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Photo-induced motion of azo dyes in organized media: from single and liquid crystals, to MOFs and machines

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The field of photo-mechanical effects is a burgeoning branch of materials science dealing with the direct transformation of light energy into mechanical motion. While the research in the field has historically focused on polymeric materials, the past decades have seen the rapid emergence of crystalline, photo-mechanically active materials capable not only of converting light into mechanical motion, but also coupling such behaviour with other materials propeties, e.g. microporosity in metal-organic frameworks (MOFs). This Highlight article focuses on the rapidly emerging, new area of photo-mechanical materials based on crystalline azobenzenes. The discovery of photo-mechanical motion in a needle-shaped crystal of an azobenzene led to an explosion of research and new developments in less than 5 years, revealing new types of photo-mechanical behaviour, crystal engineering routes to easily create libraries of crystalline photo-mechanical materials, *in situ* and real-time studies of structural changes during photo-mechanical effect using X-ray diffraction, and the discovery of new supramolecular interactions enabling the engineering of photo-mechanical azobenzene crystals at the level of molecular stacking, as well as crystal morphology.

Introduction

There has been growing interest in using small molecules as dyes and colourants for thousands of years now, from the earliest urges of humans to colour our bodies, cave walls and clothing, and then later our food, shelters, and artistic canvases. More advanced applications of chromophores then developed over the past few centuries in early chemistry laboratories, in the form of visible sensors of local environments such as pH paper and titration indicators, where colours switched with chemical change. Azobenzene in particular then started to emerge as a prime choice for such switching.[1–7] A third wave of dye molecule development was seen in recent decades, where optical, electro-optic, and photonic properties could be switched rapidly and reversibly with light, to store and process information optically, and where azobenzene once again featured prominently.[1] A most recent area of azo dye research, however, is the control of macroscopic mechanical motion directly with visible light, akin to the reversible shape-change of retinal in rhodopsin when it absorbs a single photon and isomerizes, enabling vision.[2] Such photo-mechanical effects were in fact observed first 60 years ago during studies on textile processing, when Merian reported curious macroscopic motions of then-new nylon fibres dyed with azobenzene, when they were exposed to light. In those observations, the irradiated nylon filaments shrank upon irradiation with a Xenon daylight lamp,[3] the shrinking resulting from the reversible *trans*↔*cis* geometric isomerization of the molecules bearing the azo chromophore (**Figure 1a**). The energy absorbed by the molecules in the process of isomerization was transferred, although with low efficiency, to the surrounding polymer matrix, driving an overall contraction of under 0.1% of the original length. Further research into this curious phenomenon allowed the magnitude of contraction to be gradually increased to up to 1% of the original length, simply by increasing the loading of the dye.[4,5]

Following from these original observations of photo-mechanical effects in textile fibres, much of the early research was concentrated on amorphous polymers, which later were found to be less effective in the transduction of energy of light into mechanical motion. Ordered materials, such as liquid crystalline elastomers (LCEs), proved superior in actuation force and response speeds, and offered the further advantage of control over the direction of actuation *via* polarization.[7] Ultraviolet (UV) irradiation of azobenzene-containing LCEs was found to disturb the mesogen alignment in the surface layers of the film, due to *trans*↔*cis* isomerization generating asymmetric strain, causing bending of the film in a predetermined direction.

Moving fully to single crystals in principle offers an even faster and more efficient energy transduction owing to their higher order and rigidity.[8] This Highlight focuses on the new observations of motility of azobenzene chromophores in single crystals and as parts of open metal-organic frameworks (MOFs), which offer attractive material pathways to construct complex functional architectures activated by visible light.[9,10]

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Azobenzene isomerization in crystals

Trans↔*cis* isomerization for reversible photo-mechanical motion

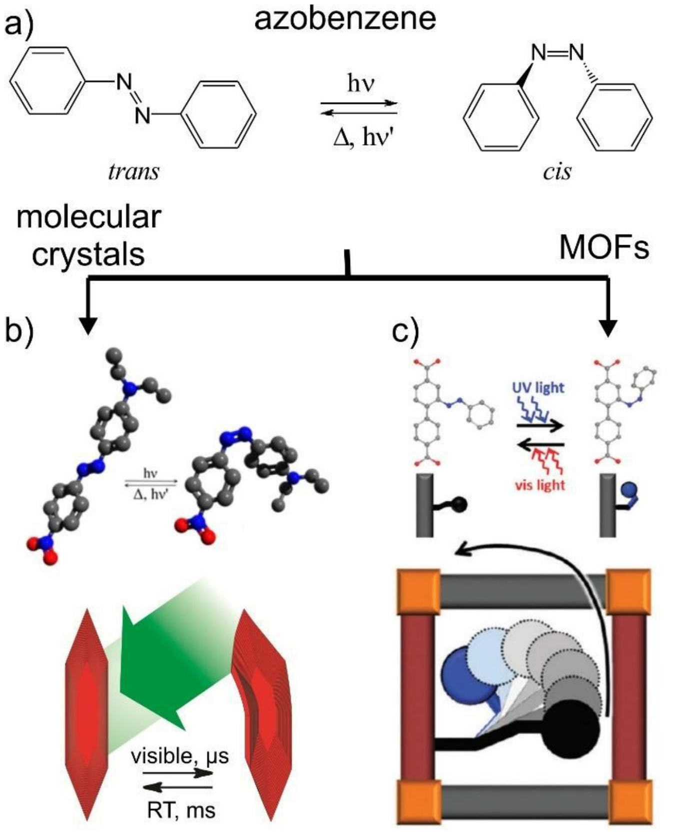

Figure 1. a) Isomerization of azobenzene chromophore driving the change of crystal shape (b) or altering the pore size in a MOF (c). Reproduced with permission from references 9 and 10. Copyright Wiley 2013 (b) and RSC 2015 (c).

For a long time, research into the photo-mechanical properties of azobenzene photoswitches was limited to polymeric and liquid-crystalline materials. One potential reason for this was a general assumption, corroborated by the experimental and computational studies of azobenzene molecules on surfaces of metals,[11-13] that the large steric demand of azobenzene isomerization would make such a process near-impossible in a densely packed crystalline environment. However, the explosion of research activity in photo-mechanically active crystalline systems, inspired to the greatest extent by the seminal investigations of the Irie group on light-induced switching of diarylethenes in single crystals,[14-17] led to a recent re-investigation of the possibility of azobenzene isomerization in crystals and, therewith, crystalline azobenzenes as photo-mechanical solids. A major breakthrough in the development of crystalline azobenzene photo-mechanical systems came with the report of Koshima *et al.*, describing that thin plates of a crystalline amino-substituted azobenzene, when irradiated with UV light, bend away from the source or radiation. (Figure 2).[18a] The bending was accompanied with a concomitant change of the absorption profile of the crystal and roughening of the crystal surface, as determined by atomic force microscopy (AFM) measurements. Once bent, the crystals were found to slowly return into the initial shape, tens of seconds after the end of irradiation.

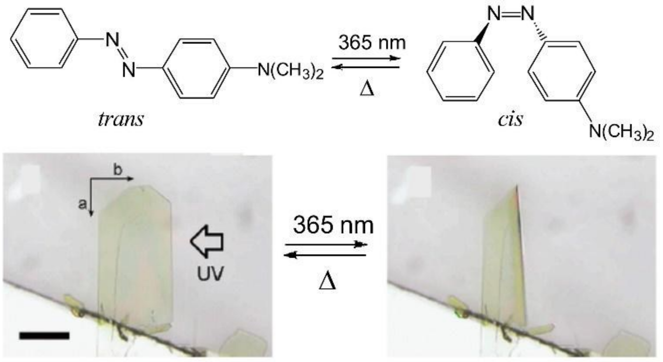

Figure 2 UV light induced azo isomerization leads to bending of a crystal of dimethylaminoazobenzene. Figure reproduced with permission from reference 18. Copyright 2009 American Chemical Society.

The photo-mechanical behaviour of azobenzenes, which was at that point unprecedented, was readily observed for crystals of yet another chemically similar amino-substituted azobenzene chromophore.[18b] Soon after, the ability to bend azobenzene crystals using visible light was demonstrated by Bushuyev *et al.*,[9] who investigated a family of pseudostilbene chromophores bearing 'push-pull'-substituents, *i.e.* azobenzene molecules substituted on opposite ends with electron-withdrawing and –donating substituents. This substitution pattern results in a red-shifted absorbance and much shorter *cis*-state lifetimes,[9] meaning that crystals of 'push-pull' pseudostilbenes can readily undergo photo-mechanical bending by irradiation with visible light. Moreover, the very short thermal half-lives of the photochemically generated *cis*-azobenzene chromophore caused the crystals to rapidly revert (within seconds) to their original shape.

In all the reports described thus far, the critical parameter for effective crystal actuation was found to be the thickness of the crystal being irradiated. Overall, the best photo-mechanical responses appear to result from crystals whose thickness is in the range between 0.7 µm and 3 µm. One of the challenges in developing crystalline photo-mechanical actuators is that conventional solution-based crystallization techniques often yield crystals too thick for photo-mechanical applications. A potential solution to this problem has recently been demonstrated by Lee *et al.*, who utilized meniscus-confined solidification techniques to prepare azobenzene-containing nanowires ranging from 200 nm to 1000 nm in diameter.[19] The small dimensions enabled photo-mechanical bending motion of such wires at UV light irradiation powers as low as 0.8 mW/cm^2. The nanowires were subsequently used to prepare optically-driven mechanical tweezers, capable of lifting and moving a 4 µm diameter polystyrene particle. In order to advance the understanding and the rational development of photo-mechanical actuators, several mathematical models have been recently proposed.[20a,b] Particularly relevant for developing azobenzene-based crystalline photo-mechanical actuators is the work of Nath *et al.*[20c], who utilized a pseudostilbene-type chromophore

Disperse Red 1 to develop a model of photo-mechanical bending. This model went beyond the classical bilayer model and was able to account for the special gradient in the product/reactant ratio and the time profiles of the forward and the reverse isomerization reactions in a slender crystal.[20]

Photo-mechanical activity of *o*-fluoro-stabilized *cis*-azobenzenes

While photo-mechanical effects were observed in crystals of azobenzenes and pseudostilbenes, the notably metastable nature of the *cis*-isomer meant that only very limited evidence of the *trans-cis* isomerization was available for those systems, gathered mostly *via* spectroscopic and AFM studies. A means to circumvent this persistent obstacle in mechanistic understanding of photo-mechanical bending of azobenzene crystals was offered by the discovery of a novel class of *o*-fluoroazobenzenes, possessing ultra-long thermal half-lives of the *cis*-isomer. The pioneering report by the Hecht group that *cis*-azobenzene structures are stabilized *via* fluorination[21] was soon followed by a study from our group, which addressed the crystal structures of *cis*-isomers of 4,4’-diiodooctafluoroazobenzene (**1**) and its bromo-analogue (**2**) **(Figure 3a)**.[22] Irradiation of the needle–shaped crystals of either **1** or **2** revealed unexpected irreversible photo-mechanical behaviour, as the crystals were found to bend away from the light source upon irradiation with visible light, for permanent and controllable shaping of a crystal (**Figure 3b**). At the same time, the crystals after irradiation exhibited sufficient crystallinity for structural analysis by X-ray diffraction, which revealed a crystal-to-crystal transformation in which the initial single crystal of the fluorinated azobenzene was converted into an oriented array of polycrystals of the corresponding *trans*-isomer. The crystal-to-crystal nature of the transformation provided the first crystallographic evidence that the photo-mechanical bending of crystalline azobenzenes can take place *via* light-induced *cis*→*trans* isomerization.

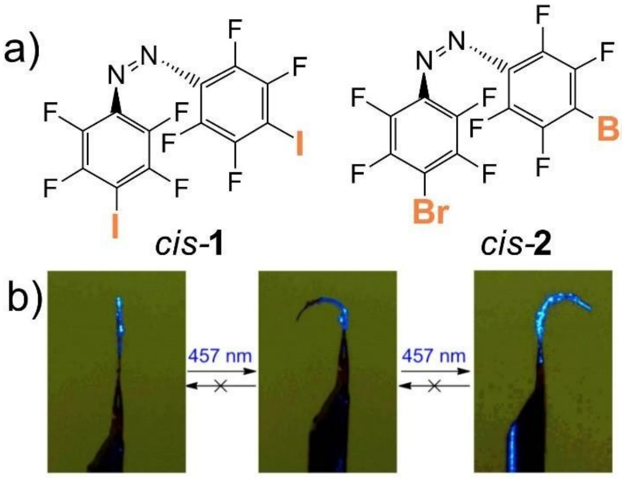

Figure 3 a) *cis*-isomers of *o*-fluorinated azobenzenes (**1**) and (**2**) b) Irreversible bending of a crystal of (2) in 488 nm light proceeds away from the irradiation source: (left) crystal before irradiation; (centre) after irradiation from the right (right) after irradiation from the left. Figure reproduced with permission from reference 22 Copyright 2013 American Chemical Society.

The polarizable iodo- and bromo-substituents in the 4-positions of molecules of **1** and **2** offer a potential handle to generate a library of photo-mechanical materials through a crystal engineering[23] route. Specifically, Bushuyev and co-workers[24] have utilised **1** and **2** as halogen bond donors in the design of cocrystals[25,26] with molecules capable of acting as halogen bond acceptors. This simple and synthetically facile route to new azobenzene-based materials, based on supramolecular derivatization *via* halogen bonding,[27] enabled the systematic construction of new photo-mechanical materials and investigation of crystal structure factors central to photo-mechanical behaviour. In particular, cocrystallization of *cis*-**1** and **2** with aromatic halogen bond acceptors, including as *trans*- and *cis*-*bis*(pyridyl)ethylene (*trans*- and *cis*-**bpe**, respectively) and *trans*-azopyridine (**apy**)[24] (**Figure 4a**) gave rise to a family of five structurally similar materials with different photo-mechanical responses. Notably, the crystal bending magnitude and irradiation power required to induce such motion differed dramatically along this series. While high angle of deflection of the tip of the bending crystal were achievable for the cocrystal (*cis*-**1**)(*cis*-**bpe**) (**Figure 4b**), only modest bending (*ca.* 3°-4°) was observed for (*cis*-**1**)(**apy**), even upon increasing the power of irradiation almost 40-fold, from 5 mW/cm^2 to 200 mW/cm^2.[24]

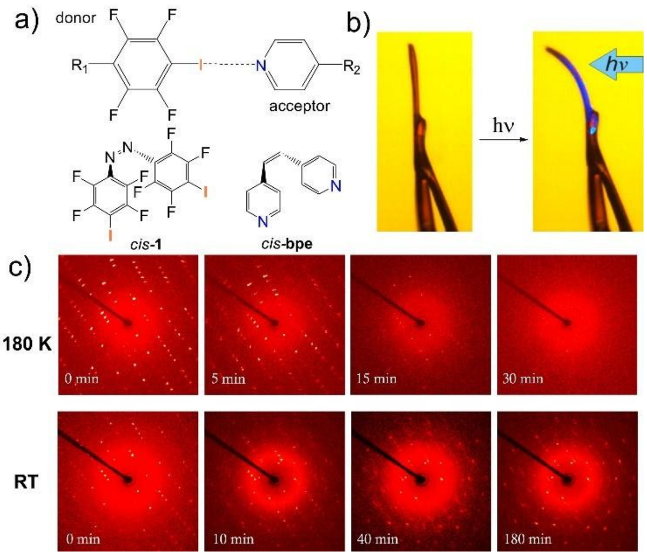

Figure 4 a) Halogen-bonding donor-acceptor motif utilized to prepare photo-mechanical cocrystals of *o*-fluorinated azobenzenes based on *cis*-**1** and *cis*-**bpe**. b) Irreversible bending of a single crystal of (*cis*-**1**)(*cis*-**bpe)** away from the 488 nm light source. c) Variable temperature x-ray diffractograms collected during irradiation: experiment at 180 K shows compete amorphization of a sample, while room temperature irradiation leads to gradual appearance of a new crystal phase of (*trans*-**1**)(*cis*-**bpe**) in a crystal-to-crystal manner. Figure reproduced with permission from reference 24 Copyright 2016 Royal Society of Chemistry.

The ease of photo-mechanical bending observed for the (*cis*-**1**)(*cis*-**bpe**) cocrystal, compared to the other members of the halogen-bonded photo-mechanochemical cocrystal family was attributed to its lower crystallographic density, *i.e.* the available volume *per* non-hydrogen atom in the unit cell.

The photo-induced transformation of (*cis*-**1**)(*cis*-**bpe**) cocrystals was also found to be of crystal-to-crystal type,[28] which was exploited for the first *in situ* study of structural changes taking place during photo-mechanical bending of an azobenzene crystal. The collection of X-ray crystal diffraction data on a continuously irradiated cocrystal of (*cis*-**1**)(*cis*-**bpe**) confirmed the *cis*→*trans* photoisomerization during the photo-mechanical bending.[24] Moreover, the analysis of diffraction images for a crystal undergoing photoisomerization at different temperatures provided a strong indication that the transformation actually takes place *via* an amorphous intermediate. In particular, diffraction monitoring of a cocrystal of (*cis*-**1**)(*cis*-**bpe**) upon laser irradiation at cryogenic conditions (180 K, Figure 4c) revealed only the gradual and complete loss of diffraction spots. In contrast, monitoring of a (*cis*-**1**)(*cis*-**bpe**) cocrystal irradiated at room temperature revealed a smooth replacement of its diffraction spots of with those consistent with (*trans*-**2**)(*cis*-**bpe**) (Figure 4c).[24] The photo-reaction proceeded in a strongly topotactic manner,[29] *i.e.* the daughter (*trans*-**2**)(*cis*-**bpe**) cocrystal domains were always in identical orientation to the parent (*cis*-**1**)(*cis*-**bpe**) cocrystal, independent of the orientation of the light source or its polarization. These *in situ* studies suggest that the photo-mechanical motion in (*cis*-**1**)(*cis*-**bpe**) proceeds with the retention of a considerable level of order, including the retention of the halogen-bonded structure, upon isomerization.

To a large extent, all so far reported studies of photo-mechanical bending of fluorinated *cis*-azobenzenes have been facilitated by their notably needle-shaped morphology. Indeed, fluorinated *cis*-azobenzenes with very diverse substitution patterns were all found to exhibit a similar morphology, prompting Bushuyev *et al.* to conduct a detailed investigation of their crystal packing.[30] Careful analysis of available structures provided strong evidence of a previously not described, highly persistent self-assembly motif in the structures of fluorinated *cis*-azobenzenes, involving close contacts between the azo nitrogen atoms group and the fluorinated phenyl moieties of nearest-neighbour molecules.[30] These short interactions were found to provide strong stabilization (on the order of magnitude of 30 kJ mol^{-1})[31] for the formation of *cis*-azobenzene stacks (Figure 5a), reminiscent of a column of Pringles™ potato chips. The analysis of the intermolecular interactions in the crystal structures of all investigated fluorinated *cis*-azobenzenes, as well as their halogen-bonded cocrystals with aromatic and aliphatic cocrystal formers revealed this azo···phenyl[30] stacking as the dominant stabilizing reaction, explaining the high preference of these materials for needle-shaped crystal morphology. Indeed, in all cases investigated the long axis of the crystal corresponded with the direction of the azo···phenyl molecular stacks.

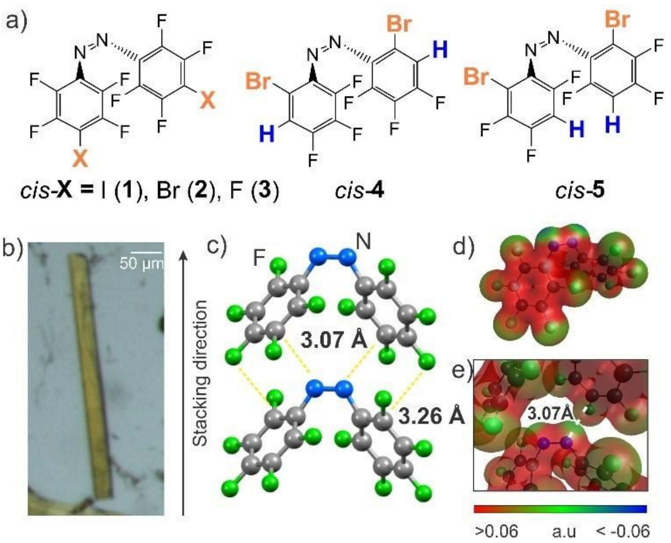

Figure 5 Fluorinated *cis*-azobenzenes **1**-**5** (a) exhibit needle-like crystal morphology (b) owing to the stacking interaction between the azo-group nitrogen and the electron-poor C-F and *para* position halogen and C-F bond of the subsequent unit (c) The interaction can be visualized on the electrostatic potential plot (d and e) Figure reproduced with permission from reference 30 Copyright 2016 Royal Society of Chemistry.

The robustness of the azo···phenyl interaction was tested by varying the substitution on the phenyl rings of fluorinated azobenzenes, and was found to persist upon changing the position of the heavy halogen atom substituent (*i.e.* bromine), or varying the number and position of fluorine and hydrogen atoms on the aromatic ring. Importantly, the interaction was found to persist in related halogen-bonded cocrystals, offering a means to arrange aliphatic and aromatic halogen bond acceptor molecules in a columnar fashion (Figure 6).

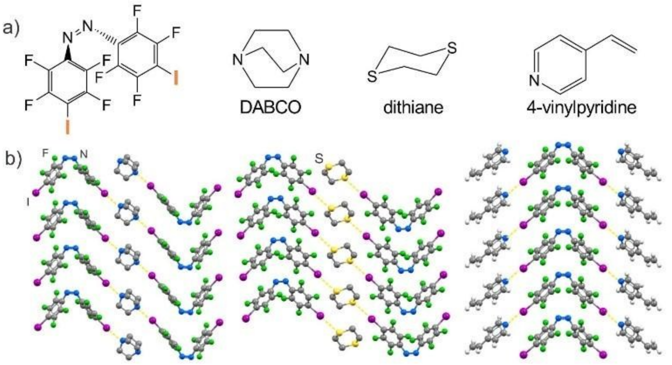

Figure 6 Cocrystallization of 1 with various halogen bond acceptors (a) yielded crystal structures with persistent azo···phenyl stacking (b), which in turn results in predictable columnar arrangement of halogen bond acceptor molecules. Figure reproduced with permission from reference 30 Copyright 2016 Royal Society of Chemistry.

Motions of azobenzenes in periodic framework architectures

A new research direction in solid-state reactions of azobenzenes was opened with the development of metal-organic frameworks (MOFs) and related crystalline framework materials.[32] Specifically, the development of robust MOF designs that can withstand harsh environmental conditions and be functionalized after synthesis, whilst retaining a high level of microporous surface area,[33,34] inspired research of photo-switchable materials. The ultimate goal of such work is the development of microporous solids capable of light-responsive absorption of gases, *e.g.* carbon dioxide (Figure 7).[35,36] Consistent with the view that azobenzene chromophores will be most likely to undergo photochemical isomerization when used as pendant groups on MOF linkers, photo-active azobenzene-substituted MOFs were prepared and successfully tested to regulate methane absorption.[37] While the azobenzene chromophore usually does not act as a truly bi-stable switch, due to a very short lifetime of the *cis*-isomer, Castellanos *et al.* recently reported a MOF material, involving *o*-fluorinated azobenzenes having *cis*-isomers of enhanced stability, that are addressable by green and blue light and has potential as a bi-stable materials for gas storage.[38]

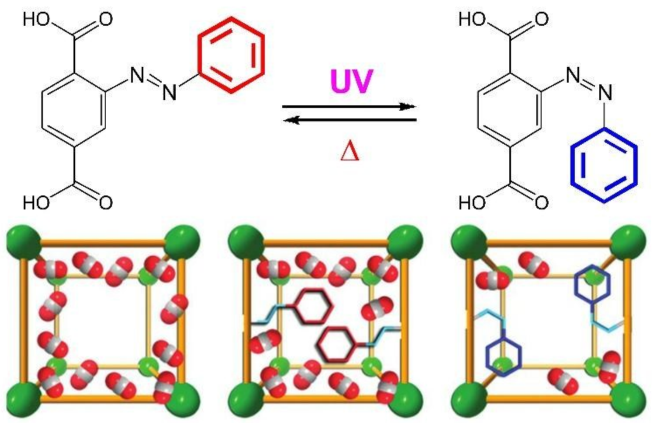

Figure 7 (Top) Isomerization of the azobenzene ligand within a MOF PCN-123. (Bottom) Schematic illustration of CO_2 uptake in the parent MOF-5 structure and PCN-123 network in a *trans*- and *cis*-states. Figure reproduced with permission from reference 35. Copyright 2012 American Chemical Society.

A simple and elegant approach to photo-switchable gas absorption in MOFs was more recently proposed by Lyndon *et al.* Instead of covalently modifying a MOF or a MOF linker unit, they opted for post-synthetic treatment of the surface of a MOF by methyl red azobenzene dye, coating the framework surface and preventing CO_2 absorption.[39] Upon irradiation with light, photo-chemical isomerization of the azobenzene led to pore opening, facilitating the sorption of more CO_2 in the MOF. In the same vein, photochromism of azobenzene molecules inside the pores of a MOF was shown by the Kitagawa group to direct structural changes in the framework, enabling regulation of gas absorption.[40] The incorporation of azobenzene chromophores as a guest molecule into the network led to a structural transformation from a tetragonal to an orthorhombic MOF upon UV irradiation, associated with drastically different gas uptake profiles. Whereas most described research is performed under the assumption that switching of azobenzene is only possible in a MOF when chromophores are used as pendant groups,[36] a highly exciting recent report by Baroncini *et al.* may warrant a closer inspection of this idea. They demonstrated that tetrameric star-shaped azobenzene molecules assembled a porous network and then underwent reversible isomerization aided by partial amorphization of the sample.[41] The isomerization in its turn changes the porosity and consequently the gas uptake of the network.

While most of the effort in photo-responsive MOFs has so far been directed towards the study of azobenzene chromophores, it is worth noting that work in this nascent field has also utilised other types of photo-switchable units. For example, Walton *et al.* produced photochromic architectures employing diarylethene chromophores.[42,43] For example, irradiation of a crystal of the material UBMOF-1 with UV-light was found to change the crystal colour into red, indicating a successful ring closure reaction of the diarylethene chromophore. In contrast to previously investigated photochromic molecular crystals,[14] the introduction of the diarylethene photochromes into the MOF prevented the reverse photoisomerization. Reversible switching of the diarylethene unit inside a framework structure was since achieved by Luo *et al.*, in materials which allowed light-triggered desorption of up to 75% of CO_2 guest upon UV and visible irradiation.[44]

Azobenzene-containing liquid-crystal elastomers: Half-way between crystals and polymers

Despite the advantages in the rates of energy transduction offered by crystals, polymeric materials are more likely to be utilized for potential device prototypes due to ease of fabrication, size- and shape-control, and processability. In this context, LCEs offer control over the direction of photo-mechanical motion *via* the axis of light polarization,[7] a change in axis or location of the azo chromophore within the film,[45] or the axis of cut of the film.[46] Directionality of the photo-mechanical actuating motion allowed the development of mechanical prototypes for several simple proof-of-principle photo-mechanical 'machines' powered by light. In one such prototype, a continuous belt of azobenzene film laminated onto a thin polyethylene (PE) sheet was used as a belt to rotate a set of pulleys by simultaneous UV and visible light irradiation of two different regions of the film (Figure 8a).[47] Laminating a free standing film in two different positions, on the other hand, created a simple arm-like device, with separately addressable 'elbow' joints. Sequential bending and unbending of the azo-treated segments allowed for precise positioning of the film in space, imitating robotic arm motions *via* these 'artificial muscles'[48] (Figure 8b).

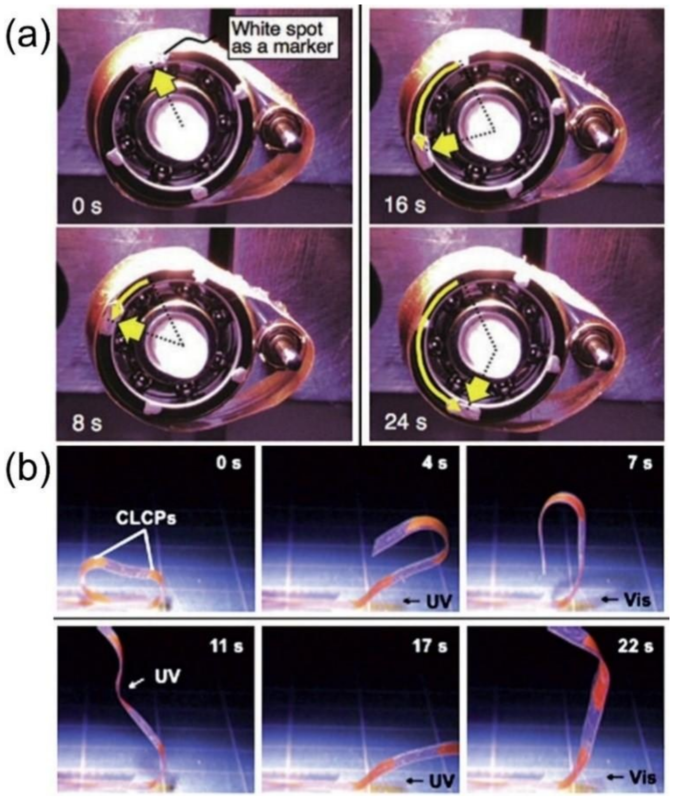

Figure 8 a) Series of photographs showing the rotation of a light-driven plastic motor with a LCE laminated film moved by simultaneous irradiation with UV and visible light. Figure reproduced with permission from reference 47Copyright 2008 Wiley. b) Series of photographs of the flexible 'robotic arm' motion of an azo-LCE laminated film induced by irradiation with UV and visible light. Arrows indicate the direction of light irradiation. Figure reproduced with permission from reference 45. Copyright 2009 Royal Society of Chemistry.

More recent notable advances in the field of photo-mechanical LCE devices report the development of more complex movement patterns and designs that respond to a broader range of stimuli with better addressability or spatial precision. Impressive control over the helical motion of azobenzene-containing liquid crystalline polymer springs may was achieved by the direction of cut of the film, and can be envisaged as a bio-mimic of the extensile function of plant tendrils.[46] The helical deformations were pre-programmed by including chiral azobenzene dopants and controlling the relative orientation of the aligned liquid-crystals. Chiral dopants induce left-handed or right-handed twists in the liquid crystalline film. Depending on the direction of the cut of such a film it will curl, twist, or do both upon irradiation with light. Complex extensile and contractile coiling and twisting helical motions are possible, and mechanical energy can be exported from the system by the use of a pair of magnets.

Conclusions and outlook

This brief overview attempted to capture the very recent development of a new family of photo-mechanical materials, based on light-induced switching between azobenzene isomers. Investigated historically almost exclusively in the context of polymer, gel or liquid crystal matrices, the 2009 discovery of photo-mechanical bending of azobenzene crystals inspired an explosive growth into an area of new azobenzene-based crystals. In a very short time span, this new field demonstrated reversibly switched photo-mechanical behaviour, as well as the ability to shape crystals irreversibly. The application of principles of supramolecular chemistry and crystal engineering now allows libraries of photo-mechanical materials to be generated by cocrystallisation, based on a small number of photo-active building blocks. A significant contribution in that context has been the discovery of fluorinated *cis*-azobenzenes with enhanced stability, enabling the first real-time structural studies of photo-mechanical behaviour, the discovery of new supramolecular motifs for controlling the arrangement of molecules and crystal morphology, types of photo-mechanical behaviour and the design of photo-addressable microporous solids. Moreover, the molecular structures of such *cis*-azobenzenes appear to be readily amenable to derivatization under mild conditions,[49] potentially opening routes to further azo-based solids. Overall, the area of azobenzene-based crystalline materials, that sprang into existence not even 5 years ago is now a thriving field which offers much promising potential as photomechanical materials for next-generation applications because of their ease of incorporation, and efficient and robust photochemistry. This highlight described some exciting new photo-mechanical effects observed recently in crystals, cocrystals, and frameworks containing azobenzene. In these and various other systems, full macroscopic light-driven actuation has now been demonstrated, representing promising materials for 'artificial muscles' driven by light. In some of these systems more complex two- and even three-dimensional motions have now been achieved, which are competitive and promising for many future applications one might envisage as sunlight-powered actuators, 'photo-motors', and 'molecular machines'.[50] Clearly, there are outstanding challenges in the further development of this exciting field, such as crystal fatigue and reversibility. Currently, the most promising strategy for developing highly reversible photo-mechanical crystals is through further miniaturization, below micrometre size.[9,18,19] A potential direction for further studies may involve the determination of structural correlation between the molecular displacement in the crystal and the bending angle that was previously performed for plastically bent organic crystals.[51] Such correlation may help better understand the underlying mechanism and facilitate the development of actuators exhibiting high efficiency of transforming light into of photo-mechanical motion.

Acknowledgements

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