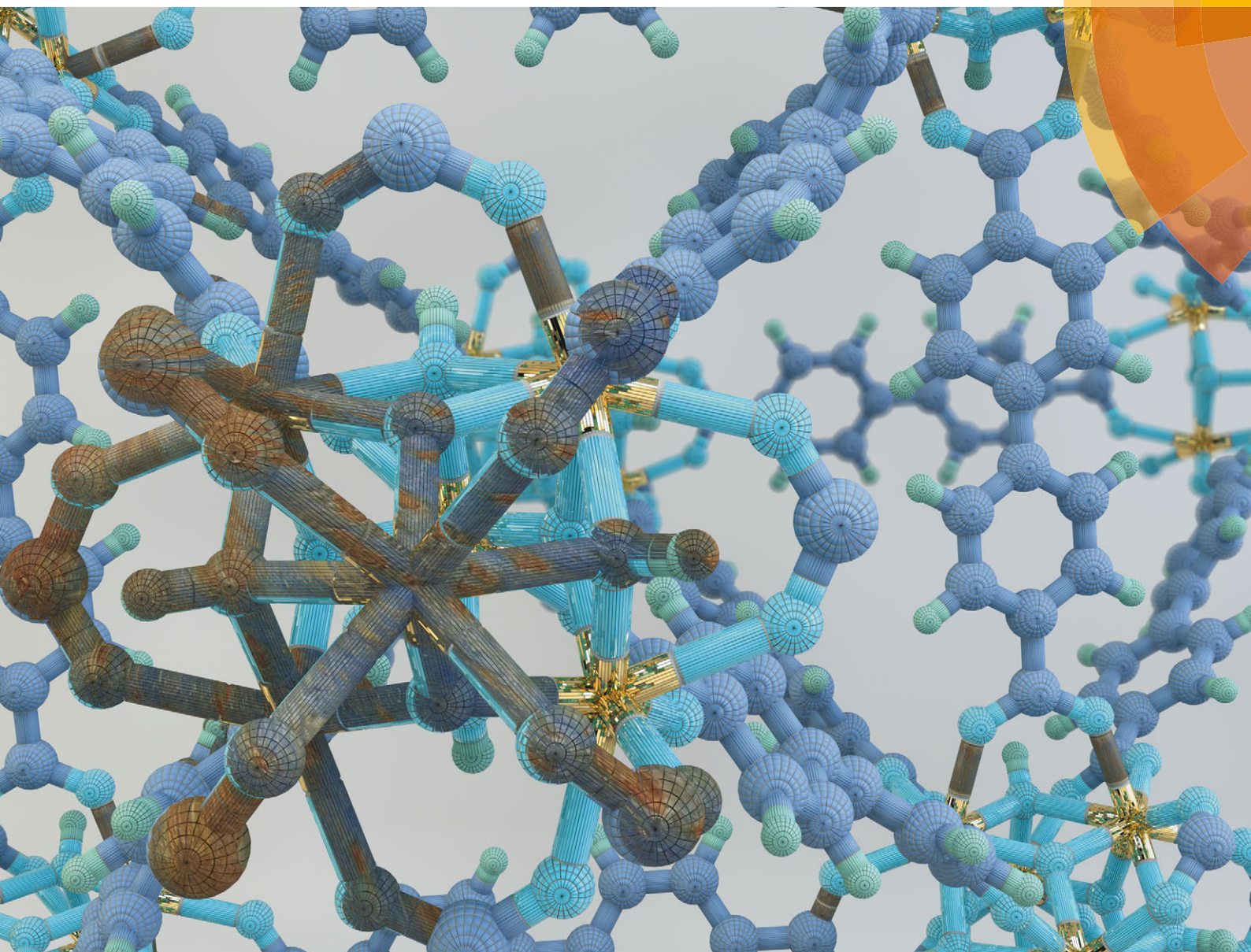


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# Determining the structural stability of UiO-67 with respect to time: a solid-state NMR investigation†

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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,

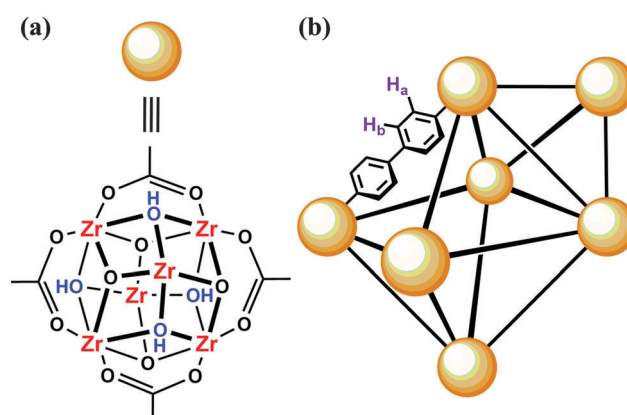


Fig. 1 (a) Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> cluster showing 4 of the 12 μ-BPDC units. (b) Schematic drawing of UiO-67 illustrating how the BPDC units link Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> clusters to one another to form both octahedral- and tetrahedral-shaped pores.

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





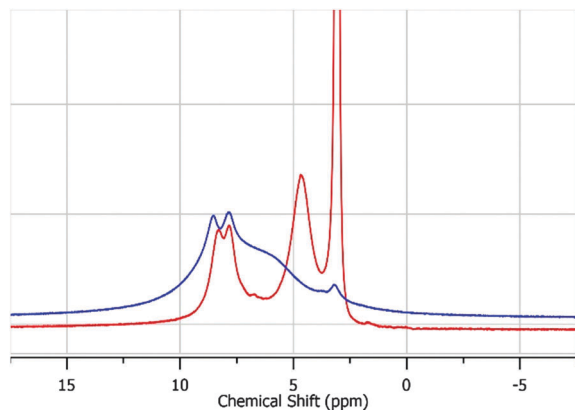


Fig. 2 (red)  $^1\text{H}$ -NMR of UiO-67 immediately after vacuum filtration. (blue)  $^1\text{H}$ -NMR of UiO-67 6 days after vacuum filtration. The corresponding  $^{13}\text{C}$ -NMRs can be seen in Fig. S2 (ESI†).

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†); 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†). 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

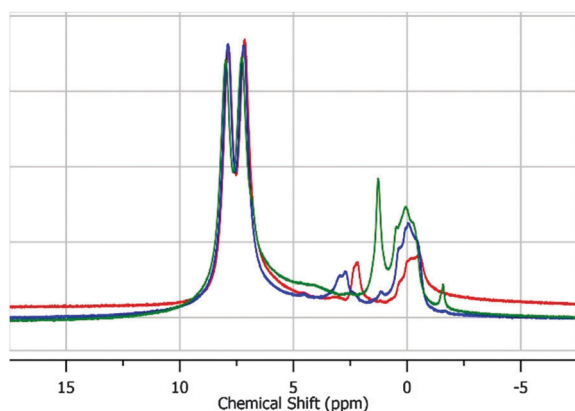


Fig. 3 (red)  $^1\text{H}$ -NMR of UiO-67 immediately after thermal activation from methanol. (blue)  $^1\text{H}$ -NMR of UiO-67 4 days after thermal activation. (green)  $^1\text{H}$ -NMR of UiO-67 1 month after thermal activation. The corresponding  $^{13}\text{C}$ -NMRs can be seen in Fig. S3 (ESI†).

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†). 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†).<sup>17</sup> 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  $500\text{ m}^2\text{ g}^{-1}$  indicating

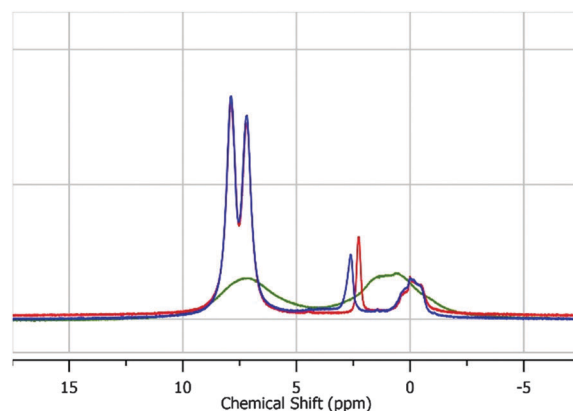


Fig. 4 (red)  $^1\text{H}$ -NMR of UiO-67 immediately after thermal activation from acetone. (blue)  $^1\text{H}$ -NMR of UiO-67 4 days after thermal activation. (green)  $^1\text{H}$ -NMR of UiO-67 1 month after thermal activation. The corresponding  $^{13}\text{C}$ -NMRs can be seen in Fig. S4 (ESI†).



**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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## Notes and references

- (a) J. A. Mason, M. Veenstra and J. R. Long, *Chem. Sci.*, 2014, **5**, 32–51; (b) B. Li, H.-M. Wen, W. Zhou and B. Chen, *J. Phys. Chem. Lett.*, 2014, **5**, 3468–3479; (c) O. K. Farha, A. Ö. Yazaydin, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944–948; (d) J. B. DeCoste, M. H. Weston, P. E. Fuller, T. M. Tovar, G. W. Peterson, M. D. LeVan and O. K. Farha, *Angew. Chem., Int. Ed.*, 2014, **53**, 14092–14095; (e) Y. Liu, Z. U. Wang and H.-C. Zhou, *Greenhouse Gases: Sci. Technol.*, 2012, **2**, 239–259.
- (a) D.-X. Xue, Y. Belmabkhout, O. Shekhah, H. Jiang, K. Adil, A. J. Cairns and M. Eddaoudi, *J. Am. Chem. Soc.*, 2015, **137**, 5034–5040; (b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105–1125; (c) E. Barea, C. Montoro and J. A. R. Navarro, *Chem. Soc. Rev.*, 2014, **43**, 5419–5430; (d) B. Van de Voorde, B. Bueken, J. Denayer and D. De Vos, *Chem. Soc. Rev.*, 2014, **43**, 5766–5788; (e) S. Qiu, M. Xue and G. Zhu, *Chem. Soc. Rev.*, 2014, **43**, 6116–6140.
- (a) C. Y. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 15858–15861; (b) T. Zhang and W. Lin, *Chem. Soc. Rev.*, 2014, **43**, 5982–5993; (c) S. Jin, H.-J. Son, O. K. Farha, G. P. Wiederrecht and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 955–958; (d) K. Meyer, M. Ranocchiari and J. A. van Bokhoven, *Energy Environ. Sci.*, 2015, **8**, 1923–1937.
- (a) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815–5840; (b) G. Lu and J. T. Hupp, *J. Am. Chem. Soc.*, 2010, **132**, 7832–7833; (c) Y. Cui, B. Chen and G. Qian, *Coord. Chem. Rev.*, 2014, **273–274**, 76–86.
- (a) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011–6061; (b) C. M. McGuirk, M. J. Katz, C. L. Stern, A. A. Sarjeant, J. T. Hupp, O. K. Farha and C. A. Mirkin, *J. Am. Chem. Soc.*, 2015, **137**, 919–925; (c) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459; (d) L. Ma, C. Abney and W. Lin, *Chem. Soc. Rev.*, 2009, **38**, 1248–1256; (e) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196–1231.
- (a) 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; (b) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851; (c) S. J. Garibay and S. M. Cohen, *Chem. Commun.*, 2010, **46**, 7700–7702; (d) M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, *Chem. Mater.*, 2010, **22**, 6632–6640; (e) L. Valenzano, B. Civalieri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700–1718; (f) M. J. Katz, J. E. Mondloch, R. K. Totten, J. K. Park, S. T. Nguyen, O. K. Farha and J. T. Hupp, *Angew. Chem., Int. Ed.*, 2014, **53**, 497–501; (g) S.-Y. Moon, G. W. Wagner, J. E. Mondloch, G. W. Peterson, J. B. DeCoste, J. T. Hupp and O. K. Farha, *Inorg. Chem.*, 2015, **54**, 10829–10833; (h) M. J. Katz, R. C. Klet, S.-Y. Moon, J. E. Mondloch, J. T. Hupp and O. K. Farha, *ACS Catal.*, 2015, **5**, 4637–4642; (i) J. M. Taylor, T. Komatsu, S. Dekura, K. Otsubo, M. Takata and H. Kitagawa, *J. Am. Chem. Soc.*, 2015, **137**, 11498–11506.
- (a) N. Planas, J. E. Mondloch, S. Tussupbayev, J. Borycz, L. Gagliardi, J. T. Hupp, O. K. Farha and C. J. Cramer, *J. Phys. Chem. Lett.*, 2014, **5**, 3716–3723; (b) J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. DeMarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair, R. Q. Snurr, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 10294–10297.
- (a) D. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z. Wei and H.-C. Zhou, *Angew. Chem.*, 2012, **124**, 10453–10456; (b) Z.-Y. Gu, J. Park, A. Raiff, Z. Wei and H.-C. Zhou, *ChemCatChem*, 2014, **6**, 67–75.
- (a) J. Jiang, F. Gándara, Y.-B. Zhang, K. Na, O. M. Yaghi and W. G. Klemperer, *J. Am. Chem. Soc.*, 2014, **136**, 12844–12847; (b) S.-Y. Moon, Y. Liu, J. T. Hupp and O. K. Farha, *Angew. Chem., Int. Ed.*, 2015, **54**, 6795–6799.
- (a) Y. Huang, W. Qin, Z. Li and Y. Li, *Dalton Trans.*, 2012, **41**, 9283–9285; (b) H. R. Abid, H. M. Ang and S. Wang, *Nanoscale*, 2012, **4**, 3089–3094.
- J. B. DeCoste, G. W. Peterson, H. Jasuja, T. G. Glover, Y.-G. Huang and K. S. Walton, *J. Mater. Chem. A*, 2013, **1**, 5642–5650.
- J. E. Mondloch, M. J. Katz, N. Planas, D. Semrouni, L. Gagliardi, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2014, **50**, 8944–8946.
- (a) S. Liu, Z. Yue and Y. Liu, *Dalton Trans.*, 2015, **44**, 12976–12980; (b) X. Zhu, B. Li, J. Yang, Y. Li, W. Zhao, J. Shi and J. Gu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 223–231.
- Caution:** desorption of solvent can cause damage to the rotor.
- W. Salomon, C. Roch-Marchal, P. Mialane, P. Rouschmeyer, C. Serre, M. Haouas, F. Taulelle, S. Yang, L. Ruhlmann and A. Dolbecq, *Chem. Commun.*, 2015, **51**, 2972–2975.
- (a) H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10525–10532; (b) G. C. Shearer, S. Chavan, J. Ethiraj, J. G. Vitillo, S. Svelle, U. Olsbye,



- C. Lamberti, S. Bordiga and K. P. Lillerud, *Chem. Mater.*, 2014, **26**, 4068–4071; (c) P. Ghosh, Y. J. Colon and R. Q. Snurr, *Chem. Commun.*, 2014, **50**, 11329–11331; (d) M. J. Cliffe, W. Wan, X. Zou, P. A. Chater, A. K. Kleppe, M. G. Tucker, H. Wilhelm, N. P. Funnell, F.-X. Coudert and A. L. Goodwin, *Nat. Chem.*, 2014, **5**, 4176; (e) C. A. Trickett, K. J. Gagnon, S. Lee, F. Gándara, H.-B. Bürgi and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2015, **54**, 11162–11167.
- 17 J. E. Mondloch, O. Karagiari, O. K. Farha and J. T. Hupp, *CrystEngComm*, 2013, **15**, 9258–9264.
- 18 T. D. Bennett and A. K. Cheetham, *Acc. Chem. Res.*, 2014, **47**, 1555–1562.
- 19 Attempts to measure  $^{91}\text{Zr}$ -SS-NMR exhibited no discernible signal for UiO-67. NOESY-rfdr experiments showed signals between ligand protons, but no other interactions were observed.

