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Review

The lighter side of MOFs: structurally photoresponsive metal–organic frameworks.

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Metal–organic frameworks (MOFs) have emerged over the past two decades as highly promising materials in the gas storage and separation arenas, with the potential to act as rapid uptake/rapid release sorbents for CO_2, CH_4 and H_2 that may have significant impact in energy and sustainability technologies. However, a small but growing subset of the MOF community have been developing alternative, light-induced applications of MOFs. This review briefly outlines some of these exciting diversions from the 'traditional' applications of MOFs and focusses particularly on the design strategies of those frameworks that undergo photoinduced structural change. These strategies are classified as either i) the imposition of photoresponsivity by a photoresponsive guest; ii) post-synthetic modification (PSM) of frameworks to add in photoresponsive groups; iii) synthesis of MOFs with linkers that support pendant photoresponsive groups; and, perhaps the most challenging, iv) synthesis of MOFs from linkers that themselves have intrinsic structural photoresponsivity such that their structure is altered on illumination. Examples are given of each approach, future applications are proposed, and strategic pathways to next-generation photoresponsive frameworks are discussed.

Introduction

Commonly cited for their excellent gas storage capability,[1-13] reports of new and modified microporous metal-organic frameworks are increasingly focussing on their more niche properties, that allow them to truly be described as stimuli-responsive functional materials.[14] Interest in previously neglected properties such as mechanical behaviour,[15-19] defects,[20-25] and surface behaviours[26-29] is growing rapidly. It is in this context that this review seeks to further divert attention from the vast corpus of porosity and gas sorption literature (estimates of the number of published MOF articles ranges from ~30,000 upwards)[‡] towards a smaller, but by no means insignificant subset of these fascinating materials: those that are photoactive.

Photoactive frameworks have been reported with potential applications as luminescent sensors for small molecules,[30-47] photochromic and thermochromic materials,[48,49] ion sensors,[46,50,51] metal-extraction materials to make "solar energy converters" that evolve hydrogen,[52] photoactive matrices for the generation of metallic microstructures,[53] photocatalysts,[54,55] semiconductors[56] and two-photon patterning hosts.[57] Broadly, we can identify five categories of photoactive frameworks. The first and largest of these is simply MOFs that demonstrate interesting or useful absorption and luminescence properties, but do not involve a significant photoinduced *structural* rearrangement. Luminescent MOFs have been reviewed several times in recent years[58-61] and therefore only brief examples of the most significant areas in which some of these materials may find application will be given here. Within the category of 'static' luminescent framework materials are also composite examples of encapsulation of luminescent chromophores and dyes in MOFs that rely on the typically disordered uptake of photoactive guests into frameworks,[47,62] but those that are not structurally photoresponsive are outside the scope of this review.

The remaining four categories describe frameworks that undergo a structural change on photoirradiation; a property that, in a recent MOF review of more broadly stimuli-responsive MOFs, Coudert neatly terms "photoresponsivity".[14] The term photoresponsivity incorporates the concept of going beyond simple photoluminescence or photoinduced energy/electron transfer processes to exploit the intrinsic structural functionality that is afforded by well-designed framework host materials. The motivation of this review is primarily to highlight the design strategies of the four categories of *photoresponsive* framework. The categories are: **i)** frameworks that have had structural photoresponsiveness imposed on them by the adsorption of a photoresponsive guest; **ii)** frameworks that have been post-synthetically modified (PSM) from a non-photoresponsive form to one that contains a structurally photoswitchable moiety; **iii)** materials in which photoinduced structural change is caused by a chromophore or moiety pendant to the framework linker (*i.e.* not directly involved in framework connectivity; although, of course, the steric bulk of a pendant group can affect the topological outcome of a MOF synthesis); and, perhaps the most interesting category, **iv)** MOFs containing a

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photoresponsive linker which causes a marked structural change on photoirradiation. Key examples of each design strategy to make these new functional materials are given, along with potential applications and developing techniques for the characterisation of these fascinating materials.

'Static' luminescent MOFs and their applications: a brief perspective

There have been numerous reports of luminescent coordination polymers and coordination networks over the last 15 years, with one of the first examples explicitly describing the absorption and emission properties of a metal-organic framework by Chen *et al.*, who reported the primarily ligand-based emission between 400 – 600 nm of the $[Zn(bpy)_2(BDC)]_\infty$ framework (bpy = 2,2'-bipyridine, BDC = 1,4-benzenedicarboxylate).[63] Since then, a burgeoning literature has extensively described luminescent frameworks and their applications, most commonly as sensors for small molecules. Reviewing these articles reveals that approximately half describe primarily organic linker-based emissive behaviour, just over a quarter describe emission due to transition metal-based excited states and the remainder exploit lanthanides as their primary photoactive component.[§] Despite the relative paucity of this field when compared with the whole MOF body of literature – over 5000 articles on MOFs have been published in 2015 alone[§§] – the number of examples of structurally static, luminescent MOFs significantly outweighs all the structurally photoresponsive materials described below, which combined make up less than 20 examples.

Several important applications of emissive frameworks have arisen in the field, primarily based around luminescent sensing of guest species that are adsorbed by the frameworks. The largest subset of these sensors is the detection of high explosives and nitroaromatics.[30-41] Other notable examples include: exploitation of an $[In(OH)(BDC)]_\infty$ framework (BDC = 1,4-benzenedicarboxylate) as an artificial 'nose' to detect chemical odorants (e.g. cinnamon, vanillin and cumin) by emission changes on adsorption into the porous, hexagonal, rod-like structure;[43] the use of the copper-based MOF, Cu-TCA (H_3TCA = tricarboxytriphenyl amine), to detect NO, an important biological small molecule, in aqueous solution and in living cells;[44] the MOF $[Cd_3(L)(H_2O)_2(DMF)_2]_\infty$ (L = hexa[4-(carboxyphenyl)oxamethyl]-3-oxapentane) reported in 2012, based on a Cd_3-containing node, that acts as an acetone detector;[45] the exploitation of the characteristic emission of Eu^{3+} in 2014 in a $[Eu(bpydb)_3(HCOO)(\mu_3\text{-}OH)_2(DMF)]_\infty$ framework ($bpydbH_2$ = 4,4'-(4,4'-bipyridine-2,6-diyl) dibenzoic acid) for the sensing of small organic molecules and inorganic ions;[46] also in 2014, the adsorption of Tb^{3+} ions into both CPM-5 and MIL-100(In), MOFs based on In-nodes and the BTC ligand (BTC = 1,3,5-benzenetricarboxylate), yielding materials that act as luminescent oxygen sensors;[47] and, in an interesting variation on the simple perturbation of emissive properties by guest adsorption, in 2010 a detection system for Cu^{2+} ions was reported which employed a Zn^{2+}-based MOF that can undergo transmetallation, replacing Zn^{2+} ions with Cu^{2+} and resulting in a strongly photoluminescent framework.[50] While this final example arguably undergoes a form of structural change with an accompanied change in photoresponse, it is not actually light-driven.

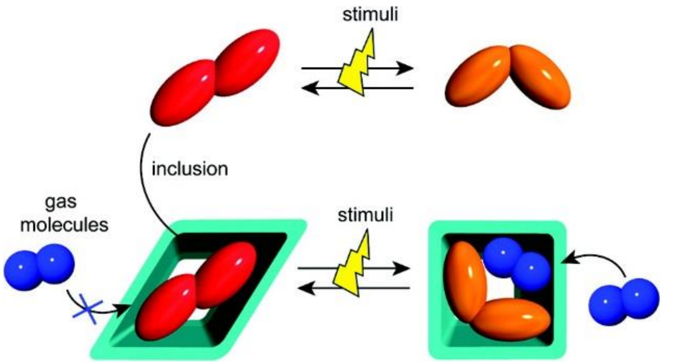


Fig. 1 Schematic illustration of the inclusion of *trans*-azobenzene (*red*) into the $[Zn_2(BDC)_2(\text{triethylenediamine})]_\infty$ MOF and subsequent light-induced isomerisation to the *cis*-isomer (*orange*) with accompanying porosity and framework structural changes. Reprinted with permission from ref 72. Copyright 2012 American Chemical Society.

Of the other applications listed in the introduction, one of the most intriguing is the use of MOF-5 as a single-crystal matrix in which photopatterning with a laser can be used to convert the Zn_4O nodes into larger Zn_4O_{13} clusters within single crystals via a multiphoton absorption process.[53] The zinc oxide clusters thus formed act as quantum dots, nanometre-sized semiconducting particles with inherent photoactivity and potential for applications in solar cells,[64-67] light emitting devices[68-70] and as photocatalysts.[71] In this instance, the framework is essential as the terephthalate linker units act as antennae to enable effective energy transfer between nodes. This irreversible process, reported in 2011 by De Vos *et al.*, is an ingenious approach to the formation of a nanoscale patterned functional material.[53]

Structurally photoresponsive frameworks

i) Structural change imposed by photoactive guests

The strategy herein is to take an existing MOF and load it with a guest that acts as the photoresponsive species. Irradiation then imposes a material property change that results from guest structural change and, in the most advanced examples, concomitant framework structural alteration.

Possibly the most famous of these materials is that reported in 2012 by Kitagawa *et al.*, who loaded the host framework $[Zn_2(BDC)_2(\text{triethylenediamine})]_\infty$ with azobenzene in the *trans*-configuration at 120°C, removing excess *trans*-azobenzene under reduced pressure.[72] The empty framework has a tetragonal 'square-grid' structure that distorts to an orthorhombic net on inclusion of *trans*-azobenzene (Figure 1); a similar distortion is observed on loading the framework with benzene. On irradiating the *trans*-azobenzene *in situ*, it undergoes partial isomerisation to *cis*-azobenzene (*cis*/*trans* ratio of 38:62) and forces an incomplete host framework structure change, such that a proportion of the structure is

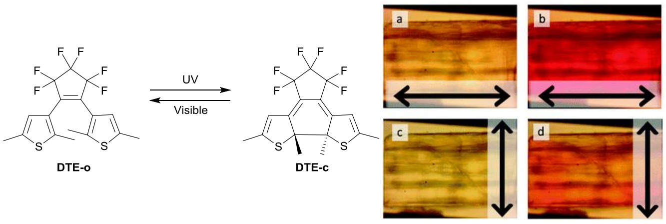


Fig. 2 *Left:* Photoisomerism of diarylethene (DTE) from the open form (DTE-o) to/from the ring-closed form (DTE-c). *Right:* Polarised light images of the MOF single crystal containing **DTE** before (a, c) and after (b, d) irradiation with 365 nm light (arrows indicate plane of polarisation). Adapted from ref 74 with permission from The Royal Society of Chemistry.

once again in the tetragonal crystal system (see schematic Fig. 1). Extending the irradiation time increases both the proportion of *cis*-azobenzene and the proportion of the structure in the tetragonal configuration, and the irradiated state is stable on a timescale of months, rather than the days seen for *cis*-azobenzene in solution. Most importantly for gas-storage applications of this approach, the porosity and N_2 uptake of the host material is significantly lower when the guest is in the *trans*-form than when the photoisomerisation has occurred.

Notably in this example, the control experiment was to incorporate *cis*-stilbene into the framework, which retained its tetragonal structure on guest inclusion, helping to confirm the structural assignment of the photoswitched MOF$\supset$azobenzene inclusion compound. In a subsequent report in 2014 by Glebov *et al*., an alternative, larger pore framework was used for the incorporation of *trans*-stilbene, and the photochemistry of the supramolecular inclusion compound studied.[73] The quantum yield of *trans-cis* photoisomerisation of stilbene in the MOF was comparable to that observed in solution (~0.2) and significantly higher than that of solid *trans*-stilbene, but no significant framework structure change was observed, highlighting the importance of commensurability between guest molecule and host pore sizes if such a change is desired (e.g. to control material porosity).

An alternative chromophore type that has been employed to induce material photoresponsivity in MOFs are diarylethenes, exemplified in Figure 2 (*left*).[74] These photochromic compounds undergo a bond-forming reaction on exposure to UV light, which can be typically reversed by irradiating with visible light. This photoreversible behaviour makes them particularly interesting as a photoswitchable unit, due to the entirely 'non-contact' nature of the driving force for structural change. Furthermore, one can envisage sunlight as the energy source for this change, with suitable optical filters used to switch between UV and visible solar irradiation.

In 2013, Benedict *et al.* described the formation of a MOF inclusion compound based on the same framework employed by Kitagawa, $[Zn_2(BDC)_2(\text{triethylenediamine})]_\infty$, but instead loaded the MOF with the diarylethene DTE-o (Figure 2, *left*).[74] Irradiation of fully loaded single crystals results in an immediate colour change from pale yellow to dark red, with the coloured crystals showing a strong linear dichroism consistent with the formation of the ring-closed DTE-c form with its long-axis aligned towards [001] (Figure 2, *right*). Unfortunately a single-crystal X-ray structure could not be obtained, even with such aligned guest molecules; a problem ascribed to both inhomogeneous filling and positional disorder of the guest. The photoconversion could be reversed using visible light and cycled with moderate success, although a small proportion of the DTE-c form remained even after prolonged visible light excitation.

In related work, Laedwig and co-workers took the same approach but with a different type of material – a "porous aromatic framework", PAF-1.[75] Describing in 2015 the inclusion complex of PAF-1 and diarylethene, the ability to photoswitch the uptake of CO_2 was demonstrated, whereby under irradiation CO_2 is desorbed rapidly but in the dark CO_2 can be readily adsorbed into the material.

ii) Post-synthetically modified photoresponsive frameworks

A relatively straightforward strategy to incorporate photo-functionality into a framework material would appear to be to take an existing framework and synthetically modify it to add a chromophore. However, this is technically challenging as there are often non-trivial issues with incomplete modification or with disorder in the PSM product framework. One of the key examples of this approach that demonstrates these issues nicely is that of Long *et al.*, who in 2007 described their modification of the well-studied $[Zn_4O(BDC)_3]_\infty$ framework.[76] Exploiting the terephthalate aromatic rings as binding sites, they heated chromium hexacarbonyl and the MOF together in a sealed tube to yield a modified framework in which $[(\eta^6\text{-arene})Cr(CO)_3]$ piano-stool complexes had been formed. The same approach was partially successful for the incorporation of $Mo(CO)_6$. While it was possible to obtain infrared spectroscopic evidence of the PSM product, and indeed of photoproducts of photoinduced CO dissociation in the presence of N_2 or H_2, the inherent disorder of the arene binding sites, even at an apparent 100% loading of Cr (calculated by acid-digestion of the MOF and recording NMR spectra of the metal-coordinated linker), makes obtaining a crystal structure of the PSM product impossible.

An alternative approach is to use light to perform the post-synthetic modification process, yielding a photoactive PSM product framework. We have already briefly described the photopatterning of MOF-5 to yield entrapped quantum dots within the MOF,[53] and in the next section we will describe a framework that demonstrates a similar photoinduced-PSM strategy to yield a luminescent framework.

iii) Frameworks with photoresponsive pendant groups

The common design strategy in this section is the utilisation of linkers that are best described as containing a photoactive moiety that is not a necessary component of the framework linkages, most evident in the examples that contain pendant groups. The advantages of this strategy over the guest-incorporation approach are clear – the photoactive moiety is covalently bound to the framework and does not rely on a

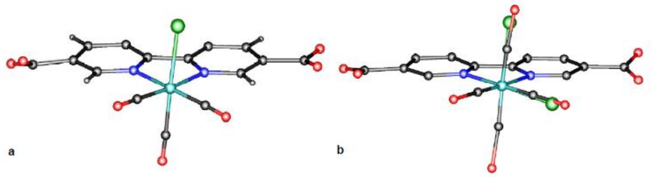


Fig. 3 Views of the single crystal X-ray structure of the (diimine)Mn(CO)$_3$Cl moiety in **MnMn** illustrating *fac-mer* isomerisation. (a) shows the initial *fac*-configuration of the CO groups and (b) shows the post-irradiation chloride occupancy (30%) in the equatorial positions consistent with partial conversion to the *mer*-configuration. Adapted with permission from ref 82. Copyright 2010 Nature Publishing Group.

potentially difficult and inefficient guest adsorption process. Unlike the PSM approach, X-ray structure characterisation is also simpler as percentage conversion is no longer a hurdle (the photoactive component is present on all linkers from the outset) and guest disorder may be reduced or completely removed. An added feature of this strategy is that it is often synthetically simpler to modify existing linkers to form frameworks with groups that 'protrude' into MOF pores than it is to produce robust photoresponsive linkers with a structural change along the MOF linkage, which often have very distinct geometric constraints that limit the possible topologies and framework connectivity that can be achieved.

We have direct experience of this approach as both a means to produce photoresponsive single crystals to examine the photoreactivity of particular chromophores in a framework environment, and to make materials with which to develop and demonstrate the emerging field of X-ray photocrystallography.[77-89] In 2009 we reported a combined spectroscopic and crystallographic study on the $[Mn(DMF)_2[LM(CO)_3Cl]]_\infty$ (L = 2,2'-bipyridine-5,5-dicarboxylate; M = Re (**ReMn**) or M = Mn (**MnMn**)) which contains an (M(diimine)(CO)$_3$Cl) unit as the linker, with the CO groups *facially* coordinated, combined with Mn nodes to form the 3D structure.[82] Ultrafast time-resolved FTIR and spatially resolved Raman mapping were used to characterise the short-lived excited states (picosecond – nanosecond) of the parent *fac*-isomer and to determine the conditions required for photoinduced *fac-mer* isomerisation to occur. The initial photoproduct of UV irradiation is actually two dicarbonyl intermediates, one of which returns to the parent *fac*-isomer, with the other leading to *mer*-isomer formation.[85] We also reported the crystal structure of the mixed-isomer final product, which demonstrated *ca*. 30% photoconversion from *fac*- to *mer*-isomer (Figure 3).

The structural change in this material is relatively small, but makes an excellent demonstration of the advantages of characterisation via both the photocrystallographic and the more traditional vibrational spectroscopic methods. There are several important examples of much more porous framework materials in which pendant chromophores undergo significant structural changes that affect the gross material properties.

One such example, reported in 2010 by Cohen *et al*., is that of an irreversible photoprocess that directly causes a MOF structural change to produce a luminescent species,[90] a strategy with clear parallels to the irreversible photopatterning of MOF-5 to produce quantum dots within the framework. In Cohen's *photoinduced-PSM* Zn-MOF example, the linkers (2-((2-nitrobenzyl)oxy)terephthalic acid and 2,3-bis((2-nitrobenzyl)oxy)terephthalic acid) had been designed with nitrobenzyl side-groups. Photocleavage of these bulky nitrobenzyl substituents from the aromatic cores of the UMCM-1-OBnNO$_2$ and UMCM-1-(OBnNO$_2$)$_2$ MOF linkers opened up the pore structure, increasing the uptake of N$_2$ and the BET surface areas by as much as 25%. The product MOFs UMCM-1-OH and UMCM-1-CAT, respectively, display blue fluorescence that is absent from the parent frameworks. While this is an elegant demonstration of the photocontrol of porosity and emissive behaviour, it is a one-shot methodology and the lack of reversibility limits its application to essentially that of a synthetic tool.

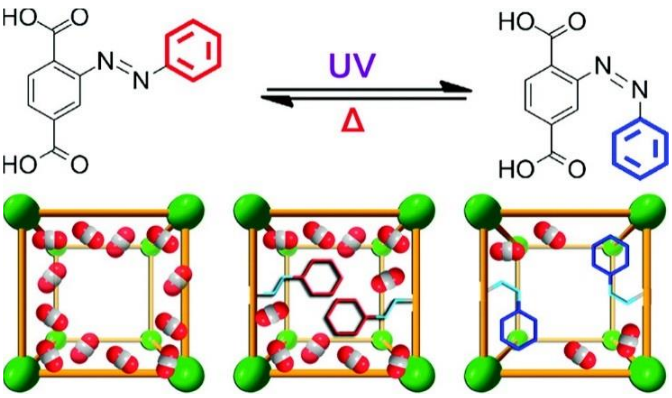


Fig. 4 *Top:* Photoinduced *trans*-to-*cis* isomerisation of the ligand of PCN-123 and thermally induced *cis*-to-*trans* back-isomerisation. *Bottom:* Schematic illustration showing the proposed CO$_2$ uptake in MOF-5, PCN-123 *trans*, and PCN-123 *cis*. Reprinted with permission from ref 91. Copyright 2012 American Chemical Society.

In a return to the popular azobenzene group, Zhou *et al*. reported in 2012 a modified form of the common benzene dicarboxylate linker, 2-(phenyldiazenyl)terephthalate, which they used to form the Zn-based MOF PCN-123 (Figure 4).[91] The framework component is isostructural with unmodified MOF-5. Despite the ordered framework, the orientation of the azobenzene groups could not be controlled and so X-ray crystallography could not distinguish the different orientations of the pendant arms in the pores, which have four-fold positional disorder. UV irradiation of PCN-123 results in a slow *trans-cis* isomerisation of the azobenzene groups, requiring several hours of irradiation (Figure 4). This slow conversion was ascribed to steric hindrance among the azobenzene groups in each cavity, combined with relatively low light penetration into the core of the crystals.

It is not clear if there is a required synergy between adjacent azobenzene groups for isomerisation to occur, a feature that could presumably be tested by measuring conversion rates as a function of photon flux, but the observation that conversion of *trans*- to *cis*-azobenzene continued after UV irradiation had finished would suggest that some sort of concerted triggering of structure change was occurring. The primary result of the photoisomerisation was a decrease in the material's CO$_2$ uptake, which dropped by as much as 54% on formation of the *cis*-isomer, an effect ascribed to blocking of the main

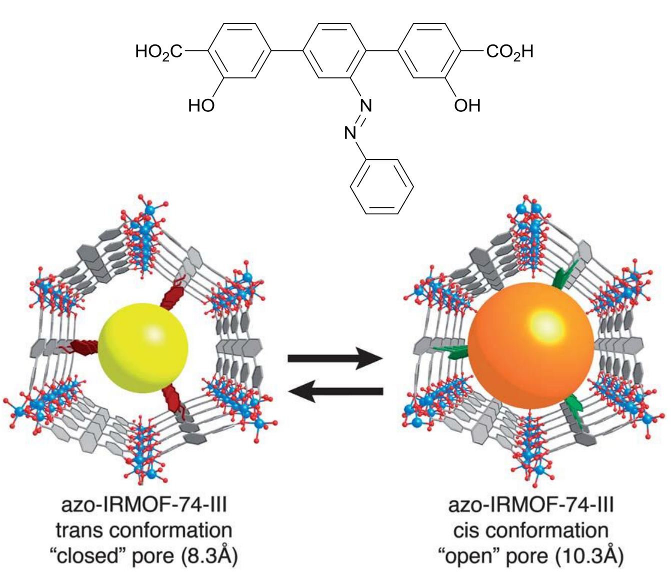


Fig. 5 *Top:* Linker used to form azo-IRMOF-74-III. *Bottom:* Idealised pore volume in the open- and closed-conformations of Mg-MOF azo-IRMOF-74-III. Reproduced from ref 93 with permission from The Royal Society of Chemistry.

adsorption sites near the metal clusters by the phenyl rings of the *cis*-azobenzene molecules. The photoswitching of CO_2 adsorption capacity was shown to be reversible by visible light irradiation or thermal back-conversion to the *trans*-azobenzene form, making these materials very interesting, albeit slow-acting, photoswitchable sorbents for CO_2.

In an interesting detour from photoresponsive MOFs, Zhou *et al*. went on from this study to subsequently report in 2014 an azobenzene-functionalised metal-organic cuboctahedron constructed from an azobenzene-substituted isophthalic acid and dicopper paddlewheel units that exploits similar principles to form an optically responsive guest capture and release material.[92] The group were able to demonstrate photoswitching of uptake and release of methylene blue in several different solvent mixtures.

By extending the terephthalic acid-based azobenzene-modified linker of Zhou *et al*. to a linear three-ring linker, Yaghi *et al*. were able to construct a MOF containing pendant azobenzene and Mg nodes that is essentially isoreticular with the MOF-74 series, which they designated azo-IRMOF-74-III (Figure 5).[93] Instead of capturing and releasing CO_2, the researchers describe the uptake and phototriggered release of a small molecule propidium iodide dye. This material operates by the azobenzene group sterically blocking the pores in the *trans*-isomer, but once converted to the bent *cis*-isomer the pore void space markedly increases (Figure 5).

Taking the strategy of optically triggered release of guest molecules from a framework one step further and combining it with the also growing field of surface-mounted MOFs (SURMOFs), Wöll and co-workers have recently described a two-component approach to a functional guest storage material.[94] In the examples above, incorporation of the azobenzene (or other pendant groups) occupies some of the existing pore space of the MOF, reducing its overall capacity to store guest species. In an elegant sidestepping of this hindrance, Wöll *et al*. grew a two-component material on a gold surface. The first component is a $[Cu_2(BDC)_2(BiPy)]$ (BiPy = 4,4'-bipyridine) framework that is not photoresponsive. In a process described as "installing a vertical compositional gradient", a second MOF is grown on top of the first. The second framework caps the pores of the first and simultaneously contains pendant azobenzene groups dangling from the terephthalate linkers in a similar manner to the examples described above. By using the second layer as a 'capping layer', guests loaded into the first layer can be controllably trapped or released through the photoactive layer (Figure 6).

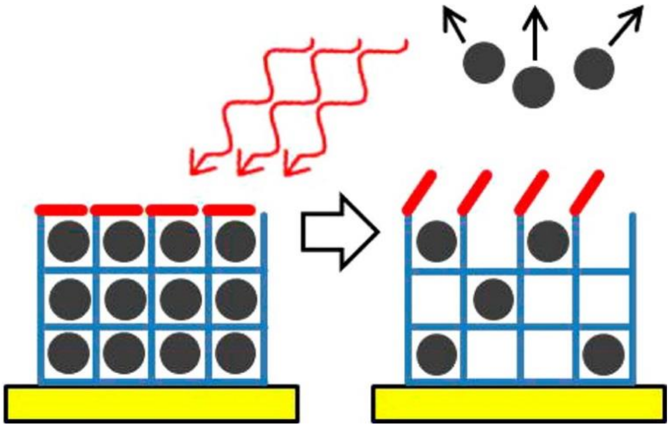


Fig. 6 A schematic representation of the surface-mounted two-component framework system whereby the blue framework acts as molecular container and the top layer, an azobenzene-containing framework layer, acts as a photoswitchable gate to the egress of the guest. Reproduced with permission from ref 94. Copyright 2014 American Chemical Society.

Notably, in studying the uptake and release of butanediol from the system, the researchers proposed that the retarded release observed when the azobenzene moieties are in their *cis*-isomer form was primarily due to the larger dipole moment of the *cis*-form interacting with the guest as it tries to diffuse out, *not* as a result of greater steric pore blocking by the *cis*-isomer. This observation has potentially significant implications for the intelligent design of future 'photogating' systems, clearly indicating that both steric and electronic factors are important in the choice of photoactive molecules. Furthermore, the researchers propose that in future multicomponent systems, two different photoresponsive species could be used that operate at different wavelengths, opening up a pathway to the design of photon-driven molecular pumps.

iv) Frameworks with structurally photoresponsive linkers

The most challenging to synthesise and to successfully characterise, this category encompasses some of the most exciting photoresponsive framework materials reported to date. The challenges described above in undertaking photocrystallographic measurements all apply; it is not trivial to make a crystalline material in which photoinduced structural change isn't either i) too hindered by the solid-state environment that only low conversion is achieved; or ii) too great, such that the crystalline material is destroyed.

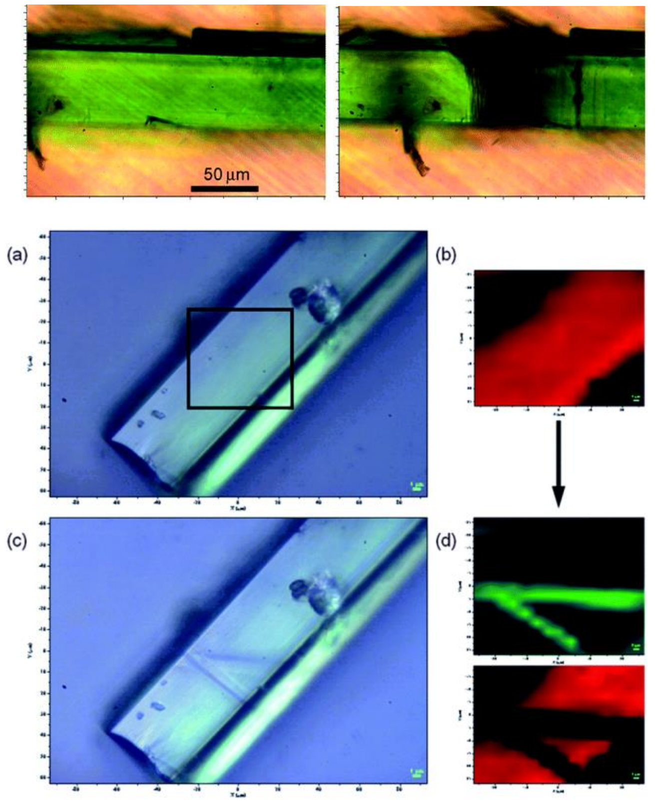
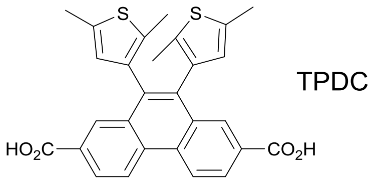


Fig. 7 *Top:* Optical image of a green **ReCu** crystal before (*left*) and after (*right*) irradiation. *Bottom:* Crystal surface before (a) and after (c) surface has been 'written' using UV laser irradiation, while (b) and (d) show the same area 'read' (mapped) by Raman spectroscopy. Adapted from ref 86 with permission from The Royal Society of Chemistry.



Scheme 1 9,10-bis(2,5-dimethylthiophen-3yl)-phenanthrene-2,7-dicarboxylate.

These challenges are well-highlighted by attempts to extend the **ReMn** studies described in the previous section to a framework material in which it was hypothesised that photoinduced electron-transfer from a Re-based state could be used to drive structural change in Cu(II)-containing nodes.[86]

This hypothesis lead to the design and synthesis of $[[Cu(DMF)(H_2O)[LRe(CO)_3Cl]]\cdot DMF]_\infty$ (**ReCu**), a material containing the Re-diimine chromophore described in section **(iii)** above, along with Cu(II) nodes in a somewhat unusual coordination geometry. Unfortunately, while the photoreduction of the Cu(II) centre (attributed to photoinduced electron transfer from the excited Re-chromophore) was demonstrated using a combination of vibrational and EPR spectroscopies, sufficiently high conversion to collect an X-ray crystal structure without significant damage to the crystals was not possible (Figure 7).

The photoprocess was also unfortunately irreversible, a consequence of decomposition of the relatively unstable Re(II) species formed after photoinduced electron transfer to the copper. Despite these difficulties, it was possible to 'write' on the crystals without them degrading by using a low-power UV laser (325 nm) on a Raman microscope, rapidly swept back and forth across the crystals, and to spatially map the structural change from the crystals using a longer wavelength laser (785 nm) on the same microscope (Figure 7). This 'writing' on crystals is also reminiscent of the aforementioned laser-induced quantum dot formation within MOF-5,[53] and a combination of both approaches could perhaps lead to design of spatially-resolved quantum-dot arrays within single crystals.

There are still only few examples of MOFs that contain photoresponsive linkers that themselves change structure on irradiation. In a follow-up to the pendant diarylethene work described above, Benedict and co-workers have described a strategy for the design and synthesis of carboxylated diarylethene molecules to use as MOF linkers and reported several examples of frameworks synthesised from these linkers.[95,96] In the first of these reports, two bis-carboxylated dithien-3-ylphenanthrenes were synthesised in reasonable yield via a five-step route. One of these, 9,10-bis(2,5-dimethylthiophen-3yl)-phenanthrene-2,7-dicarboxylate (TPDC, Scheme 1) was successfully employed in the synthesis of a Zn-based MOF which is isomorphous in structure to the analogous IRMOF-10 framework that utilises a biphenyl-4,4'-dicarboxylate linker. The TPDC ligand displays strong crystallographic disorder in the MOF, having high site symmetry and eight distinct possible conformations in the structure. UV irradiation of the chromophore-containing MOF caused a distinct colour change from essentially colourless to red crystals, consistent with formation of the ring-closed form of the linker. Irradiation with visible light was not able to completely reverse this colour change, but by acid-digesting the red crystals and investigating the nature of the recovered material, formation of an undesirable coloured fatigue product was ruled out. Therefore the researchers proposed that the incomplete recovery of the colourless ring-open form was a consequence of local chemical environment supressing the ring opening reaction.

Fig. 8 Reversible photoinduced CO_2 uptake in MOF Zn-(AzDC)(4,4'-BPE)$_{0.5}$. Reproduced with permission from ref 97. Copyright 2013 Wiley-VCH.

The final example of a photoresponsive MOF is one that appears to have bypassed many of the difficulties of the above systems and incorporates not one but two different photoresponsive linkers. Reported by Hill, Lyndon and co-workers in 2013, the pillared framework [Zn(AzDC)(4,4′-BPE)$_{0.5}$]$_\infty$ contains the AzDC (dicarboxylated azobenzene) linker, which forms sheets within the framework, and 4,4′-BPE (*trans*-1,2-bis(4-pyridyl)ethylene), an analogue of the common MOF pillar 4,4′-bipyridine (Figure 8).[97]

As a result of the two photoresponsive groups, irradiation of the framework causes what initially appears to be a ‘squeezing’ effect, such that adsorbed species can be rapidly desorbed in the presence of light. The framework is triply interpenetrated, which may be the basis of some of the crystalline stability to photoinduced structural change, and may partially explain why no structure change is observable by synchrotron X-ray diffraction – the structure change was described as essentially a bending of the linkers on a local scale that is not propagated in an ordered fashion throughout the whole crystal or all the nets. This was corroborated by spectroscopic measurements, by changes in the infrared spectrum relating to bending modes of the linkers. Desorption of CO_2 from the dark-state when irradiated was as much as 64% under dynamic conditions (42% under static conditions). This remarkable behaviour readily demonstrates the potential for applications in low-energy carbon dioxide capture and release, and also points to the structural behaviour of the framework as being truly dynamic.

Conclusions

Photoresponsive metal-organic frameworks are a relatively young class of porous materials, with their potential applications widely unmapped. ‘Static’ luminescent frameworks have been thoroughly investigated, forming the foundations of current research into more advanced materials. Photoinduced structural alteration can be achieved through the incorporation of photoactive guest molecules, and a primary benefit of this strategy is the extensive range of guests able to form inclusion complexes with any given framework. Alternatively, existing frameworks can be post-synthetically manipulated to afford photoresponsivity, albeit with difficulty. Photoactive moieties can be included as part of the building blocks of a metal-organic framework. Luminescent pendant groups can be affixed to organic linkers prior to framework construction. By incorporating photoactive moieties into the linker pre-construction, the problem of potentially complex interactions of host molecules with a photoactive guest can be mitigated. The design and implementation of a structurally photoresponsive linker in a framework avoids possible complications with guest molecule inclusion, and reduces protruding steric clashes of pendant groups within framework pores and channels. However, investigation into this area is still relatively new. The vast library of potentially structurally photoresponsive compounds that could be modified to form suitable linkers from which to synthesise MOFs enables novel design of photoactive frameworks, provided geometric constraints can be met. Efforts to develop alternate structurally photoresponsive materials are ongoing in our lab and others. The recent pioneering example of a triply-interpenetrated framework from Hill *et al.*[97] which avoids several of the issues discussed in this review gives promise for the development of further conceptually analogous frameworks.

Computational support is essential to the field of porous frameworks, both for understanding of properties and, increasingly, for structure prediction.[98-100] Once the field of prediction of likely MOF structures from metal/linker combinations has developed sufficiently, we fully expect it will be possible to also predict hypothetical frameworks that will survive, or even promote, photoinduced structural change.

Given the traditional functions of metal-organic frameworks are gas sorption and separation, the employment of MOFs for photocatalytic water splitting,[101] as a photodynamic therapy (PDT) anti-cancer agents[102] and for the detoxification of chemical warfare agents[103] demonstrates the development of a much broader application basis for photoactive frameworks. Interest is growing into the impact of intrinsic framework flexibility[14,104] and how mechanical properties can be affected by the incorporation of photoresponsive guests, such as dye molecules.[105] Alternative smart porous materials are also gaining significance, with examples of photoresponsive covalent–organic frameworks (COFs)[106] and porous–aromatic frameworks (PAFs)[75] appearing in recent literature. All of these developments make photoresponsive smart materials a rapidly developing field, with the potential for exciting advances in coming years. A thorough comprehension of the requisite construction techniques for these materials could give way to the design of specifically engineered frameworks as highly targeted substrate specific smart porous materials and rapid-response functional materials.

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Notes and references

‡ A Web of Science search performed on 18/11/2015 for “metal organic framework” returned >29,000 results.

§ Based on empirical analysis of a Web of Science search performed on 19/11/2015 using the search terms “luminescent metal-organic framework”, “metal-organic framework emission” and “metal-organic framework luminescence”.

§§ Based on a Web of Science search performed on 19/11/2015 using the search term “metal organic framework”, restricted to articles published in 2015.

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