

WIR SCHAFFEN WISSEN – HEUTE FÜR MORGEN



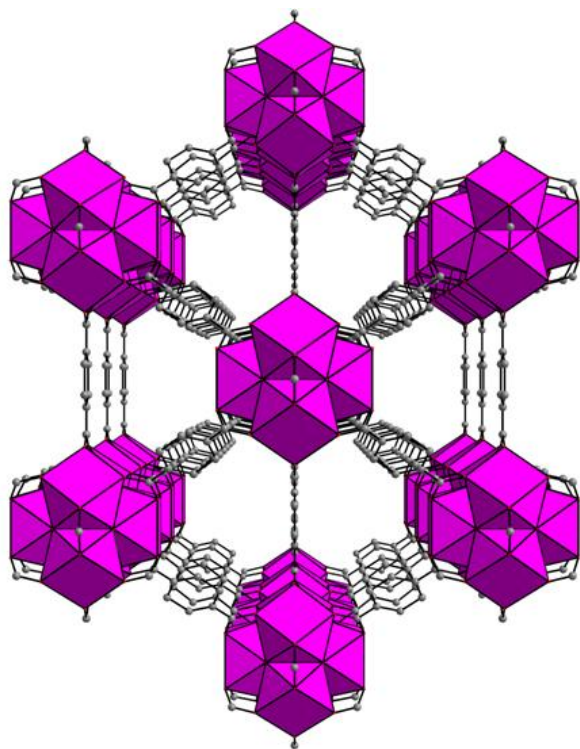
Dr. Marco Taddei ([marco.taddei@psi.ch](mailto:marco.taddei@psi.ch)) :: Paul Scherrer Institut

# UiO-66: a Case Study Metal-Organic Framework

Catalysis Class (529-0502-00L) – 25-27/05/2016

- Why UiO-66?
- Crystal structure
- Properties
- Synthesis and functionalization
- Defects
- Applications in catalysis

# Why UiO-66?



- Cheap (based on  $Zr^{4+}$  and terephthalic acid)
- High porosity
- High thermal stability
- High stability to hydrolysis
- Easy to synthesize
- Extremely versatile

The asymmetric unit is the smallest group of crystallographically independent atoms needed to build up the overall crystal structure.

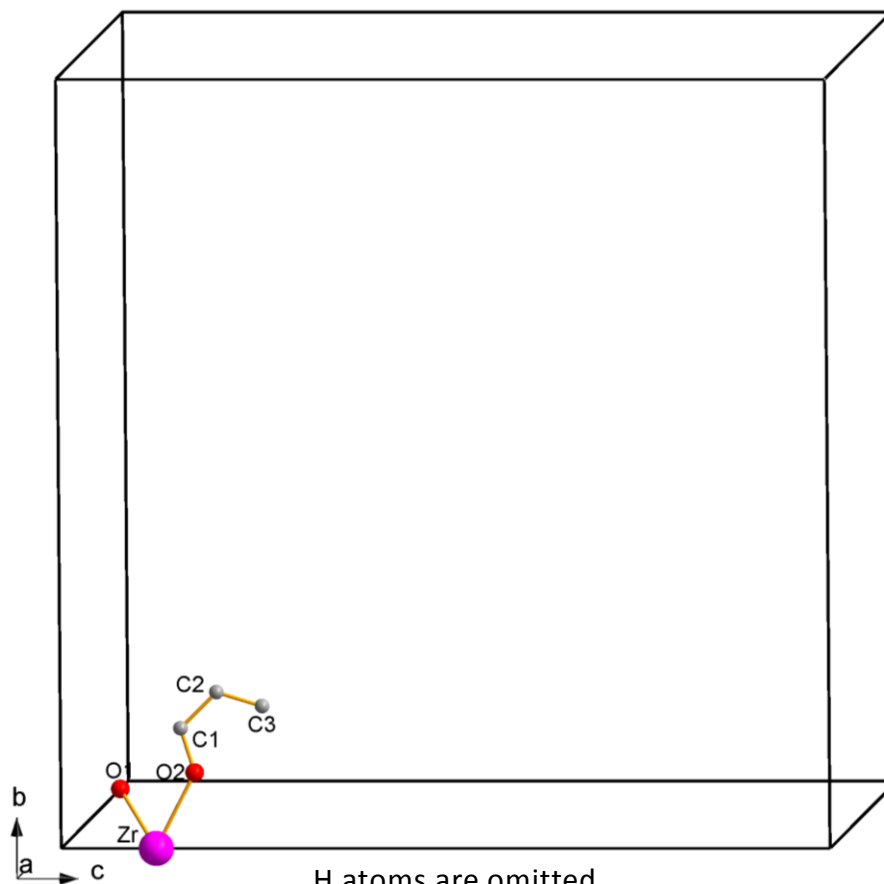
Symmetry: cubic

Space group:  $Fm-3m$

$a = 20.7465 \text{ \AA}$

$V = 8929.65 \text{ \AA}^3$

Asymmetric unit content: 1 Zr, 2 O, 3 C



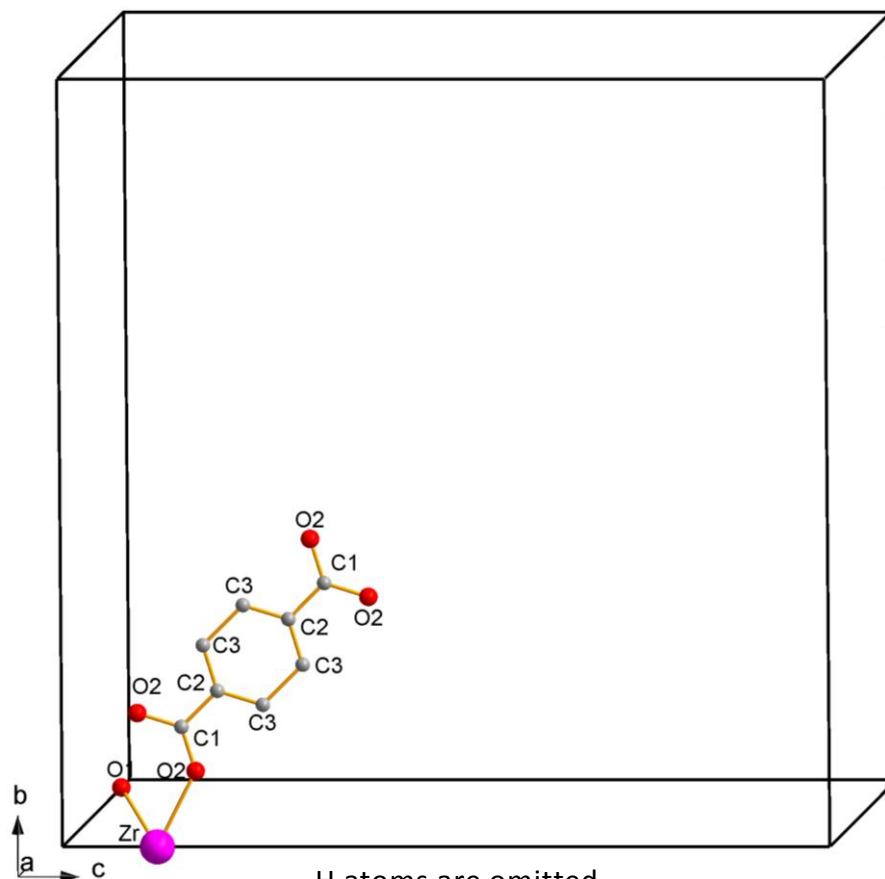
By defining the coordinates of the atoms in the asymmetric unit, we define the position of all the other atoms in the unit cell, which are generated by symmetrical transformations.

Symmetry: cubic

Space group:  $Fm-3m$

$a = 20.7465 \text{ \AA}$

$V = 8929.65 \text{ \AA}^3$



The content of the asymmetric unit is not representative of the chemical composition of the crystal!

«Special positions» exist inside the unit cell, which are related to symmetry operators.

Symmetry: cubic

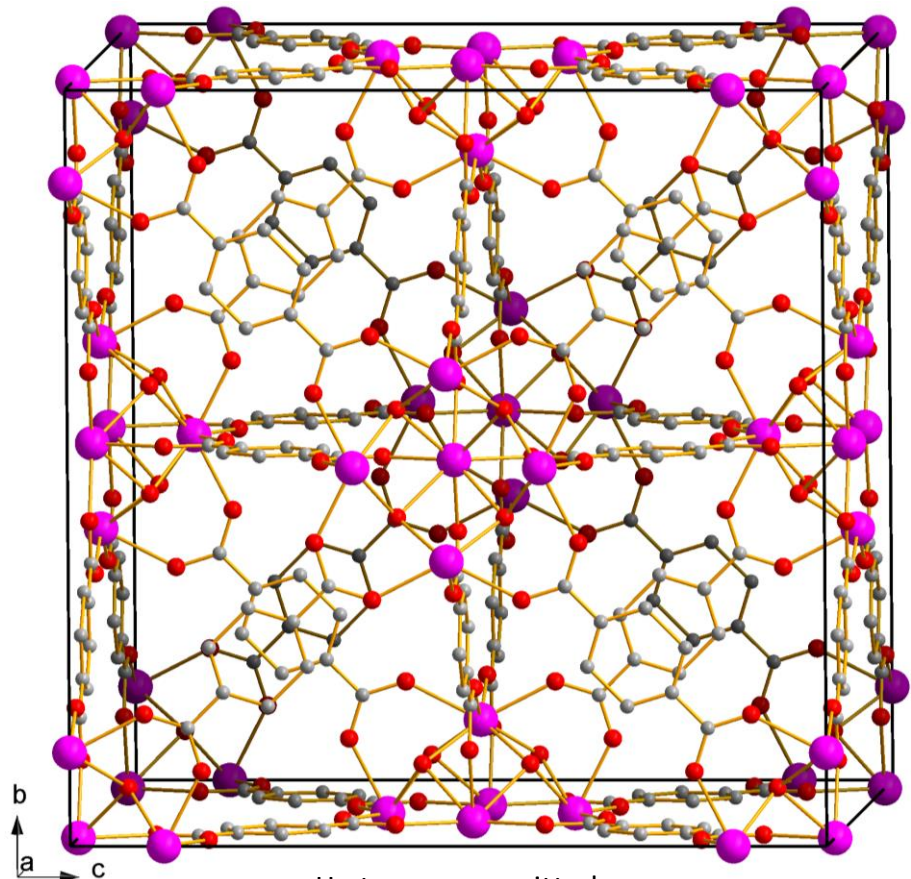
Space group:  $Fm-3m$

$a = 20.7465 \text{ \AA}$

$V = 8929.65 \text{ \AA}^3$

Asymmetric unit content: 1 Zr, 2 O, 3 C

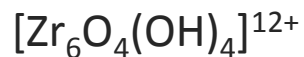
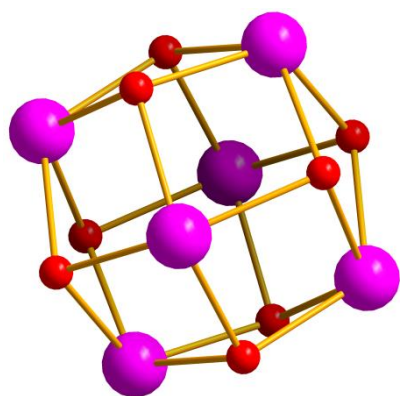
Unit cell content: 24 Zr, 128 O, 192 C



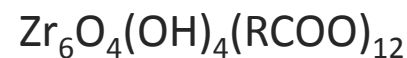
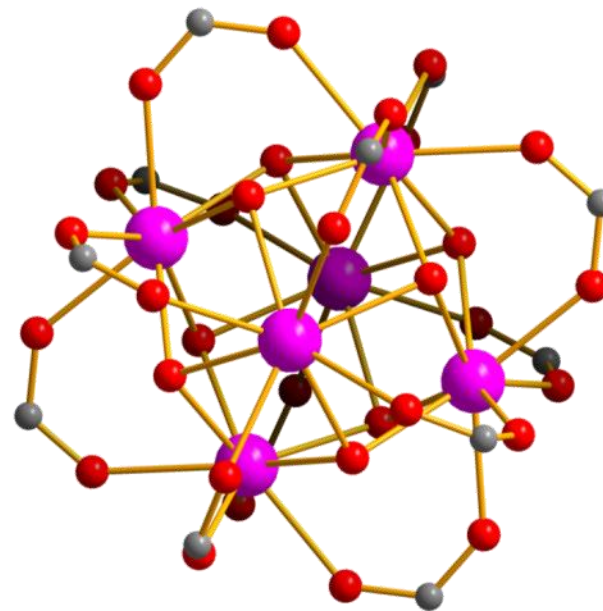
H atoms are omitted

$Zr_6O_4(OH)_4$  clusters are the cornerstones upon which the three-dimensional framework of UiO-66 is built. The clusters have specific geometrical and symmetrical features that «drive» the assembly of the crystal structure. Such species are normally termed «secondary building units» (SBUs).

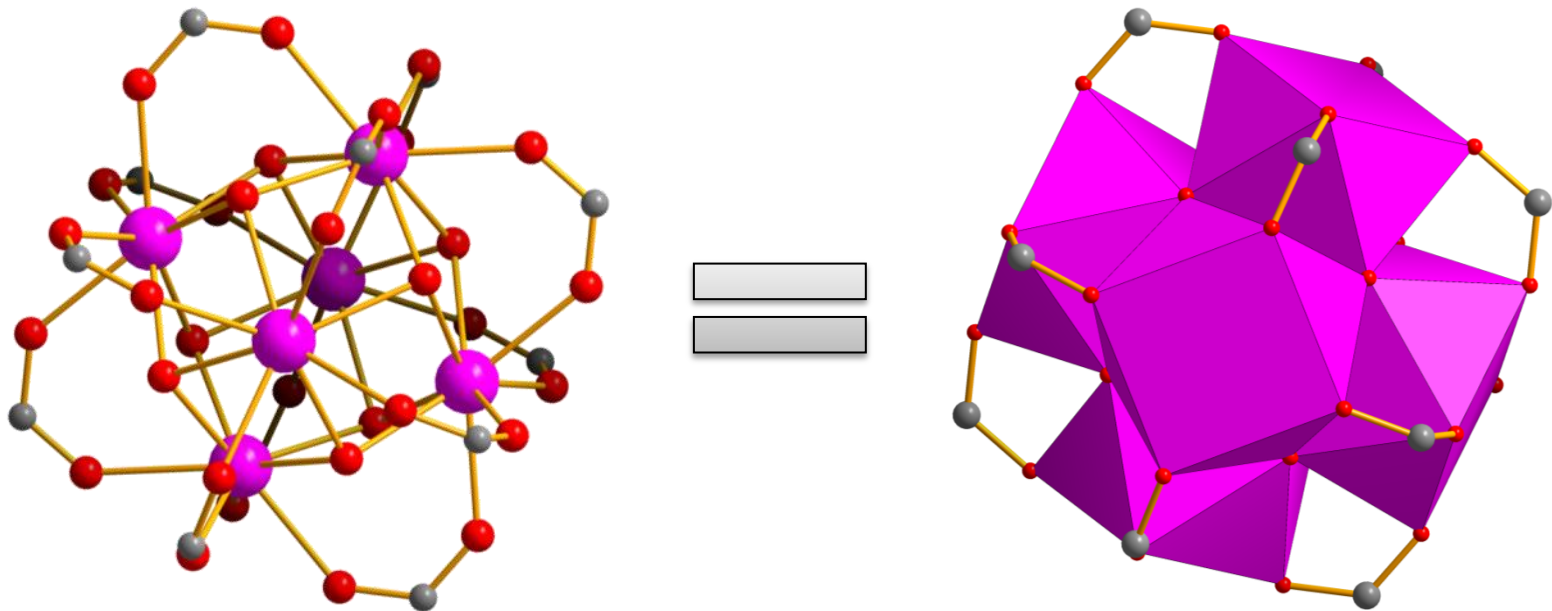
Each cluster is decorated with twelve carboxylate groups coordinated to the metal atoms.



12 RCOO<sup>-</sup>



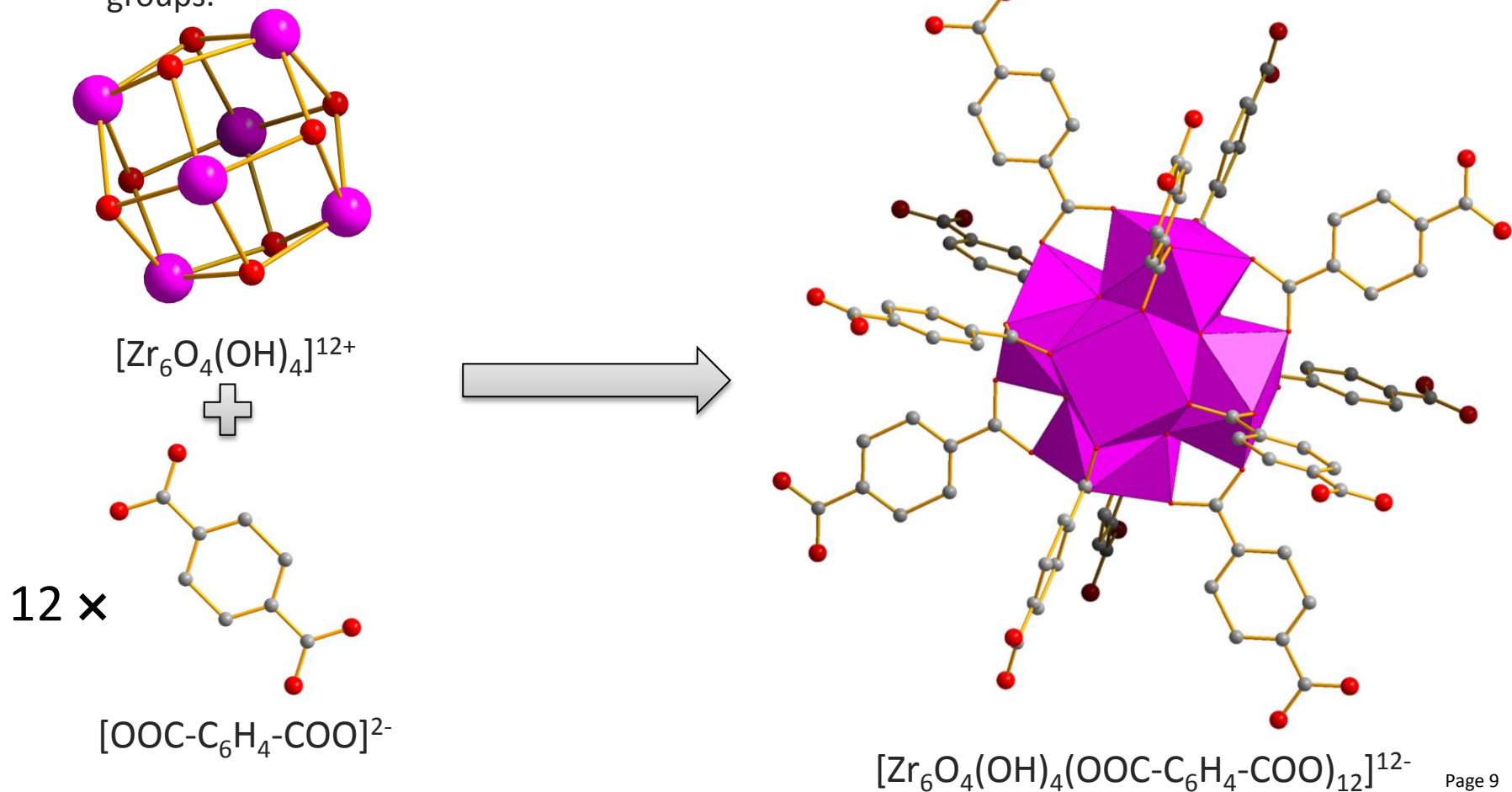
Polyhedra can be used to simplify the crystal structure and make its visualization easier.





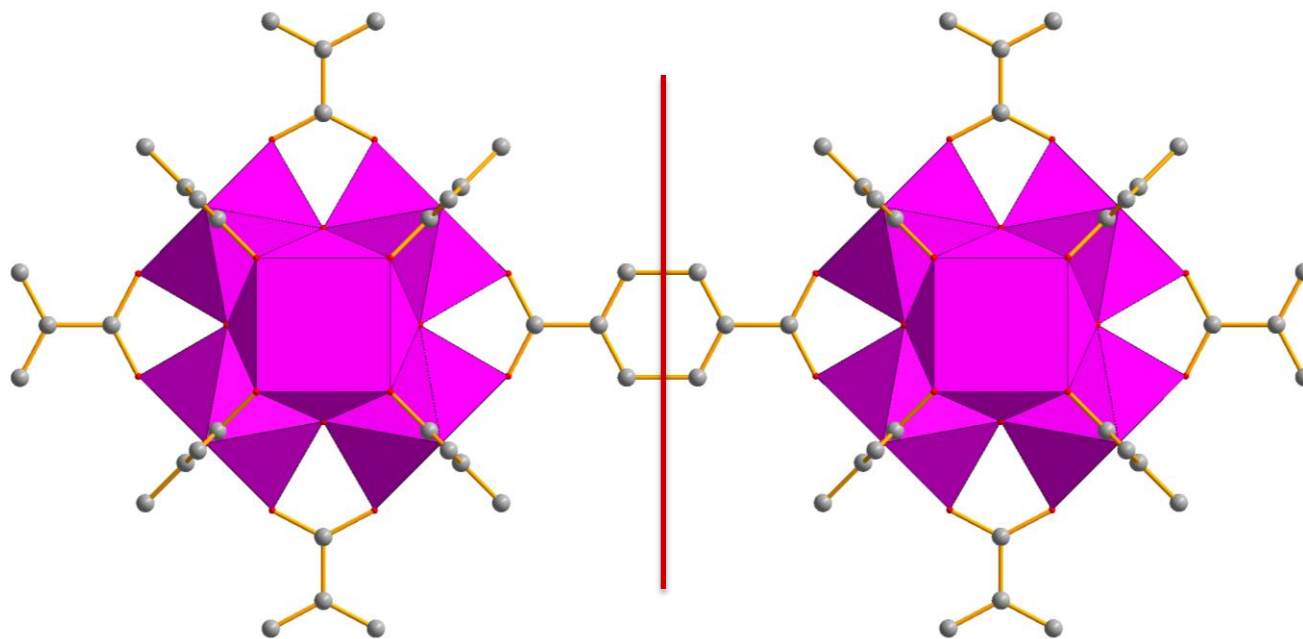
UiO-66 is a «coordination polymer». The monomers, AKA «building blocks», are bdc and  $Zr_6O_4(OH)_4$  clusters.

Twelve bdc linkers coordinate to the metal atoms of the cluster with one of their carboxylate groups.

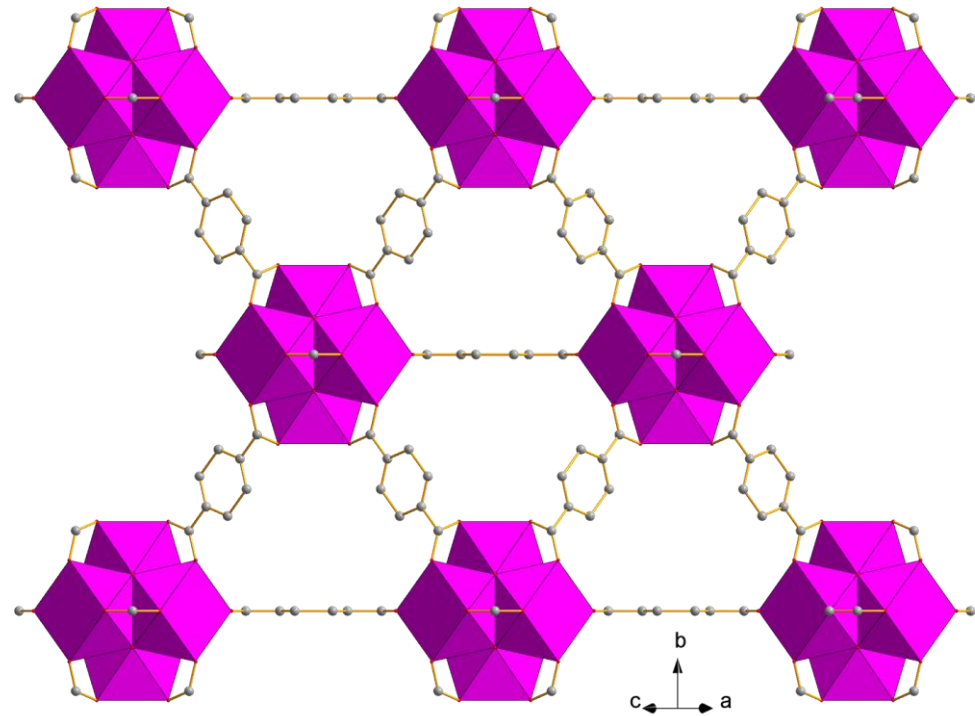
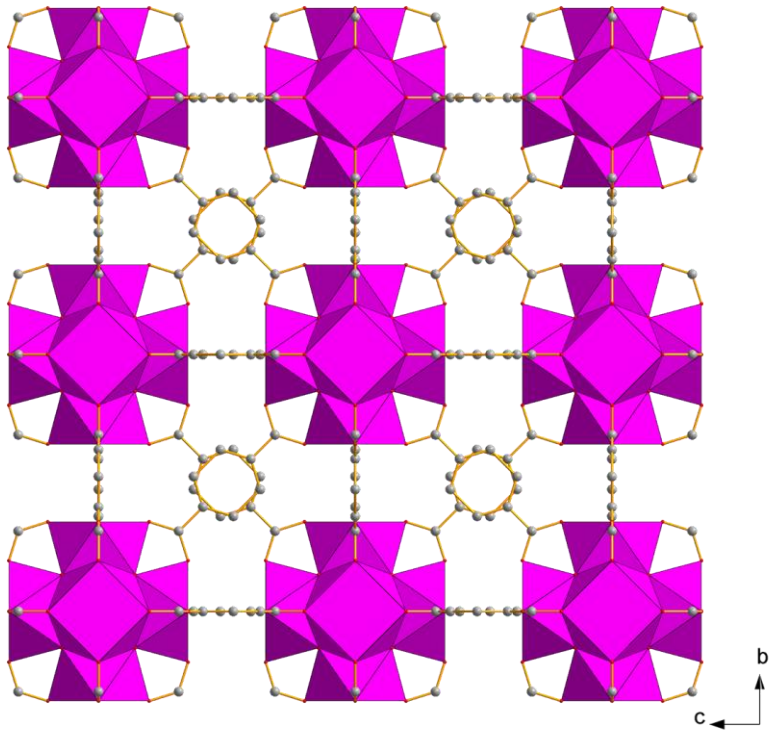


Every bdc linker is shared between two clusters. In this way, each  $[\text{OOC-C}_6\text{H}_4\text{-COO}]^{2-}$  unit contributes with a single negative charge to every cluster.

In other words, every cluster is decorated by twelve «half-bdc» ligands, thus leading to the electroneutral formula  $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{OOC-C}_6\text{H}_4\text{-COO})_6$ .



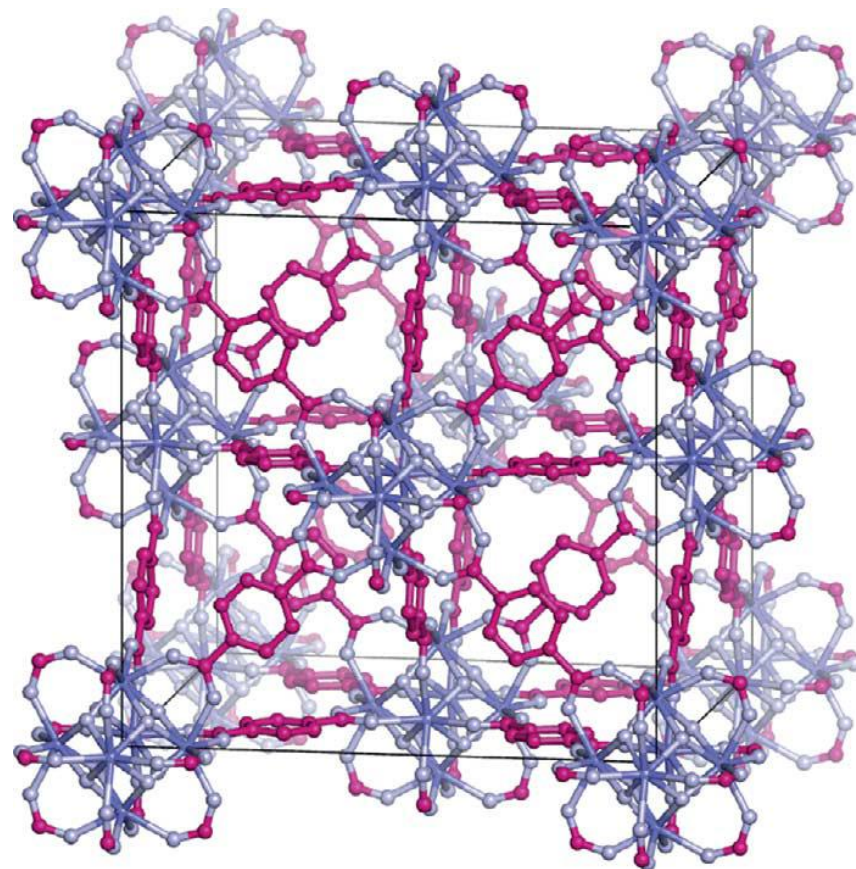
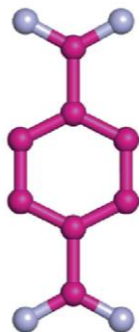
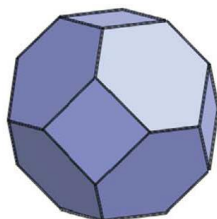
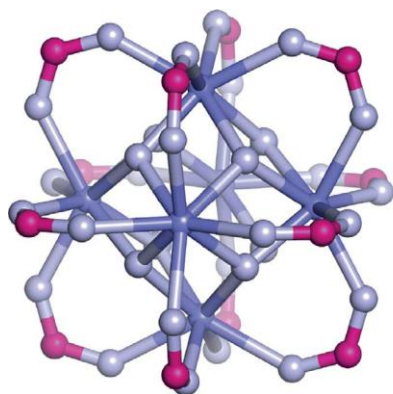
Two different views of the crystal structure.



# Crystal structure

A simplified modular representation helps in having a clearer picture of the crystal structure.

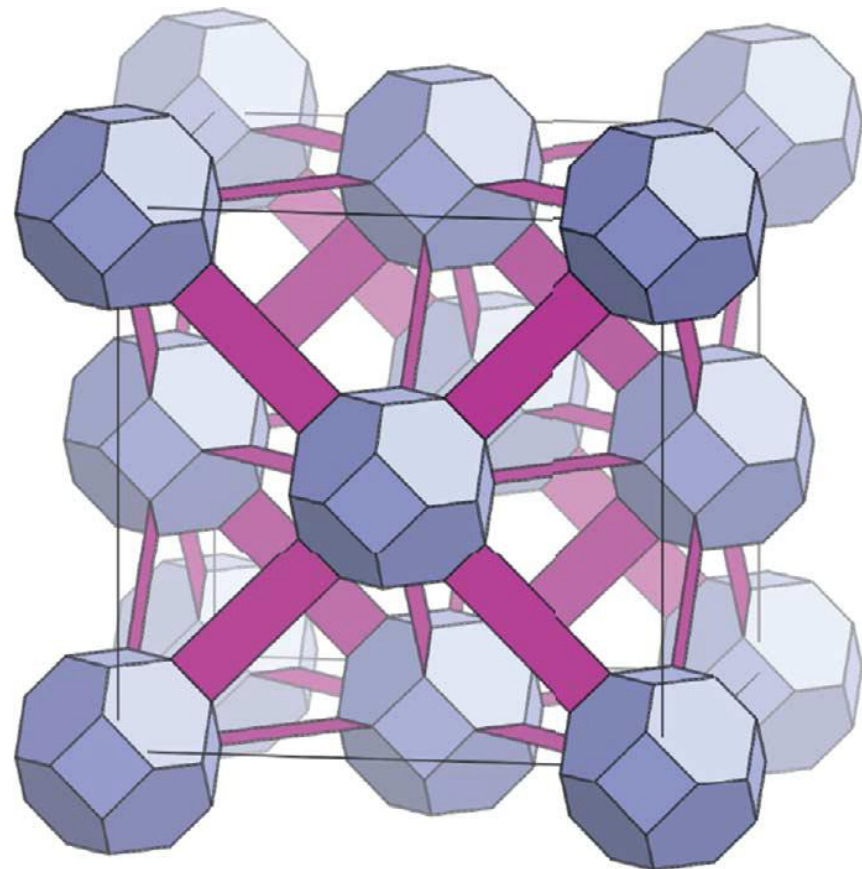
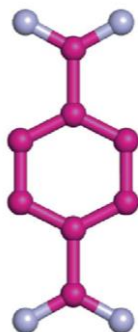
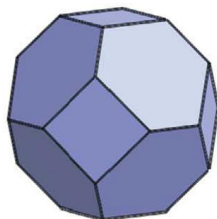
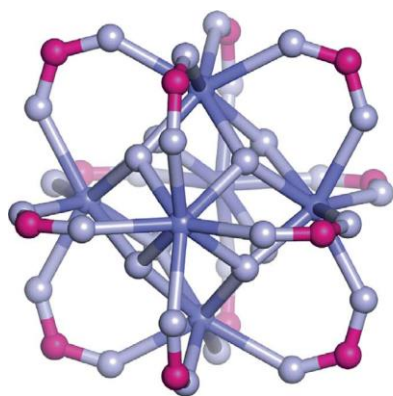
We can think of the building blocks as a molecular version of LEGO bricks.



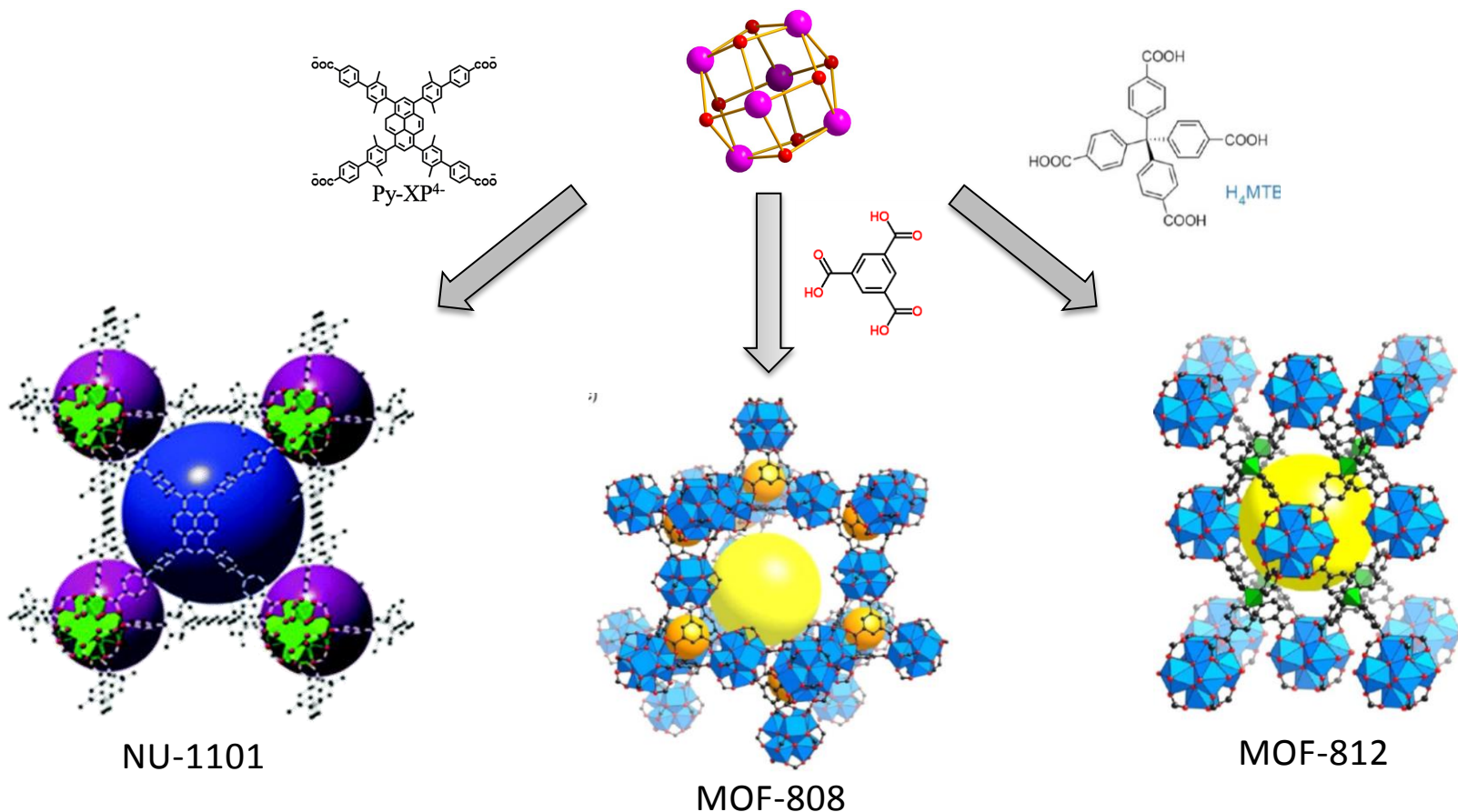
# Crystal structure

A simplified modular representation helps in having a clearer picture of the crystal structure.

We can think of the building blocks as a molecular version of LEGO bricks.

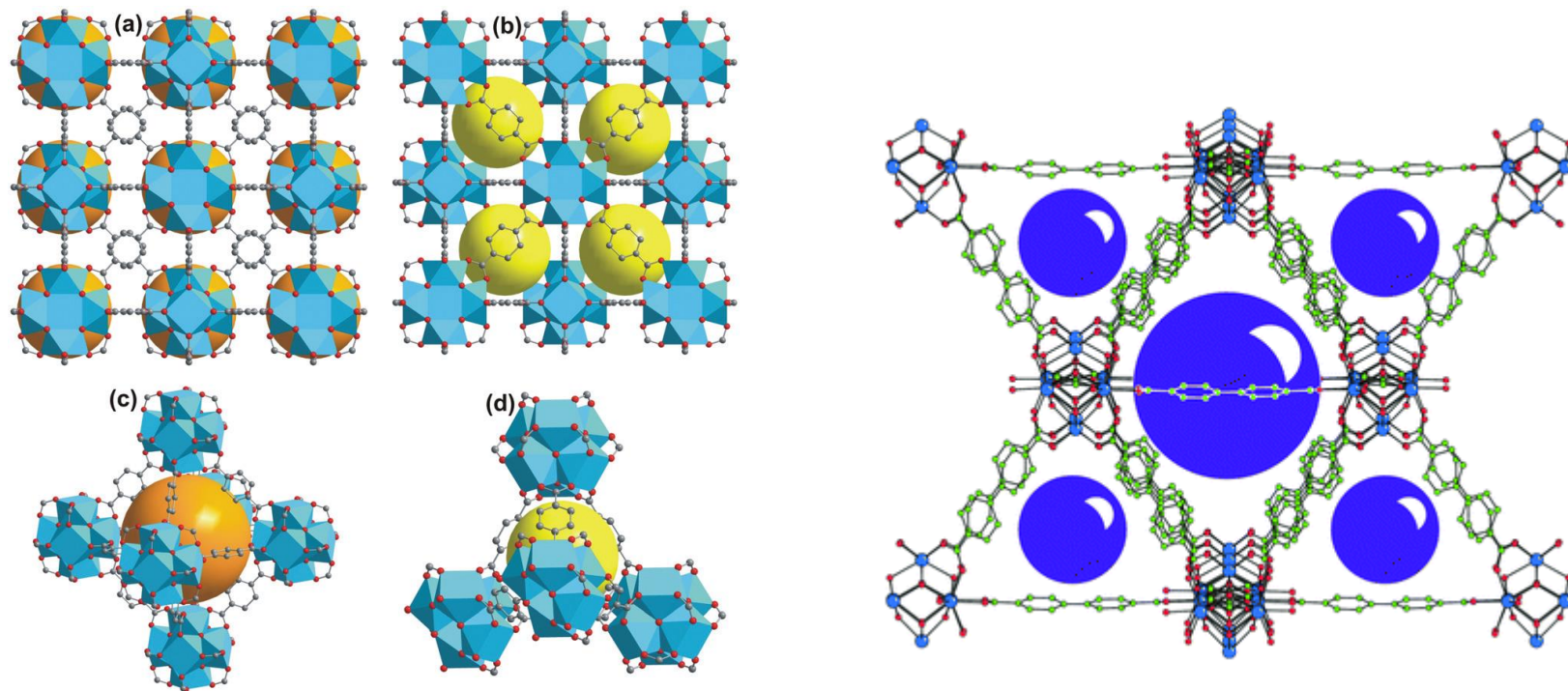


UiO-66 is the progenitor of a family of zirconium-based MOFs: the same  $Zr_6O_4(OH)_4$  clusters found in UiO-66 serve as SBUs for a whole class of materials displaying a wide range of topologies, accessible by employing linkers having specific geometrical and symmetrical features.



The framework of UiO-66 features two types of cages: octahedral (orange in the left figure, 9 Å diameter) and tetrahedral (yellow in the left figure, 7 Å diameter).

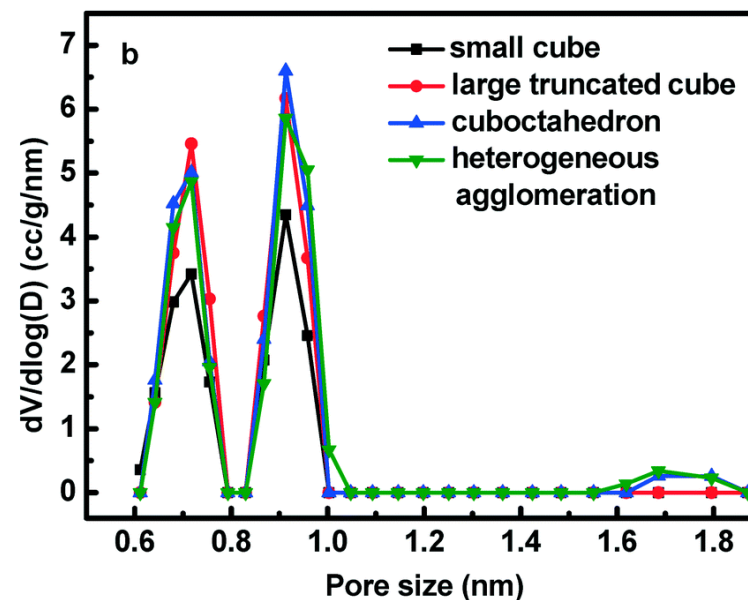
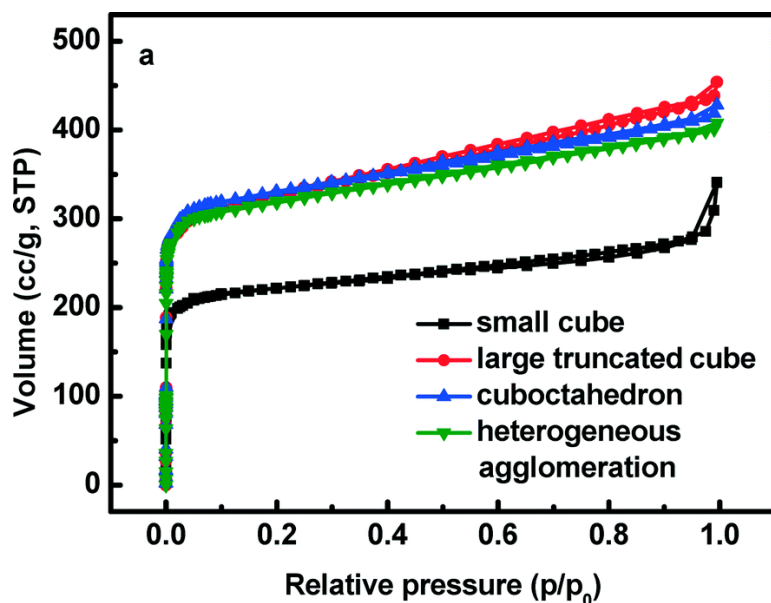
These cages are accessible to guest species, but they are normally filled with solvent molecules, which can be removed by heating under vacuum.



The accessible space inside the framework can be measured by means of nitrogen physisorption analysis performed at 77 K.

Surface area (calculated using the BET theory), pore volume and pore size distribution are the most important parameters extracted from the adsorption isotherm.

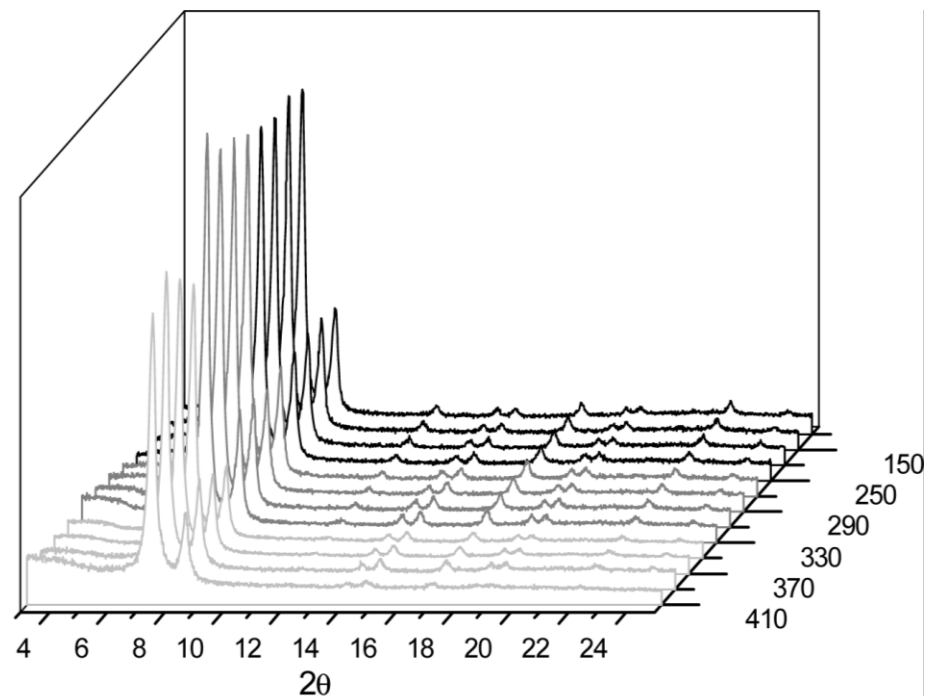
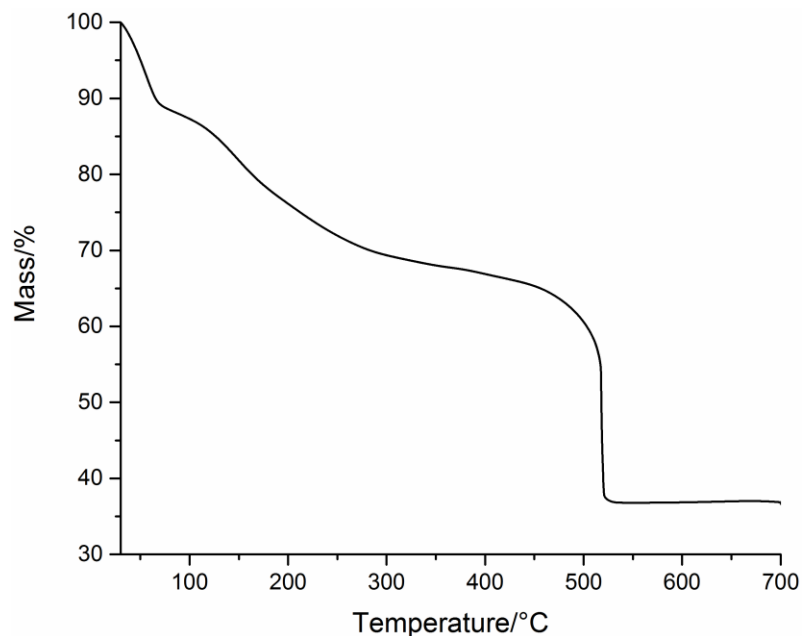
BET surface area  $\approx 1200 \text{ m}^2 \text{ g}^{-1}$ , Pore volume  $\approx 0.44 \text{ cm}^3 \text{ g}^{-1}$



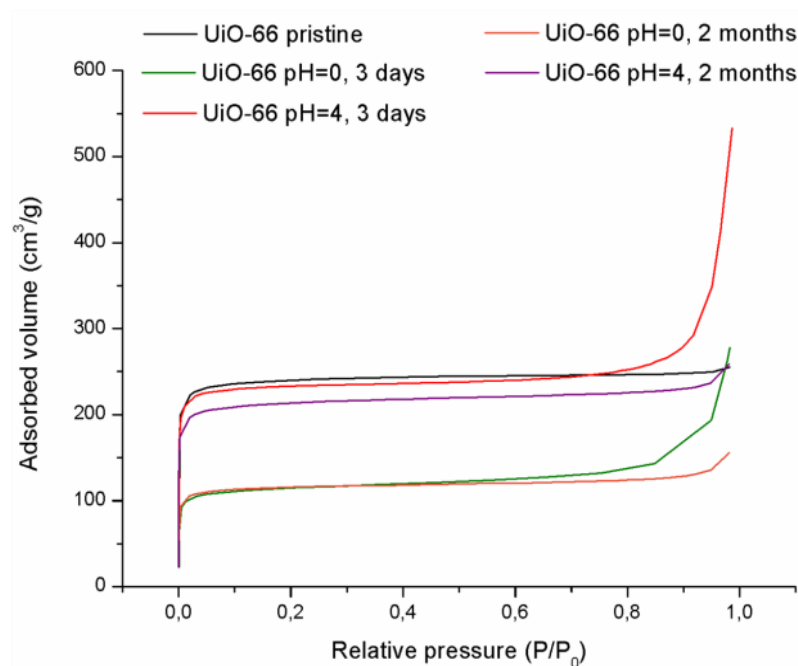
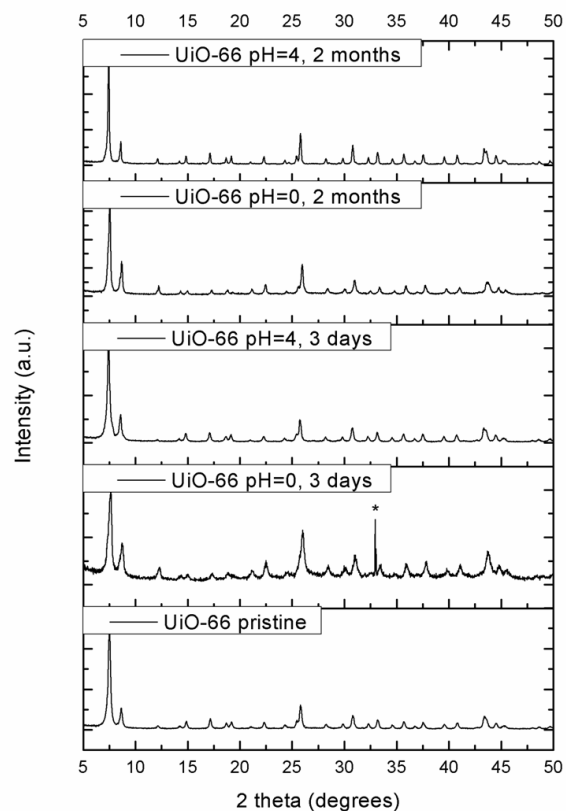


Thermal stability is investigated by means of thermogravimetric analysis and temperature-dependent X-ray diffraction.

Decomposition of the framework starts at about 450 °C. Before this temperature the compound loses weight due to desorption of solvent from the pores and dehydroxylation of the clusters.



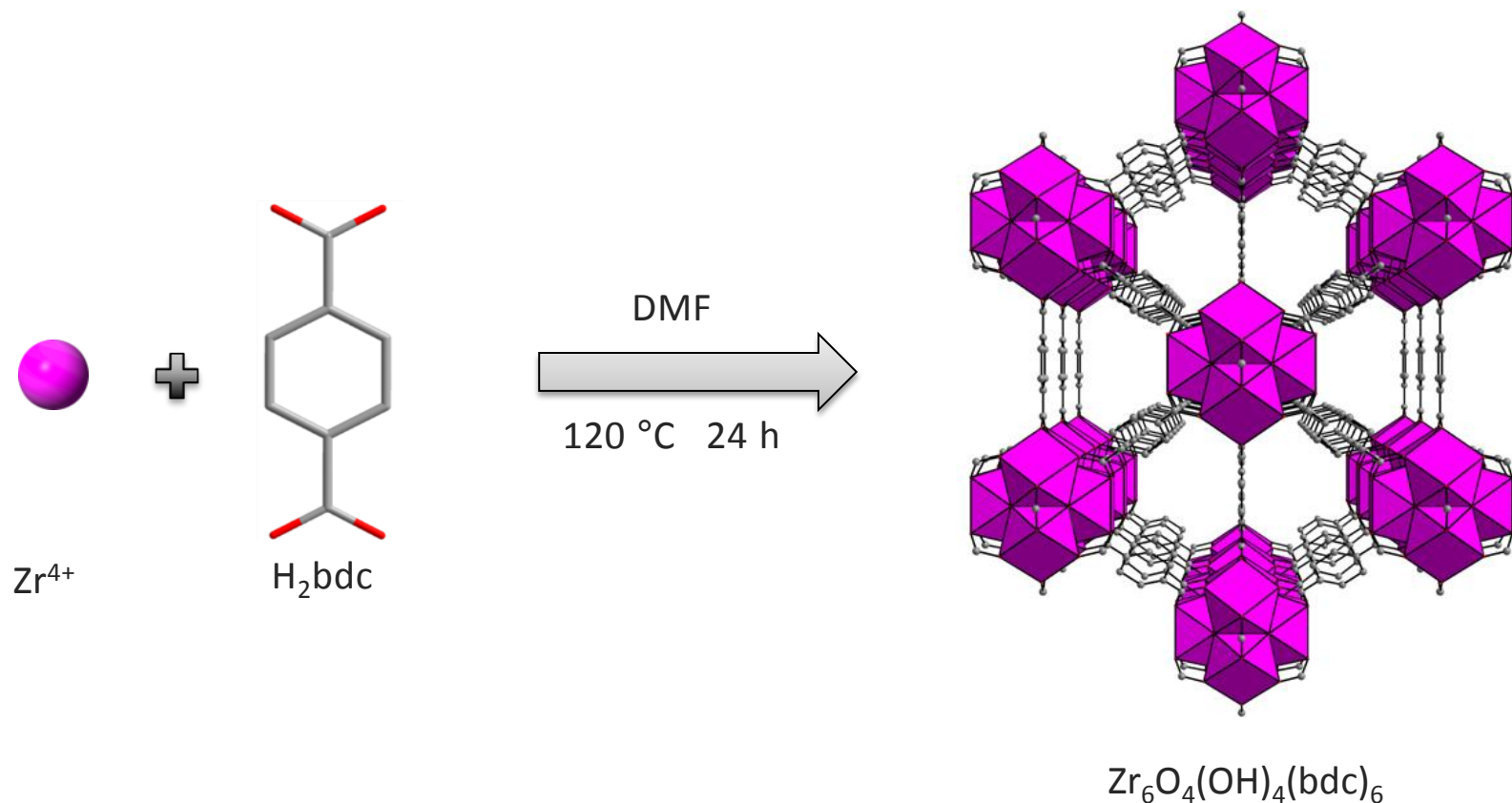
Chemical stability is assessed by treating the material in several solvents and in different conditions (pH, temperature). Of particular interest for practical application is the stability towards hydrolysis, due to the ubiquitous nature of water.



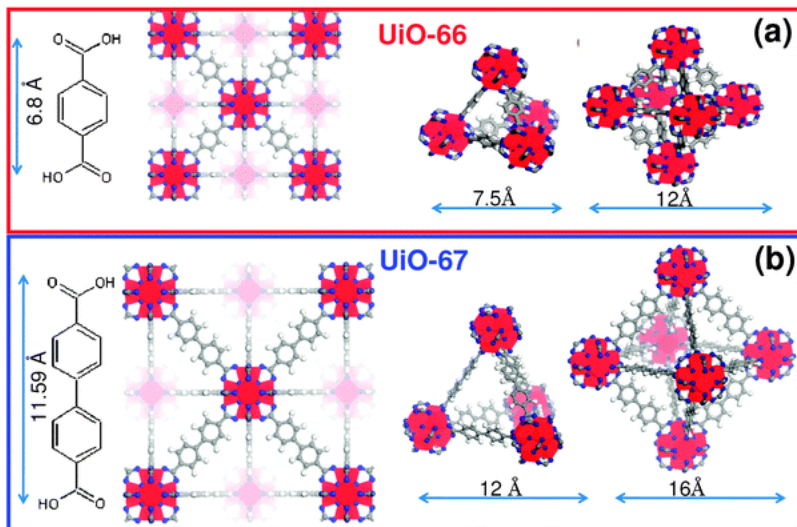
# Synthesis and functionalization

Solvothermal synthesis: the reaction mixture is heated in a sealed vessel under autogeneous pressure.

The MOF is formed by self-assembly of the building blocks and precipitates due to its insolubility in the reaction environment.



Isorecticular synthesis: using a linker with the same geometry but different length, a crystal structure having the same connectivity (topology) but larger cages is formed.

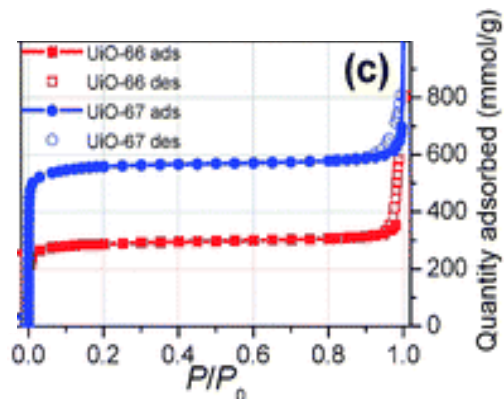
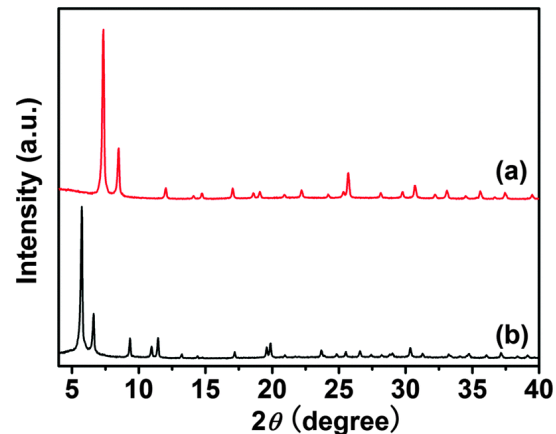


BET surface area

UiO-66 = 1052 m<sup>2</sup> g<sup>-1</sup>

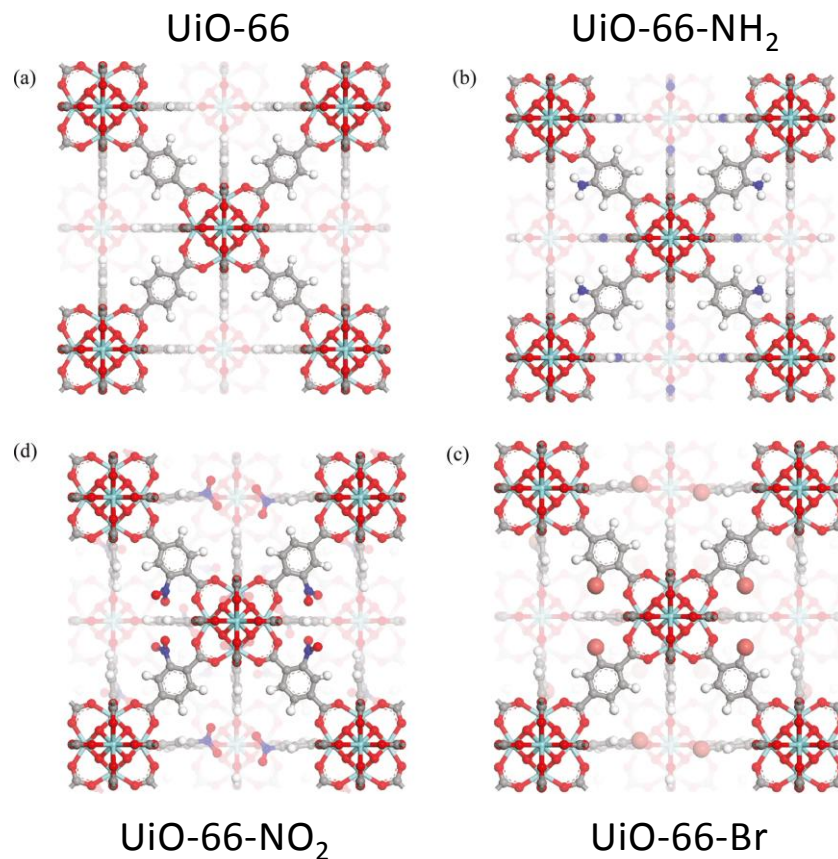
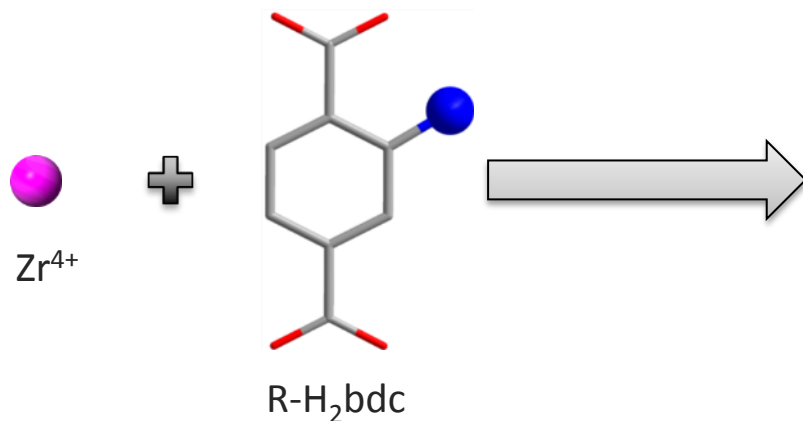
UiO-67 = 2105 m<sup>2</sup> g<sup>-1</sup>

UiO-67 is less stable than UiO-66

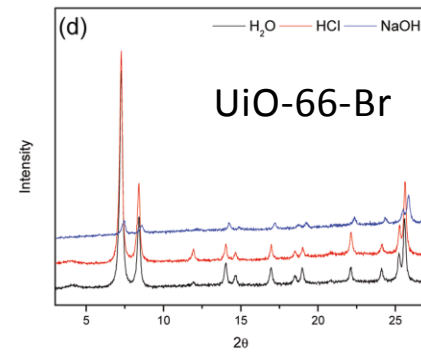
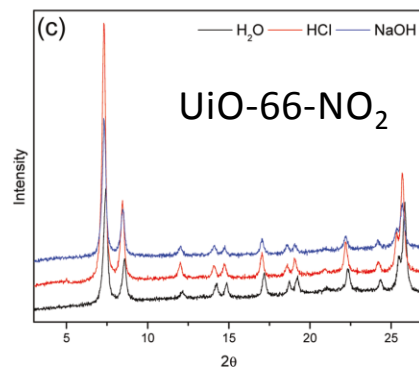
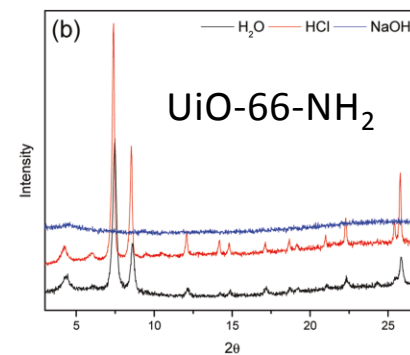
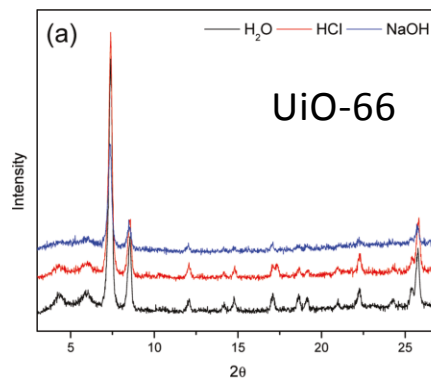
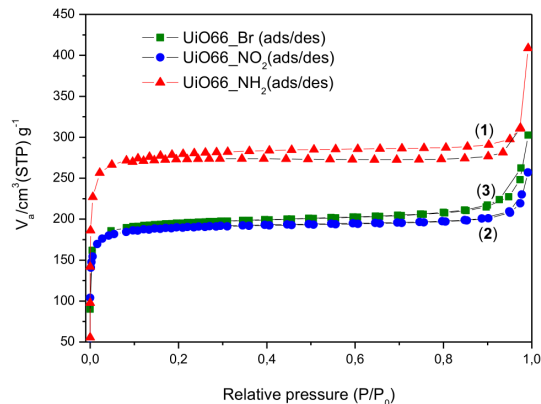
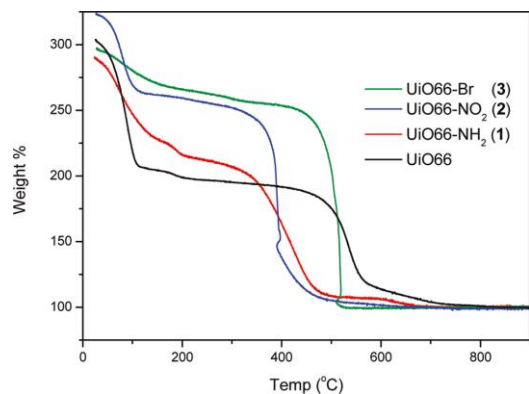


# Synthesis and functionalization

Isorecticular synthesis: using a linker with the same geometry of bdc and a functional group attached to the aromatic ring, a crystal structure having the same connectivity (topology) and functionalized framework is obtained.



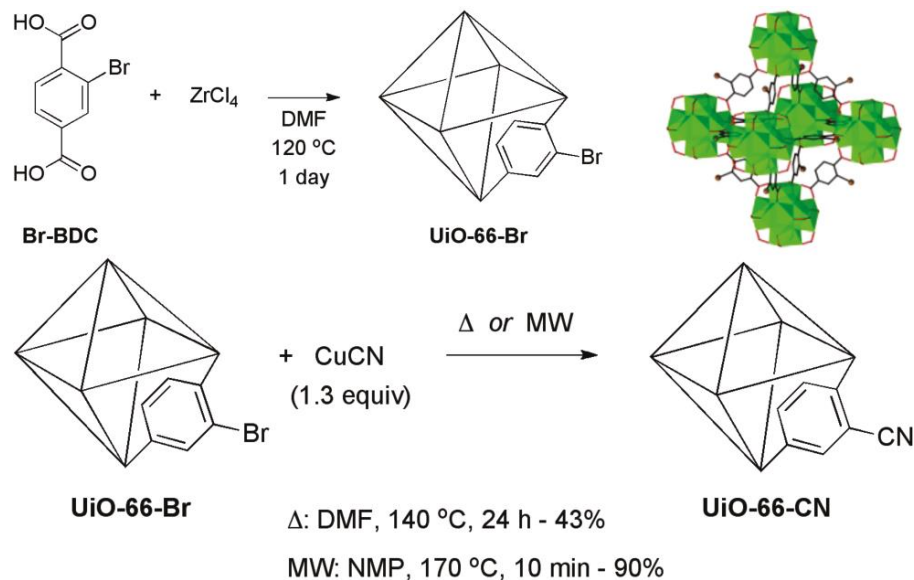
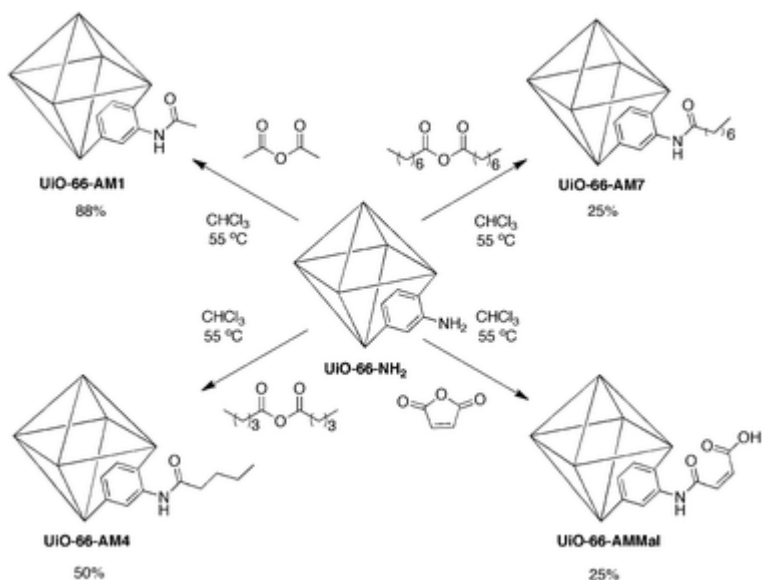
The presence of functional groups in the framework has an effect on the properties and the reactivity of the MOF.



BET surface area: UiO-66 = 1300 m<sup>2</sup> g<sup>-1</sup>, UiO-66-NH<sub>2</sub> = 1250 m<sup>2</sup> g<sup>-1</sup>,  
 UiO-66-Br = 899 m<sup>2</sup> g<sup>-1</sup>, UiO-66-NO<sub>2</sub> = 856 m<sup>2</sup> g<sup>-1</sup>

# Synthesis and functionalization

Functionalized UiO-66 is an excellent platform for post-synthetic modification (PSM). In PSM, porosity of the MOF allows reactive species to diffuse into the crystal structure and come in contact with the functional groups decorating the framework. MOF pores are microreactors!



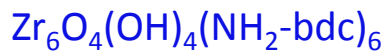
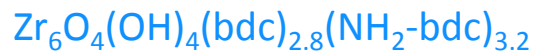
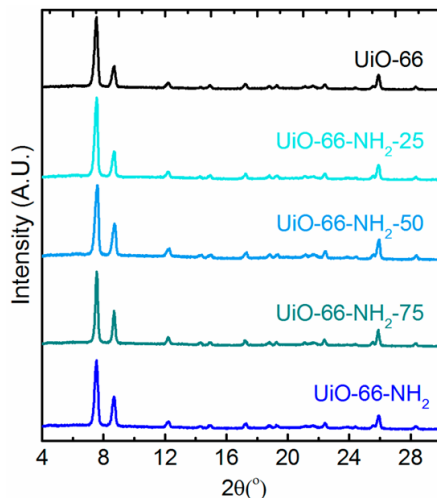
# Synthesis and functionalization

An effective way to modulate the properties of a MOF is the mixed-linker approach (MIXMOFs).

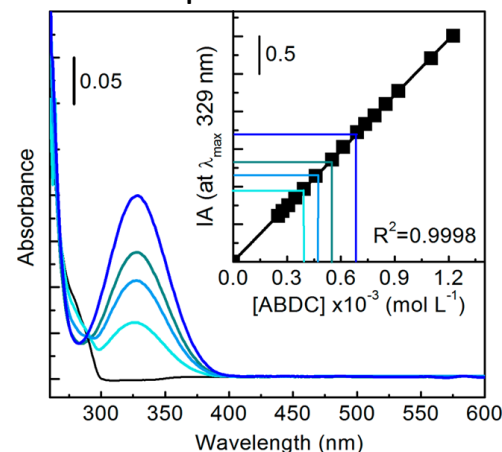
Two (or more) linkers are used as starting materials, yielding a framework where they are randomly dispersed.

The properties of the resulting material are a combination of those of the pure MOFs.

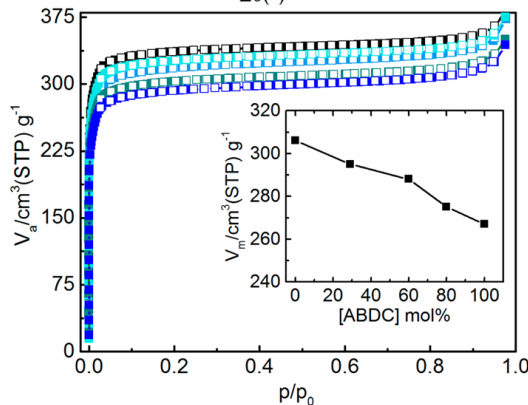
PXRD



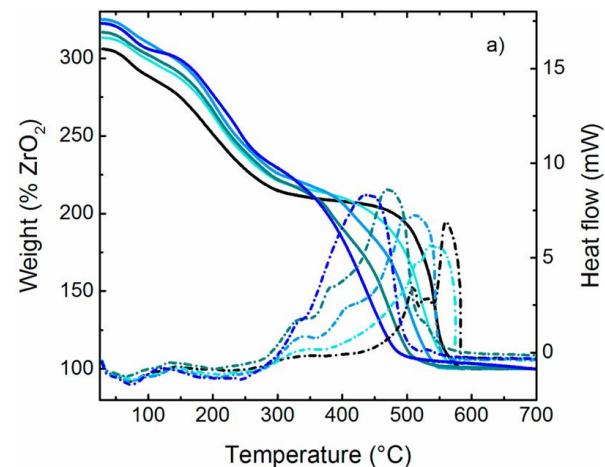
UV-Vis Spectroscopy



Gas sorption



TGA

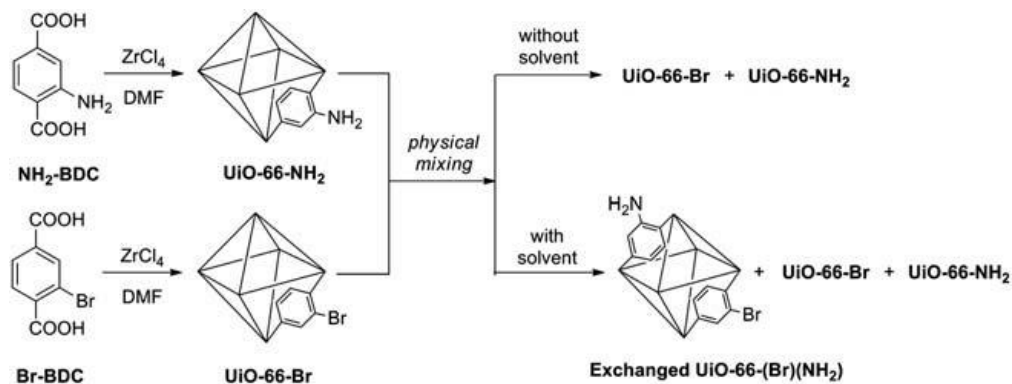




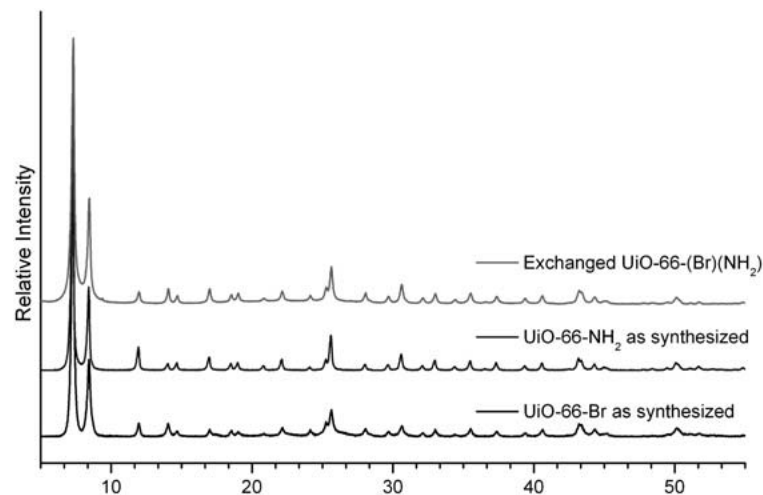
# Synthesis and functionalization

A powerful alternative route to prepare MIXMOFs is post-synthetic exchange (PSE). It is a solvent-mediated process and it occurs preferentially in polar solvents.

Solid-solid PSE occurs by simply soaking two differently functionalized materials in a solvent, yielding a MIXMOF.



## Solid-solid PSE



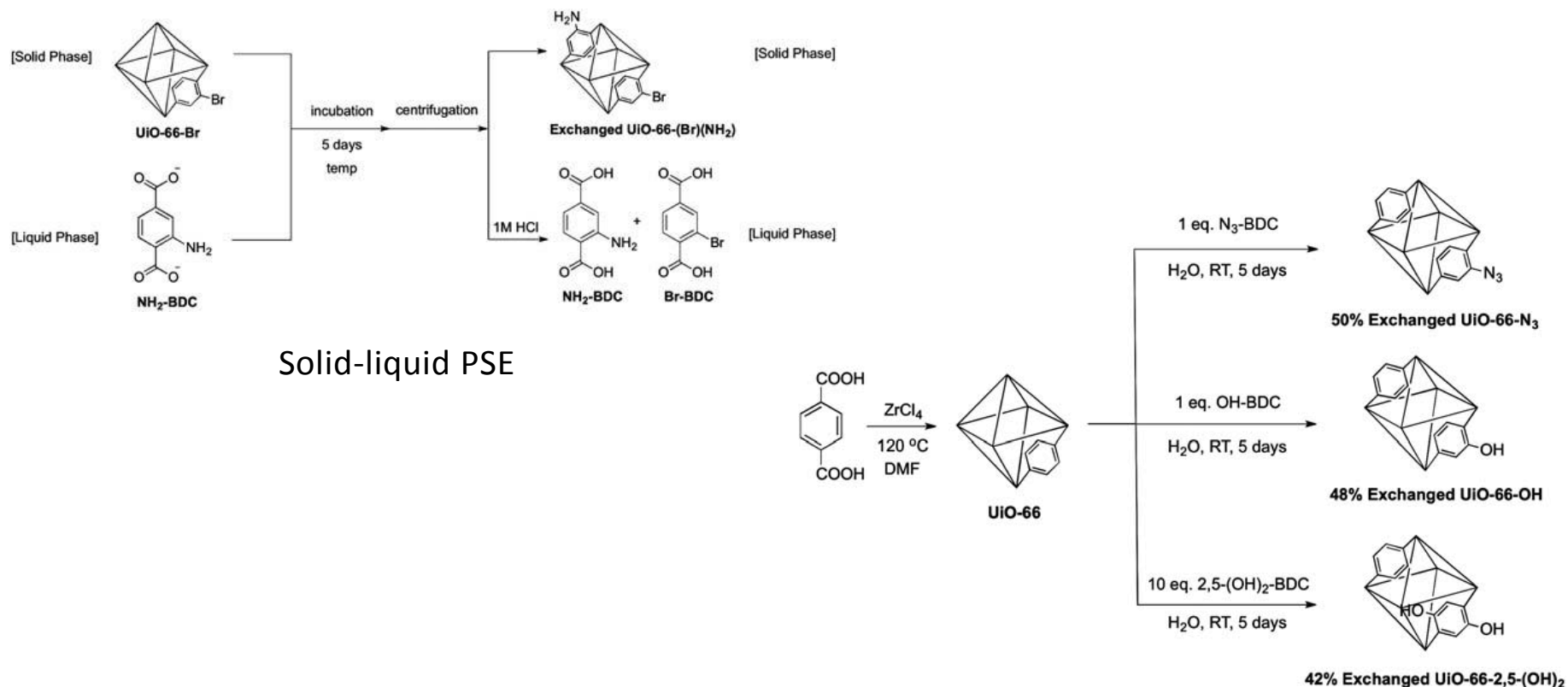
Entry	Conditions <sup>a</sup>	Number of particles—exchanged : UiO-66-Br : UiO-66-NH <sub>2</sub>	Percentage of particles exchanged (±2%) <sup>b</sup>
1	CHCl <sub>3</sub> , RT	387 : 548 : 898	21%
2	CHCl <sub>3</sub> , 55 °C	785 : 469 : 583	43%
3	MeOH, RT	677 : 644 : 540	36%
4	MeOH, 55 °C	1243 : 250 : 486	63%
5	DMF, RT	1165 : 235 : 606	58%
6	DMF, 55 °C	1344 : 259 : 336	69%
7	DMF, 85 °C	1419 : 187 : 530	66%
8	H <sub>2</sub> O, RT	882 : 420 : 332	54%
9	H <sub>2</sub> O, 55 °C	1549 : 119 : 276	80%
10	H <sub>2</sub> O, 85 °C	1907 : 13 : 56	97%

<sup>a</sup> UiO-66-NH<sub>2</sub> (0.1 mmol) and UiO-66-Br (0.1 mmol) were placed in a dram vial with 2 mL of the solvent indicated for 5 days. <sup>b</sup> (number of particles with both ligands)/(total number of particles).

# Synthesis and functionalization

Solid-liquid PSE is performed by soaking the MOF in a solution of the desired ligand. For practical purposes, this is the most useful type of PSE.

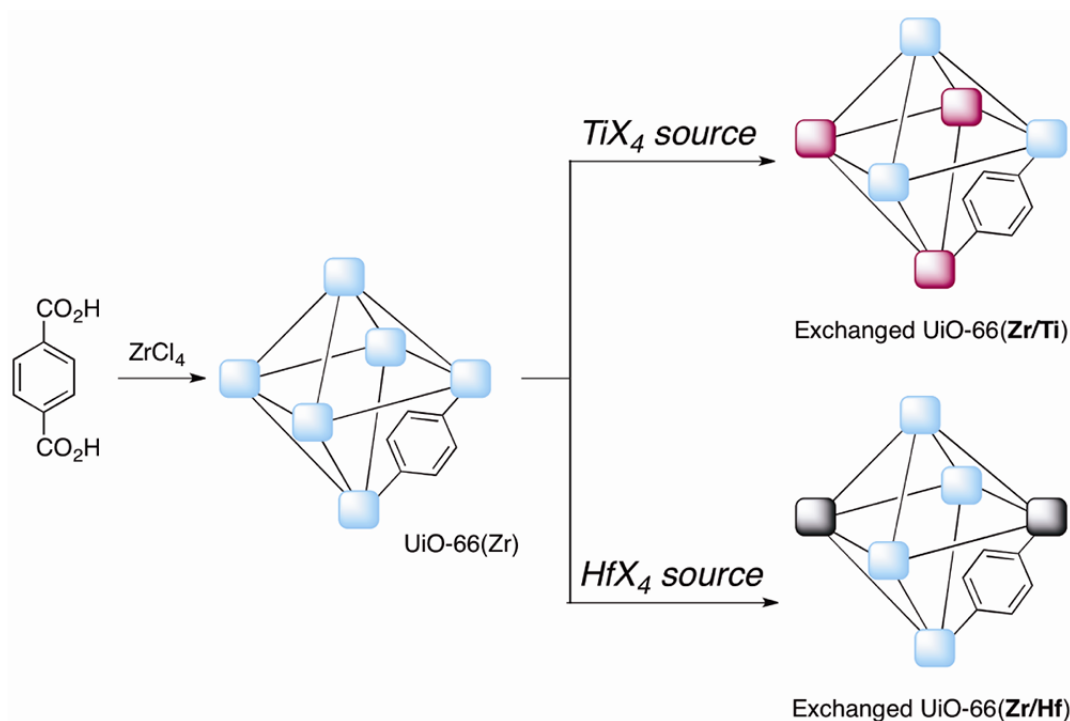
Some materials that cannot be obtained with other synthetic methods have been successfully prepared via PSE.



# Synthesis and functionalization

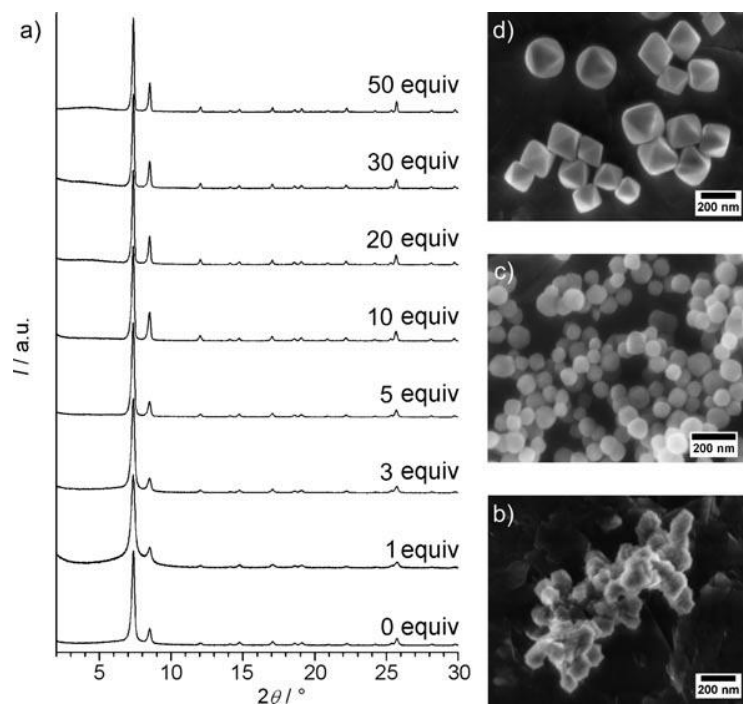
The metal ions constituting the clusters can also be PSEd by soaking the common UiO-66(Zr) in a solution of  $\text{Ti}^{4+}$  or  $\text{Hf}^{4+}$ , leading to mixed-metal UiO-66.

This is the only available route to introduce  $\text{Ti}^{4+}$  in the clusters.



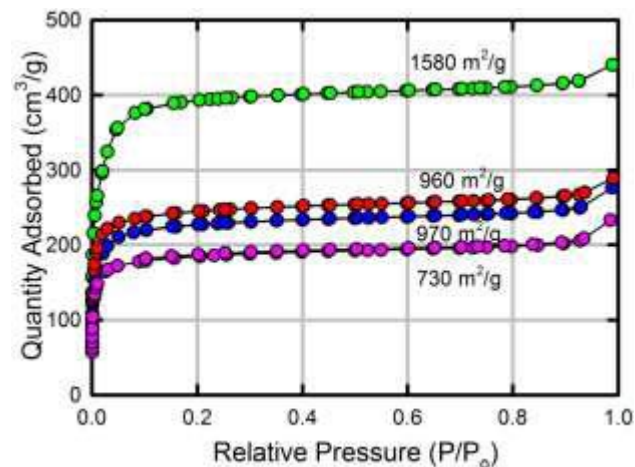
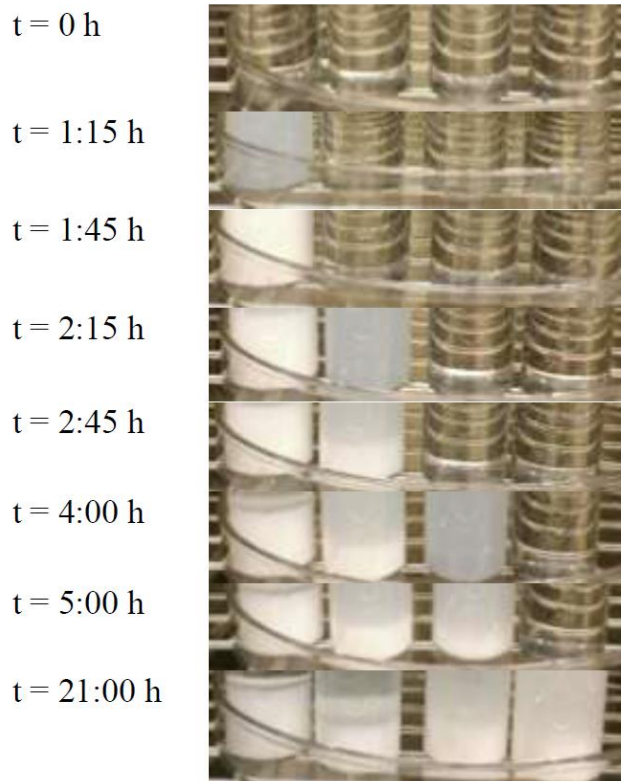
Precise control of crystal size is a topic of great interest in MOF chemistry. Large crystals are desirable for detailed structural characterization, whereas for most practical applications small crystals are preferred due to decreased diffusion limitations.

Monocarboxylic acids are employed as «coordination modulators» for UiO-66. They are believed to compete with bdc for coordination to the clusters, slowing down the precipitation rate of the MOF and allowing the growth of larger crystals.



Commonly used modulators include: acetic acid, formic acid, benzoic acid, trifluoroacetic acid.

«Protonation modulation» involves the addition of strong inorganic acids (typically HCl), thus inhibiting dissociation of H<sub>2</sub>bdc to bdc and consequently slowing down the precipitation rate.



Green: 1 mL

Red: 0.5 mL

Blue: 0.25 mL

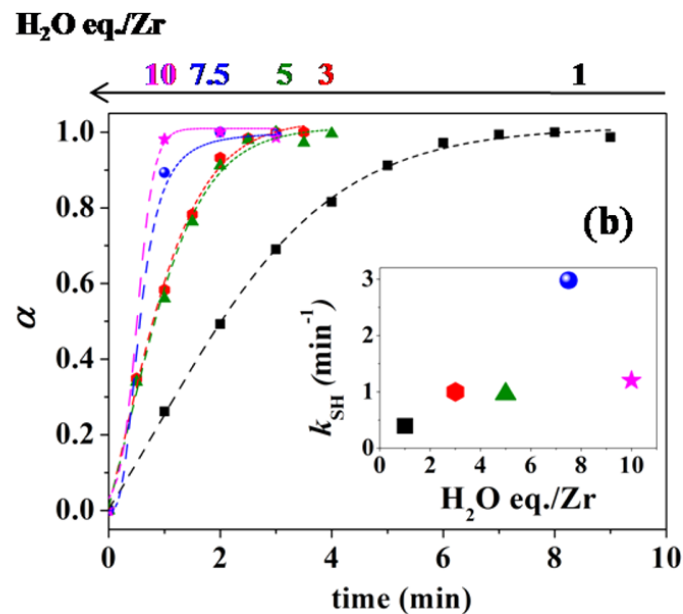
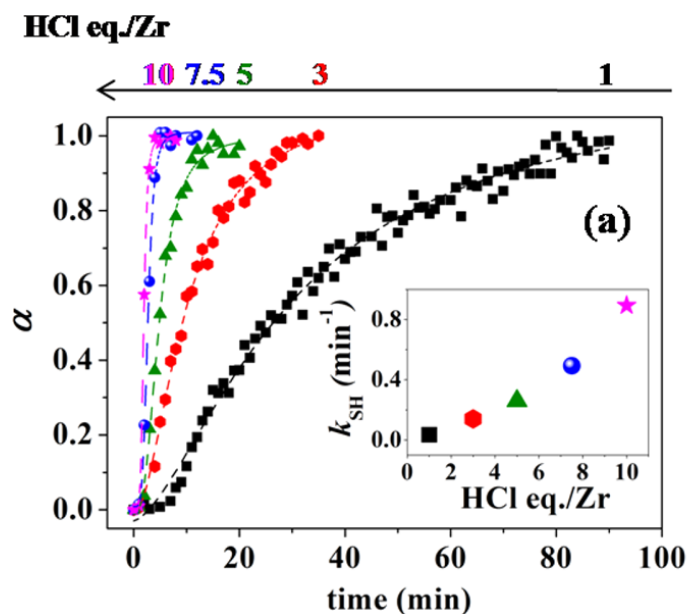
Purple: 0.1 mL

Amount of HCl 37% added: 1 mL 0.5 mL 0.25 mL 0.1 mL

# Synthesis and functionalization

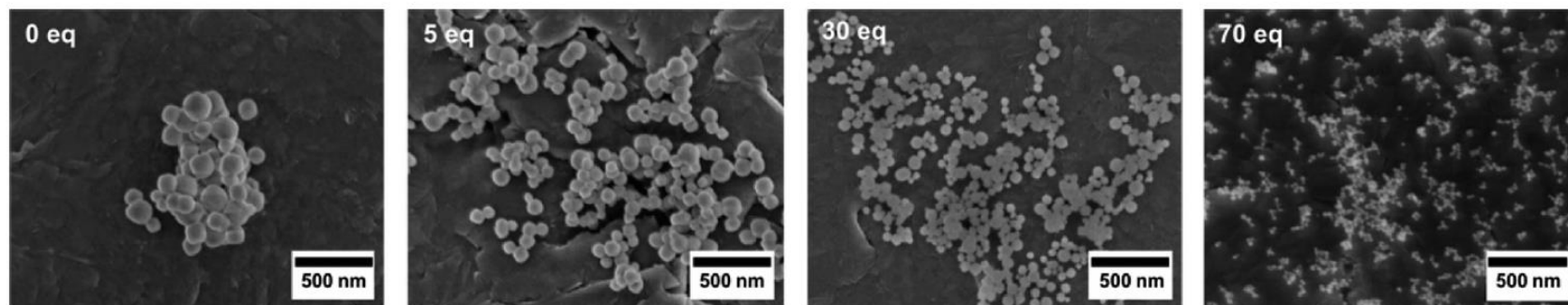
Nonetheless, addition of 37% HCl also means addition of water. It was demonstrated that water has an accelerating effect on the formation of UiO-66. This is due to the fact that the clusters contain oxide and hydroxide ligands, which arguably come from deprotonation of water.

Addition of pure water enhances the kinetics of reaction and leads to growth of smaller crystals.



Nonetheless, addition of 37% HCl also means addition of water. It was demonstrated that water has an accelerating effect on the formation of UiO-66. This is due to the fact that the clusters contain oxide and hydroxide ligands, which arguably come from deprotonation of water.

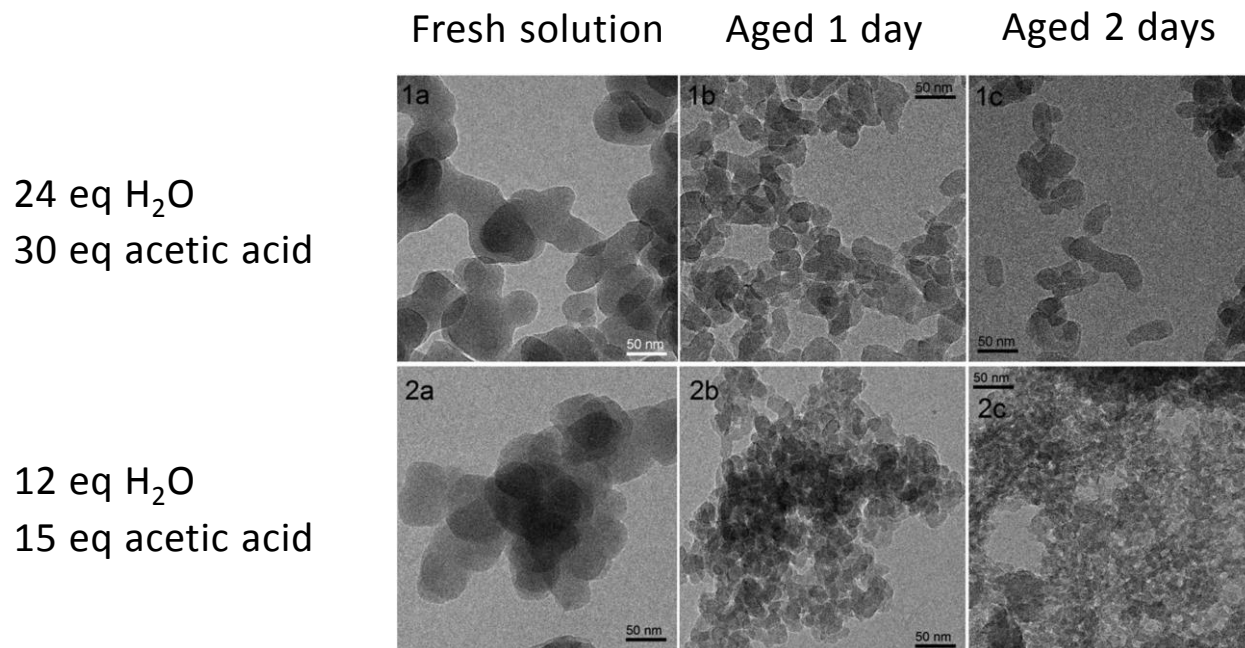
Addition of pure water enhances the kinetics of reaction and leads to growth of smaller crystals.



**Fig. 11** SEM images obtained from Zr-fumarate MOF synthesised with various amounts of water  $x$  added to a DMF-based synthesis ( $\text{ZrCl}_4/\text{H}_2\text{fum}/\text{formic acid}/\text{water}/\text{DMF}$  1: 3: 70 :  $x$ : 500, 100 °C).

# Synthesis and functionalization

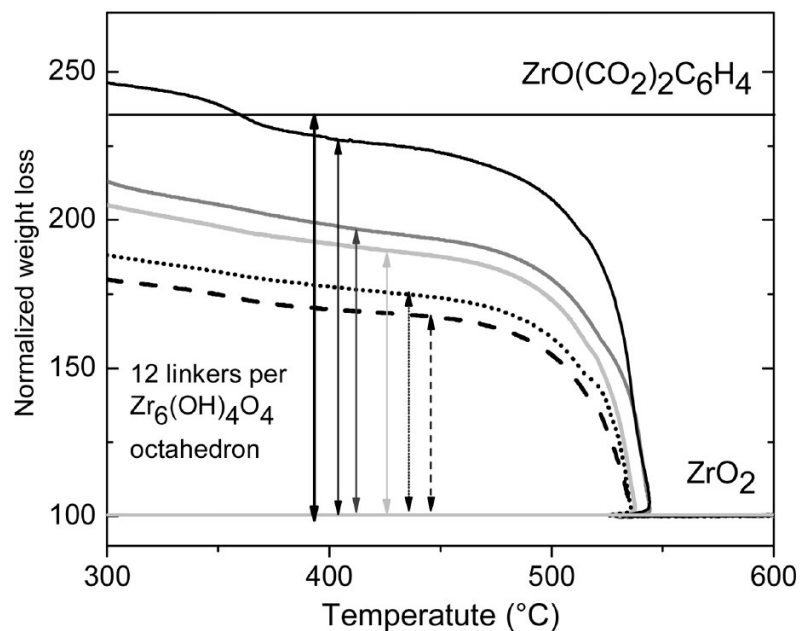
It was recently discovered in our group that crystal size can be modulated by aging a solution of Zr in DMF in the presence of different ratios of additives (water and acetic acid) prior to the addition of the ligand. Longer aging times lead to smaller crystallites. Water is responsible for the aging effect, while acetic acid plays a role in modulating the extent of crystal size reduction.





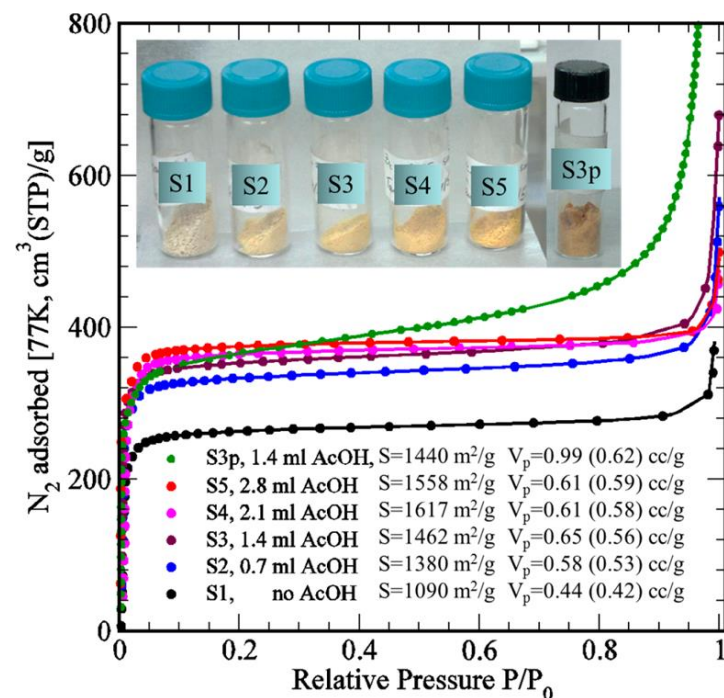
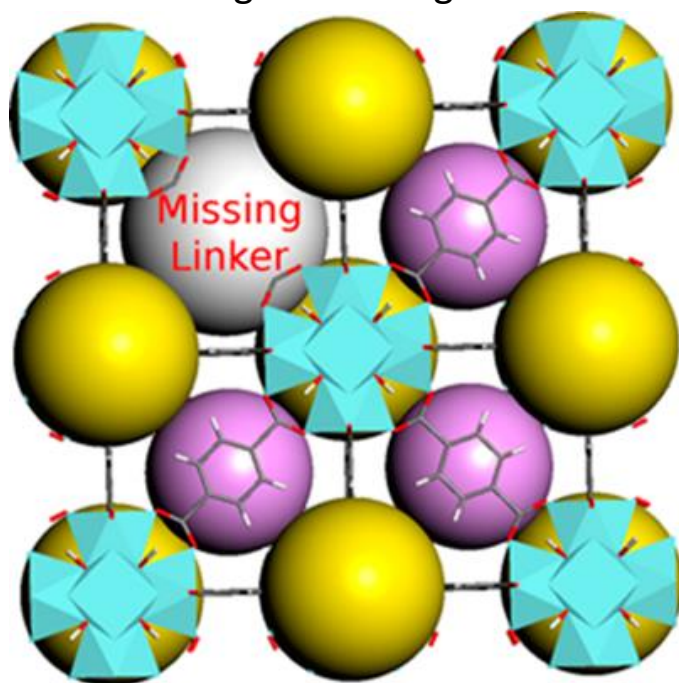
The presence of defects in the structure of UiO-66 was first observed in 2011, revealed by thermogravimetric analysis: the experimental weight loss above 400 °C is often smaller than the ideal loss in case of a non-defective framework.

The PXRD pattern does not show significant correlations with the amount of defects. This is due to the fact that diffraction is dominated by the inorganic part of the framework.



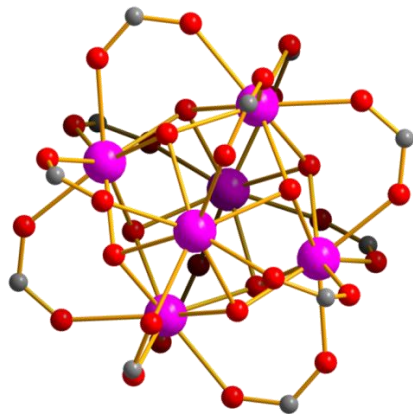
Later on, it was shown that the addition of monocarboxylic acids as modulators favors the formation of «missing linker defects», supposedly by remaining coordinated to the clusters at the solid state. The presence of defects is associated to an increase of porosity.

Neutron diffraction showed that these defects are not ordered and can be crystallographically described by reducing the occupancy of the carbon atoms constituting the bdc ligand.

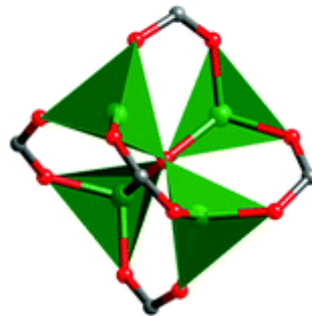


The reason why UiO-66 can stand the presence of missing linker defects (up to 25% of the total linkers can be lost without collapse of the framework) is thought to be the high degree of connectivity of the clusters. 25% of defects means taking away 4 out of 12 linkers, still leaving 8 of them holding the structure up.

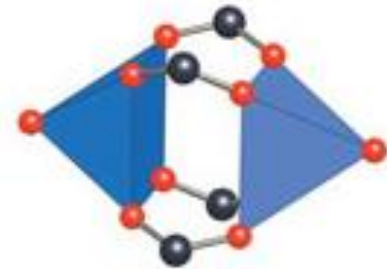
Other MOFs based on less connected SBUs do not survive the removal of linkers.



UiO-66: 12-connected SBUs



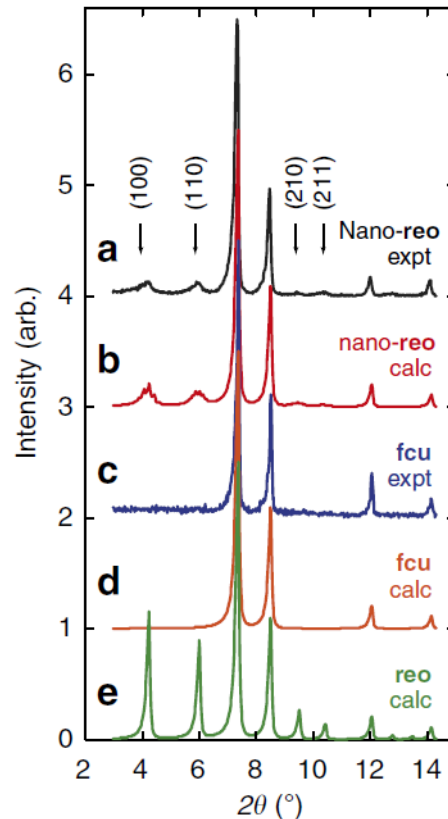
MOF-5: 6-connected SBUs



HKUST-1: 4-connected SBUs

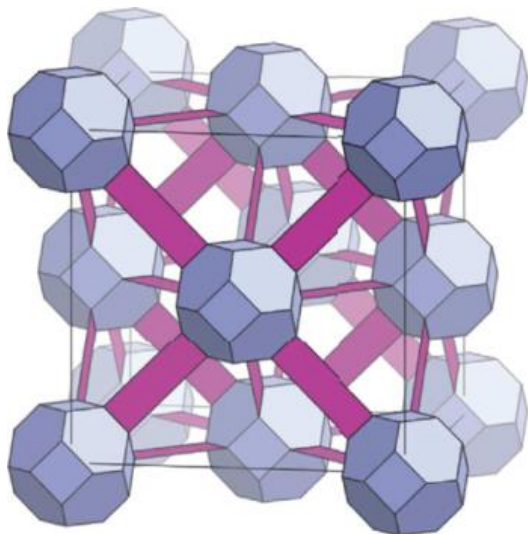
Another type of defects was described in 2014: «missing cluster defects». This time, PXRD can detect the presence of defects, thanks to the appearance of some weak peaks that are symmetry forbidden in the  $Fm-3m$  unit cell of UiO-66.

These peaks can be assigned to a less symmetrical unit cell having space group  $Pm-3m$ .

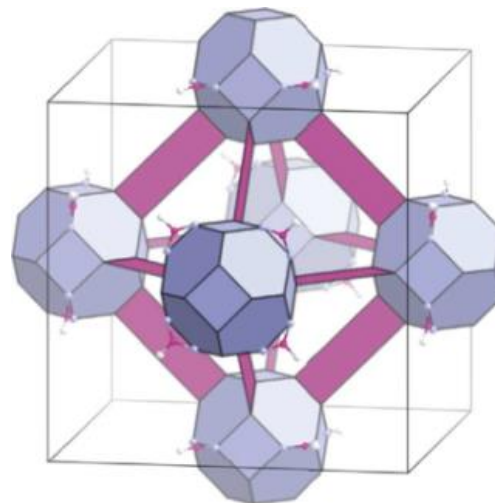


The «forbidden» peaks are generated by an additional crystalline phase having different topology (reo) from that of common UiO-66 (fcu).

In the unit cell of the reo phase, the clusters sitting on the corners of the unit cell are «removed» together with all of their twelve ligands, leaving an 8-connected framework in which formate anions fill the empty coordination sites in the clusters.

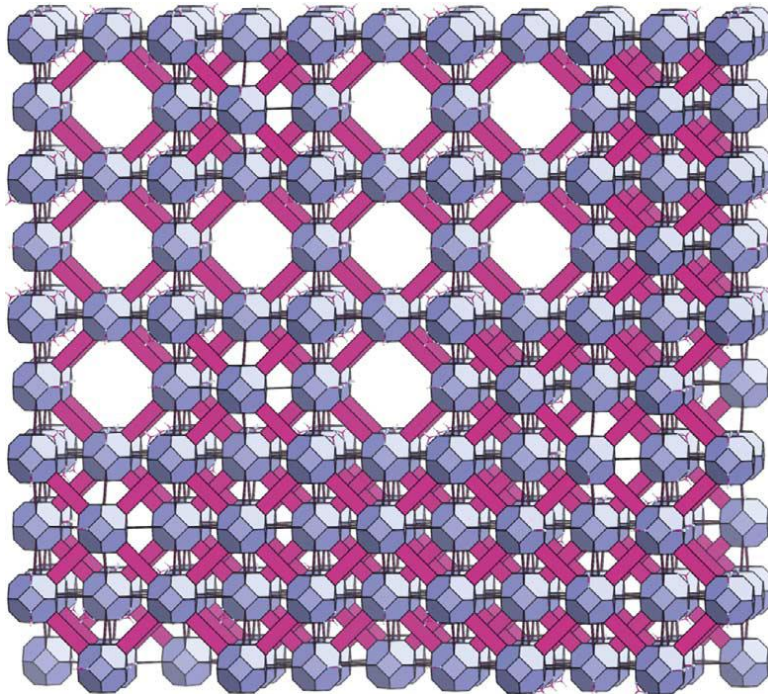


$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_6$   
fcu,  $Fm-3m$



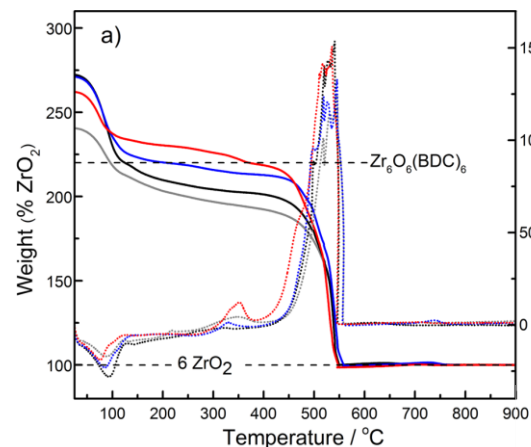
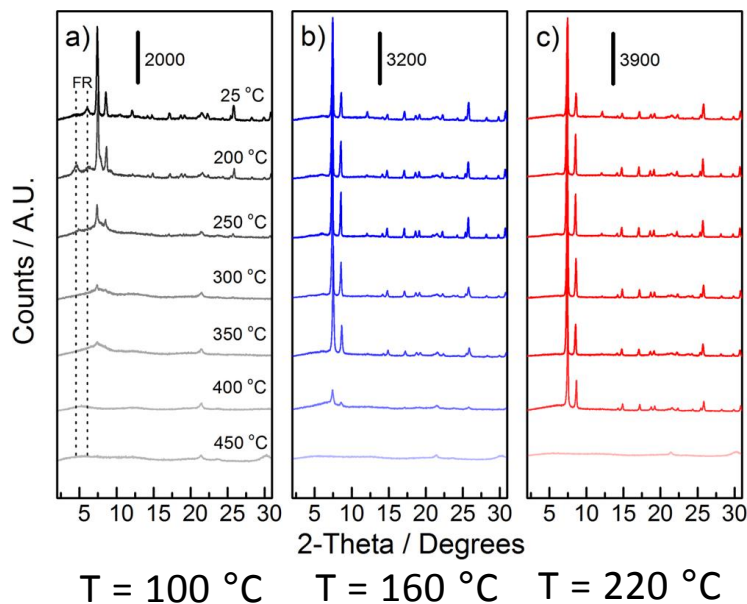
$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_4(\text{HCOO})_4$   
reo,  $Pm-3m$

The reo phase is embedded in the form of «correlated nanodomains», constituted of a few unit cells, in a defect-free fcu matrix: defective UiO-66 can be seen as a gruyere, where the cheese is the «perfect» fcu framework and the holes are the nanoregions of defective reo phase.

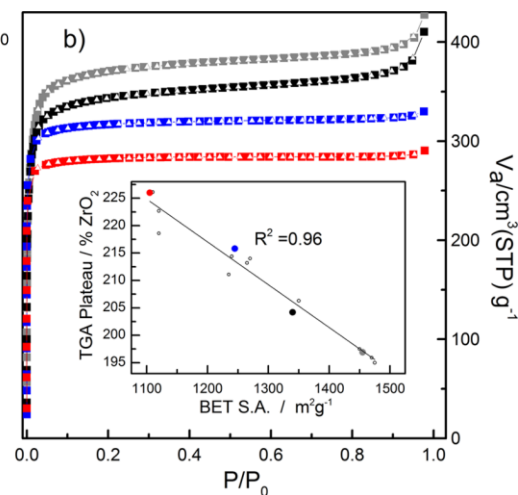


Missing cluster defects have a significant influence on the stability of the framework, which decreases as the amount of defects increases.

The amount of defects can be tuned by controlling parameters such as temperature, ligand/metal ratio and workup procedure.



Gray = 1:1 L/M,  $100^\circ\text{C}$   
 Black = 2:1 L/M,  $100^\circ\text{C}$   
 Blue = 2:1 L/M,  $160^\circ\text{C}$   
 Red = 2:1 L/M,  $220^\circ\text{C}$





ChemComm

COMMUNICATION

View Article Online

View Journal | View Issue

## A robust, catalytic metal–organic framework with open 2,2′-bipyridine sites†

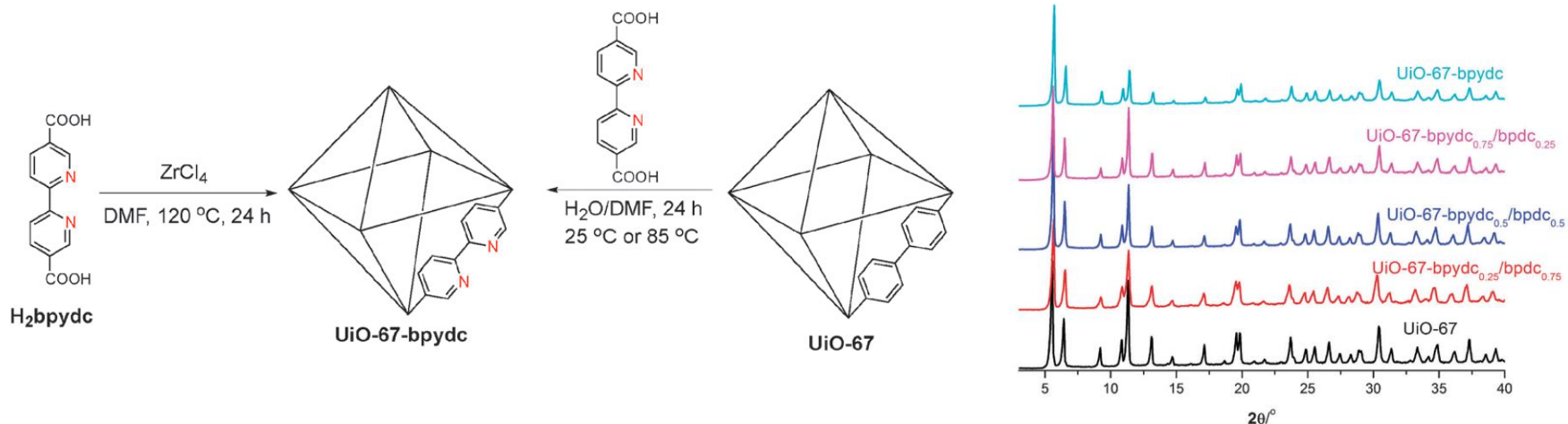
Cite this: *Chem. Commun.*, 2014, 50, 4810

Received 3rd March 2014,  
Accepted 19th March 2014

Honghan Fei and Seth M. Cohen\*

UiO-67 incorporating 2,2′-bipyridine-5,5′-dicarboxylic acid as a linker was prepared by both direct synthesis and PSE.

2,2′-bipyridine has no affinity for Zr, therefore it does not interfere with the formation of the UiO-67 structure.





# Applications in catalysis

PSM of UiO-67-bpydc<sub>0.5</sub>/bpdcc<sub>0.5</sub> was performed in acetonitrile solution containing PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> at 65 °C afforded nearly quantitative metalation of all the bipyridine sites, giving a material of formula Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(PdbpydcCl<sub>2</sub>)<sub>3</sub>(bpdcc)<sub>3</sub>. The crystal structure was not affected by metalation.

The MOF was tested as a catalyst for the Suzuki-Miyaura coupling, displaying excellent performances over several cycles. The material did not undergo significant leaching of Pd and loss of crystallinity.

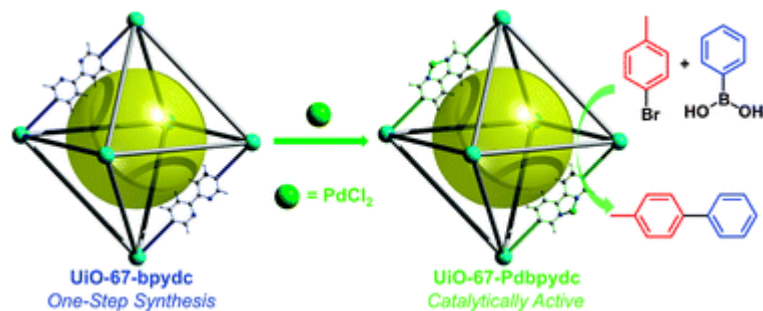


Table 1 Suzuki-Miyaura coupling reaction of 4-bromotoluene and phenylboronic acid<sup>a</sup>

Entry	Catalyst	Pd (mol%)	MOF (mol%)	Yield <sup>b</sup> (%)
1	Blank	0	5	0
2	UiO-67	0	5	0
3	UiO-67-bpydc <sub>0.5</sub> /bpdcc <sub>0.5</sub>	0	5	0
4	PdCl <sub>2</sub>	2.5	0	54(3)
5	Pd(OAc) <sub>2</sub>	2.5	0	51(6)
6	Pd/C (10 wt% Pd)	2.5	0	63(7)
7	UiO-67-Pdbpydc <sub>0.5</sub> /bpdcc <sub>0.5</sub>	2.5	5	89(1)

<sup>a</sup> Reaction conditions: 4-bromotoluene (1.0 mmol), phenylboronic acid (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2.0 mmol) in 5 mL toluene, was heated at 95 °C for 16 h. <sup>b</sup> Yield based on GC-MS analysis, an average value of three runs (error in parentheses).

ChemComm

Cite this: *Chem. Commun.*, 2012, **48**, 11656–11658[www.rsc.org/chemcomm](http://www.rsc.org/chemcomm)

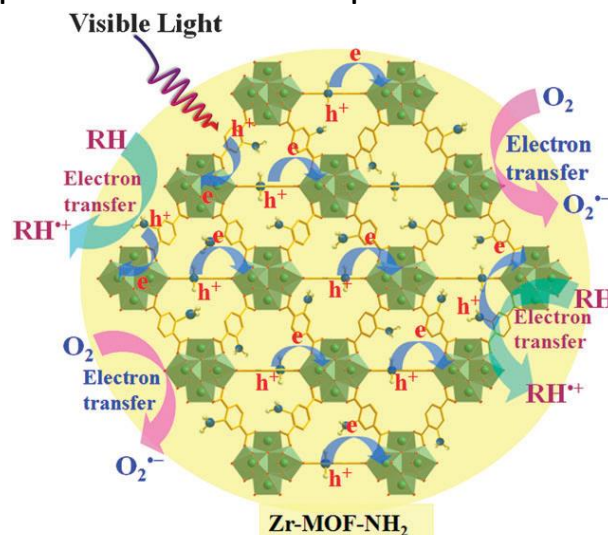
COMMUNICATION

**Amine-functionalized zirconium metal–organic framework as efficient visible-light photocatalyst for aerobic organic transformations†**Jinlin Long,<sup>\*ab</sup> Sibowang,<sup>a</sup> Zhengxin Ding,<sup>a</sup> Shuchao Wang,<sup>b</sup> Yangen Zhou,<sup>a</sup>  
Ling Huang<sup>\*bc</sup> and Xuxu Wang<sup>a</sup>

Received 28th June 2012, Accepted 8th October 2012

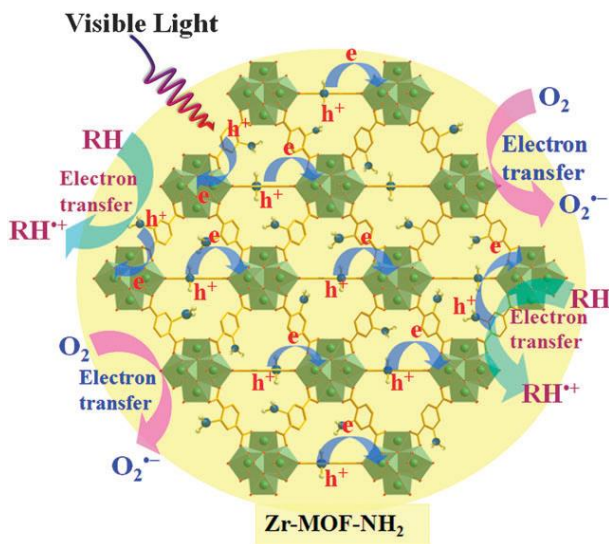
DOI: 10.1039/c2cc34620f

Functionalization of UiO-66 with amino groups makes the material able to absorb visible light. Absorption is due to the conjugated p electron transition from the amine-containing chromophores to the Zr centers and makes the material able to generate electron-hole pairs that can be exploited for catalytic purposes.



Aerobic oxidation of several substrates (alkenes, alcohols, cycloalkanes) was accomplished by exploiting UiO-66-NH<sub>2</sub> as a photocatalyst.

In the process, O<sub>2</sub> captures one electron while the hydrocarbon species captures one hole, generating very reactive radical ion species.



**Table 1** Photocatalytic activity of UiO-66-NH<sub>2</sub> for organic transformations

Substrate <sup>a</sup>	Solvent	Conversion (%) (TOF/h <sup>-1</sup> )	Selectivity (%)	
			Aldehyde/ ketone	Epoxide
β-Methylstyrene	CH <sub>3</sub> CN	14.0 (1.234)	79.1	20.9
	TFT	10.3 (0.908)	76.9	23.1
	Acetone	7.8 (0.687)	80.1	19.9
Styrene	CHCl <sub>3</sub>	9.1 (0.802)	81.0	19.0
	DMF	13.4 (1.181)	57.0	43.0
	CH <sub>3</sub> CN	7.7 (0.766)	83.4	16.5
	TFT	3.8 (0.378)	81.0	19.0
1,2-Diphenylethylene	Acetone	6.7 (0.666)	83.9	16.2
	CHCl <sub>3</sub>	5.3 (0.527)	91.6	8.4
	DMF	2.2 (0.219)	70.1	29.9
Cyclooctene	TFT	0.5 (0.031)	35.0	65.0
	CH <sub>3</sub> CN	0.7 (0.043)	73.1	26.9
Benzyl alcohol <sup>b</sup>	CH <sub>3</sub> CN	0.8 (0.070)	0.0	100
	TFT	0.5 (0.044)	0.0	100
Cyclohexanol <sup>c</sup>	CH <sub>3</sub> CN	11.1 (1.227)	100	0.0
	TFT	13.1 (1.448)	100	0.0
	Acetone	7.5 (0.829)	100	0.0
	CHCl <sub>3</sub>	8.0 (0.884)	100	0.0
	DMF	5.4 (0.597)	100	0.0
Hexyl alcohol <sup>d</sup>	CH <sub>3</sub> CN	2.8 (0.308)	100	0.0
	TFT	2.7 (0.297)	100	0.0
	CHCl <sub>3</sub>	1.6 (0.176)	100	0.0
Cyclohexane <sup>e</sup>	Acetone	2.1 (0.231)	100	0.0
	CH <sub>3</sub> CN	0.9 (0.082)	100	0.0
	CH <sub>3</sub> CN	0.1 (0.009)	100	0.0

<sup>a</sup> Standard reaction conditions: 1200 rpm stirring speed, 12 h reaction time, light intensity ca. 270 mW cm<sup>-2</sup>, light irradiation area of ca. 1.5 cm<sup>2</sup>. Main products are either benzaldehyde or epoxide. Products are <sup>b</sup>benzaldehyde, <sup>c</sup>cyclohexanone, <sup>d</sup>hexanal and <sup>e</sup>cyclohexanone.

ChemComm

COMMUNICATION

View Article Online

View Journal



Cite this: DOI: 10.1039/c5cc00686d

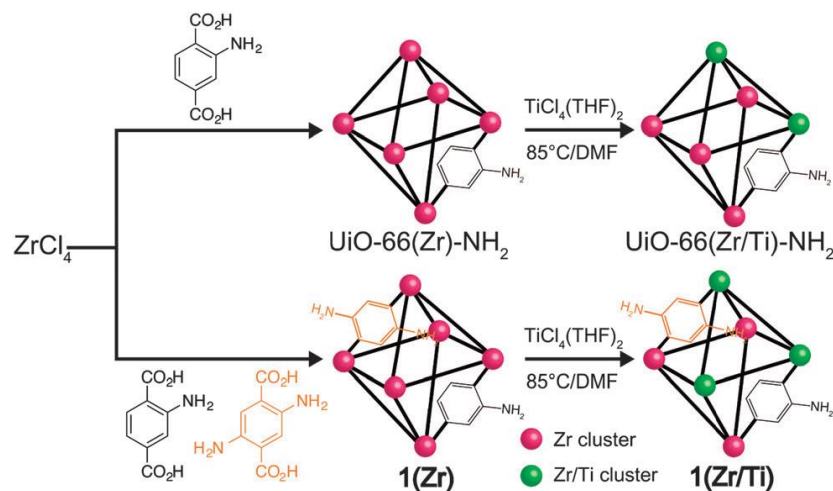
Received 24th January 2015,  
Accepted 18th February 2015

## Photocatalytic CO<sub>2</sub> reduction by a mixed metal (Zr/Ti), mixed ligand metal–organic framework under visible light irradiation†

Yeob Lee,<sup>a</sup> Sangjun Kim,<sup>b</sup> Jeung Ku Kang<sup>\*bc</sup> and Seth M. Cohen<sup>\*a</sup>

Three years later, the system was further modified by introducing a diaminated linker by direct synthesis and successively Ti in the clusters by PSE.

The new material has formula  $Zr_{4.3}Ti_{1.7}O_4(OH)_4(NH_2bdc)_{5.17}(NH_2bdcNH_2)_{0.83}$ .



Both the diaminated linker and the Ti in the clusters contribute to enhance the photocatalytic properties of the material: the linker introduces new energy levels that improve charge transfer to the substrate, whereas Ti lowers the redox potential energy of the clusters, allowing to generate electron-hole pairs with longer lifetime. The MOF was used as a catalyst for reduction of carbon dioxide to formic acid.

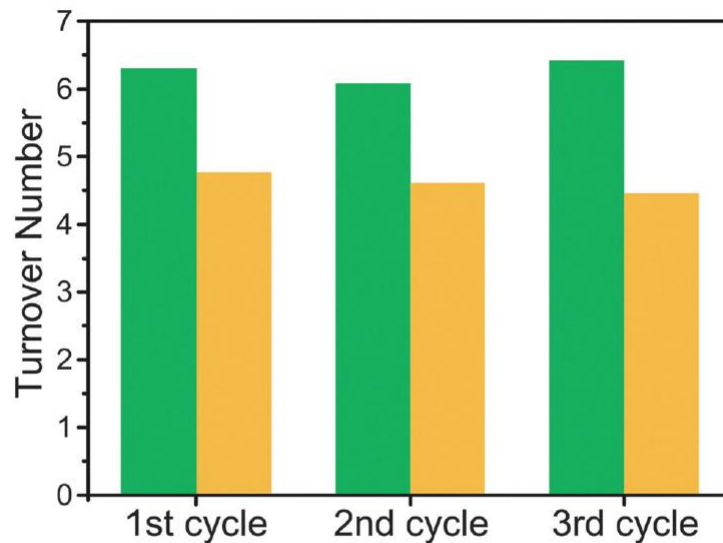
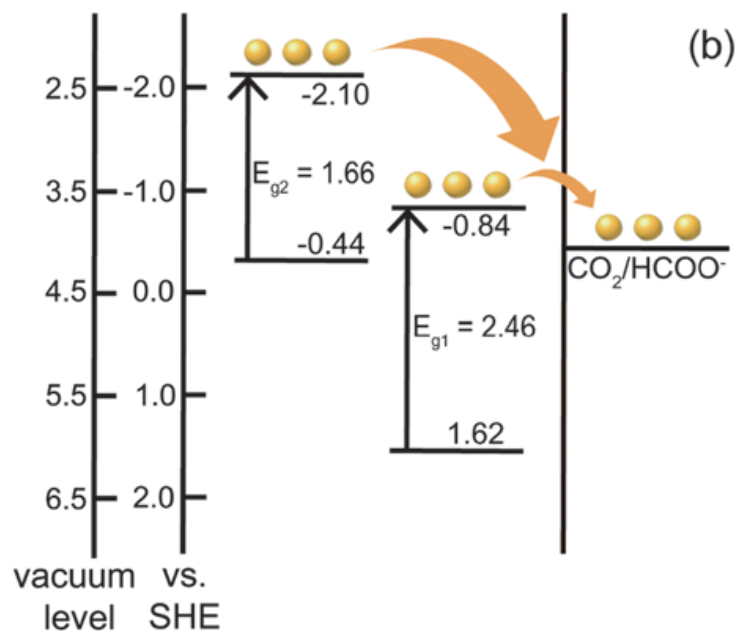


Fig. 2 Turnover numbers of **1(Zr/Ti)** (green) and UiO-66(Zr/Ti)-NH<sub>2</sub> (gold) for photocatalysis of CO<sub>2</sub> to HCOOH over three cycles. Samples were recovered after each cycle and reused under identical reaction conditions.

**J | A | C | S**  
 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

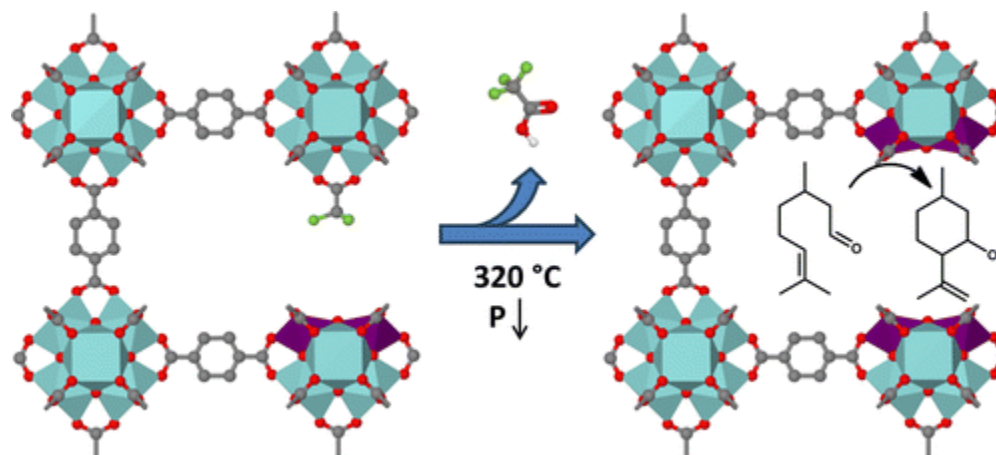
Communication

pubs.acs.org/JACS

## Synthesis Modulation as a Tool To Increase the Catalytic Activity of Metal–Organic Frameworks: The Unique Case of UiO-66(Zr)

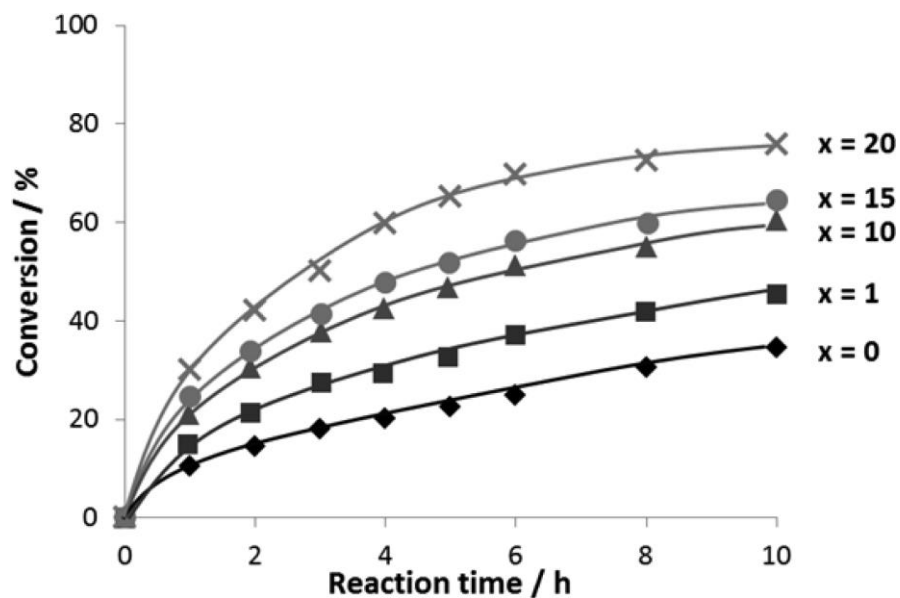
Frederik Vermoortele,<sup>‡</sup> Bart Bueken,<sup>‡</sup> Gaëlle Le Bars,<sup>§</sup> Ben Van de Voorde,<sup>‡</sup> Matthias Vandichel,<sup>†</sup>  
 Kristof Houthoofd,<sup>‡</sup> Alexandre Vimont,<sup>§</sup> Marco Daturi,<sup>§</sup> Michel Waroquier,<sup>†</sup> Veronique Van Speybroeck,<sup>†</sup>  
 Christine Kirschhock,<sup>‡</sup> and Dirk E. De Vos<sup>\*,‡</sup>

Use of modulators can result in the formation of defects and incorporation of modulator molecules in the framework. Activation in vacuum at high temperature leads to removal of trifluoroacetic acid and formation of coordinatively unsaturated sites in the clusters, which display Lewis acidity and can catalyze the cyclization of citronellal.



Catalytic activity is dependent on the amount of modulator used in the synthesis: more modulator means more Lewis-acid sites after activation.

Addition of HCl enhances the incorporation of modulator in the structure, improving the catalytic activity.



x = equivalents of modulator used

