HIGHLIGHT

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We survey the importance of correlated—as opposed to random—disorder in metal–organic frameworks (MOFs), focusing on correlations in vacancy arrangements, composition, and linker orientations in some canonical systems. We explore the link to physical and chemical properties, and highlight the various experimental and computational tools available for characterising and interpreting correlated disorder in MOFs.

1 Introduction

The discovery of disordered,1 defective,2,3 amorphous,4 and even liquid5,6 metal–organic frameworks (MOFs) has forced a paradigm shift in our collective understanding of MOF structural chemistry.7 Having long focused on the elegant control possible over crystalline network structures,8,9 the field is now increasingly exploiting the presence and nature of disorder in MOFs as an important design tool with which to tune their physical and chemical properties.10,11

Disorder is sometimes random; more often it is correlated.12 A vacancy at a linker site in an otherwise crystalline MOF, for example, may affect the likelihood for neighbouring linkers also to be vacant. Such vacancy correlations can propagate throughout a structure, collectively determining a variety of bulk properties—including porosity.2,13 Likewise, mixed-metal and/or mixed-linker MOFs can have non-statistical distributions that determine their corresponding chemistry; such is the basis, after all, of the ‘multivariate’ MOF approach which exploits compositional heterogeneity to improve functionality.14 And in orientationally-disordered MOFs, correlations in linker orientations can also affect mechanical and host/guest responses.15 These various distinctions are illustrated schematically in Fig. 1. It is no accident then that controlling the correlations within disordered MOFs—whether involving vacancy, composition, or linker orientation distributions—is an essential aspect of defect engineering.2,16–18

Distinguishing correlated disorder from random disorder is often a nontrivial experimental and computational challenge. Conventional crystallography, which has played such an important historical role in MOF science, probes only the average structure of materials: it is demonstrably insensitive to correlations within disordered states.19 Yet a number of developments have now converged to equip us, as a community, with the tools needed to probe correlated...
The importance of vacancy correlations in other MOF systems is also increasingly apparent. In the aluminium carboxylate MOF AlTz-53-DEF, for example, correlated linker vacancies facilitate a remarkable reversible switching between sql and kgm network topologies during desolvation/resolution cycles [Fig. 2(c)].14 Even for the well-known MOF-5, adsorption isotherms are sensitive to the distribution of linker vacancies—a result demonstrated using grand canonical Monte Carlo (GCMC) simulations.12 A similar link
Dense coordination networks can harbour disordered correlated vacancy distributions, the form and origin of which we expect may prove relevant in due course to the behaviour of MOFs. For example, Prussian blue analogues (PBAs) are highly defective cyanide frameworks with the pcu topology. Single-crystal X-ray diffraction measurements of PBAs reveal highly structured diffuse scattering, which has recently been interpreted using the three-dimensional difference pair distribution function [3D-APDF] approach [Fig. 2(d)]. The scattering arises from correlated hexacyanometallate vacancies, which avoid occupying neighbouring sites. A key point is that the precise correlations—which control the sorption and transport characteristics of the resulting pore network—can be tuned by variation in PBA composition and synthesis route. Conceptually similar vacancy patterns are found in the thiocyanate analogues, albeit with long-range order. And in formate perovskites, cation vacancies again interact by avoiding neighbouring sites; this leads to a disorder/order transition in [GUA] Mn$_x$-Fe$_{2-x}$/3(HCOO)$_3$ (GUA$^+$ = guanidinium cation) at $x_{ord} \approx 0.6$.51

![Fig. 2](image.png)

**3 Compositional disorder**

It is now well established that many MOF architectures are tolerant to the incorporation of multiple different metals and/or linkers within the one material. In such cases an obvious consideration is whether composition is homogeneously distributed or varies in some nonstatistical way—e.g. domain formation or core-shell architectures. The multivariate MOF (MTV-MOF) paradigm, and strategies such as sequential linker installation (SLI), have at their heart the concept that the spatial arrangement of different linkers or metals within a given MOF architecture is key to function.

The sense one gets is that, other than for very dilute mixtures, truly-random compositional distributions are conspicuously rare in MOFs. Clearly, kinetics of crystallisation play an important role here; for example, the different nucleation rates of Zn- and Co-containing imidazolate frameworks allow the one-port formation of mixed-metal frameworks with core-shell architectures. Likewise, precursors with different kinetic stabilities can be chosen cleverly to control the degree of mixing during synthesis of mixed-metal coordination polymers. But there are thermodynamic considerations at play too: a comprehensive DFT study has highlighted the dual roles of charge distribution and size-mismatch in determining the balance between mixing and segregation. Such considerations may rationalise the preferential formation of CeZr$_5$ clusters in mixed-Ce/Zr UiO-66 samples, as evidenced by X-ray absorption fine structure (EXAFS) measurements and as implicated in their catalytic behaviour.

In addition to DFT calculations and EXAFS measurements, a variety of techniques offer sensitivity to the spatial distribution of components in compositionally disordered MOFs. Electron microscopy allows direct visualisation of the heterogeneous disorder within MOFs.
Highlight

Fig. 3 Determining compositional correlations in compositionally disordered MOFs. (a) STEM-EDX images of transition-metal segregation in the mixed-metal Zn/Ni/MnCID-5 ⊂ G MOF.58 Adapted from ref. 58 with permission from the American Chemical Society. (b) REDOR-NMR decay curves are sensitive to the degree of clustering/anticlustering of individual linkers in mixed-linker MOFs (LC = large clusters, SC = small clusters, Alt = alternating).54 Adapted from ref. 54 with permission from the American Association for the Advancement of Science. (c) Atom probe tomography allows the sequencing of metal-oxide rods in multivariate MOF-74.62 Here the method is shown to differentiate ‘duplicate’ (D), random (R), and ‘insertion’ (I) sequences. Adapted from ref. 62 with permission from the American Association for the Advancement of Science. (d) The in-plane methylimidazolate (mIm) stretching region of the IR spectra of mixed-metal (Zn/Cd) ZIF-8 derivatives is sensitive to the relative populations of Zn–mIm–Zn, Zn–mIm–Cd and Cd–mIm–Cd linkages. These populations can be extracted using non-negative matrix factorisation and used to derive models of the Zn/Cd distribution, which is found to involve clustering.63 Note the greater-than-statistical population of Zn4/Cd4 four-rings (experimental Zn4/Cd4 populations as solid bars; statistical populations as open bars). Adapted from ref. 63 with permission from the Royal Society of Chemistry.

Just as enzymes derive their function from the precise spatial arrangement of different components—e.g. the amino-acids of their protein backbone—the vision with compositionally complex MOFs has always been one of controlling heterogeneity to optimise a particular chemical or physical property.11 A simple but effective example is the recent demonstration of correlation-dependent photocatalysis in a mixed-linker UiO-68 derivative.66 But this vision is not unique to the MOF field: indeed, conventional solid-state chemistry has long exploited the use of solid solutions and inhomogeneity in this general way. A good example is that of the relaxor ferroelectrics, such as PbMg1/3Nb2/3O3, where the structural complexity responsible for their useful dielectric properties emerges naturally from an interplay between composition and lattice geometry.67 We anticipate the design rules developed to control complexity in these inorganic materials may yet have a role to play in MOF science.12

4 Orientational disorder

Whenever the nodes or linkers of a MOF have lower point symmetry than that of the corresponding site in the MOF lattice, the issue of orientational disorder arises.12,68 A longstanding example is that of the IRMOF series, where orientational disorder follows from asymmetric substitution of terephthalate linkers.69 Because the pores of MOFs are surrounded by multiple neighbouring linkers, the chemical and physical pore environments are affected by the presence or absence of correlations in linker orientations. Hence the distinction between random and correlated disorder in such systems may be crucial for interpreting a variety of host/guest phenomena. Such is the case in the CAU-1 family, for example, for which hyperpolarised 129Xe NMR spectroscopy has been used to identify correlations in side-chain orientations, in turn reflected in the experimental Ar sorption isotherms.70 So too in the IRMOF-3-AMPh system (AMPh...
MOF is found in DUT-8(Ni), a pillared paddle-wheel MOF with 2,6-naphthalenedicarboxylate (NDC) linkers. The origin of disorder in this system is the existence of two degenerate NDC orientations. Each orientation introduces an offset—either up or down—in the positions of the neighbouring paddlewheel pillars. Since the lozenge-shaped pores of DUT-8(Ni) are flanked by four NDCs, there is a natural constraint that two must step up and two step down—aft er all, the total offset on traversing a loop around the pore must vanish to zero. The six possible NDC arrangements satisfying this rule partition into a set of four with a C2v-symmetric pore structure, and a set of two with a D2d pores. Neighbouring pores share edges, such that a large and complex configurational landscape emerges, characterised by different spatial arrangements of pore geometries. Remarkably, the adsorption and desorption of different solvent molecules drives the system reversibly across this landscape—the strength of host/guest interactions overcoming the ~20 kJ mol⁻¹ barrier to NDC ‘flips’ [Fig. 4(b)]. The recent development of efficient and accurate MOF force fields may allow computational insight into the mechanism for this unusual disorder–disorder switching.

The extent to which orientational disorder is static or dynamic depends on the reorientation barrier height, and if this barrier is commensurate with the available thermal energy then one expects to observe an order/disorder transition. There are plenty of examples in the literature, but we focus here on the case of the hybrid perovskite [NPr₄][Mn(N(CN)₂)₃]—not technically a MOF but relevant nonetheless because its MOF-like framework structure

denotes a phenylamide substituent), where linker orientations can be ordered or disordered a ccording to a clever choice of synthesis approach; the two polymorphs have profoundly different H₂ sorption profiles [Fig. 4(a)].

Just as linker orientations influence pore chemistry, so is it that guest adsorption can affect the correlations in linker orientations. Perhaps the clearest example in a disordered geometries. Remarkably, the adsorption and desorption of different solvent molecules drives the system reversibly across this landscape—the strength of host/guest interactions overcoming the ~20 kJ mol⁻¹ barrier to NDC ‘flips’ [Fig. 4(b)]. The recent development of efficient and accurate MOF force fields may allow computational insight into the mechanism for this unusual disorder–disorder switching.

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exhibits a particularly useful barocaloric effect exploitable in solid-state cooling. The conformations of the flexible \([\text{NPr}_4]^+\) extra-framework cations and orientations of the dicyanamide linkers couple: they are disordered at temperatures above 331 K and ordered below. The transition between the two states is accompanied by a large change in both entropy and volume. The latter confers sensitivity to pressure—the disordered state can be re-ordered by squeezing, which is the basis for a barocaloric heating/cooling cycle [Fig. 5]. Correlations within the disordered state, although still poorly understood, influence the barocaloric entropy change and reduce the critical pressure needed for each cooling cycle. In the parallel field of magnetocalorics—based on the order and disorder of magnetic spins—correlated disorder and the geometric frustration from which it arises are well-known to increase cooling efficiency. We therefore anticipate that similar design principles will prove valuable in exploiting orientational disorder in hybrid frameworks and MOFs alike.

5 Conclusions and outlook

Perhaps our central thesis is that MOFs are fundamentally predisposed to correlated disorder. On the one hand, they have many compositional and configurational degrees of freedom—so there will always be a strong entropic driving force for disordered states. And, on the other hand, interactions between neighbouring nodes, or neighbouring linkers, or between host and guest are rarely negligible, such that disorder is unlikely to be random. Sometimes this distinction between random and correlated disorder will be unimportant, but we hope to have identified in this brief review a range of physical and chemical properties for which the distinction is crucial.

An historical barrier to studying and exploiting correlated disorder in MOFs has been the ostensible insensitivity of experimental techniques to its presence and nature: conventional crystallography is the obvious culprit here. But there are now many different experimental and computational tools available with the relevant capabilities. The hurdle that unquestionably remains is that of developing rigorous strategies for exercising synthetic control over correlated disorder. To this end we have flagged the interplay between composition and network geometry, and also the role of local-symmetry lowering as potential mechanisms for driving very specific types of correlated disordered states. The balance of kinetic and thermodynamic control during synthesis is clearly also to be decisive in many cases.

Looking forward, the field shares much of its aims with those of multivariate MOF chemistry: ultimately, correlated disorder is a form of structural complexity that might be exploited in e.g. catalysis or information storage or selective host/guest chemistry. An intriguing recent development along similar lines is the concept of using correlated disordered states as intermediates in materials synthesis to target low-dimensional phases. But we note in conclusion the possible additional importance of different types of correlated disorder in MOFs to those outlined here— involving e.g. frustrated magnetism, local charge ordering, or cooperative spin-state transitions. We see enormous potential in combining the unconventional physics of correlated disordered states with the scope for exquisite control over geometry for which MOFs are renowned.

Conflicts of interest

There are no conflicts to declare.

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