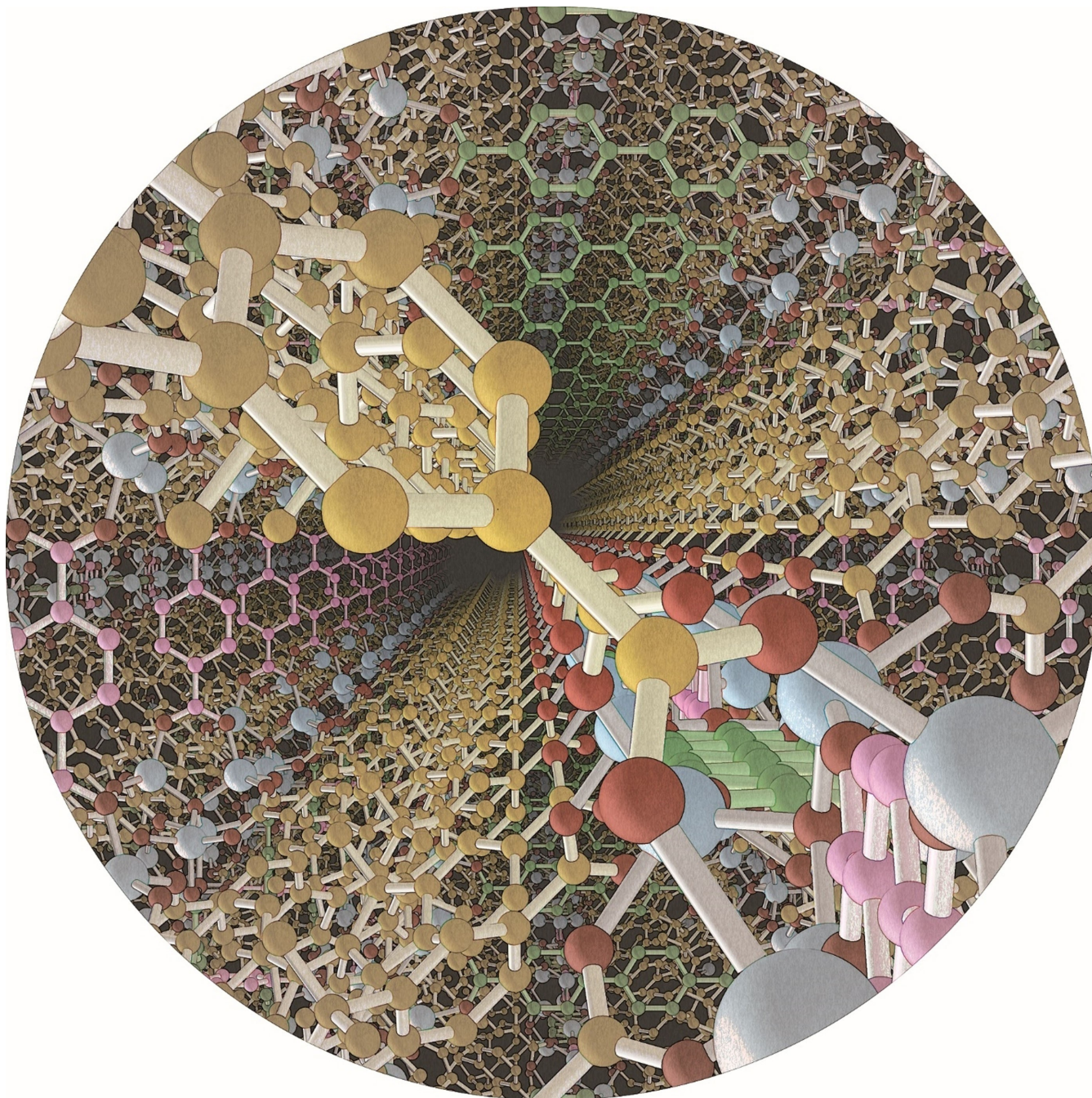


Metal-Organic Frameworks

How to cite: *Angew. Chem. Int. Ed.* **2023**, *62*, e202306341
doi.org/10.1002/anie.202306341

Multicomponent Metal-Organic Frameworks

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Abstract: Metal-organic frameworks (MOFs) are constructed from metal ions or clusters and organic linkers. Typical MOFs are rather simple, comprising just one type of joint and linker. An additional degree of structural complexity can be introduced by using multiple different components that are assembled into the same framework. In the early days of MOF chemistry, conventional wisdom held that attempting to prepare frameworks starting from such a broad set of components would lead to multiple different phases. However, this review highlights how this view was mistaken and frameworks comprising multiple different components can be deliberately designed and synthesized. When coupled to structural order and periodicity, the presence of multiple components leads to exceptional functional properties that can be understood at the atomic level.

1. Introduction

Synthetic materials are generally very simple being composed of a limited number of constituents. In contrast, structural complexity is a hallmark of biological materials. Importantly, this complexity is not accompanied by chaos; instead, there is structural order and uniformity. The combination of complexity and order translates into exquisite functional behaviour and arguably life itself. This provides inspiration for coupling complexity to order in synthetic materials.

What might be achieved by synthesizing MOFs from multiple components?^[1] The portfolio of design blueprints for frameworks can be expanded since the topologies of the building blocks becomes more diverse. New perspectives on framework architectures and pore chemistry are delivered by knowledge regarding materials that are synthetically accessible. Complex arrays of functional groups can be generated with precision, order and periodicity. This underpins structure–activity relationships that can be understood at the atomic level. The question of which moieties and with which arrangement give rise to a particular property can be addressed with certainty. Ultimately, emergent properties that arise from cooperative interactions among individual components may be observed.

In this review, the important distinction between *multicomponent* and *multivariate* MOFs is maintained (Figure 1). In multicomponent MOFs, the building blocks occupy distinct framework sites, whereas in multivariate MOFs the building blocks occupy the same framework sites. We also note that our review is not intended to be comprehensive, but to highlight representative examples.

2. What Kind of Building Blocks are Suitable for Multicomponent MOFs?

Multicomponent MOFs fruitfully combine complexity with order. Their complexity arises from the presence of two or more linkers or two or more metals. Their order stems from the precise positioning of each component with regularity and periodicity.

The ordered complexity of multicomponent MOFs underlies functional properties that are not possible in simpler materials. Since the components of multicomponent MOFs are arranged in sequence each pore is repeated throughout the lattice with strict periodicity. Since the framework components have well-defined spatial relationships to each other, their functional properties can be understood with precision. This is especially important where those properties rely on an array of specific interactions with incoming guest molecules.

Multicomponent MOFs differ from their conventional counterparts by being built up from multiple—rather than solitary—building blocks. In general, when complex structures are built up by the self-assembly of smaller subcomponents, identical such subcomponents are used. This is advantageous since fewer recognition, discrimination, and error-correcting events are required during the self-assembly process.^[2] If these processes are imperfect then the final assembly may suffer from irregularities and disorder. Using viruses as an example, the tobacco mosaic virus comprises an RNA strand coated with 2130 identical proteins. While the self-assembly process is intricate, its fidelity and the high symmetry of the final structure arises from the regularity of the protein sub-components and the noncovalent interactions between them.^[3]

Some crystals are known to have a multiplicity of molecular components arranged in order. This is well illustrated by pharmaceutical cocrystals where “*two or more components form a unique crystalline structure having unique properties*”.^[4] While solvates and clathrates are also types of multicomponent crystals, it is more relevant to draw parallels between multicomponent MOFs and cocrystals comprising two or more large molecules.^[5] Ternary and quaternary cocrystals have been realized by careful consideration of the noncovalent interactions between the components. The central challenge in their production is the existence of alternative crystallisation pathways that lead to single-component crystals. These pathways exist because the interactions between molecules in cocrystals are weak and they are strongly influenced by solvent and temperature. In

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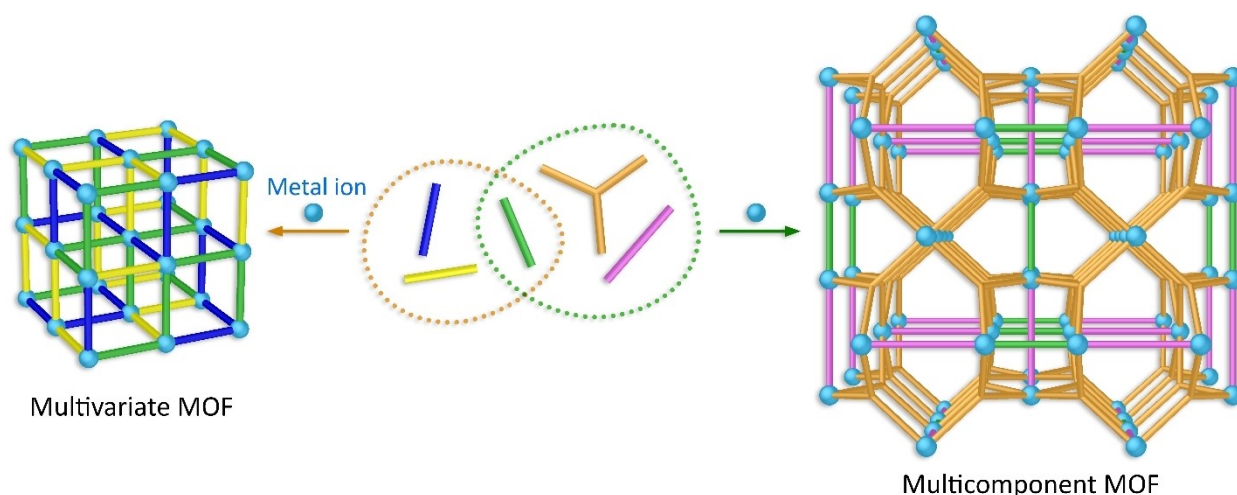


Figure 1. Metal-organic frameworks with multiple components. Building blocks that are geometrically similar to one another in terms of length and symmetry will co-assemble into multivariate (MTV) MOFs. Building blocks that are geometrically different to one another can form multicomponent MOFs in which they each building block is located in a specific position. Metal nodes are indicated by blue spheres.

contrast, multicomponent MOFs can be designed and realised in a more systematic way since the competing reaction pathways appear to be better differentiated in energetic terms and the reaction conditions can be tuned to follow the desired pathway in a more reliable way.

The formation of multicomponent MOFs relies on three successful processes: the (i) integration of the multiple components into a common framework, (ii) placement of each component in a unique framework position, and (iii) suppression of competing phases (side-products). For this to be achieved, the components must be sufficiently distinct from one another to enable recognition, discrimination, and error-correcting processes during self-assembly. They must also be compatible for co-assembly into a common framework. For example, while the bdc (1,4-benzenedicarboxylate, Figure 2) linker is chemically distinct from its deuterated analogue bdc- d_4 , the differences are subtle, and these linkers are unlikely to be differentiated. Therefore, a *multivariate* framework would be generated in which the two linkers occupy the same lattice sites at random. On the other hand, since the bpdc (biphenyl-4,4'-

dicarboxylate) linker is longer, bpdc and bdc cannot occupy the same framework sites. Simultaneously, bdc and bpdc are sufficiently compatible with one another so that they can be integrated into the same framework (SUMOF-4 (see below)). This compatibility draws from the isorecticular principle, which holds that structurally-related building blocks will give rise to topologically identical, or “isorecticular” frameworks.^[6] The question of competing product phases arises with SUMOF-4 since MOF-5 could be formed from the bdc linker and IRMOF-9 from the bpdc linker. These competing reaction pathways are suppressed during the synthesis of SUMOF-4 by adjusting the H₂bdc:H₂bpdc ratio and the reaction conditions.

How different do linkers need to be to enable their differentiation during framework assembly? While this depends on many details that are particular to a given framework, it is possible to make some generalizations:

- (i) the linkers will have different lengths, and/or
- (ii) the linkers have different symmetries, and/or
- (iii) the linkers will have different donor groups.



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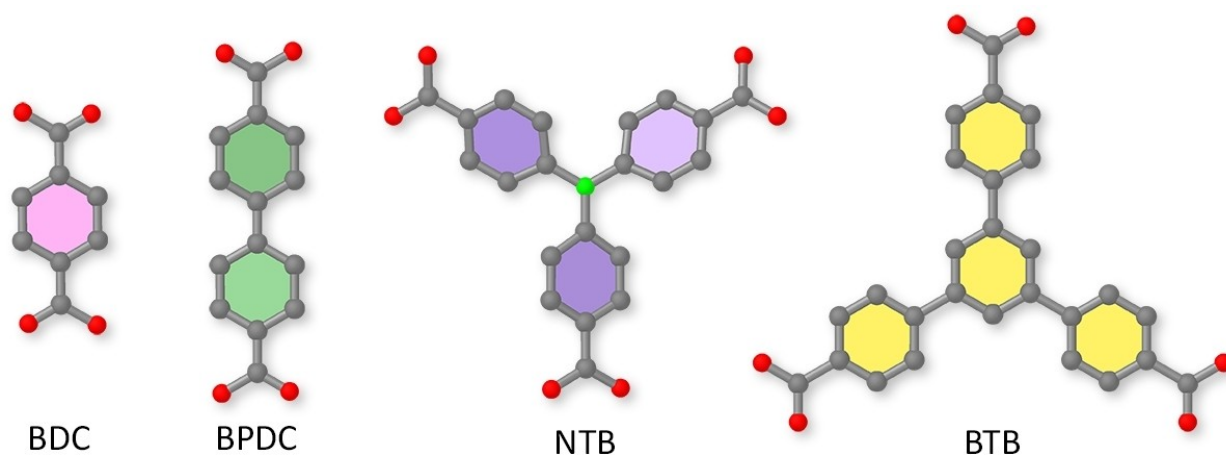


Figure 2. The structures of a selection of ligands commonly encountered in multicomponent MOFs. Hydrogen atoms are omitted for clarity. Color code: C, gray; O, red; N, green.

Point (i) is nicely exemplified by SUMOF-4, while point (ii) is illustrated by a comparison of bdc and btb (benzene-1,3,5-tribenzoate, Figure 2). Bdc is a ditopic bis(carboxylate) linker while btb is a tritopic tris(carboxylate) linker, so their different symmetries and ways of connecting metal clusters allow for their easy differentiation. We will encounter linkers that exemplify point (iii) in the next paragraph.

So far, our discussion has focused on organic linkers, but similar concepts can be applied to multicomponent MOFs built up from two or more different metal ions. The discrimination of metal ions during framework assembly will allow them to occupy distinct lattice sites based on the hard-soft-acid-base (HSAB) principle. Linkers with hard and soft donors coassembled in FDM-6, with the zinc(II) ions engaging exclusively with the hard carboxyl groups and the copper(I) ions coordinating to the pyrazolate nitrogen donors. In contrast, random *multivariate* frameworks are produced where the metal ions are not discriminated, for example in $[\text{Zn}_{1-x}\text{Cu}_x(\text{bdc})(\text{dabco})_{0.5}]$ ($\text{dabco} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane}$).^[7]

3. Multicomponent MOFs with Two Ligands

When two ligands are combined with a metal cluster to form a metal-organic framework, in principle there are three potential phases:

- (i) linker A can produce its own MOFs,
- (ii) linker B can produce its own MOF, or
- (iii) linkers A and B can coassemble into the same ternary (three-component) MOF.

The principles of multicomponent MOF formation are well illustrated by SUMOF-4, $[\text{Zn}_4\text{O}(\text{bdc})_2(\text{bpdc})]$, which is a cubic framework built up from bdc, bpdc and Zn_4O clusters (Figure 3).^[8] The resemblance to MOF-5 can be appreciated: the bdc linkers that lie along one crystallographic axis in MOF-5 have been replaced by bpdc linkers

in SUMOF-4 while the cubic **pcu** topology is maintained. In this light, SUMOF-4 conforms to the principles of isorecticular chemistry.

The report of UMCM-1 set the scene for the field of multicomponent MOFs.^[9] Notably, UMCM-1 represented an entirely new framework type: there was no pre-existing blueprint for the design of this MOF. It comprises btb and bdc ligands together with Zn_4O clusters with the formula $[\text{Zn}_4\text{O}(\text{btb})_{4/3}(\text{bdc})]$ (Figure 4). Four btb ligands and two bdc ligands connect to each zinc(II) cluster and the framework adopts the **muo** topology. A challenge in the synthesis of UMCM-1 is the existence of competing frameworks. Under similar conditions, the bdc linkers can form MOF-5 while the btb linkers can produce MOF-177, $[\text{Zn}_4\text{O}(\text{btb})_2]$. Fortunately, UMCM-1 can be clearly differentiated from these competing phases by optical microscopy since its crystals have a needle-like morphology as opposed to the prismatic shapes of MOF-5 and MOF-177. The correct feed ratio of the bdc and btb linkers is crucial to obtain phase-pure UMCM-1. Specifically, the $\text{H}_3\text{btb}:\text{H}_2\text{bdc}$ feed ratio used in the synthesis must lie between 2:3 and 1:1. Notably, the bdc:btb ratio in the product is 4:3, which lies outside of this range of feed ratios i.e. the amount of H_2bdc in the reaction mixture has to be increased above the level found in UMCM-1 itself. This difference between the required feed ratio and the ratio in the framework itself is a common observation in multicomponent MOFs. In UMCM-1, btb is more likely to be incorporated to a framework since it has three carboxyl groups while bdc only has two. A complementary perspective is obtained by converting the $\text{H}_3\text{btb}:\text{H}_2\text{bdc}$ ligand feed ratios (2:3 to 1:1) into a feed ratio of the carboxyl groups themselves (three for the btb ligand; two for the bdc ligand). This equates to a requisite feed ratio of “btb carboxyl groups” to “bdc carboxyl groups” of 1:1 to 3:2. The ratio of btb and bdc present in UMCM-1 itself (4:3) lies in this range.

A series of MOFs related to UMCM-1 has been reported. These MOFs, UMCM-2–UMCM-5, comprise Zn_4O clusters and btb linkers in combination with various

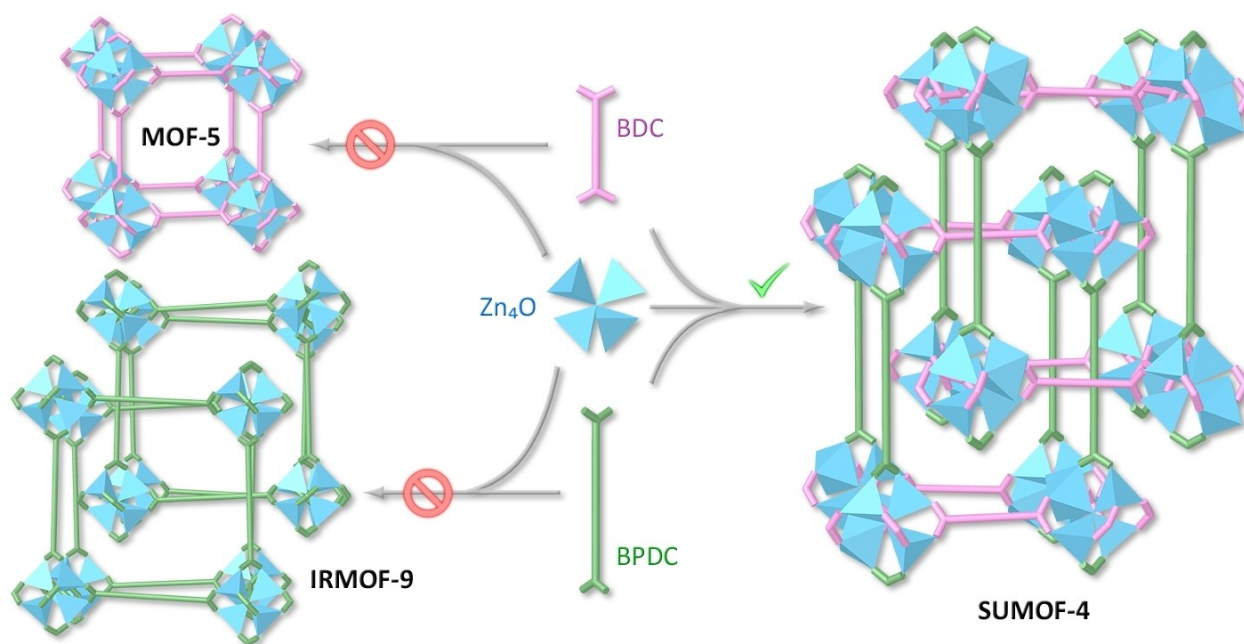


Figure 3. The assembly and structure of SUMOF-4, $[\text{Zn}_4\text{O}(\text{bdc})_2(\text{bpdc})]$, a multicomponent MOF comprising bdc and bpdc linkers and Zn_4O clusters. MOF-5 and IRMOF-9 are potential competing phases, but their formation is suppressed. Color code: Zn, blue. bdc and bpdc linkers are shown in pink and green, respectively.

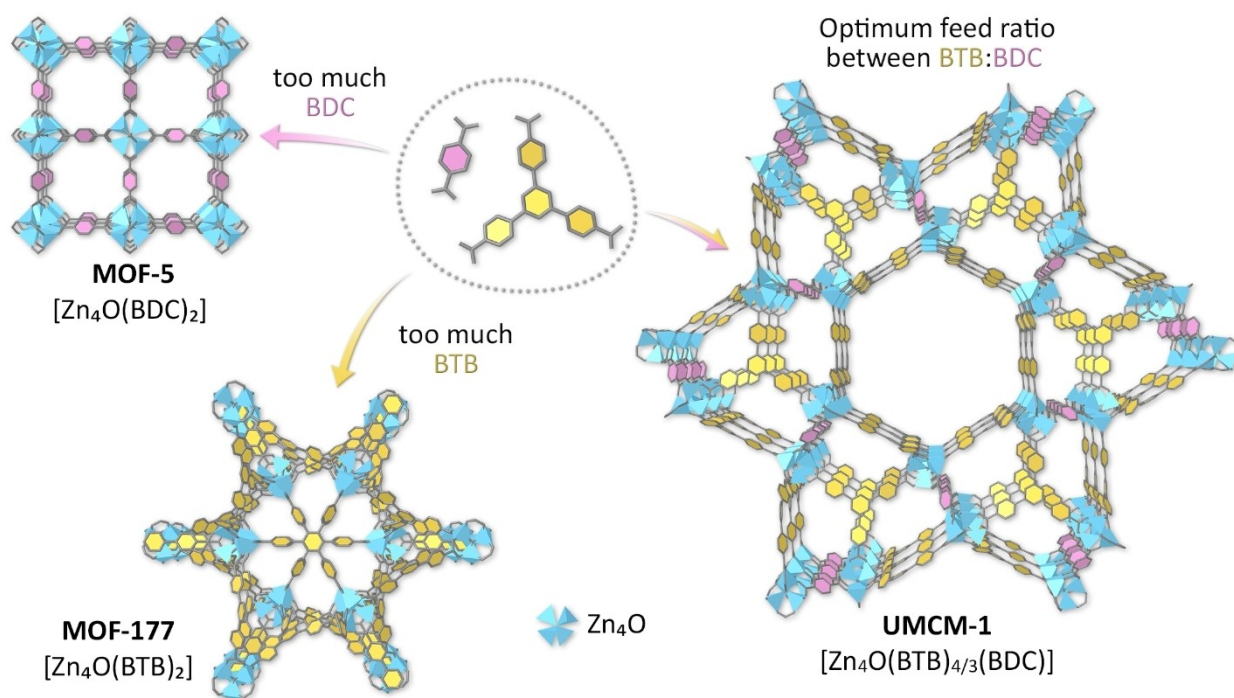


Figure 4. The assembly and structure of the multicomponent UMCM-1 framework, $[\text{Zn}_4\text{O}(\text{btb})_{4/3}(\text{bdc})]$. UMCM-1 can be formed phase-pure with certain btb:bdc ratios. Outside of this “sweet spot” MOF-5 or MOF-177 appears as a competing phase. Color code: Zn, blue. BDC and BTB linkers are highlighted in pink and yellow, respectively.

ditopic, linear bis(carboxylate) linkers.^[10] The tritopic ntb linker ($\text{H}_3\text{ntb} = 4,4',4''\text{-tricarboxytriphenylamine}$) was also used as a substitute for btb. While the formula of these materials is uniformly $[\text{Zn}_4\text{O}(\text{tritopic})_{4/3}(\text{ditopic})]$, the ar-

rangements of the ligands differ substantially. As a consequence, the network topologies are diverse. An exception is UMCM-5, which is an analogue of UMCM-1. In this case, the isorecticular principle is applicable since the bdc linker of

UMCM-1 is simply replaced by the NDC (1,4-naphthalenedicarboxylate) linker.

Circling back to the question of how different the linkers need to be to enable their differentiation during framework assembly yet be mutually compatible, UMCM-1–UMCM-5 highlight the importance of the distance between their donor groups (length). The ratio of the lengths of the ditopic and tritopic linkers that successfully gave multicomponent MOFs lies between 0.73 and 1.02. Outside of this range they are incompatible with one another. As an example of an unsuccessful combination, bpdc and btb are not known to coassemble into a common framework with Zn_4O clusters.

In terms of MOFs with different metal clusters, DUT-23 comprises btb linkers together with 4,4'-bipyridine (bipy) and dinuclear zinc(II) paddlewheel nodes.^[11] The carboxylate groups of the btb linkers coordinate in the equatorial positions of the paddlewheels. This produces a neutral underlying subnet with the **pto** topology. The neutral bipy ligands can coordinate via their nitrogen donor atoms in the axial sites of the zinc(II) paddlewheels to link adjacent subnets into a lattice with **ith-d** topology.

Compatible length ratios were also key to the design of the multicomponent quaternary MUF-32 (Figure 5).^[12] This MOF comprises a $[Zn_2(ntb)_{4/3}]$ subnet (**pto** topology) with dinuclear zinc(II) paddlewheels that are connected by the carboxylate groups of ntb linkers. Bipy and dabco linkers connect adjacent nets giving the overall formula $[Zn_2(ntb)_{4/3}(bipy)_{1/2}(dabco)_{1/2}]$ in a network that now has **ith-d** topology. These frameworks are able to sustain high levels of ligand vacancy defects. Since the bipy and dabco linkers are neutral, their absence has no impact on the charge balance of the material. Their absence has a limited impact on the structural integrity of the framework since the underlying $[Zn_2(ntb)_{4/3}]$ subnet is “load bearing” whereas the neutral ditopic linkers are largely “decorative”. The integrity

of the material is maintained even when only 20% of the bipy/dabco linkers are present.

MIL-142(Fe) is a multicomponent MOF with bdc and btb ligands and it has the formula $[Fe_3O(H_2O)_2(Cl)(bdc)(btb)_{4/3}]$ (Figure 6).^[13] Each iron(III) trimer is connected by two bdc and four btb linkers to produce an array of superoctahedral clusters. The power of the isorecticular principle is evident when the bdc linker is elongated to a longer linear ditopic carboxylate linkers while the network structure is retained. This gives rise to a series of analogues (MIL-142B–MIL-142E). The isorecticular principle was again fruitfully employed to make a number of analogues of MIL-142 using scandium(III) in place of iron(III).^[14] These metals share similar coordination preferences and characteristics. In the scandium examples, the tritopic btb linker was replaced by 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzoate (tatb) and 4,4',4''-(pyridine-2,4,6-triyl)tribenzoate (ptb) while maintaining the parent network structure. Careful optimization of the feed ratio of $ScCl_3$, H_2bdc and H_3tatb allowed for the synthesis of MIL-142(Sc)-tatb ($[Sc_3O(H_2O)_2(OH)(bdc)(tatb)_{4/3}]$) in a crystalline form with a high surface area. It is notable that the ideal feed ratio of the H_2bdc and H_3tatb linkers is 1:1, which matches the stoichiometry of the parent MOF. Unlike UMCM-1, this feed ratio does not have to be adjusted for the different number of carboxyl groups of the linkers.

The analysis of MOF networks can be used to design multicomponent MOFs, as nicely demonstrated by sph-MOF-1.^[15] The term **sph** refers to the topology of the network of this MOF. It has the formula $[Tb_6(\mu_3-OH)_8(tia)_2(btcb)_2(H_2O)_6]$ ($tia = 4H-1,2,4$ -triazol-4-yl)isophthalate, $btcb = 4,4',4''$ -(benzene-1,3,5-tricarboxyl)tri(azanediy)l-tribenzoate). The **sph** net can be deconstructed into two underlying subnets: a **spn** net and a **hxg** net (Figure 7). The **sph** net was realized by the solvothermal reaction of $Tb(NO_3)_3$, H_2tia , and H_3btcb in DMF/water. The **spn** subnet

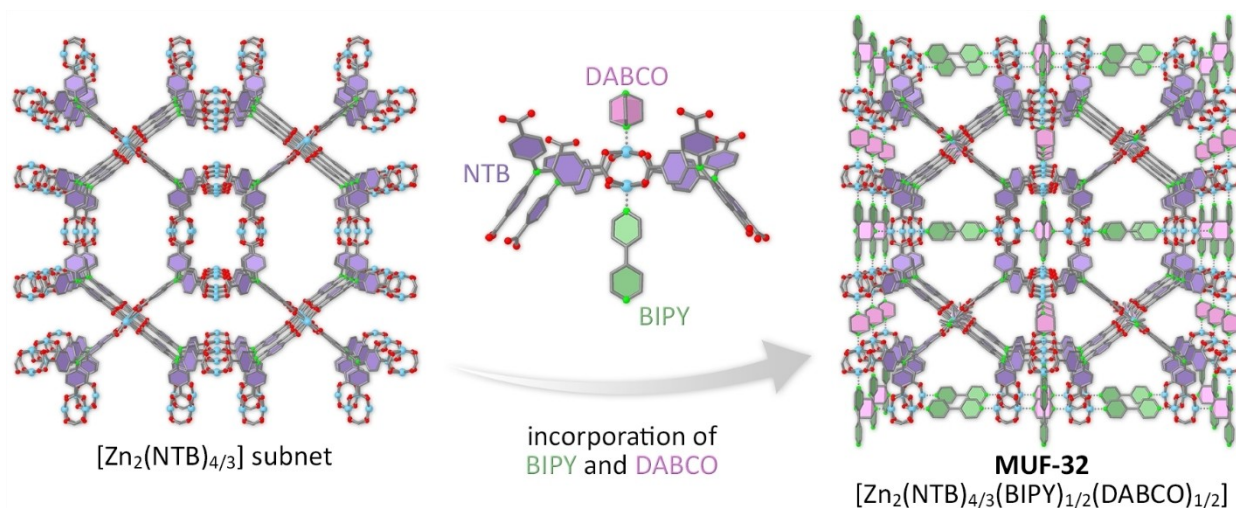


Figure 5. The assembly and structure of the multicomponent MUF-32 framework, $[Zn_2(ntb)_{4/3}(bipy)_{1/2}(dabco)_{1/2}]$. Its structure can be visualized as a hypothetical $[Zn_2(NTB)_{4/3}]$ subnet that is linked by bipy and dabco ligands in the axial paddlewheel sites. The framework can sustain high levels of vacancy defects when these neutral ligands are absent. Color code: Zn, blue; O, red; C, gray; N, green. bipy, dabco and ntb linkers are shown in green, pink and violet, respectively.

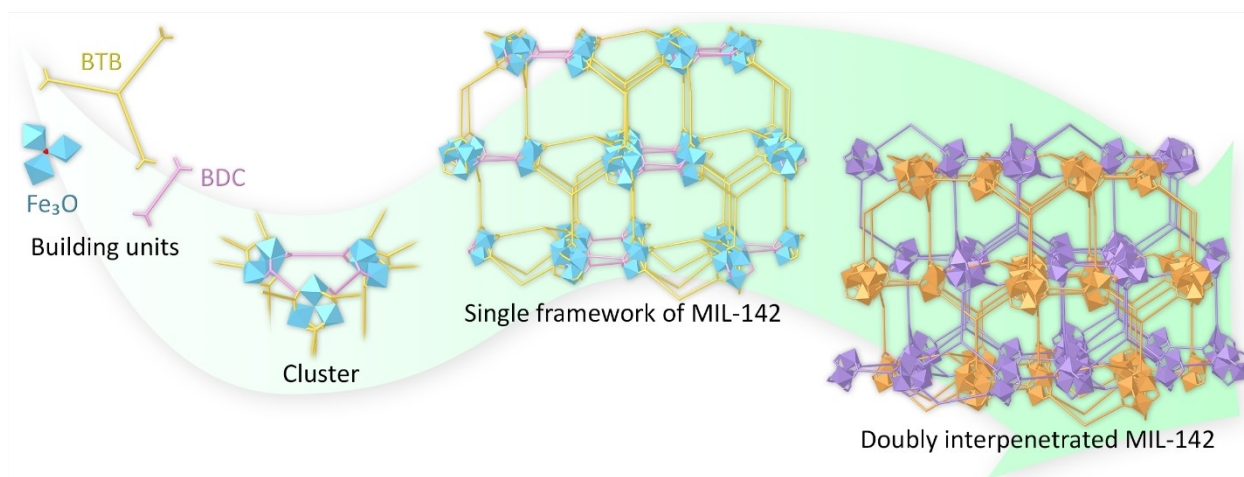


Figure 6. The structure of the multicomponent MIL-142(Fe) framework, $[\text{Fe}_3\text{O}(\text{H}_2\text{O})_2(\text{Cl})(\text{bdc})(\text{btb})_{4/3}]$, with only the bdc and btb ligands shown for clarity. Color code: Fe₃O, blue; btb, yellow; bdc, pink.

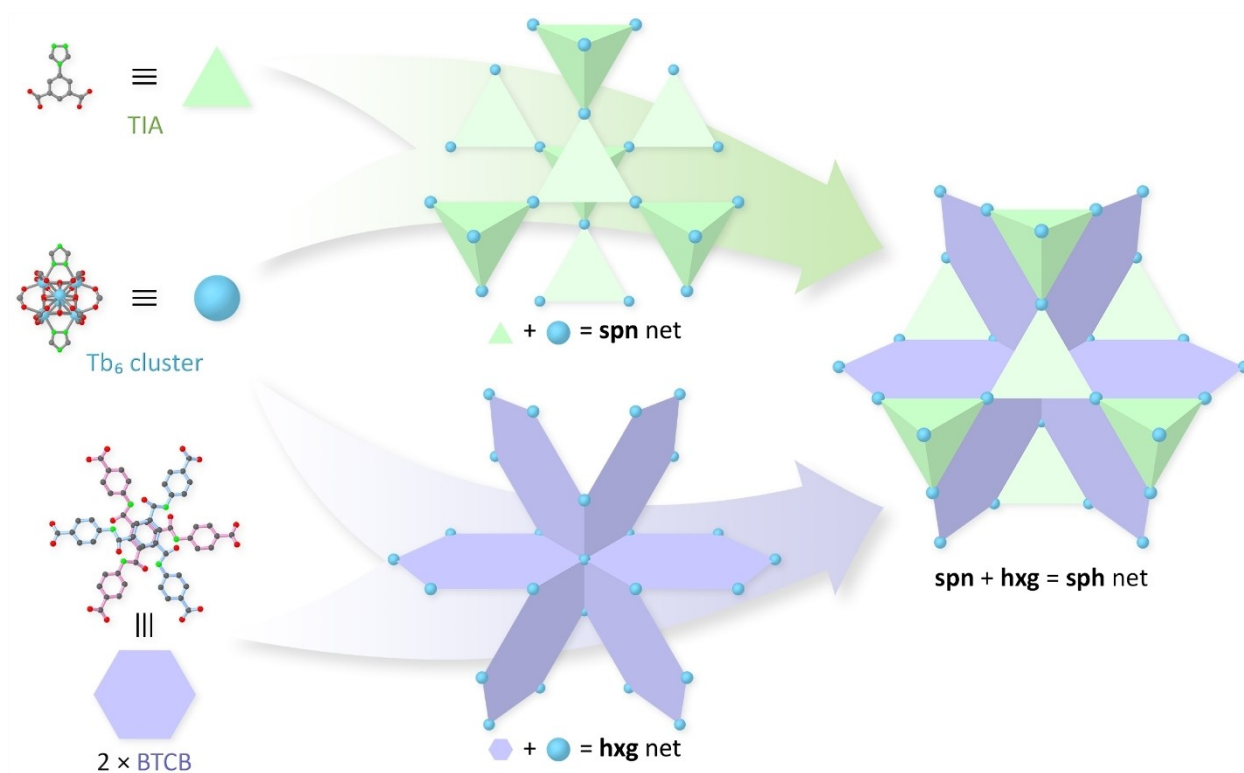


Figure 7. The structure of the multicomponent sph-MOF-1 framework, $[\text{Tb}_6(\mu_3\text{-OH})_8(\text{tia})_2(\text{btcb})_2(\text{H}_2\text{O})_6]$. The sph-MOF-1 framework can be deconstructed into two underlying nets: **spn** (from tia and the terbium clusters) and **hxg** (from btcb and the terbium clusters). These conceptual nets merge into the final **sph** net. Color code: Tb₆-cluster, blue; btcb, violet; tia, green.

is generated by a combination of the tia linkers and hexanuclear terbium(III) clusters, and it was produced independently in Tb-spn-MOF-1, $[\text{Tb}_6(\mu_3\text{-OH})_8(\text{tia})_2(2\text{-fba})_6(\text{H}_2\text{O})_6]$ (2-fba = 2-fluorobenzoic acid). In sph-MOF-1, the btcb linkers also coordinate to the terbium clusters. Taken alone, this combination produced a **hxg** subnet. The overall **sph** network topology arises from merging the **spn** and **hxg** subnets. The compatibility of the tia and btcb linkers in sph-

MOF-1 was carefully assessed based on their relative lengths and the geometric requirements of the **sph** network. Ligands suitable for isorecticular analogues were identified based on their metric parameters, and the power of this strategy was demonstrated by the successful synthesis of MOFs sph-MOF-2–sph-MOF-4. The deliberate design of multicomponent MOFs using merged nets complements earlier exam-

ples of topology-driven approaches with DUT-23 and MUF-32 (vide infra).

Using kinetically labile ions to generate multicomponent MOFs is advantageous since it permits reversible self-assembly during framework growth. This allows the framework components to assume ordered, regular positions rather than being locked into a random orientation. Frameworks that are well ordered are likely to lie at deep thermodynamic minima. In contrast, the slow metal-ligand substitution reactions of kinetically inert metal ions are generally incompatible with the bond reversibility required for error-correcting and healing processes. This is illustrated by multicomponent MOFs produced from the inert metal ion zirconium(IV) and a combination of bdc and dobdc ligands (dobdc = 2,5-dihydroxy-1,4-benzenedicarboxylate).^[16] While both linkers are incorporated into a common framework, named ZRD-DOB, ¹H NMR spectroscopy indicated the presence of ligand vacancy defects, which stem from error correction and healing processes being outpaced by framework growth. These defects indicate a lack of framework periodicity, therefore the material constitutes a range of different cluster and pore environments. In a related example, linear bdc and zig-zag fumarate (fum) linkers were combined into a multicomponent zirconium(IV) MOF, [Zr₆O₄(OH)₄(bdc)₃(fum)₃], using a one-pot process.^[17] Each hexanuclear zirconium cluster is a 12-connected node coordinated to six bdc and six fum linkers. The linkers occupy specific positions in the framework, however ¹H NMR spectroscopy showed that ligand-vacancy defects were prevalent.

4. Multicomponent MOFs with Three Ligands

Quaternary MOFs comprise four components. Typically, this is a set of three linkers in combination with a metal cluster. The presence of three linkers in a synthetic “brew” accentuates the phase problem since an even wider array of frameworks are potential side-products. Despite these challenges, quaternary MOFs can routinely be synthesized in phase-pure form and free of defects and disorder. Because the position of each linker in the lattice is determined by its backbone structure, regularity prevails over randomness.

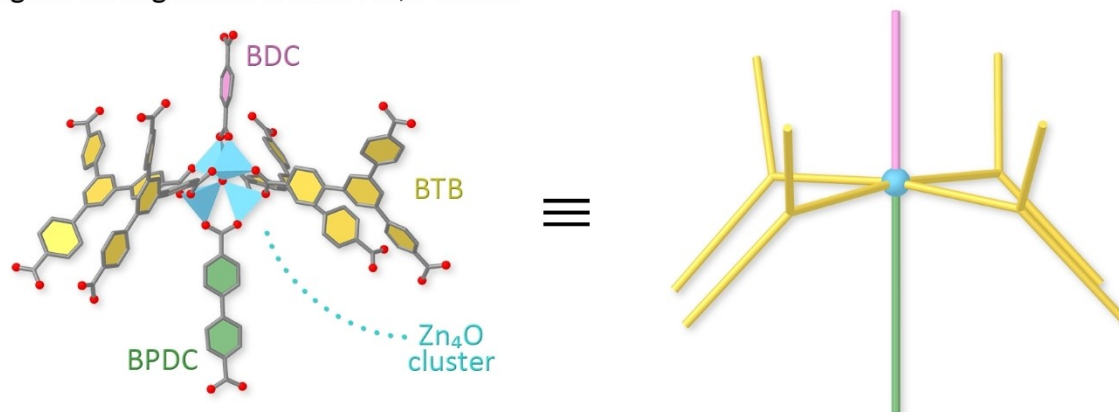
In MUF-7a, the linkers bdc, bpdc, and btb are combined with Zn₄O clusters to give [Zn₄O(btb)_{4/3}(bdc)_{1/2}(bpdc)_{1/2}] (Figure 8a). Despite the number of possible competing phases, MUF-7a can be prepared in a pure form in high yield.^[18] As observed for UMCM-1, it was found that ditopic linkers should be present in the feed mixture in slightly larger quantities than those required stoichiometrically. Since the bdc, bpdc, and btb linkers are geometrically distinct from one another, they occupy specific positions in the MUF-7 lattice. This circumvents randomness in the framework structure therefore there are no observable defects or disorder.

MUF-7a is modular and the individual components can be replaced by substituted analogues while maintaining the **ith-d** topology. Functional groups can be installed on the

linkers to build up “programmed pores”: precisely tuned pore spaces (Figure 8b). Since these linkers are included in predetermined positions, these functional groups systematically vary the pore spaces and are positioned precisely with respect to one another.

MUF-7 is somewhat sensitive to water vapor, which means that it cannot be handled in open air without the risk of losing crystallinity and porosity. This can complicate applications such as catalysis and gas adsorption. MUF-77 is a closely-related MOF that is much more stable towards water vapour and can be conveniently handled in open air without the risk of framework collapse.^[19] The key difference between MUF-7 and MUF-77 is the nature of the tritopic tris(carboxylate) linker. In MUF-7 this linker is btb while in MUF-77 it is hmmt (5,5',10,10',15,15'-hexamethyltruxene-2,7,12-tricarboxylate), which has a truxene core (Figure 9). The truxene core is much more rigid than the phenyl ring in btb, which counteracts any ligand exchange reactions with incoming H₂O that would lead to pore collapse. In MUF-77, bdc, bpdc, and hmmt combine with Zn₄O clusters to yield [Zn₄O(hmmt)_{4/3}(bdc)_{1/2}(bpdc)_{1/2}]. As in MUF-7, the framework adopts the **ith-d** network topology. The hmmt linker features methyl groups that can be replaced by other alkyl groups up to 10 carbon atoms long to generate an isorecticular series of materials. Similarly, the bdc and bpdc struts can be replaced by functionalised analogues in accordance with the isorecticular principle.^[20] These functional groups decorate the framework pores in a preconceived way. Since three functional groups can be introduced in total (one each on the truxene, bdc and bpdc linkers), the framework pores can be “programmed” with arrays of functional groups (Figure 9). Catalytic properties can be introduced organocatalytic substituents on one of the linkers. Groups on the other linkers can then systematically modify the catalytic properties, such as the enantiomeric excess of the reaction products,^[21] the reaction rate and the selection between multiple competing reaction channels e.g. aldol and Henry reactions.^[22] Without overstating the biological relevance of these materials, it can be noted that programmed pore environments have a degree of structural and functional resemblance to enzymes. Such frameworks may not mimic enzyme behaviour *per se*, but allow the lessons of small molecule catalysis and supramolecular chemistry to be applied to heterogeneous catalysts. The ability to introduce functional elements in predetermined positions in MUF-77 materials has also been leveraged to tune their emission (luminescence) profiles. By taking advantage of functional groups placed on all three ligands, MOFs that emit white light could be designed and synthesized.^[23]

UMCM-10 is a pillared layer quaternary MOF. Its 2-dimensional layers comprise ntb and bdc coordinated to Zn₄O clusters.^[24] The pillar is provided by 2,2',6,6'-tetramethylbiphenyl-4,4'-dicarboxylate (tm-bpdc) giving an overall formula of [Zn₄O(ntb)(bdc)_{1/2}(tm-bpdc)]. The linear linkers are required in greater amounts than given by the stoichiometry of the framework, which is consistent with their relative number of carboxyl groups. The isorecticular principle can be gainfully employed to produce UMCM-11

(a) Ligand arrangement around Zn_4O cluster

(b) Various pore environments

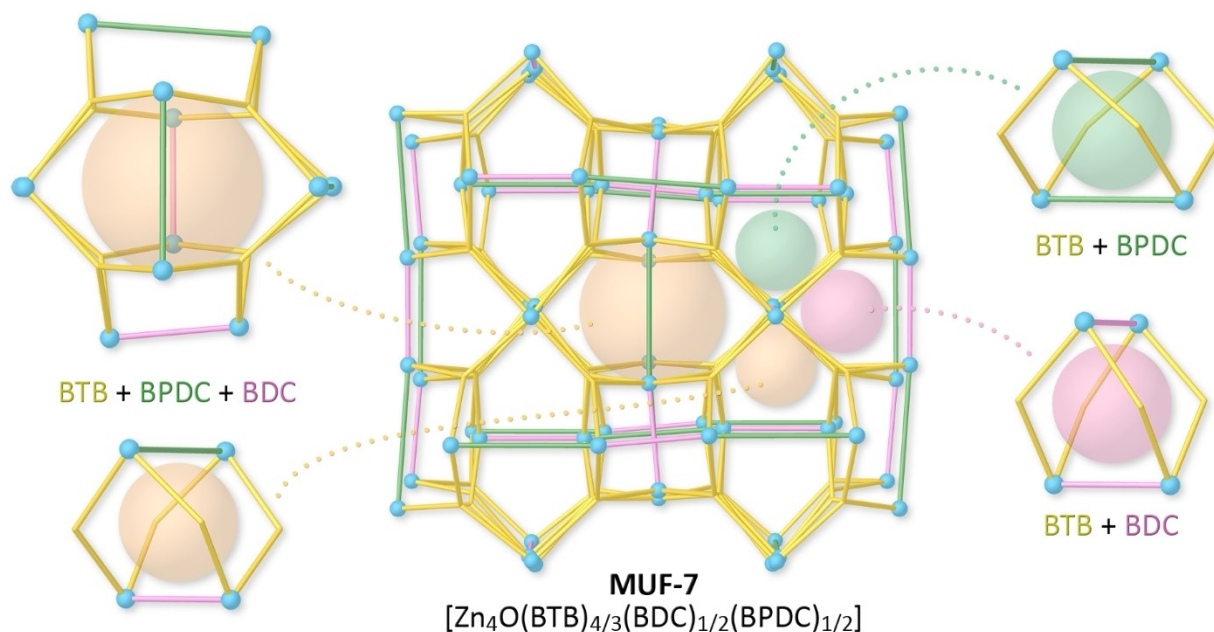


Figure 8. Structure of the multicomponent MUF-7 framework $[Zn_4O(btb)_{4/3}(bdc)_{1/2}(bpdc)_{1/2}]$. (a) Linker sphere around the Zn_4O SBU and (b) different types of pores in MUF-7 that can be programmed by introducing three different functional groups to the three different linkers. Color code: Zn, blue. Bdc linkers in pink, bpdc linkers in green, and BTB linkers in yellow.

and UCMC-12 by extending the length of the pillaring linker with an acetylenic or phenyl ring spacer.

TPMOF-2 is a quaternary framework that is assembled from zinc(II) ions and tz, tdc and bdc linkers (tz = 1,2,3-triazolate; tdc = 2,5-thiophenedicarboxylate), which build up a **lon** network with the overall formula $[(CH_3)_2NH_2]_2[Zn_8(tz)_6(tdc)_3(bdc)_3]$.^[25] By drawing on the isorecticular principle, related materials could be made by replacing the bdc with other linear linkers such as 2,6-ndc. The core trigonal prismatic node was retained in related materials with **jea** and **xai** topologies. These multicomponent MOFs were constructed by replacing the bdc in TPMOF-2 by the *tritopic* linkers ntb and btb and by the *tetratopic* tcpp (tetrakis(4-carboxyphenyl)porphyrin) linker.

FDM-6 is a multicomponent MOF that is constructed from PyC (4-pyrazolecarboxylate) and bdc linkers together with two distinct roles for the metal ions.^[26] In one role, the zinc(II) forms a conventional Zn_4O cluster, while the other role involves assembly of three copper(I) centres and three pyrazolate groups into $Cu_3(PyC)_3$ units. This generates FDM-6 ($[Zn_4O(Cu_3(PyC)_3)_4/3bdc]$), which is isorecticular to UCMC-2. The structural relationship between FDM-6 and UCMC-2 can be appreciated by viewing the tritopic metal-organic linkers that are structurally akin to btb. The expansion of the bdc linker to 2,6-ndc in FDM-8 is accompanied by a switch from the **umt** topology to the **ith-d** topology (Figure 10). FDM-8 extends the structural features of FDM-6 and leverages the diversity of both the metallic and ligand structural elements for the design of a *five-component*

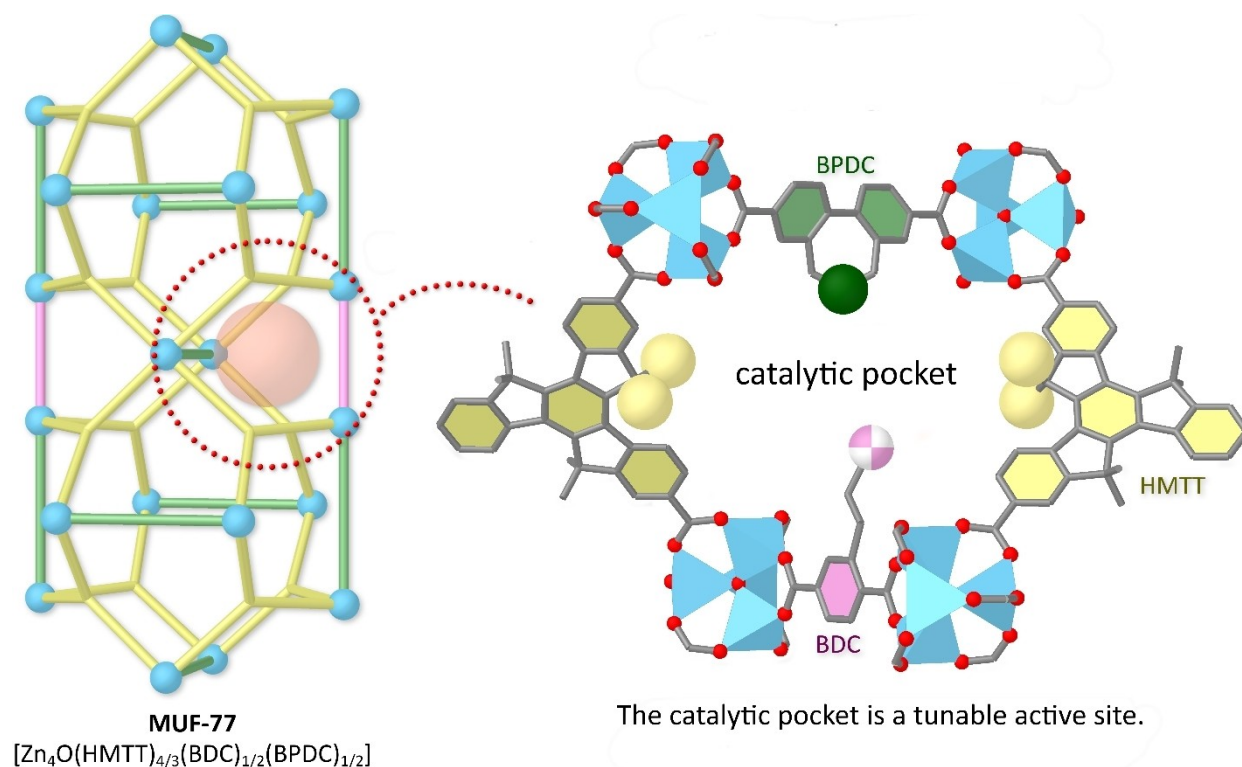


Figure 9. The structure of the multicomponent MUF-77 framework, [Zn₄O(hmtt)_{4/3}(bdc)_{1/2}(bpdc)_{1/2}]. The pore environment is an active site that can be deliberately programmed e.g., a catalytic group can be attached to one of the linkers and the catalysis properties tuned by functional groups attached to the other linkers. Color code: Zn, blue; bdc, bpdc, and truxene linkers are shown in pink, green, and yellow, respectively.

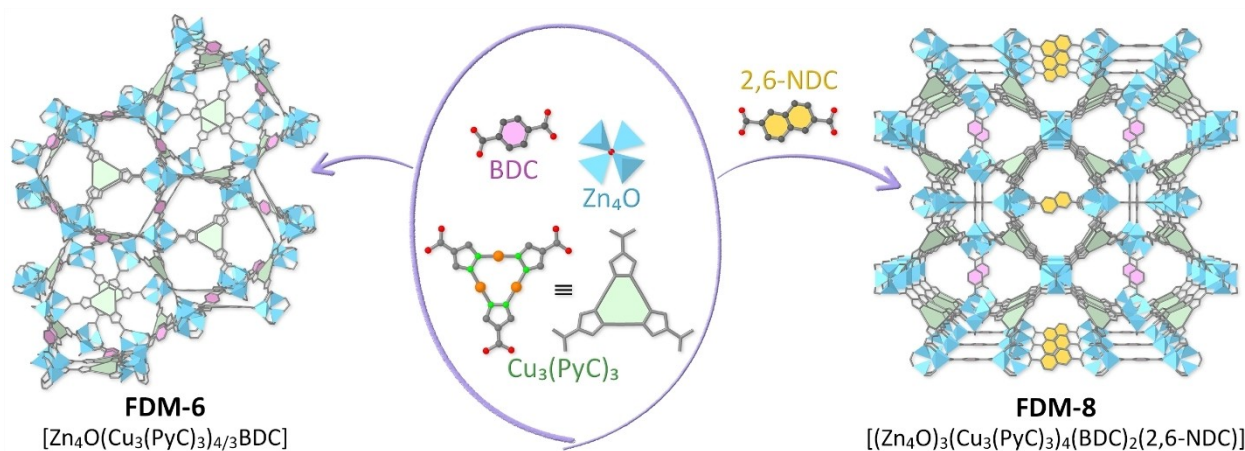


Figure 10. The assembly of FDM-6, [Zn₄O(Cu₃(PyC)₃)_{4/3}bdc], which has four components in order. In inclusion of 2,6-ndc leads to FDM-8, [(Zn₄O)₃(Cu₃(PyC)₃)₄(bdc)₂(2,6-NDC)], which has five components in order. Both frameworks comprise the C₃-symmetric Cu₃(pyC)₃ metalloligand. Color code: Zn, blue; Cu, orange; C, gray; O, red; N, green. bdc, 2,6-ndc and Cu₃(PyC)₃-moieties are highlighted in pink, yellow, and green, respectively.

(quinary) MOF.^[27] The Cu₃(PyC)₃ once again defines a tritopic metallo-linker. This combines with Zn₄O clusters and bdc and 2,6-NDC to assemble the three ligands and two metal ions into FDM-8 with the formula [(Zn₄O)₃(Cu₃(PyC)₃)₄(bdc)₂(2,6-ndc)]. Alternative reaction products are avoided by careful optimization of the reaction conditions.

In combining three linkers and two different metal clusters, FJU-6 is another quinary MOF.^[28] It comprises two-dimensional sheets of trigonal Co₃(OH) clusters and a combination of bdc and ina (isonicotinate) linkers. Hexanuclear cobalt(II) clusters then act as pillars between the 2D layers and connect the ina with the third linker (btb). By

using substituted analogues of each of the three ligands, a diverse set of isorecticular MOFs could be prepared.

It is interesting to consider how multicomponent MOFs nucleate and grow. For example, do all of their components simultaneously assemble at the earliest stages of crystal nucleation? Or is a precursor phase initially established, potentially form just one or two of the linkers, which then transforms into another phase as the crystals develop? We have addressed these questions by synthesizing multicomponent MOFs in *flow* and monitoring the appearance of products over the initial stages of framework growth by synchrotron PXRD in real time.^[29] Upon mixing zinc(II) acetate, H₂bdc and H₃btb, the components required for UCMC-1, MOF-5 is actually observed at the earliest stage of crystal growth. UCMC-1 takes over as the dominant product after an induction period. On the other hand, a mixture of zinc(II) acetate, H₂bdc, H₂bpdc and H₃btb leads directly to MUF-7 at the onset of nucleation: a multicomponent MOF is formed directly without the appearance of any other frameworks in this case.

5. The Distinction Between Multicomponent and Multivariate MOFs

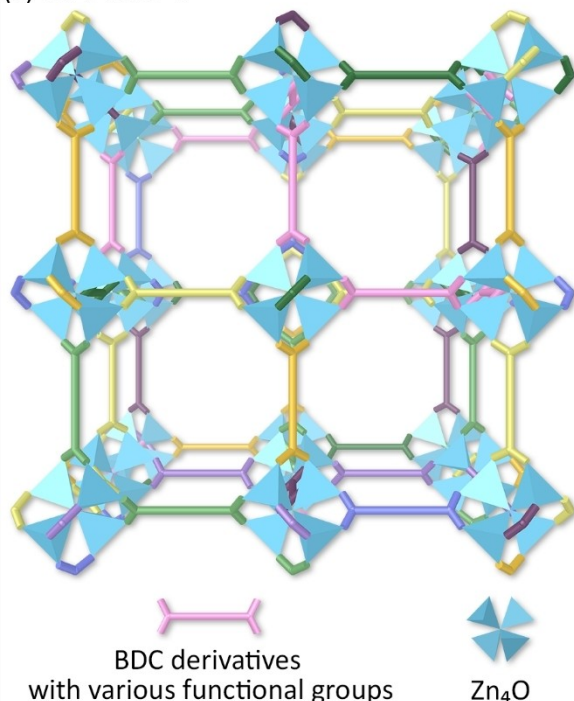
Multivariate (MTV) MOFs are built up from multiple components that are able to assume the same positions in the framework lattice.^[30] For example, if MOF-5 is synthesized from a mixture of bdc and a set of analogues with the

same backbone but appended functionalities (e.g., 2-amino-1,4-benzenedicarboxylate, bdc-NH₂), the bdc and bdc-NH₂ linker linkers will be incorporated more-or-less indiscriminately into the growing framework. (Figure 11a). Similarly, MOF-74 may comprise a rich variety of metal(II) ions arranged randomly in the framework (Figure 11b). Multivariate MOFs have parallels with solid-state materials such as minerals, zeolites, alloys, and solid solutions, which have lattice sites that can be randomly occupied by different species. This comes about because the differences between the linker are too subtle to be recognized during framework assembly (this can be viewed as the ability to evade error-checking processes during self-assembly). In addition, entropic factors favour frameworks with mixed components as opposed to partitioning of the components into separate framework regions or even distinct materials.

Multivariate MOFs lack uniformity in both their framework and pore structures. Therefore, different parts of the MOFs will have different functional properties. For example, in a multivariate MOF that exhibits catalytic activity, individual pores will have turnovers and selectivities that are distinct from their neighbours the activity arising from one pore regions may even counteract one another. The observed activity will be a sum of these individual contributions. The key challenge here is to design multivariate MOFs in which the benefits accrued from the diversity of linkers in multivariate MOFs are not offset by pore heterogeneity.

Multivariate MOFs find their niche where distinct properties arise by varying the ratios of the framework

(a) MTV-MOF-5



(b) MTV-MOF-74

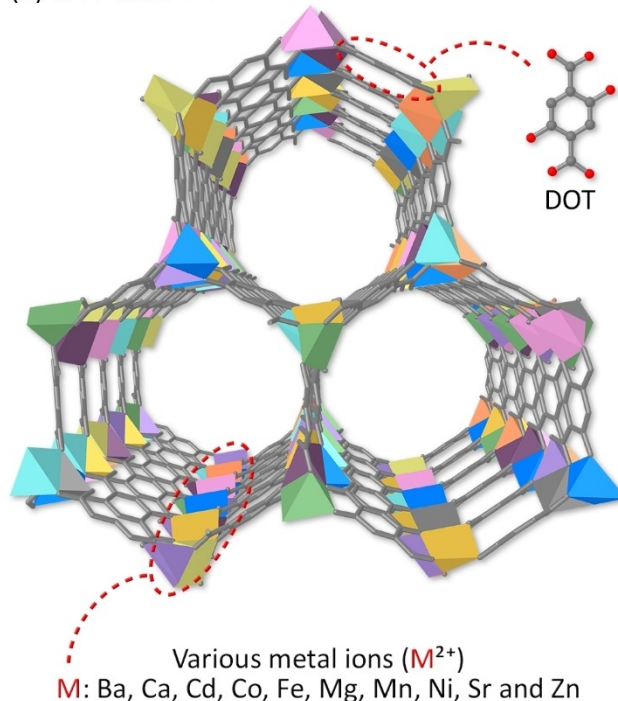


Figure 11. (a) Multivariate MOF-5, which is built up using a set of different linkers that have a common bdc backbone. (b) Multivariate MOF-74, which is built up using an array of divalent metal ions linked by 2,5-dioxidoterephthalate.

components. For example, MOF-333 ([Al(OH)(pzdc)], pzdc=1-H-pyrazole-3,5-dicarboxylate) has a high affinity for water vapor and the step in its adsorption isotherm occurs at a relatively high partial pressure of water vapour.^[31] The position of this step can be moved to lower partial pressure values in multivariate analogues of MOF-303 in which some of the pzdc linkers are replaced by 2,4-furandicarboxylate (fdc). Similarly, the flexibility of MUF-15-OMe in response to gas adsorption has been tuned by incorporating various amounts of isophthalic acid in place of its methoxy-substituted analogue,^[32] and acetylene uptake can be tuned by the ratios of substituted bdc linkers in multivariate zinc(II) MOFs.^[33]

6. Summary and Outlook

The most important perspective on multicomponent MOFs is also the simplest: they can be made! The “phase problem” relating to the competing reaction pathways can be overcome by selecting appropriate building blocks and reaction conditions. Complexity can be achieved and—importantly—it is not accompanied by chaos. The building blocks are coded, and this code is translated into specific sequential arrangements.

The coupling of complexity to order elevates the functional attributes of multicomponent beyond conventional materials since well-defined, periodic pore environments are created. Tuning the pore environments allows for functional properties that cannot be achieved in simpler materials. Complementary interactions between functional groups become possible and the structural complexity inherent to biological materials comes within reach.

Multicomponent MOFs thus offer new perspectives on both structural and functional properties. Motifs with complementary features, such as chirality, catalysis, reactivity, spin, or electron donor/acceptor behaviour can be deliberately brought into proximity in well-defined environments. Interesting catalytic, redox, optical, magnetic, and electronic properties are thus enabled.

Acknowledgements

We thank group members—past and present—for their enthusiastic pursuit of multicomponent MOFs for their architectural beauty and extraordinary properties. Open Access publishing facilitated by Massey University, as part of the Wiley - Massey University agreement via the Council of Australian University Librarians.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Complexity · Metal-Organic Frameworks · Porous Materials · Multicomponent · Multivariate

- [1] a) Q. Pang, B. Tu, Q. Li, *Coord. Chem. Rev.* **2019**, *388*, 107–125; b) M. Viciano-Chumillas, X. Liu, A. Leyva-Pérez, D. Armentano, J. Ferrando-Soria, E. Pardo, *Coord. Chem. Rev.* **2022**, *451*, 214273.
- [2] L. M. Greig, D. Philp, *Chem. Soc. Rev.* **2001**, *30*, 287–302.
- [3] A. Klug, *Philos. Trans. R. Soc. London Ser. B* **1999**, *354*, 531–535.
- [4] G. P. Stahly, *Cryst. Growth Des.* **2007**, *7*, 1007–1026.
- [5] N. A. Mir, R. Dubey, G. R. Desiraju, *Acc. Chem. Res.* **2019**, *52*, 2210–2220.
- [6] a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469–472; b) H. Jiang, D. Alezi, M. Eddaoudi, *Nat. Rev. Mater.* **2021**, *6*, 466–487.
- [7] O. Kozachuk, K. Khaletskaya, M. Halbherr, A. Bétard, M. Meilikhov, R. W. Seidel, B. Jee, A. Pöpl, R. A. Fischer, *Eur. J. Inorg. Chem.* **2012**, 1688–1695.
- [8] Q. Yao, J. Su, O. Cheung, Q. Liu, N. Hedin, X. Zou, *J. Mater. Chem.* **2012**, *22*, 10345–10351.
- [9] K. Koh, A. G. Wong-Foy, A. J. Matzger, *Angew. Chem. Int. Ed.* **2008**, *47*, 677–680.
- [10] K. Koh, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.* **2010**, *132*, 15005–15010.
- [11] N. Klein, I. Senkowska, I. A. Baburin, R. Gröner, U. Stöck, M. Schlichtenmayer, B. Streppel, U. Mueller, S. Leoni, M. Hirscher, S. Kaskel, *Chem. Eur. J.* **2011**, *17*, 13007–13016.
- [12] S. J. Lee, C. Doussot, A. Baux, L. Liu, G. B. Jameson, C. Richardson, J. J. Pak, F. Trouselet, F.-X. Coudert, S. G. Telfer, *Chem. Mater.* **2016**, *28*, 368–375.
- [13] H. Chevreau, T. Devic, F. Salles, G. Maurin, N. Stock, C. Serre, *Angew. Chem. Int. Ed.* **2013**, *52*, 5056–5060.
- [14] R. R. Prasad, C. Pleass, A. L. Rigg, D. B. Cordes, M. M. Lozinska, V. M. Georgieva, F. Hoffmann, A. M. Slawin, P. A. Wright, *CrystEngComm* **2021**, *23*, 804–812.
- [15] H. Jiang, J. Jia, A. Shkurenko, Z. Chen, K. Adil, Y. Belmabkhout, L. J. Weselinski, A. H. Assen, D.-X. Xue, M. O’Keeffe, *J. Am. Chem. Soc.* **2018**, *140*, 8858–8867.
- [16] H. Kim, D. Kim, D. Moon, Y. N. Choi, S. B. Baek, M. S. Lah, *Chem. Sci.* **2019**, *10*, 5801–5806.
- [17] A. M. Tollitt, R. Vismara, L. M. Daniels, D. Antypov, M. W. Gaultois, A. P. Katsoulidis, M. J. Rosseinsky, *Angew. Chem.* **2021**, *60*, 26939–26946.
- [18] L. Liu, K. Konstas, M. R. Hill, S. G. Telfer, *J. Am. Chem. Soc.* **2013**, *135*, 17731–17734.
- [19] L. Liu, S. G. Telfer, *J. Am. Chem. Soc.* **2015**, *137*, 3901–3909.
- [20] a) A. Alkaş, L. E. Friche, S. N. Harris, S. G. Telfer, *Chem. Eur. J.* **2020**, *26*, 10321–10329; b) A. Alkaş, J. Cornelio, S. G. Telfer, *Chem. Asian J.* **2019**, *14*, 1167–1174; c) L. K. Macreadie, E. J. Mensforth, R. Babarao, K. Konstas, S. G. Telfer, C. M. Doherty, J. Tsanaktisidis, S. R. Batten, M. R. Hill, *J. Am. Chem. Soc.* **2019**, *141*, 3828–3832.
- [21] L. Liu, T.-Y. Zhou, S. G. Telfer, *J. Am. Chem. Soc.* **2017**, *139*, 13936–13943.
- [22] T.-Y. Zhou, B. Auer, S. J. Lee, S. G. Telfer, *J. Am. Chem. Soc.* **2019**, *141*, 1577–1582.
- [23] J. Cornelio, T.-Y. Zhou, A. Alkaş, S. G. Telfer, *J. Am. Chem. Soc.* **2018**, *140*, 15470–15476.

- [24] A. Dutta, A. G. Wong-Foy, A. J. Matzger, *Chem. Sci.* **2014**, *5*, 3729–3734.
- [25] J.-S. Qin, D.-Y. Du, M. Li, X.-Z. Lian, L.-Z. Dong, M. Bosch, Z.-M. Su, Q. Zhang, S.-L. Li, Y.-Q. Lan, S. Yuan, H.-C. Zhou, *J. Am. Chem. Soc.* **2016**, *138*, 5299–5307.
- [26] B. Tu, Q. Pang, H. Xu, X. Li, Y. Wang, Z. Ma, L. Weng, Q. Li, *J. Am. Chem. Soc.* **2017**, *139*, 7998–8007.
- [27] B. Tu, L. Diestel, Z.-L. Shi, W. R. L. N. Bandara, Y. Chen, W. Lin, Y.-B. Zhang, S. G. Telfer, Q. Li, *Angew. Chem. Int. Ed.* **2019**, *58*, 5348–5353.
- [28] L. Liu, Z. Yao, Y. Ye, Y. Yang, Q. Lin, Z. Zhang, M. O’Keeffe, S. Xiang, *J. Am. Chem. Soc.* **2020**, *142*, 9258–9266.
- [29] B. He, L. K. Macreadie, J. Gardiner, S. G. Telfer, M. R. Hill, *ACS Appl. Mater. Interfaces* **2021**, *13*, 54284–54293.
- [30] a) J. Bitzer, W. Kleist, *Chem. Eur. J.* **2019**, *25*, 1866–1882; b) A. Helal, Z. H. Yamani, K. E. Cordova, O. M. Yaghi, *Natl. Sci. Rev.* **2017**, *4*, 296–298.
- [31] N. Hanikel, X. Pei, S. Chheda, H. Lyu, W. Jeong, J. Sauer, L. Gagliardi, O. M. Yaghi, *Science* **2021**, *374*, 454–459.
- [32] O. T. Qazvini, V.-J. Scott, L. Bondorf, M. Ducamp, M. Hirscher, F. O.-X. Coudert, S. G. Telfer, *Chem. Mater.* **2021**, *33*, 8886–8894.
- [33] M. Bonneau, C. Lavenn, J.-J. Zheng, A. Legrand, T. Ogawa, K. Sugimoto, F.-X. Coudert, R. Reau, S. Sakaki, K.-i. Otake, *Nat. Chem.* **2022**, *14*, 816–822.

Manuscript received: May 8, 2023

Accepted manuscript online: June 21, 2023

Version of record online: July 4, 2023