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A Study on Switching in Metal-Organic Frameworks

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Abstract

In recent years, metal-organic frameworks (MOFs) have become an area of intense research interest because of their adjustable pores and nearly limitless structural diversity deriving from the design of different organic linkers and metal structural building units (SBUs). Among the recent great challenges for scientists are included switchable MOFs and their corresponding applications. Switchable MOFs are a type of smart material that undergo distinct, reversible, chemical changes in their structure upon exposure to external stimuli, yielding important

technological applicability. Although the process of switching shares similarities with flexibility, very limited studies have been devoted specifically to switching, while a fairly large number of research reports and reviews have been assigned to flexibility in MOFs. This perspective focuses on the properties and general design of switchable MOFs. The switching activity has been delineated based on the cause of the switching: light, spin crossover (SCO), redox, temperature and wettability.

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2. MOF switching with light
3. MOF switching with temperature and pressure
4. MOF switching with redox
5. MOF switching with guests

1. Introduction

MOFs are a new generation of crystalline porous materials composed of organic linkers (ligands) connecting metal centers or clusters. These materials have unique structural features such as permanent, regular porosity and large internal surface areas.^[1-5] The enormous variety in MOF structures arises from the diversity of metal SBU and organic linker choice, leading to an extensive spectrum of physical and chemical properties.^[6-10] This, along with the presence of various interactions, including hydrogen bonding, van der Waals interactions, π - π stacking, and metal coordination, have made MOFs promising, diverse technological compounds. Expressly, the uniquely tunable structural properties of MOFs have endowed them with potential applications in diverging areas such as gas storage and separation, sensing, and catalysis.^[11-21]

Due to the last few years of progress in supramolecular chemistry, switchable molecules have captured widespread attention. Although the denotation of “switching”^[22-25, 93, 94] has been

variably employed in the literature, for the purposes of limiting the scope of this review the term “switch” will signify any system that, upon promotion by a particular, external stimulus such as light, temperature, or electrical field, undergoes a reversible and controllable transformation between two or more distinct molecular states, commonly illustrated by isomerization, bond breaking or formation, the gain or loss of electrons, or conformational changes. Under ideal conditions, it is assumed that every stage in the transformation of a reversible process is in equilibrium with the next state and the just prior state, so that infinitesimally small reversal steps along the reaction coordinate will yield a state indistinguishable to that from before the process began. By controllable, it is meant that the applied stimuli is assumed to be the principal instigator in the change of state. In other words, the transformational energy barrier that exists between the states should be in excess of what the thermal energy at observation conditions could overcome. Through this reasoning, is it possible that a structure that is not considered a switch at higher temperatures, may fit the conditions to be termed a switch at lower temperatures although for simplicities sake, these will not be highlighted herein. Finally, distinct implies that the transformation between these states produces some change in properties discrete enough to be observable and distinguished from one another using modern characterization techniques. For these reasons mass transport, gradual swelling, simple, inconspicuous hinging motions, and other phenomena which are either not reversible, do not entail intramolecular change, do not possess a significant enough activation energy to be well controllable (such as for small but additive lengthening or shortening of bonds), or whose states are too similar and cannot be distinguished from one another will not be included in this report.

Switching processes are one of the key strategies in the adsorption/desorption control of materials. However, compounds that perform well as switches in solution may encounter

difficulties in the solid state such as incomplete conversions from the greater restriction of movement in the solid state. In fact, switchability in molecules in the solution state does not always translate to a molecule with switchability in the solid state. Conversely, molecules which do not exhibit switching in solution may gain this capacity in the solid state.^[26, 27]

The advantage of immobilizing switchable molecules into porous materials is that the molecules can be incorporated into the solid state where extra pore space permits maintained mobility of the molecule. To date, a variety of stimuli-responsive, dynamic, and flexible materials have been documented. The high porosity of MOFs makes them ideal for the immobilization of switchable materials for usage in solution as well as in the solid state. In addition, the high degree of tunability of MOFs can be exploited to optimize the response and access to various stimuli. As the MOF synthetic toolkit expands, the realization of MOFs with targeted designs becomes increasingly facile.^[20, 28] Moreover, computational studies have been successful owing to the regularity and crystallinity of MOF structures, with recent high-throughput screening studies helping to guide experimentalists.^[29-33] *In situ* or post synthetically, structural and pendant ligands, primary and auxiliary metals and metal clusters, as well as pore sizes, shape, acidity, and hydrophobicity modifications can direct the uptake capacities, selectivity, sensitivity, and mobility of MOFs and MOF components.^[20, 28] MOFs feature greater surface areas and higher degrees of tunability than other porous materials such as zeolites, essential for applications including selective catalysis and low density, high capacity gas storage. Compared to porous polymers, MOF crystallinity, periodicity, and permanent porosity make characterization by x-ray diffraction techniques more amenable. Finally, while covalent organic frameworks are often lighter and larger pore structures are more stable than in MOF counterparts, MOFs boast more diverse synthetic conditions and the additional tunability provided by the

metal structural building unit (SBU) can permit facile incorporation of photochemical properties, catalytic centers, and gas sorption sites.^[11-21]

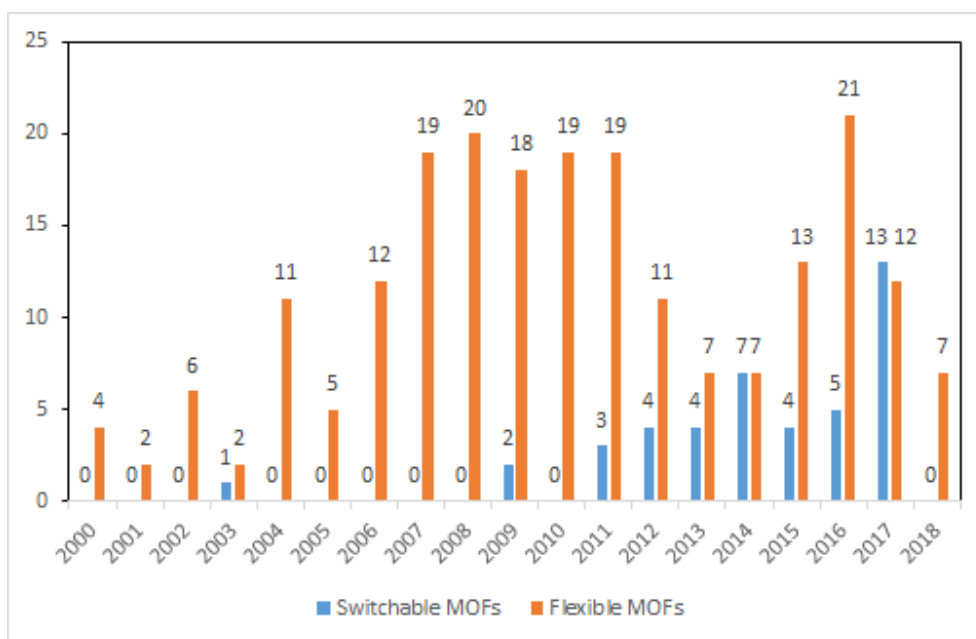
Flexible MOFs possessing the ability to structurally adapt under particular circumstances without the loss of structural integrity are often referred to as 3rd generation MOFs, or soft porous crystals.^[2] While this umbrella label includes switchable MOFs, not all 3rd generation MOFs are switches. For instance, flexible MOFs can undergo reversible phase changes, such as from crystalline to amorphous or crystal to crystal transformations, as well as volume changes in response to stimuli but they are not always switches if these changes do not occur on an intramolecular level or if the differences in states are not considerable enough to differentiate, as is often the case in swelling and mass transport-reliant changes.

Herein, the subject of our discussion will focus on switchable MOFs rather than the loftier topic of dynamic and flexible MOFs. Despite fairly extensive studies carried out on dynamic and flexible MOFs, studies on switchable MOFs were very limited until 2009 (Scheme 1). Table 1 lists some switchable MOFs that have been reported, their switching mechanisms, and their applications. As shown in Table 1, there are many ways to impose switching features on MOFs:

- a) Insertion of a switchable guest molecules into the MOF's pores;^[27, 34, 35]
- b) Functionalization of side groups on the linkers;^[36, 37]
- c) Direct incorporation of switching ligands as the MOF backbone.^[38-40]

Light stimulation is the most common stimulus employed for switching in MOFs although variety exists in whether the light excites metal ions in the MOF, structural ligands, pendant ligands, or guest species. In particular, azobenzenes (AZBs) are among the best candidates for molecular switches, either as guest molecules or as side groups. However, other stimuli have also

received recognition including redox, guests, temperature, and pressure. The subcategories of this review have been selected and organized based upon the type of stimulus applied to yield a switching response.



Scheme 1. The number of published articles including switchable and flexible MOFs each year.

Table 1. Features and suggested or examined applications of select switchable MOFs

MOF	Switchable Component	Switching Mechanism	Stimulus	Application(s)	Reference
$\text{Cu}_2(\text{F}_2\text{AzoBDC})_2(\text{dabco})$	F_2AzoBDC ligand	<i>Cis/Trans</i> isomerization	Light	H_2 hydrocarbon separation	[33]
$\text{Zn}(\text{L})-(\text{bpd}) \cdot \text{solvents}$	Diarylethene derivative ligand	Ring opening/closing	Light	CO_2 storage/release	[60]
UiO-66-TCPP-BCDTE	BCDTE ligand	Ring opening/closing	Light	$^1\text{O}_2$ generation	[30]
$\{[\text{Eu}(\text{BA})(\text{Bpybc})_{1.5}(\text{H}_2\text{O})] \cdot 2\text{NO}_3 \cdot 5\text{H}_2\text{O}\}_n$	Bpydc ligand	Light-induced radical generation/oxidative quenching	Light and Redox	Readout/Data Storage	[82]
UiO-66-PNIPAM	PNIPAM coating	Coil-globule transition	Temperature	Small organics storage and release (resorufin, caffeine, procainamide)	[91]

PC-PCN	BPDTE ligand	Ring opening/closing	Light	None mentioned or examined	[46]
SO-PCN	BPDTE ligand	Ring opening/closing	Light	¹ O ₂ generation and photocatalytic oxidation of DHN	[46]
2,6-Naph(COOLi) ₂	Ligand carboxylate groups	Lithium intercalation	Redox	Heat-responsive switching devices	[35]
[Fe(pz)M(CN) ₄]	Metal environment	Spin state stabilizations	Guest	Memory devices	[74], [75]
MOF-808-SP	Spiropyran ligand	Ring opening/closing	Light and Temperature	Gas separation	[57]
UBMOF-3	TPDPy ligand	Ring opening/closing	Light	None mentioned or examined	[49]
AMOF-1	Metal environment	Quenching by Cu ²⁺ guest	Guest	Cation (Cu ²⁺) sensing	[50]
Azo-IRMOF-74-III	Azobenzene ligand	<i>Cis/Trans</i> isomerization	Light	Dye (propidium iodide) storage and release	[32]
PCN-123	Azobenzene ligand	<i>Cis/Trans</i> isomerization	Light or Temperature	CO ₂ storage/release	[43]
CAU-5	AzoBiPyB ligand	<i>Cis/Trans</i> isomerization	Light or Temperature	Gas storage/release	[48]
PSZ-1	Imidazolate-based diethylenethene ligand	Ring opening/closing	Light	Aromatic hydrocarbon filter	[56]
Cu ₂ (AzoBPDC) ₂ (AzoBiPyB) SURMOF	AzoBPDC and AzoBiPyB ligands	<i>Cis/Trans</i> isomerization	Light	H ₂ :CO ₂ separation	[97]
ECIT-20	BPE ligand	[2+2] reaction	Light and Temperature	Allyl alcohol removal, conversion, and release	[62]
Zn(AzDC)(4,4'-BPE) _{0.5}	BPE and azobenzene ligands	<i>Cis/Trans</i> isomerization	Light	CO ₂ storage/release	[55]
[Zn ₂ (terephthalate) ₂ (trienhylenediamine)] _n □AB	Azobenzene ligand	<i>Cis/Trans</i> isomerization	Light or Temperature	Optical, electric, and magnetic devices	[54]
JUC-120	BSP guest	Ring opening/closing	Light	Photonic and optical devices	[58]
UiO-67	Azobenzene guest	<i>Cis/Trans</i> isomerization	Light	H ₂ :CO ₂ separation	[31]
[Fe(pmd)-(H ₂ O){M(CN) ₂ }]·H ₂ O (M=Ag or Au)	Fe(II) environment	Spin state stabilizations	Temperature	Sensory and memory devices	[72]
[Fe ^{II} (Hbpt)Pt(CN) ₄]·1/2Hbpt·1/2CH ₃ OH·5/2H ₂ O	Fe(II) environment	Spin state stabilizations	Temperature	Memory devices	[68]
Fe ₂ [Nb(CN) ₈]·(4-pyridinealdoxime) ₈ ·2H ₂ O	Fe(II) environment	Spin state stabilizations	Temperature and pressure	Memory devices and optical information storage and displays	[71]
SALI-R ³⁽⁺⁾	Semirotaxane ligand	Semirotaxane dumbbell site preference	Redox	Molecular electronic devices	[96]
TMU-34	H ₂ DPT ligand	Deprotonation of tetrazine moiety	Redox	Chloroform detection	[83]

i-motif DNA-modified UMCM-1	i-motif DNA	DNA folding and unfolding	Redox	Storage/release of rhodamine 6G	[99]
G-quadruplex DNA-modified UMCM-1	G-quadruplex DNA	DNA folding and unfolding	Redox	Horseradish peroxidase mimic	[99]
UiO-68-OH	Hydroquinone ligand	Hydroquinone/quinone transformation	Redox	Storage devices	[77]
NU-1000-FC ²⁺	[2]catenane	Partially restrained relative motion	Redox	Molecular electronic devices	[80]
MIL-100(Al)@Fe(sal ₂ triene)	Fe(II) environment	Spin-state stabilization	Guest	Sensing devices	[115]
MOF-5	Metal environment	Introduction of intermediate energy levels	Guest	Pyridine sensor	[116]
PCN-250	Azobenzene ligand	<i>Cis/Trans</i> isomerization	Pressure	CH ₄ uptake	[111/98]
ZAG-6	1,4-cyclohexanedicarboxylate ligands	Uncoiled/coiled transformation	Pressure	Proton conduction	[110]
DUT-8(Ni)	Percolating carbon nanoparticles	Disruption of nanoparticle network with increasing volume	Guest	Sensing in industrial feed streams, VOC filtration, gas storage	[40]
ELM-11	Percolating carbon nanoparticles	Disruption of nanoparticle network with increasing volume	Guest	Sensing in industrial feed streams, VOC filtration, gas storage	[40]
{Fe(pyrazine)[Pt(CN) ₄] ₂ }	Fe(II) environment	Spin-state stabilization	Guest	None mentioned or examined	[64]
{[Ag ₁₂ (S ^t Bu) ₆ (CF ₃ CO ₂) ₆] ₁₀ .5[Ag ₈ (S ^t Bu) ₄ (CF ₃ CO ₂) ₄](tpe) ₂ (DMAC) ₁₀] _n }	tpe ligand	Steric restriction of internal ligand rotations	Guest	Sensing and light-emitting devices	[117]
MAMS-1	Pendant <i>t</i> -butyl groups	Steric restriction to <i>t</i> -butyl rotation	Temperature	H ₂ :CO ₂ separation	[41]
DUT-49	9,9'-([1,1'-biphenyl]-4,4'-diyl)bis(9 <i>H</i> -carbazole-3,6-dicarboxylate) ligand	Bending and straightening of ligand	Pressure	Micropneumatic devices, self-propelling systems, mechanical actuators	[100]

2. MOF Switching with Light

Light is a simple and practical stimulus that provides fast, clean, remote-controllable transition between states.^[41, 42] Particularly, wavelengths near the visible spectrum are nondestructive, high

resolution, produce few side products, and are easily accessible in the form of sunlight.^[42, 43]

Photochromic molecules are compounds that reversibly change their molecular and electronic state upon exposure to light stimulus. Generally, photoresponsive molecules exhibit potential as sensors, switches, and memory and optical data storage media. For instance, a number of organometallic molecules have been widely investigated and used in technologies such as organic light-emitting diodes (OLEDs), fluorescent probes, and laser dyes.^[44-46]

Attracted by what an organometallic chemistry and materials science hybrid could offer to these technologies, photoresponsive MOFs are a new class of MOF that have recently garnered significant research interest.^[47] Conceptually, MOFs are appropriate structures for the encasement of optically active agents because entrapment of these molecules into MOFs' pores prevents agglomeration and subsequent self-quenching. However, one concern to deliberate on is that photochromic molecules often cannot effectively switch and exhibit their optimal optical activity in the solid state since their motion is restricted by intramolecular interactions in dense crystalline packing.^[23] Therefore, it is essential that the switchable species is not restrained to the point of inactivity once incorporated into a MOF.

Azobenzenes are one of the most studied photochromic molecules. This molecule possesses an azo bond that can be switched from a thermally stable *trans* isomer to a metastable *cis* isomer upon irradiation with UV and visible light irradiation. Isomeric conversion of azobenzene is rapid and reversible, changing the structure and polarity such that the distance between the two para carbon atoms in the *trans* and *cis* forms are 9 Å and 5.5 Å, respectively.^[36, 42, 48]

Azobenzenes are undoubtedly one of the most popular species hosted in light-stimulated switchable MOFs.^[49, 50] In fact, an azobenzene pendant moiety was the switching piece in the first photoswitchable MOF, CAU-5.^[51] As pendant groups, azobenzene units retain their

switchability without significant fettering. In addition, upon *cis/trans* switching, dangling azobenzene groups can modify the pore environment enough to give rise to interesting properties and applicability.

The openness of the MOF PCN-123's pores was studied in the work of Zhou et al. by exploiting the reversible photoresponse of a pendant azobenzene group.^[43] This switching in turn modified the framework's CO₂ adsorption capacity. Although the *cis* isomer offers larger pore space in PCN-123, it is the *trans* isomer that displays the greater CO₂ uptake by allowing increased access to the metal clusters, the main site for CO₂ adsorption. Of particular interest was the fact that the decrease in CO₂ uptake after UV treatment was only about 26.6%, whereas this value approached 53.9% 5 hours after UV irradiation. The authors suggest there may be synergism at work, whereby the *trans-to-cis* transformation of the azobenzene ligand encourage the isomerization of other azobenzene ligands. Well-designed experimental or theoretical insight into this synergistic effect could prove useful to control the speed of these conversions in future materials.

Seeing the potential these materials could have in gas capture and separation, studies have been conducted on MOF films with switchable azobenzene groups. In one example, Knebel et al. designed a MOF, Cu₂(F₂AzoBDC)₂(dabco).^[37] This MOF, containing a difluorinated azobenzene derivative, was capable of switching upon exposure to green or violet visible light, avoiding the potential destruction of organic and biological materials caused by UV light irradiation (figure 1). Additionally, the use of visible light increases the isomerization yields through avoiding competition with LMCT promoted by UV light in Cu-paddle-wheel structures. MOF film on mesoporous Al₂O₃ supports separated H₂:hydrocarbon mixtures while being unable

to separate H₂:CO₂ mixtures. For this reason, they attributed the modulation of H₂:hydrocarbon separation by

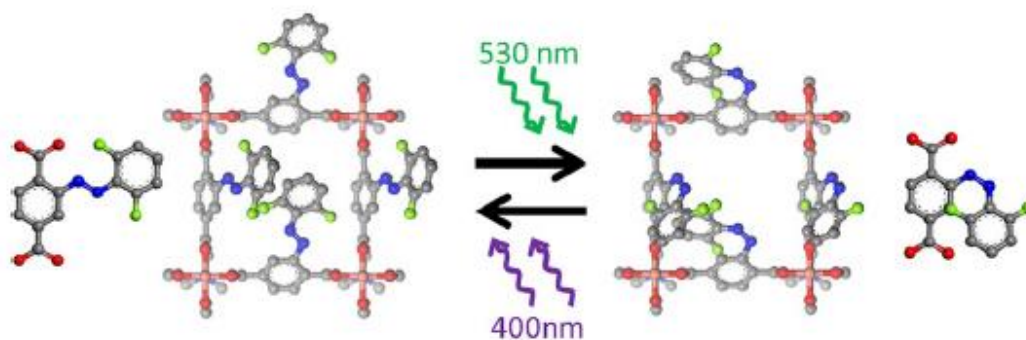


Fig. 1. a) Structure of Cu₂(F₂AzoBDC)₂(dabco) with fluorinated azobenzene side groups which undergo reversible trans- (left) to-cis (right) isomerization by irradiation with green light (530 nm) and from cis-to-trans by irradiation with violet light (400 nm). The photoswitchable linker F₂AzoBDC is portrayed next to the MOF structure. Carbon atoms are grey, oxygen red, copper salmon, fluorine green, and nitrogen blue. For clarity, the hydrogen atoms are not shown. (Reproduced with permission from [37]. Copyright © 2017, John Wiley and Sons).

visible light irradiation to relate to pore opening/blocking effects of the *cis/trans* isomers of F₂AzoBDC, rather than any changes in polarity or metal-site access. Also employing minor modifications to the linker, Wang and coworkers assembled a pillared-layer structure MOF with two unique pendant azo linkers, AzoBPDC and AzoBiPyB, on a porous α -Al₂O₃ support.^[51] This assembly permitted precise control of the H₂:CO₂ separation factor from 3 to 8. The successful use of modified azobenzene linkers suggests the exploration of more azobenzene modifications. Changes to the electron distribution near and around the azo bond or adjustments to the degree of bulkiness on the pendant ligand will undoubtedly affect the wavelength of switching, the

completeness of switching, and/or the amount of blocking around the metal clusters or the pores.

However, such investigations still need to be thoroughly undertaken.

Besides gas separation capabilities, incorporation of a dangling azobenzene group can result in further interesting applications upon guest encapsulation. For instance, azo-IRMOF-74-III, an analogue to MOF-74, was capable of trapping and releasing fluorescent cargo propidium iodide thanks for pore blocking effects of the azo ligand in the *trans* conformation.^[36] Interestingly, Heinke's group took the direction of loading proton conductors 1,4-butanediol and 1,2,3-triazole as guests into a surface-mounted MOF, $\text{Cu}_2(\text{F}_2\text{AzoBDC})_2(\text{dabco})$ on a quartz.^[52] Experimentally, the *trans* conformation in the azo linker resulted in higher conductivity, and thereby freer movement of the proton conductors, while the *cis* conformation showed reduced conductivity, suggesting more restraints to the guest molecules' movement. Using quantum chemical calculations and IR spectroscopy, they could assert that the *cis* conformation allows for stronger hydrogen bridging between the azo nitrogen and the guest molecules, slowing their travel. Finally, Meng et al. exploited the susceptibility of metallofullerene spins through inclusion into a MOF with pendant azobenzene units.^[53] The differences in dipole moment of the linker as well as the π - π interactions with the fullerene guest resulting in reversible, marked changes in magnetic properties. However, upon irradiation times past 30 minutes, no further differences in EPR spectra were observed. This seems to be in contrast to the synergistic effects observed in PCN-123 and this difference may be due to the strong host-guest interactions between the MOF and fullerenes as well as isomerization hindrance due to the metallofullerene's sheer size.

Azobenzenes as guest molecules can also provide application as separation membranes. In one instance, a thin film of UiO-67 deposited on an $\alpha\text{-Al}_2\text{O}_3$ support was loaded with azobenzene guest molecules.^[35] Although the azobenzene guests showed π -interactions with the MOF

framework, they were still able to switch under UV irradiation, producing two distinct states with discernable variation in $H_2:CO_2$ permeance, which were credited primarily to the gating effect of azobenzene rather than electrostatic changes. Kitagawa's group noticed an interesting transformation when azobenzene guest molecules were stimulated inside of a flexible zinc framework.^[54] Conformational isomerism of the guests triggered a structural adjustment in the host framework from a tetragonal to an orthorhombic symmetry (figure 2). This process of guest-to-host structural transmission is a keystone example to inspire the further incorporation of switchable moieties into flexible frameworks as guests with the potential to convert generally flexible frameworks into switchable ones, producing additional, unexplored smart porous materials.

The question inevitably arises as to if switchable linkers can be incorporated into MOFs as integral, critical parts of a framework's walls, rather than as pendant groups or guest molecules. The primary obstacle in these attempts is the overall rigidity that the linker would have to overcome in order to maintain switchability. However, Lyndon et al. have reported a MOF, $Zn(AzDC)(4,4'-BPE)_{0.5}$ composed of two linkers both capable of *cis/trans* isomerization located perpendicular to

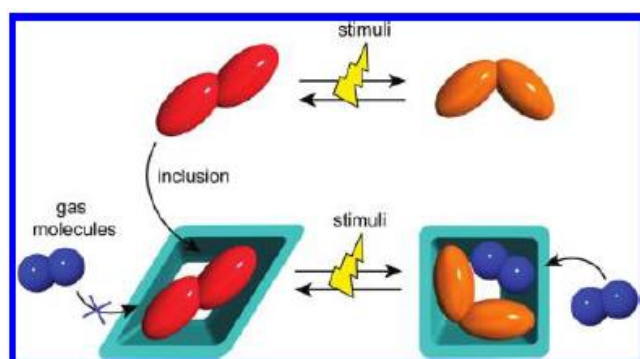


Fig. 2. Structural transition of guest molecules leading to a conformational change in the host. Red and orange objects represent *trans*-AB and *cis*-AB, respectively. (Reproduced with permission from [54]. Copyright 2012. American Chemical Society).

one another (figure 3).^[55] While this result was captivating, changes in the framework due to isomerization of the ligands were localized and transient. The quick transitions back to their more stable isomers were likely due to the already established crystallinity of the MOF framework as well as from stresses from existing as a triply interpenetrated framework. Nevertheless, this study sets up precedence for future research into switchable integral MOF ligands as well as questioning how much removing interpenetration would emancipate the linkers to allow for slightly more permanent switching between states.

Dithienylethenes are another family of photoresponsive organic groups applied in the preparation of switchable MOFs. Triggered by UV or visible light, dithienylethenes undergo reversible ring opening/closing. Diarylethene derivatives such as dithienylethenes are distinguished in the excellent thermal stability of both the open and closed isomers, limiting the extent of unintended back reaction to the more thermally stable isomer over time. Dithienylethenes display desirable

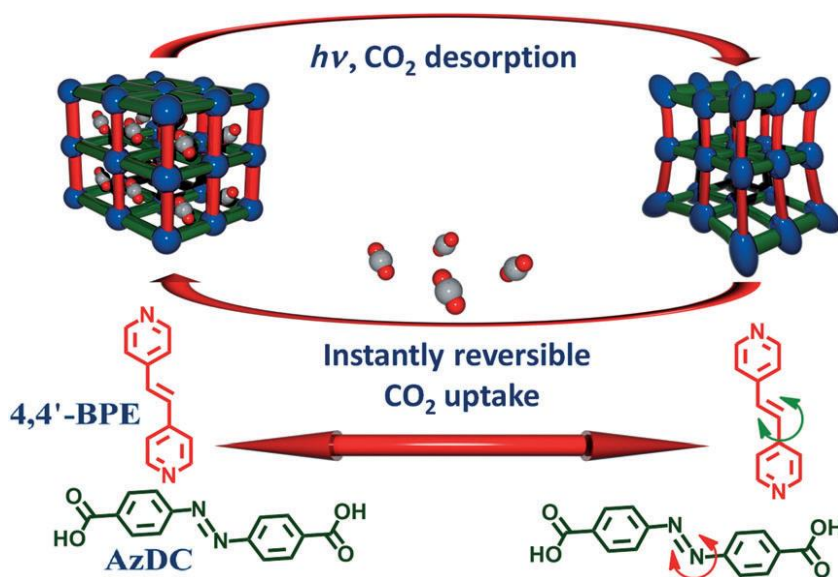
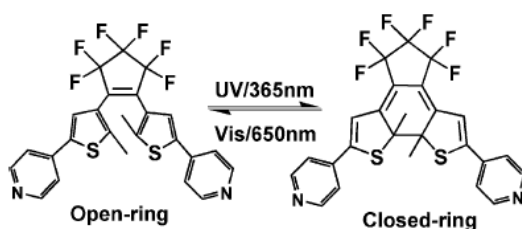


Fig. 3. Photo-switching of an AzDC-functionalized MOF molecule capable of reversible CO₂ uptake. (Reproduced with permission from [55]. Copyright © 2013, John Wiley and Sons).

properties in photochromic studies such as large optical differences between states, thermal stability, fatigue resistance to photochromic performance, and rapid responses in the solid state.

The first dithienylethene MOF included the photochromic species as guest molecules within a Zn-based host.^[56] Shortly afterwards, a dithienylethene was employed as a secondary structural ligand (figure 4).^[57] This ligand utilizes pyridine donor ligands on the dithienylethene moiety along with carboxylate-donating BPDC ligands to assist in stabilizing the framework. The resulting MOF demonstrated excellent controlled CO₂-adsorption/release with desorption

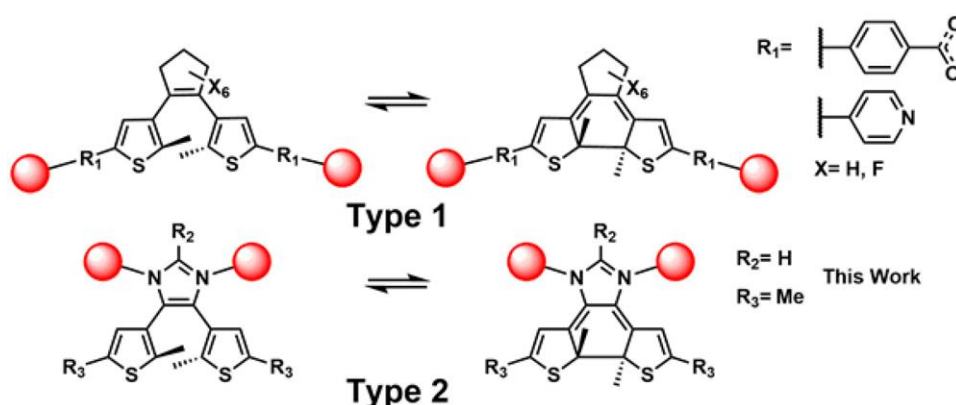


capacities around 75% using static irradiation.

Fig. 4. Reversible interconversion of a diarylethene derivative under UV or visible light irradiation. (Reproduced with permission from [57]. Copyright © 2014, John Wiley and Sons).

Striving for more efficient switching, Benedict's group sought to develop a dithienylethene-incorporated MOF with less geometric restrictions than its predecessors. To this end, rather than attaching the coordinating groups to the thienyl portion, whereby repeated photoisomerization exerts stress and damage to the MOF scaffold, a Zn-MOF, UBMOF-3, was successfully produced with ditopic linkers bearing modified dithienylethene species protruding the switchable

thienyl moiety into the MOF's pores.^[58] Following this success, this linker motif was then included into the larger pores of a ZIF-70 framework using solvent assisted linker exchange to produce PSZ-1.^[59] As was hypothesized, the resulting switchable MOF underwent up to 5 open-close cycles with no noticeable damage to the structure. Additionally, the dithienylethene linker is photobleached in solution whereas incorporation to PSZ-1 prevents this photoinactivation. The material was then used for the separation of aromatic hydrocarbons, to confirm a difference in pore properties between the open and closed states. In the open form, toluene, naphthalene, and pyrene all pass through the material similar to unmodified ZIF-70. However, if the material is irradiated with UV light to produce the closed form, the elution of the aromatic species are all



halved. Because the retention times between all species are similar, they propose that the differences in retention times are due to electronic effects rather than steric blocking of pore space. Reversible modification of a MOFs' pores with an input as facile as light irradiation without damage to the overall structure is an exciting concept to decrease costs by bestowing reusability and durability to smart materials.

Fig. 5. Dithienylethene-based linkers (spheres: metal nodes) (Reproduced with permission from [59]. Copyright 2017. American Chemical Society).

In two examples highlighting interesting applications of the dithienylethenes, the photoswitchable linker was installed in conjunction with a Zn-TCPP photosensitizer ligand to generate molecular dyad MOFs.^[46] The appropriate energy state of the dithienylethene linker in its open position is too high to accept energy from the excited state of TCPP. In this case, energy transfer occurs between the excited Zn-TCPP linker to triplet oxygen to produce singlet oxygen. In contrast, the closed state of the dithienylethene linker is lower in energy and capable of accepting energy from the excited state, minimizing the formation of singlet oxygen. This MOF's catalytic performance was then demonstrated via the photooxidation of 1,5-dihydroxynaphthalene. In a study following, TCPP and the dithienylethene, in varying ratios, were added *in situ* to the synthesis of UiO-66.^[34] Compared with the use of a photosensitizer and a switch separately in solution, incorporation into a MOF ensures relative closeness of the two species and thereby more efficient transfer of energy. This singlet oxygen generating MOF was employed in successfully controllable *in vitro* photodynamic therapy. Interestingly, although the authors note the substituent effect on dithienylethene switches that results in loss of fatigue resistance upon repeated cycling,^[60] the unmodified dithienylethene system was still selected. Far less studied in MOFs than azobenzenes or dithienylethenes, spiropyrans are an alternative class of photoactive molecule that are capable of reversibly converting between a colorless "closed" spiropyran form (CSP) under the influence of visible light or heat, and a colored "open" merocyanine form (OMC) upon UV light irradiation. Rather than *cis/trans* isomerization as in the case of azobenzenes, and similar to dithienylethenes, spiropyrans undergo reversible ring opening/closing switching mechanism. Although spiropyrans were previously incorporated into a MOF (JUC-120) using microwave-assisted crystallization inclusion method,^[61] they were also inserted post-synthetically into MOF-

808 through replacement of solvent occupied sites on the Zr_6 nodes with a precursor (1-(carboxymethyl)-2,3,3-trimethyl-3*H*-indol-1-ium) followed by addition of and condensation with 2-hydroxy-5-nitrobenzaldehyde to produce the spiropyran-bearing MOF (figure 6).^[62] Switching of this auxiliary ligand using visible or UV light modulated the CO_2 uptake of the framework. The open spiropyran isomer boasted a higher CO_2 uptake than the closed isomer, attributed to the charges around the nitrogen and oxygen atoms in the open form which should cause a greater affinity for CO_2 .

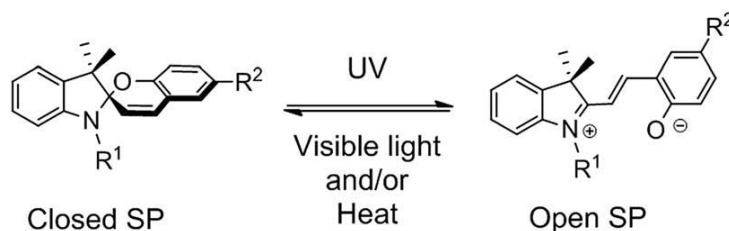


Fig. 6. Reversible isomerization between spiropyran (left) and merocyanine (right). (Reproduced with permission from [62]. Copyright © 2016, Royal Society of Chemistry).

Recently, Heinke's group conducted an in-depth study into conductance modulation in a UiO-67 scaffold with embedded spiropyran photoswitches.^[63] Although previous studies had shown regulation of conductivity upon isomerization in single molecules and self-assembled monolayers of spiropyran, utilization of these concepts in a three-dimensional material is novel and could proffer untapped potential. In addition to documenting a 10 fold spike in current upon irradiation with UV light, they also noted the relatively slower isomerization back to the closed form, performed cycling experiments and noticed a small decrease in performance between cycles attributed to the fatigue effect mentioned earlier, applied density functional theory to suggest a charge hopping mechanism of charge transfer, addressed the electron density of the

frontier orbitals and the electronic couplings to assert that the greater degree of electron coupling in the open form is spiropyran facilitates charge hopping and electron conductance. Such a detailed report provides inspiration to optimize this and similar switchable conducting materials through adjusting the distances between and distribution of spiropyran molecules. Additionally, modifications to the structure of the spiroyrans themselves should enable access to more diverse properties. For instance, the targeting of more accessible (for cheaper devices) or less accessible (more selective devices) switching wavelengths may be achievable through the addition of electron withdrawing or electron donating groups. Alternatively, increasing the disparity in conjugation between open and closed isomers could produce a larger difference in electron coupling and therefor electronic conductance.

In one intriguing, unorthodox approach, Gong et al. demonstrated a photo-activated, gas-solid reaction between structural 1,2-di(4-pyridyl)ethylene (BPE) linkers and introduced allyl alcohol.^[64] In contrast to the *cis/trans* isomerization of azobenzenes and ring opening/closing of spiroyrans and dithienylethenes, the double bond in the center of the BPE linkers undergoes a reversible, asymmetric [2+2] cycloaddition reaction with allyl alcohol. This platform behaves as a highly efficient, reusable, safe capture and release switching platform for toxic allyl alcohol. More importantly, this work promotes deeper consideration for switchable, light-controlled, reaction-based devices.

Finally, although the rise of molecular shuttles, switches, and motors has lead to a collection of mechanically interlocked materials being installed into MOFs, these either have unpredictable or uncontrollable Brownian-like motion or indistinguishable, degenerate switching states.^[92] Of late, molecular motors, capable of controllable, unidirectional motion, have been implemented into MOF systems. One such system was a light-driven rotor protruding into the MOF's pores but

covalently linked to the backbone ligand.^[65] The initial rotation utilized light stimulus however the second step required heat input. These immobilized rotor struts were capable of full, repeatable 360° unidirectional rotation. Although applicability of ‘moto-MOFs’ may not be near realization, it is easy to imagine these materials could aid in carefully controlled fluidic mass transport or gas diffusion applications, whereby the MOF scaffolding provides a base by which to eliminate and unproductive movements.

Isomerization of the three most commonly employed photoswitching molecules, azobenzenes, dithienylethenes, and spiropyrans, were described. When switchable moieties are integrated into MOFs, they can profit from sieving and protection by the framework. Additionally, MOFs can mitigate challenges such as aggregation and self-quenching by immobilizing switches in regulated distances and installation percentages. These studies have illustrated consequences of placement (structural, pendant, or guest) and functionalization of the switchable moieties, particularly regarding potential damage to the hosting framework, the wavelength of switching necessary, and steric facilitation or hindering of isomerization. The studies mentioned have explored the application of the resulting materials in the capture, storage, and/or release of gaseous molecules, pairing with a photosensitizer to generate singlet oxygen, conductivity switching, and modulation of magnetic susceptibility. Studies utilizing switchable components as part of the MOF backbone are lacking and more insight into this area would help to fill out the current literature. Inclusion of photoswitchable constituents beyond azobenzenes, dithienylethenes, and spiropyrans is one direction that this field will doubtlessly be pursued. Of particular interest would be further exploration of MOFs impregnated with photoactivated molecular motors. Molecular tweezers could in principle work well with the filtering due to MOF structures, producing stable, highly-selective capturing devices. Additionally, designing

MOFs with built in tracks for synthetic molecular walkers could produce interesting selective mass transport. “Moto-MOFs” are certain to evolve with help from the vigorous advances being made with molecular motors. Finally, although it was not emphasized, many of the MOFs discussed suffer from interpenetration, reducing the amount of pore space available for switching and effectively restricting the application potential of the material. As control over MOF interpenetration improves, studies should keep in mind these new strategies in synthesizing future switchable MOFs.

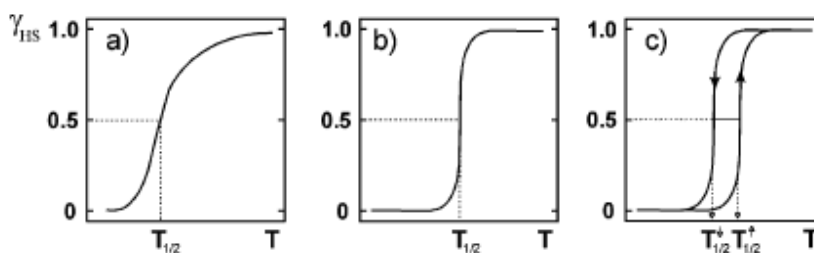
3. MOF Switching with Temperature and Pressure

Temperature is a scalar stimulus akin to light in its accessibility and prevalence in the realm of switchable smart materials. Although less accessible, pressure is another straightforward, scalar stimulus that, like temperature, is often used in conjunction with or interchangeably with other stimulus-based switching systems. For instance, the light-switchable azobenzene ligands discussed in the previous section have been observed capable of also switching with the application of heat or sufficient pressure.^[43, 54, 66] Multiplying the variety of switchable MOFs is the switchable reaction produced upon stimulation. Similar to how light-sensitive species may react by *cis/trans* isomerization, ring opening/closing isomerization, excitation of a photosensitizer, or other bond rearrangement, breaking, or formation reactions, species which are receptive to temperature and pressure may switch in the form of *cis/trans* isomerization, spin crossover, rotation around single bonds, proton transfer, and globule/coil conversions.

Compounds that are capable of spin crossover (SCO) have recently garnered significant attention. SCO describes a change in spin state common in the 3d-orbitals of octahedral metal centers with d^4 - d^7 electronic configurations and is induced by external stimuli spanning temperature, pressure,

light, magnetic field, solvent, pH, and ligand exchange. Moreover, combinations of spin states of non-degenerate metal centers can enhance the diversity of ‘states’. Materials capable of SCO are highly sought after for the development of microsensors, memory devices, data storage devices, and displays. High work density, accompanied by the ability to operate at ambient temperatures, is desirable for practical purposes.

Figure 7 illustrates three types of SCO that are commonly observed. Metal–ligand bonds are typically weaker in the HS state and the transition from LS to HS leads to a greater volume of material. As temperature increases, the fraction of HS states (γ) may increase gradually (Fig. 7a). This type of SCO is most appropriate for sensing. Secondly, the fraction of HS states may increase suddenly as temperature rises (Fig. 7b), ideal for switching applications. A final SCO profile details a sudden jump in γ with the presence of hysteresis upon subsequent cooling (Fig. 7c), appealing for the construction of memory devices, optical displays, and magnetic devices.^[67, 68, 69] Modulation of hysteresis may be accomplished using powerful intermolecular interactions such as hydrogen bonding and π – π interactions.^[69, 70, 71] SCO compounds which demonstrates thermal hysteresis at room temperature are most useful for application as memory devices.^[67] Spin states may be indirectly tracked on account of observable structural changes accompanying the spin transitions. Because electron distribution, and consequently quadrupole moment, at the nuclei changes, Mössbauer spectroscopy is a suitable characterization method for these compounds. UV/Vis, IR, and Raman spectroscopies and DSC are also appropriate methods for identification due to the variations in optical properties, bond vibrations, and heat content of the



states, respectively.

Fig. 7. Schematic illustrations of the main types of SCO phenomenon, where the y axis is fraction HS (γ , often shown as x) and the x axis is temperature (T): (a) gradual (b) abrupt (c) abrupt with thermal hysteresis. (Reproduced with permission from [67]. Copyright 2015. Royal Society of Chemistry).

The d^6 Fe(II) ion (usually in the form of $[\text{Fe}^{\text{II}}\text{N}_6]$ structures) is an ideal SCO switch with noticeable popularity in SCO research. Transitions in Fe(II) ions are frequently carried out by temperature or visible light as the energy inputs undergoing marked changes in bond distances, cooperativity, and magnetic response between the low-spin (LS) and high-spin (HS) states. The fundamental electronic states of the Fe(II) ion are given in Scheme 2. The $^1\text{A}_1(\text{t}_2\text{g}^6)$ state is a low-spin ground state while $^5\text{T}_2(\text{t}_2\text{g}^4\text{e}_\text{g}^2)$ is a thermally accessible high-spin states.

In 2011, an iron-based SCO MOF was introduced by Ohkoshi et al stimulated by light.^[72] However, *ab initio* investigation into the SCO phenomenon of this material predicted spin state transitions between the low-spin state, intermediate state, high-spin state (HS-1), and a second high-spin state (HS-2) generated by pressure or temperature. These spin state changes manipulated the bond lengths and bond angles and in turn the relative energy levels, Fe-N hybridization, and hopping interactions. However, only the transition between the low-spin and first high-spin state via temperature has been observed and so future research to realize these predicted states and transitions, or the reasons for their inaccessibility, is still necessary.

Compared to simple single-step SCO transitions with only two states, stepwise SCO possessing intermediate states enables more sophisticated control over a myriad of device technologies,

particularly in memory storage. Hofmann-type SCO-MOFs with the ability to adapt for distorted geometries may show durable intermediate magnetic phases. In fact, Jun Tao et al. obtained a 3D Hofmann-type SCO-MOF $[\text{Fe}^{\text{II}}(\text{Hbpt})\text{Pt}(\text{CN})_4] \cdot 1/2\text{Hbpt} \cdot 1/2\text{CH}_3\text{OH} \cdot 5/2\text{H}_2\text{O}$ (Hbpt = 4,4'-(1H-1,2,4-triazole-3,5-diyl)dipyridine) which undergoes incomplete, reversible, three-step SCO.^[73] Further developments and discoveries regarding MOFs capable of SCO, especially those containing multi-step SCO and SCO near room temperature, will lead to key developments in various advanced switching devices, particularly data storage and memory devices.^[67] Specifically, well-organized, multiple SCO-capable metal-containing MOFs should be surveyed in order to access enhanced cooperativity and new spin states, which would allow for the fabrication of more complicated devices without excessive escalation in costs or device size.

As stated, the application of temperature or pressure can produce several responses in switchable materials. Some of these responses generate observable properties that may seem counterintuitive. In one such case, Dan Zhao's group exfoliated and purified nanosheets of MAMS-1, a nickel-based MOF with robust bonds within a layer, with connected layers affixed to one another through individually weak van der Waals interactions.^[74] This MOF possesses two distinct, perpendicular apertures. The smaller apertures are situated perpendicular to the membrane and gated by pairs of *tert*-butyl groups whereas the larger aperture is hydrophilic and located parallel to the main body of the membrane. The permeance of CO_2 is abnormally low – lower than the smaller He and H_2 gasses as well as larger O_2 , N_2 , and CH_4 , signifying it is not due to size effects. Rather, this is attributed to the hydrophilic and “ CO_2 -philic” internal surface of the larger pores which CO_2 molecules effectively stick to, reducing complete permeation of this species. They then noticed an interesting feature of the H_2/CO_2 mixture separation. Typically, heating a material will result in expansion of the lattice and increased gas permeance according

to the Arrhenius equation. This is known as positive thermal expansion. More unusual to materials, but common in MOFs, is the opposite process whereby the material contracts upon heating, known as negative thermal expansion. It was previously demonstrated that heating of MAMS-1 enhance accessibility through the MOFs' openings through intensifying the motion of the dangling *tert*-butyl groups.^[75] Consequently, although heat-induced contraction of the framework is predicted for most MOFs,

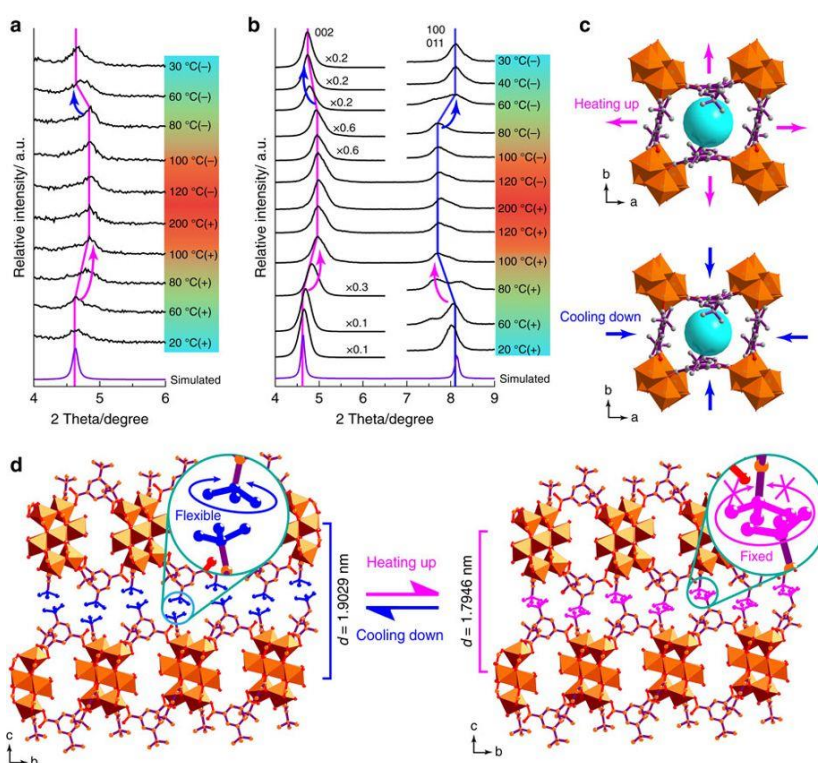


Fig. 8. PXRD patterns of (a) 2D membrane and (b) bulk MAMS-1, highlighting shifting peaks when sample is exposed to different temperature. (c) Schematic representation of expansion and shrinkage of pore space viewed along the *c*-axis during heating and cooling. (d) Schematic representation of expansion and shrinkage of pore space viewed along the *a*-axis during heating a cooling, with the discrepancy in freedom of rotation of pendant *t*-butyl groups emphasized. (Reproduced with permission from [74]. Copyright 2017, Springer Nature Publishing AG).

energizing of these functional group via heating may act counter to the gas permeation influences of this effect. They found that the lattice expands in the *ab* plane with heat input but that the interlayer distances contract in the *bc* plane. Rather than movement of the *t*-butyl groups being enhanced, the contraction of the lattice forces these species closer to one another, effectively reducing available space for movement. Overall, while the CO₂ permeance remains relatively constant, this fact results in a material capable of controllable, cyclable H₂ permeance and hence a temperature-dependent separation factor. Elaboration into materials with multiple gas permeation pathways, structural flexibility, and additional performance from pendant groups is an interesting manner to expand the already vast tunability of MOF separation membranes.

In an alternative approach, the benefits of thermoresponsive polymers can be endowed through appendage onto a MOF's surface. Nagata et al. affixed the heat-sensitive PNIPAM polymer to a UiO-66 base.^[76] Below the critical temperature, or the cloud point T_c , of 32 °C, PNIPAM adopts a coiled conformation and above this temperature, the coils collapse into a less ordered globule conformation. Contraction into the globule form acted as enough of a physical diffusion barrier for UiO-66-PNIPAM to be used as a temperature-dependent storage/release of organic guest molecules resorufin, caffeine, and procainamide up to three cycles without change to the release behavior. Notably, UiO-66-PNIPAM could not entrap larger molecules like protoporphyrin IX however PNIPAM modification of MOFs with larger pores may be able to fill this hole.

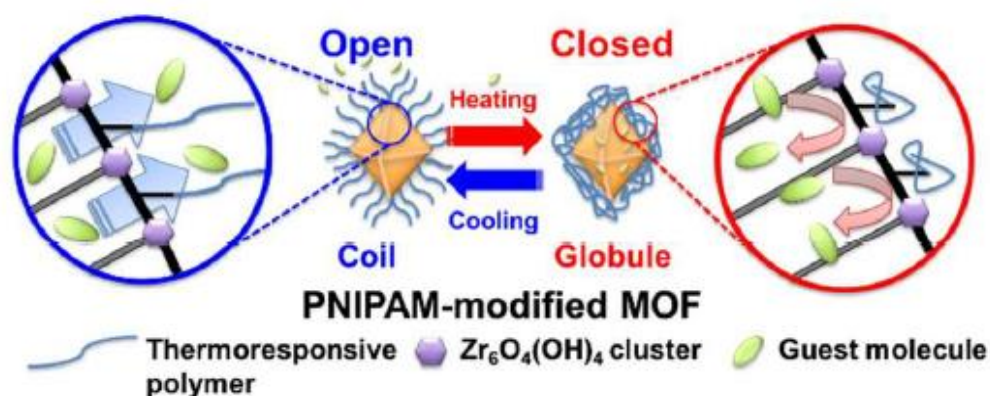


Fig. 9. Schematic showing PNIPAM-modified UiO-66. At lower temperatures, PNIPAM adopts a solvated, 'coiled' conformation, allowing for guest molecule diffusion into and out of the MOF (left). At higher temperatures, PNIPAM adopts a globule conformation, closing off the pores of the MOF, effectively trapping the internal guest molecules. (Reproduced with permission from [76]. Copyright © 2015, Royal Society of Chemistry).

Appliance of pressure to MOFs rarely yields reversible reactions and when it does, it is almost exclusively in the form of amorphization or single-crystal-to-single-crystal transformations. Therefore, reversible bond formation/breaking or rearrangement in response to pressure are novelties lacking in investigation. Another rarity mentioned previously are switching moieties incorporated as essential structural components in MOFs, which often results in the loss of switchability due to the overall stiffness imparted by integration into a crystalline network. Switching can disrupt the structure enough to result in collapse or damage. Therefore, evidence of switching with integral ligands with maintenance of crystallinity are notable. In one instance, PCN-250 was shown capable of sequential phase transformation by isomerization about the azo bond in a structural azobenzene ligand.^[66] Two derivatives of PCN-250 were isolated after 19 MPa and 150 MPa of applied pressure displaying different ratios of switched/unswitched azobenzene ligands and volumetric CH₄ uptakes.

Ortiz et al. reported on a zinc alkyl gate (ZAG) MOF, ZAG-6, a wine rack motif framework composed of Zn clusters and 1,6-hexanebisphosphonate chains.^[77] Naturally, this organic species adopts an uncoiled chain conformation. Compression via pressure induces a structural transition in this ligand to a coiled chain in concurrence with a reversible proton transfer between a phosphonate group and a guest water molecule. Moreover, the relative enthalpies of the coiled ligand with neutral guest water molecules and the coiled ligand with protonated guest water

molecules are similar enough to suggest that this proton is fairly delocalized in this conformation, making ZAG-6 a candidate as a switchable proton conductor.

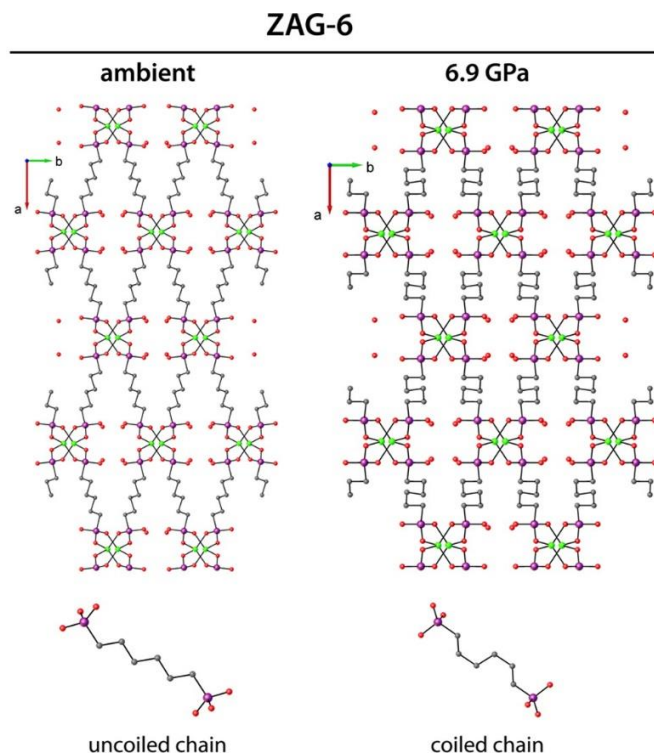


Fig. 10. Structure of ZAG-6 at ambient (left) and pressurized (right) conditions with the difference in organic linker conformation accentuated below. (Adapted and reproduced with permission from [77]. Copyright 2014. American Chemical Society).

Pressure and temperature are interesting stimuli partially due to the various occasions in which they arise. In some industrial processes, failure of pressure-relieving mechanisms or unplanned for accumulation of heat can be dangerous. Smart materials with switch-off capabilities may work to prevent further build-up (as in the case of thermal runaway) and minimize damage to surrounding components. Therefore, although these switching cases may be secondary functions, such safety features can easily be envisioned as essential to meet industrial standards or consumer expectations in the near future.

4. MOF Switching with Redox

Redox switches are capable of switching between two redox states upon the addition or removal of electrons.^[24, 78, 79] For redox switches to prove useful, the on and off states should be structurally distinctive with sufficiently distinguishable characteristics for detection,^[79] most often through variations in the geometry and/or the electronic configuration of the compound.^[24] To assure reversibility, the oxidation and reductions should not be so harsh that the coordination bonds between the ligands and metal clusters suffer and are unable to rejoin to yield the original structure.

Redox switching on the structural ligands in MOFs should occur while maintaining structural integrity and crystallinity.

In one successful example of a redox-induced switchable MOF, a Zr-oxo MOF, UiO-68-OH, possesses hydroquinone ligands that are oxidized to quinone ligands by addition of iodobenzene diacetate.^[80] During this process, the colorless MOF crystals transform to yellow crystals, with a visibly observable core-shell intermediate, and a fluorescence shift from blue to mostly nonfluorescent. The switching cycle could be completed through oxidation by ascorbic acid back to UiO-68-OH for up to three cycles. Similarly, TMU-34, a Zn-based MOF was exposed to an extensive range of volatile organic compounds (VOCs) comprising methanol, ethanol, formaldehyde, acetone, formic acid, acetonitrile, chloroform, bromoform, dichloromethane, diethyl ether, tetrahydrofuran, *n*-hexane, toluene, xylene, and styrene.^[81] Astonishingly, only chloroform produced a color change (from yellow to pink) perceptible by the naked-eye, which was attributed to oxidation by chloroform of the V-shaped H₂DPT ligands to planar DPT ligands.

The quick response time, low detection threshold, and selectivity in the presence of other VOCs position TMU-34 as a promising colorimetric chloroform sensor requiring no extraneous instrumentation.

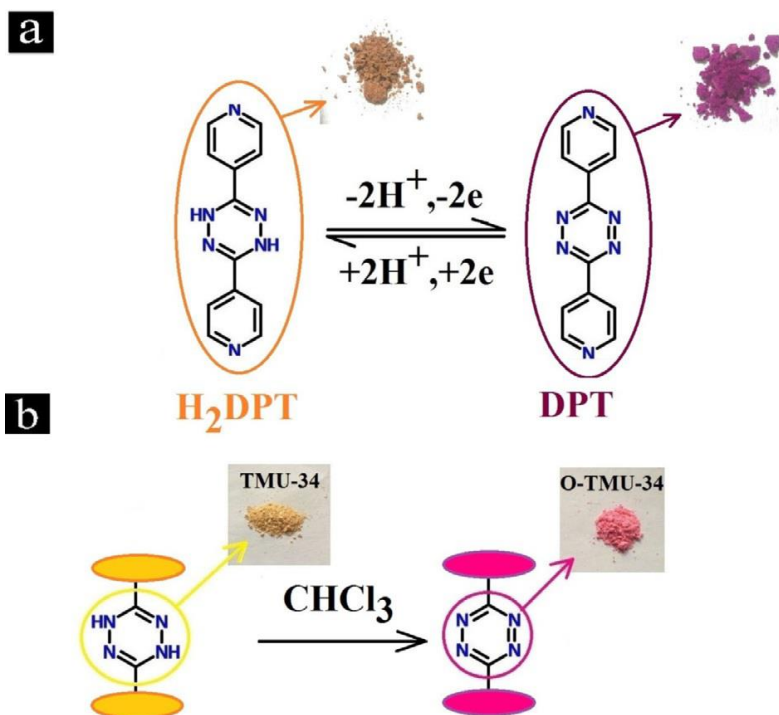
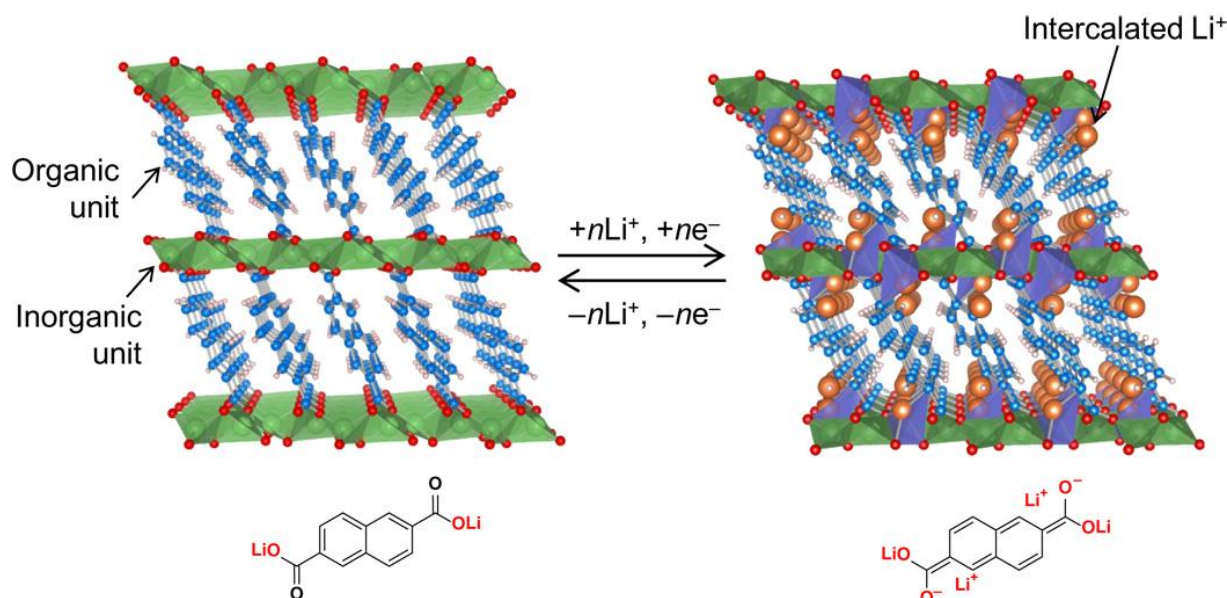


Fig. 11. (a) Switching of H₂DPT to DPT upon oxidation. (b) Images illustrating the visual changes of TMU-34 from a yellow color before addition of chloroform as an oxidant to a pink color in O-TMU-34 after oxidation. (Reproduced with permission from [81]. Copyright © 2017, John Wiley and Sons).

Disruption of essential metal-ligand coordination bonds in MOFs is a less explored manner of redox switching in MOFs owing to the risk of structural collapse associated with this method. Nevertheless, Ogihara et al. reported a MOF with switchable electronic conduction whose switching behavior is controlled through reversible Li intercalation.^[39] The introduction of these lithium species provides an additional electron hopping pathway while maintaining structural integrity, thermal stability, and ionic conductivity. These results are informative to the pursuit of

safer battery electrodes with shutdown functions. This reversible intercalation of lithium is reminiscent of lithium intercalation into graphite anodes in lithium ion batteries. Since lithium dendrite formation is one of the greatest restraints to lithium battery improvements, it may be



fruitful to investigate how these mechanisms of intercalation differ, and whether MOFs like this could provide a protective coating on the anode to temporarily store lithium ions, preventing build up and subsequent dendrite formation while the high porosity of MOFs may still allow for efficient lithium-diffusivity to and away from the anode.

Fig. 12. Illustration of reversible lithium intercalation between organic linkers and inorganic units in 2,6-Naph(COOLi)₂. (Reproduced with permission from [39]. Copyright 2017, AAAS.)

With recent advances in understanding the biological relevance and programmability of DNA-switches, DNA-modified MOFs as a means to endow switchability could soon become more popular and practical. Kahn et al. explored the various applicability of three DNA/MOF hybrids loaded with rhodamine 6G, differing in regards to the DNA sequences appended to the MOF

surface: i-motif, triplex DNA nanostructures, or G-quadruplex DNA.^[82] i-motif DNA-modified MOFs were reversibly pH responsive, in which a pH of 5.5 coiled the DNA around the MOF, withholding the internal dye cargo, whereas a pH increase to 7.4 dissociated the organization of these DNA strands, releasing the cargo. To postulate the applicability of DNA/MOF hybrids, K⁺-stabilized hemin/G-quadruplex/MOF composites were synthesized. This complex was shown to catalyze the oxidation of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid). Upon the addition of 18-crown-6-ether to remove the coil-stabilizing potassium cations, the catalytic ability of this system is switched off. This study suggests DNA-functionalization of MOFs as an easy way to apply switchability for applications such as turn on/off catalysis and control guest uptake and release devices.

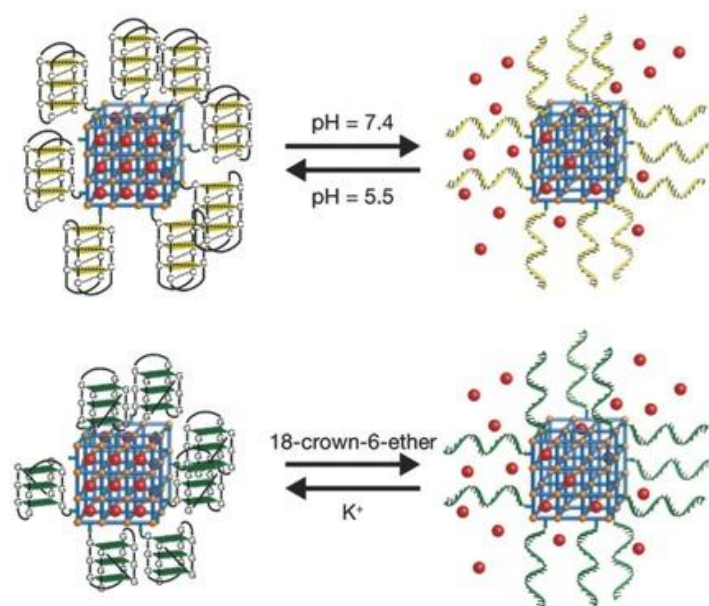


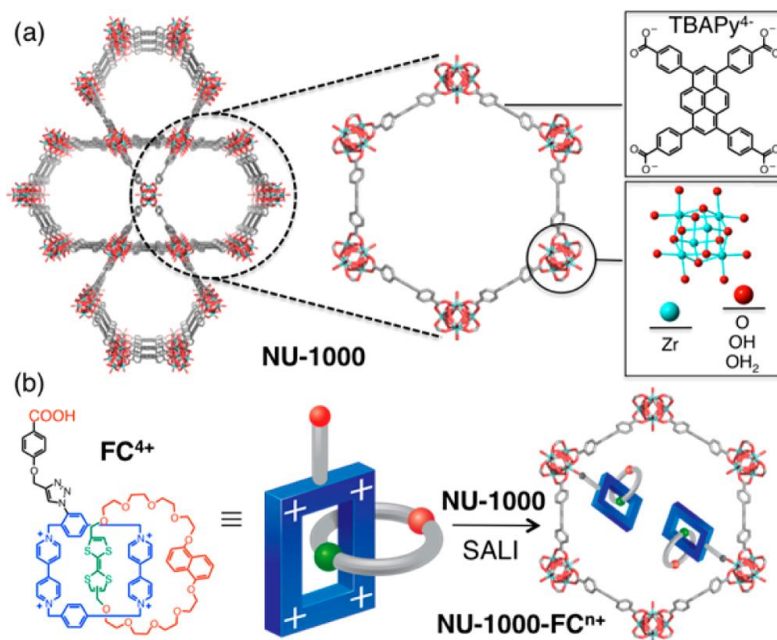
Fig. 13. Illustrated depictions of pH and K⁺ switching in an i-motif gated MOF and a G-quadruplex gated MOF. (Reproduced with permission from [82]. Copyright 2017, John Wiley and Sons).

Bistable mechanically interlocked molecules (MIMs) have unique abilities in redox switching applications. Although the random movements of most switchable MIMs in solution lead to a net zero switching, the highly ordered spaces in MOFs are ideal platforms to host MIMs for organized and unidirectional movement.^[83] Rotaxanes and catenanes are two of the most popular and well-developed MIMs. Rotaxanes are mechanically interlocked molecules consisting of a macrocycle threaded through an axis terminated on both ends by a bulky group to prevent unthreading of the macrocycle. This ring can shuttle reversibly between two or more positions along the axis and convert electrical or chemical stimuli to mechanical energy. Catenanes are mechanically interlocked molecules composed of two or more interlocked macrocycles. These rings can be controllably rotated relative to one another through redox-active functional groups. Additionally, the presence of weak interactions such as hydrogen bonding in each of the two states often results in changes in chemical and physical properties.^[24, 84, 85]

Hupp et al. realized that sufficient pore space exists within NU-1000 for the post synthetic installation of and proper operation of a functionalized, redox-activated [2]catenane, FC^{4+} with two nondegenerate switching states.^[85] Inclusion into a MOF scaffold acts to eliminate cancellation of work due to random motion, the spacious pores of NU-1000 are well-suited for retention of their switching capability after incorporation, and the use of post synthetic installation allows for a more diverse array of switchable moieties to be used. The highly organized incorporation of a bistable MIM into the highly stable NU-1000 with the preservation of activity is an important step towards the development of new electronic devices to make use of molecular motors while protecting them from threats of external degradation.

In another case, Zhang et al. designed a 3D polyrotaxane framework, $\{[Eu(BA)(Bpybc)_{1.5}(H_2O)] \cdot 2NO_3 \cdot 5H_2O\}_n$, (HBA = benzoic acid, $H_2BpybcCl_2$ = 1,1'-bis(4-

carboxybenzyl)-4,4'-bipyridinium dichloride), that showed reversible photochromism and



luminescence modulation.^[86] UV light irradiation of the framework produces a deep blue color likely due to the formation of viologen radicals. Subsequent oxidation of the framework via exposure to oxygen converts this reduced, radical “off” state to the neutral, bleached “on” state (scheme 3). This example highlights the potential for future MOF structures to themselves act as the novel molecular motors on a supramolecular scale.

Fig. 14. (a) The structure of NU-1000 composed of tetratopic carboxylate ligands and Zr₆ clusters with emphasis on the large pore area (carbon atoms are gray, oxygen red and zirconium blue). (b) Chemical and cartoon structures of [2]catenane FC⁴⁺ as well as NU-1000-FCⁿ⁺ produced after solvent assisted linker installation. (Reproduced with permission from [19]. Copyright 2016. American Chemical Society).

The development of MOFs capable of controlled redox reactions or MOFs as suitable hosts for redox-active molecules via post-synthetic modification make them appropriate for the design and

construction of novel molecular switches in applications such as nanoelectronics,^[87] molecular machines,^[24] drug delivery,^[78] and energy storage devices.^[88]

5. MOF Switching with Guests

Guest molecules are an easy to implement stimuli for switching. However, in most studies, guest molecules inhabiting MOF pores are handled like impurities to be removed before application or characterization.^[89] In spite of this, MOF electronic, magnetic, and scintillation properties can be incredibly susceptible to their internal environments and hence the guests inhabiting them should be treated as an additional dimension of tunability. In terms of switchability requirements, guest interactions with the MOF host should be relatively strong, reversible, and alter or create new properties by virtue of their infiltration.

The majority of SCO compounds are non-porous – freeing the way for MOF contributions to the field. Porosity allows for easy electronic state perturbations through absorption of guest molecules as well as potential for sensing- or capture-based applications. In one instance, a Fe(sal₂trien) moiety was introduced into a MIL-100(Al) framework.^[90] This Fe(sal₂trien)⁺ species shows solvent-dependent spin states at room temperature, correlating principally with the degree of interaction with said solvent via hydrogen bonding. It was observed in the EPR spectrum, absorption spectrum, and magnetic properties that dehydration amplifies the fraction of high-spin: low-spin states in the MOF. Modulating the spin states of a porous material using a solvent such as water is a step toward cheaper, greener, more accessible, switchable SCO complexes.

With a wider scope of considered guest molecules, Southon et al. examined $[\text{Fe}^{\text{II}}(\text{pz})\text{Ni}^{\text{II}}(\text{CN})_4] \cdot x\text{Guest}$, a material capable of bistability at room temperature.^[91] From analysis of the adsorption of water, methanol, ethanol, acetone, acetonitrile, and toluene, a few conclusions were drawn. First, it was noted that inclusion of larger guests could more affectively suppress the switching transition. Second, steric bulk considerations are the dominant factor in the resulting SCO temperature. As the temperature of the system falls, the kinetic dimensions of the guest also decrease, leading to weaker interaction with the host. At a certain point, guests are small enough so that crossover at the metal centers would reoptimize the interactions with the guests and minimize the overall energy of the system. Third, the mechanistic conclusion drawn from this system is unique in that the temperature of SCO is primarily motivated by the degree of host-guest interaction energy rather than stabilizations to spin states directly by the guest molecules. Fully reversible guest adsorption in this framework produces interesting memory effects with step-wise pseudo reversibility. Within the framework's bistable temperature, the MOF in the high spin state can be converted to the low spin state configuration through introduction of acetonitrile. Interestingly, removal of the acetonitrile leaves the evacuated framework in its low spin state. Although the framework can then be returned to the high spin state by a similar procedure using acetone as a guest, this resulting effect can itself be a useful magnetic function. At 310 K, this memory process can proceed alternatively from the low-spin MOF with acetonitrile guests, to the evacuated high-spin form, and then to the high-spin MOF with acetonitrile guests. Regarding future studies, the authors wisely suggested that further study into more than just the size of the guest (the shape and orientation for instance) and its effect on responsive SCO MOFs. After these prerequisites are investigated, it would also be interesting to consider the polarity and electronegativity of the guests in order to develop more complicated

frameworks capable of SCO responses based upon host-guest interaction energies as well as variations in spin-state energies induced by guest molecules.

Steric and electronic considerations are also both possibilities with guest-induced luminescent switching in MOFs. In a silver MOF possessing tpe ligands, it was learned that the presence of dimethylacetamide molecules restrict the eight rotors present in the tpe ligands.^[91] As the MOF is exposed to the atmosphere, DMAC molecules slowly exit the framework, freeing up the tpe to adopt various conformations and producing a reversible change from blue to yellow fluorescence. To verify this inference, the fluorescence characteristics with DMF, THF, toluene, and Et₂O were also examined. Variances in polarity of the guest molecule demonstrated inconsequential effect on the fluorescence. However, disparities in switching rates were observed and were correlated to the varying boiling points of the guests. The influence of larger or smaller guests was not discussed – which could prove interesting considering the conclusion that restriction of tpe rotations are the origin of this MOF's switchable fluorescence.

In contrast to guest-induced adjustments to fluorescence, guests have additionally been utilized to tune phosphorescence of MOF frameworks. Although phosphorescence is frequently studied with rare-earth or noble metal-containing MOFs, the anionic MOF AMOF-1 initially demonstrates green phosphorescence due to MLCT from the cadmium-containing SBUs to the organic linkers and initial (Me₂NH₂)²⁺ guest molecules.^[93] Metal-cation doping in this MOF produces marked adjustments in phosphorescence emission wavelengths and emission intensities due to the introduction of additional, intermediate energy levels to or by which charge density from the Cd²⁺ or π -density from the ligand phenyl rings can transfer or be quenched, respectively. Due to the extreme difference in phosphorescence intensity before and after Cu²⁺ doping, AMOF-1 could function as a Cu²⁺-sensitive switch. MOF-5 is another framework shown to

possess highly controllable phosphorescence with pyridine guest-based switching behavior.^[94] Within the relatively large channels of MOF-5, pyridine and TPA ligands interact in a π - π manner, increasing the wavelength of the emitted luminescence. Facile pyridine guest removal was accomplished through simple heating of the sample to 50 °C, returning the framework to its original color.

Guest-MOF materials can be difficult to understand and analyze due to their understudied possession of supramolecular identity in communication with molecular identity.^[89] Guests may encourage a MOF to switch through maximization of interactions between the two or through the introduction of intermediate energy states to accept or donate charge density. Generally, guest studies have focused on a limited selection of solvents or cations. The next step in understanding these interactions is to observe guest interactions in variable pore environments and defect extent. Additionally, long term-studies regarding guest-filled MOFs exposed to ambient conditions are necessary to understand passive escape or replacement of guests.

Conclusion

Herein were discussed the general design, mode of operation, and applications of switchable MOFs.

The installation of switchable moieties as integral, pendant, or guest species were briefly compared with an emphasis on maintenance of switchability and host integrity. Light, temperature, pressure, redox, and guests were highlighted by cause of being among the more common investigated stimuli for MOF-based switching. However, more unconventional stimuli, such as application of a potential, do exist but their resulting switching mechanisms are currently more obscured.^[34, 36]

Pursuing the development of MOFs with switchable processes offers valuable opportunities ascribed to their highly crystalline, and hence characterizable, tunable structures. Meticulous selection of central MOF components such as organic linkers and metal SBUs, synthetic conditions to promote an assorted array of porosity, topology, and organization, and post synthetic modifications from an actively expanding toolkit position MOFs as a pliable platform to fit a grand collection of applications. These components may work individually or in concert when exposed to precise stimuli generating the switching activity. Conversely, these adaptable properties have earned MOFs a disparaging reputation as a 'jack of all trades, master of none'. In their current state, this may very well be the case. However, with the ever-expanding levels of tunability, including the successful imbuing of switchable behavior with a wide scope of stimuli, is further placing MOF and MOF composite materials as undeniably valuable multi-functional smart materials. Only time remains in the way of determining whether MOFs will bloom into a go-to material for practical purposes or whether limitations in synthesis, such as difficulties in obtaining single crystals or processing of some MOFs into films or monoliths, stability, which typically requires the use of a limiting selection of metals and coordination groups to reinforce, and properties, as is seen in the intricacy involved in developing electrically conductive MOFs, a recently more confronted issue that fights against the directionality of metal bonds to generally redox-inactive ligands, could in some way be inherently insurmountable.

Switchable MOFs are promising compounds for many applications requiring separation and purification of gas mixtures or highly efficient gas sorption. Other methods to accomplish these tasks may depend on vacuum or heating. In juxtaposition, the use of inexpensive, less energy demanding, and accessible stimuli like sunlight in porous MOF-based systems make them very valuable compared to other methods. In addition, design of systems aimed at the adsorption and

release of guest molecules under the influence of external stimuli provide potential applications in drug-delivery, adaptable surface coatings, optical, electrical, memory and magnetic devices. Although multiplicity in stimuli for a single MOF is one future course leading to multifunctional materials reminiscent of gel and other supramolecular assembly counterparts and can also be interesting from a curiosity standpoint, reliable control of switchability in a more practical perspective may require fine-tuning to assure only a single, specific stimulus can enact switching and to eliminate unintentional switching. Further insight into the role of framework topology, concentration of defects, and interactions between multiple switching moieties within a single framework would enable more informed engineering of MOF materials. Understanding of these fundamental behaviors may avoid extensive loss of time and resources chasing new applicability, putting the cart before the horse so to speak. Limited research has been devoted to these less glamorous, yet promising avenues and systematic investigations that further the understanding of the meaningful relationships between structural aspects and resulting behavior in turn will facilitate the expansion of productive, controllably switchable MOF materials.

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