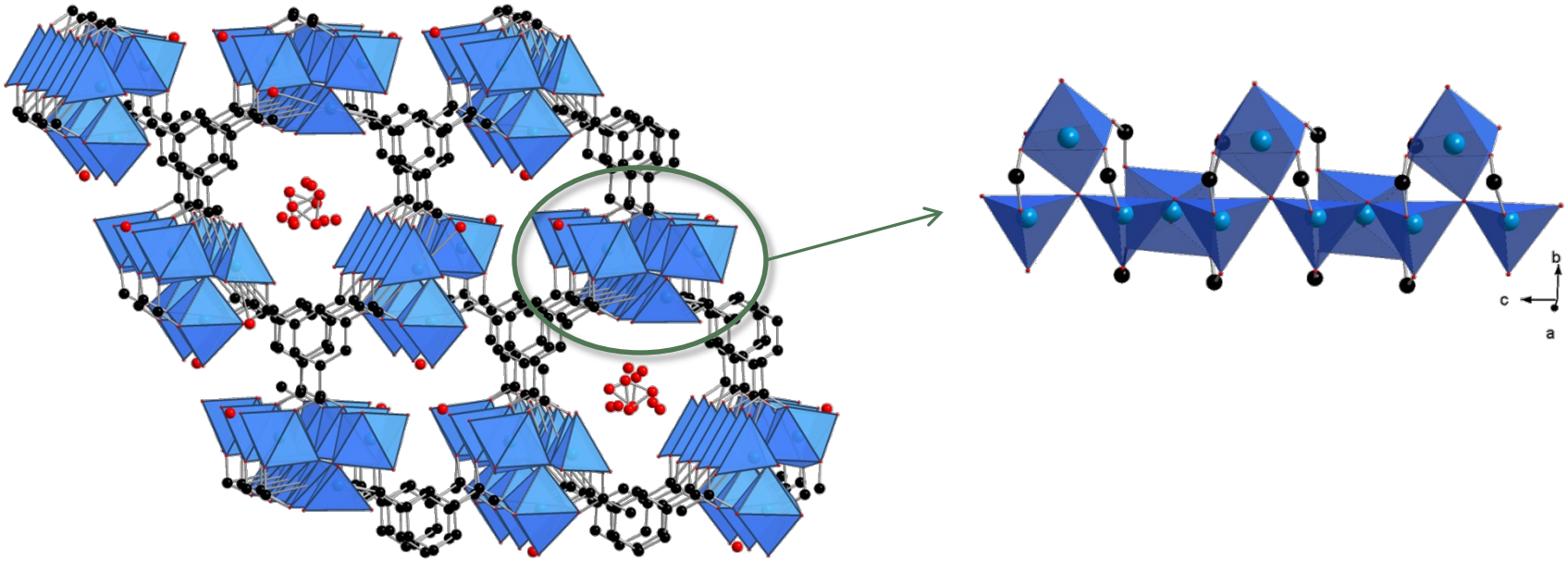
Can we synthesize hydrostable MOF via ‘rational design‘?



- lucky guess 
- numerous trials 

Zn-benzene-1,3,5-tricarboxylate

T. Birsa Čelič, M. Mazaj, N. Guillou, E. Elkaïm, M. El Roz, F. Thibault-Starzyk, G. Mali, M. Rangus, T. Čendak, V. Kaučič, N. Zabukovec Logar, *J. Phys. Chem. C,* **2013**, *117*, 14608.



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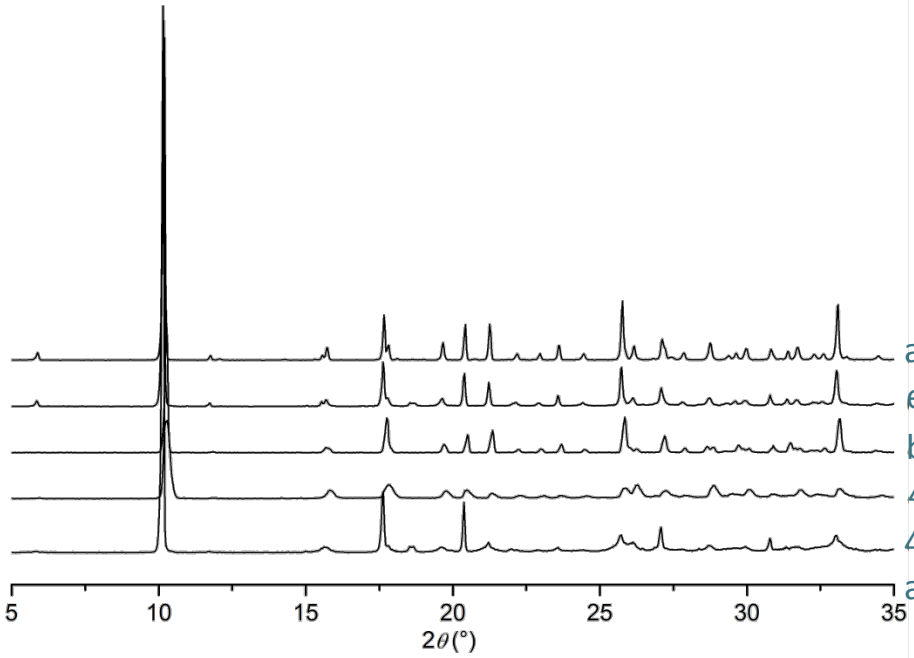
Zn-benzene-1,3,5-tricarboxylate



as-synthesized
exposure to 90% RH
boiling in water
40 cylces water adsorption/desorption
40 cylces water adsorption/desorption and additional exposure to 90% RH

Zn-benzene-1,3,5-tricarboxylate

Factors governing hydrostability:

- **Metal-to-ligand bond strength:** Zn-O < Cu-O < Cr-O < Fe-O
- **Basicity of ligand:** carboxylates << imidazoles
- **Coordination number, oxidation number :** $ML_3 < ML_4 < ML_5 < ML_6 < ML_7 < ML_8$

  $M^{2+} < M^{3+} < M^{4+}$

- **Metal building unit dimensionality :**

  0-D clusters < chains < lamellar structures < 3-d frameworks

This MOF structure should NOT be resistant to water at all!

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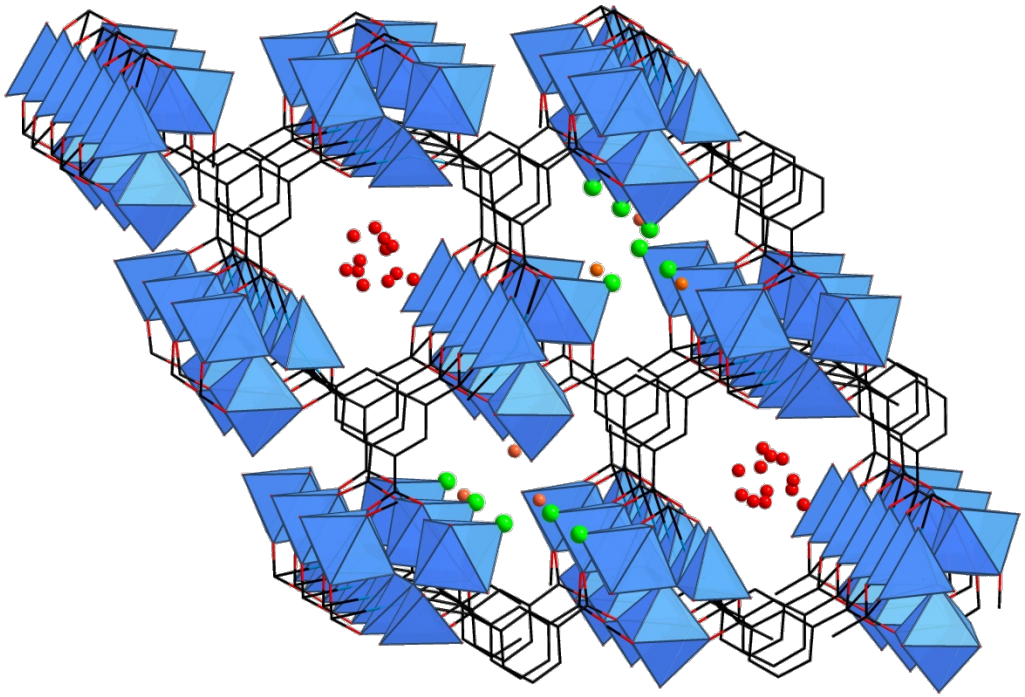
Zn-benzene-1,3,5-tricarboxylate



adsorbed water in clusters

individually adsorbed water molecules

coordinated water molecules

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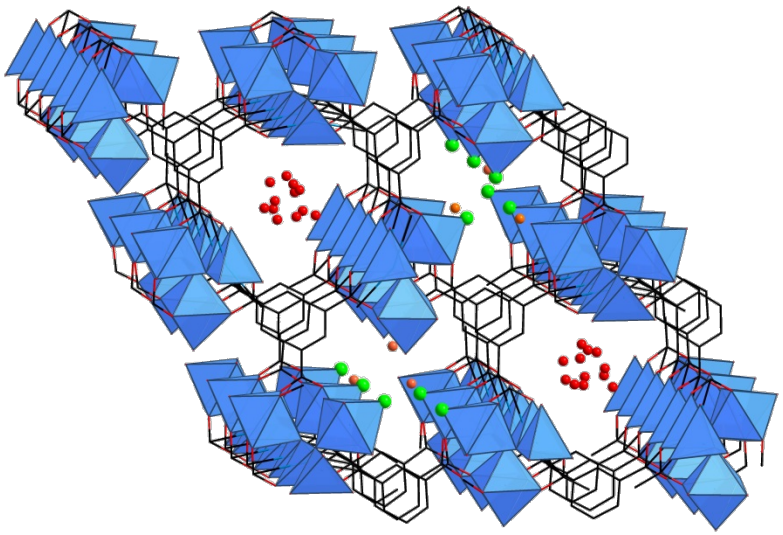
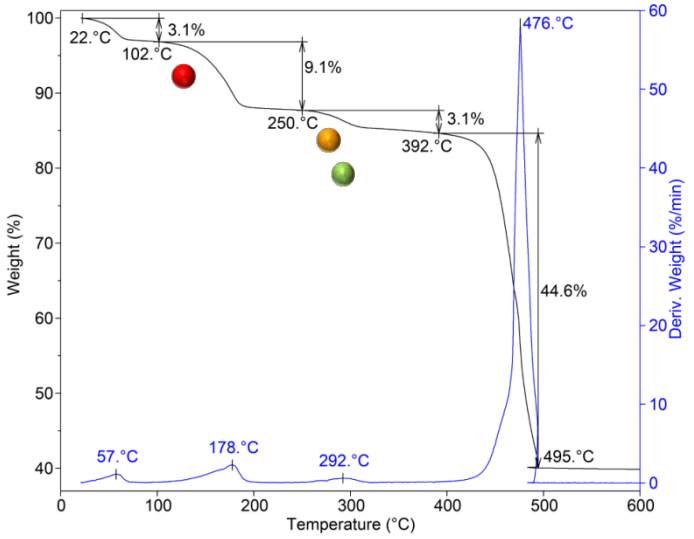
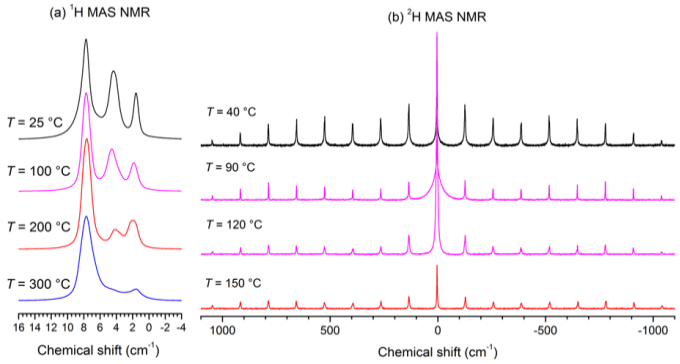
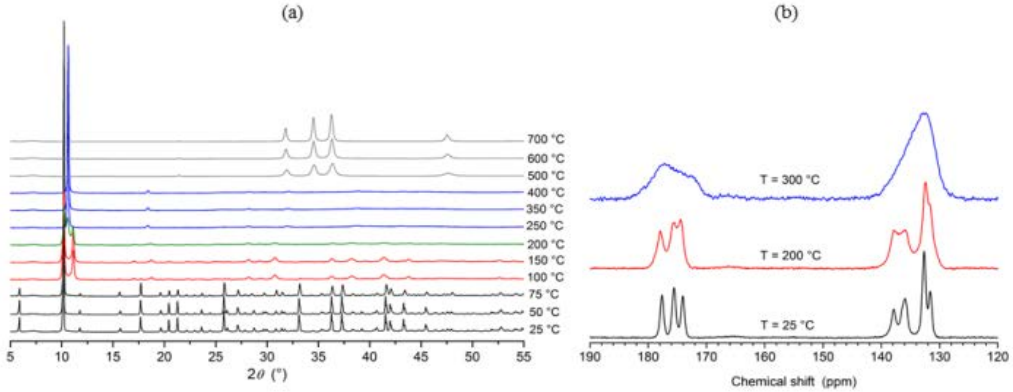
Zn-benzene-1,3,5-tricarboxylate









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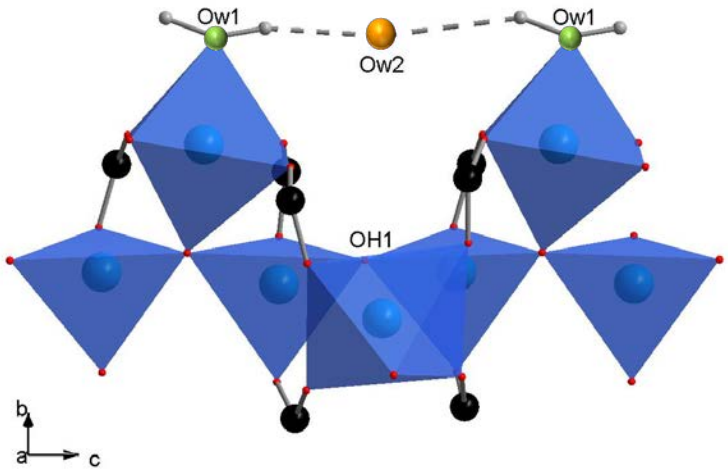
Zn-benzene-1,3,5-tricarboxylate



Ow2 stabilizes the whole framework through strong H-bonds

Ow2 is responsible for hydrostability of Zn-BTC

It is hard to predict hydrostability of MOF structures in advance.

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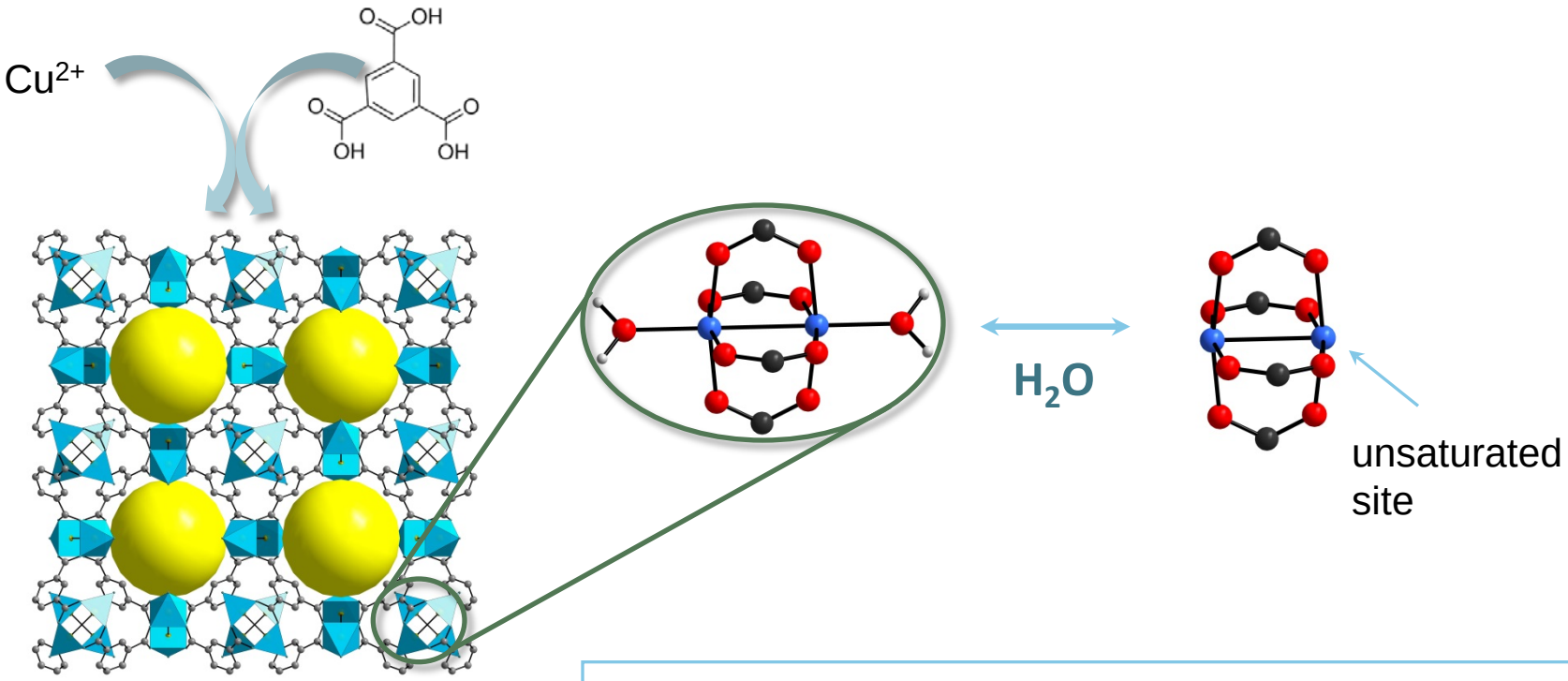
$Cu_3(BTC)_2$- HKUST-1



pore size – 9.8 Å

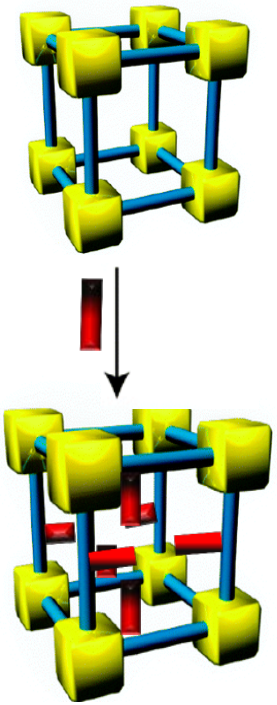
S_{BET} ~ 1500 m^2/g

Drawback

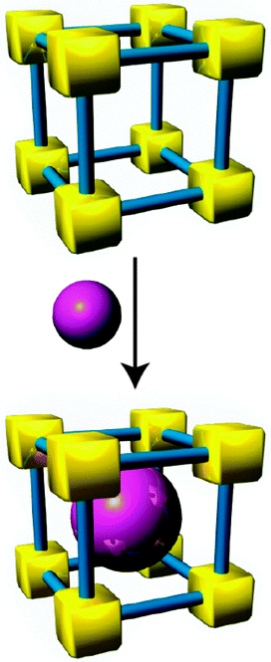
Structure is unstable under humid environment

Approaches to increase stability of MOFs under humid conditions

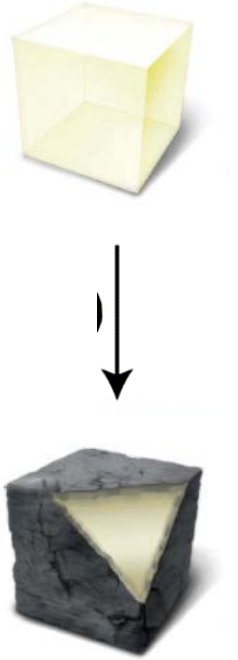
Ligand functionalization



Metal species encapsulation



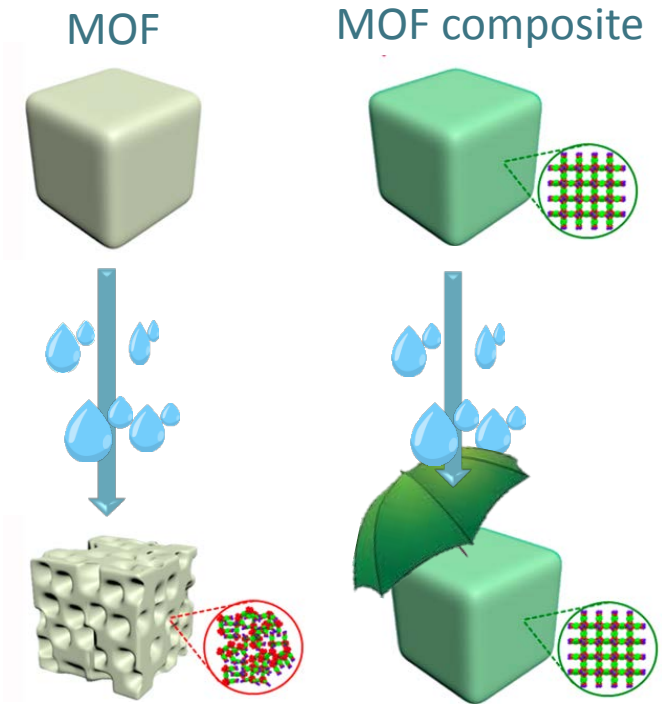
Carbon coating



In all cases we are dealing with partial pore blocking!

Enhanced hydrostability of MOFs

Concept - incorporation (protection) of MOFs within the hydrophobic matrix

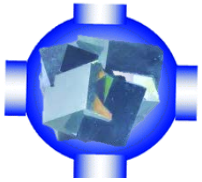


Hydrophobic matrices:
- mesoporous silica
- macroporous polymer

(1) Incorporation of MOF within silica matrix

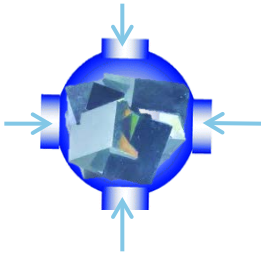
Choice of silica matrix

Sufficiently large pores



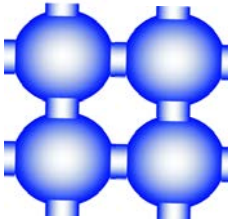
enabling confined MOF growth

3-D pore system



accessibility to MOF is unobstructed

Ordered pores

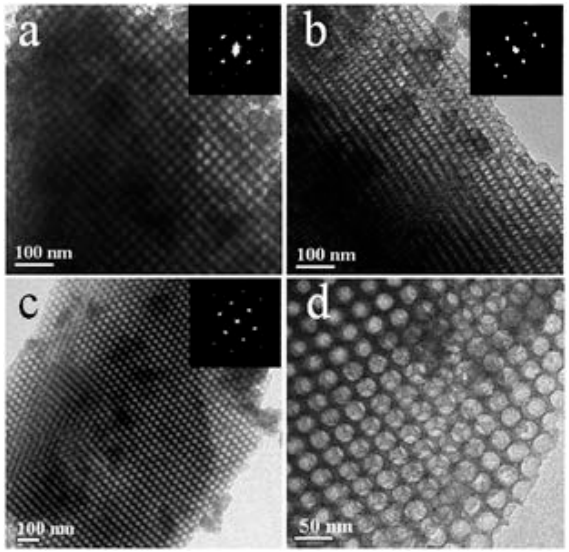


better control over the confined MOF growth

UL-FDU-12

Pore diameter – 30 nm
Pore volume – 1 cm^3/g

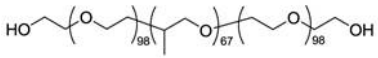
Cubic spherical-shaped pore system



(1) HKUST-1/FDU-12

Preparation

Pluronic F127

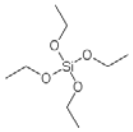


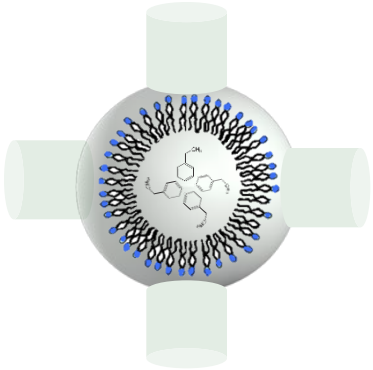
HCl (2M)

KCl

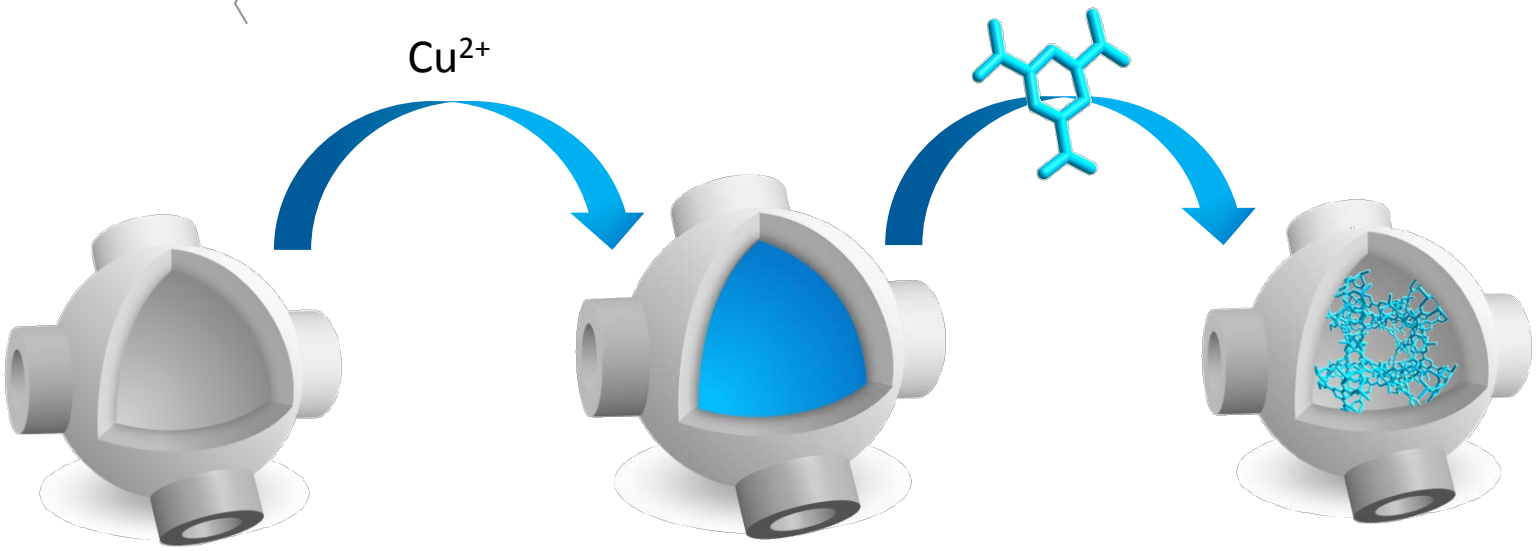
ethylbenzene

TEOS





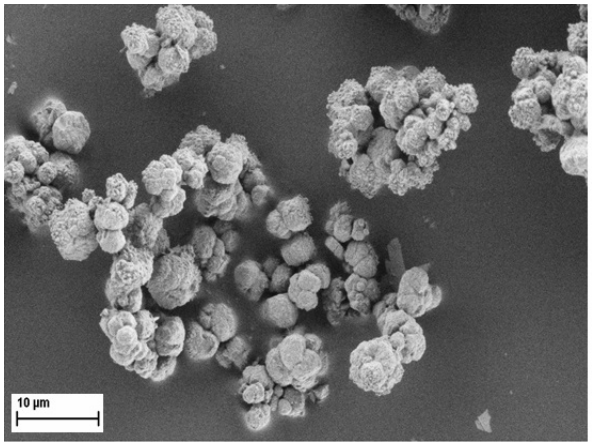
Cu^{2+}



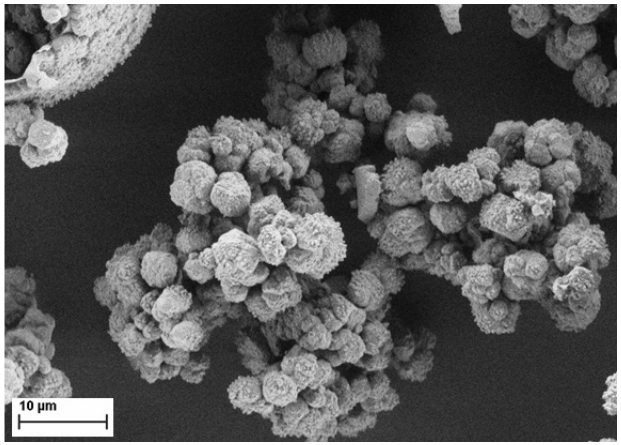
M. Mazaj, T. Čendak, G. Buscarino, M. Todaro, N. Zabukovec Logar, submitted to *Chem. Mater*.

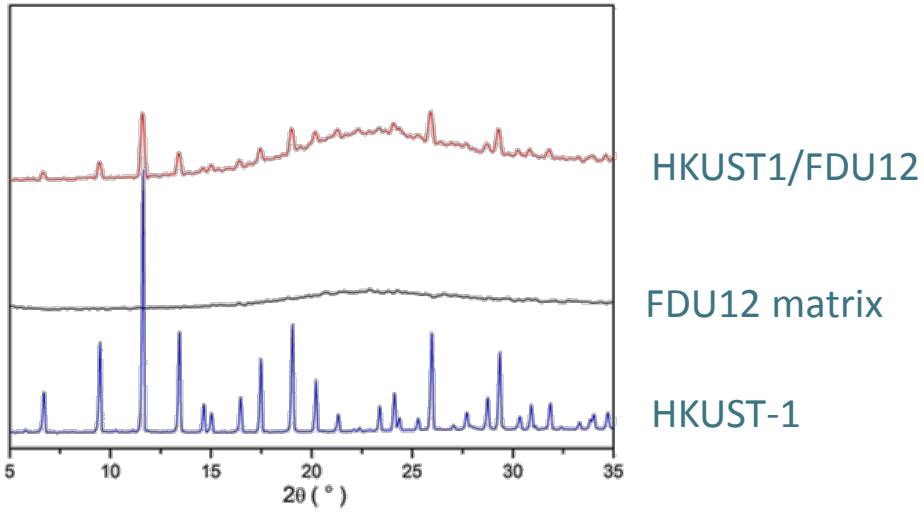
(1) HKUST-1/FDU-12

FDU-12 matrix



HKUST-1/FDU-12





HKUST1/FDU12

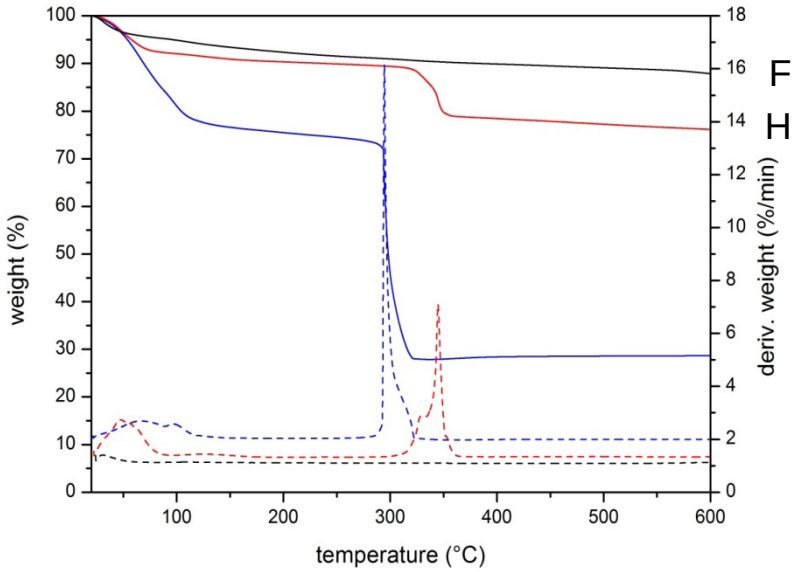
FDU12 matrix

HKUST-1

HKUST-1/FDU-12

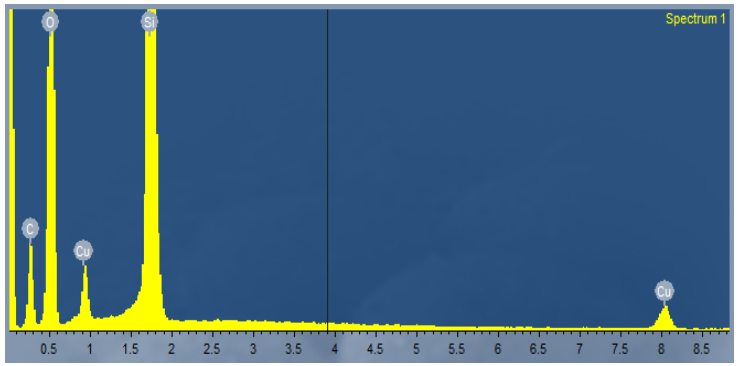
MOF content

TG



EDS

HKUST-1/FDU-12 contains 5.5 wt.% of Cu



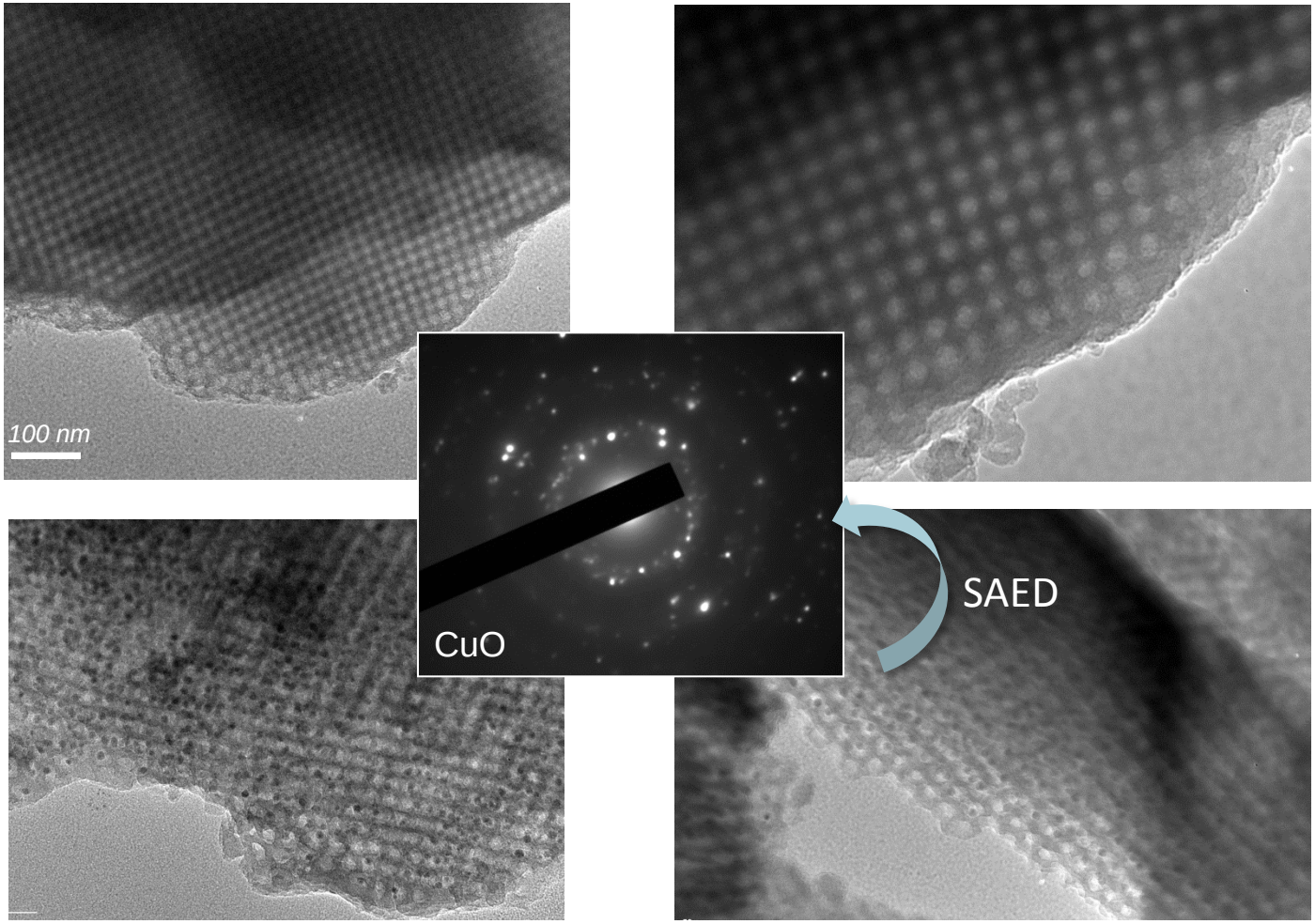
MOF content deduced from

TG – 21 wt.%
EDS – 19 wt.%

cca. 50% of mesopores are occupied with MOF material

(1) HKUST-1/FDU-12

Is HKUST-1 really incorporated within FDU-12 matrix?



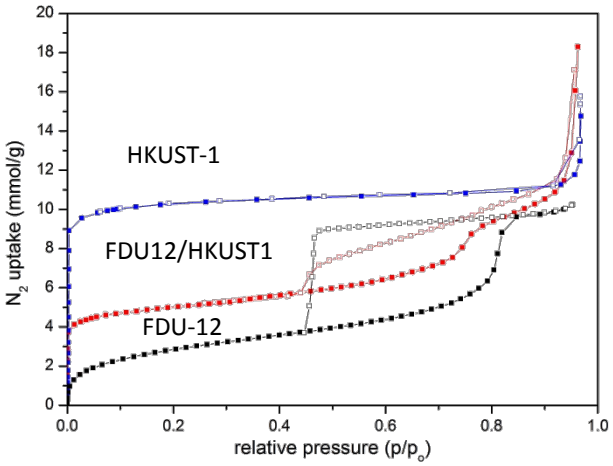
FDU-12

HKUST-1/FDU-12

(1) HKUST-1/FDU-12

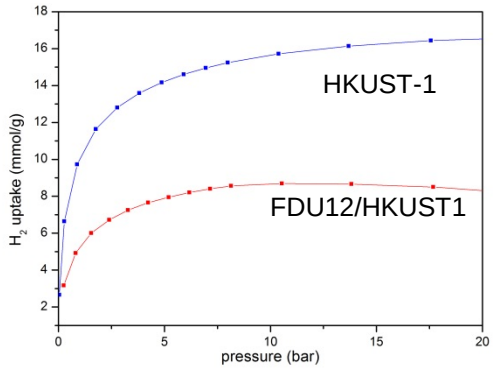
Sorption properties

N_2 – 77K

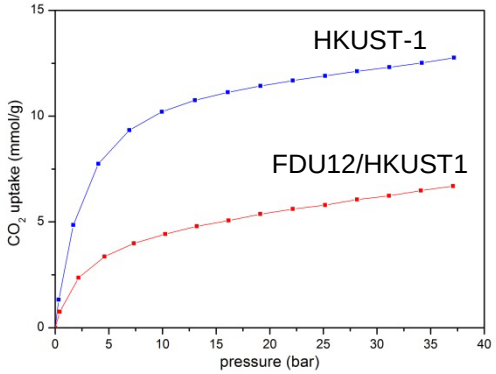


material	S_{BET} (m^2/g)	V_{mes} (cm^3/g)	V_{mic} (cm^3/g)	d_{mes} (nm)	d_{mic} (nm)
FDU12-NH_2	72	0.68	0.05	19.2	-
HKUST1	1211	-	0.49	-	2.5
FDU12-HKUST1	374	0.54	0.38	19.2	2.3

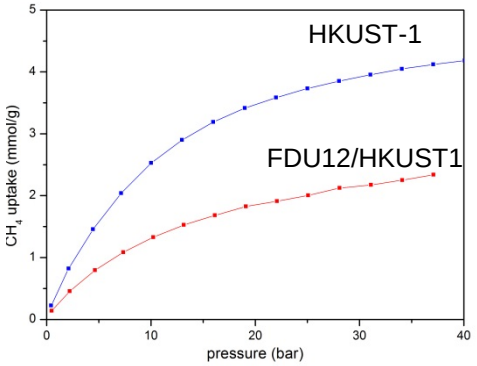
H_2 – 77K



CO_2 – 298K



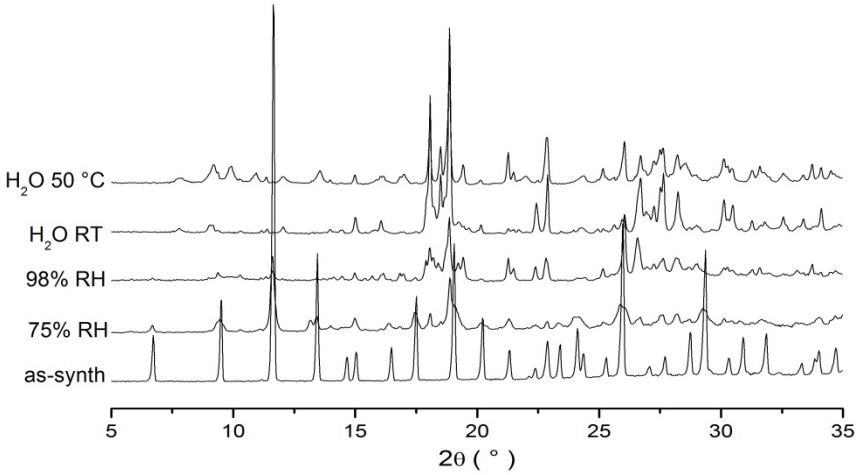
CH_4 – 298K



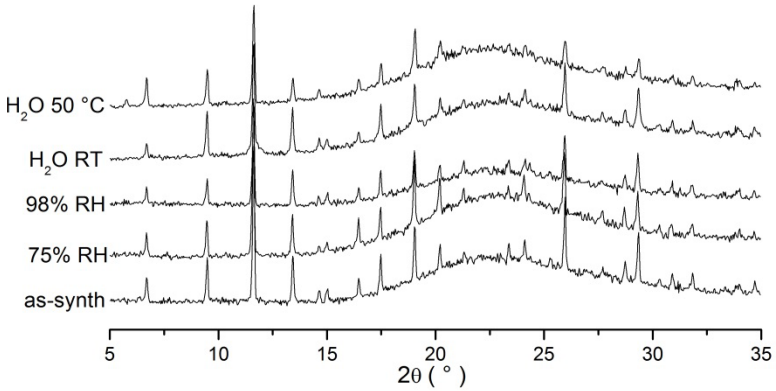
(1) HKUST-1/FDU-12

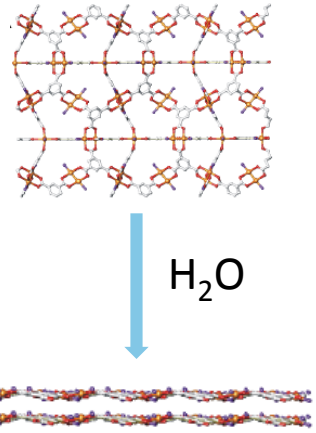
Stability in water

HKUST-1

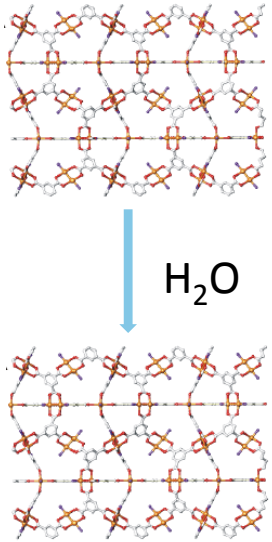


HKUST-1/FDU-12



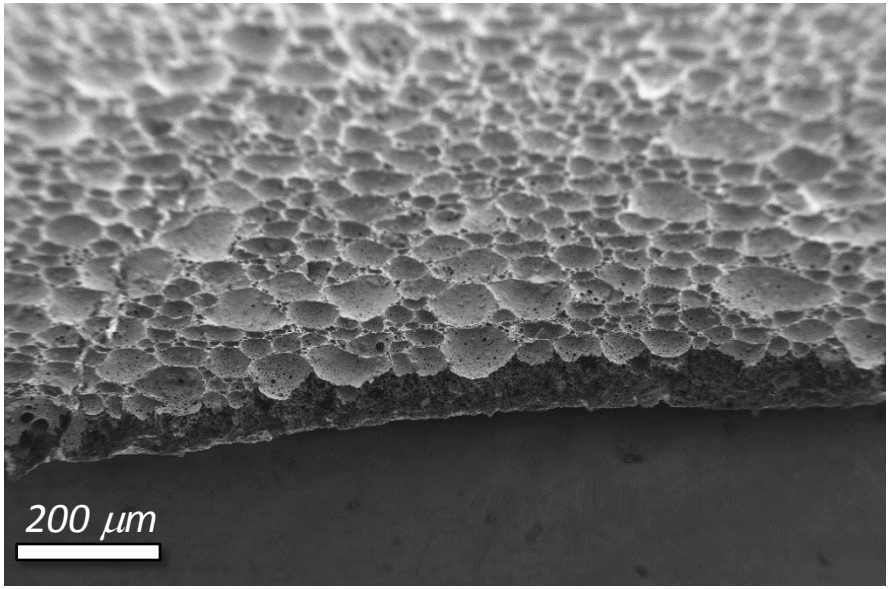


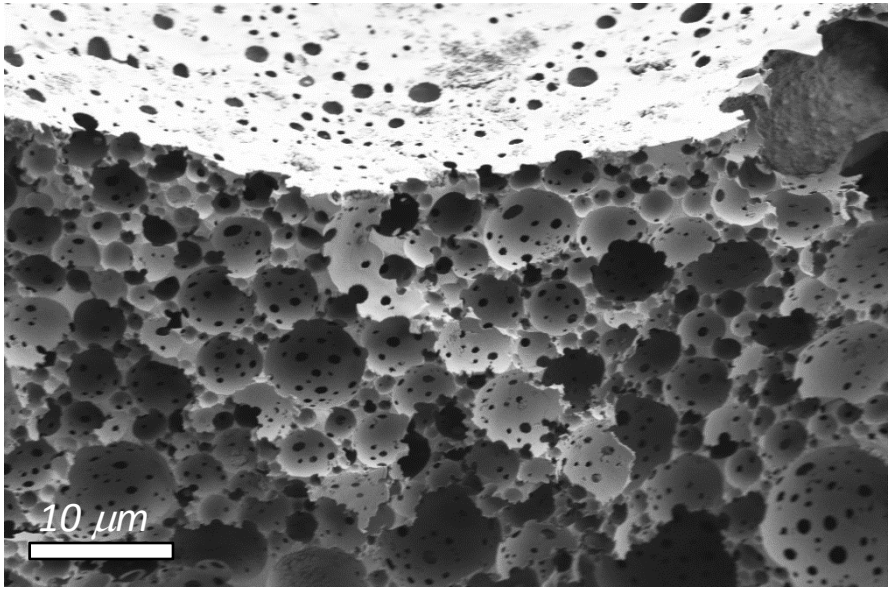
$Cu_2OH(BTC)(H_2O)]\cdot 2H_2O$



$Cu_3(BTC)_2$

(2) MOF/polyHIPE composite membrane





(2) MIL-100/polyHIPE

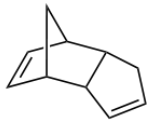
Preparation

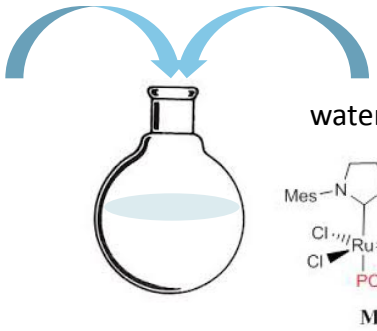
Pluronic L121

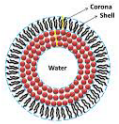
dicyclopentadiene

toluene

MIL-100(Fe)

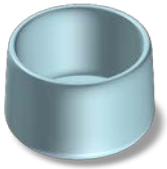






pickering emulsion

casting into mould



polymerization
80 C, 2h

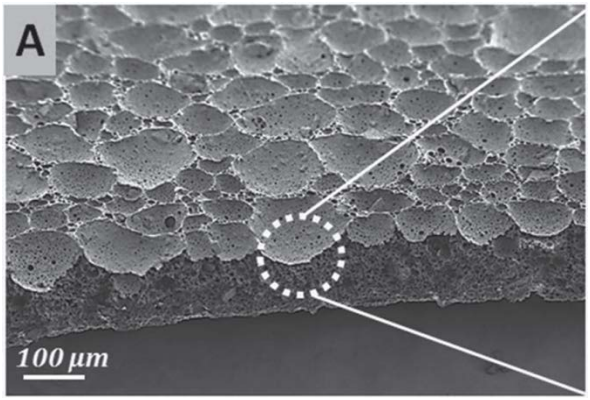
S. Kovačič, M. Mazaj, M. Ješelnik, D. Pahovnik, E. Žagar, C. Slugovc, N. Zabukovec Logar, *Macromol. Rapid Commun.* **2015**, *36*, 1605.

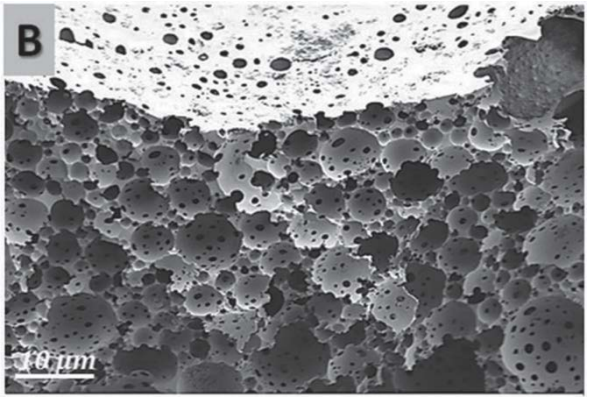
(2) MIL-100/polyHIPE

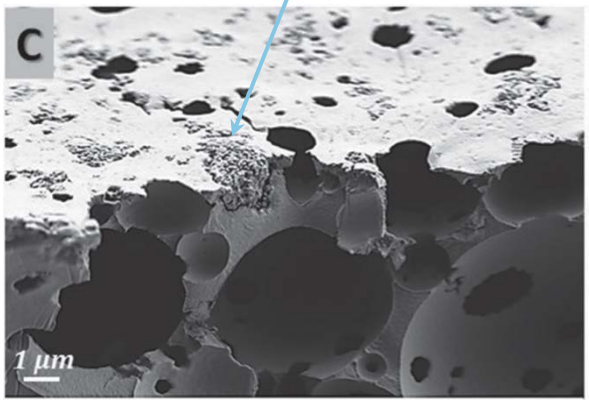
polyHIPE membrane

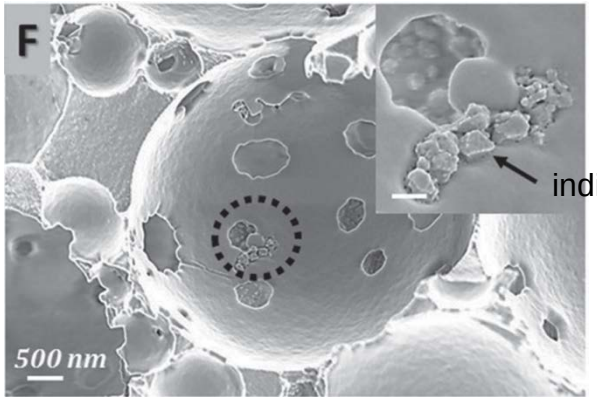
macropores with windows

aggregates of nanoparticles





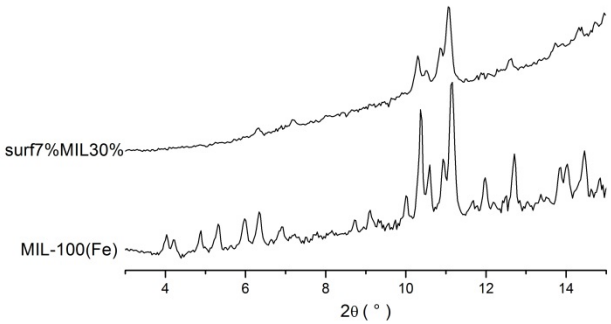




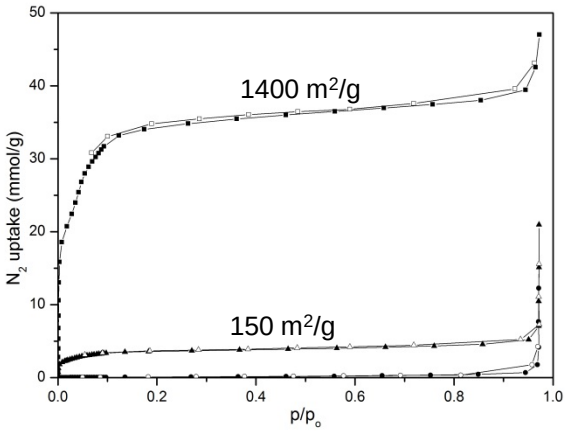
individual crystals

(2) MIL-100/polyHIPE

XRD



N_2 sorption



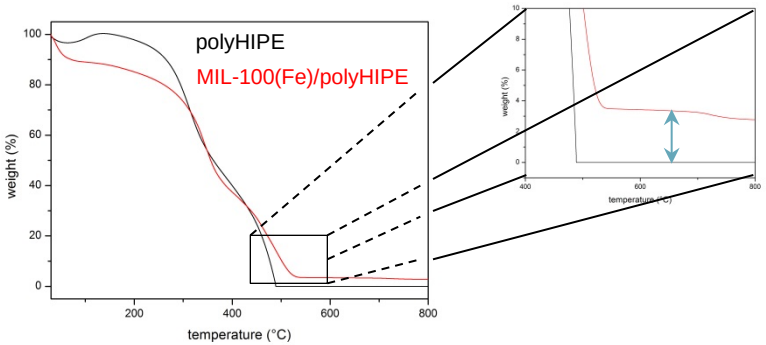
MIL-100(Fe)

MIL-100(Fe)/polyHIPE

polyHIPE

cca. 85% of active MIL-100(Fe) is accessible

TG

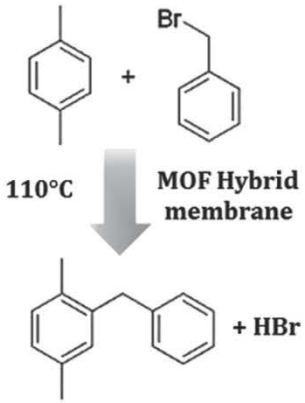


Δwt ~ 3.4 %

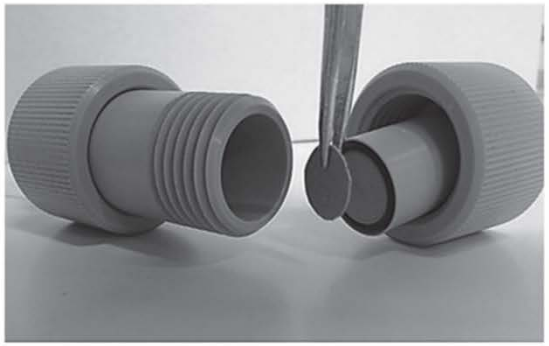
Amount of MIL100(Fe) in the polymer matrix is cca. **14 wt%.**

(2) MIL-100/polyHIPE

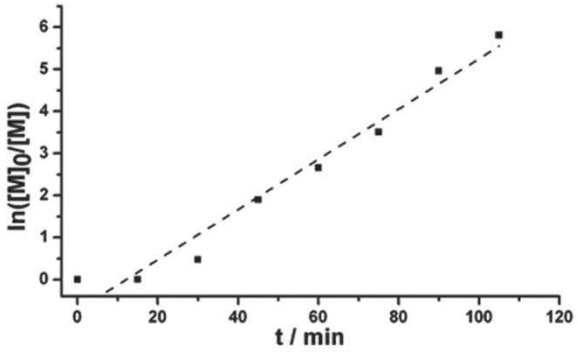
Potential catalyst



Friedel-Krafts benzylbromide coupling



flow-through reactor mode
110 °C, residence time 2s,
flow rate 0.01 ml/min

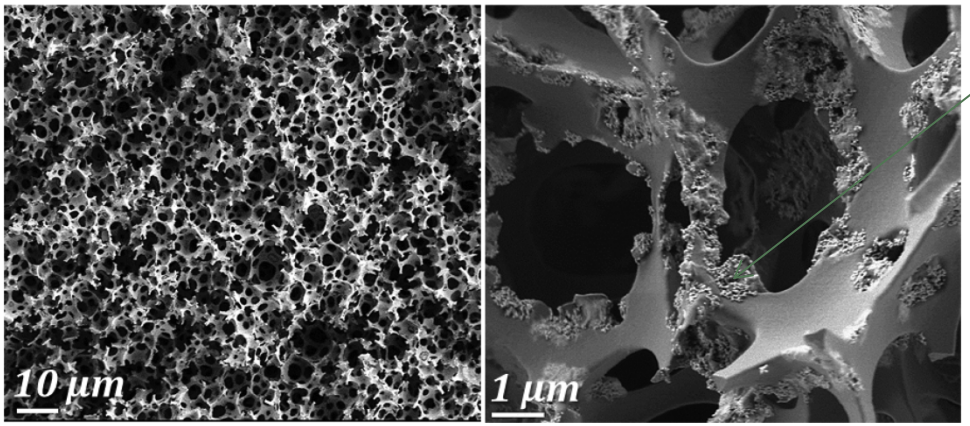


1st order reaction kinetics

MIL-100(Fe) – batch reactor – **99% conversion**
MIL-100(Fe)/polyHIPE – flow-through reactor – **7% conversion**

50 % of acid sites are accessible

- **MOF was used to stabilize polyHIPE**
- **Can we stabilize MOF using polyHIPE?**
- **Maximium 14 wt% of MOF loading was achieved. How can we increase loading?**

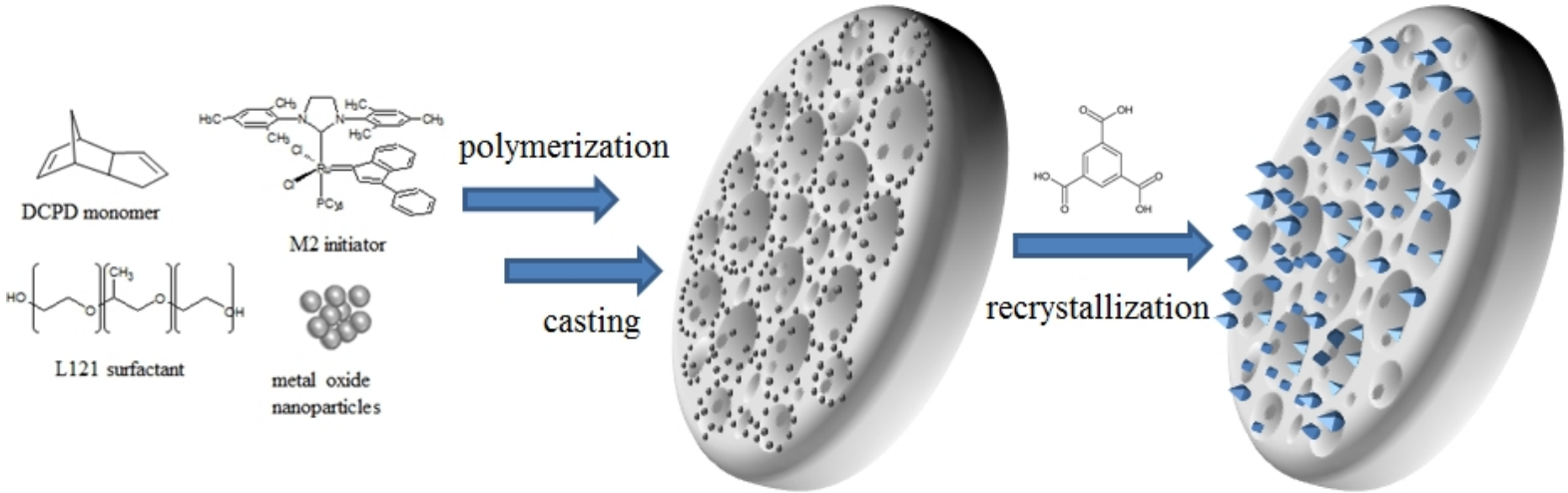


ZnO@polyHIPE
30 wt% of ZnO on polyHIPE matrix

metal-oxide@polyHIPE composite acting used as precursor for MOF@polyHIPE?

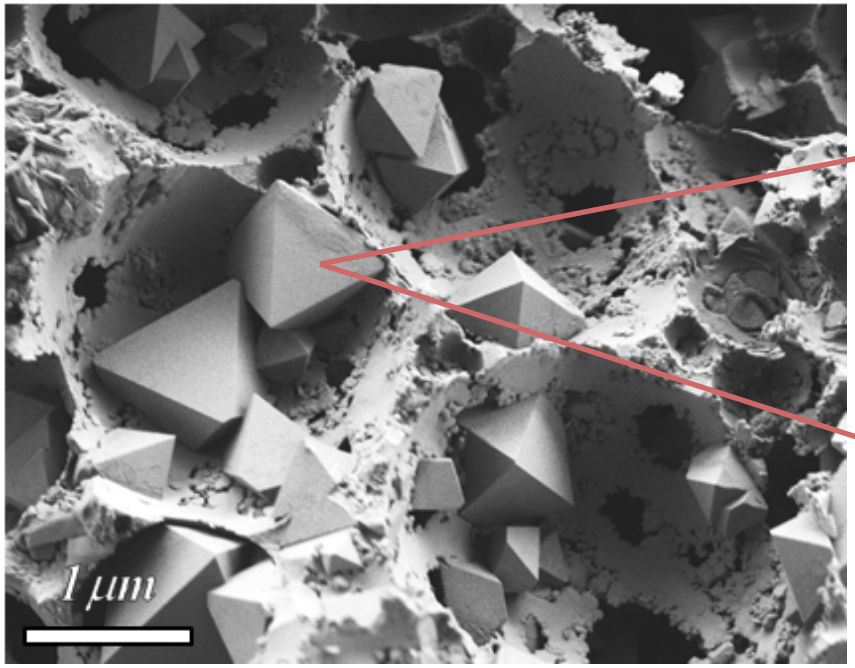
S. Kovačič et al. *ACS Appl. Mater. Intefaces* **2014**, *6*, 19075.

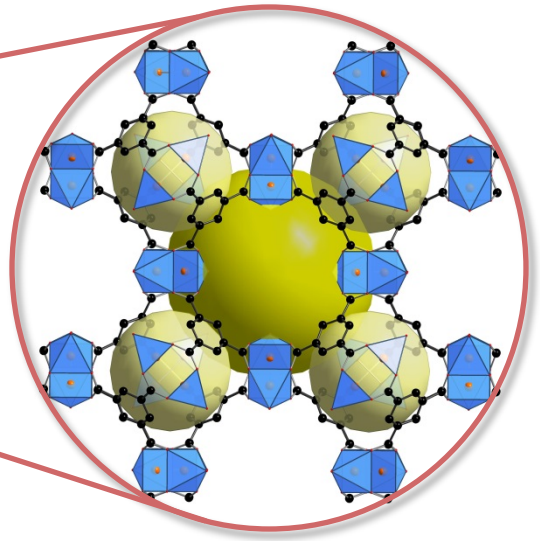
Recrystallization of CuO@polyHIPE into HKUST1@polyHIPE



M. Mazaj, N. Zabukovec Logar, E. Žagar, S. Kovačič, *J. Mater. Chem. A,* **2017**, *In Press*

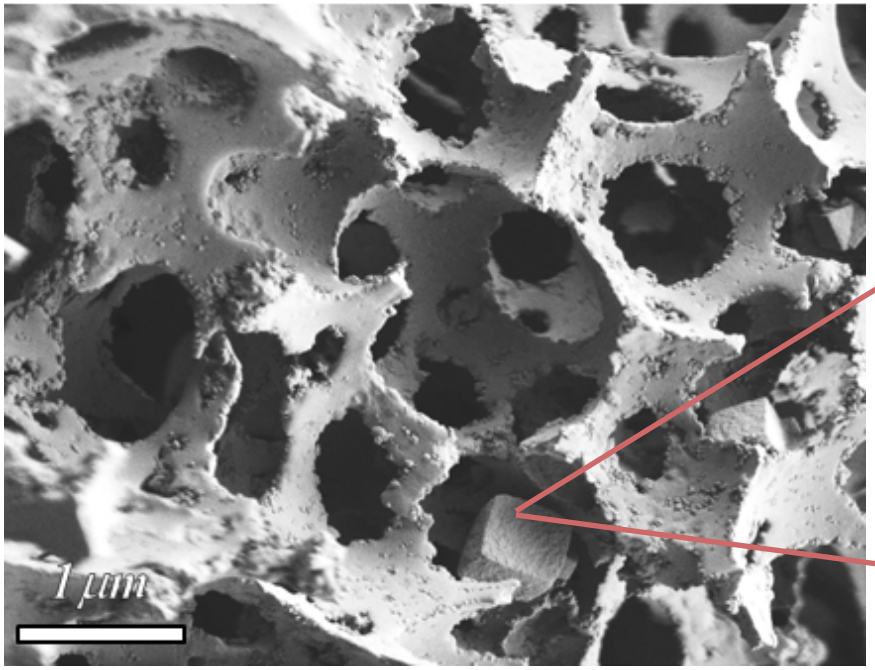
Recrystallization of CuO@polyHIPE into HKUST1@polyHIPE

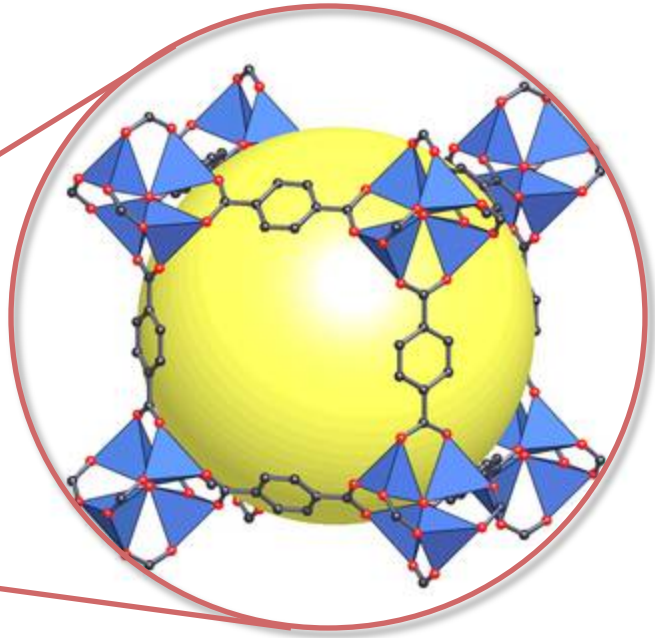




M. Mazaj, N. Zabukovec Logar, E. Žagar, S. Kovačič, *J. Mater. Chem. A,* **2017**, *In Press*

Recrystallization of ZnO@polyHIPE into MOF-5@polyHIPE





M. Mazaj, N. Zabukovec Logar, E. Žagar, S. Kovačič, *J. Mater. Chem. A,* **2017***, In Press*

- HKUST1@polyHIPE contains 75 wt% of HKUST-1

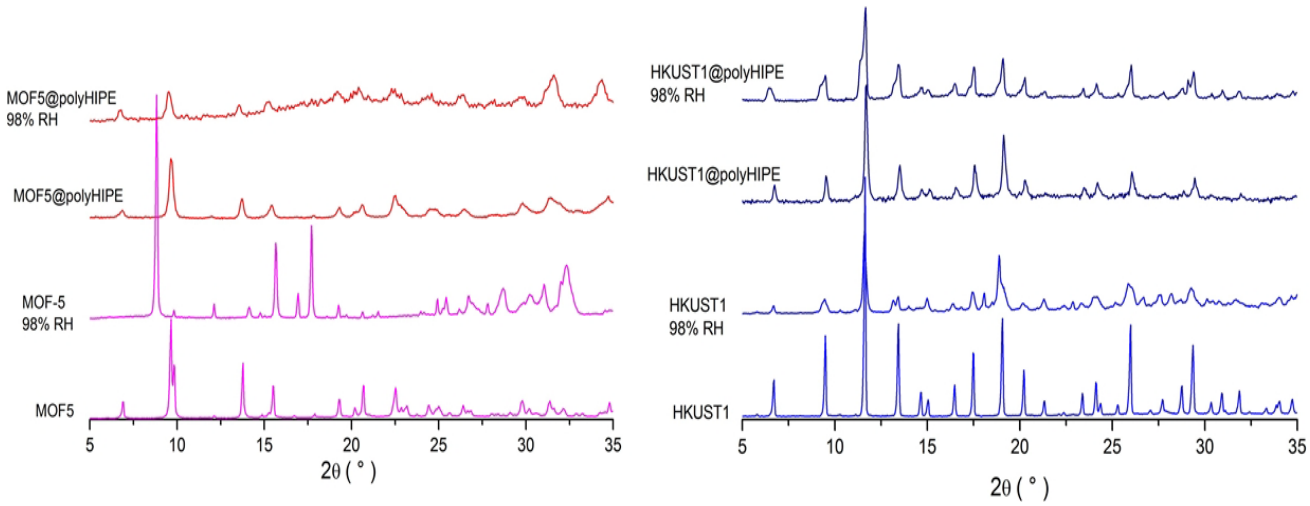
- MOF5@polyHIPE contains 55 wt% of MOF-5

Material	wt.%	MOF-S_{BET} (m^2/g)	S_{BET}-m (m^2/g)	S_{BET}-c (m^2/g)	η
MOF5/polyHIPE	55.1	2501	1298	1401	0.93
HKUST1/polyHIPE	75.4	1211	794	921	0.86

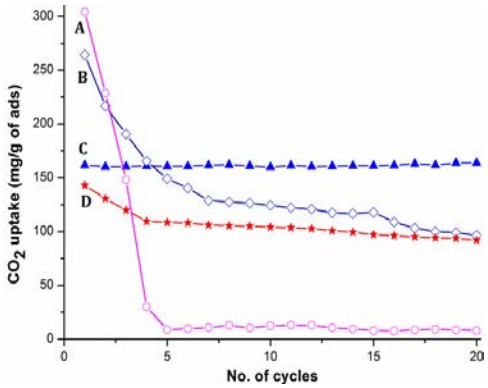
Embedded MOFs are highly accessible!

M. Mazaj, N. Zabukovec Logar, E. Žagar, S. Kovačič, *J. Mater. Chem. A,* **2017**, *In Press*

What about hydrostability?



CO_2 cycling under humid conditions:



HKUST1@polyHIPE

HKUST-1
MOF5@polyHIPE

MOF-5

Cycle experiment:

CO_2 adsorption (25 °C, 1 bar)
Exposure to 50 %RH
Degassing

M. Mazaj, N. Zabukovec Logar, E. Žagar, S. Kovačič, *J. Mater. Chem. A*, **2017**, *In Press*

Conclusions

Hydrostability of MOFs can be significantly enahnced by immobilization in different hydrophobic porous matrices without losing accessibility for gas molecules.

MOF/polyHIPEs also enable unlimited shaping possibilities.

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Co-workers from Department for Inorganic Chemistry and Technology

Department for Polymer Chemistry and Technology

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Gianpiero Buscarino
Michaela Todaro

Thank you for your attention!