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MOF defects under control: insights into the missing linker sites and their implication in the reactivity of Zr-based frameworks.

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Metal-Organic Frameworks · Defects · Catalysis · Zr-based MOFs · Solvothermal Synthesis
Modulated Synthesis of MOFs.

Abstract: For the 3D Metal-Organic Frameworks, MOFs, the presence and nature of structural defects has been recognized as a key factor shaping the material's physical and chemical behaviour. In this work, the formation of the “missing linker” defects has been addressed in the model biphenyl-4,4'-dicarboxylate (bpdc)-based Zr MOF, UiO-67. The defect showed strong dependence on the nature of the modulator acid used in the MOF synthesis; the defects, in turn, were found to correlate with the MOF physical and chemical properties. The dynamic nature of the Zr_6 (node)-monocarboxylate bond showed promise in defect functionalization and “healing”, including the formation of X-ray quality “defect-free” UiO-67 single crystals. Chemical

transformations at defect sites have also been explored. The study was also extended to the isorecticular UiO-66 and UiO-68' systems.

1. Introduction.

Research into regular metal-organic frameworks (MOFs) has experienced a spectacular growth, due, in part, to the possibility of controlling the material's property via a judicious choice of just two building units: linkers and nodes.¹ The latter structural element has spanned a range of metal ions, bimetallic units (e.g. Cu₂) and clusters, the latter famously exemplified by the Zr₆ oxometallate cluster node introduced in 2008 by Lillerud and co-workers.² Prior to this seminal report,² discrete octahedral Zr₆ clusters had already been studied by Schubert *et al*³ in the context of the carboxylate-assisted sol-gel formation of zirconia. The idealized cluster was thus formulated as Zr₆(μ³-OH)₄(μ³-O)₄(μ²-O₂CR)₁₂ (Figure 1), with the six Zr ions occupying the vertices of an octahedron held together by 12 μ² carboxylate edges. Importantly, it was shown early on by Schubert, Gross and co-workers that a cluster-bound carboxylate ligand could be exchanged for an external carboxylate without affecting the cluster core (Figure 1).^{3c}

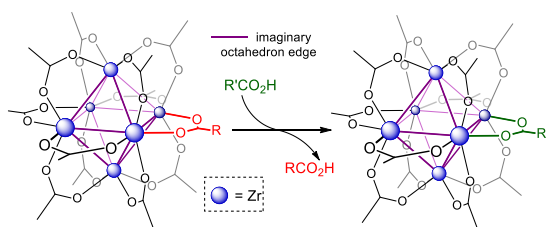


Figure 1. The structure and dynamic nature of the basic Zr₆(OH)₄(O)₄(μ²-O₂CR)₁₂ cluster core (capping μ³-OH and μ³-O groups omitted).

Thus, in the prototypical UiO-66 MOF structure each Zr₆ node is bound (ideally) to 12 terephthalate ligands acting as the struts/linkers.² This family of Zr-based structures has shown

promise in a wide range of applications^{4,5} including catalysis,⁴ gas storage,^{5a,b} and heavy metal capture^{5c} (to name just a few), due, in large part, to the elevated stability of such materials. For the broader UiO family, the suffix following the UiO designator is defined by the linear linker diacid, as in the isorecticular series UiO-66 (*p*-phenylene diacid), UiO-67 (4,4'-biphenylene diacid) and UiO-68 (4,4''-terphenylene diacid). MOFs based on the Zr₆ cluster are usually prepared via a solvothermal reaction between a simple Zr(IV) precursor (e.g. ZrCl₄ or ZrOCl₂) and the diacid.

Importantly, in 2009, Gross, Serre et al. showed that the labile nature of the Zr₆-monocarboxylate linkage (Figure 1) can be exploited to form Zr-MOFs using pre-formed Zr₆ methacrylate clusters under mild conditions, allowing for the synthesis of the otherwise inaccessible UiO-66-type zirconium muconate.^{7a} This publication served as the basis of the “acid modulation” in the synthesis of UiO-66, whereby a reaction between the Zr(IV) precursor and the ligand is performed in the presence of a monocarboxylic acid additive, aiding the method reproducibility and product crystallinity.⁷

Such acid modulation has since become ubiquitous for the synthesis of Zr-MOFs, including the development of space-time efficient large scale synthesis of UiO-66.⁸ In view of the precedents,^{7a} such acid-modulated reaction might begin with a rapid formation of the soluble discreet modulator-capped Zr₆ clusters, which would then assemble into the final 3D structure via reversible ligand exchange with the ditopic linker acid (Figure 2).

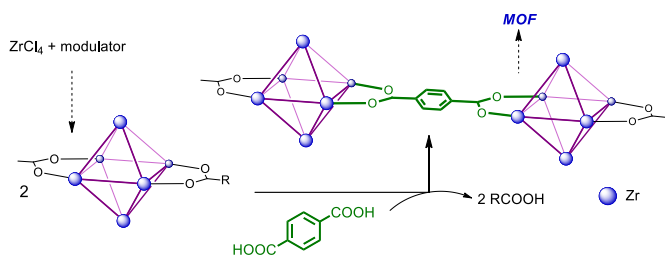


Figure 2. A modulated stepwise growth of the UiO-type Zr MOF network.

On the “flipside” of acid modulation is the possibility that some of the modulator remain in the structure, leading to network containing missing linker defects (Figure 3).^{4b,d,9} Such defect tolerance is quite unique to Zr-based MOFs, and is due to their high degree of connectivity, preventing the structure collapse.¹⁰ The presence of missing linker defects has been demonstrated to have a dramatic effect on the MOF gas sorption capacity,^{9,10} catalytic activity^{4b,d} and stability.¹¹ For UiO-66, a correlation between acetic acid modulation and the degree of structural defects has been elegantly demonstrated; with the acetates shown by to occupy the “missing-linker” edges of the cluster.^{9a}

Working with the next higher homologues, UiO-67, we have now established that acid modulator is a powerful tool to control the particle properties, and that a variety of acids can be used, each leading to a unique set of MOF properties.

2. Experimental Section

2.1. General Details. All air- or water-sensitive reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Water was obtained from a deionized water source provided by ICIQ. Powder X-ray diffraction (PXRD) patterns were recorded on a D8 Advance Series 2 θ / θ powder diffraction system using CuK $_{\alpha}$ 1-radiation in transmission geometry. Nitrogen isotherms were measured on Autosorb iQ adsorption analyzer (Quantachrome). Measurements were performed at 77 K and the temperature was held constant using liquid N₂. Surface areas of activated zirconium-based MOFs were calculated from nitrogen isotherms based on the adsorption model of Brunauer-Emmet-Teller (BET). The pressure range used to calculate the BET surface area was selected so it fulfills the two “consistency criteria.”

2.2. Example of Modulated Synthesis: Preparation of UiO-67f. *The solvothermal synthesis was conducted in a glass jar equipped with a Teflon-lined screw tap.* The solid $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1.2 g, 3.7 mmol) was dissolved in a mixture of DMF (100 mL) and HCOOH (4 mL) under a 5 min sonication. The 4,4'-biphenyldicarboxylic acid (1 g, 4.1 mmol) was added and the mixture was sonicated for an additional 5 min. The jar was then stored undisturbed for 24 h in a temperature-controlled oven preheated to 120 °C. At this point, a part of the supernatant solution was decanted, and the remaining resulting precipitate was separated by centrifugation, washed with DMF (4 x 50 mL). Each washing cycle consisted in adding the DMF, stirring (with spatula) to achieve a homogeneous suspension, allowing the mixture to repose for 30 min, and then isolating the precipitate by centrifugation. The same procedure was then repeated with acetone washes (5 x 50 mL). To remove solvents from pores, the material was evacuated for 12h at room temp., and then for 6 h at 120 °C (ramp 1C/min). Yield: 0.95 g. See Supp. Info for product characterization.

3. Results and Discussion

3.1. Acid Modulation for UiO-67. Parting from the recently published small-scale synthesis (~50 mg) of UiO-67 modulated by the formic acid,^{5b} we began by identifying more practical conditions allowing for a 20-fold increase of the initial synthesis scale and 4-fold decrease in reaction time, while retaining material's high quality. Thus, a controlled solvothermal reaction of $\text{ZrOCl}_2 \cdot \text{hydrate}$ with H_2bpdc in the presence of approx. 30 equiv of formic acid in DMF, followed by thorough washings and evacuation, affording ~1 g batches of the activated UiO-67. The powder X-Ray diffraction (pXRD) pattern and the Brunauer–Emmett–Teller surface area of the newly synthesized UiO-67 (BET SA = 2600 m²/g) match the literature data for the smaller-scale preparation, confirming the reproducibility and scalability of the method. At this point, the presence of the

formic acid modulator in the final structure was confirmed by the characteristic formate $^1\text{H-NMR}$ resonance (8.1 ppm) in the acid-digested samples of the activated UiO-67. From the relative peak area, the material was formulated as $\text{Zr}_6\text{O}_4(\text{OH})_4\text{L}_{5.6}(\text{form})_{0.8}$ ($\text{L} = \text{H}_2\text{bpdc}$), i.e. with roughly 1 out of 12 linkers missing on each Zr_6 node (entry 1, in Table 1).

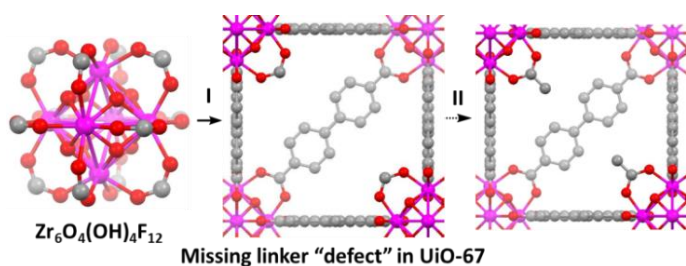


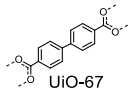
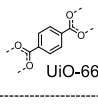
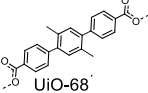
Figure 3. I - Proposed scheme for "defect" Zr-MOF formation using H_2bpdc as a ligand in the presence of excess formic acid modulator. **II** – Replacing of anions, capping defects, with an organic acid (acetic here).

Going a step further, it was found that, in addition to the formic acid, several common acid additives were all able to afford highly-crystalline samples of UiO-67 (Figure S1), with the modulator retained in quantities ranging from 0.35 per Zr_6 cluster (PhCO_2H), up to 0.8 molecules per Zr_6 (AcOH) (Tables 1, S1). Further insight into modulator effect was provided by TEM, where the particle size and morphology were found to vary from 20-50 nm spherical nanoparticles obtained using formic or acetic acid up to single crystals obtained via benzoic acid modulation (Tables 1, S2). The defect content was directly reflected in the BET SA (N_2 sorption @ 77K, Figure S2; Table 1). Given that materials with missing linkers (or nodes) tend to have lower sample densities, and since BET SA is calculated on a per gram basis,^{9a,10b} samples of UiO-67f were found to feature the highest surface area, consistent with its increased missing linker percentage and the highest molecular weight difference between the missing linker and the modulator taking its place.

The shapes of the isotherms demonstrate a mesoporosity step attributed to missing linkers^{9d} at around 0.14 P/P0 in all UiO-67 except for the largely “defect-free” UiO-67**b**. The material UiO-67**h** obtained with the aid of hydrochloric acid demonstrates the lowest porosity, suggesting a poor modulating ability for HCl. As expected, by increasing the initial ligand/Zr ratio from 1.1 to 1.6, the missing linker content was decreased by 40% in the case of formic acid and by 60% for acetic acid modulation. In contrast, the reaction time (1-10 days) did not significantly affect the amount of defects (Table S3).

As already mentioned, the linker size in UiO-67 lies between that of UiO-66 (terephthalate), and the less well developed terphenyl-based UiO-68, for which only the ligand-substituted derivatives are known. Thus, a subset of the modulators was applied to the synthesis of UiO-66 and UiO-68', the latter built using the 2',5'-dimethyl-[p-terphenyl]-4,4''-dicarboxylic acid (Table 1).¹² While the resulting UiO-68' was found to be largely modulator-free ($n = 0.2$), in the case of UiO-66 the approach led to modulator incorporation at the missing linker sites in amounts ranging from $n=0.6$ per cluster (acetic) to 3.5 (benzoic).

Table 1. Composition and properties of *de-novo* synthesized MOFs. MOFs formulated as $[\text{Zr}_6\text{O}_4(\text{OH})_4] \text{L}_{(6-0.5n)}\text{A}_n$ (L = ditopic linker acid; A = modulator anion).

	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	<i>nd</i>	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* Zr₆ cluster according to ¹H 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.

As was the case with UiO-67, TEM imaging of the newly synthesized UiO-66 and 68 showed that benzoic acid provides the largest particles, and formic acid the smallest. The highest surface area for our UiO-66 samples was observed for UiO-66**b**, in principle in agreement with its high defect content (3.5 out of 12 linkers missing on each Zr₆ cluster). Such simple correlation, however, was taken with caution, given that the very high surface area (60% more than theoretically predicted for a perfect structure)^{5a} would not result from a simple ligand substitution with the bulky and heavy benzoate. It is likely that the material features another type of defects, where the entire metal clusters are missing from the structure, and with those Zr₆ clusters adjacent to the resulting vacancies being capped by the modulator. The existence of such defects has been demonstrated for a related MOF *via* X-Ray diffraction studies.¹³

3.2 Dynamic Ligand Exchange and “Healing”. Given the dynamic nature of the Zr₆–monocarboxylate bonds,^{3,14} we wondered whether the modulator acid units at the defects sites could exchange a posteriori for another acid. Indeed, the treatment of UiO-67**f** and UiO-67**b** (0.8 and 0.35 modulator anions per cluster) with a solution of acetic acid led to new UiO-67 samples

which contained 0.8 and 0.3 acetate anions per cluster, respectively. For the MOFs prepared using the hydrochloric acid modulator, the missing linker defects, if present, are assumed to be capped by the –OH units, and are difficult to quantify directly. In this case organic acid treatment was found to be very useful, since defect content may then be determined by the organic acid uptake. Using this approach, the number of missing linkers in UiO-66**h** was found to be approx. 4 per cluster, in good agreement with ref. 9e where it was determined based on porosity experimental and computational studies. The reverse process is also possible, as observed in the hydrolytic removal of the acetates from UiO-67**a** by treatment with diluted hydrochloric acid. In addition to defect quantification purposes, the method could serve as a straightforward approach for the introduction of new functional substituents into Zr-MOFs. Thus, the formic acid treatment of UiO-66**b** led to the benzoate being replaced with lighter formate, leading to the predicted increase in both the nitrogen uptake (Figure S4) and the surface area (1600 m²/g, the highest among the UiO-66 samples studied here). Additionally, the method is promising for the introduction of aminoacids into Zr-MOF, as seen upon treating UiO-67**f** with *L*-proline hydrochloride, leading to a complete exchange of the formate for the amino acid. The method may open the door to new chiral materials for separation and catalysis applications.

Next, we wondered whether a defect-containing Zr-MOF could be similarly “healed” by infusing it with excess of the corresponding dicarboxylic acid linker (similarly to recently reported ‘linker installation’ phenomena¹⁵), which of course, would only be viable for systems with just the “missing linker”, and not in those missing entire nodes. In principle, the latter might be then distinguished from the former by the ease with which the newly incorporated ligand diacids (presumably just lining the lacunary sites) might once again be replaced by another acid. Hence, samples of UiO-67**a**, **b** and **f** were treated with a solution containing H₂bpdca for 48 hours at 120

°C. Indeed, in all cases the ^1H NMR spectra of the digested samples showed the virtual disappearance of the modulator (Figure S3). The treated samples demonstrated improved isotherms shapes (Figure S5), but also decreased N_2 uptake indicating the proportionally higher weight and steric bulk contribution of the H_2bpdc comparing to the smaller modulator acids. Furthermore, submitting samples of the healed UiO-67b to this treatment led to very low acetic acid reuptake (likely on the surface) consistent with true defect repair. In fact, crystals of the healed UiO-67b were found suitable for X-Ray diffraction, which incidentally had not been reported when this work was initiated. Although during the course of this work a synchrotron single-crystal UiO-67 structure was reported,¹⁶ in our case, the structure was solved using a conventional diffractometer (Figure 4, Table S5). The 3D architecture of UiO-67 determined by both methods is the same.

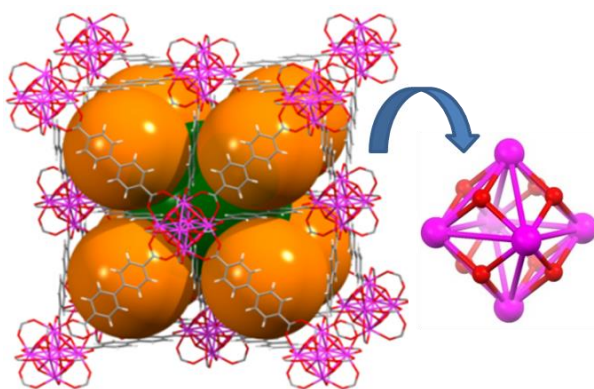


Figure 4. A fragment of “healed” UiO-67b crystal structure demonstrating the overall topology, with the two types of pores (larger green and smaller orange) schematically indicated with spheres (left). Structure of $\text{Zr}_6\text{O}_4(\text{OH})_4^{12+}$ cluster (right). Hydrogen atoms are omitted for clarity. Colors corresponding to atoms: C (grey), O (red), Zr (purple).

In contrast, an acetic acid treatment of the “healed” UiO-67a and UiO-67f led to the reincorporation of the acid in ratios close to those found in the freshly synthesized MOFs. This phenomenon is interpreted as showing that the linker diacid had been incorporated by bonding through only one of the carboxylate groups, which would make them labile for subsequent exchange. This, in turn, likely indicates that MOFs prepared using acetic and formic acids as modulator contain not just missing linkers, but rather entire missing node (i.e. Zr_6) defects (Figure 5).

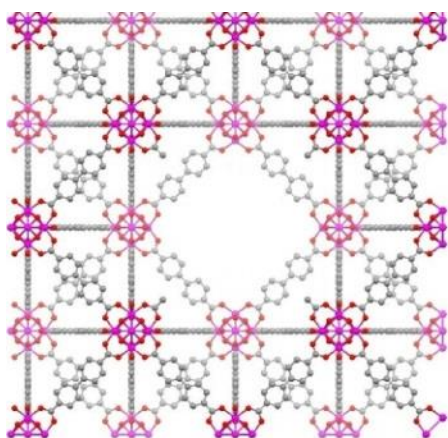


Figure 5. A cartoon illustrating the proposed missing-node defect in UiO-67a.

From the point of view of using MOFs as heterogeneous catalysts, the metal-based chemistry at the node is a highly promising field of study.^{4b,d,f,h} Given, however, that the incorporation of additional metals (including d-elements) in MOFs might be necessary, we wondered how the modulation in a MOF synthesis affects its ability to take up simple metal salts. As a test, a Cr(III) salt was chosen in light of the metal’s broad catalytic potential. It was found that exposing the high-defect samples of UiO-67f and UiO-66f to a solution of $CrCl_3 \cdot 3THF$ (a $CrCl_3$ salt soluble in organic solvents) led to the sample color change from white to purple, consistent with chromium incorporation (Figure S6). The ICP analysis of the UiO-66Cr and UiO-67Cr thus obtained show a

4.5 and 3.4 wt. % Cr, respectively. While this Cr(III) uptake did not affect the material's pXRD pattern or the particles sizes and morphology (as judged by TEM), the N₂ sorption (Figure 6) in a UiO-67Cr sample (upon activation) did show decrease in N₂ uptake, with a surface area drop from 2600 m²/g down to 2000 m²/g.

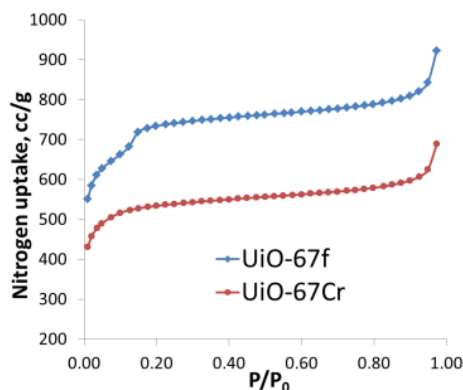
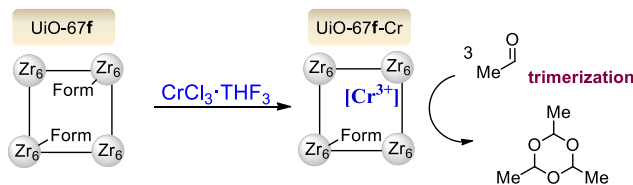


Figure 6. Nitrogen sorption at 77K for UiO-67Cr compared with the parent UiO-67f.

Although the mode of coordination of Cr(III) is currently unclear, we believe that the high uptake is due to the defect sites, as has been previously proposed for other 3d metal cations (V, Mn, Fe, Co, Ni) incorporated at the Zr₆-oxo clusters.^{17, 4f} Consistent with this hypothesis, the nearly defect-free sample of UiO-67b led to a very modest final Cr content (1.4%).

In our study we obtained two types of potent heterogeneous catalysts Zr-MOF-Cr (“chromated” Zr-MOFs) and Zr-MOF-h (HCl modulated MOFs, containing Lewis acidic Zr-OH sites). As a model reaction to test catalytic activity of our materials we selected acetaldehyde self-reaction which is an industrially attractive process that can lead to many different products.¹⁸ We have found that in the presence of UiO-66Cr and UiO-67Cr (0.5 mole %) acetaldehyde self-cyclize at room temperature with conversion up to 96% correspondingly, and paraldehyde (Scheme 1) as a

sole industrially valuable¹⁹ product. A test reaction with $\text{CrCl}_3 \cdot 3\text{THF}$ as a homogeneous reference gave similarly good results (92% of paraldehyde using 2 % Cr) though.



Scheme 1. Defect-promoted chromium(III) uptake in UiO-67f.

4. Conclusions

In conclusion, it was found, that the number of missing linkers in a Zr-MOF is mainly determined by both ligand and modulation acid structure. The dynamic nature of coordination bonds allowed us to replace anions on defect sites. This was applied not only to further quantify missing linkers, but also as a new straightforward method of introduction functional species into readily available Zr-MOFs. On the other hand it was for the first time used for MOF “healing”, leading to defect-free UiO-67 material. Strong effect of defect structure on reactivity of Zr-MOFs was observed. New MOF-catalyzed acetaldehyde self-reactions were developed.

ASSOCIATED CONTENT

Supporting Information.

Detailed experimental procedures and data (synthesis and catalysis protocols, powder X-Ray diffractograms, BET sorption measurement details, TEM and SEM images). This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

Any additional relevant notes should be placed here.

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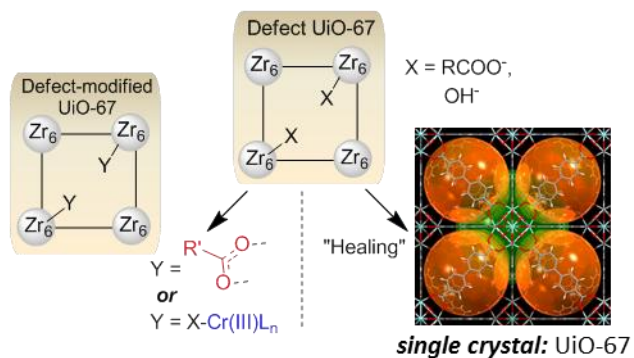
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The formation of the UiO-67 family of Zr MOFs is explored here through the prism of their acid-modulated growth, showing it to be key factor in controlling the MOF defect content, porosity, particle size and morphology. The dynamic nature of the resulting Zr_6 -monocarboxylate ("missing linker") defect sites is explored for UiO functionalization (through acid exchange), "healing" and the introduction of a catalytically active M(III) cation.