[Supporting Information (SI) to accompany:]

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

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Experimental

Synthesis of UiO-67

UiO-67 was synthesized according to the method of Katz et al.[1] Briefly, $ZrCl_4$ and biphenyl-4,4-dicarboxlic acid (BPDC) were heated at 80 °C overnight in a DMF solution containing 0.375 M HCl (0.5mL in a 15mL DMF solution). The MOF was subsequently cooled, filtered, washed 2x with DMF, 3x with methanol, and subsequently allowed to dry for an hour. For the initial studies (Fig. 2 in the main text), the samples were worked up according to the method of Katz et al (as briefly mentioned herein).[1] However, for the remainder of the manuscript (Fig. 3 and onwards), after the MOF was synthesized and subsequently centrifuged and washed with DMF 3x (10 mL), then the MOF was solvent-exchanged for Methanol, acetone, or CH_2Cl_2 daily for 4 days and subsequently filtered and immediately heated in a vacuum oven at ca. 90 °C.

Surface area measurements were determined on a Micromeritics Tristar instrument at 77 K. All samples were heated at 90 °C overnight in a vacuum oven prior to measurements.

Solid-State NMR of UiO-67

All spectra were obtained at 298 K using a Bruker Avance II 600 spectrometer, equipped with a SB Bruker 4mm MAS double-tuned probe operating at 600.33MHz for ^1H and 150.97 MHz for ^{13}C. Chemical shifts were referenced to tetramethylsilane (TMS) using adamantane as an intermediate standard for ^{13}C. The samples were spun at 15 kHz. Cross-polarization (CPMAS) spectra were collected with a Hartmann-Hahn match at 62.5 kHz and 100 kHz ^1H decoupling, with a contact time of 2 ms, a recycle delay of 3 s and 1 k scans.

N_2 Isotherms

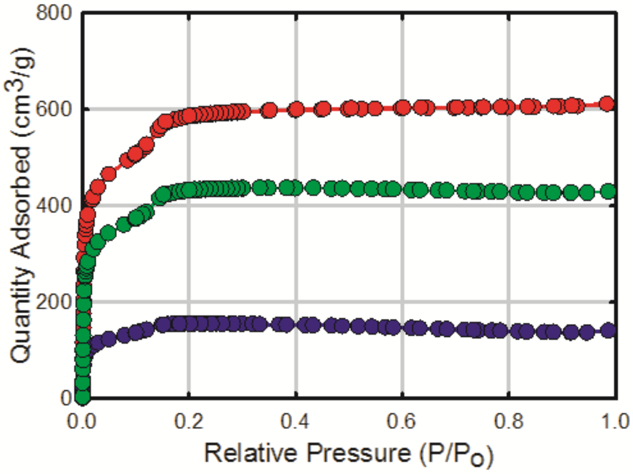

Fig. S1: $N_{2(g)}$ isotherms of UiO-67 collected at 77 K. (red) Isotherms of UiO-67 activated immediately after filtration. (blue) Isotherms of UiO-67 activated 6 days after filtration. (green) Isotherms of UiO-67 activated immediately after filtration but re-activated and measured after 1 month.

^{13}C-NMR of UiO-67

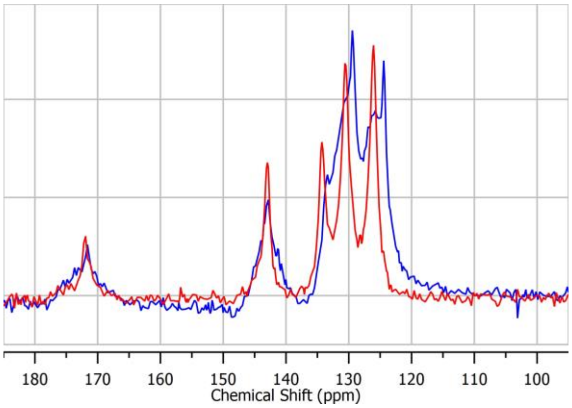

Fig. S2: (red) ^{13}C-NMR of UiO-67 immediately after vacuum filtration. (blue) ^{13}C-NMR of UiO-67 6 days after vacuum filtration. Note the increase in breadth of the ^{13}C peaks which is indicative of an amorphous material being present.

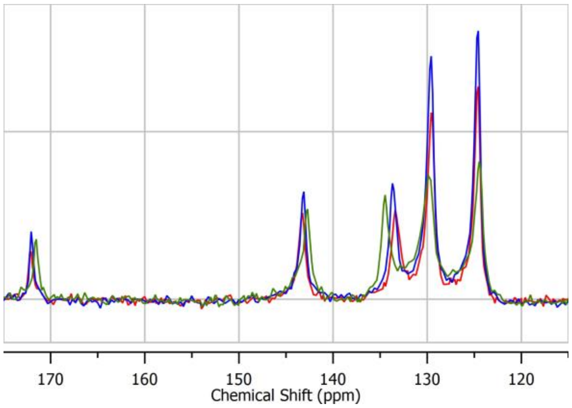

Fig. S3: (red) ^{13}C-NMR of UiO-67 immediately after thermal activation from methanol. (blue) ^{13}C-NMR of UiO-67 4 days after thermal activation. (green) ^{13}C -NMR of UiO-67 1 month after thermal activation.

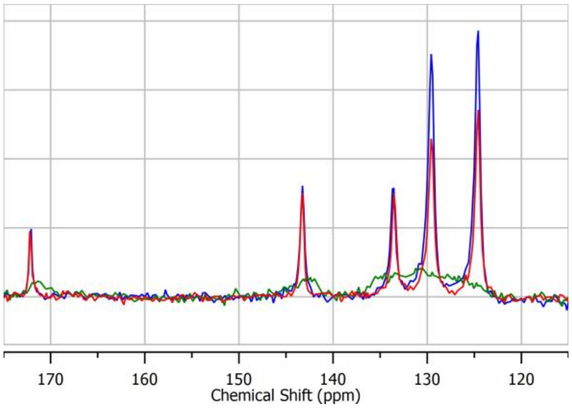

Fig. S4: (red) ^{13}C-NMR of UiO-67 immediately after thermal activation from acetone. (blue) ^{13}C-NMR of UiO-67 4 days after thermal activation. (green) ^{13}C-NMR of UiO-67 1 month after thermal activation. Note that when activated from acetone, the MOF remains unaltered over the course of a week, but at the one-month period it becomes completely amorphous indicating that the MOF succumbs to collapse.

^{1}H-NMR of UiO-67 activated from CH_2Cl_2

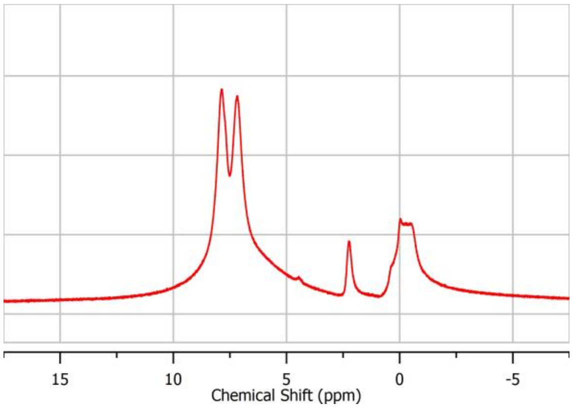

Fig. S5: (red) ^{1}H-NMR of UiO-67 immediately after thermal activation from CH_2Cl_2. The presence of an additional, albeit low intensity, hump at ca. 6 ppm is indicative of amorphous material suggesting that CH_2Cl_2 is not an ideal solvent for the activation of UiO-67.

References

1. M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449-9451.