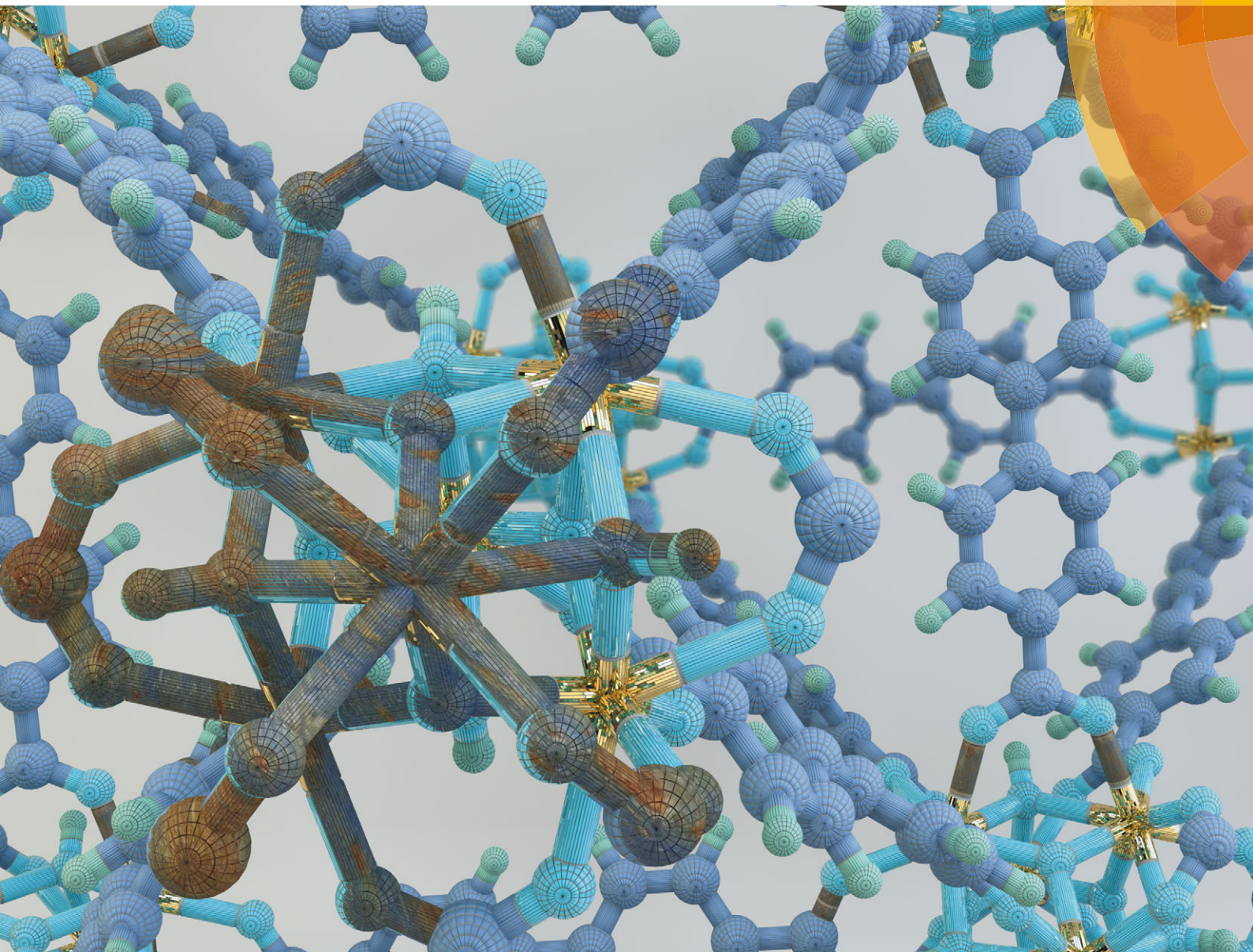


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## Determining the structural stability of UiO-67 with respect to time: a solid-state NMR investigation†

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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,<sup>1</sup> chemical separations,<sup>2</sup> light-harvesting,<sup>3</sup> sensing,<sup>2b,4</sup> and catalysis<sup>5</sup> 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,<sup>6</sup> NU-1000,<sup>7</sup> PCN-222,<sup>8</sup> and MOF-808.<sup>9</sup> The interest in these MOFs stems from their thermal, chemical, and mechanic stability making them ideal for many applications.<sup>6d,10</sup>

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<sup>2</sup> g<sup>-1</sup> to 10 m<sup>2</sup> g<sup>-1</sup> 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<sub>2</sub>.<sup>11</sup> 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,

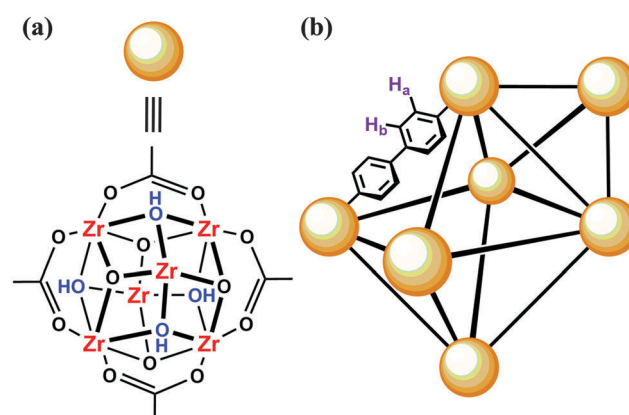


Fig. 1 (a) Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> cluster showing 4 of the 12 μ-BPDC units. (b) Schematic drawing of UiO-67 illustrating how the BPDC units link Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> clusters to one another to form both octahedral- and tetrahedral-shaped pores.

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.<sup>12</sup>

Given the utility of UiO-67,<sup>5b,6h,13</sup> 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).<sup>6a</sup> UiO-67 was subsequently filter-dried (*ca.* 1 h). The samples of DeCoste *et al.*<sup>11</sup> 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, <sup>13</sup>C-NMR spectra, and <sup>1</sup>H-NMR spectra of CH<sub>2</sub>Cl<sub>2</sub>-activated UiO-67. See DOI: 10.1039/c5cc09919f





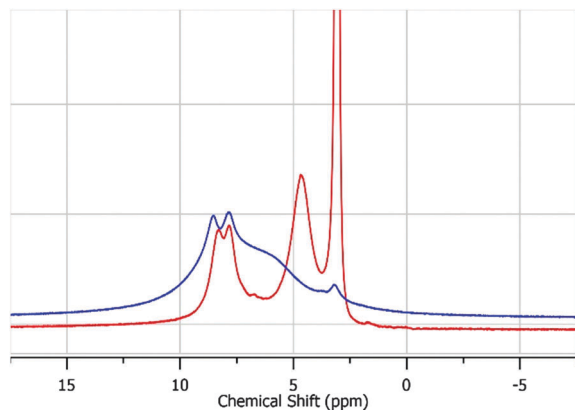


Fig. 2 (red)  $^1\text{H}$ -NMR of UiO-67 immediately after vacuum filtration. (blue)  $^1\text{H}$ -NMR of UiO-67 6 days after vacuum filtration. The corresponding  $^{13}\text{C}$ -NMRs can be seen in Fig. S2 (ESI $^\dagger$ ).

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  $\text{H}_a$  and  $\text{H}_b$ ).

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.<sup>14</sup> 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  $500\text{ m}^2\text{ g}^{-1}$  (Fig. S1 in the ESI $^\dagger$ ); this is in contrast with the SA of freshly-prepared and thermally activated UiO-67 which exhibited a BET SA of  $2000\text{ m}^2\text{ g}^{-1}$  (Fig. S1 in the ESI $^\dagger$ ). These results are consistent with the work by DeCoste *et al.*<sup>11</sup>

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

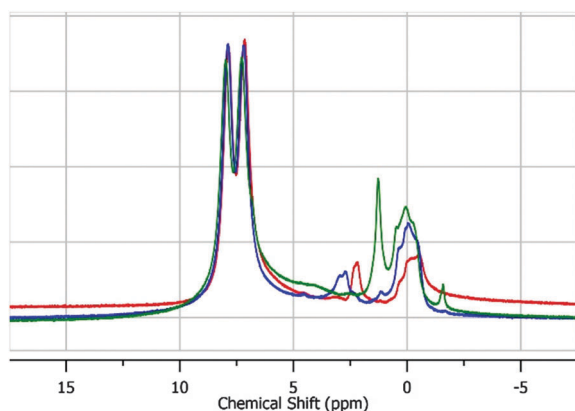


Fig. 3 (red)  $^1\text{H}$ -NMR of UiO-67 immediately after thermal activation from methanol. (blue)  $^1\text{H}$ -NMR of UiO-67 4 days after thermal activation. (green)  $^1\text{H}$ -NMR of UiO-67 1 month after thermal activation. The corresponding  $^{13}\text{C}$ -NMRs can be seen in Fig. S3 (ESI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

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).<sup>15</sup> The remaining resonance at 0 ppm, which is only slightly visible in the spectra by Dolbecq *et al.*,<sup>15</sup> we attribute to linker deficiencies (*i.e.*, defect sites comprised of Zr-bound OH and  $\text{H}_2\text{O}$  moieties on the  $\text{Zr}_6(\text{OH})_4\text{O}_4^{12+}$  node) within the porous framework.<sup>6a,h,16</sup>

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  $1500\text{ m}^2\text{ g}^{-1}$  (Fig. S1 in the ESI $^\dagger$ ). 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.<sup>12</sup>

As a function of time however, the spectra in Fig. 3 show that the  $\mu^3\text{-OH}$  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 $^\dagger$ ).<sup>17</sup> Samples activated from dichloromethane (Fig. S5, ESI $^\dagger$ ) 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  $500\text{ m}^2\text{ g}^{-1}$  indicating

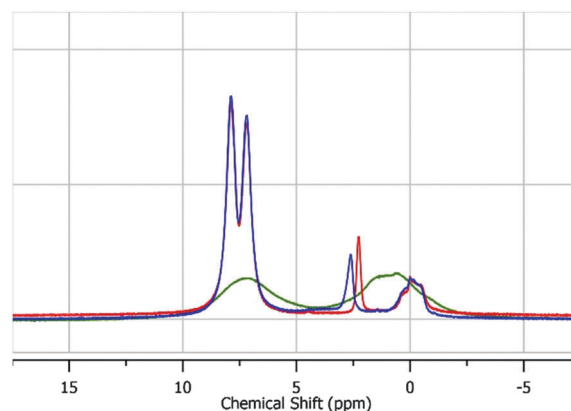


Fig. 4 (red)  $^1\text{H}$ -NMR of UiO-67 immediately after thermal activation from acetone. (blue)  $^1\text{H}$ -NMR of UiO-67 4 days after thermal activation. (green)  $^1\text{H}$ -NMR of UiO-67 1 month after thermal activation. The corresponding  $^{13}\text{C}$ -NMRs can be seen in Fig. S4 (ESI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



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

| Activation method      | Time (days) | BET SA (m <sup>2</sup> g <sup>-1</sup> ) | SS-NMR observations   |
|------------------------|-------------|--|---|
| MeOH Wash              | 0           | 2000                                     | MeOH present  |
|                        | 6           | 500                                      | Crystalline and amorphous   |
| Thermal from MeOH      | 0           | 2000                                     | Defects present (0 ppm)   |
|                        | 4           | —  | $\mu^3$ -OH shifts downfield, increased defect density                            |
|                        | 30          | 1500                                     | $\mu^3$ -OH shifts upfield, increased defect density, onset of amorphous material |
| Thermal from acetone   | 0           | 2000                                     | Defects present (0 ppm)   |
|                        | 4           | —  | $\mu^3$ -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;<sup>18</sup> 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.<sup>19</sup> As evident by the changing chemical shift of the  $\mu^3$ -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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