

Microsymposium

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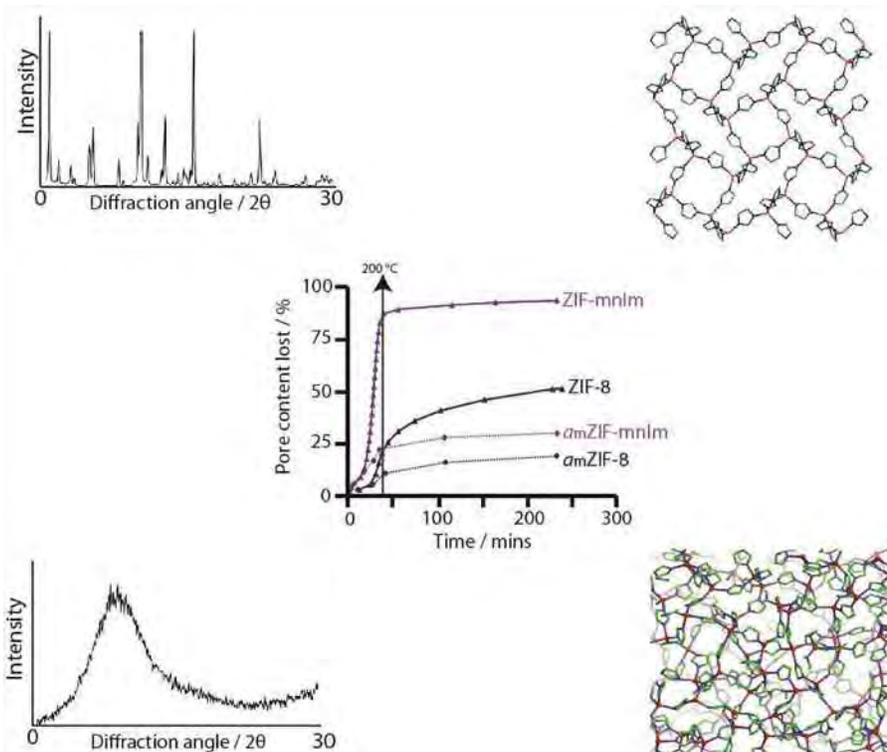
Amorphous Metal-organic Frameworks: Structure, Properties and Application

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A small but growing number of cases of MOFs lacking the long-range order characteristic of crystalline structures are steadily capturing scientific interest (though they remain woefully under represented), despite the phenomenon being known in inorganic zeolites. The majority of work has been performed on a sub-family of MOFs called zeolitic imidazolate frameworks (ZIFs), which consist of tetrahedral metal centers (typically Zn²⁺ or Co²⁺), connected by Imidazolate-type (C₃H₃N₂⁻) organic ligands in zeolitic topologies. Recently, we discovered that ZIFs could be amorphized by ball-milling and heating, and that the resultant amorphous material has a similar topology to that of silica glass. (Bennett et al., 2010, Bennett et al., 2011) Similarly, they can also be amorphized by pressure, though there is considerable debate about the reversibility of the process. Amorphous MOFs, whilst significantly harder to characterise, are more mechanically stable than their well-known crystalline counterparts. They also offer routes to functional glass materials, through melting of functionalised parent frameworks (incorporating lanthanide ions or chiral ligands). Some of these glasses have been shown to be topologically 'perfect' with fragilities lower than that of aSiO₂. Recently, we have shown that the release in-vitro of ibuprofen and caffeine stored within ZIF-8 can be tailored by ball-milling inducing collapse of the framework, whilst I₂ has also been irreversibly captured using similar methodology. (Bennett et al., 2013) Significant challenges exist in exploring the field of amorphous hybrid frameworks, though access to a multitude of functional materials is indeed a worthwhile reward.

[1] Bennett, T. D., Goodwin, A. L., Dove, M. T., Keen, D. A., Tucker, M. G., Barney, E. R., Soper, A. K., Bithell, E. G., Tan, J. C. & Cheetham, A. K. (2010). *Phys Rev Lett* 104., [2] Bennett, T. D., Cao, S., Tan, J. C., Keen, D. A., Bithell, E. G., Beldon, P. J., Friscic, T. & Cheetham, A. K. (2011). *J Am Chem Soc* 133, 14546-14549., [3] Bennett, T. D., Saines, P. J., Keen, D. A., Tan, J. C. & Cheetham, A. K. (2013). *Chem-Eur J* 19, 7049-7055.



Keywords: Metal-organic Framework, Amorphous, Properties