SUMMARY

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PROJECT ACRONYM: MOF-ET-WORK

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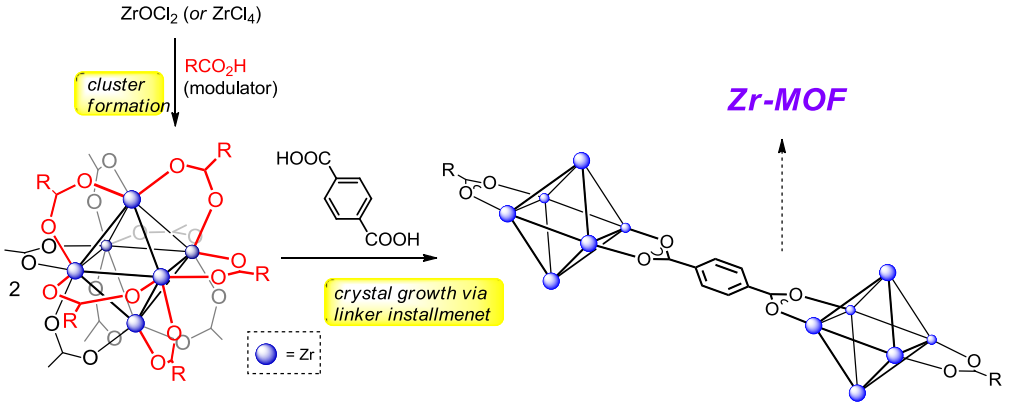
Overview of the Results

***The premise*.** This postdoctoral Marie Curie project dealt with the application of metal-organic frameworks as a platform for selective catalytic processes. From the outset, and following a previous experience by the fellow O. Gutov, Zr-based MOFs were chosen as a system that would provide the highest mechanical and chemical stability. This family of MOFs is constructed using octahedral Zr_6 clusters linked by poly-carboxylate struts. The initial report of such a construct came from the laboratories of K. P. Lillerud (Lillerud *et al*, 2008) and described a metal-organic framework assembled from Zr_6 clusters linked by terephthalic acid struts. The 12 cluster edges are each formed by a μ^2 carboxylate units, and the 8 faces are capped, in alternating fashion, by μ^3-OH and μ^3-O units; this leads the material formulation as $Zr_6(O)_4(OH)_4\mathbf{L_6}$. The terephthalate-based prototype is called UiO-66 (reflecting its ***U**niversitet **i O**slo* origins), and a large number of analogues have been prepared, many of which (such as UiO-67, UiO-68) are isoreticular with UiO-66. This family of MOFs is currently one of the sturdiest, both chemically and mechanically, making it an attractive platforms for the design of catalytic (and, overall, functional) materials. Particularly important is a relatively high (though, perhaps, not as high as was originally hoped for) resistance of Zr-based based MOFs to hydrolysis.



Scheme 1. The modulation phenomenon illustrated for the formation of UiO-66 MOF.

Most commonly, UiO-66 is prepared solvotehrmally by storing (undisturbed) a mixture of a Zr(IV) chloride with the terephthalic acid in DMF at 100-120 ^{o}C. Though not fully understood, the assembly is thought to begin with an initial formation of the Zr_6 octahedra, followed by their assembly into the 3D cubic network. Importantly, these syntheses are commonly performed in the presence of an excess (≥30 equiv) of mono-dentate carboxylic acid, such as acetic or benzoic acid, which acts as a modulator in the crystal growth. The modulator acid is assumed to aid in the initial formation of the Zr_6Mod_{12} species, which would then slowly assemble through carboxylate exchange (Scheme 1). In fact, in his previous work (Northwestern U) Dr Gutov had investigated the use of formic acid in UiO-67 synthesis, showing it to be a superior modulator (Hupp, Farha *et al*). Arguing in favor of the stepwise mechanism is the report by Gross, Schubert *et al*. on the synthesis of a UiO-type MOF using pre-formed and isolated Zr_6 methacrylate clusters.

Understanding the Zr MOF defects. The present Marie Curie project has been designed aiming to benefit from Dr. Gutov's expertise in MOF with the host group's experience in catalytic materials. It was envisaged that the UiO-66 platforms could be particularly effective as it is tolerant of a wide range of substituent on the dicarboxylate linker, enabling the introduction of functional groups, sich as ligands. At the initial stages, quantities of UiO-66 and UiO-67 functionalized with an NH2 group were prepared. Subsequent work on post-synthetic ligand synthesis and metal complex introduction led to the observation of significant interference from the material itself. Specifically, even the parent UiO-66 and UiO-67, in principle unsuitable for metal binding, were found, in some cases, to exhibit significant uptake of metal salts. This uptake, however, was highly synthesis dependent. This phenomenon was traced to the presence of defects within the MOF network, with the quantity and type, in turn, dependent on the modulator and conditions employed. In the simplest cases, a defect consists of a missing linker site, with the corresponding cluster edges capped by the modulator, as illustrated in Figure 1.

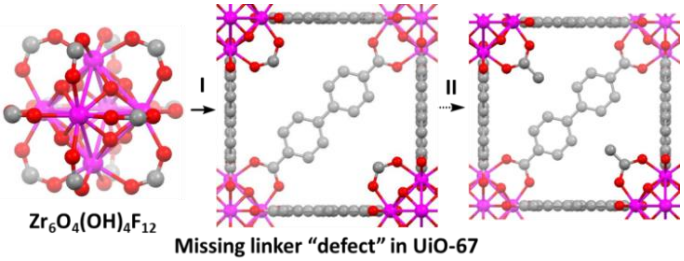
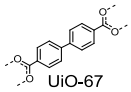
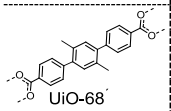


Figure 1. **I** - Proposed scheme for "defect" Zr-MOF formation using H_2bpdc as a ligand in the presence of excess formic acid modulator. **II** – Replacing of anions, capping defects, with an organic acid (acetic here).

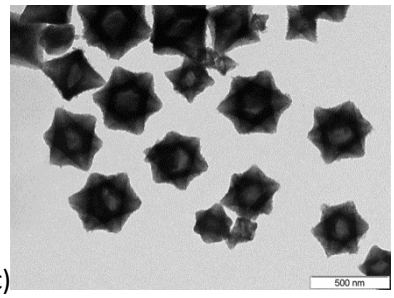
At this point, it was clear that any further development of this MC project would require a detailed understanding of the defect phenomenon, unavailable at the time this work began. Therefore, an

ample study was conducted aiming to understand the relationship between the modulator employed and the properties of the resulting material. The study also facilitated the group's entry into the MOF field. Necessary equipment was also acquired at this point, including a temperature-controlled oven and a medium-potency centrifuge for sample work up. At this stage, we also established fluid contacts with the facilities (ICIQ, URV, others) for MOF characterization. The study covered the three common structures, namely that based on the terephthalic acid (UiO-66), the biphenyl-dicarboxylic acid (UiO-67) and the methyl-substituted terphenyl dicarboxylic acid (UiO-68Me). The modulators explored were benzoic acid, acetic acid, trifluoroacetic and, formic acid and HCl. The study allowed, for the first time, to establish a relationship between the modulator employed and the defect content, porosity and crystallinity of the resulting MOF. Thus, while the canonical defect-free MOF formulation is $Zr_6(O)_4(OH)_4\mathbf{L_6}$, the samples obtained were better described as $[Zr_6O_4(OH)_4]\boldsymbol{L}_{(6\text{-}0.5n)}Mod_n$ (***L*** = ditopic linker acid; Mod = modulator anion). Hence, the *n* parameter here describes the defect contents, and varies widely across the systems studies; this, in turn, has a profound effect on particle size and morphology, as well as on gas uptake (Table 1, Figure 2).

Table 1. Composition and properties of *de-novo* synthesized MOFs. MOFs formulated as $[Zr_6O_4(OH)_4]\boldsymbol{L}_{(6\text{-}0.5n)}Mod_n$ (***L*** = ditopic linker acid; Mod = modulator anion).

linker	modulator	***n***[a]	MOF	surf. area (m^2/g)	size (nm)[b]
 UiO-67	formic	0.8	UiO-67**f**[c]	2600	50
	benzoic	0.35	UiO-67**b**	2400	7500
	trifluoroacetic	0.4	UiO-67**t**	2350	20
	acetic	0.8	UiO-67**a**	2100	350
	hydrochloric	*nd*	UiO-67**h**	1470	250
 UiO-66	formic	0.6	UiO-66**f**	1250	10
	benzoic	3.5	UiO-66**b**	1520	300
	acetic	1.6	UiO-66**a**	1130	10
	hydrochloric	--	UiO-66**h**	1450	200
 UiO-68'	acetic	0.2	UiO-68'**a**	3600	1000
	benzoic	0.2	UiO-68'**b**	3200	12000

[a] ***n***: number of modulator groups per Zr_6 cluster according to ^{1}H NMR; [b] average particle size determined by TEM/SEM; [c] the letter index at the end of MOF code defines for modulating acid used in the synthesis.

A. (acetic) 

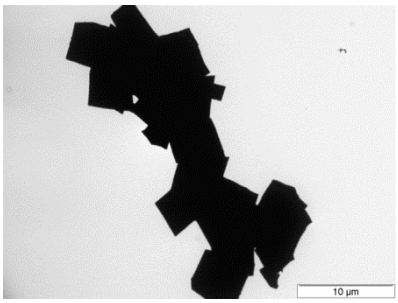
B (benzoic. 

Figure 2. Difference in morphology between samples of UiO-67 prepared via acetic and beznoic acid modulation.

As part of this study, the dynamic nature of the defect sites was also explored as a tool to MOF modification. Thus, missing linker sites were found amenable to simple carboxylate exchange, and even allowed for MOF healing, a process whereby the defects are eliminated by post-synthetic installation of the missing linkers. Importantly, the work allowed for the single crystal structure determination of UiO-67, which up to that point was only structurally described based on powder X-Ray structure (Figure 3).

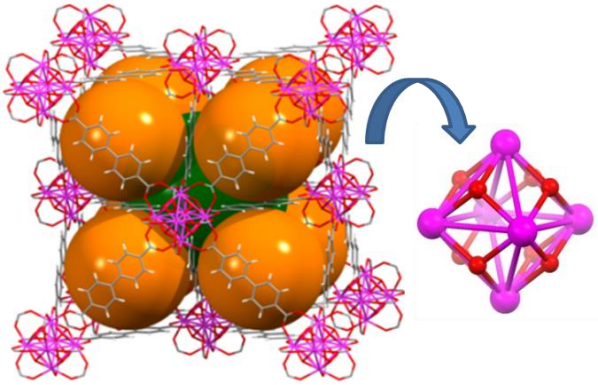


Figure 3. A fragment of "healed" UiO-67**b** crystal structure demonstrating the overall topology, with the two types of pores (larger green and smaller orange) schematically indicated with spheres (left). Structure of $Zr_6O_4(OH)_4^{12+}$ cluster (right). Hydrogen atoms are omitted for clarity. Colors corresponding to atoms: C (grey), O (red), Zr (purple).

Importantly, the high defect content was correlated with the ability of a MOF to soak up metal ions. As an example, the high defect content samples of UiO-66f (via formic acid modulation) exhibited high affinity for Cr(III) ions, which can be appreciated even visually (Figure 4).

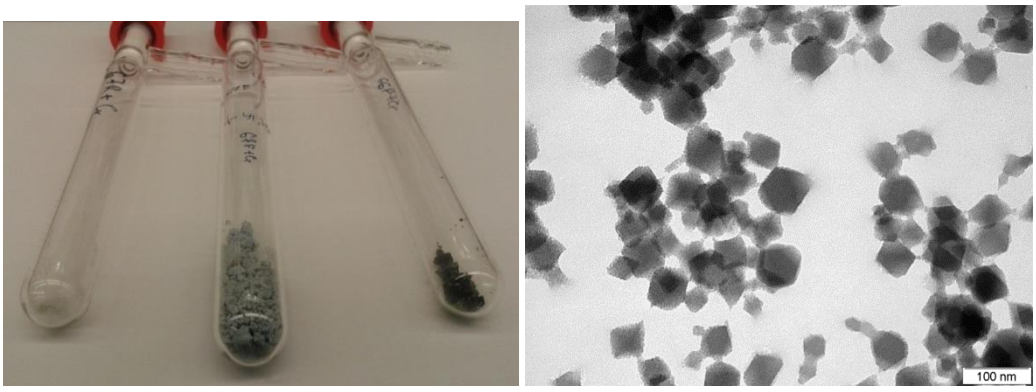
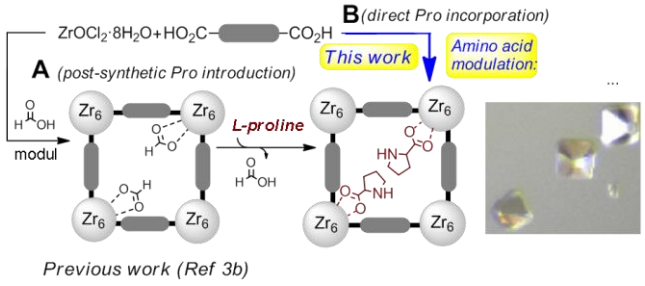


Figure 4. left) Images of the chromium-treated samples: "healed" UiO-66b, UiO-67f-Cr (left) and UiO-66f-Cr (right). b) TEM image of UiO-67Cr.

This work was reported with the MC fellow as co-corresponding author:
Metal–Organic Framework (MOF) Defects under Control: Insights into the Missing Linker Sites and Their Implication in the Reactivity of Zirconium-Based Frameworks
O. V. Gutov*, M. González Hevia, E. C. Escudero-Adán, and A. Shafir*, *Inorg. Chem.* **2015**, *54*, 8396–8400. Cited: 9 times in 1 year.

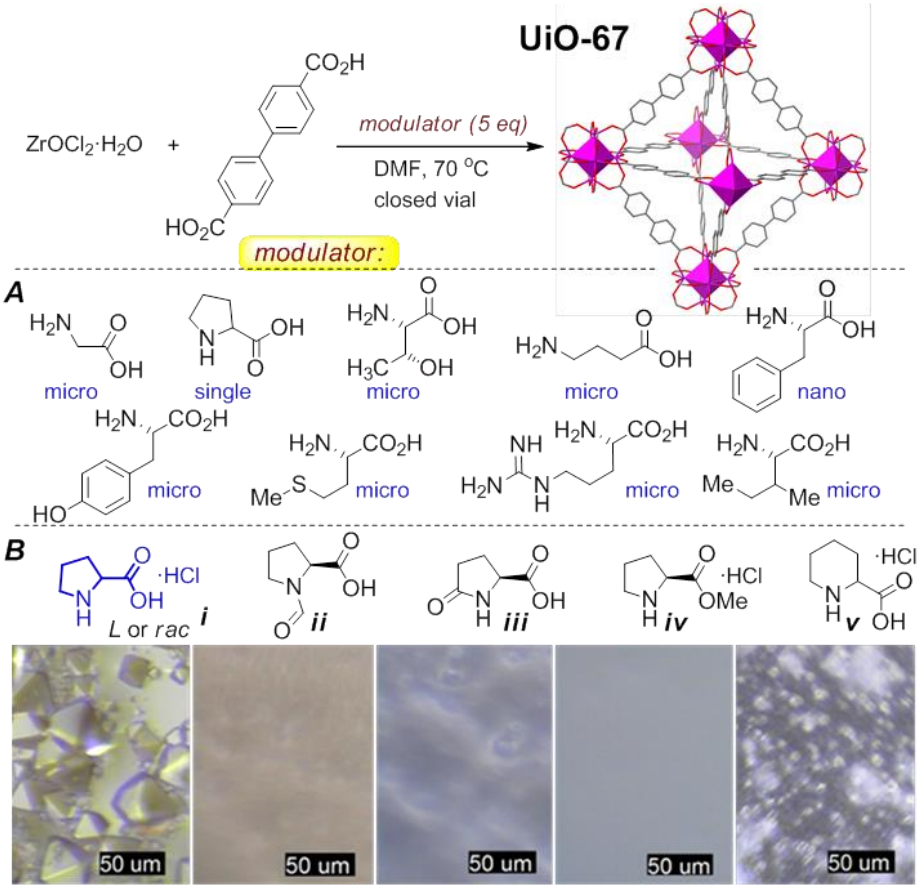
Proline as superior modulator in Zr MOF synthesis. During our work on defect control, we also found that *L*-Proline (L-Pro) could be incorporated at missing linker defect sites by treating samples of UiO-67 (Scheme 2A), which contained formate-capped defects, with L-Proline hydrochloride. This led us to ponder the possibility of achieving Zr-MOFs containing L-Pro (or other amino acids) directly through modulation with the corresponding amino acid (Scheme 2B). Independently, in 2015 Forgan and coworkers exploited the excellent modulating abilities of L-Pro and studied the phenomenon of amino acid modulation.



Scheme 2. A) Anchoring of L-Pro onto Zr-MOF (ref. 3b); B) amino-acid modulated MOF synthesis.

For the modulated synthesis of metal-organic framework, the solubility of the modulator acid in the reaction medium is likely a key factor for efficient growth of the 3D network. For several amino acids, including L-proline, the free base form proved largely insoluble in DMF, and showed poor modulating

ability in the preparation of Zr-MOFs. Experimentally, converting the amino acids into the corresponding hydrochlorides proved crucial to ensure their solubility in DMF and enabled their use as modulators in the syntheses of Zr-MOF.



Scheme 5. A) Amino acid screen in UiO-67 synthesis; B). Proline vs analogues in modulated synthesis.

As a key finding, it was discovered that most of the amino acids tested were competent as modulators in the growth of both UiO-66 and UiO-67. Importantly, proline proved to be an exceptional modulator for the synthesis of UiO-67, leading to the formation of single crystalline samples with only 5 equiv of the modulator. One may recall that typical modulator loading are 30-50 equiv (Figure 5). Addition experiments were carried out in order to pinpoint the structural parameters responsible for proline's unique modulation capacity; interestingly, any structural modification proved detrimental, including the usage of the analogous 6-membered pipecolinic acid (entry **vi**), which suggests subtle conformational effects on modulating ability.

Applying proline modulator to other linkers led to the synthesis of several of these in the form of X-ray quality single crystal. As a proof of concept, in addition to re-determining the single crystal

structures of UiO-67 and of a methylated UiO-68 derivative (also known as PCN-56), we now prepared and solved the single crystal structure of the previously unknown UiO-67Cl, and of the NU-801, synthesized from the 1,4-benzenediacrylic acid (Figure 1, Method A). The structure of the latter had previously been determined from powder X-Ray analysis, and the new determination corroborates the previous structure. Two such examples are illustrated in Figure 5.

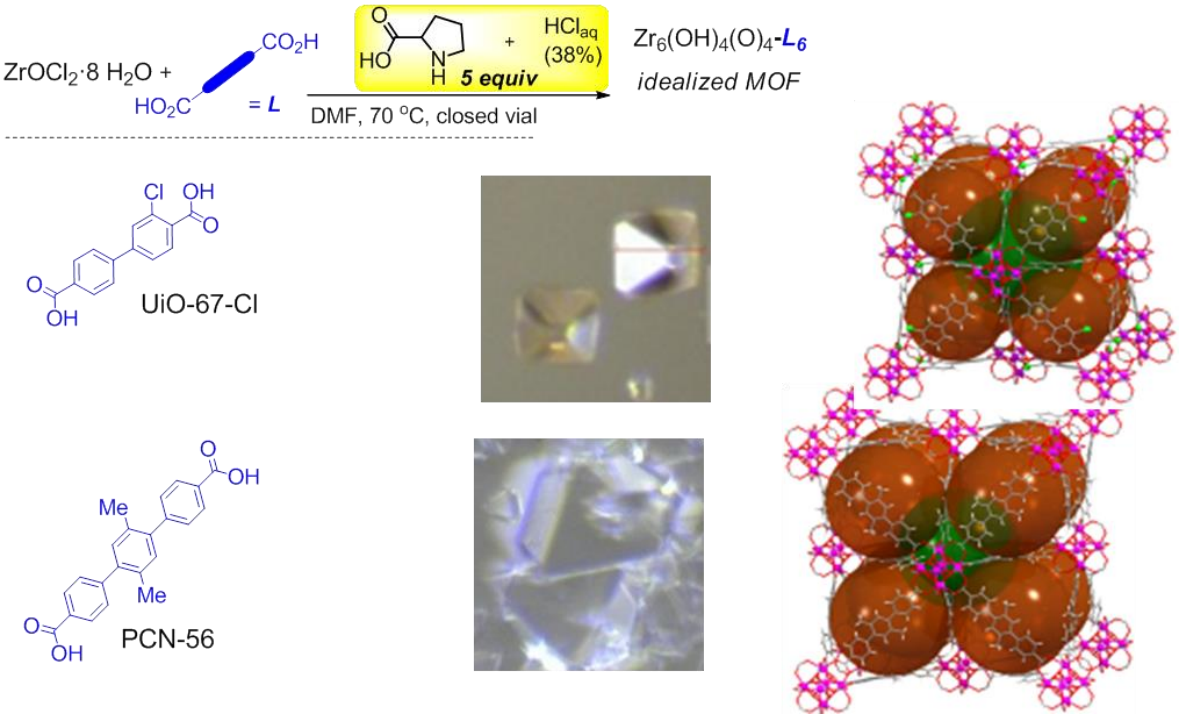


Figure 5. Two examples of proline-modulated formation of single crystals of Zr MOFs.

As an interesting finding, the muconate-derived framework presents a structure different from that previously determined from pXRD. While the reported structure featured the muconic acid in the s-cis conformation with a framework essentially identical (through disorder) to UiO-66, the single crystal structure of the material obtained here via proline modulation (Method B) is constructed with linkers in the extended s-trans conformation (Figure 6).

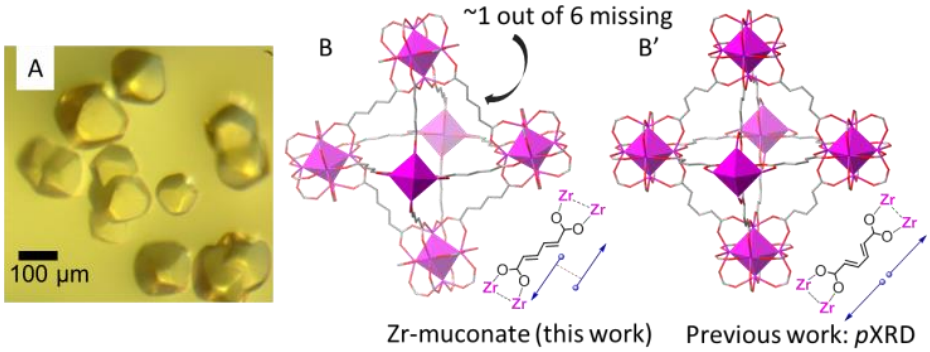


Figure 6. A) Crystal of the Zr muconate obtained by Method B, and B) the material's single crystal X-ray structure. For comparison, the pXRD structure for the material synthesized from Zr6 methacrylate ¡is shown as B'.

A second corollary of amino acid modulation is the potential entry into amino acid-containing MOF structures. We found a roughly inverse correlation between amino acid incorporation and crystal size/quality. This opens the door for future incorporation of bigger biomolecules (peptides etc.) and the the design of new hybrid materials for separations and catalysis. Finally, the amino acid modulated Zr-MOFs demonstrated improved CO2 capture capacity comparing to non-functionalized material.

This work has been submitted and is currently under revision

Modulation by amino acids: towards superior control in Zr-MOFs synthesis

O. V. Gutov,* S. Molina, E C. Escudero-Adán, A. Shafir* *Chem. Eur. J.* Under revision

Zr MOFs in catalysis. As mentioned, earlier, the earlier stages of this project consisted in the development of parameters necessary for the control of the properties of Zr MOFs. As we and others have shown, this knowledge was rather fragmented regarding the phenomenon of Zr MOF defects, the effect of modulation on MOF properties and the lack of precise control over particle size and porosity. Having gained significant knowledge in these aspects, the last part of this project has focused on the design of Zr MOF for industrially relevant catalytic processes. This work is currently in advanced stages, and will be reported in due course.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