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Flexibility and disorder in metal–organic frameworks

Thomas D. Bennett,*[a] Alain H. Fuchs,[b] Anthony K. Cheetham[a] and François-Xavier Coudert*[b]

Metal–organic frameworks (MOFs), or networked solids containing both inorganic and organic moieties linked in an infinite array, have received considerable attention in the past two decades. Significant advances in creating chemically complex structures of increasing internal surface areas have been made, building on the deliberate assembly of rod-like components into the scaffolding like structures reported by Robson in 1990. Early priority was given to the creation of what where considered at the time to be rigid structures, in order to support the presence of large internal cavities, with an eye on applications such as fluid adsorption, separation and catalysis. Whilst still true for some UiO-type frameworks (Yot, DOI: 10.1039/C5DT03621F), our perception of MOFs as structurally intransigent materials is now being challenged.

In this issue, we provide examples of this recent research on MOF flexibility, such as the synthesis and breathing ability of novel MIL-53 derivatives (Stock, DOI: 10.1039/C5DT03510D; Walton, DOI: 10.1039/C5DT03438H), and a short review of those MOFs containing neutral N-donor ligands (Ghosh, DOI: 10.1039/C5DT03443D). Such examples of MOF flexibility, and the complexities of their structural behaviour, are even more pronounced when assessing the response of several Zn-based MOFs to heat (Kim, DOI: 10.1039/C5DT03710G; Barbour, DOI: 10.1039/C5DT01927C), and the guest diffusion of ZIF-8 under tensile or shear deformation (Zheng, DOI: 10.1039/C5DT03861H). Reports of wide-ranging, dynamic MOF responses to pressure (Clearfield, DOI: 10.1039/C5DT03228H) serve to further shift the research focus onto the flexible behaviour of MOF systems, which is of great importance, and consequence, for their application in gas sorption and separation (Howarth, DOI: 10.1039/C5DT03436A; Leuking, DOI: 10.1039/C5DT03432A; Tanaka, DOI: 10.1039/C5DT03476K; Llewellyn, DOI: 10.1039/C5DT03591K). One of the greatest challenges in the field going forwards is thus perhaps to exercise some control over this inherent degree of flexibility (Senkovska, DOI: 10.1039/C5DT03504J).

As rigidity and order are intertwined, so perhaps are flexibility and disorder. Research presented here on the latter ranges from cation solid-solutions in Zn/Co triazole systems (Gandara, DOI: 10.1039/C5DT03856A) and mixed linker Zn(BDC)(DABCO) systems (Burrows, DOI: 10.1039/C5DT04045K) to those which are entirely X-ray amorphous (Horike, DOI: 10.1039/C5DT03286E). Examples are also presented on how to characterize more subtle degrees of structural disorder, such as in the case of MIL-47(V) (Heinen, DOI: 10.1039/C5DT03399C). Work by Sarkisov (DOI: 10.1039/C5DT03498A) on IRMOF-1 not only illustrates the unexpected presence of disorder in prototypical MOFs such as IRMOF-1, but also provides a demonstration of defects in MOFs, in what some may consider a natural consequence of disorder. A short review by Farrusseng focuses on the link between these defects and the catalytic properties of MOFs (DOI: 10.1039/C5DT03522H).

It is perhaps a natural progression, given the field's continuing maturity, that researchers from domains outside of what we might we associate with classical MOF chemistry are starting to contribute. Articles on the non-linear optical properties of MOF-dye composites (Qian, DOI: 10.1039/C5DT03466C), screening of linker candidates under large deformations (Greaney, DOI: 10.1039/C5DT03511B), the application of counting theory and rigidity rules to MOFs (Marmier, DOI: 10.1039/C5DT03586D) and application of soft matter modelling techniques such as coarse-grained simulations (Schmid, DOI: 10.1039/C5DT03865K) are fitting testament to our continuing ability to explore this rich and diverse field.

Whilst it has ultimately proved impossible to mention all of the included research papers here, we encourage you to discover their diversity, excellence and novelty by reading this themed collection. Of course, none of this would be possible without the efforts and contributions of our colleagues, in both submitting and reviewing the papers presented here. We also want to thank all participants to the CECAM Workshop on Flexibility and Disorder in Metal–Organic Frameworks (Website: http://molsim.info/MOF-flexibility-disorder/), held in June 2015

[a]*Department of Materials Science and Metallurgy, 27 Charles Babbage Road, University of Cambridge, CB3 0FS, UK. E-mail: tdb35@cam.ac.uk*
[b]*Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France. E-mail: fx.coudert@chimie-paristech.fr*

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at Chimie ParisTech, organized in conjunction with this themed issue. The discussions in Paris clearly demonstrated both how far we have progressed and the numerous open questions remaining on the road ahead of us, highlighting the vitality of this field of research.

Finally, we would like to extend our sincere thanks to the staff at *Dalton Transactions*, and in particular Guy Jones and Laurent Mathey, for their dedication, enthusiasm and hard work in bringing together this issue.

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