Review

Flexibility in Metal–Organic Frameworks: A Basic Understanding

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Abstract: Much has been written about the fundamental aspects of the metal–organic frameworks (MOFs). Still, details concerning the MOFs with structural flexibility are not comprehensively understood. However, a dramatic increase in research activities concerning rigid MOFs over the years has brought deeper levels of understanding for their properties and applications. Nonetheless, robustness and flexibility of such smart frameworks are intriguing for different research areas such as catalysis, adsorption, etc. This manuscript overviews the different aspects of framework flexibility. The review has touched lightly on several ideas and proposals, which have been demonstrated within the selected examples to provide a logical basis to obtain a fundamental understanding of their synthesis and behavior to external stimuli.

Keywords: metal–organic frameworks; flexibility; mechanical properties; secondary building unit; characterization

1. Introduction about Metal–Organic Frameworks (MOFs) and Their Structure

Coordinated polymeric materials were first discovered by Kinoshita in the late 1950s [1,2], and Berlin [3], then Block [4] followed his footsteps in the 1960s. In the last century, many great scientists focused their research on understanding the behavior of these porous materials [5]. The term MOF dates to the late 1990s in which Kitagawa [6], Yaghi [7] and Férey [8] primed a quantum leap in understanding, advancing the synthesis of such hybrid materials. The pioneering work of these scientists and their outstanding discoveries in MOFs is highly appreciated. Their studies and descriptions of the science (or art) of their synthesis and characterization have engendered vast literature, as numerous books and review articles attest. Moreover, recent research affords access to a much wider range of investigational and synthesis techniques.

Structural formulas of various degrees of an infinite number of combinations and permutations between metal centers with either a tetrahedral or an octahedral array of organic rod-like connecting units resulted in successfully synthesizing thousands of MOFs. From these newly discovered

scaffolding-like materials, flexible frameworks with dynamic properties are rather limited, and only quite a few have been thoroughly investigated [6].

The flexible features of some of these porous materials are intriguing for so-called "smart" materials in that they could structurally respond to an external stimulus. The flexibility of the MOF(s) might play a crucial role in the MOF(s) interfacial structure, and thus in their compatibility.

The fundamental understanding of MOFs flexibility introduces a desire to interpret the flexibility phenomena by studying the properties of individual organic linkers and metal nodes of specific MOFs. To this end, literature has devised a variety of ways to classify and envision their composition, size, and shape.

Full characterization should be reserved for MOFs with interesting flexible behavior, and adequate explanation should be devoted to this. The goal of this review is to be able to cite as much detail and as many needed examples to reach a fundamental and comprehensive understanding of MOFs' flexibility, its origin, and control methods.

In this review, three main themes will be discussed: (i) the flexibility behavior and the dependence of the chemical identity and physical state of the framework on its organic linkers and its metal nodes, (ii) phenomena of flexible MOFs, how to control it and its application; this theme is predicated on the forms of adsorbed species on the flexible framework (guest–host, guest–guest, and host–host interaction), and (iii) the observations on which these themes will be expressed in a real application and not merely as theory statements.

To explore the flexibility of MOFs, help in adjacent areas of science such as reticular chemistry and joint experimental–modeling is needed. This review will give a literature analysis of the main advances in flexible MOFs up until 2018, where synthetic strategies, characterization, and application are thoroughly discussed.

1.1. Origin of MOFs Flexibility

The design and synthesis of flexible scaffold-like material depend on the choice of the scaffolding elements as metal nodes and organic linkers. It is worth mentioning that the choice of metal centers would depend partially on the framework building process to be used [5]. However, organic linkers bearing functional groups are gaining more attention, and play a major role in flexibility, e.g., rigid MOFs with flexible ligands Thus, any of the three possible sources contribute to the flexibility of MOFs. Two speculations can be offered in this respect: (i) the source of the flexibility and (ii) the way the flexible MOF behaves toward external stimuli. The structure and functionality depend on the deliberate way of construction and assembly on either the two components or the nature and type of connection linking them.

The rational and intelligent design of the coordinating ligand and metal nodes have been the subject of much interest and attention to synthesize a wide range of scaffolding-like solids with unusual and useful properties. Essentially, most of the research has been adequately focusing on the conceivable linking of the scaffold-like compounds using the supramolecular building blocks (SBBs) or the secondary building units (SBUs) and the molecular linkers [9–12]. In principle, MOFs with a high degree of rigidity are synthesized using fixed organic building blocks (based on phenyl rings or multiple bonds, rigid benzene di-, tri-, and tetra-carboxylic acids, terephthalic acid, azolate-based ligands, as well as their derivatives). Such frameworks usually show relatively high thermal and mechanical stability and are capable of retention of porosity upon guest solvents removal. It should not come as a surprise that the properties of MOFs with flexible ligands cannot determine the whole framework if it is flexible or not. As the nature of the resulting frameworks cannot only be determined by the linkers' flexibility or rigidity since in some cases, flexible ligands can be used to build both robust and flexible MOFs. However, in view of the above remarks concerning the nature of flexibility, attention is needed when choosing the source of flexibility. In general, there is an obvious difference between flexible MOFs and MOFs with flexible ligands (FL-MOFs). The latter corresponds to MOFs

with one flexible component in the framework. The organic linker's rigidity or flexibility is not directly linked to the nature of the framework.

What is not generally recognized is the probable role of the connection of metal nodes and organic linker and the functionality of an organic ligand, as a connector to design and tune flexible structures [6].

MOFs that are capable of responding to external stimuli, their entire framework is dynamic, and their response represents in conformational mobility combined with coordination preferences, can be classified as flexible MOFs [13]. Such response depends on the choice of a metal compound, or on whether the linkers can rotate, twist or bend. This unique feature significantly improves the performance of the MOF in several applications such as storage, separation, sensing, and others. In contrast with the discovery of rigid MOFs, at present, misconceived thinking still appears in other areas of design, synthesis, and applications of flexible MOFs. This review will provide insight into seminal examples from different laboratories to get a profound understanding of the structure and bonding of individual elements and their properties controlling characterizations and applications.

1.2. The Flexibility of Linkers/Functionalized Linkers

Linkers have a large impact on the final nature of this kind of porous material. Linkers or ligands are defined as bridging organic elements, which connect the aggregates or metal centers into prolonged framework structures. The geometry, length, functionality, and connectivity of a linker will direct the resulting structure of the framework [14–16]. For example, changing the linker connectivity and fixing the cornerstone geometry can result in a very different framework with different properties. Many studies have found that such linkers may allow conformational diversity owing to their potential energies, which can be expressed by their binding strengths [17]. Their response to external stimuli can occur through a variety of mechanisms such as rotation of the host framework between a metal ion and an organic ligand, rotation around single bonds within an organic ligand or displacement of sub-networks.

The following types of linkers provide a flexible structure with dynamic behavior:

1. Aliphatic carbon chain; intrigue significant interest in flexible MOFs synthesis because of the ability to reorient themselves in response to external stimuli [18,19]. The greater the length of the chain, the greater is the variety of possible reorientation.
2. Aromatic rings with the capability of rotation or movement of dangling side chains of the organic ligands [20].
3. Ligands with an open structure. This type of ligand depends on the formation of coordination bonds with the central metal atom M. The decrease of the dentation gives multiple degrees of rotational freedom of the ligand around the inorganic moiety. The ratio of the metal/linker (M/L) and linker/linker (L/L) and the synergistic effect of metal nodes and organic linker on framework flexibility are major-league factors that play a vital role in determining the degree of flexibility [21,22].
4. Linkers' surfaces can also be used as anchoring points for introducing additional functionalities to tailor the framework flexibility by the substituent effects at the linker [23]. Such functionalization results in multivariate MOFs (MTV-MOFs).

The methods that are used to modify the backbones' flexibility of the framework may be put into two general classes: (a) application of specific organic synthetic strategies with a particular selection of the electron withdrawing or donating nature of the "contributing" functional linkers, and (b) incorporation of extended conjugated aromatic systems to the linker(s) itself. Furthermore, the shape, the size, and the shared angle between the functional group added onto the main linker, play a role in identifying the structure of the MOF and its overall network topology [15,24,25]. Asymmetric linkers also contribute to tuning the topological flexibility of the network [26,27].

In view of the almost endless ways that a linker(s) can manifest itself, a benchmark class of MOFs based on carboxylate linkers or functionalized 1,4-benzenedicarboxylate (BDC) linkers have been extensively explored so far. Recently these types of linkers have been dominant in the field of flexibility recognition of MOFs.

1.2.1. Carboxylate Linkers and Their Isomerism Features

Férey and Serre proposed several empirical rules concerning the impact of the carboxylate linkers on the flexibility of MOFs [28]: (i) The first rule states that ditopic carboxylate ligands, which are linked to two metal clusters or SBUs, are favorable for the design of flexible MOFs. Hence, the inorganic cornerstones, which own a mirror plane with the carboxylate linkers, have the ability to permit framework swelling; MIL-88 is a prized example to study this rule. (ii) The second rule is about the ratio of the number of carbons of the carboxylate surrounding the cluster to the number of metallic atoms within the cluster (C/M), several studies demonstrated that if this ratio is higher than or equal 2, then the brick possibly allows swelling. Mill-88 is demonstrative once again of this theory with a C/M = 2. However, this rule needs to be delineated by other MOFs. (iii) The third rule states that on the contrary to ditopic carboxylate ligands, tri- or tetra-topic carboxylate linkers prohibit the breathing in MOFs. Presumably, the forgoing rules represent the main structural requirements for the flexibility phenomenon.

Kitagawa and his group [29] investigated the linker rotation of pyridinedicarboxylic acid linker (PDC) in $\{[Cd_2(pzdc)_2L(H_2O)_2]$ $5(HO)$ $(CH_3CH_2OH)\}_n$. The PDC linker, which bears ethylene glycol side chains, acts as a molecular gate with locking/unlocking interactions when this coordination polymer is triggered by guest inclusion, see Figure 1.
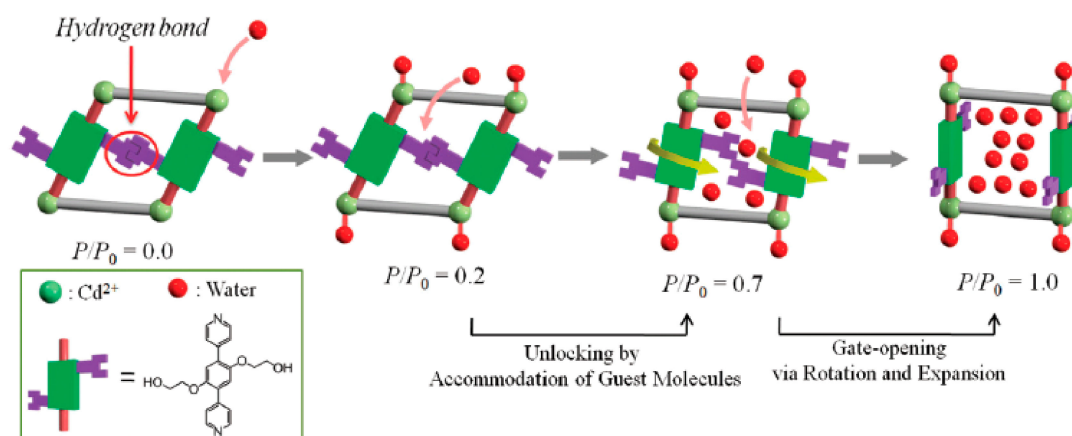
Figure 1. Schematic representation of the structural transformations triggered by water adsorption [29].

Particular ligand functionalization can modify conformational flexibility [30]. The extra decoration on the pores using functionalized linker molecules can add some complexity to their properties [31,32]. For example, adding a group which can interact through their hydrogen bonding such as –NH$_2$, –COOH and OH, will lead to a higher degree of deprotonation and higher density of open metal sites, and hence the ratio of M/L will increase [22,33]. Fischer's group created a library of functionalized BDC-type linkers, with minimal additional dangling side groups and diverse functionalities by varying chain length at different positions of the benzene core [30].

MIL-53 and MIL-88 are two types of flexible MOFs that belong to the third-generation porous materials. Their fascinating properties attracted attention for experimental and theoretical linker functionalization investigations [34,35]. Ahnfeldt et al. investigated the insertion of amine-bearing organic linkers in MIL-53. The structure contained linkages of AlO$_4$(OH)$_2$-octahedra with 1,4-benzenedicarboxylic acid; such inclusion resulted in a slight expansion of the unit cell volume [36]. The observation of this process has provided fundamental clues to understand the

importance of functionalization, making it possible to point out that the type of functionalization will strongly depend on the type of desired application.

1.2.2. Mixed-Linker

Emphasis is being placed on improving the properties of linkers by mixing various organic linkers. Such a combination can have a higher degree of flexibility. Yaghi and coworkers followed this strategy in order to synthesize 18 one-phase MTV of MOF-5 starting with eight types of functionalized 1,4-BDC organic linkers. The resulting series of MOFs contained distinct functionalities [37].

Another well-studied example concerning mixed-linker structures was presented by Seo and coworkers [29], where they investigated the pillared-layer MOFs. This type of MOFs is featured by their structural elasticity, the interpenetration of their layers, and flexibility. A simple modification of the dipyridyl linker can change the channel size and functionality as well as adjust the degree of flexibility and hydrophobicity of the framework while maintaining its pillared layer structure. Sen et al. [38] have also demonstrated the effectiveness of using a mixed ligand system to enhance the functional property of aromatic carboxylate linkers. As the resulting MOFs gave rise to sustained flexibility, i.e., using a semi-flexible tricarboxylic acid ligand H_3L and pyridyl-based co-ligand under solvothermal/hydrothermal conditions to synthesize Cd(II) coordination polymers. The aromatic polycarboxylate co-ligands have an important effect on the features and the overall structures of Cdbmb polymers (bmb= (1,4-bis(2-methylbenzimidazol-1-ylmethyl) benzene)), concerning their construction, flexibility, coordination modes, etc. [39,40]. Reflection on some of these examples leads to the conclusion that the flexibility of MOFs has mainly been accredited to a conformation change of the flexible organic linkers [13,41].

### 1.3. Flexibility of the Metal Nodes

The inorganic brick or the so-called metal nodes provides the local structure of the overall framework. These inorganic nodes, which can either be metal clusters or metal ions [42], are the place where flexibility and transformation could start as many of metals clusters/ions are not permanently quiescent but in a state of temporary stability until exposure to external stimuli, and then it takes different shapes.

In many cases, the metal nodes of the framework do not follow the symmetry of the overall structure. Several studies have pointed this issue out, and the changes that occur when external stimuli induced those structures [43–46]. Thus, the structure at the metal node will also play a critical factor in controlling the flexibility of the framework. One criterion for distinguishing flexible MOFs from rigid MOFs is (i) the changed coordination environment of metal ions [47,48]. Other criteria have been proposed such as (ii) the deformed configuration/connectivity of secondary building units (SBUs) containing metal ions in response to the removal or binding of coordinative molecules [49]. Furthermore, observational studies demonstrated that the framework flexibility have a tendency to scale inversely with metal–ligand interaction strength [50,51].

The presence of some unpaired electrons in the chains of the metal centers can also delimit the dynamic behavior by puckering and slightly modifying the overall contraction or elongation distances between adjacent metal centers [52]. MIL-53(M) can be taken as a prototypical example to explain the role of the metal nodes in the overall framework flexibility. Several structures can be composed by varying the metal M as such $[M(OH) (BDC)_2]n$. (M = Cr [53], Sc [54], In [55], Ga [56], Al [57], Fe [58]). The beneficial interplay with the choice of the metal center will result in different flexible behavior, MIL-53(Cr) exhibits an improved ability for pore opening upon dehydration [53]. A transition from large pores (LP) to narrow pores (NP) was detected upon applying a mercury intrusion–extrusion test using a mechanical pressure below 500 MPa on MIL-53(Cr) and MIL-53(Al), mercury penetration took place within pores larger than 3 nm. The result of this test demonstrated that MIL-53(Al) solid was shown to exhibit an irreversible contraction, while MIL-53(Cr) undergoes a reversible structure change under similar conditions, see Figure 2 [59]. Such impressive behavior can be explained only on

the basis of corner-sharing chains of $AlO_4(OH)_2$ octahedra, which lead to stiffness of structure upon inducing a pressure [60].
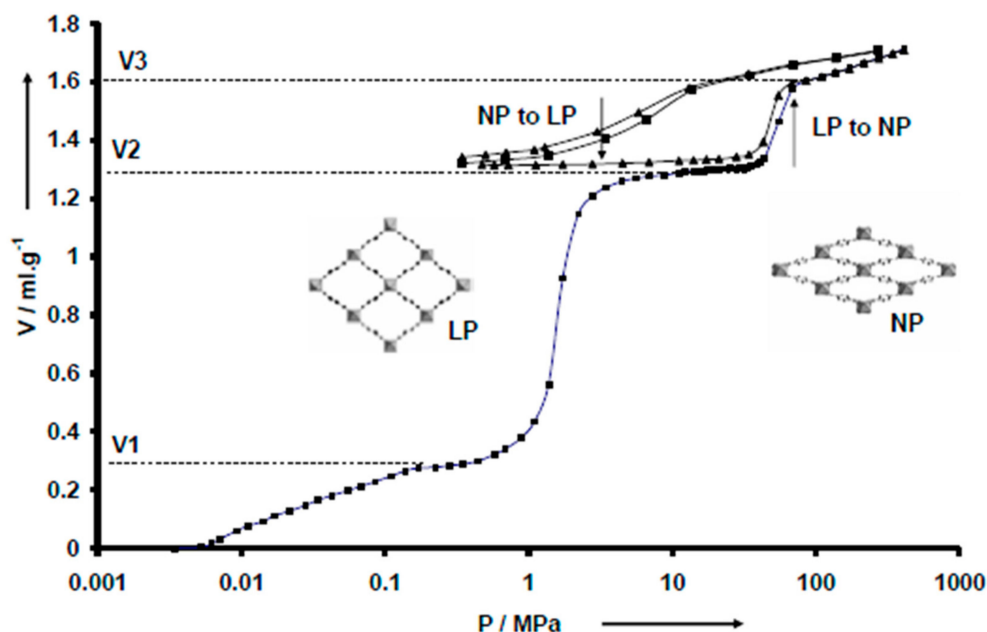
Figure 2. Large pores (LP) to narrow pores (NP) transition in MIL-53(Cr) sample upon intrusion–extrusion of mercury: cumulative intruded volume versus applied pressure. The arrows show the steps that correspond to the LP to NP transition. Squares: first intrusion–extrusion cycle. Triangles: second intrusion–extrusion cycle [59].

In summary, to design flexible MOFs, it is not enough to introduce specific types of metal nods/ions, linkers or their functionalities, but a smart functionalization and gentle interplay must exist between them concerning concentration, location, and distance of individual elements of the framework. Therefore, it is expected to see some parallelism between the effects of metals nodes and organic linkers and how the overall framework can respond to any changes in temperature, pressures or guest molecules.

## 2. General Aspects of Framework Flexibility

Several phenomena have been addressed with regards to framework flexibility. For each phenomenon, detailed and profound insight into the structure and the connectivity of individual MOFs' element is needed. Moreover, a look over their structural transition during exposure to external provocations to discern which factors may be improved during an application with particular reference to apparently anomalous behaviors. Flexible MOFs perform in an extraordinary stimuli-responsive fashion. When a researcher discusses the dynamic behavior of flexible MOFs upon exposure to external stimuli; three different conceptual levels of response should be borne in mind; (i) host coordination network structure (cage), (ii) the crystal structure, and (iii) the overall particle structure [20]. In order to simulate the stereo-dynamic behavior of third generation MOFs, the action of certain external stimuli such as light, temperature or pressure is needed. The type of the stimuli has a sole behavior on the obtained response from the targeted framework. Several important consequences then follow. The degree of responsive will depend on the potential of an architectural framework to restructure itself according to stimuli-dependence behaviors. Gate opening, phase change, and change in the cell parameters could present such responses. Several natural stimuli used to irritate the structural transition such as:

- Exposure to temperature. When MOFs are exposed to different temperatures; a change in the linker's conformation can be observed (e.g., rotation of aromatic rings or the movement of dangling side chains of the organic ligands) [35,61–63].
- Exposure to external pressure. Mechanical stability of the framework can be affected upon exposure to pressure [61,64,65].
- Insertion/removal of guest molecules [66,67], to study guest-dependent dynamic behavior since the framework can expand or contract upon guest exchange.
- Light can also be used as a stimulus for the dynamic movement of MOFs [68,69]. Switching between cis–trans/LP–NP transition upon interaction with light [68–70].

2.1. Breathing, Swelling, and Linker Rotation

2.1.1. Breathing

In the early stage of research, most dynamic behaviors were related to the presence or removal of guest molecules, known as the host–guest interaction [6,71]. At the outset, breathing effects were considered in many laboratories; despite the variety of MOFs, only several classes exhibit the unique breathing phenomena in which the frameworks can easily change and adapt its structure upon host–guest interaction. Breathing phenomenon is caused by the existence of "weak points" in the framework at which substantial geometrical changes can occur. Figure 3 displays the three principle breathing cases of MIL-53 [72].
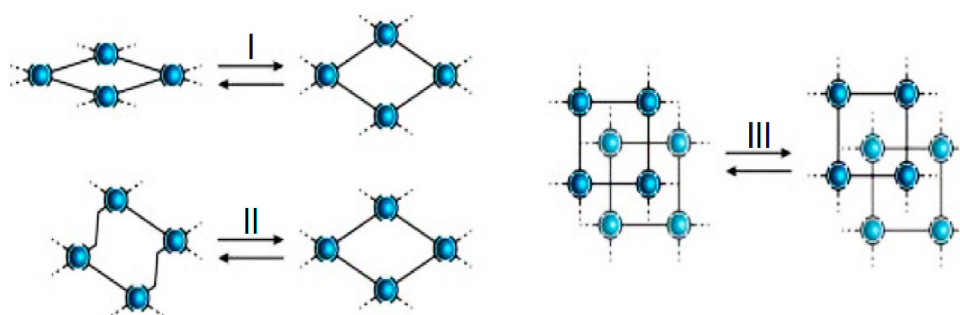
Figure 3. Types of breathing: (I) flexibility of the inorganic building units (IBUs), (II) structural changes of the linker molecules, and (III) shift of interpenetrated or interwoven frameworks [72].

- The dynamic behavior of the inorganic building units (IBU) e.g., Figure 3 (I), is subject to the ordered rotation of the ligand molecules or a hinge motion of the linkers [28,73,74]. These dynamic behaviors result in opening or closing of pores and accordingly affect the loss/uptake of guest molecules. Carboxylate ligands are considered an example for weak IBU since they are capable of switching their binding mode in the so-called kneecap mechanism in which the ligand rotates around the O–O-axis of the carboxylate group.
- When organic linkers with reversible structural and low energy are considered, one must keep in mind that guests' exposure will lead to many isomerized linkers; see Figure 3 (II). The reversible photoisomerization of azobenzene molecules with alternating UV/visible light irradiation is a good example of such type of flexible transformation [75].
- The free pore volume of interlocked linkers and interpenetrated networks can also act as a weak point; see Figure 3 (III). In this case, breathing arises by shifting the individual frameworks against each other by van der Waals interactions [76,77].

After evoking the weak points in a framework, it is worth recalling types of MOFs that exhibit flexibility under the inclusion/evacuation of guests within the coordination framework, according to the structural dimensionality, see Figure 4 [71].
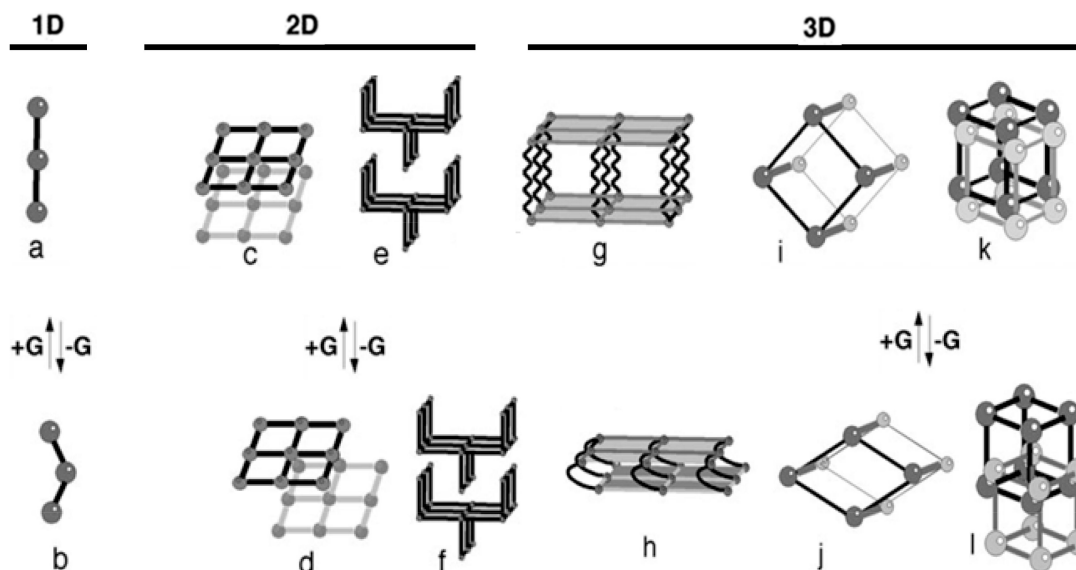
Figure 4. Illustration of dynamic behaviors of the metal-organic frameworks' (MOFs) structure under the incorporation/removal of the guest molecule [71].

The first category corresponds to MOFs with 1D channels with diamond or square cross-sections. This type are known as pillared MOFs in which rod-like linkers are connecting the metals. The pillaring linkers of the frameworks are flexible as they can expand or shrink (elongated or shortened) upon probe molecule inclusion [78,79].

The second category presented are rigid MOFs with 2D layers covalently connected with flexible pillars in an overlaid or shifted manner [80]. Generally, a strong framework–guest interaction can result in a significant perturbation of the cell volume of the so-called sponge-like MOFs. e.g., elongation of pillars results in the framework expansion during absorption of guest molecules while the frameworks shrink upon the removal of guest molecules. Moreover, the rotation of organic moieties resulting from strong guest–host interactions, persuades the volume change [80,81]. An interesting and potentially very useful property of this category is that the topology of the framework preserves its single crystallinity upon the adsorption of guest molecules. A salutary example of this case can be presented by a bilayer framework synthesized from bismacrocyclic Ni(II) and BTC (BTC = 1,3,5-benzenetricarboxylate) ligand. This framework presents a sponge-like behavior, shrinking and swelling according to the number of guest solvent molecules contained within the networks [82].

The last category is presented by interpenetrated 3D grids that contain layers connected covalently with flexible pillars. The introduction of guest molecules causes the sliding of the adjacent interpenetrated net and hence cause the pores to open or close upon the adsorption of guest molecules whilst keeping the same topology [78,83]. Some of the 3D frameworks are densely packed in the deficiency of guests and introducing of molecules engenders a sliding of one network [28]. This classification provides confidence that a wide range of scaffolding-like solids should provide accessible structures regardless of their dimension.

A particularly well-studied example concerning the breathing phenomena in MOFs is given by flexible chromium terephthalate. This MOF consist of 3D metal (III) terephthalates with 1D-pore channels of disordered BDC linkers. Llewellyn and coworkers investigated the CO_2 separation over MIL-53. This MOF shows a selective flexible by means of breathing during CO_2 adsorption. The breathing behavior is attributed to the disordered BDC linker since it switched from NP to LP upon hydration and dehydration respectively, with a 50% volume increase without any change in the topology (Figure 5) [84]. The large breathing effect is ascribed to the deficiency of the hydrogen-bond interactions between the hydrogen atoms of water molecules and oxygen atoms of the carboxylic

group and the μ2-hydroxo group. As exposure is increased, the framework structures are ever more densely packed.
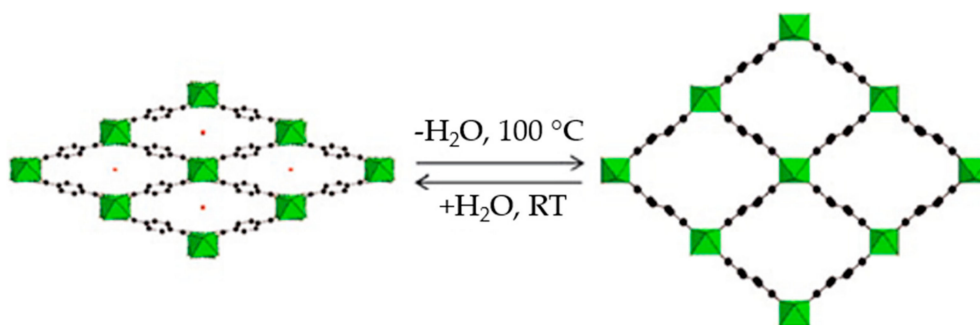

Figure 5. Breathing behavior of MIL-53(Al, Cr) [84].

2.1.2. Swelling

In contrary to the well-studied MOFs that display such distinct transitions such are those with a pillared structure, there have however been several studies investigating MOFs that exhibit large flexibility and continuous breathing behavior without defined transitions. Such behaviors are erratic and are not fully understood but highly sought after [34,85]. The common name of such behavior is often referred to as "swelling behavior." The swelling mode is featured by gradual enlargement of the MOF unit cell volume without a change in the shape of the unit cell shape or the space group.

MIL-88 is a prime example of swelling behavior as it exhibits a large breathing behavior resulted from pore size change during solvation and desolvation [79]. It could swell upon immersion in liquids with variations in accessible free cell volumes from 85% to 230% depending on the nature/length of the organic spacer (see Figure 6) [35,85].
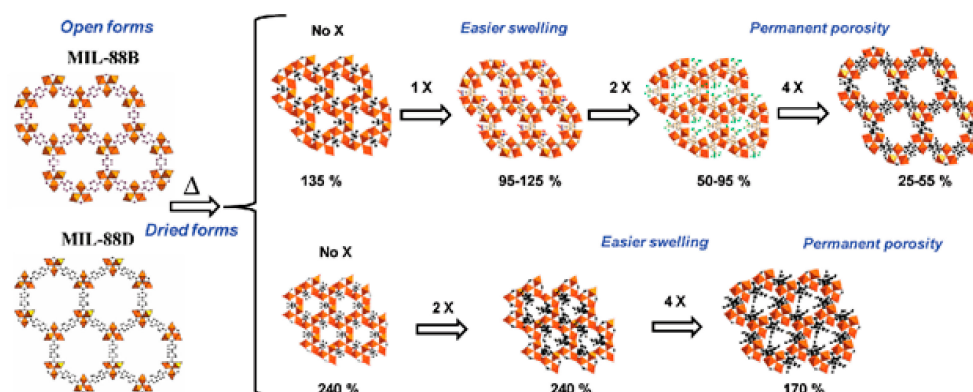

Figure 6. Illustration for swelling phenomena of the structure and the flexibility of the MIL-88B and MIL-88D modified solids as a function of the number of functional groups (X) per spacer (on the top) [35].

Another study was done on MIL-88, by Ramsahye and his group. They studied the impact of n-hexane adsorption over MIL-88 and modified MIL-88. During adsorption, the external surface of the structure opens the pore sufficiently for the first molecules to be able to diffuse into the framework and thus initiating a pore swelling. However, the modified MIL-88 shows only a small cell volume contraction of about 20% upon drying and thus bears a pore size in its dried state over 5 Å [86].
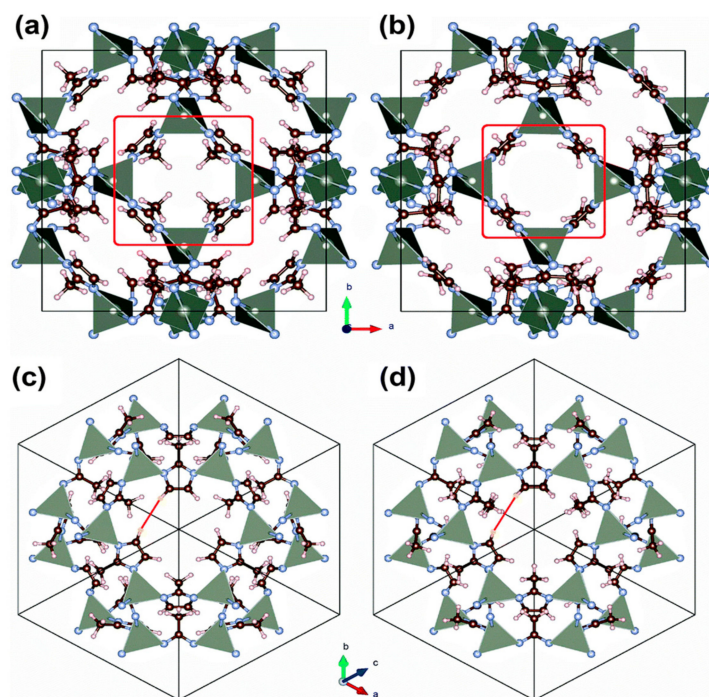
2.1.3. Linker Rotation

Linker rotation or gate opening behavior is described as a (continuous) transition where the fragments of a linker can rotate around a certain axis. It is important to note that linker rotation is not

essentially accompanied by crystallographic phase transitions [52,87]. That kind of dynamic behavior results in a significant change in the inner geometry of the pore, as well as the positions of possible gas uptake [88]. Figure 7 shows the rotational behavior of the aromatic ring within the linker structure around a certain axis within the void.
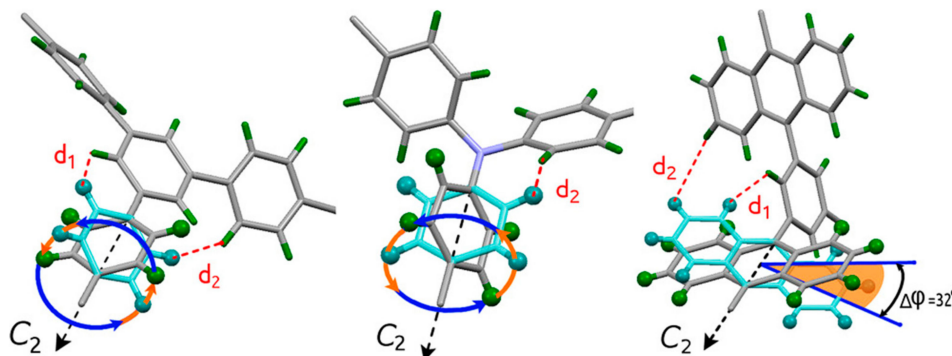
Figure 7. Illustration of aromatic ring linker rotation for isostructural (3,24)-connected porous materials, MFM-112a, MFM-115a, and MFM-132a, with different linker backbone functionalization [88].

Fairen-Jimenez and his group [89] presented an experimental–theoretical study on the gate opening of ZIF-8, in which a reversible linker reorientation was observed on the organic linker of the MOF (methylimidazole linker) upon the application of high pressures (14–700 bar). The size of the pore window increased as the implemented pressure increased, see Figure 8.

Figure 8. Linker reorientation can be observed on the linker of ZIF-8 viewing from the axis direction (**a**), and the diagonal direction (**c**), the corresponding structure of ZIF-8 loaded with N_2, (**b**,**d**) [90].

The distinctive characteristic between linker rotation/gate opening behavior and breathing phenomena is that the rotational movement by the linker results in the expansion of the pore windows while a change in the unit cell of the crystal occurs during breathing.

2.2. Thermo-Responsivity

Temperature plays a distinct part in characterizing the conformational change of flexible MOFs [51,52,91]. Some of the flexible MOFs show a drastic change in their transition state from narrow pore (NP) state at low temperatures, to large pore (LP) structures upon reaching the threshold temperature.

It is worth mentioning in such responsive behavior, increasing the side chain length and angles results in a decrease in the transition temperature. On the contrary, the more polar the linker, the higher the transition temperature, as the pillars rotation eventually ends up in the opening of the pore space [92,93].

Going back to the prominent example, when inducing a high temperature to MIL-53(Cr) an increase in the rotational motion of the phenyl rings occurs and consequently a transition to the open form. Therefore, changing the nature of the aromatic spacer has a strong impact on the flexible character of these solids [54]. Figure 9 displays thermo-responsive behavior of the Sc–OH–Sc chain in MIL-53(Sc) upon heating to 623 K, as it leads unit cell expansion.
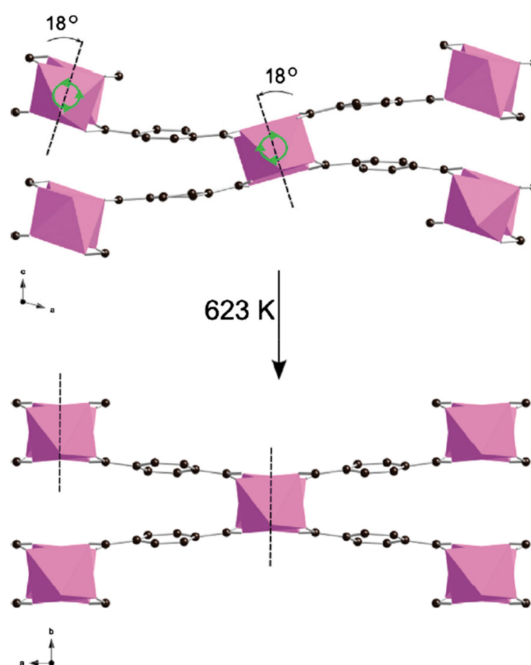
Figure 9. Effect of heating on Sc–OH–Sc chain in MIL-53(Sc). The dashed line represents the plane of the infinite Sc–O–Sc chains [54].

2.3. Mechanical Properties, Elasticity

Pressure plays a major role in several practical applications. Thus studying its effect has triggered the interest of many researchers as applying pressure on specific framework imparts the flexibility to allow drastic perturbations on their structural characteristics.

Until now, some pressure-induced behaviors of flexible MOFs have been investigated [94–97]. However, the number of MOFs that have been exposed to mechanical stress is trivial in comparison to the immense number of MOFs that have been produced [61]. Chapman and Moggach groups have borne out the significance of applying small pressures upon single crystals with porous frameworks to study the structural changes upon the framework response [51,98,99]. Their unique studies demonstrated that pressure offers a unique meaning to thoroughly explore the often-complex structure–function relationships of flexible MOFs since it was evident that their porous nature gives an additional dimension upon exposure to high pressure. Notable flexible behavior was noticed when frameworks with metal polyhedra were exposed to high pressure. Polyhedral metal is considered as a vital sign of

highly flexible and high elastic MOFs, as it can relax, rotate and change the unit cell volume when external pressure is induced [100].

Figure 10 provides a basis for understanding the possible unit cell transformations of MOFs upon pressure, as illustrated exposure [101]:

- Amorphization, e.g., pressure-induced amorphization of ZIF-4 [102].
- Compression, e.g., the linear compressibility of MIL-53(Al) [102].
- Reversible phase transition, e.g., ZIF-8 [98].
- Phase formation (bond rearrangement), e.g., a pressure-induced bond rearrangement in $[tmenH_2][Er(HCOO)_4]_2$ [64].

This classification does not, however, point uniquely to any of the reversible behavior, as a truly flexible material should show reversible behavior under pressure relief, e.g., many compression cases are fully reversible, such as ZIF-8, after the pressure has changed back to the initial conditions [65,99,101,103]. However, some structural transformations resulting from pressure stimuli are not necessarily reversible.
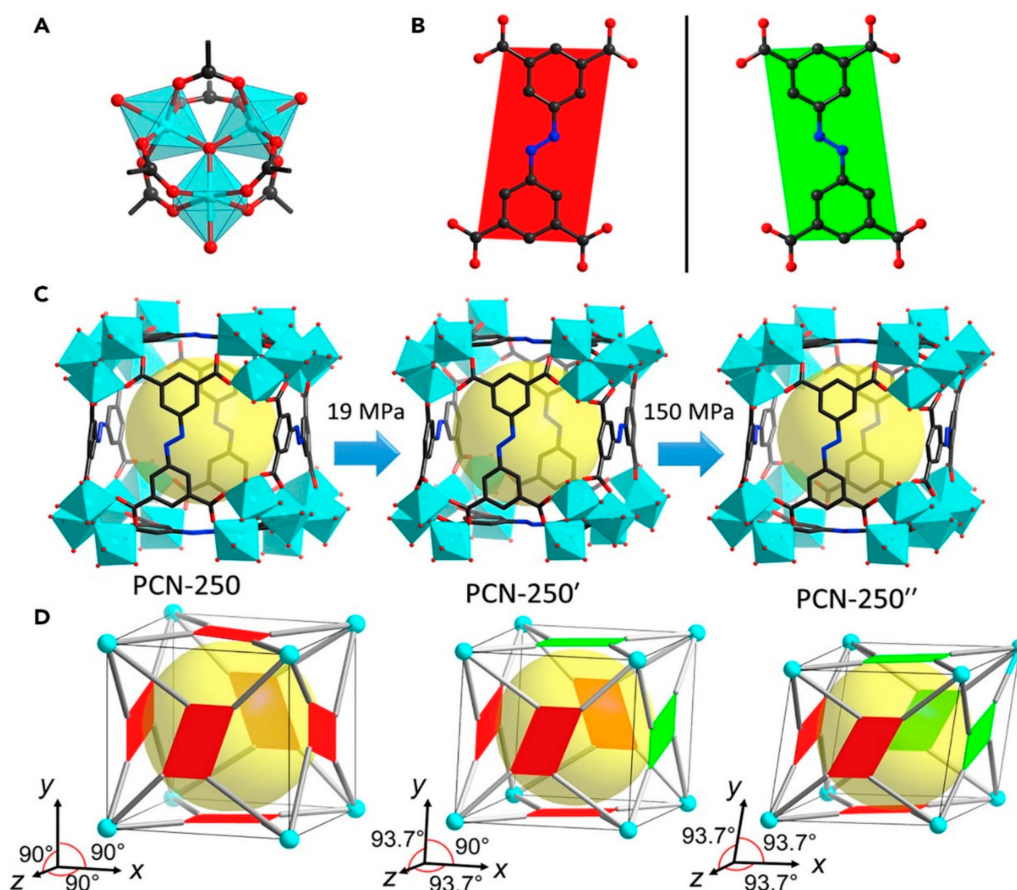

Figure 10. Shows the illustration of possible transformations that PCN-250 can undergo upon applying mechanical pressure such as the inclination of the unit cell and flipping of linkers, (**A**–**D**) Structure of (**A**) Fe_3-μ_3-oxo cluster; (**B**) ABTC linkers with different configurations; (**C**) comparison of the crystal structures of PCN-250, PCN-2500, and PCN-25000; (**D**) scheme representation of the structural transformation including the inclination of unit cell and flipping of linkers. [101].

2.4. Photo-Responsiveness

A number of proof-of-concept research studies support unique behavior upon interaction of MOFs with light, which provide the basis for identifying structure–function relationships of photo-switches phenomena. The photo-responsive frameworks classified into three main generations [104]. The first

generation contains MOFs with thermally or optically functional pendant groups to the overall framework. These groups acts as responsive soldiers within these frameworks, and they alter their conformation upon light exposure. Commonly, this kind of MOFs are synthesized using azobenzene and its derivatives due to their photochromic molecules that can undergo clean, efficient, and extrinsic reversible photoisomerization [105]. Stock and his group have pioneered this fact as they studied porous twofold interpenetrated MOF which contains an azo-functionality that protrudes into the pores. Exposure of this MOF to UV-light of a wavelength of 365 nm triggers the cis–trans transformation of the linker, while back switching has been noticed when irradiated with a wavelength of 440 nm (See Figure 11) [106].
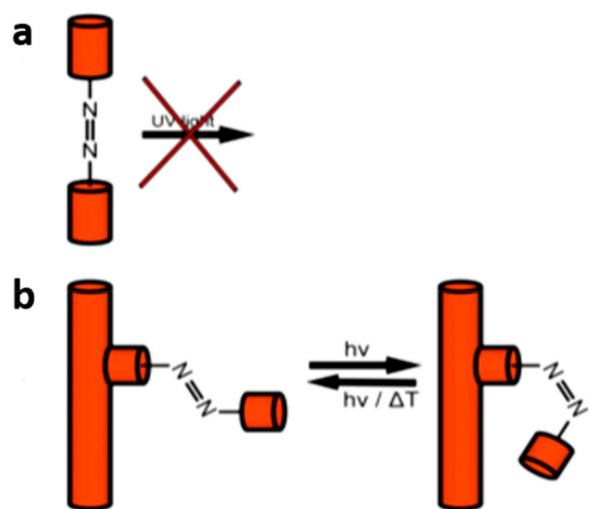
Figure 11. Photo-switchable azobenzene side groups. (**a**) Azo-linker as part of the backbone of the MOF, (**b**) azo-group covalently attached to the inner pore wall and extended into the pore [106].

It is evident that the cis–trans transition and guest's photo isomerization could lead to drastic changes in the gas adsorption properties. Most attention is usually paid to the MOFs with of azobenzene-functionalized linker. Brown and co-workers examined a photo-switched characteristic of azobenzene-functionalized linker hosted by IRMOF-74-III framework $[Mg_2(C_{26}H_{16}O_6N_2)]_n$. The authors observed a switching from the trans-conformer to the cis-conformer upon arousing this MOF with light. Furthermore, a distance increment between the para-carbon atoms in azobenzene molecule from 8.3 Å to 10.3 Å was also remarked [106]. In a more recent study, Park and his group examined the reversible alteration of CO_2 uptake upon light exposure or thermal treatment. It was observed that the reversible alteration of the azobenzene has a significant effect on the framework's capacity of CO_2 uptake. Particularly, when the azobenzene is in the cis form, the framework has a significantly lower CO_2 uptake in contrast to the material framework when the linker is in the trans-form [70]. This concept was studied by other research groups and further exploited with a different host framework, e.g., that some host frameworks forbid and block the cis–trans transformation as in case of azobenzene in MIL-53(Al) [107]. One drawback for this generation is that switching is strongly hindered due to the fact that the azo groups are an integral part of the linker molecules. Thus, this type has not been revealed to date.

In contrary to the first generation, the second generation includes MOFs which are synthesized by protruding azo groups into the pores of the linker, in another word the photo-responsive unit is directly incorporated to the "backbone" of the linker as a side chain. It was ascertained that the photo-switching properties of azobenzene side-chain fully retained its photoisomerization ability, with a change in pore dimensions upon light exposure [106,108–110].

In analogy to the preceding examples, Modrow and his group [108] introduced the azo functional group to the Cr-MIL-101-NH$_2$ mesoporous cages. Photo-responsive behavior of this MOF was tested

by CH_4 adsorption experiments (Figure 12). Upon interaction of the prepared MOFs with sporadic irradiation of UV-Vis light, a variation in the CH_4 sorption behavior was perceived, e.g., an increase of the cis-isomer concentration. The rise in the CH_4 adsorption capacity is attributed to the change of the polarity, dipole moment and free space for each conform [70,108].
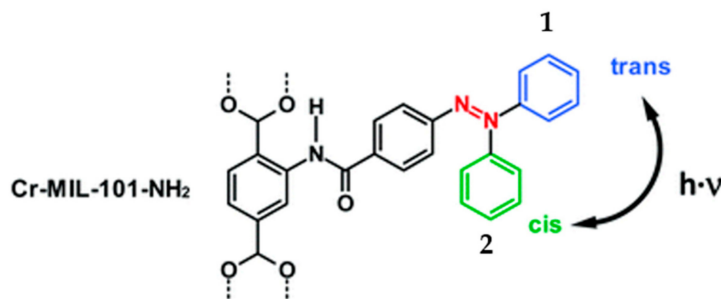
Figure 12. The product of Cr-MIL-101-NH$_2$ with p-phenylazobenzoylchloride (**1**) and 4-(phenylazo)phenylisocyanate (**2**). Blue amide and green urea [108].

The third generation includes frameworks that change themselves, upon exposure to light. This kind of dynamic photo-switching MOFs is difficult to synthesize, and it is considered as the most affected light-induced transformation. Lyndon and his group performed a very interesting study to employ MOFs with photo-switching behaviors in low-energy CO_2 capture and release. They conducted their study on a triple interpenetrated framework (Zn(AzDC)(4,4'-(BPE)0.5) using UV light. The results revealed that an immediate discharge of up to 64% of the adsorbed CO_2 using broadband radiation, similar to concentrated solar sources. Moreover, a fully reversible response has been noticed [105]. In summary, different modes of attachment lead to different photo-switching behavior.

This brief survey must suffice to introduce a pervasive phenomenon, which must often affect the structure of MOFs with flexible nature, and hence their responsive behaviors: this will be a recurring item in the application section.

3. How to Control MOFs Flexibility

Either modifying the organic linker or the metal ion can easily tune the structure of a MOF. Reactions such as Friedel–Craft acylation or Lewis acid catalyzed alkylation and reactions involving the amide formation and nucleophilic substitution, can be applied in order to introduce flexibility into the backbone of the MOF [111,112].

3.1. Ligand Control

Alternative techniques are adopted, when active species fail to be incorporated within a framework. Solvent assisted ligand incorporation (SALI), is a technique that allows the addition of new active species into zirconium based MOFs (Zr-MOF), through simple acid-base chemistry [113]. These catalytic functions are either added at the linker, or the Zr oxide node, or through pores encapsulation [114]. Deria and co-workers were able to successfully incorporate perfluoro alkane carboxylates of various chain lengths on the Zr$_6$ nodes of NU-1000 through the SALI technique. Catalytic functionality is introduced through the ionic bonding of the OH groups on the NU-1000 node and the carboxylate group of the perfluorinated chain (Figure 13) [115–117].
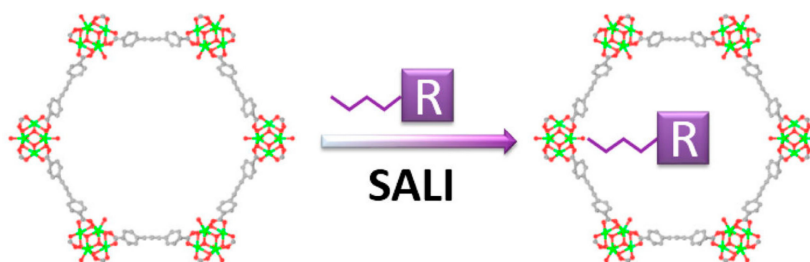
Figure 13. Solvent-assisted ligand incorporation onto Zr-nodes of NU-1000. Perfluoro alkane carboxylates were successfully incorporated on the Zr6 nodes of NU-1000 [114].

3.1.1. Linker Substitution

The choice of organic linker highly affects the flexibility behavior of the MOF. Adsorption properties, as well as network porosity and flexibility, will be highly influenced by the selected linker within a MOF structure.

The adsorption behavior of a series of isoreticular Cr (III) or Fe(III) dicarboxylates labeled MIL-88A–D was studied by Serre and co-worker [34]. The difference between the four MIL-88 is the choice of organic ligand which is as follows: dicarbox = fumarate (88A); terephthalate (1,4-BDC) (88B); 2,6-naphthalene dicarboxylate 2,6 NDC) (88C); and 4-4′-biphenyl dicarboxylate (4-4′-BPDC) (88D). Upon adsorption, the interaction between guest molecules and MIL-88 caused noticeable breathing motion for the MIL with the linker with the longest chain length. The longer the length of the linker, the higher the ratio of the cell volume of the open form to that of the dried solid (1.85 for MIL-88A to 3.3 for MIL-88D). Water stable isoreticular phosphonate-based Cu-MOFs, having both phosphonate and N-heterocyclic linkers, were first synthesized by Taddei and co-workers. The flexibility of this specific catalyst was studied by varying the choice of the linker. When *N*,*N*,*N*′,*N*′-tetrakis (phosphonomethyl) hexamethylenediamine (denoted as L) and 1,2-bis-(4-pyridyl)ethane (denoted as etbipy) were used as organic ligands for the construction of $Cu_3(L)(etbipy)_2$ framework, a reversible breathing effected was noticed. On the contrary, when replacing one of the mentioned linkers with a more rigid linker such as etbipy with 4,4′-bipyridyl, the breathing effect during dehydration was irreversible [118].

Vermoortele and coworkers studied the effect of linker substitution on a series of functionalized UiO-66 (Zr). They were able to prove, through molecular modeling calculations, that the activity of UIO-66 with coordinatively unsaturated sites was drastically increased when functionalized linkers were added to the framework. Therefore, when the nitro substitution was added, the activation free energy of the reaction was lowered due to low adsorption capacity [119].

3.1.2. Linker Rotation

A breathing MOF can be formed by applying the concept of linker rotation. In order to obtain a "gate" effect, allowing the pores to open and close freely, the linker must rotate between fixed positions (see Figure 14) [74,120].
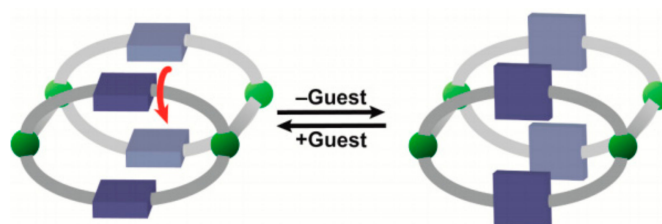
Figure 14. Ligands can rotate to open and close the pore, upon adsorption and desorption respectively. Green spheres represent metal centers or secondary building units (SBUs), gray represents rigid portions of the ligand, and blue components represent flexible portions of the ligand [74].

Functional groups that are added into the linker have a major effect on the rotational behavior of the ligand. The introduction of four CH_3 groups in the aromatic linker of MIL-53(Cr), causes the phenyl rings to rotate by 90°, preventing the adsorption of guest molecules [121,122]. The host–guest interaction of some gases and liquids during adsorption/desorption, tend to also control the flexibility of some MOFs [74]. In the case of MIL-53, the adsorption of carbon dioxide, water, and some hydrocarbons tend to control the size and the structure of the pores from large rectangular to narrow trapezoids [123].

In the case of MIL-88, the absence of any sort of linkage between its "equatorial" trimers, causes the framework to swell upon hydration, leading to the adsorption of large molecules. The free rotation of the COO groups around the single carbon–carbon bond causes this type of swelling in addition to the change in the dihedral angle between the COO plane and the trimers plane (Fe–Fe–Fe) [85].

3.1.3. Post-Synthetic Modification (PSM)

The steric hindrance of the functional groups that are incorporated within the MOF framework tends to reduce the flexibility of the ligands. Rigid phenyl rings or heterocycles are such an example. Incorporation of such groups can be predefined, either during synthesis or through post-synthetic modifications (PSM) [124]. The secondary building units (SBU) approach can also be used in order to incorporate some functional groups within the framework [34,125]. Monocarboxylic acids with different backbones were added to the framework of JLU-Liu4 (JLU—JiLin University) during synthesis. The inclusion of small carboxylic acids (formic acid and acetic acid) resulted in a gate opening behavior during adsorption. On the contrary, when bulkier carboxylates such as benzoic acid and cinnamic acid were added a different structural transformation was observed. For MOF containing benzoic acid, classical breathing behavior was attained, while a step-wise increase in the unit cell was observed for cinnamic acid MOF [126].

Horcajada and coworkers analyzed the flexibility of MIL-88 after a few ligand modifications through the introduction of functional groups onto the aromatic rings. Different flexibility behaviors were observed for iron (III) 4,40-biphenyl dicarboxylate and iron(III) terephthalate MIL-88, due to different steric and intermolecular interactions between the phenyl rings. The bigger the size of the functional group that was introduced, the smaller the breathing amplitude [35].

3.2. Metal Ion Modification

Since a MOF is a combination of organic linkers and metal nodes, the flexibility will depend on the type of metal node and how it is connected to the linker. For cobalt-based MOF, Co(BDP) (BDP = 1,4-benzene dipyrazolate), the framework adapts five structural transitions during the adsorption of nitrogen at 77 K [61,127]. Upon adsorption, a breathing effect is noticeable, and the geometry of the framework adopts a tetrahedral form, which is caused by the long 0.26 nm Co–N bond [127]. Even though Cr^{3+} and Fe^{3+} possess similar electronegativities and ionic radii, MIL-53(Fe) and MIL-53(Cr) show different behavior towards the sorption of CO_2. The interaction of guest molecules with MIL-53 upon adsorption is highly affected by the choice of the metal ion within the framework [127,128].

Greathouse and Allendorf studied the intramolecular interaction behavior of Zn ions and water oxygen atoms upon the adsorption of water on MOF-5. MOF-5 is composed of Zn_4O clusters bridged with BDP organic ligands; each Zn ion is coordinated by one inorganic O atom (O1) and three BDC O atoms (O2). Changes in Zn coordination with increasing water content were observed [129]. Molecular dynamics simulations show that there are three possible interaction routes between water and MOF-5. The first is a direct attack on the ZnO_4 tetrahedron, where a water oxygen atom replaces an O atom of the coordinating MOF. The second is a possible interaction between the water hydrogen atom and O_2, and the third interaction is the interaction of H atom to one or more ZnO_4 tetrahedra (Figure 15). Greathouse and Allendorf suggest a possible modification of the metal–linker interaction so that the framework can withstand stronger metal–water interaction.
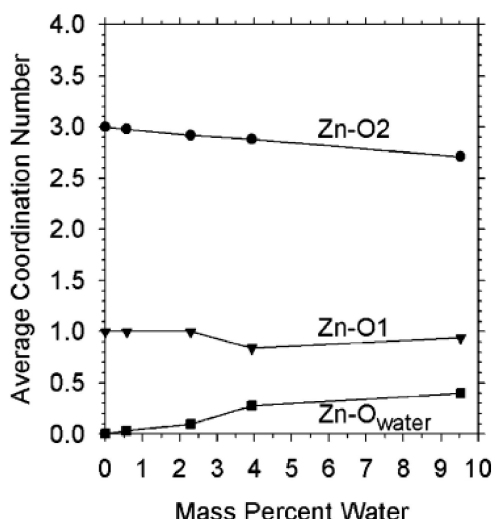
Figure 15. Zn coordination behavior upon water adsorption. Zn retains tetrahedral coordination, but the relative amounts of BDC oxygen (O2) and inorganic oxygen (O1) decrease as they are replaced by water oxygen atoms [129].

4. Characterization Techniques to Detect Flexibility

Understanding the dynamic and structural changes in flexible MOFs is key in order to be able to explain potential behavior and possible framework modification [52]. The mechanical properties of flexible porous MOFs can be studied through different methods such as mercury porosimetry. This method relies on the intrusion of mercury molecules within the pores at a specific pressure. The transition between LP to NP can be analyzed by applying mechanical pressure [59]. Other spectroscopy techniques that are used to study the flexibility behavior of MOFs are mentioned in this section.

4.1. Nuclear Magnetic Resonance (NMR)

The detection of flexibility through NMR allows monitoring of the structural changes of the host during adsorption. For instance, [129]Xe NMR spectroscopy relies on the adsorption of xenon gas to study the Xe chemical shift as an indicator of the extended transition from LP to NP. Springuel-Huet et al. were able to perform in-situ [129]Xe adsorption NMR experiments on the flexible MIL-53(Al) material at different pressures and temperatures [130]. They based their findings on the chemical shift of Xe to study the local Xe amount and the transformation from LP to NP form.

The transformation of an anisotropic framework was studied by Murdock and coworkers using a ^{13}C cross polarization magic-angle-spinning (CP-MAS) NMR. They were able to directly monitor phenyl rotation as a function of solvation [74,131]. Results show that this spectroscopic method is a powerful tool to monitor the breathing effect in MOFs.

^{2}H NMR spectroscopy can also be used to characterize the dynamic behavior of many catalysts, like porous coordination polymers (PCPs). Horike et al. synthesized a new class of PCPs with rotational organic groups and regulated their dynamic motion by guest sorption [132]. ^{2}H NMR spectra were recorded for the same sample at different temperatures in order to demonstrate the change in the topology of the framework with temperature as well.

4.2. Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction (PXRD) is another powerful analytical technique that can be used to determine structural transformation in flexible MOFs [60]. The freedom of motion of polar linker groups in the framework of IRMOF-2 was investigated by Winston et al. The framework of IRMOF consists of octahedrally coordinated zinc oxide clusters linked by the bromoterephthalate group.

These groups contain a rotatable bromo-p-phenylene moiety [133]. The XRD for IRMOF-2 yielded good agreement with the published data for the atomic positions showing eight-fold disorder of the bromine.

Devic and co-workers used a combination of techniques in order to evaluate the effect of the functional group X (X = –Cl, Br, CH_3, NH_2, $(CO_2H)_2$), of a series of functionalized flexible MIL-53(Fe)–X during adsorption of CO_2. Different diffraction patterns were obtained, indicating the effect of the functional group on the pore opening during adsorption from NP to LP [134]. An example is given in Figure 16, showing the difference between spectra of MIL-53(Fe) with and without a functional group.
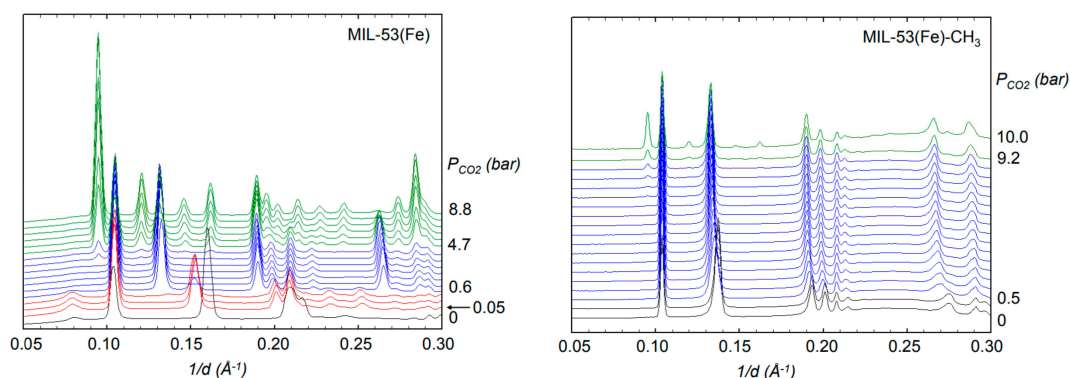
Figure 16. CO_2 adsorption on MIL-53(Fe) –X (X = –CH_3) at 230 K followed by PXRD. Spectra were recorded at different pressures. Black: anhydrous closed pores form; red: intermediate form; blue: NP form and green: LP form [134].

4.3. Infrared Spectroscopy (IR)

Infrared spectroscopy is a vibrational method often used to determine the chemical and structural changes of the host framework caused by the interaction of the skeleton with the guest molecule. Salles and coworkers, relied on IR spectroscopy to study the pyrazolate ring stretch vibrations in Co(BDP), during N_2 adsorption at 100 K. As the pressure is increased, the C–N stretching vibrations of the pyrazolate rings undergo different transition states. In situ infrared spectra were recorded to show the transition from NP to intermediate phase ip1 and ip2 (at 0.01 and 0.023 bar, respectively), see Figure 17 [127].
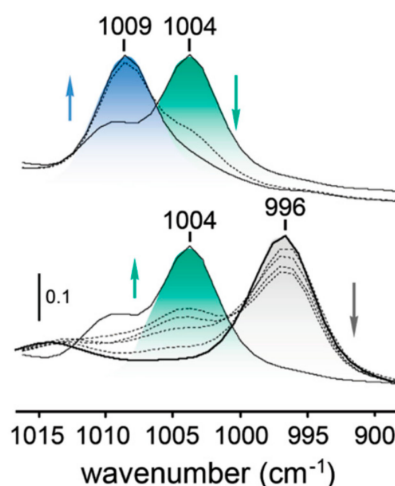

Figure 17. In situ infrared spectra of Co(BDP), during N_2 adsorption at 100 K. Phase transitions from the dry form (gray) to ip1 (green) and ip2 (blue). Reprinted [127].

4.4. Raman Spectroscopy

The structural flexibility of a MOF plays an important role in the separation of CO_2 and CH_4. Hamon et al., studied the effect of flexibility of MIL-53(Cr) on the breakthrough curves, during the adsorption of a mixture of CO_2 and CH_4 [135]. They examined the NP/LP fraction through Raman spectroscopy, by varying the ratio of CO_2 to CH_4. As the concentration of CO_2 increases, the narrow pores open up and CH_4 molecules are pushed out of the NP to accommodate CO_2 molecules.

Figure 18 shows the consistency of integrated Raman band intensities of adsorbed CO_2 and CH_4 molecules with the adsorption isotherms. These results show that Raman spectroscopy is a useful technique to track the concentration of the adsorbed species in situ.
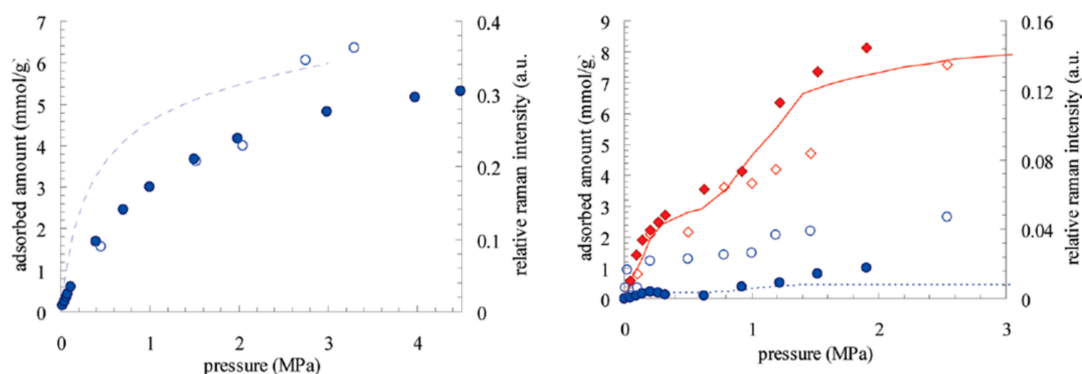
Figure 18. Adsorption isotherms of CO_2 (♦) and CH_4 (●) on MIL-53(Cr) at 303 K compared to the relative Raman intensity of CO_2 (◊) and CH_4 (○). Gas composition CO_2:CH_4, left: 0–100 and right: 50–50. The simulation of CO_2 is represented in full line and in dashed for CH_4 [135].

5. Application

There is already a very considerable literature on the synthesis and application of rigid MOFs, and no doubt, its growth is set to continue. However, interest has been shown during the last years in the remarkable properties of the third generation MOFs such as flexibility, large surface area, and high porosity, giving those properties particular attention in numerous applications, especially in the area of storage and separation, sensing, and guest capture processes.

The value of good theoretical studies or explanation of the flexibility of MOFs lies in its ability to correlate a wide range of observed phenomena through useful applications, such as selective gas separation [136–138], molecular recognition [139], catalytic process [140], sensing [141], and biomedical application (i.e., controlled drug release) [142]. Each application has its own set of requirements when it comes to choosing the correct type of MOF, depending on the intended use; this section will focus on what is desired for the efficient application of flexible MOFs. BASF is the only chief company known to be working towards the industrial-scale synthesis of MOFs [143,144], they offered six MOFs only two with flexible nature, namely ZIF-8 and MIL-53(Al) (corresponding to Basolites A100 and Basolites Z1200 respectively). A general industrial application for different flexible MOFs is still awaited.

5.1. Catalytic Application

Given the importance of MOFs during the past two decades, it is surprising that so little research has been devoted to the industrialization of flexible MOFs in catalytic reactions. The researchers and licensors are concerned with the industrial application of flexible MOFs to the particular problems that led to the development of those catalysts. This neglect is perhaps explained by observing that flexible MOFs are not stable under different operating conditions and different reactions.

Das and coworkers [140] pioneered the utilization of the pores of a flexible MOF as a catalyst to monitor the cyanosilylation and Knoevenagel reaction. During the reaction changes in the space and shape of the voids were detected. Those changes were induced by the introduction of guest molecules

inside the cavity. The dynamic change of the pore space triggered the interest in intense research in investigating other chemical and biological reactions inside the pores of flexible MOFs. Since flexible MOFs are still only of limited interest as catalysts for several reactions, a more expectant statement cannot be determined, because the breadth of these studies is still not extensive.

5.2. Separation

By choosing the appropriate physical form of the framework, MOFs can be used in various types of selective gas separation applications. The framework is considered a vital element in determining remarkable separation. Stavitski and coworkers investigated the separation of CO_2 from a mixture of gases through NH_2-MIL-53(Al) [145]. Figure 19 shows the structures and relative energies of NH_2-MIL-53 materials and their complexes with CO_2. The confinement of the CO_2 molecule within the NP and LP NH_2-MIL-53(Al) structures is also given. The outstanding high efficiency in capturing CO_2 molecules is attributed to the flexibility of the framework and its capacity to modify the structure upon gas adsorption.
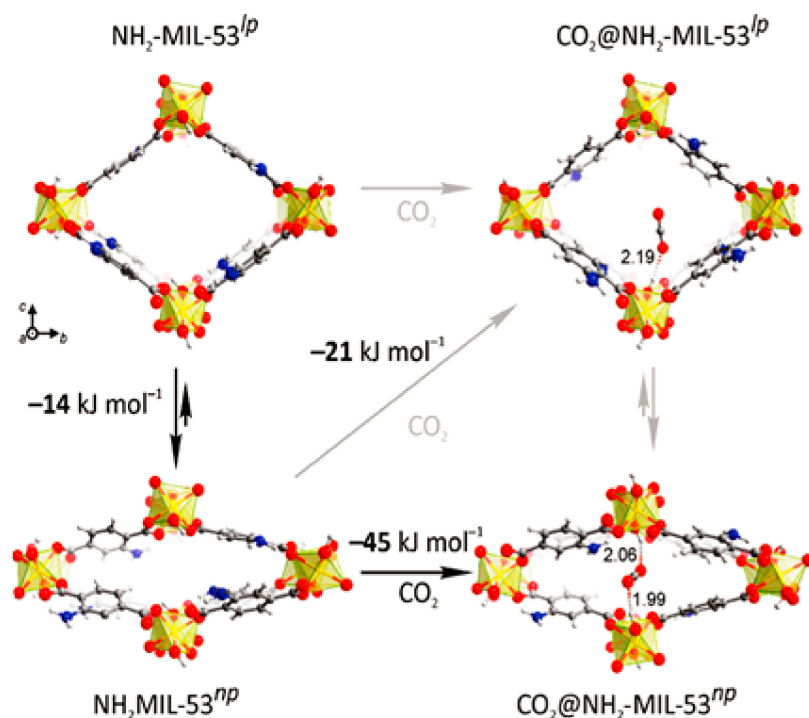

Figure 19. Structures and relative energies of NH_2-MIL-53 materials and their complexes with CO_2 [145].

Pressure swing separation is an essential application for flexible MOFs [145].

Kim and coworkers [138] investigated the textural properties of NH_2 MIL-53(Al) upon CO_2/N_2 separation. This MOF shows high selectivity towards CO_2 adsorption and remarkable structural flexibility during six cycles of pressure swing adsorption–desorption. In this respect, it is worth mentioning that the adsorption isotherms of flexible MOF follow different isotherms. Therefore, their behavior cannot be classified according to the IUPAC scheme because such MOFs can undergo structural changes during adsorption [146].

Li and coworkers [147] also studied the challenging separation of a mixture with similar molecular size "propyne/propylene" over rigid–flexible MOF. This type of MOF is of particular interest with regards to its unique properties since it can function at the low-pressure range as well as high-pressure range, where it transforms into a flexible MOF. In their study, ELM-12 was studied as it has a rigid square-grid copper bipyridine scaffold with dynamic dangling OTf^- (OTf^- = trifluoromethanesulfonate) groups. It was noticed that the strong binding affinity of ELM-12 towards C_3H_4 increased with

increasing pressure, contrary to ELM-12 adsorption capacity towards C_3H_6. Therefore this type of MOF could be applied to separate different types of gas mixtures with similar molecular size. Their results expanded the dictionary of application of third generation porous MOFs for combined separation/purification applications. Much attention has been given to investigate the ability of flexible MOF in liquid phase separation due to their capability of fine control guest uptake compared to conventional inorganic structures. For example, flexible porous MIL-53(Fe) was used as a stationary phase during the application of HPLC, to separate xylene isomers from mixtures of BTEX (benzene, toluene, ethylbenzene, and the three xylene isomers) [148]. Figure 20 shows that the xylene isomers are well separated.
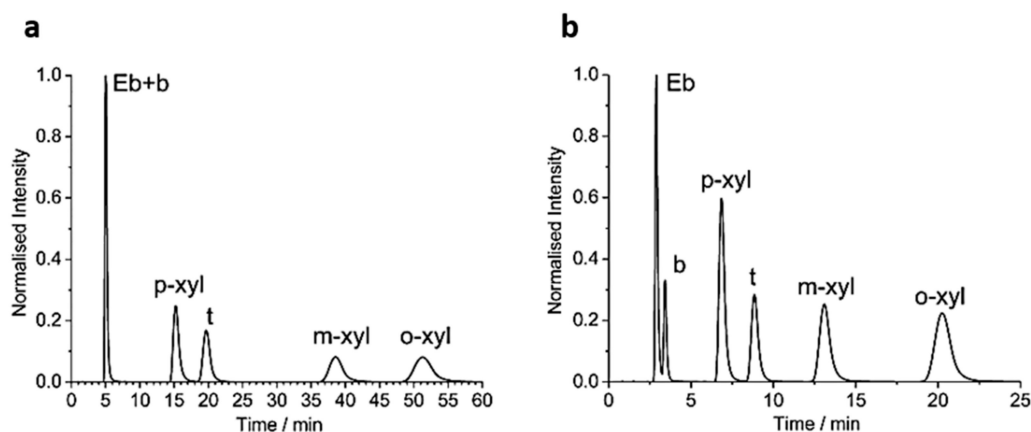

Figure 20. Chromatograms of the BTEX (benzene, toluene, ethylbenzene, and the three xylene isomers) on MIL-53(Fe) at 293 K (**a**) and 323 K (**b**) [149].

5.3. Guest Capture

For fundamental studies, there is much to be said about using flexible MOFs in controllable capture and release, particularly in gas capturing via host−guest interactions or the pore structure state. This intriguing aspect deserves investigating due to its importance in some applications such as drug delivery application.

A seminal work based on the controllable gas capturing and releasing was reported by Matranga and co-workers [149]. They investigated 3D and 1D porous coordination polymers (PCP), with different degrees of flexibility and similar gate opening pressure response towards CO_2. Their results revealed a change in the pore structure of both PCPs upon gas sorption, regulated domain growth, and ligand reorientation accordingly. In a more precise description, the length of the linker spacing and consequent size of the void spaces changes in a controlled manner.

In an exciting study to investigate the metal-ion-capture properties, Thallapally and co-workers [48] studied the potential of the trinuclear cluster with a flexible ligand MOF [Mn_3 (L)$_2$]$^{-2}$·2[NH_2 (CH$_3$)$_2$]. 9DMF to capture harmful divalent transition-metal cations. This MOF sequesters itself by deformation of its trinuclear cluster and the coordination of additional metal ions such as Cu^{2+}, and Ni^{2+}. The results revealed that the MOF displayed a high capture selectivity initiating from the coordination interaction of targeted ions and the framework via cooperative breakage/formation of a metal−carboxylate, see Figure 21.
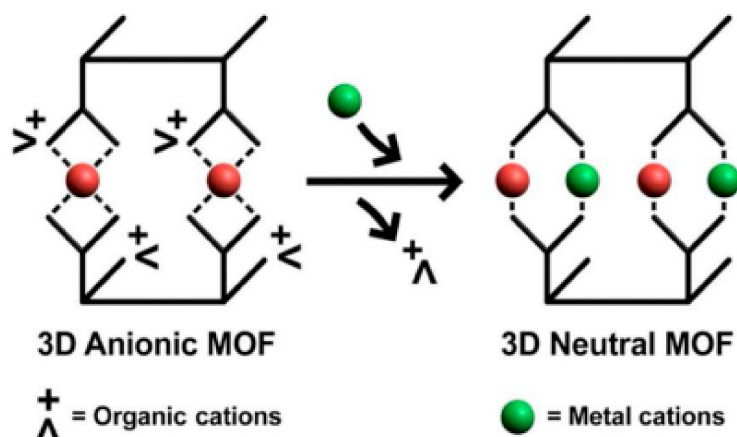
Figure 21. Scheme showing the incorporation of transition metal (TM^{2+}) cations into the anionic networks to afford neutral and heterobimetallic systems via ligand directing single-crystal-to-single-crystal structural rearrangement [48].

5.4. Sensing

Flexible MOFs with a reversible structural flexibility accompanied with (i) distinct color-changing and/or (ii) crystal size deformation or change the framework structures from closed to open forms upon thermal stimuli or gas uptake demonstrated their ability in the smart sensing application. Such composites would selectively adsorb gases for which interactions with the composites were strong enough to change the framework structures. This has been the subject of some recent research. Yanai and his group investigated the role of host–guest interactions of the fluorescent guest molecules and flexible structure and their effect on sensing mechanism. Their study tested the selective detection of CO_2 and C_2H_2 over DSB@[Zn_2(BDC)$_2$dabco]$_n$ (DSB—distyrylbenzene). This MOF showed different fluorescence responses towards CO_2 and C_2H_2 [150]. It is now possible to dive deeper into the versatile sensing and switching fluorescent MOFs. For example, Dong and his group adopting the concepts of this material to study the potential and behavior of a new type of flexible emissive silver-chalcogenolate cluster-based MOF (SCC-MOF) for the adsorption of the volatile organic compound "VOCs." This MOF showed unparalleled distinctly different visible luminescence colors upon chloromethanes adsorption (CH_2Cl_2, $CHCl_3$, CCl_4) [151]. In summary, the general desire to engage flexible MOFs that have detectable relevance to industrial applications, triggers scientists to invest in academic laboratories in order to remove the barriers towards large-scale applications.

6. Conclusions

The purpose of this review is to try to construct a map to guide the reader through the literature on the types, nature, control, and characterization of flexible MOFs. In order to evolve some general principles, this review delineated the main features and outlined the strategy to be adopted in their design in order to find the desired route for any application. Many excellent reviews and books shed light on the advances in both theoretical thinking and skillful experimental on the rigid MOFs. However, theoretical and experimental studies that deal with flexible MOFs are lacking, and any attempt to rationalize the changes in their structure through the external stimuli to the industrial application is still missing. In this review, a short but informative account of the literature on flexible MOFs has been investigated and guidance provided to the reader to see wherein the complications lie in their design and accordingly their responsive behavior. In conclusion, smart manipulation of metal–ligand coordination along with their general responsive stimuli can lead to outstanding third generation porous material that covers a wide variety of applications.

Abbreviations

ABTC	Azobenzenetetra carboxylate
BDC	Benzene dicarboxylate
BDP	1,4-benzene dipyrazolate
BHE-bpb	2,5-bis(2-hydroxyethoxy)-1,4-bis(4-pyridyl)benzene
bmb	1,4-bis(2-methylbenzimidazol-1-ylmethyl) benzene
BPE	Bis-pyridyl ethylene
BTC	Benzene tricarboxylate
CP	Closed Pores
SCC	Chalcogenolate cluster
FL-MOFs	Flexible ligand metal organic framework
H3L	5-(2-carboxybenzyloxy)
HKUST-1	Hong Kong University of Science and Technology
IBU	Inorganic building unit
IR	Infrared spectroscopy
JLU-Liu4	JiLin University
L	Linker
LP	Large Pores
M	Metal
MIL	Materials of Institute Lavoisier
MTV	multivariable
NMR	Nuclear Magnetic Resonance
NP	Narrow pores
PCP	Porous coordination polymers
PDC	Pyridine dicarboxylic acid
PSM	Post-synthetic modifications
PXRD	Powder X-ray diffraction
Pz	pyrazolate
Pzdc	2,3-pyrazinedicarboxylate
SALI	Solvent assisted ligand incorporation
SBBs	Supramolecular building blocks
SBUs	Secondary building units
TM	Transition metal
VOC	Volatile Organic Compound
ZIF	Zeolitic Imidazolate Framework
ZIF-8	$[Zn(mIm)_2]n$ (mIm, also Im) = 2-methylimidazole

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