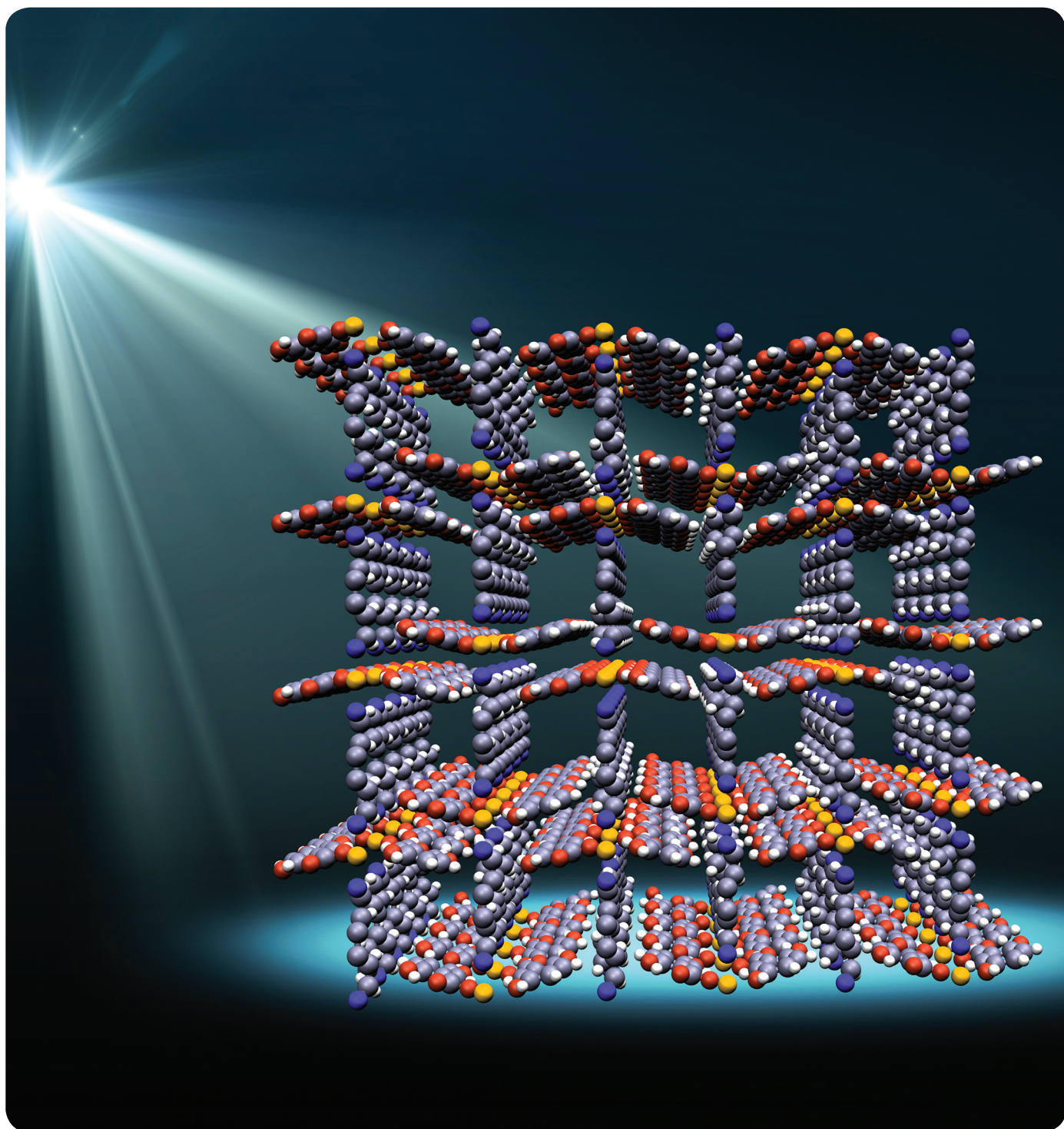




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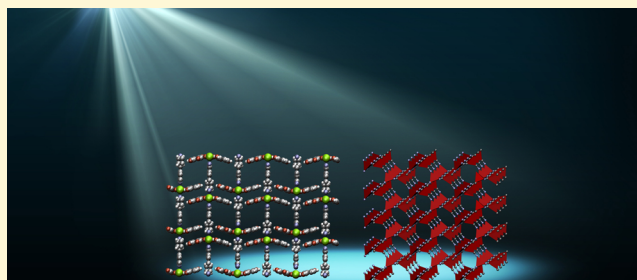
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Responsive Metal–Organic Frameworks and Framework Materials: Under Pressure, Taking the Heat, in the Spotlight, with Friends[†]

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ABSTRACT: Recent years have seen a large increase of the research effort focused on framework materials, including the nowadays-ubiquitous metal–organic frameworks but also dense coordination polymers, covalent organic frameworks, and molecular frameworks. With the quickly increasing number of structures synthesized and characterized, one pattern emerging is the common occurrence of flexibility. More specifically, an important number of framework materials are *stimuli-responsive*: their structure can undergo changes of large amplitude in response to physical or chemical stimulation. They can display transformations induced by temperature, mechanical pressure, guest adsorption or evacuation, light absorption, etc. and are sometimes referred to as *smart materials*, *soft crystals*, or *dynamic materials*. This Perspective highlights recent progress in this field, showcasing some of the most novel and unusual responses to stimuli, as well as advances in the fundamental understanding of flexible framework materials.



■ INTRODUCTION

The last 15 years have seen the emergence of new classes of crystalline framework materials, based on relatively weaker bonds (coordinative bonds, π – π stacking, hydrogen bonds, or some covalent bonds) compared to inorganic dense and nanoporous materials (such as oxides and zeolites). The most studied of these new materials are the now ubiquitous metal–organic frameworks (MOFs), with more than 20,000 papers published, 15,000 structures on record at the Cambridge Crystallographic Data Centre, and over 170 review articles dedicated to this topic. However, other classes of crystalline framework materials have attracted attention from the research community, including covalent organic frameworks (COFs), porous molecular organic solids, and other molecular framework materials.

Within such a large number of new materials synthesized and characterized, one of the empirical patterns that is appearing is the common occurrence of *flexibility* of these framework materials, i.e., whose structure exhibits dynamics or potential for deformations of large amplitude. In particular, there is a rapidly increasing number of framework structures whose flexibility manifests in the form of *transformations induced by external stimulation of physical or chemical nature*: changes in temperature, mechanical constraints, guest adsorption, light exposure, etc. A number of different terms have been used to qualify this behavior, including *smart materials*, *soft crystals*,¹ *dynamic frameworks*, or *flexible frameworks*. I will employ here the term *stimuli-responsive* to qualify those framework materials that undergo changes of large amplitude in response to external stimulation.

Given the large number of known stimuli-responsive framework materials and the rapid pace at which both novel materials

as well as novel responses of known materials are reported, several reviews of these flexible materials have been published, focusing mostly on MOFs and dense coordination polymers.^{1–6} In this Perspective, I will highlight the recent progresses in this field in a somewhat more general view, including other framework materials along with MOFs. I will showcase some of the most novel and unusual responses to stimuli, as well as advances in the fundamental understanding of flexible framework materials, and point out the open questions and avenues of inquiry that seem, from my perspective, necessary for future research to address.

■ RESPONSE TO PRESSURE: MECHANICAL PROPERTIES

Framework materials demonstrate a wide variety of behavior in their response to the application of mechanical pressure, as illustrated in Figure 1. This diversity of the mechanical behavior of materials as a function of topology, even at a constant chemical composition, has been well established for inorganic materials, and in particular in the field of zeolites. For metal–organic frameworks, though, mechanical properties are not among the “standard” physical characterization data typically reported for new materials, mostly because the inherent difficulties in determining them reliably for relatively small crystal sizes. The past few years have nevertheless seen some systematic efforts at measuring mechanical properties,⁷ including bulk modulus (through high-pressure crystallography), directional Young’s moduli and hardnesses (through nanoindentation of mono-

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Responses to pressure

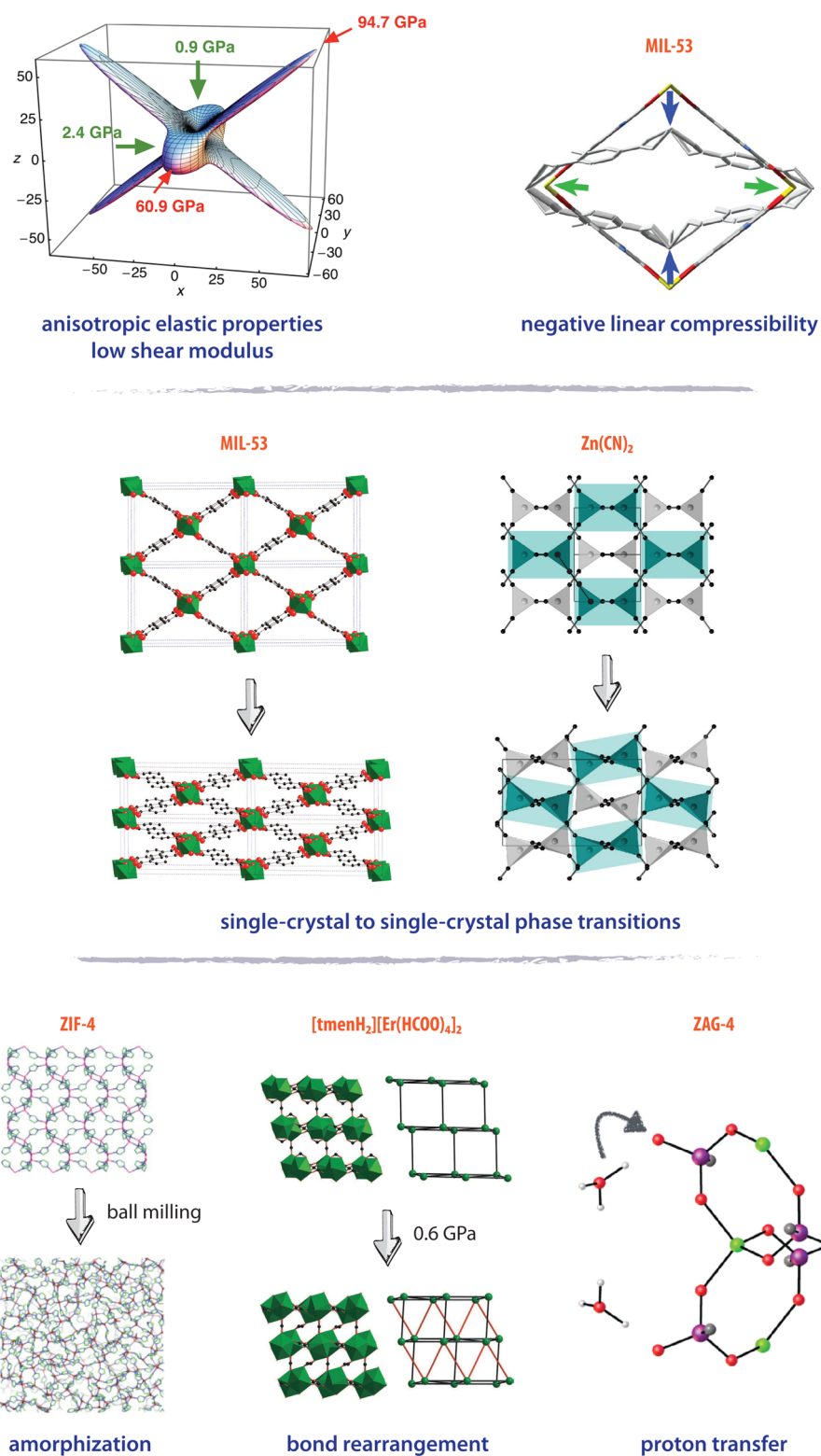


Figure 1. Illustration of some possible responses to the application mechanical pressure. Top-left: extremely anisotropic directional Young's modulus²³ (left) and negative linear compressibility¹⁴ (right) of MIL-53(Al) 1p phase; middle: pressure-induced phase transitions in MIL-53(Al)³⁰ (left) and Zn(CN)_2 ³² (right); bottom left: pressure-induced amorphization of ZIF-4;³⁸ bottom center: pressure-induced bond rearrangement in $[\text{tmenH}_2][\text{Er}(\text{HCOO})_4]_2$;⁴⁴ bottom right: pressure-induced proton jump in ZAG-4.⁴⁷ Adapted with permission from refs 30, 32, 38, 44, and 47. Copyright 2011, 2013, 2014 American Chemical Society. Copyright 2011 Royal Society of Chemistry. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

crystals),^{8,9} or full second-order elastic tensors (from Brillouin scattering experiments or quantum chemistry calculations).¹⁰

Within the elastic regime, an important number of metal–organic frameworks have demonstrated anomalous mechanical responses: these materials respond to external pressure by deformations of large amplitude or counterintuitive direction. The most typical example of anomalous mechanical behavior is *negative linear compressibility* (NLC), in which the material under compression expands along certain directions, while undergoing a reduction in volume (as mandated by thermodynamics). This desirable property can be leveraged for applications in sensors and actuators or to design nanocomposite materials with zero linear compressibility in a specific direction. NLC is extremely uncommon in inorganic solids overall¹¹ but appears more prevalent in framework materials. It was first evidenced in MOFs silver(I) 2-methylimidazolate¹² and $[\text{NH}_4][\text{Zn}(\text{HCOO})_3]$,¹³ where in both cases it is due to “wine rack” motif in their framework topology. Thus, occurrence of NLC in other framework materials with a wine rack-type framework seems likely, as well as for some other framework types exhibiting a similar “hinging” mechanism. This is particularly true of MOFs, where such motifs are relatively common, and there have now been several experimental confirmations published.^{14,15} But this is also true of other framework materials, including molecular frameworks zinc dicyanoaurate¹⁶ and silver(I) tricyanomethanide,¹⁷ as well as zeolite frameworks GIS, SOS, and ATT, which are predicted to feature NLC in their all-silica form.¹⁸

Another class of anomalous mechanical behavior is the occurrence of *very low elastic moduli*. MOFs, coordination polymers, and other molecular framework materials have, as a whole, lower elastic moduli (stiffness) than inorganic materials such as zeolites,⁷ due to the weaker interactions involved in their 3D network. This is seen experimentally by relatively lower values of bulk modulus or Young's modulus. However, in addition to this general effect, some framework materials show specifically lower moduli for some deformation modes, typically shearing modes, with large-amplitude responses to small external constraints. This was first evidenced experimentally in the case of ZIF-8, with a shear modulus of ~ 1 GPa that was considered remarkably low.¹⁹ Though there has been to my knowledge no other experimental measurements of shear modulus since then, both theoretical calculations of elastic constants and pressure-induced amorphization experiments²⁰ show that low shear moduli are the norm, rather than the exception, for highly porous metal–organic frameworks. Many of the more porous (less dense) MOFs have shown sub-GPa shear modulus in their evacuated state.²¹ The downside of such high flexibility is, as seen in many cases, a limited mechanical stability upon solvent removal and evacuation of the porous frameworks.

Other anomalous mechanical behaviors observed in framework materials include *auxeticity*, i.e., the existence of directions of *negative Poisson's ratio*. Auxetic crystals exhibit the counterintuitive of getting thicker when stretched along certain directions. From a practical point of view, large values of negative Poisson's ratio are thought to give rise to good indentation resistance and fracture toughness.²² This is not an uncommon phenomenon, even for crystalline materials, and its occurrence in some zeolitic frameworks has been thoroughly studied and rationalized in the 1990s. The search for this property has only very recently been addressed in MOFs, so far entirely through computational methods, but already a number of structures have been predicted to be present with large auxeticity.^{23–25} Recent systematic studies of elastic properties of

pure-silica zeolitic frameworks have shown the prevalence of negative Poisson's ratio to be around one-third,¹⁸ giving high hopes that promising highly auxetic MOF candidates can be selected by computational screening of known and hypothetical structures. Recently, we have even proposed a candidate structure for a *completely auxetic* zeolitic framework, for which the Poisson's ratio would be negative in all directions—something that has only ever been observed in barium and samarium alloys so far.²⁶

Finally, among the variety of elastic behavior of framework materials, one of the unusual responses observed in some materials is an *extreme anisotropy of their elastic moduli*. This translates into very anisotropic responses to mechanical constraints, with some crystal directions exhibiting deformations of much larger amplitude than others, either upon isotropic stress (hydrostatic compression) or uniaxial loading. This phenomenon is highly dependent on the topology of the material's framework, which is in all cases the root of the anisotropy: deformations directly involving compression or tension of the framework's linker (the *struts*) have very high elastic moduli, while those involving weaker interactions (the *hinges* of the framework) have much lower stiffness. In metal–organic frameworks, the contrast between the strong intramolecular interactions (covalent bonds of the linkers, some coordinative bonds) and the weak intermolecular interactions (dispersive interactions, π – π stacking, hydrogen bonds, etc.) can lead to extreme anisotropy, with up to 2 orders of magnitude in difference between the strongest and lowest moduli.²³ This extreme elastic anisotropy, coupled with the existence of modes of low deformation, is a *key signature* of highly flexible materials, such as the so-called “breathing” MOFs.²⁴ In some very recent work, my group has shown that this signature, relatively easy to check using quantum chemistry calculations, can be used as first step in a computational methodology for predicting the flexibility of crystal structures. Using it, we recently predicted an adsorption-induced large-pore phase in MOF CAU-13,²⁷ a prediction that was later validated experimentally.²⁸

■ RESPONSE TO PRESSURE: PHASE TRANSITIONS

In addition to the unusual elastic responses described above, some framework materials undergo larger-scale deformations under high pressure, usually in the form of pressure-induced phase transformations. These pressure-induced structural transformations are triggered by the application of large hydrostatic pressure (GPa-scale) onto the crystals via a nonpenetrating pressure-transmitting fluid, and monitored in situ by diffraction methods. There has been a large increase of such studies in the past few years, typically with single-crystal samples loaded in a diamond anvil cell and intense synchrotron radiation used for X-ray diffraction measurements. Such setups obviously permit only compression experiments but not measurements of the behavior under tension.

Among the recent literature on high pressure crystallography of framework materials, a somewhat recent phenomenon is the observation of *pressure-induced single-crystal to single-crystal transitions*. While most of the earlier work on flexible MOFs dealt with adsorption-induced transitions (the so-called “breathing” and “gate opening” transitions; see the section below on adsorption), later works showed that such phase transitions in multistable materials could also be triggered by mechanical constraints rather than adsorption. This was very clearly demonstrated by Beurroies et al., who showed that the large-pore to narrow-pore phase transition of the “breathing” MIL-

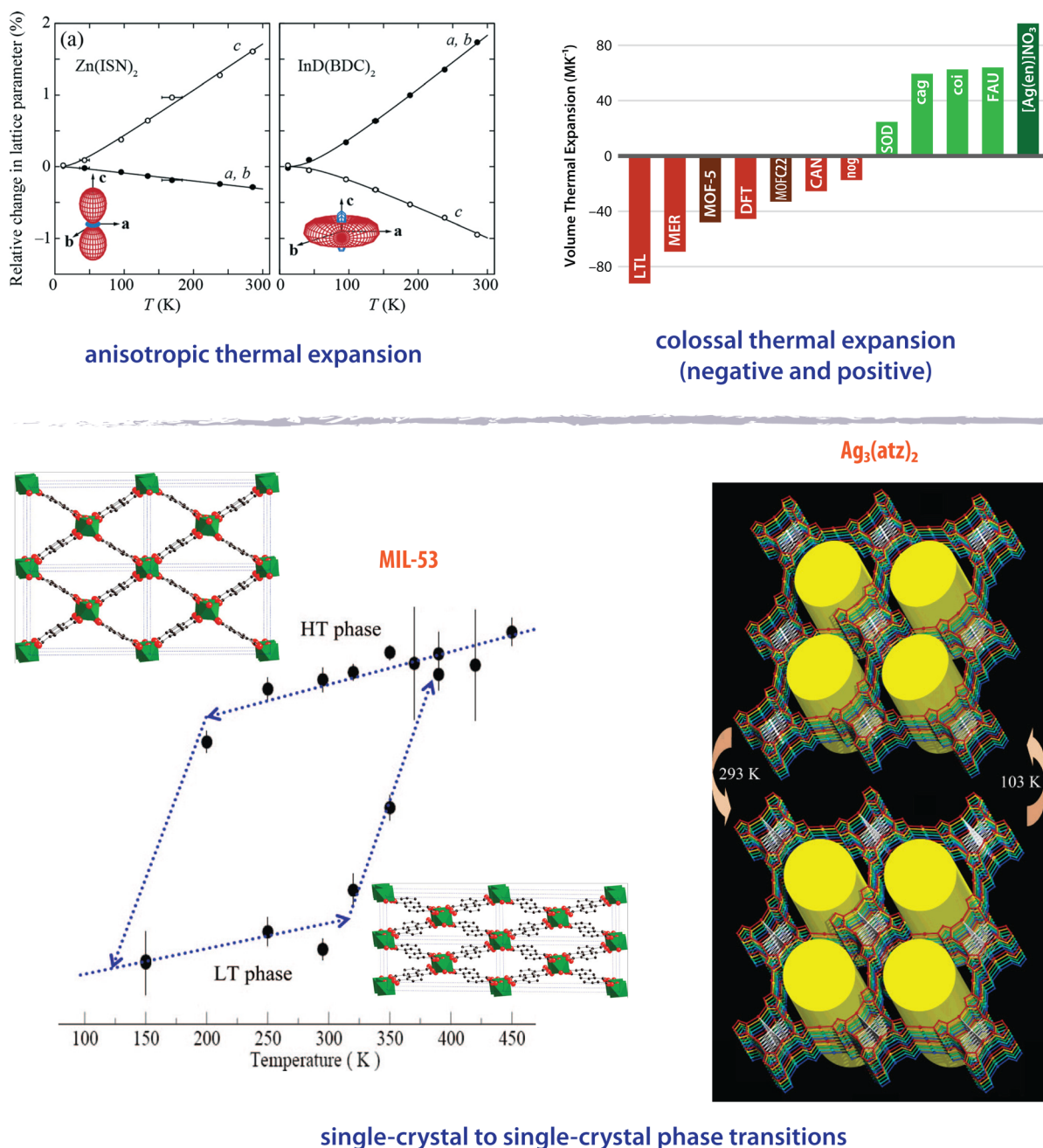


Figure 2. Illustration of responses to temperature changes. Top left: anisotropic thermal expansion in Zn(ISN)₂ and InD(BDC)₂;⁶² top right: predicted values of volumetric thermal expansion in unsubstituted ZIF frameworks, compared to other framework materials;²¹ bottom: temperature-driven phase transitions in MOFs MIL-53(Al)⁶⁴ and Ag₃(atz)₂.⁶⁰ Adapted with permission from refs 21, 60, 62, and 64. Copyright 2008, 2014 Royal Society of Chemistry. Copyright 2014 AIP Publishing LLC.

53(Cr) framework could be triggered by isostatic compression in liquid mercury.²⁹ It was later shown, based on theoretical calculations comparing the compression-induced transition and the CO₂ adsorption-induced transitions, that both were in fact the same transition,³⁰ i.e., that the frameworks react in the same way to stress exerted “from the outside” in the form of mechanical pressure and to stress exerted “from the inside” in the form of adsorption-induced stress (a well-known phenomenon in the field of adsorption³¹).

Since that seminal work, other pressure-induced phase transitions have been observed in MOFs and in framework materials more generally. Such transitions lead to the formation of a denser phase under high pressure, usually accompanied by a

lowering of symmetry and distortion of the framework or metal center coordination from the ambient phase. A typical example of this behavior is that of dense molecular framework zinc cyanide, Zn(CN)₂, which under hydrostatic compression at ~1.5 GPa undergoes a reversible phase transition to a high-pressure phase.^{32,33} This transition involves a buckling of the Zn–CN–Zn linkage from a linear conformation in the ambient phase to a displaced CN[−] anion and shorter Zn⋯Zn distance in the high-pressure phase. Examples among metal–organic frameworks include the aluminum-based MIL-53(Al);¹⁴ MIL-47, a vanadium-based MOF with the same wine rack topology as the MIL-53 family, and whose “breathing” transition has so far only been triggered by adsorption but only by compression;³⁴ Co₂(4,4’-

bipyridine)₃(NO₃)₄)³⁵ and computational predictions of a pressure-induced transition in NOTT-300.²⁷

It is clear from the above list that pressure-induced crystal-to-crystal transitions in flexible metal–organic frameworks are quite rarely observed, in contrast with dense inorganic materials. Indeed, the most commonly observed response of MOFs under high pressure is *pressure-induced amorphization*. This has been very well documented and thoroughly studied in the family of zeolitic imidazolate frameworks (ZIFs). All ZIFs studied so far have shown pressure-induced amorphization at modest, industrially accessible pressure, though the conditions and results vary depending on parameters such as pressurization conditions, framework topology and porosity, presence of guest inside the pores, etc. For example, the prototypical ZIF-8 amorphizes irreversibly under mechanical compression as low as 0.3 GPa³⁶ as well as under mild ball-milling.³⁷ In the denser ZIF-4, a *reversible* amorphization occurs at slightly higher hydrostatic pressure (0.35 GPa) in the evacuated state, but the presence of DMF molecules in its pores shifts amorphization to higher pressure and leads to the existence of an intermediate crystalline phase.³⁸ The mechanism behind pressure-induced amorphization of ZIF-4, ZIF-8, and other porous ZIFs was also investigated from a theoretical point of view, showing that the crystal-to-amorphous transition is triggered by a mechanical instability under compression, due to shear mode softening of porous ZIFs.^{21,39} This also explains why amorphization is shifted to higher pressure for guest-filled materials: the presence of guests in the pores increases the elastic moduli of the framework, including its shear modulus, thus requiring higher pressure for the shear-mode softening to lead to amorphization.

It may at first sound like the common occurrence of amorphization of porous framework materials under pressure is a bad thing, as it marks the upper limit of their mechanical stability. As such, one can try to design novel robust materials with higher mechanical stability and amorphization pressures. But amorphization in itself can also be leveraged for practical purposes, for example, for the irreversible trapping of adsorbed species^{40,41} or as a route to synthesize *amorphous MOFs*, a novel subclass of framework materials with high mechanical and thermal stability.⁴²

■ RESPONSE TO PRESSURE: CHEMICAL REACTIONS

Among the wide variety of framework materials' response to pressure, there is a third category that has merely begun to emerge. It represents a very uncommon, yet highly desirable, behavior: *pressure-induced chemical reactions*, i.e. reversible transformations leading to a different chemical state or framework coordination through bond breaking and formation. Pressure-induced bond rearrangement, and in particular *reversible* pressure-induced bond rearrangement, is a very rare phenomenon in materials science, and there are, to my knowledge, only two examples of this behavior in the current literature on framework materials, both reported in 2014. The first one is a reversible *pressure-induced bond rearrangement* in erbium formate MOF [tmenH₂][Er(HCOO)₄]₂ (tmenH₂²⁺ = N,N,N',N'-tetramethylethylenediammonium).⁴³ This material shows a first order phase transition under compression at ~0.5 GPa, in which its framework transforms from a 6-connecting uninodal *vmd* net to an 8-connecting *vmt* net.⁴⁴

The second example is found in the zinc alkyl gate (ZAG) family of zinc phosphonate MOFs.⁴⁵ Two materials from this family, ZAG-4 and ZAG-6, exhibit negative linear compressibility at high pressure,⁴⁶ due to a *pressure-induced reversible proton*

transfer between an included water molecule and the linker's phosphonate group.⁴⁷ This phenomenon was revealed by combining high-pressure single-crystal X-ray crystallography and quantum mechanical calculations and has potential applications as a pressure-switchable proton conductor.

Both of these recent examples of very rare pressure-induced chemical reactions show just how deep the field of MOFs response to pressure is, and how novel and unsuspected phenomena may arise in the future when mechanical properties of framework materials are more systematically studied.

■ RESPONSE TO TEMPERATURE

Temperature, because of its scalar nature and limited practical range, may at first be seen as a rather boring stimulus. Yet framework materials demonstrate a wide variety of behavior in response to temperature changes; some of the most striking examples are depicted in Figure 2.

The first unusual thermal property of complex molecular and metal–organic frameworks is the prevalence of *negative thermal expansion* (NTE) among them, and its occurrence in relatively large temperature ranges often including room conditions. Materials with a negative thermal expansion coefficient contract when heated,⁴⁸ a property desirable for many practical applications in materials and composites engineering. NTE, which is found in several zeolite frameworks,^{49,50} is also found to be quite common in molecular frameworks (e.g., Zn(CN)₂,⁵¹ Cd(CN)₂,⁵² Ag₃[Co(CN)₆]⁵³) and metal–organic frameworks, including some of the archetypal MOFs, like HKUST-1,⁵⁴ MOF-5,⁵⁵ other members of the IRMOF family,⁵⁶ and many ZIFs.²¹ This propensity for NTE has been attributed to the presence of many soft (low frequency) transverse vibrational modes in the frameworks, and in particular the vibration modes of the linkers out transverse to the metal–metal axes. The magnitude of the (negative) volumetric thermal expansion coefficients of these materials have been called “large”, “pronounced”, or “exceptional” depending on the authors. The current record holder for volumetric NTE is a defect-rich UiO-66(Hf) material,⁵⁷ which reaches the condition set for “colossal” NTE at $\alpha_V = dV/V dT \sim -100 \text{ MK}^{-1}$,⁵³ while this same order of magnitude has also been computationally from some ZIFs.²¹

In addition to the common occurrence of negative volumetric thermal expansion among framework materials, their very nature also enables them to boast *highly anisotropic thermal expansions*, for the same reasons that they exhibit mechanical anisotropy and NLC. Thus, there have been several recent reports of framework materials showing strongly anisotropic thermal expansion, with crystallographic directions showing large contrasting positive and negative expansions.^{58–60} In particular, one of the interesting avenues of research in this area is the possibility to optimize the thermal response of materials by changes in their structure, linker functionalization, and the presence of guest molecules. Some examples have already started to appear in the literature,⁶¹ along with theoretical analyses of the effects of framework geometry and chemistry on the thermal behavior.⁶² This paves the way for the design of novel materials with targeted thermal properties.

In addition to the linear thermal responses, quantified by thermal expansion coefficients, some framework materials also display *temperature-driven crystal-to-crystal phase transitions*. These correspond to first-order structural transitions observed under heating or cooling of materials, usually with wide hysteresis and discontinuous changes in the unit cell parameters and symmetry.

The driving forces and determining factors behind such transitions depend on the specifics of the intra- and intermolecular interactions in the material but generally result from the balance between four different terms:⁶³ (i) distortion energy of the metal coordination; (ii) long-range dispersive interactions, favoring the denser structures; and (iii) the *PV* term in the enthalpy, favoring denser structures at high pressure. In addition to those four enthalpic terms, the balance also involves (iv) entropic contributions, which generally favor higher-symmetry and more open structures due to larger contributions to the vibrational entropy. These energetic and entropic contributions have been particularly well studied in one of the few examples of temperature-driven crystal-to-crystal transitions in MOFs, namely, the MIL-53 family of materials. The temperature-driven transition in the evacuated MIL-53(Al) was originally observed experimentally by Liu et al.⁶⁴ and was later studied from the theoretical point of view by combining quantum chemistry calculations,⁶⁵ first-principles molecular dynamics, and thermodynamic models.⁶⁶ A similar approach combining in situ X-ray diffraction experiments with first-principles simulations was followed by Chen et al. to investigate the temperature-triggered structural transformations in MIL-53(Sc).⁶⁷

Apart from the MIL-53 family of materials, very few framework materials (and even fewer MOFs) show temperature-induced transitions. Examples reported in the literature include a monoclinic/orthorhombic transition in germanium MFI-type zeolites (with very little structural differences between the two phases),⁶⁸ some dense coordination polymers,^{69,70} and metal-organic framework $\text{Ag}_6\text{Cl}(\text{3-amino-1,2,4-triazolate})_4$.⁷¹ In contrast, it may be of interest to note that many more heating-induced structural transitions are reported on as-synthesized MOFs: those transitions are not actually driven by temperature directly, but rather by the solvent or guest evacuation that takes places upon heating (and are thus guest-induced structural transitions, as described in the section below).

Finally, a last category in the array of framework materials' responses to temperature is that of *thermal amorphization*, or crystal-to-amorphous structural transitions. Temperature-induced amorphization of MOFs is a relatively novel phenomenon, with relatively few reported cases of controlled high-temperature amorphization with full characterization of the amorphous phase. This subject has been spearheaded in particular by Bennett et al., who showed controlled thermal amorphization of ZIFs with various topologies yielded an amorphous *a*-ZIF framework, with a network topology comparable to that of silica glass and with mechanical properties intermediate between porous and dense crystalline ZIFs.^{72,73} I expect that this research in this new area will rapidly expand, especially in light of exciting new results on the formation of hybrid glasses from metal-organic framework liquids.⁷⁴

■ RESPONSE TO ADSORPTION OR GUEST EVACUATION

The interplay between the flexibility of MOFs and porous molecular frameworks and the adsorption of guests within their pores has been one of the most studied areas of framework flexibility. This is at least in part because such transitions are rather readily observed during routine characterization experiments, such as solvent exchange or solvent evacuation upon activation of an as-synthesized material, common nitrogen adsorption isotherms for the characterization of the pore volume or surface area, or measurement of the adsorption capacity of CO_2 , CH_4 , and other strategic small gas molecules. There are

thus a very large number of known guest-responsive framework materials, including some very eye-catching phenomena: *gate opening* transitions in layered or interdigitated frameworks (crystal-to-crystal transition from a nonporous to a porous state);^{75,76} *breathing* transitions in wine-rack frameworks such as the MIL-53 family;⁷⁷ continuous *swelling* upon solvent uptake as in MIL-88;⁷⁸ multistep adsorption with multiple well-defined intermediate states;⁷⁹ reversible crystal-to-crystal and crystal-to-amorphous transitions upon solvent evacuation, etc.^{80,81} These phenomena have been well studied, and several reviews on the topic have appeared.^{1–4}

In this section of the Perspective, I selectively highlight some of the recent results reported in this area, which I think will lead the way to substantial new developments in the future, bring new fundamental understanding, and raise unanswered questions or are simply beautiful or unexpected results.

One of the areas that has seen a large expansion recently is the use of *high-pressure intrusion of liquids* inside porous materials, often triggering structural transformations of the host. The setup for such experiments is typically that of high-pressure crystallography (see section Response to Pressure: Phase Transitions), with simple molecular fluid or fluid mixture (water, methanol, ethanol, etc.) used instead of the typically nonpenetrating pressure transducers (e.g., silicon oil or Fluorinert). This particular type experiment is not entirely new, with some studies on HKUST-1⁸² and ZIF-8⁸³ dating back to 2008, but it has recently seen a renewed interest.^{84–86} However, these results are generally difficult to interpret, because two competitive phenomena are intertwined: (i) adsorption of fluid inside the porous material, which in itself can lead to contraction, expansion, or structural transitions in the host and (ii) compression of the {host + guest} system, whose behavior under compression can be very different from the host itself (a phenomenon sometimes called “hyper-filling”⁸² or “over-hydration”⁸⁷). The general trends observed, however, roughly parallel what has been known in inorganic porous materials such as zeolites: the presence of guests inside the pores increases elastic moduli and diminishes compressibility, while improving resistance to delaying the onset of pressure-induced amorphization.^{88,89} Finally, it is worth noting that high-pressure fluid intrusion has potential applications in energy storage and as molecular springs and shock absorbers.^{86,90,91}

One particular striking result in this area is the possibility to use *high-pressure fluid adsorption to create novel porous phases* from an initially dense framework material. Lapidus et al. reported in 2013³³ that the application of GPa-scale pressure using a fluid of small polar molecules could create new porous polymorphs, starting from dense molecular framework $\text{Zn}(\text{CN})_2$. Moreover, different compression fluids can lead to different porous topologies: diamondoid, pyrite, and lonsdaleite topologies, obtained respectively by intrusion of water, methanol, and a methanol/ethanol/water mixture (see Figure 3). All three topologies constitute novel porous phases of zinc cyanide, which had never been obtained through direct synthesis.

The creation of new porous phases and the associated volume increase (near 2-fold) are quite counterintuitive, because compression of a material usually gives rise to denser structures, and have not been explained in the literature. They can however be understood by considering the thermodynamics of the full {deformable solid + fluid} system in the osmotic ensemble:⁹² the free energy stabilization due to the fluid intrusion counterbalances the free energy penalty of the less dense polymorphs.⁹³ Moreover, the details of the host-guest interactions determine

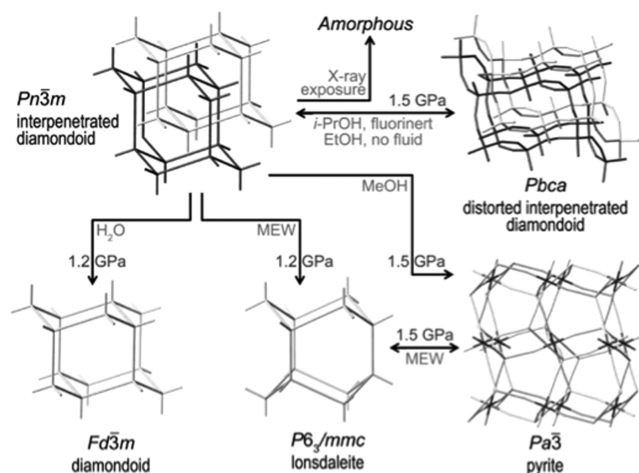


Figure 3. Summary of the fluid intrusion-induced phase transitions in $\text{Zn}(\text{CN})_2$. Reproduced with permission from ref 33. Copyright 2013 American Chemical Society.

what polymorph is obtained under intrusion of a given fluid: the host–guest interactions influence the adsorption isotherms in each phase and thus modify the thermodynamic grand potential of each phase, stabilizing a given phase more than another, and leading to the thermodynamically controlled structural transition upon intrusion. As a consequence, fluid adsorption under high pressure appears as a truly groundbreaking method with broad potential for the synthesis of novel porous framework materials, either from already porous phases or from dense starting materials.

Another fascinating trend in the study of guest-induced structural transitions are the recent achievements in characterizing in detail the *mechanisms, kinetics, and transient states* of such transitions. These studies offer unparalleled insight into the fundamental nature and microscopic mechanism of the flexibility of MOFs, by combining multiple *in situ* structural and spectroscopic techniques (sometimes spatially resolved) and computational chemistry tools. One example is the very recent study of a structural transition of $\text{Zn}_2(\text{ndc})_2(\text{bpy})$:^{94,95} this doubly interpenetrated MOF, in its as-synthesized state, converts to a triply interpenetrated framework upon desolvation and evacuation of the DMF molecules inside its pores. Aggarwal et al. showed in 2014 that this transformation occurs in a single-crystal to single-crystal fashion, without partial dissolution and regrowth of the framework.⁹⁶ On the basis of computational arguments, they propose a mechanism for the transition, involving a concerted process of coordination bond cleavage and reformation facilitated by transverse sliding of pillared layers. This represents a significant advancement in the understanding of

how adsorption-induced (or, in this case, desorption-induced) phase transitions can happen at the scale of an entire crystal, something that has been lacking so far for even the most studied “breathing” materials.⁹⁷

Another such example was the observation of an transient state in the adsorption-induced structural transition of pillared MOF $\text{Zn}_2(\text{ndc})_2(\text{dabco})$.⁹⁸ By using synchrotron grazing incidence diffraction measurements to determine separately the structures of a crystal’s bulk and surface, Kondo et al. showed that, upon adsorption of bulky molecules, the $\text{Zn}_2(\text{ndc})_2(\text{dabco})$ featured a heterostructure:⁹⁹ due to slow diffusion of the guest into the crystal, and a transient state was observed with a guest-induced sheared phase at the surface coexisting with an unperturbed MOF structure in the core of the crystal (see Figure 4). This is an important conceptual step on the way to address the crucial question of the mechanism of adsorption-induced transitions at the scale of the crystal. This will help us understand important observations such as the predominantly hysteretic nature of guest-driven structural transitions, as well as the determining influence of crystal size on the macroscopic behavior under adsorption or solvent evacuation. This latter effect has been convincingly established in a few cases, such as the experimental observations in MOFs MIL-53,^{100,101} $\text{Zn}(\text{ip})(\text{bipy})$,¹⁰² $\text{Cu}_2(\text{bdc})_2(\text{bipy})$,¹⁰³ and ZIF-8,¹⁰⁴ and theoretical rationalizations of these behaviors.^{104,105}

■ RESPONSE TO LIGHT

Among the possible stimuli to which framework materials respond by structural transformations, pressure, temperature and adsorption are by far the most common. There are, however, a large number of other interesting potential stimuli, either physical (electric or magnetic fields, light) or chemical (pH, ionic strength, electron transfer, redox, etc.). Of these, *light* is the only stimulus that was demonstrated so far to *induce structural transformations* in framework materials, a propriety called *photoresponsivity*. The photoresponsive frameworks reported so far, mostly porous metal–organic frameworks, can be classified in three generations, as illustrated in Figure 5. The *first generation* concerns MOFs with an extrinsic photoresponse, due to loading the MOF with photoresponsive guest molecules. This approach was first demonstrated on azobenzene-loaded $\text{Zn}_2(\text{terephthalate})_2(\text{triethylenediamine})$. Yanai et al.¹⁰⁶ showed that light-induced *trans–cis* isomerization of the azobenzene guest leads to a reversible structural transformation of the flexible MOF and in turn to drastic changes in the gas adsorption properties. That approach is not universally applicable, though: in some cases, the guest’s photoisomerization is blocked by the host framework, as for azobenzene in MIL-53(Al).¹⁰⁷

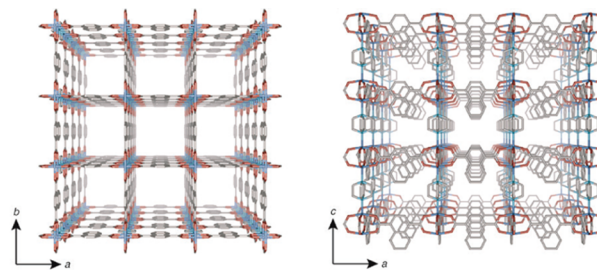
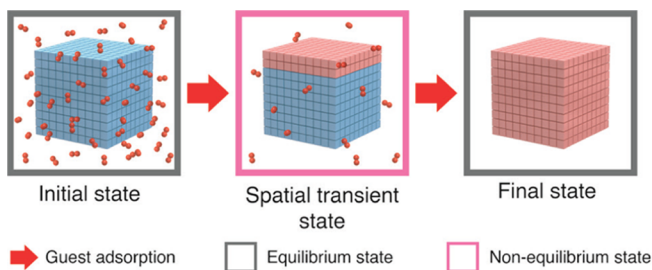
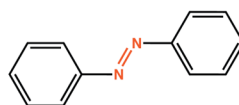
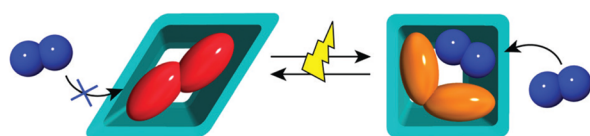


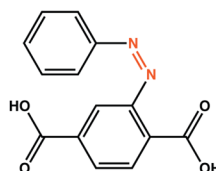
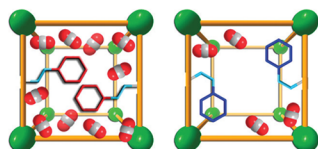
Figure 4. Observation of a transient heterostructure in $\text{Zn}_2(\text{ndc})_2(\text{dabco})$ upon adsorption of bulky molecules. Adapted with permission from ref 99. Copyright 2014 American Chemical Society.

Generation 1



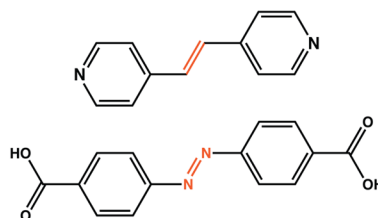
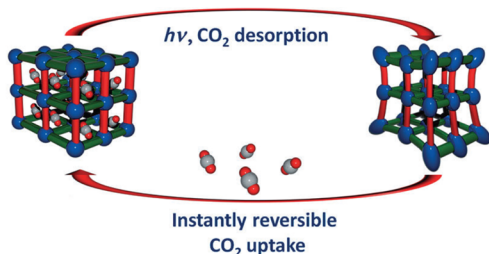
photoresponsive guest

Generation 2



photoresponsive linker side chain

Generation 3



photoresponsive linker backbone

Figure 5. Examples of the three generations of photoresponsive metal–organic frameworks. From top to bottom: azobenzene-loaded $\text{Zn}_2(\text{terephthalate})_2(\text{triethylenediamine})$,¹⁰⁶ PCN-123,¹¹² and $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$.¹¹⁴ Adapted with permission from refs 106, 112, and 114. Copyright 2012 American Chemical Society. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The *second generation* of photoresponsive MOFs incorporate photoresponsive side chains directly inside the organic linkers of the framework. This is the largest of the three categories, commonly exploiting the azobenzene moiety as a photoresponsive component covalently linked to the organic linker.¹⁰⁸ Several materials demonstrated an azobenzene side-chain full retaining its photoisomerization ability,^{109–111} with a change in pore dimensions upon light exposure. This phenomenon was also leveraged for practical applications: Park et al. reported a material that changes its CO_2 uptake capacity after light exposure,¹¹² while Brown et al. demonstrated the possibility of light-driven release of a luminescent dye initially encapsulated within the pores of a MOF.¹¹³

The *third generation* of photoresponsive MOFs is both the most promising and the most difficult to achieve: MOFs based flexible photoresponsive linkers that incorporate a photoresponsive entity directly in the “backbone” of the linker (i.e., not as a side chain). Because light will then directly affect the framework itself, this generation promises the largest and most dramatic light-induced transformations. There is, however, but one example known in this category: $\text{Zn}(\text{AzDC})(4,4'\text{-BPE})_{0.5}$. This material includes two different photoisomerizable linkers, namely, 4,4'-dicarboxylate (AzDC) and *trans*-1,2-bis(4-pyridyl)-ethylene (4,4'-BPE), to form a triply interpenetrated porous framework. It is photoresponsive, and its photoinduced framework isomerization strongly affects the pore dimensions, such that exposure to UV light can be used to trigger the uptake and release of CO_2 in real time.¹¹⁴ Another example is that of a 2D azobenzene-based COF that exhibits *trans*-to-*cis* photoisomerization under UV irradiation, inducing a decrease in crystallinity but no change in the overall structure or pore size.¹¹⁵

Finally, among the light absorption-related properties of flexible framework materials, an interesting property of quickly

rising interest is the occurrence of *guest-modulated changes in optical properties*. I list it here separately: though it is a guest-induced transformation of optical properties (and not a light-induced transformation), it has seen a recent increase in attention. In particular, a number of studies have shown that intrinsically luminescent MOFs can see their photoluminescence emission spectra greatly affected by adsorption of guests. This can occur in a direct manner, through host–guest interactions and mixing of orbitals, as is the case of MOF-5.¹¹⁶ This can also happen as an indirect effect, where the presence of the guest distorts the hosts (adsorption-induced deformation), which in turn changes the optical properties; this is the case, for example, of the “wine rack” $\text{In}(\text{OH})(\text{bdc})$ framework.¹¹⁷ This phenomenon has large potential for applications in sensing.^{118,119}

PERSPECTIVES

Ending this somewhat selective review of the recent progresses of stimuli-responsive framework materials, I would like to highlight some of the remaining open questions and avenues of inquiry that seem, from my perspective, worthwhile for future research. The first one is expanding the board on which we are currently playing the game by *designing framework materials that respond to novel stimuli*: electric or magnetic fields, pH,¹²⁰ oxidation or reduction,^{121–123} ionic strength, electron transfer, etc. All types of physical or chemical stimuli can be coupled with framework transformations. One such example is the very recent discovery of an electrically switchable MOF,¹²⁴ though the mechanism behind the observations is still uncertain. Moreover, multiple stimuli can be applied in conjunction, leading to the possibility of *multifunctional materials* whose response to a complex stimulation is not a simple combination of linear one-variable effects: such materials have been known for some time in the

fields of gels and supramolecular assemblies, and multistimuli-responsive nanoporous frameworks have started to appear recently.¹²⁵

Thus, as the number of stimuli studied increases, the dimensionality of the parameter space increases dramatically, with, e.g., temperature, mechanical pressure, adsorption (nature of the guests and fluid pressure), and light exposure varying independently. In order to understand the behavior of materials in this high-dimensional parameter space, we need to develop multicoordinate phase diagrams by a combination of experimental measurements, computational tools, and statistical thermodynamic models. Such phase diagrams, or equations of state, can then be used for higher-scale modeling to engineer devices based on multifunctional stimuli-responsive materials.

In addition to new stimuli, another way of expanding the applications of responsive framework materials is to leverage the coupling between deformation and other properties for novel applications. Current research rightly focuses a lot of effort in understanding *how* and *why* materials deform under external constraints, but we also need to better understand the physical and chemical properties of these “stimulated” states: optical properties, electronic states, polarization, magnetism, etc. This is exemplified by the recent advances in turn-on fluorescence in MOFs¹²⁶ and reports of materials with photoluminescent properties that can be shifted depending on temperature¹²⁷ or guest uptake.¹²⁸ Other properties remain to be investigated: stimuli-responsive materials, with their large responses to small stimulations, can provide excellent materials for piezoelectric, ferroelectric, piezomagnetic, and other applications.

In better understanding these properties, an important open and very broad question is that of the link between framework geometry and topology, and a material's properties. Or: *in a framework material's response, what is dictated by framework geometry and topology, and what is the influence of chemical composition?* The fundamental understanding of such relationships would enable us to provide conceptual guidelines for the design of new materials. The goal here is clearly the ability to engineer materials with specific responses, i.e., the *rational design of frameworks with tailored physical and chemical properties*, by being able to predict computationally the responses of a specific framework under various stimuli. There has already been a significant research effort on that front, focusing mostly on enumerating hypothetical frameworks^{129–131} and evaluating their static properties (adsorption capacities,¹³² relative enthalpy,^{133,134} etc.) as well as dynamic properties (such as hydrothermal stability¹³⁵ and mechanical properties^{18,21,136}). In time, more parameters will need to be incorporated than the ideal framework topology: recent studies have shown the large influence of correlated defects in the behavior of framework materials¹³⁷ and the possibility to leverage this for the design of optimized materials.^{57,138,139} There, in addition to the oft-stated goal of obtaining highly responsive materials for applications such as sensing, it is worth noting that a deeper understanding of the mechanisms of framework responses will also allow to develop materials at the other end of the flexibility spectrum, i.e., materials capable of resisting structural changes under temperature changes or pressure.

Finally, among the examples I highlighted in this Perspective, there is a clear recent trend toward providing better insight into the physical mechanisms of stimuli-responsiveness, with particular focus on space-resolved, time-resolved, and in operando measurements. Those are crucial to provide a better fundamental understanding of the nature of the transformations

triggered by complex stimuli and have practical consequences for the design of novel materials in working conditions. The typical questions that need to be answered include: *how do stimuli-induced transformations occur and propagate at the scale of the crystal? What is their kinetics and dependence on the history of the material (i.e., what determines the possible metastable states of the system)? How do crystal size, shape, and textural properties affect responsivity?*

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Notes

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