

# 'Eye' of the molecule—a viewpoint†

Seungkyu Lee  ‡ and Omar M. Yaghi  \*

Received 23rd April 2021, Accepted 19th May 2021

DOI: 10.1039/d1fd00032b

If the twentieth century was the age of precisely designed molecules, the twenty-first century is beginning to look like the age of reticulated molecules. In the spirit of the *Faraday Discussion* meeting, we wish to highlight the power of harnessing the reticulated molecule and suggest that its chemistry can be furthered by viewing our reticular structures from the 'eye of the molecule'. To clarify what is meant by this term, we wish to first take stock of the current state of reticular chemistry.

Today, reticular chemistry represents a new field of science where organic and inorganic building units are stitched together by strong bonds into crystalline, extended structures as exemplified by metal–organic frameworks (MOFs) and covalent organic frameworks (COFs).<sup>1</sup> Our ability to crystallize such strongly bonded extended structures under mild conditions and therefore preserve the integrity of the building units is the foundation of the field. It means that the characteristics of the molecule and its reactivity can be largely preserved and fruitfully used to predict its behavior upon translation into the crystallized MOF or COF structure. However, reticulation of the molecule into the framework results in a property that the molecule itself does not have: it is the space encompassed by the framework within which matter can be further manipulated and controlled. The strong bond, secondary building unit (SBU) approach launched in the mid-1990s for MOFs ensured that the framework has the architectural and chemical stability for molecules to travel in and out of the pores without collapse of the overall porous structure.<sup>2–4</sup> Expansion of the opportunities offered by this chemistry was realized with the development of COFs in 2005 and 2007, which in effect extended organic chemistry to infinite 2D and 3D covalent structures.<sup>5,6</sup>

Thus, for the first time, we as a scientific community have developed what can only be considered 'infinite' chemistry, where there are infinite numbers of building units (organic and inorganic), infinite geometrical ways of reticulating

*Department of Chemistry, University of California, Berkeley, California 94720, USA. E-mail: yaghi@berkeley.edu*

† Electronic supplementary information (ESI) available. CCDC 2079556. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1fd00032b

‡ Current address: Department of Chemistry, Northwestern University, Evanston, Illinois, 60208, United States.

them, infinite numbers of possible structures, and infinite reactions to functionalize their pores—all with unparalleled levels of molecular precision and definition. Again, this would not have been possible without the development of the crystallization strategies for strongly bonded frameworks, which are now part of the standard practices of reticular chemistry.

However, reticular chemists are beginning to take the crystallinity of reticular structures and their facile characterization by single-crystal X-ray diffraction for granted, and as a result we are experiencing a lack of precision in the description of structures. This ‘non-precision in precision land’ is a trend that might be the result of the vast amount of information made available by our success in obtaining high-quality crystals and our need to abbreviate the description of what we feel (rightly or wrongly) are routine data and observations. This sometimes translates into our published work having a crystal structure displayed as a postage stamp with no details given of how the atoms are connected, the identity of their geometries, and indeed the shape and size of the pores. It is as if the crystal structure we spent our efforts, time, and resources to achieve does not figure prominently in our analysis and conclusions. It would be unfortunate if, in our preoccupation with studying our materials’ applications, we inadvertently devalue the exquisite details crystal structures provide. The fact is that in most reticular chemistry articles, very little crystallographic information is discussed at the level of detail that the data command. We believe that such details may hold key elements of discovery and that methodical and patient ‘reading’ of them is a necessary part of reticular chemistry, and in our opinion, it should be the minimum standard for reporting our structures.

To be clear, our consideration and description of a reticular structure should be done with the precision of the ‘eye of the molecule’. In describing the crystal structure of a MOF, for example, we should consider ourselves molecules navigating the framework, looking around as we diffuse through the pores, and registering locations, geometries, metrics, interactions, and topographical information. The entire molecular ‘ecosystem’ of the framework and its interior should be subjected to the scrutiny of the eye of the molecule. In so doing, we are taking an atomically accurate survey of the structure and giving the crystallography data their due consideration. We believe discovery is there to be had or at least has a better chance of emerging when we practise careful ‘reading’ and study the crystal structure from the vantage point of what the eye of the molecule registers.

Here, we present the structure of a new MOF refined from single-crystal X-ray diffraction data and highlight its features through the eye of the molecule. We synthesized a new MOF,  $Zr_6(\mu^3-O)_4(\mu^3-OH)_4(OH)_4(H_2O)_4(BDC)_4$  (BDC: 1,4-benzenedicarboxylate), termed MOF-711. We note that the synthesis of this compound requires further optimization, but we opted to report its crystal structure as an illustrative object of this contribution. The periodic structure of MOF-711 is composed of 8-connected SBUs,  $Zr_6(\mu^3-O)_4(\mu^3-OH)_4(OH)_4(H_2O)_4(-COO)_8$ , linked to eight ditopic BDC linkers. Each SBU has six  $Zr^{4+}$  ions located on the vertices of an octahedron (Fig. 1a), and each  $Zr^{4+}$  has eight coordination sites. There are three pairs of crystallographically different  $Zr^{4+}$  centers: the first pair (Zr1) has two  $\mu^3$ -

§ CIF data have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC 2079556.

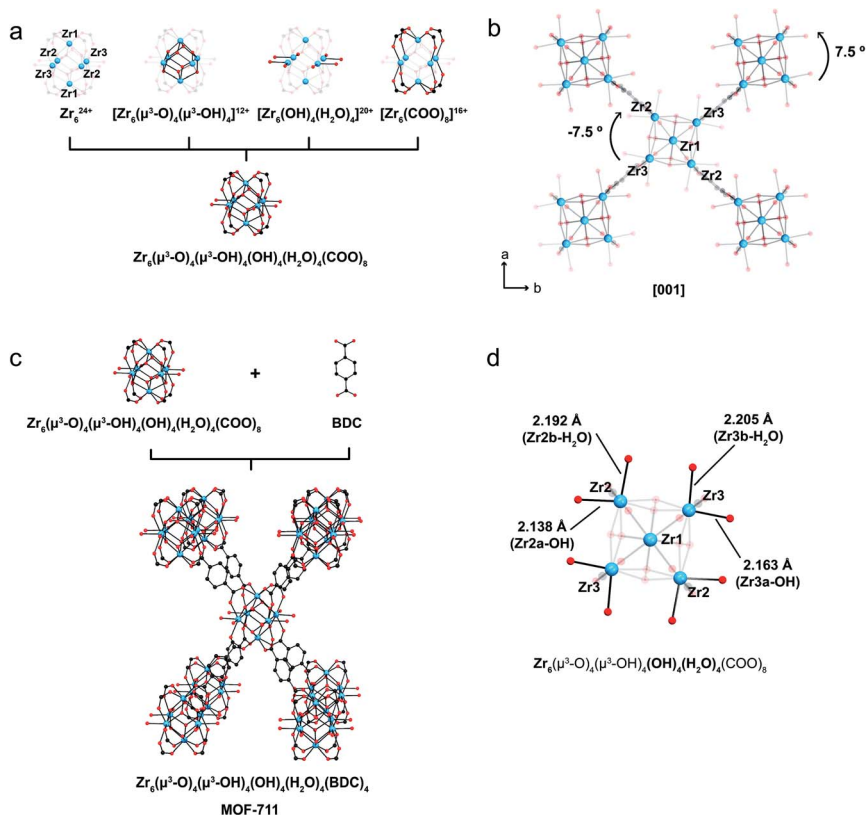


Fig. 1 Single crystal X-ray structure of  $Zr_6(\mu^3-O)_4(\mu^3-OH)_4(OH)_4(H_2O)_4(BDC)_4$  (BDC: 1,4-benzenedicarboxylate), MOF-711, showing the (a) three crystallographically unique  $Zr^{4+}$  ions Zr1, Zr2, and Zr3, highlighting for each Zr center the coordination environment within the octahedral secondary building unit (SBU), (b) connectivity of the SBUs and their rotation with respect to each other, thereby making Zr2 and Zr3 crystallographically distinct, (c) combination of the SBUs with BDC to make a 3D MOF-711 structure based on a body-centered cubic arrangement, and (d) bond lengths distinguishing the terminal water and hydroxide ligands on Zr2 and Zr3.

$O^{2-}$ , two  $\mu^3-OH^-$ , and four carboxylates from BDC linkers; the second pair (Zr2) has two  $\mu^3-O^{2-}$ , two  $\mu^3-OH^-$ , two carboxylates from BDC linkers, and two terminal  $OH^-$  and  $H_2O$  ligands; the third pair (Zr3) have exactly the same coordination as Zr2. However, rotation of the SBUs by  $\pm 7.5^\circ$  along the  $c$ -axis (Fig. 1b) makes Zr2 and Zr3 crystallographically different. Eight of the twelve edges are the carboxylates of BDC, and they are linked to other octahedra to form a body-centered cubic arrangement, **bcu** (Fig. 1c). Crystals of MOF-711 have an orthorhombic space group,  $Pn\bar{m}$ , and unit cell parameters of  $a$ : 13.4687(15),  $b$ : 14.8959(17), and  $c$ : 21.264(2) Å. Close examination of the MOF-711 structure reveals that it can be conceptually derived from UiO-66 (space group:  $Fm\bar{3}m$ ) by removing 4 linkers in the same plane from the 12 linkers coordinated to the SBUs of UiO-66, absent any rotation of the SBUs with respect to each other.<sup>7</sup>

We note that Zr2 interacts with the terminal ligands more strongly [Zr2–OH distance: 2.1382(48) Å and Zr2–H<sub>2</sub>O: 2.1919(54) Å] than Zr3 [Zr3–OH: 2.1629(45) Å and Zr3–H<sub>2</sub>O: 2.2051(42) Å] (Fig. 1d). The assignment of OH<sup>−</sup> and H<sub>2</sub>O was done based on distances, in that the Zr–OH<sup>−</sup> distance is significantly shorter than the Zr–OH<sub>2</sub> distance, and this is in agreement with the charge consideration. Thus, each SBU has eight terminal ligand coordination sites of four different types (two on Zr2: Zr2a and Zr2b and two on Zr3: Zr3a and Zr3b, where ‘a’ represents the coordination sites for OH<sup>−</sup> and ‘b’ represents the coordination sites for H<sub>2</sub>O) that could potentially serve as Lewis acidic open metal sites for various addition and substitution reactions with incoming basic molecules (Fig. 1d).

MOF-711 has a three-dimensional pore structure, where three intersecting pores run along the *a*, *b*, and *c* directions with diameters of 16.3 × 7.12, 16.3 × 5.69, and 7.12 × 5.69 Å<sup>2</sup>, respectively (Fig. 2a–d). Molecules traveling along the *a*-direction through the largest pore opening would frequently contact Zr2a and Zr3a coordination sites, which interact with the terminal ligands more strongly than Zr2b and Zr3b. Molecules traveling along the *b*-direction would interact with Zr2b and Zr3b. Diffusion of molecules traveling along the *c*-direction would be relatively slow due to the smallest pore opening.

In this description, we have presented the structure of MOF-711 at a detail level to allow the reader an appreciation of the structure and the coordination environment of each of the metal ions without necessarily having the benefit of the figures. We wish to remark that our description is in no way unique, but we hope that our attempt at clarity in structure description has been successful and that it might serve as at least a minimum standard to be followed in future published reticular chemistry research. There is certainly a need for computer programs to aid in providing full structure descriptions. This would greatly enhance our

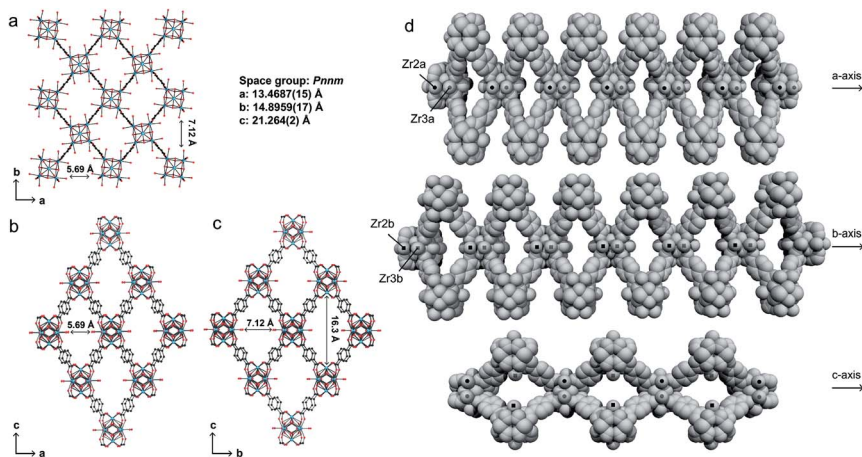


Fig. 2 (a)–(c) The crystal structure of MOF-711 shown along the three axes to emphasize the existence of three types of channels whose dimensions are indicated and measured by the van der Waals edges of the outermost atoms. (d) Cut-away view of the channels along all three axes to show the atomic ‘topography’ of the space encompassed by MOF-711. Exposed terminal ligands coordinating to the different Zr open metal sites are indicated with circles and squares in a black and gray color scheme.

rigorous description, documentation, and systemization of what the eye of the molecule registers as it moves around these reticular structures. We propose that the topic presented in this viewpoint be discussed at the *Faraday Discussion* meeting and that an agreed-upon protocol be pursued for displaying and describing MOF and COF structures from the eye of the molecule, and only then can the full development of their chemistry and applications be realized.

## Conflicts of interest

The authors have no conflicts of interest.

## Acknowledgements

Support for the synthesis and the characterization of MOF-711 was provided by the Joint KACST-UC Berkeley Center of Excellence for Nanomaterials and Clean Energy Applications, Riyadh, Saudi Arabia.

## Notes and references

- 1 O. M. Yaghi, M. J. Kalmutzki and C. S. Diercks, *Introduction to Reticular Chemistry: Metal–Organic Frameworks and Covalent Organic Frameworks*, Wiley-VCH, Weinheim, 2019.
- 2 O. M. Yaghi, G. Li and H. Li, Selective binding and removal of guests in a microporous metal–organic framework, *Nature*, 1995, **378**, 703–706.
- 3 H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, Establishing microporosity in open metal–organic frameworks: gas sorption isotherms for Zn(BDC) (BDC=1,4-benzenedicarboxylate), *J. Am. Chem. Soc.*, 1998, **120**, 8571–8572.
- 4 H. Li, M. Eddaoudi, M. O’Keeffe and O. M. Yaghi, Design and synthesis of an exceptionally stable and highly porous metal–organic framework, *Nature*, 1999, **402**, 276–279.
- 5 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O’Keeffe, A. J. Matzger and O. M. Yaghi, Porous, crystalline, covalent organic frameworks, *Science*, 2005, **310**, 1166–1170.
- 6 H. El-Kaderi, J. R. Hunt, J. L. Mendoza Cortez, A. P. Côté, R. Taylor, M. O’Keeffe and O. M. Yaghi, Designed synthesis of 3-D covalent organic frameworks, *Science*, 2007, **316**, 268–272.
- 7 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, A new zirconium inorganic building brick forming metal–organic frameworks with exceptional stability, *J. Am. Chem. Soc.*, 2008, **130**, 13850–13851.