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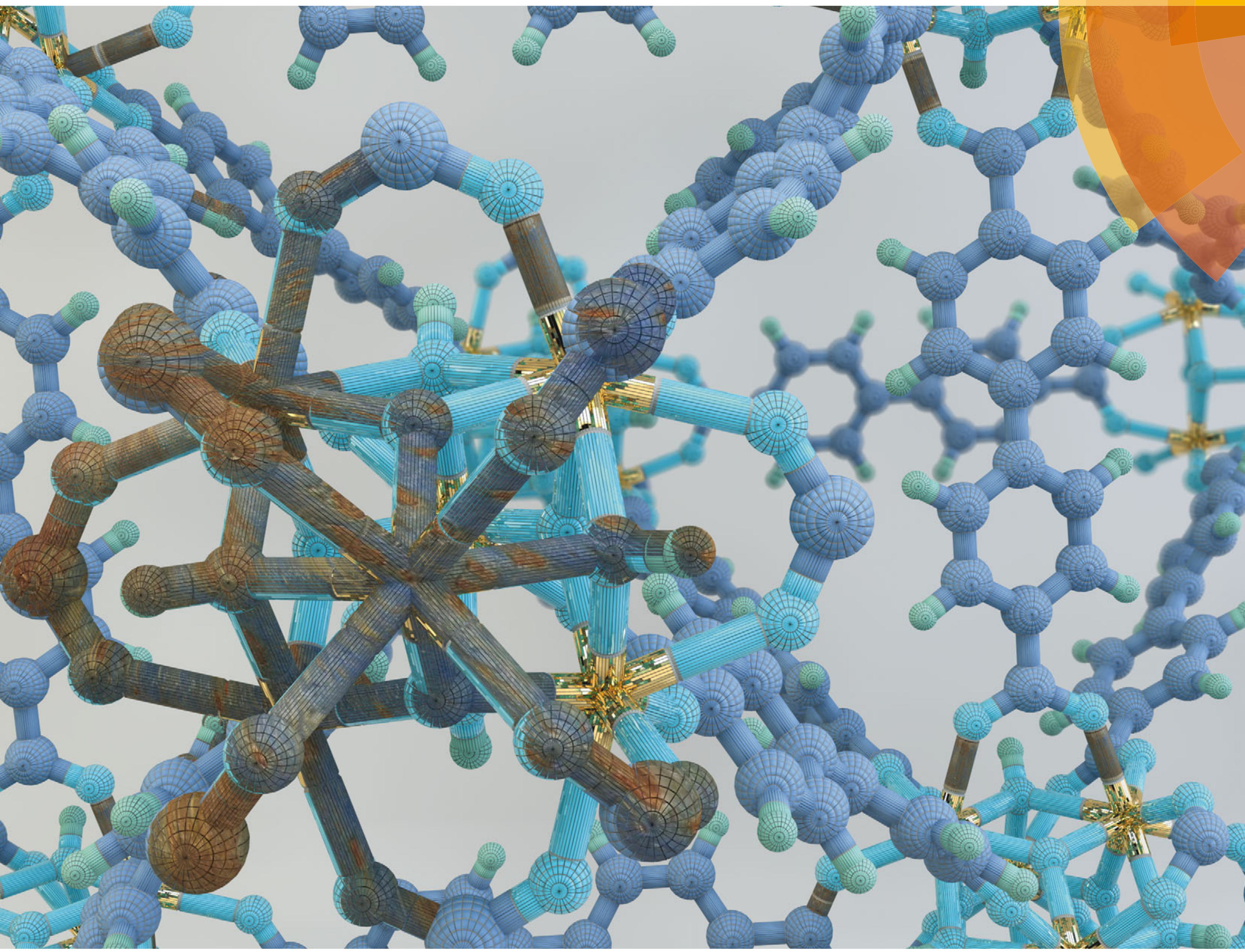

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Determining the structural stability of UiO-67 with respect to time: a solid-state NMR investigation†

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The stability of UiO-67 has been questioned for some time. We have used solid-state NMR to investigate the temporal stability of this MOF. Proper activation is necessary to achieve optimal surface area. However, even with proper activation, the long-term (30+ days) fate of UiO-67 is hydrolysis of the linker-metal bonds and, ultimately, pore collapse.

Metal–organic frameworks (MOFs) are porous materials formed *via* coordination of bridging organic ligands (linkers) with inorganic metal cations/clusters (nodes). With judicious choice of these components, MOFs with applications in gas-storage,[1] chemical separations,[2] light-harvesting,[3] sensing,[2b,4] and catalysis[5] have been realized. One family of MOFs which are becoming ubiquitous in these applications is the Zr-cluster-containing family of MOFs, including, but not limited to, UiOs,[6] NU-1000,[7] PCN-222,[8] and MOF-808.[9] The interest in these MOFs stems from their thermal, chemical, and mechanic stability making them ideal for many applications.[6d,10]

With respect to both anecdotal evidence as well as literature precedence, UiO-67 (Fig. 1) has had a precarious history. DeCoste *et al.* demonstrated that the internal surface area (SA) of UiO-67 decreased from 2145 $m^2\ g^{-1}$ to 10 $m^2\ g^{-1}$ after the MOF was exposed to 90% relative humidity. Similarly, when soaked in water, UiO-67 was found to be unstable; powder X-ray diffraction data (pxrd) indicated the presence of ZrO_2.[11] Although the instability is attributed to hydrolysis of the bonds between the linker and node, FTIR data showed no vibrational changes to corroborate this.

In a related manuscript, Mondloch *et al.* have proposed an alternate hypothesis. When UiO-67 was activated (*i.e.*, the process of removing solvent from the porous frameworks) from water, then there was no notable porosity remaining. However, if water in the pore was replaced with acetone prior to activation, then the porosity remained; similar results were obtained when UiO-67 was boiled in water prior to solvent exchange. Thus, rather than an inherent instability in the MOF it was proposed that capillary-force driven collapse, due to improper activation, is responsible for the proposed instability.[12]

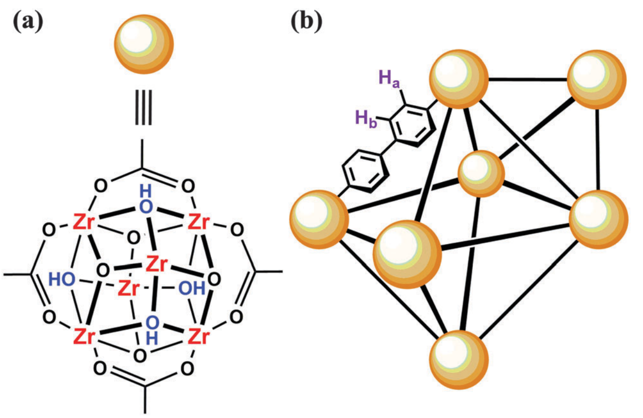

Fig. 1 (a) $Zr_6O_4(OH)_4$ cluster showing 4 of the 12 μ-BPDC units. (b) Schematic drawing of UiO-67 illustrating how the BPDC units link $Zr_6O_4(OH)_4$ clusters to one another to form both octahedral- and tetrahedral-shaped pores.

Given the utility of UiO-67,[5b,6h,13] we were interested in further probing its stability. Specifically, we are interested in investigating the long-term stability of UiO-67 with respect to time. We turned our attention to solid-state NMR (SS-NMR) as a probe for the potential structural changes that occur within this MOF. Unlike pxrd, which is sensitive to crystalline materials containing high Z nuclei, SS-NMR is equally sensitive to both amorphous and crystalline materials. Furthermore, SS-NMR has the potential to independently report on each nucleus.

UiO-67 was synthesized by the method of Katz *et al.* (See ESI,† for further details).[6a] UiO-67 was subsequently filter-dried (*ca.* 1 h). The samples of DeCoste *et al.*[11] were similarly filtered.

As expected, despite the apparently dry UiO-67, the SS-NMR indicates that freshly-prepared UiO-67 (Fig. 2 red trace) shows

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† Electronic supplementary information (ESI) available: Experimental details, ^{13}C-NMR spectra, and ^{1}H-NMR spectra of CH_2Cl_2-activated UiO-67. See DOI: 10.1039/c5cc09919f

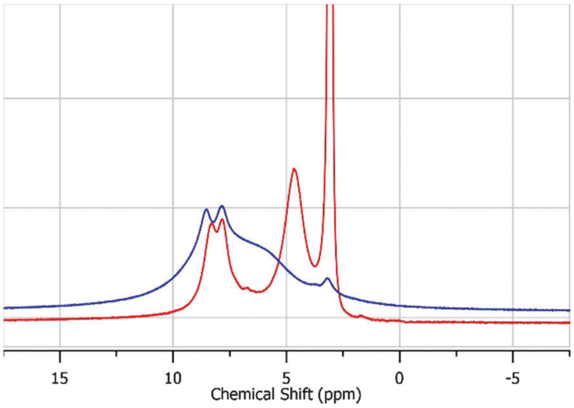

Fig. 2 (red) ^{1}H-NMR of UiO-67 immediately after vacuum filtration. (blue) ^{1}H-NMR of UiO-67 6 days after vacuum filtration. The corresponding ^{13}C-NMRs can be seen in Fig. S2 (ESI†).

remanence of methanol (3.05 ppm, 4.65 ppm) within the pores of the MOF; the remaining resonances at 7.82 and 8.29 ppm belong to the biphenyl protons (Fig. 1 H_a and H_b).

When freshly-prepared UiO-67 was left out for 6 days, the SS-NMR indicated that the majority of the methanol signals were greatly diminished.[14] However, a new broad-featureless resonance upfield of the linker protons (6.29 ppm) with a concomitant broad resonance buried at 8.51 ppm was observed. This feature is indicative of the formation of an amorphous material. Concomitantly, the Brunauer–Emmett–Teller (BET) SA of the 6-day old sample was a mere 500 $m^2 g^{-1}$ (Fig. S1 in the ESI†); this is in contrast with the SA of freshly-prepared and thermally activated UiO-67 which exhibited a BET SA of 2000 $m^2 g^{-1}$ (Fig. S1 in the ESI†). These results are consistent with the work by DeCoste *et al.*[11]

In order to further probe whether hydrolysis of the Zr-carboxylate bonds or capillary-force driven collapse is the culprit, we repeated the experiment with UiO-67 which was solvent exchanged (4 days) and subsequently filtered and thermally activated. As illustrated in Fig. 3, there are three distinct regions at *ca.* 0 ppm, 2.5 ppm, and 7.5 ppm; the latter two resonances have been attributed to the linker (7.5 ppm) and the bridging hydroxides (Fig. 1) on the node (2.5 ppm).[15] The remaining resonance at 0 ppm, which is only slightly visible in the spectra by Dolbecq *et al.*,[15] we attribute to linker deficiencies (*i.e.*, defect sites comprised of Zr-bound OH and H_2O moieties on the $Zr_6(OH)_4O_4^{12+}$ node) within the porous framework.[6a,h,16]

Unlike the filter-dry sample which contains pore-bound solvent (Fig. 2), over the course of a month, the BET SA of activated UiO-67 merely decreased to 1500 $m^2 g^{-1}$ (Fig. S1 in the ESI†). The SS-NMR (Fig. 3) shows nearly no evidence for the broad featureless hump in Fig. 2 suggesting that the origin of the decrease in SA for filter-dried UiO-67 (Fig. 2) is due to capillary-force driven collapse.[12]

As a function of time however, the spectra in Fig. 3 show that the μ^3-OH resonance (2.5 ppm) shifts with a concomitant increase in the intensity of the defect-based protons at 0 ppm. The latter implies that hydrolysis occurs over time leading to an increased defect density. Thus, in addition to capillary-force-driven collapse, the process of node-hydrolysis occurs slowly over time even in properly-activated UiO-67. However, given the nominal decrease in SA over the course of a month, the MOF is clearly able to tolerate some hydrolysis of the linker-Zr bonds.

In order to probe the generality of our observations, we repeated the experiment with acetone and dichloromethane as the exchanged solvent (Fig. 4, Fig. S4 and S5, ESI†).[17] Samples activated from dichloromethane (Fig. S5, ESI†) showed evidence of amorphous material and was not further examined; we hypothesize that the low miscibility of water with dichloromethane, and thus a less-efficient solvent exchange, is responsible for the degradation of the MOF.

However, when acetone was utilized (Fig. 4) the SS-NMR of the MOF initially indicated a more stable MOF with respect to hydrolysis (*i.e.*, the peaks at 0 ppm do not shift or increase in intensity). However, after a month, the MOF was found to be completely amorphous with a BET SA of 500 $m^2 g^{-1}$ indicating

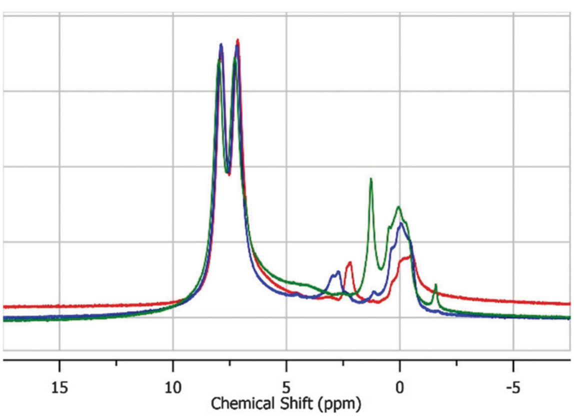

Fig. 3 (red) ^{1}H-NMR of UiO-67 immediately after thermal activation from methanol. (blue) ^{1}H-NMR of UiO-67 4 days after thermal activation. (green) ^{1}H-NMR of UiO-67 1 month after thermal activation. The corresponding ^{13}C-NMRs can be seen in Fig. S3 (ESI†).

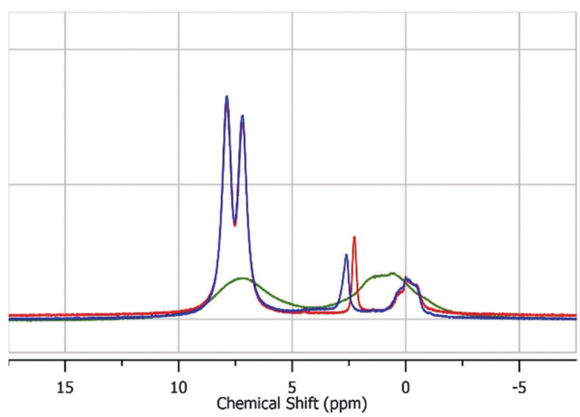

Fig. 4 (red) ^{1}H-NMR of UiO-67 immediately after thermal activation from acetone. (blue) ^{1}H-NMR of UiO-67 4 days after thermal activation. (green) ^{1}H-NMR of UiO-67 1 month after thermal activation. The corresponding ^{13}C-NMRs can be seen in Fig. S4 (ESI†).

Table 1 Summary of SS-NMR observations correlated to BET SA and activation method and solvent

Activation method	Time (days)	BET SA ($m^2 g^{-1}$)	SS-NMR observations
MeOH Wash	0	2000	MeOH present
	6	500	Crystalline and amorphous
Thermal from MeOH	0	2000	Defects present (0 ppm)
	4	—	μ^3-OH shifts downfield, increased defect density
	30	1500	μ^3-OH shifts upfield, increased defect density, onset of amorphous material
Thermal from acetone	0	2000	Defects present (0 ppm)
	4	—	μ^3-OH shifts downfield, no change in defect density
	30	500	Completely amorphous
Thermal from DCM (ESI)	0	—	Amorphous material observed

that, eventually, the MOF succumbs to hydrolysis;[18] ultimately, we expect a similar fate to methanol-exchanged UiO-67.

As summarized in Table 1, SS-NMR in combination with SA measurements were used to examine the stability of UiO-67 with respect to time.[19] As evident by the changing chemical shift of the μ^3-OH and defect-based resonance, SS-NMR is a key tool for the understanding of the dynamic behaviour within MOFs. With respect to the stability of UiO-67, we observed that when solvent molecules remain inside the pore for a few days, then UiO-67 collapses rapidly. However, when solvent is removed at elevated temperatures, then UiO-67 remains stable for at least a month. Inevitably, hydrolysis, caused by the relative humidity, degrades the MOF beyond its structural integrity. In our hands, if kept dry or in solution, UiO-67 remains intact.

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19 Attempts to measure ^{91}Zr-SS-NMR exhibited no decernible signal for UiO-67. NOESY-rfdr experiments showed signals between ligand protons, but no other interactions were observed.