21

Dynamic Frameworks

21.1 Introduction

Reticular chemistry is concerned with linking molecular building units through strong bonds into well-defined extended structures such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) [1]. The resulting materials are known to be architecturally stable and to sustain permanent porosity. This is generally attributed to the strong directional bonding making up the backbone of these materials. The large accessible internal voids within the structures of MOFs and COFs further endow them with the seemingly contradictory prospect of large amplitude motion of their constituents in the solid state, an aspect rarely achieved in conventional extended structures. To understand this, it is instructive to consider what criteria need to be met to create extended solids capable of motion of their constituents without collapse or deterioration of the overall structure. Two general points need to be considered: (i) the constituents must be able to move about without interfering with each other which makes the use of open porous frameworks a necessary requirement, and (ii) specific weak points must be introduced in the structure to control where the motion is to take place. Both aspects can be addressed in reticular chemistry. The construction from molecular building units affords porous reticular frameworks with pre-determined composition and ensures the prospect of distinctly different kind of bonds within one single framework. Different strategies can be applied to target MOFs/COFs capable of large amplitude motion in the solid state and they can be categorized based on the prevalent modes of framework dynamics. In general, we distinguish four distinct cases: (i) Synchronized global dynamics where two or more discrete configurations of the framework backbone exist and can be interconverted by an external stimulus such as gas pressure or temperature. (ii) Synchronized local dynamics where the backbone remains unaffected but a synchronized motion of functionality appended to the backbone can be triggered by an external stimulus. (iii) Independent local dynamics where the backbone of the framework is held together by mechanical rather than chemical bonds thus allowing for motion of the framework constituents without the need for making or breaking of covalent bonds and no need for an external stimulus, and (iv) independent local dynamics where mechanically entangled species are appended to the backbone

Introduction to Reticular Chemistry: Metal-Organic Frameworks and Covalent Organic Frameworks,
First Edition. Omar M. Yaghi, Markus J. Kalmutzki, and Christian S. Diercks.

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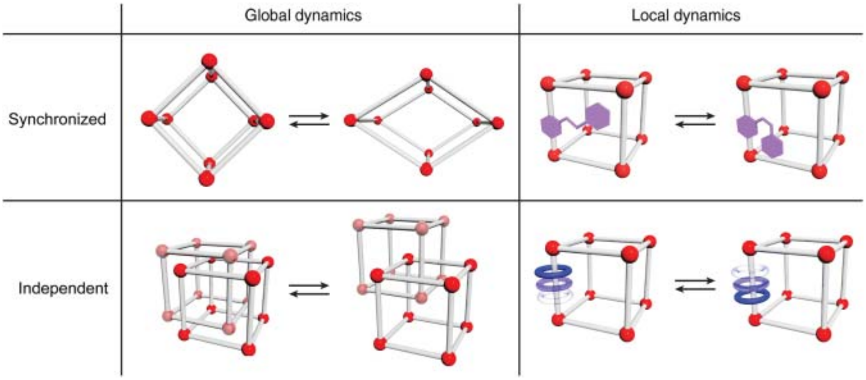

Figure 21.1 Representative modes of dynamics in extended framework structures. The dynamics can be either global and affect the entire backbone of the framework or local and independent of the framework backbone. Additionally, we distinguish synchronized dynamics, where distinct states are accessed that are structurally well-defined from independent motion in frameworks where the motion is not synchronized throughout the entire framework. Global synchronized dynamics are found in so-called "breathing" MOFs. Local dynamics are found in frameworks with molecular switches appended to their backbone. Global independent dynamics are found in interpenetrated or woven frameworks where the mechanically entangled substituents show large degrees of freedom of motion without the need for making or breaking of bonds. Similarly, local independent dynamics are found in frameworks with mechanically entangled rings appended to their backbone.

and move without affecting it (Figure 21.1). In this chapter we conceptualize the different modes of dynamics in extended framework structures and highlight their respective underlying design principles.

21.2 Flexibility in Synchronized Dynamics

In "flexible" MOFs and COFs the framework gets flexed meaning that a force is exerted on the material to bring about the structural change. On a molecular level this translates into making and breaking of bonds or distortions in bond lengths and angles. In this context the motion of the framework can be global when the entire backbone of the framework is dynamic, or local when the motion is independent of the backbone. Global flexibility in MOFs is found in "breathing MOFs" which, when triggered by an external stimulus, show substantial changes in their internal void space. Local flexibility can be achieved by decorating the backbone of a framework with molecular switches that can accommodate two (or more) distinct conformations without affecting the integrity of the framework. In both cases the dynamic motion of the constituents is ordered and gets triggered by an external stimulus which supplies the necessary energy for the structural change to occur.

21.2.1 Synchronized Global Dynamics

It was found that certain MOFs undergo reversible structural phase transitions in response to external stimuli (e.g. guest inclusion, heat, gas pressure, etc.), often accompanied by drastic changes in pore volume resulting from the expansion or contraction. In general, such materials cooperatively switch between two or more distinct states with full retention of long-range order, a phenomenon commonly referred to as "breathing." The resulting large amplitude structural motion is in stark contrast to what is observed in traditional crystalline solids, where such motion would result in structure collapse. The crystallographically well-defined transitions of breathing frameworks not only allow for the unambiguous elucidation of the individual states but furthermore provide a handle for the identification of the inherent structural features that endow these otherwise rigid frameworks with flexibility. Upon exposure to external stimuli flexible frameworks distort at their weakest points, and in this regard several structural components feature prominently: (i) MOFs comprising rod secondary building units (SBUs) and square-shaped 1D pore systems, (ii) discrete SBUs with flexible coordination geometry around the metal centers, and (iii) MOFs comprising inherently flexible linkers [2].

21.2.1.1 Breathing in MOFs Built from Rod SBUs

The first example of a MOF exhibiting large amplitude structural flexibility was MIL-53, a framework of general composition ($M^{3+}(OH)(BDC)$, where M = Al, Fe, Cr, Sc, Ga) [3]. In the crystal structure, one-dimensional rod SBUs are linked by BDC linkers to afford a three-dimensional **sra** topology extended structure featuring square shaped 1D channels along the crystallographic *c*-axis (Figure 21.2). Upon exposure to external stimuli of different nature, three distinct phases of (Cr)MIL-53 are observed; as-synthesized (*as*), narrow pore (*np*), and wide pore (*wp*). In (Cr)MIL-53-*as* ($V = 1440\ \text{A}^3$) the channels are occupied by disordered H_2BDC molecules. Upon heating to 573 K these unbound moieties are removed resulting in (Cr)MIL-53-*wp* ($V = 1486\ \text{A}^3$) and subsequent cooling in air leads to (Cr)MIL-53-*np* with significantly decreased pore volume ($V = 1012\ \text{A}^3$). In these fully reversible phase transitions, both, the inorganic SBU, as well as the entirely sp^2 hybridized linker remain unchanged. Consequently, the origin of flexibility must be due to the junction between these two constituents. Indeed, crystallographic data corroborates that the weak point in the structure is in fact the coordination geometry around the octahedral Cr^{3+} ions. This manifests itself in rotation of the linker around the carboxylate O–O axis during the phase transitions, resulting in the corresponding dihedral angles between the O–Cr–Cr–O and the O–C–O planes of 177.51° for (Cr)MIL-53-*as*, 180.1° for (Cr)MIL-53-*wp*, and 139.1° for (Cr)MIL-53-*np*, respectively. More generally it is observed that in the absence of guests and at low temperature the framework has narrow pores and in the presence of guest molecules or at high temperature the pore opens up to yield (Cr)MIL-53-*wp* (Figure 21.2) [4]. It must be noted that in this case, the presence of square-shaped tetragonal pores is crucial in that it allows for the linker to rotate around all SBUs in a synchronized manner. During the framework distortion the carboxylate binding groups rotate around the O–O axis in a "knee cap" like motion.

The importance of this finding is illustrated by comparison to MIL-68 ($M^{3+}(BDC)(OH)$, where M = V, Fe, Al, In), a MOF of the same chemical composition and with the same SBU as MIL-53, but of different structure type.

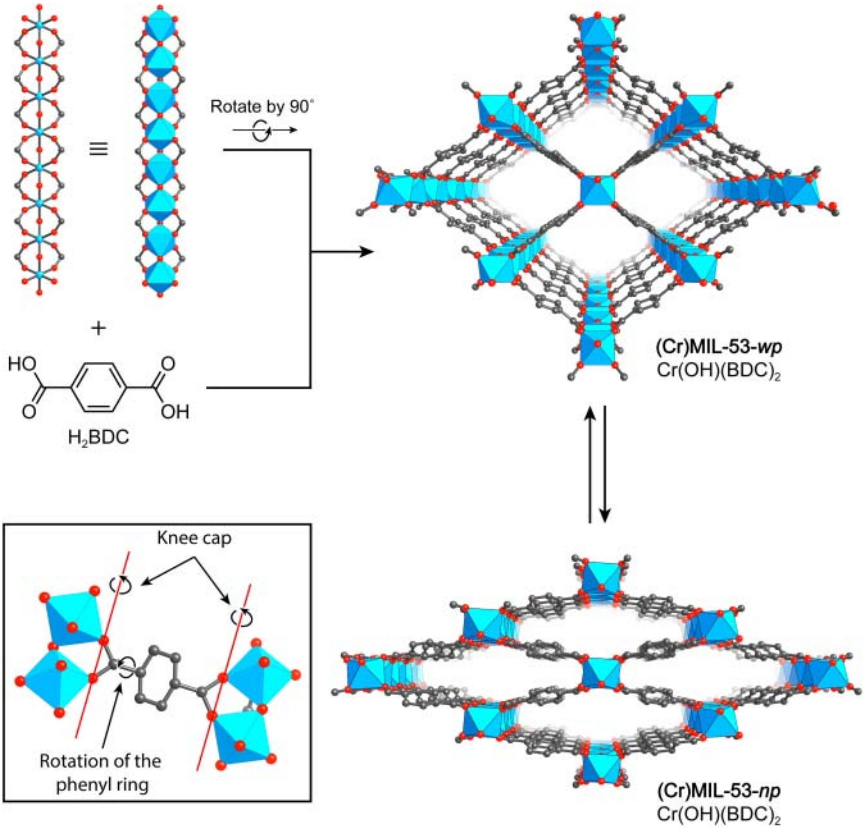

Figure 21.2 Breathing behavior of (Cr)MIL-53, constructed from linear rod SBUs and BDC linkers. In the presence of guests and at elevated temperatures the framework features wide trapezoidal channels along the crystallographic *c*-axis. Upon cooling to room temperature and/or removal of guest molecules the framework distorts by rotation around the carboxylate O–O axis in a "knee cap" fashion assisted by rotation of the central phenyl ring of the BDC linker, thus resulting in narrow trapezoidal pores. The framework distortion is fully reversible. All hydrogen atoms are omitted for clarity. Color code: Cr, blue; C, gray; O, red.

In contrast to the square-shaped pores of MIL-53, MIL-68 has a **rad** net with parallel hexagonal and triangular channels running along the crystallographic *c*-axis. As a result, synchronized rotation of the linker around the SBUs is prohibited and consequentially MIL-68 does not display a breathing behavior [5].

21.2.1.2 Breathing in MOFs Built from Discrete SBUs

Discrete SBUs can also lead to flexible frameworks. The fact that the inorganic SBUs are 0D not 1D enables a higher degree of flexibility, the main source of which still comes from the rotation of chelating linkers around the metal centers. However, in contrast to 1D rod SBUs the expansion/contraction motion in the case of discrete SBUs is not necessarily restricted to two dimensions.

Intuitively flexible structures expand upon inclusion and contract when the guest is expelled. Contrarily, the opposite is observed in the breathing behavior

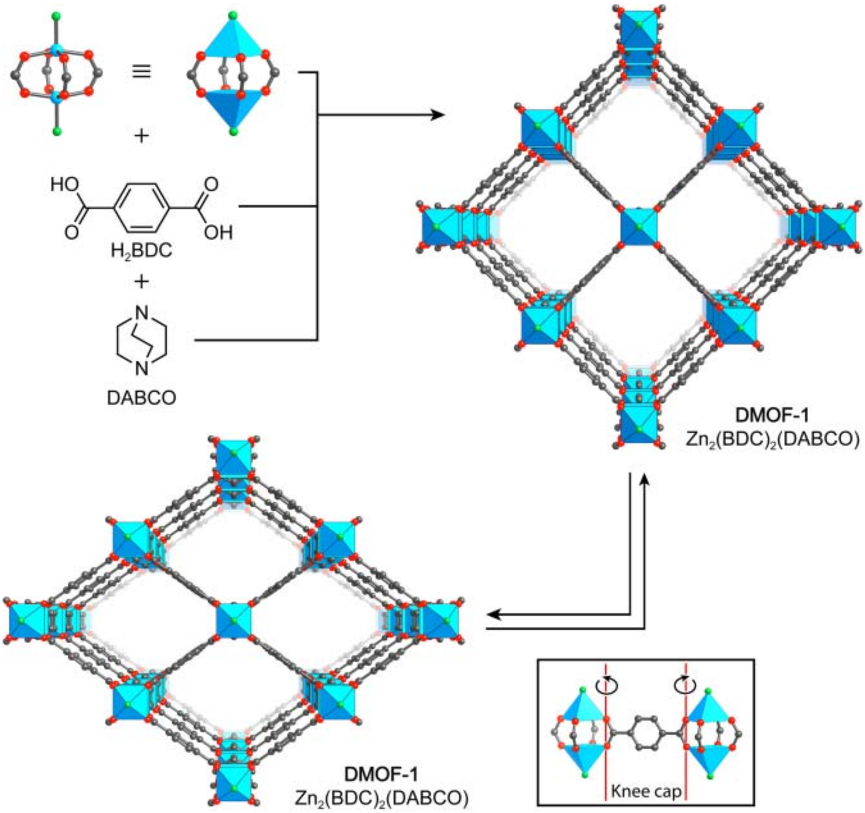

Figure 21.3 DMOF-1 is constructed from copper paddle wheel SBUs that are connected by BDC linkers to yield $Zn_2(BDC)_2$ square grid layers. These layers are pillared by DABCO molecules to yield a framework with underlying **pcu** topology. The empty framework features wide tetragonal channels along the crystallographic *c*-axis. Upon inclusion of benzene molecules, the pore aperture adopts a narrow trapezoidal shape. The weak point in the structure is the carboxylate metal coordination which can rotate along the carboxylate O—O bond. All hydrogen atoms are omitted for clarity. Color code: Zn, blue; C, gray; N, green; O, red.

of DMOF-1 ($Zn_2(BDC)_2(DABCO)\cdot 4DMF$, where DABCO = 1,4-diazabicyclo [2.2.2]octane). DMOF-1 is composed of dinuclear paddle wheel SBUs, which are bridged by linear ditopic BDC linkers to form distorted 2D square-grid ($Zn_2(BDC)_2$) layers (Figure 21.3). The axial sites of the paddle wheels are occupied by DABCO pillars to extend the 2D layers into a 3D framework of **pcu** topology. The evacuated open framework with tetragonal square-shaped channels shrinks upon inclusion of benzene into a trapezoidal conformation. Again, the weak point of the structure is the coordination environment around the inorganic SBU. A decrease in volume accompanies this distortion (1147.6 to 1114.2 $Å^3$) with the thermodynamic driving force being favorable host–guest interactions [6].

Reticulation of iron acetate with H_2NDC (naphthalene-2,6-dicarboxylic acid) yields (Fe)MIL-88(C) ($Fe_3(O)(OH)(H_2O)_2(NDC)_3$) of **asc** topology (Figure 21.4).

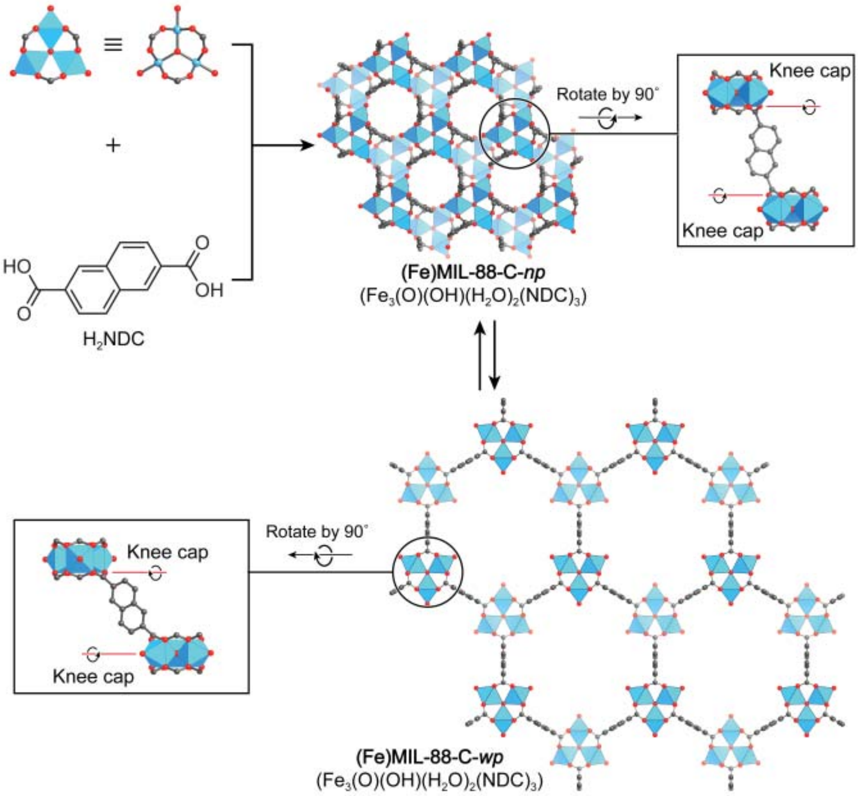

Figure 21.4 Flexibility in the 3D **acs** topology framework (Fe)MIL-88(C) constructed from linear ditopic BDC linkers and discrete Fe$_3$(O)(OH)(H$_2$O)$_2$ SBUs. Distortion of the O–O axes of the carboxylates coordinated to the SBU by 30° in a "knee cap" kind of fashion due to favorable interactions with DMF translates into an increased SBU–SBU distance and a concomitant increase in the unit cell volume of 230%. All hydrogen atoms are omitted for clarity. Color code: Zn, blue; C, gray; N, green; O, red.

The framework shows a breathing behavior with a difference in unit cell volume between the *np* and the *wp* form of up to 230%. This is remarkable, especially when compared to MOFs based on rod SBUs which display only up to 40% difference in unit cell volume between their respective *np* and *wp* phases. In the case of (Fe)MIL-88(C) the closed form minimizes lattice energy and exists in the absence of guests. To accommodate guest inclusion, the carboxylates coordinated to the trimeric metal SBUs can rotate around the O–O axis by up to 30°, thus extending the SBU–SBU distance which in turn leads to an expansion in all three lattice dimensions in a manner akin to swelling. Selective adsorption toward guests of different chemical nature is observed. Specifically, (Fe)MIL-88(C) expands from a unit cell volume of 2120 Å^3 in the dry *np* state to 5695 Å^3 upon exposure to DMF in the *wp* state. In contrast, in the presence of water, methanol, and lutidine, the unit cell remains largely unaltered (2270 Å^3) [7].

21.2.1.3 Flexibility Through Distorted Organic Linkers

Rigidity of organic linkers is considered a necessary requirement for the construction of architecturally stable frameworks. In rare cases, bending of these presumably inflexible units can however be induced by external stimuli to provide for flexibility, as illustrated by DUT-49 (Cu_2(BBCDC), where BBCDC = 9*H*-carbazole-3,6-dicarboxylate) [8]. DUT-49 is constructed from copper paddle wheel SBUs and tetratopic H_4BBCDC linkers. In the structure, the paddle wheel SBUs are connected by carbazole-3,6-dicarboxylate moieties to form cuboctahedral MOPs (see Chapter 21) [9]. These 12-c tertiary building units (TBUs) are connected by linear biphenyl links to yield a framework of overall **fcu** topology (Figure 21.5). The framework has a hierarchical pore structure with three distinct kinds of pore: 12 Å large cuboctahedral cages, 18 Å large tetrahedral cages, and 26 Å large octahedral cages [8]. In stark contrast to commonly observed gas adsorption behavior of microporous solids, which display an increase of gas uptake with increasing external gas pressure, DUT-49 exhibits an unusual negative gas adsorption isotherm [10]. Spontaneous desorption of gas is observed (10 and 30 kPa for methane and *n*-butane, respectively) upon increasing the gas pressure. Careful examination of single crystal X-ray diffraction data reveals that the framework undergoes a dramatic contraction (61% decrease in pore volume) caused by rotation of the TBUs induced by a severe distortion of the linker backbone (Figure 21.5). Theoretical calculations suggest that the high level of strain on the organic molecule can be compensated for by the energy benefits provided by greater methane affinity of the contracted/smaller pores. Such framework deformation results in decreased porosity and release of previously adsorbed gas [11].

The aforementioned three modes of flexibility only represent the most common scenarios reported for breathing MOFs. In these cases, the entire framework undergoes synchronized phase transitions induced by external stimuli. The weak points in the structure can either be the coordination junction between chelating linkers and SBUs or the organic linkers themselves.

21.2.2 Synchronized Local Dynamics

In breathing MOFs the backbone of the framework is distorted significantly upon framework expansion/contraction. Over time this can lead to structure deterioration. To circumvent the need for the frameworks' backbone to distort, molecular photoswitches (i.e. organic molecules which change their conformation or structure upon interaction with light) are implemented into MOFs by appending them to the organic linkers. In this way the pore size, shape, and hence the ability to adsorb certain guests, are directly be controlled by light irradiation. The most common way to introduce photoswitches is their addition as a functional side group to the linker. Even though there is a wide range of different molecules that show switching upon irradiation with light, thus far only the prototypical azobenzene photoswitch has been incorporated into MOFs. In most cases the azobenzene photoswitch dangles into the pore and after light

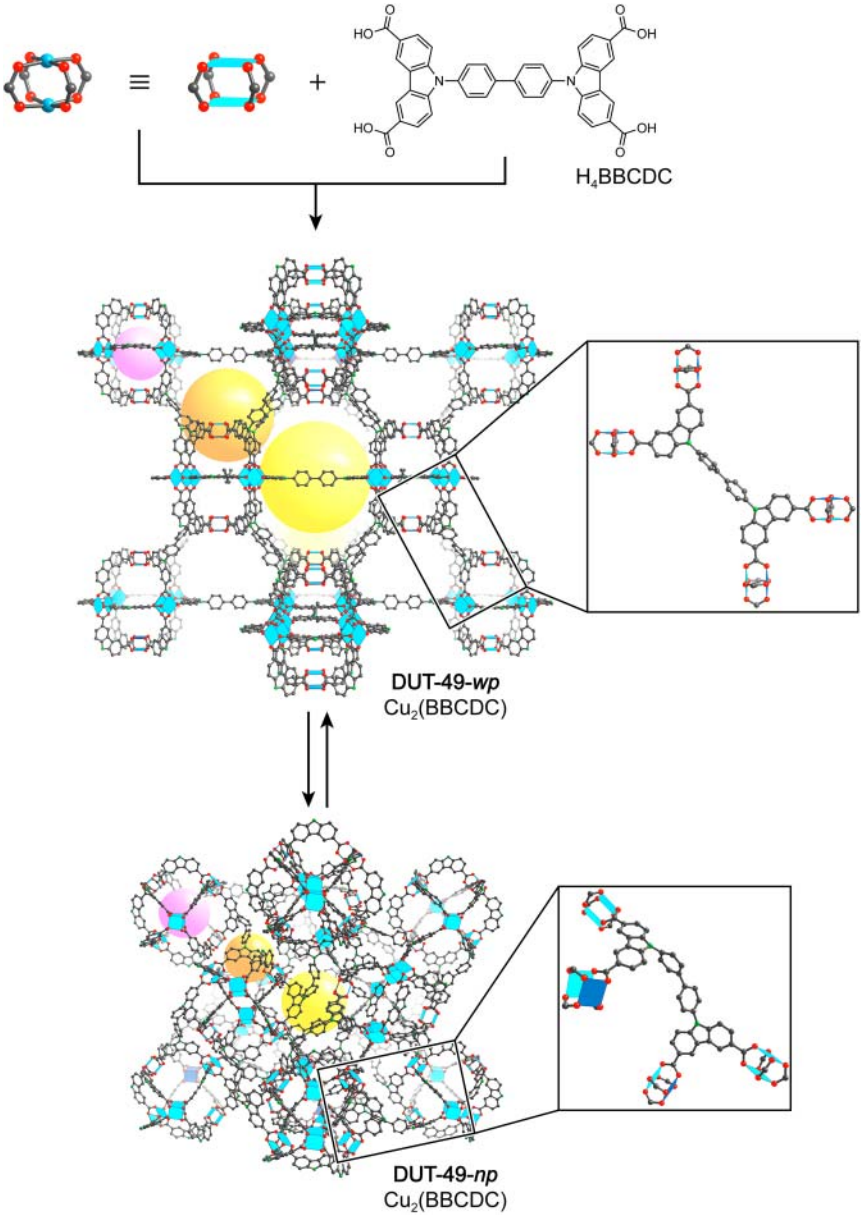

Figure 21.5 DUT-49 is constructed from cuboctahedral 12-c TBUs formed from paddle wheel SBUs and carbazole-3,6-dicarboxylate moieties of the linker. These TBUs are connected by biphenyl bridges to yield a framework of **fcu** topology. Upon adsorption of methane (10 kPa) and butane (30 kPa) the framework shows negative gas adsorption due to structural rearrangement induced by bending of the organic linker which decreases the internal pore volume of the structure. All hydrogen atoms are omitted for clarity. Color code: Zn, blue; C, gray; N, green; O, red.

exposure (365 nm) changes from a *trans* configuration to a *cis* configuration. This is usually accompanied by a substantial change in the pore aperture and thus the accessibility of the internal void space. The switching back to the initial state can be triggered by either absorption of light of a higher wavelength (440 nm) or by heating thus rendering the whole process reversible. IRMOF-74-III(azo) (Mg(azo-DOT-III)$_2$) is an isoreticular analog of the prototypical **etb** topology MOF-74. It is constructed. from 1D SBUs that are connected by azo-DOT-III linkers. The structure of IRMOF-74-III(azo) features mesoporous hexagonal 1D channels running along the crystallographic *c*-axis. (Figure 21.6) [12]. Each azo-DOT-III linker in IRMOF-74-III(azo) is decorated with a photoswitchable azobenzene unit, which can be converted between its *cis* and *trans* conformation

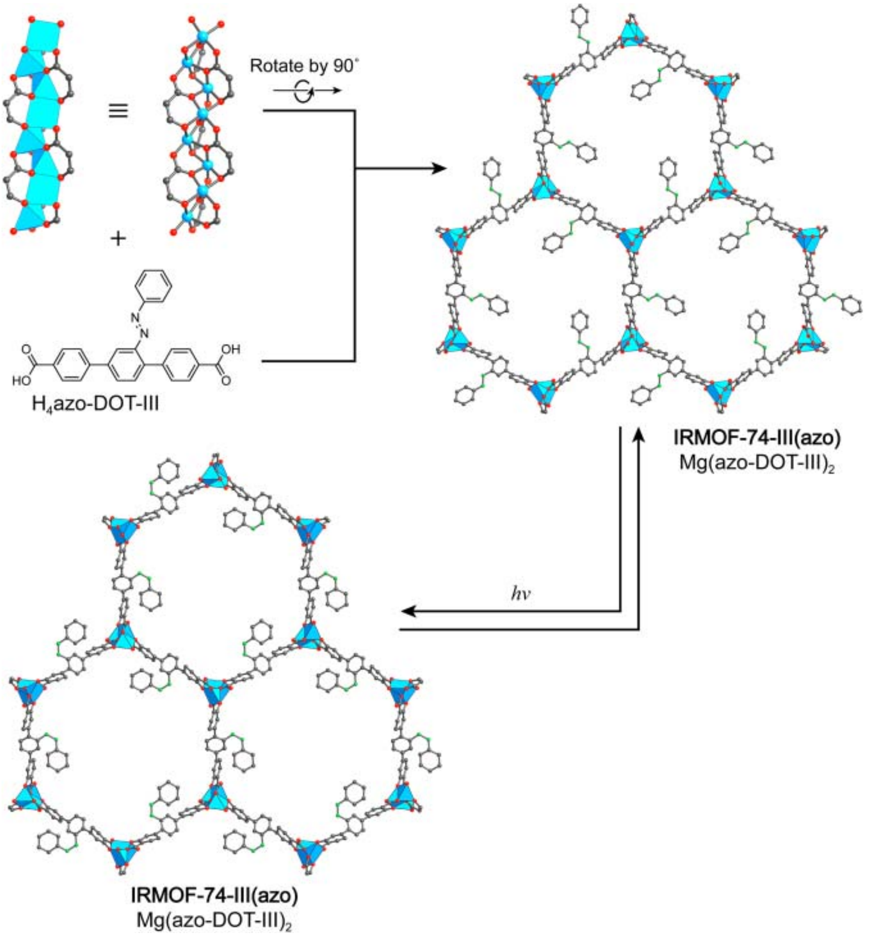

Figure 21.6 Local synchronized dynamics in the **etb** topology IRMOF-74-III(azo) constructed from rod SBUs and azo-DOT-III linkers. Isomerization of the appended photoswitches between the *cis* and the *trans* conformation is affected by irradiation with light of 408 nm in wavelength. This motion occurs uniformly throughout the framework and is independent of the framework backbone. All hydrogen atoms are omitted for clarity. Color code: Mg, blue; C, gray; N, green; O, red.

by excitation at 408 nm. This switching is independent of the framework backbone but directly affects the pore aperture of the material which expands from 8.3 Å in the *trans* conformation to 10.3 Å in the *cis* conformation. The utility of this switching is highlighted by the controlled loading and release of a propidium iodide dye. Spectroscopic studies show no release of the luminescent dye under ambient conditions but upon irradiation of the MOF at 408 nm, the rapid wagging motion inherent to the repetitive isomerization of the azobenzene functionality triggers the release of the dye from the pores.

While in photoswitchable MOFs the backbone of the framework remains unaffected of the motion of the switch, the strategy still relies on the isomerization (i.e. flexing) of covalent bonds, which is not desirable in the context of longevity and endurance of materials.

21.3 Independent Dynamics in Frameworks

A fundamentally different approach toward dynamics in extended structures are adaptive frameworks; materials where the framework dynamics are not triggered by a specific external stimulus but that can adapt, locally or globally, to various external influences. To realize such frameworks, the constituents need to be able to move freely and thus without the need for flexing of bonds. This is achieved by employing mechanical instead of chemical bonds. Mechanical bonds hold molecular entities together by physical entanglement rather than actual chemical bonding. This is advantageous in the context of dynamics because the constituents of such frameworks can move independently without parting company. Again, we distinguish global dynamics from local dynamics. The introduction of mechanically bonded rings onto the struts of an extended backbone is referred to as "robust dynamics." In this scenario, the motion of the ring is independent of the framework backbone and can occur in the absence of an external stimulus. Global dynamics are observed in extended interpenetrated structures where individual frameworks can move with respect to each other, and in 3D frameworks formed by weaving of molecular threads. It is important to note that in contrast to flexible frameworks where an external stimulus affects synchronized motions of the respective building units, adaptive dynamics based on mechanical bonding can occur in the absence of external stimuli and are therefore independent as opposed to synchronized.

21.3.1 Independent Local Dynamics

To overcome the inherent limitations of flexible frameworks with respect to longevity and endurance, mechanically interlocked molecules are inserted into the rigid framework backbone in such way that they are capable of dynamics without compromising the fidelity of the entire system (robust dynamics) [13]. The fact that in such systems the constituents are linked mechanically, not chemically, allows for large amplitude molecular motion of the units with respect to each other. On the molecular level this approach has proved fruitful for the development of molecular machines, muscles, and rotors where during a switching process only weak non-covalent bonds are broken and reformed again in a fully reversible and highly controllable fashion [14]. In the structure of MOF-1040 ($Zn_4O(BPCu)_3$, where BPCu = Cu^{2+}-4,7,10,13,16,19,22,25-octaoxa-2(2,9)-phenanthrolina-1,3(1,4)-dibenzenacyclohexacosaphane@4,4′-(1,10-phenanthroline-3,8-diyl)dibenzoate), macrocycles are mechanically appended to its backbone. MOF-1040 is prepared by reticulating copper(I)-bisphenanthroline complex-based pseudorotaxane linker H_2BPCu with Zn^{2+} ions into a framework of **pcu** topology, isoreticular to MOF-5.The single crystal structure of the twofold interpenetrated framework confirms that the chemical integrity of the copper(I)-complexed pseudorotaxane is maintained under the MOF synthesis condition. The oxidation of Cu^{1+} to Cu^{2+} within the framework can be carried out under ambient conditions without affecting the integrity of the MOF backbone, corroborating the chemical accessibility of the copper centers in the framework. In theory, upon demetallation, the discrete macrocycle that is connected to the framework only by means of mechanical bonding can move about freely on the strut between neighboring SBUs, however, in this case the demetallation of the framework does not go to completion, presumably due to steric shielding of the Cu^{1+} centers by the framework (Figure 21.7).

In contrast a MOF constructed from $Zn_4O(\text{-}COO)_6$ SBUs and tetratopic H_4BITC (18-crown-6 @ 4,4′,4″,4‴-(1,4-phenylenebis(1*H*-benzo[*d*]imidazole-2,4,7-triyl))tetrabenzoic acid) linkers, termed UWDM-4 ($(Zn_4O)_2(BITC)_3$), contains 18-crown-6 ethers on the crossbars between two triphenyl-dicarboxylic

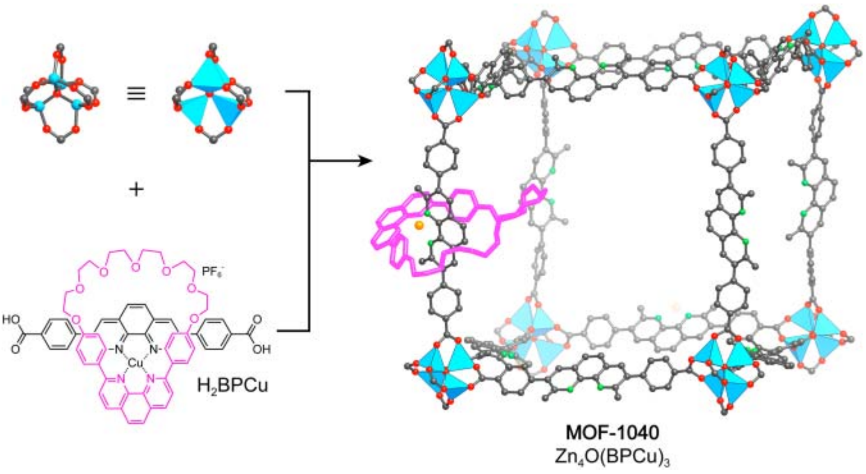

Figure 21.7 Mechanically bonded macrocycles appended to the backbone of MOF-1040. MOF-1040 is constructed from $Zn_4O(-COO)_6$ SBUs and ditopic BPCu linkers. The linker is a pseudorotaxane where the linear strut and the macrocycle are held together by coordination to a Cu(I) template. Upon reticulation the ring is trapped on the strut between two neighboring SBUs. Demetallation of the framework proves difficult due to steric shielding of the Cu(I) centers in the twofold interpenetrated structure. All hydrogen atoms and interpenetrating nets are omitted for clarity. Only one macrocycle is shown for clarity and highlighted in pink. Color code: Zn, blue; Cu, orange; C, gray; N, green; O, red.

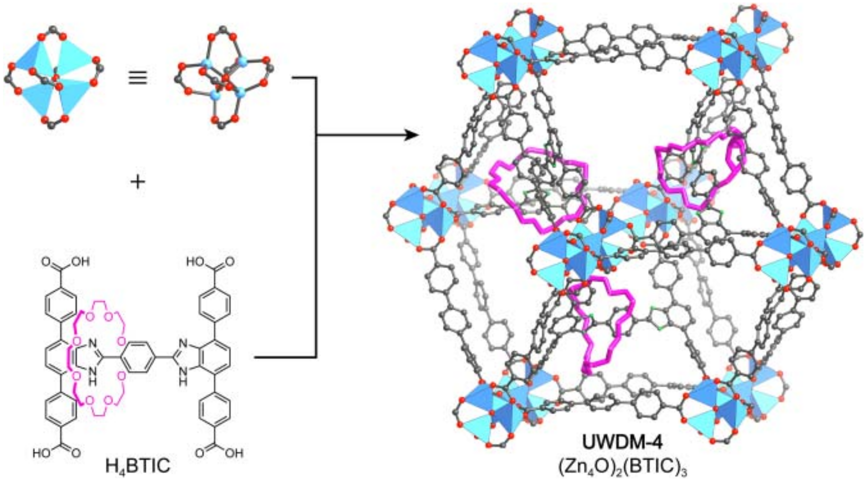

Figure 21.8 Local independent dynamics of 18-crown-6 ethers mechanically bonded to the backbone of UWDM-4. The framework is constructed from $Zn_4O(-COO)_6$ SBUs and tetratopic BITC linkers and assumes an overall **acs** topology. The 18-crown-6 ether is appended to a crossbar between two triphenyldicarboxylic acids on the linker and does not detach from the linker during the MOF synthesis despite the lack of strong chemical interactions. At room temperature the linker rapidly shuffles between two imidazole moieties on the crossbar. Only upon cooling this motion is slowed down and the macrocycle is confined to either of the two imidazole moieties on the linkers' crossbar. All hydrogen atoms and interpenetrating frameworks are omitted for clarity. Color code: Zn, blue; C, gray; N, green; O, red.

acids. In the linker the macrocycle is not bound through metal coordination but held in place by two bulky stoppers. The molecular ring can move freely but interacts preferably with the two electron deficient imidazole moieties on opposing sites of the crossbar (Figure 21.8) [15]. The translational "shuttling" of the crown ether is observed by variable-temperature solid-state nuclear magnetic resonance (NMR). At room temperature, only one resonance structure is detected for occupied and unoccupied imidazole moieties on the linker, indicating rapid shuttling of the ring between the two sites beyond the NMR timescale. Upon a decrease in temperature the shuttling motion slows down which allows for the peak to be resolved into two distinct resonance states.

21.3.2 Independent Global Dynamics

The use of mechanical bonds is not limited to the local motion of molecular fragments on a rigid backbone, but it is also possible to synthesize frameworks that are entirely constructed from mechanical bonds which allows for global dynamics and rearrangement of the whole structure without the making or breaking of chemical bonds. In principal there are three distinct cases of how a framework can be composed of mechanically linked building units. These scenarios are: (i) interpenetration of extended 3D and 2D frameworks, (ii) weaving of 1D molecular threads held together by mechanical entanglement, and (iii) a structure built up entirely from discrete (0D) interlocking rings [1]. Interpenetration of 3D and

2D frameworks is well established in solid-state materials such as MOFs, coordination networks, or inorganic extended structures. However, in the case of 3D and 2D interpenetration, the potential for motion of the fragments with respect to each other is limited because the entire extended 3D or 2D frameworks would have to be dislocated.

In contrast, the formation of extended structures based on 1D weaving or 0D interlocking offers many more degrees of freedom of the building units and thus allows for enormous spatial deviations to take place without deteriorating the overall structure. The synthesis of such structures is challenging but the reticular synthesis of COFs provides a directed and general approach to access materials with these modes of entanglement. Woven COFs have been accessed synthetically as illustrated by the 3D framework COF-505-Cu ($((\mathrm{Cu})(\mathrm{BF}_4)[(\mathrm{PDB})(\mathrm{BZ})]_{imine}$, where PDB = 0,13,16,19,22,25-octaoxa-2(2,9)-phenanthrolina-1, 3(1,4)-dibenzenacyclohexacosaphane). COF-505-Cu is built from distorted tetrahedral tetratopic functionalized copper bis-phenanthroline complexes, ($\mathrm{Cu(PDB)_2(BF_4)}$), and linear ditopic benzidine linkers through imine bond formation to give a framework of **dia** topology (Figure 21.9) [16]. In the structure

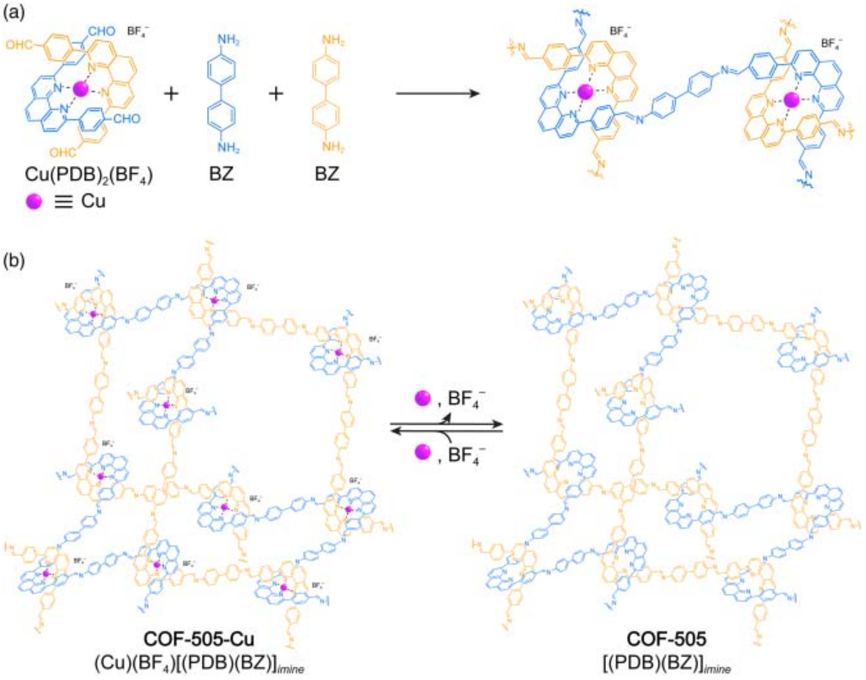

Figure 21.9 (a) Reticulation of $\mathrm{Cu(PDB)_2(BF_4)}$ with BZ by imine bond formation. (b) Illustration of one adamantane cage of the resulting COF-505-Cu and the demetallated woven framework COF-505. The reversible demetallation of COF-505-Cu results in a change of the topology of the framework from **dia** to **dia-w**. The backbone of the **dia-w** COF-505 is comprised of linear interwoven threads that are held together only by mechanical but not by chemical bonding. As a consequence the framework is endowed with many additional degrees of freedom which allow for large deviations to take place. This is evidenced in a 10-fold increase in elasticity as determined by nano-indentation by atomic force microscopy.

the copper centers only serve as templates for bringing the threads into a woven pattern instead of the more commonly observed parallel arrangement. Post-synthetically these Cu^{1+} ions can be reversibly removed and re-added without loss of the overall structure. Upon demetallation the threads in the resulting **dia-w** topology framework COF-505 ($[(PDB)(BZ)]_{imine}$) are endowed with many additional degrees of freedom for enormous deviations to take place between them, without unzipping the weaving of the overall structure. This translates into a 10-fold increase in elasticity of the material as determined by nano-indentation by atomic force microscope (AFM).

The largest degrees of freedom that can be achieved in extended frameworks based on mechanical bonds are expected in structures composed of discrete rings. The synthesis of extended structures composed of 0D rings that are held together exclusively by mechanical bonds. This synthetic target is a long-standing challenge. We expect that such structures can be achieved with a strategy akin to what has been used for the generation of woven structures [17].

21.4 Summary

In this chapter we covered the modes of dynamics in extended framework materials. The importance of both the porosity and the presence of distinctly different kinds of bonding within one single structure with respect to large amplitude motion of their constituents were examined. Modes of framework dynamics were categorized into global and local, depending on if the motion affects the entire backbone of the material or is independent of it. Such dynamic processes can be affected by a specific external stimulus which generally results in synchronized motion. Global synchronized motion is observed in flexible breathing frameworks and the weak point in the framework that distorts in response to the stimuli can be both, the inorganic SBU or the organic linker. Local synchronized motion can be achieved by appending photoswitches to the backbone of the MOF or COF. Synchronized framework dynamics rely on the making and breaking or on the flexing of covalent bonds which is detrimental in the context of material longevity. In contrast independent framework dynamics are based on mechanical bonding and only weak, non-covalent interactions need to be overcome to affect the motion. On a local level this can be achieved by appending mechanically bonded rings onto the struts of the framework and on a global level such dynamics are observed in woven materials where the 1D framework constituents are held together by mechanical bonds. It is worthwhile noting that in independent framework dynamics the motion can be autonomous as opposed to synchronized and can happen in the absence of specific external stimuli.

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