

Multivariate metal-organic frameworks

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Reticular chemistry is founded upon the principles of linking simple organic and inorganic building blocks through strong bonds to form extended, porous and crystalline solids, such as metal-organic frameworks (MOFs) [1]. This field has developed and advanced by making new structures and studying their properties for applications covering gas storage, separations and catalysis, to name a few [2]. It is striking that the large majority of MOFs being studied thus far have relatively 'simple' structures in which a small number of building units is repeated throughout the crystal. In considering the future of MOFs, it is useful to take inspiration from biological systems and the fact that these are more complex because of the large number of building units and functionality (i.e. heterogeneity) making up their structure. We believe that, in order to achieve a new level of utility for MOFs, it is important to develop strategies that use the precision with which MOFs can be made towards making them more complex. In this context, the challenge becomes how to introduce heterogeneity and still maintain ordered materials as well as the handle on characterizing them [3]. This contribution focuses on how the multivariate approach to making MOFs is a viable strategy for introducing heterogeneity while maintaining order, and how these qualities lead to a higher degree of functionality.

Although MOFs with increased complexity (i.e. more than one linker) have been reported as early as 2002 [4], the first step in truly realizing the potential of introducing heterogeneity within

MOF structures came with the discovery of multivariate (MTV) MOFs in 2010 [5]. In this report, the incorporation of up to eight distinct linker functionalities within one pure phase of MOF-5 was successfully demonstrated (Fig. 1) [5]. The MTV discovery had a profound implication: the resulting MTV-MOFs possessed properties that did not arise from linear combinations of the pure constituents. This was evidenced by one MTV-MOF-5 material exhibiting a 400% enhancement in selectivity for carbon dioxide over carbon monoxide when compared to the parent MOF-5 analogues containing only pure-link

components. Following this, the spatial apportionment of the different functionalities (small clusters, random or alternating) in MTV-MOF-5 systems was determined in the context of predicting the adsorptive properties of such systems [6]. The MTV concept was later applied to MOF-177, resulting in a 25% higher volumetric H₂ uptake in the MTV-MOF-177 material, and was extended to the inorganic secondary building units (SBUs) of MOF-74 with the introduction of multiple metals (up to 10) within the same SBU (Fig. 1) [7,8]. It is noted that, in these systems, the MTV-MOF backbone is ordered and the heterogeneity

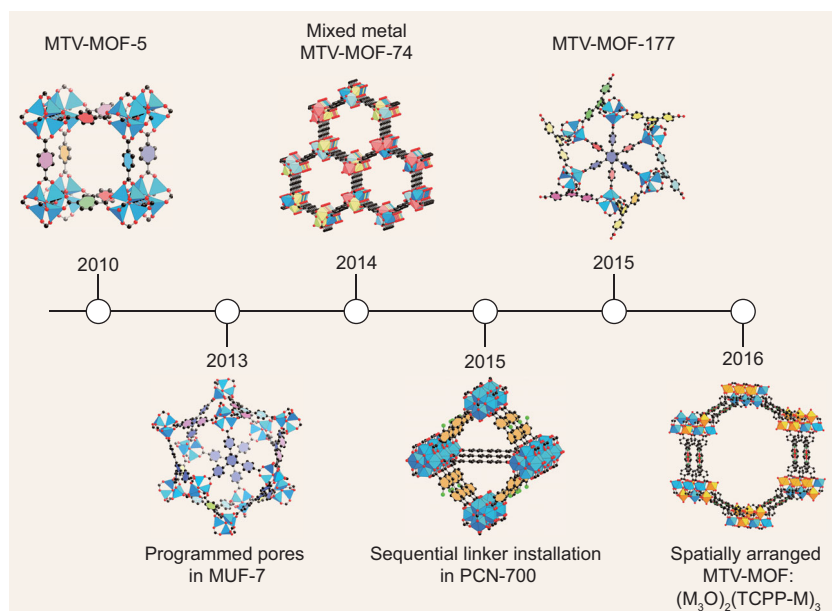


Figure 1. Representative discoveries of the multivariate approach for introducing heterogeneity within ordered MOFs. Color code: black, C; red, O; green, installed functional group; and various colored polyhedra, metal (M) atoms. H atoms are omitted for clarity. TCPP, tetrakis(4-carboxyphenyl)porphyrin.

(mixed organic functionalities or metal ions) is covalently bound at well-defined distances and ratios. Yet, even with this success, there was only limited control in placing different functionalized linkers (or metals) in exact positions throughout the MTV-MOF crystal.

In 2013, a strategy was reported to address this issue: linkers of varying symmetry and connectivity were judiciously chosen in order to obtain a MOF, MUF-7a, in which each linker was placed in pre-determined positions throughout the structure [9]. Accordingly, MUF-7a was constructed from three distinct linkers that were, in turn, functionalized to produce seven MTV-like MUF-7 analogues (Fig. 1). The beauty of this strategy was proven through the understanding that each of the three linkers occupied specific crystallographic site symmetries, which meant that, upon functionalization, no crystallographic disorder was to be observed. Introducing complexity into MUF-7a led to the exact placement of the introduced functionalities, control over the pore composition and up to 94% enhancement in CO₂ adsorption capacity. An additionally unique strategy for controlling the exact positions of functionalities was reported in 2015 (Fig. 1) [10]. In this case, terminal ligands (OH⁻/H₂O) of a Zr-based SBU were targeted for removal, thus allowing for the creation of appropriately sized pockets (16.4 and 7.0 Å). These pockets provided the requisite space needed for new linkers of varying sizes, and with varying functionalities, to be installed.

Beyond applying the MTV concept to the organic linker, the SBU also represents a viable target for achieving heterogeneity. Accordingly, it was shown that three distinct SBU geometries (Cu-based triangles, Zn-based square pyramids and Zn-based octahedra) could be combined with only one linker to construct a new mesoporous MOF, FDM-3 [11]. The endowed complexity led to precise arrangements of cages and pore apertures, thus limiting guest molecule transport to specific pathways. Recently, the MTV-SBU approach was applied to 36 porphyrin-based MOFs, in which the trigonal SBUs were composed of mixed-metal ions (Fig. 1) [12]. Remarkably,

the spatial arrangement of the multivariate metals within the SBUs of these MOFs were found to be well mixed or distributed throughout the MTV-MOF crystals in domains. In cases of the former arrangement, the MTV-MOFs were proven as kinetically more robust catalysts for the photo-oxidation of 1,5-dihydroxynaphthalene in comparison to the parent MOF structures with SBUs containing only one metal ion.

Although this is but a small sample of the progress reported for accomplishing a greater degree of heterogeneity within otherwise ordered structures, one can be assured that there is vast space left to explore. For example, performing framework chemistry, through post-synthetic modification, carries the potential of realizing pore environments with 'enzyme-like complexity' [13]. Indeed, this was recently achieved through seven successful post-synthetic reactions within the pores of an isoreticular MOF-74 system to install tripeptide functionalities. This modification afforded the resulting MTV-MOF with high catalytic selectivity resembling that of the enzyme TEV endopeptidase [13]. Significant consideration has also turned to the introduction of heterogeneity realm [14]. Furthermore, the strategy of designing dynamic, yet robust, frameworks that comprise different counting, coverage and sorting domains for guest molecules leads to MOFs with complex sets of physical properties [15]. Suffice it to say that introducing heterogeneity may be the first step in rectifying the disconnect associated with the functional capabilities of the synthetic world when compared to those observed in nature. Indeed, it is generally true that synthetic materials largely operate serially, whereas nature operates in parallel to perform a much wider array of functions at the same time. Therefore, it is a natural extension for us, as synthetic chemists, to speculate and explore how to bridge this functionality divide. In our opinion, the answer to this lies in achieving materials whose parts are many, heterogeneous and systematically varied [2].

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