

# Robust dynamics

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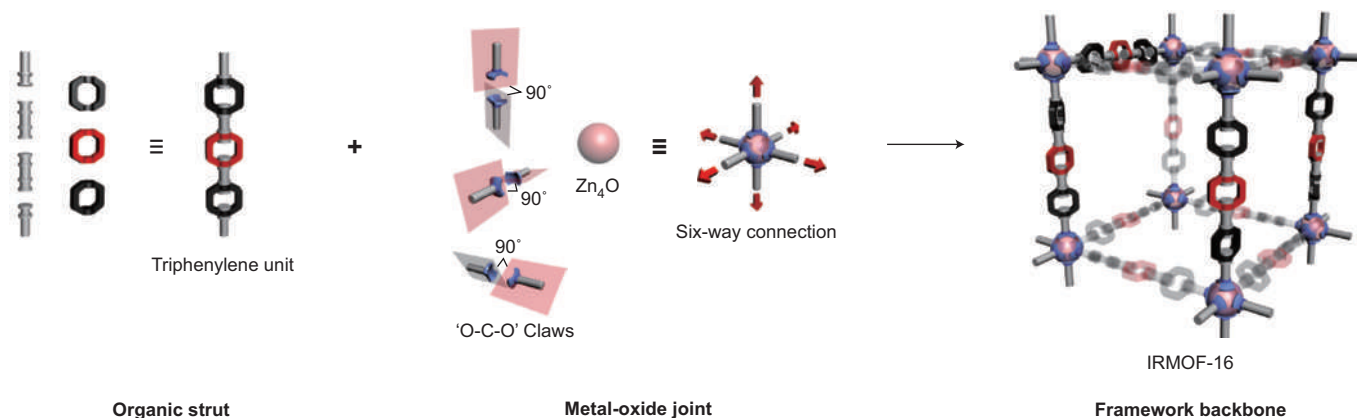
**Although metal-organic frameworks are extensive in number and have found widespread applications, there remains a need to add complexity to their structures in a controlled manner. It is inevitable that frameworks capable of dynamics will be required. However, as in other extended structures, when they are flexible, they fail. We propose that mechanically interlocked molecules be inserted covalently into the rigid framework backbone such that they are mounted as integrated components, capable of dynamics, without compromising the fidelity of the entire system. We have coined the term 'robust dynamics' to describe constructs where the repeated dynamics of one entity does not affect the integrity of any others linked to it. The implication of this concept for dynamic molecules, whose performance has the disadvantages of random motion, is to bring them to a standstill in three-dimensional extended structures and thus significantly enhance their order, and ultimately their coherence and performance.**

Stitching molecular building blocks into extended frameworks using strong bonds — reticular chemistry — is one of the most widely investigated areas in chemistry today<sup>1</sup>. A library of organic and inorganic building blocks has been used to build a large number of structures, named metal-organic frameworks<sup>2</sup> (MOFs). Generally, the MOF construct is based on the principle of linking metal-oxide joints with organic struts as illustrated in Fig. 1. This process has been repeated over and over again in various different chemical contexts to afford extensive classes of porous MOFs with a diversity and multiplicity previously unknown in the realm of artificial materials. The rigidity and directionality of the joints and struts ensure the MOFs' architectural stability and therefore permanent porosity: both are vitally important for their applications in catalysis, gas storage and separation<sup>3</sup>. It is these very same features, however, that rob MOFs of their dynamics and give rise to the question: how can we preserve the important characteristics and properties of MOFs, while accessing the dynamics that could provide the key to enhancing their functions?

An obvious strategy is to make flexible frameworks from pliable struts<sup>4</sup>. Another strategy is to use multi-interpenetrating

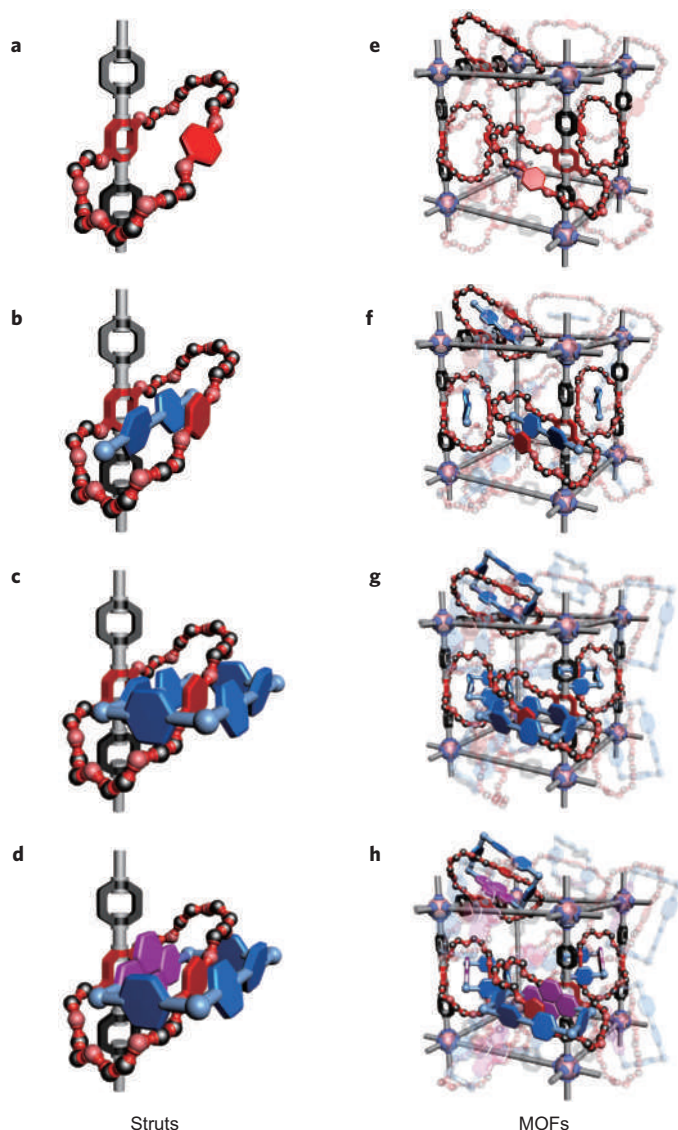
frameworks, wherein one framework shifts with respect to the others, thereby closing or opening the pores<sup>5</sup>. Both of these strategies are severely limited because frameworks that flex back-and-forth fail when subjected to further repeated dynamics, and interpenetrating frameworks are highly dependent on the uncontrollable behaviour of guests that fill their pores. In fact, this problem is not unique to MOFs — it is understood that structural failure is to be expected when the backbones of polymers and other extended structures are subjected to repeated dynamics. How then do we overcome the challenge of introducing dynamics into MOFs and, for that matter, other extended chemical structures, while retaining their robustness?

To answer this question, we turn our attention to another field of endeavour that has been progressing at an equally rapid pace of late — that of artificial molecular switches and machines<sup>6</sup>. In one of their most highly studied manifestations, they are composed (Fig. 2a–d) of circular, and sometimes also linear, components that are linked together mechanically<sup>7</sup>. Given the use of templation<sup>8</sup> in their synthesis, they are capable of elaborate and repeated dynamics,



**Figure 1 | A rare view into the construction of metal-organic frameworks (MOFs).** Herein the phenylene rings are bonded together by pivot joints to make the struts that link six-way tetra-zinc oxide clusters, likened to ball-joints, to form a MOF-5-type structure, previously named IRMOF-16. The carboxyl units act as 'claws' to keep the zinc centres in invariant positions and disallow any major structural perturbations. These features, when combined with the perpendicular orientations of all the claws, provide a glimpse into the reason for the well-known architectural stability of this MOF construct. The phenylene rings (red and black), O-C-O claws (grey and blue), and zinc oxide joint (Zn<sub>4</sub>O, pink).

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**Figure 2 | Illustrative examples of how elaborate units can be mounted onto the organic struts to introduce complexity and dynamics into MOFs.** The struts (a to d) are linked by tetra-zinc oxide centres to produce MOFs (e to h) in which the metrics of the struts and their functionality can be varied to give highly ordered 3D systems with controlled complexity and of vast openness such as to allow access to, and dynamics at, the mounted units. The polyether oxygen (pink), carbon (black) and phenylene (red) form the crown ether receptor/template (a and e), which forms pseudorotaxanes with Paraquat dication (b and f), degenerate catenanes with a cyclophane (blue) containing two Paraquat units linked by phenylene rings interlocking the crown ether (c and g), and a cyclophane (blue) containing a dimethyl diazapyrenium unit (purple) in addition to a Paraquat unit linked by phenylene rings interlocking the crown ether (d and h).

yet so far, for the most part, in an incoherent manner in solution or in condensed phases<sup>9</sup>. The problem with their present design is that they lack the rigid backbone that could provide a platform for their strategic and precise placement in two- (2D) or three-dimensional (3D) space so that they can express their dynamics — namely, the coherent switching between their mounted components.

During a switching process, only weak non-covalent bonds get broken and reformed again in a wholly reversible and highly controllable fashion<sup>79</sup>. We therefore propose that coupling the dynamics of molecular switches and machines with the rigid structures

of MOFs will yield materials that are intrinsically robust and rigid, yet dynamic — a property we term ‘robust dynamics’. The idea is that molecular switches and machines will be incorporated symmetrically into the struts of MOFs to graft dynamics onto their frameworks. In such materials, the repeated relative motions of the mechanically interlocked components will not affect the robustness of the framework backbone because their relative movements do not subject their constituent covalent bonds to undue stress and hence breakage: only non-covalent bonds are being ruptured and remade. In this way, the material’s fidelity and longevity will be overwhelmingly enhanced. It is our opinion that a system capable of robust dynamics must inevitably encompass a rigid framework into which flexible units (Fig. 2a–d) are inserted. The result of this thought process is illustrated in Fig. 2e–h, using the well-known MOF-5-type structure<sup>10</sup> and a bistable [2]catenane<sup>6,7</sup>. Here, we detail some of the underlying principles and thinking that now need to go into the blending of these two types of structural architecture, while emphasising the vast potential inherent in this union.

The process of designing a MOF structure is not unlike how we design and construct macroscopic objects such as bridges and skyscrapers; we link together girders and junctions of various shapes according to a blueprint using fasteners and rivets. The way the construction is done on the ångström or nanometre scale is to employ the chemical architect’s blueprint, which is a net — that is, a 3D array of points joined together by links, ideally related to each other by symmetry<sup>11</sup>. There is virtually a limitless number of net topologies of widely varying connectivities: we select the simplest and most symmetrical as feasible targets for synthesis. One such net is the primitive cubic topology. It is composed of two-connectors (struts or girders) that link (riveting) the vertices (junctions) leading to six-way connectivity. In our MOF-5-type structure, the intersecting points are joints with octahedral geometry. To make a MOF based on this topology, we take the phenylene ring of 1,4-benzenedicarboxylate as a two-way connector, and the zinc cluster as the six-coordinated unit and together they impose (Fig. 1) a primitive cubic structure on the MOF. Using related links, the same strategy can be applied to produce<sup>12</sup> yet more MOFs based on the same net (isoreticular) with predetermined pore sizes and shapes.

Ideally, the joints are rigid entities with well-defined geometries, which impart directionality and control over the resulting structure. By predetermining the geometry of the joint, one dictates the connectivity of the underlying net. The key to making rigid joints is to choose clusters that have an intrinsically 3D structure that is entirely composed of common-sized rings. In the case of these MOFs, the  $Zn_4O(CO_2)_6$  joints may be viewed as being made up of six 6-membered rings of  $Zn_2-O-CO_2$  composition that are sharing edges and are perpendicular to adjacent rings while also positioned (Fig. 1) opposite to other such rings. Indeed, when one considers this arrangement and the fact that the rings act as O–C–O ‘claws’, which hold the zinc atoms in position, then it becomes apparent why this construction does not shear. Once reaction conditions are identified for forming a joint, a small number of high-symmetry nets can be targeted, employing struts of the appropriate shapes and symmetries. We note that the use of joints made up of one metal atom, where no common rings exist, leads to flexing motions of large amplitude that inevitably destroy the framework, and the variable connectivity of such metal atoms preclude making frameworks by design. By contrast, metal-cluster joints ensure an invariant connectivity and therefore allow the design of frameworks, whereas the presence of multiple six-membered rings within such joints imparts that crucial but slight flexing at those joints ultimately, leading to robust structures of high fidelity. With all these considerations in mind, the stage is now set for introducing bistable catenanes and rotaxanes as two-way

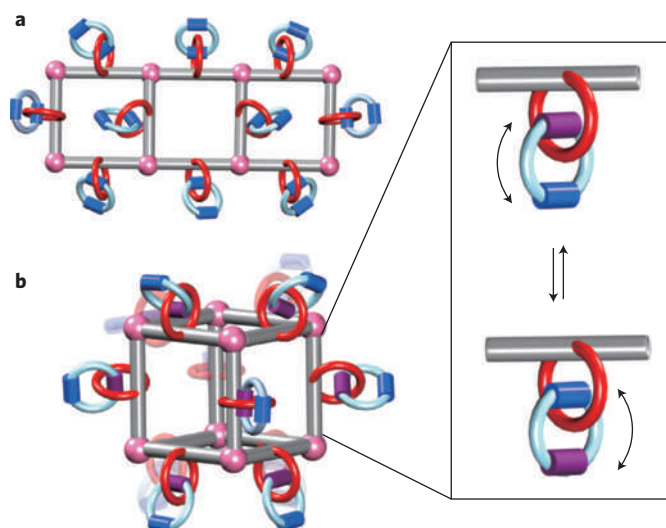
connectors into exactly the same type of net that we just described for MOF-5-type structures.

For mechanically interlocked molecules (MIMs), known<sup>13,14</sup> as catenanes (Lat. *Catena* = chain) and rotaxanes (Lat. *Rota* = wheel, axis = axle) to behave as molecular switches and machines they must incorporate two characteristic features<sup>6,7,15–17</sup>. One is that their components — two mechanically interlocked rings (Fig. 2) in the case of a bistable [2]catenane, and a ring encircling a dumbbell in the case of a bistable [2]rotaxane — must communicate with each other by means of intramolecular forces that can be modulated subsequently<sup>6,7,13–17</sup> with chemicals (for example, pH change), electricity or light, that is, redox change. The other feature is that, as a result of some judiciously chosen constitutional dissymmetry, as well as the required orthogonality to stimuli associated with the two different recognitions sites — the more interactive of which can be switched OFF and ON reversibly with complete fidelity in the presence of the weaker site. By means of this modulation, bistable MIMs can be raised from a ground to a metastable state, such that there are two translationally isomeric<sup>13</sup> forms expressing their bistability<sup>9</sup>.

The first feature is associated intimately with the efficient synthesis of bistable MIMs by protocols that rely on templation<sup>8</sup> — that is, the use of molecular recognition processes involving a steadily increasing number of intermolecular forces, which become intramolecular on the formation of a mechanical bond<sup>7</sup>, a factor that guides the assembly of the components of the bistable MIMs. It is the very fact that the non-covalent bonding, which is introduced incrementally in a step-wise manner into these bistable MIMs each time a covalent bond is formed, ‘lives on’ inside the molecules afterwards, which endows them with their unique properties. The situation is a true chicken-and-egg one: without the progressive build-up of non-covalent bonds during templation<sup>8</sup>, the outcome of a synthesis will be no better than statistical in nature — that is, the yields will be minuscule and the product will contain little or no information. One attribute of their construction feeds off the other to the extent that, if reversibility is introduced into the covalent bond-forming steps, then proofreading and error checking will often lead<sup>18</sup> to all but quantitative yields.

In pursuit of systems expressing functions, there has been a drive to self-assemble them (for example, as thiols on gold) on surfaces<sup>19</sup>, or to place them at interfaces by self-organization — for example, by Langmuir–Blodgett transfer of monolayers<sup>20</sup> of amphiphilic MIMs — to create nanoelectromechanical systems<sup>21</sup> or molecular electronic devices<sup>22</sup>, respectively. The incoherence that characterizes the operation of artificial molecular switches and machines only finds a practical expression when they are constituted as self-assembled monolayers on surfaces<sup>19</sup> or in molecular switch tunnel junctions at interfaces<sup>20,22,23</sup> one molecule thick between two electrodes. Not only do these self-assembly processes and self-organizational procedures all come with a downside in the shape of disorder, which introduces blemishes into devices, the artificial machinery is also often impeded in its function and usually becomes exhausted after tens, or, at the most, hundreds, of cycles. In other words, the distribution of orientation of the active molecules within these environments leads to their drastically reduced performance. So the inevitable question arises — how can we remove these blemishes and impediments and, at the same time, improve on the performance of molecular switches and machines?

The act of introducing MIMs into MOFs can be likened to the building of helicopters, jet planes and rockets. These particular flying machines are all constructed around robust fuselages to which engines are attached to the top, or on the sides, or at the back, or on the bottom. By appealing to a combination of robustness and motive power, we have all but overcome the hurdle of flight, which fascinated, yet evaded human beings for centuries. By the same token, we can envisage incorporating the artificial switches



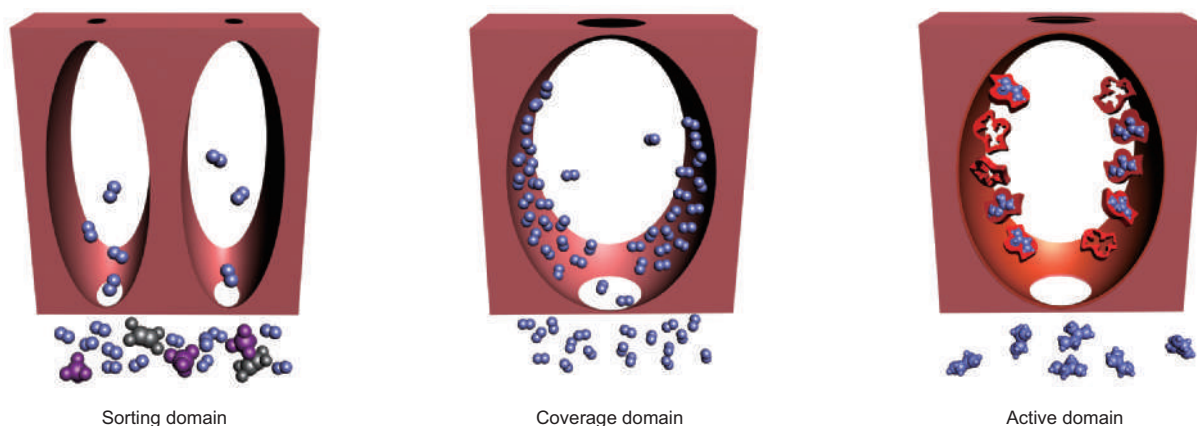
**Figure 3 | The 2D and 3D merger of MIMs and MOFs to bring about robust dynamics.** A representation of **a**, 2D and **b**, 3D MOFs incorporating units (catenated light blue and red in **a** for degenerate rings of blue positions and blue/purple for the non-degenerate bistable rings in **b**) that typically have random motions as discrete molecules, but such motions are brought to a standstill when the units are mounted covalently to the rigid framework backbone (pink spheres and grey struts). This merger between MIMs and MOFs brings order to the appended units and endows them with the ability to carry out well-defined repeated dynamics without compromising the integrity of the entire system — a concept termed robust dynamics.

and machines, as part of the two-way connectors held together by cluster joints during the template-directed synthesis<sup>8</sup> of the enabled struts. We foresee the possibility of being able to locate arrays of molecular switches and machines symmetrically and efficiently inside the 3D structures of MOFs, while retaining their inherent robustness. By virtue of the highly ordered MOF structure, its ultrahigh porosity, and facile accessibility to all its internal sites, the dynamic components of the MIMs, mounted within the extended structure provided by the MOF, will, in principle, be completely addressable and, under the right set of circumstances, behave in a coherent and reproducible manner. In essence, the random motion that plagues untethered MIMs in solution and condensed phases is curbed (Fig. 3) in MOFs.

Recently, the feasibility of mounting MIMs within MOFs has become evident from the successful introduction of a strut (Fig. 2a) into a MOF (Fig. 2e) and the formation of its [2]pseudorotaxane<sup>24–27</sup> MOF (Fig. 2f). Although MOFs incorporating the degenerate<sup>28</sup> and the non-degenerate<sup>29</sup> [2]catenane (Fig. 2c,d and g,h) have not been synthesized as yet, a 2D MOF containing the strut in Fig. 2c, as illustrated in Fig. 3a, has already been reported<sup>30</sup>. In these extended structures (Fig. 2e,f), long organic struts (~2 nm) incorporating 34- and 36-membered polyether rings<sup>27</sup> were used to build new MOFs (MOF-1001 and MOF-1002) whose structures are based on that of the MOF-5-type. The polyether chains are known to be highly dynamic in their free state, where they are folded in on themselves in the absence of guests, but are capable of readily unfolding to accommodate guests in their interior. Accordingly, this dynamic behaviour is also present in the new MOFs, in which the polyether units are found to be disordered in the crystals.

There is, however, yet another reason for the macrocycles to be disordered in MOF-1001 and MOF-1002: the presence of planar chirality. As the method of their synthesis did not permit any control over the handedness of the macrocycles, enantiomeric forms of them are presumably distributed in three dimensions throughout the crystals. In the future, however, it is going to be possible





**Figure 4 | The sorting, coverage and active domains of MOFs.** The three porous domains that the new MOFs (Figs 2 and 3) combine when they recognize and bind incoming substrates (guests). These domains are principally characterized by use of the pore opening to sort guests by shape and size selection (sorting domain), the internal adsorption sites to compact guests (coverage domain), and the crown ether receptors designed to bind guests in a stereoelectronically selective manner (active domain).

to employ asymmetric catalysis<sup>31</sup> to produce homochiral MOFs with receptors that incorporate planar chirality. Such dramatically new materials, in which the chiral receptor sites for the stereoselective docking of enantiomers are arranged precisely in space and are easily accessible to racemic analytes in a mobile phase, could revolutionize the production of chiral stationary phases for high-performance liquid chromatography for the efficient separation of enantiomeric compounds.

Remarkably, when MOF-1001 (Fig. 2e) is exposed to Paraquat dications in acetonitrile solutions, its polyether loops unfold and bind to the Paraquat guests in a stereoelectronically specific manner. The process can be repeated many times with the full preservation of the MOF backbone structure and without leaving any imprint on it. We attribute this framework fidelity to the fact that the only segments of the MOF structure that are flexible are the polyether loops, and none of their dynamics require any alteration to the metrics of the framework. It is the ideal construct because the rigidity of the framework allows the permanent openness of the structure so that guests may move in and out without obstruction and the large interstices provide sufficient space for the polyether loops to fold and unfold, and to do so independently of the framework. Therefore, the key to achieving robust dynamics in extended systems is only present in the segment of the structure where dynamics is desirable — leaving unperturbed the remainder of the structure. The stereoelectronically selective manner in which Paraquat dication is bound to the polyether loops in MOF-1001 introduces (Fig. 4) molecular recognition into porous crystals that so far have operated on either a shape/size selective or compacting capability.

Further independence of the flexible units in MOFs is potentially achieved by employing mechanically interlocked components. In principle, the synthesis of such MOFs was shown<sup>30</sup> to be feasible by the successful incorporation of degenerate, donor-acceptor [2]catenanes<sup>28</sup> into the 2D structure of MOF-1011. The layered nature of this MOF and the strong layer-layer interactions in the crystal preclude any dynamics involving the mechanically interlocked rings. Indeed, the construction of a 3D MOF structure, such as that of the MOF-5-type, would be necessary to realize the full potential of the interlocking rings' dynamics (Figs 2h and 3b). Nevertheless, it is encouraging to observe that these mechanically interlocked components, which are prototypical molecular machines<sup>6</sup>, can be mounted successfully inside extended MOF systems.

We believe that once the non-degenerate MOF-5-like structure is made, it will be just a matter of time before ultradense, 3D arrays

of molecular memory based on switchable [2]catenanes make their way into state-of-the-art device settings<sup>23</sup>. Ultradense memory, however, is the tip of the iceberg, provided it can be addressed. In the fullness of time, coupling switching with the ever-increasing capabilities of carrying out recognition processes — for example, microcontact printing on the surfaces and extending into the highly sophisticated interiors of these new switchable MOFs — will become commonplace. In principle, MOFs with molecular machinery mounted appropriately within their extended structures would not be unlike airplanes carrying their strategically mounted propeller-driven or jet engines on robust wings. One can easily conceptualize a chemical world where chameleon-like MOF crystals can be induced under the influence of chemicals (pH change), electricity (redox change) and light to travel in solution from one environment to another. In essence, the concept of robust dynamics is not only a necessary requirement for the longevity of dynamic extended structures, but it is also a strategy for adding yet another layer of complexity to the present functioning capabilities of MOFs.

The ability to build integrated systems that are capable of a complex set of functions is reminiscent of operations in the biological world. In a sense, robust dynamics is an example of how the concept of repeating dynamics, which is so prevalent in biology, can be transferred from the biological world to an artificial arena occupied by MOFs and MIMs and filled with integrated systems, without actually mimicking biology. Robust dynamics, therefore, is about concept transfer from the life sciences into the chemistry of materials. We can define<sup>32</sup> concept transfer as “adapting and applying the recognition processes, employed by living systems in achieving their forms and fulfilling their functions, to the construction of chemical systems with well-defined forms and prescribed uses”. In the wake of this definition, we propose that concept transfer, rather than trying to mimic biology, is a more viable approach<sup>33</sup> for making the next leap in the design and synthesis of useful materials. Moreover, the ordered, extended structures of MOFs and the flexibility with which they can be synthesized and functionalized with MIMs render the marriage between the two chemistries ideally suited for uncovering, testing and developing other concept transfer strategies.

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