



# Shape-Shifting Azo Dye Polymers: Towards Sunlight-Driven Molecular Devices

Oleksandr S. Bushuyev, Miho Aizawa, Atsushi Shishido, and Christopher J. Barrett\*

The development of stimuli-responsive polymers is among the key goals of modern materials science. The structure and properties of such switchable materials can be designed to be controlled via various stimuli, among which light is frequently the most powerful trigger. Light is a gentle energy source that can target materials remotely, and with extremely high spatial and temporal resolution easily and cheaply. Reversible light-control over molecular mechanical properties in particular has in recent years attracted great interest due to potential applications as optical-to-mechanical conversion actuators and ‘devices’, enabling ‘molecular robotic machines’. In this review, some recent examples and emerging trends in this exciting field of research are highlighted, covering a wide variety of polymer hosts that contain azobenzene photo-reversible switches. It is hoped that this review will help stimulate more interest towards the development of light-reversible materials for energy harvesting and conversion, and their successful incorporation into a wide variety of current and future high-tech applications in devices.

and now include many reports of real dynamic molecular systems where the machine-like action of their molecular components has been harnessed to do controlled work on their surroundings. These likely qualify as ‘molecular machines’ in most readers’ opinion, but the achievement and very definition of a machine, molecular or otherwise, has been in lively debate ever since biochemistry professor Isaac Asimov began to sketch out the early laws of robotics over 75 years ago in his sci-fi paperbacks.<sup>[4]</sup> In an effort to help guide chemists and molecular engineers now in this field, a clear language has been proposed to try and differentiate simple molecular shape switches, from complex multi-component devices that are effective in driving a system away from its equilibrium in a controlled, desired, and pre-programmed fashion.<sup>[5–8]</sup>

## 1. Introduction: Molecular Devices and Tiny Machines

Inspired by the sophistication and elegance of biological machinery, an ultimate pursuit of modern molecular-scale engineering is the design of artificial molecular devices, where complex tasks can be performed by controlling mechanical motion at the molecular level.<sup>[1]</sup> Perhaps now more than just a subject of suspect science fiction, ‘molecular machines’ are now firmly entrenched at the forefront of current molecular device engineering, as affirmed by the Nobel Prize in Chemistry in 2016,<sup>[2]</sup> and in 2017 by the first running of a Formula-1-style international nano-car race.<sup>[3]</sup> The design and synthesis of molecules that can undergo reversible and controlled structural changes with various stimuli have thus received considerable attention,

While the working principles of these molecular motors and devices are hard to compare directly to their macroscopic analogues, a *molecular machine* can be defined as a multicomponent system with specific energy input that is capable of performing a measurable and useful secondary function either at the nanoscale, or if amplified through collective action, at the macroscale.<sup>[7,8]</sup> The system should ideally perform in a reversible manner, with the capacity to enact desired and repeated mechanical operations. Temporal and spatial control over this motion, and performance of useful work, are further hallmarks of such successful machines, helping to differentiate desired and deliberately actuated mechanics that leverage Brownian motion, from undirected and uncontrolled thermal effects, and exclude warm molecules that simply vibrate, wiggle, or diffuse randomly. Of course, what will be described in this review are necessarily only crude first attempts towards *artificial* molecular machines, as our proteins and DNA for millions of years have demonstrated clear natural success of the above criteria for *natural* machines, with every fold and subsequent robot-like function.

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## 2. Molecular Photo-Switches that can be Incorporated into Polymers

The development of stimuli-responsive functional molecules is one of the key goals of current materials science. The structure and thus properties of such switchable materials can be designed to be controlled via various

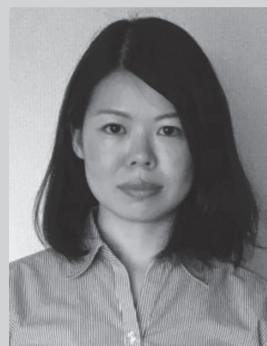
stimuli, among which light is frequently the most powerful trigger, so will be the stimulus of choice for this review. Light is a mild and gentle energy source that can target materials with extremely high spatial and temporal resolution, both easily and cheaply. The ability to drive molecular-level devices with light as a power source is attractive for many applications, as it circumvents inherent limitations to diffusion or wiring, and permits a remote (or even quite distant) battery-free power supply. Light-control over molecular properties in particular has attracted much interest in recent years. Such 'photo-switches' exhibit a reversible transformation between two chemical species with semi-stable energy states, triggered by absorption of visible light. In principle, any double-well potential system which reversibly cycles between two energy states by absorption of light can be a photo-switch, yet practical photo-reversible systems also need to switch cleanly, without the build-up of unwanted side products, and possess a sufficiently high potential barrier as to ensure the reasonable stability of both of the energy states over device-requirement timescales. A few families of parent molecules that reversibly isomerize between multiple structural geometrical configurations in response to light satisfy these criteria, and some common examples of such molecular photo-switches are presented in **Figure 1**. The most extensively employed class of small-molecule photo-switches contain azobenzene chromophores, whose isomerization between *trans* and *cis* geometric conformations about the double bond mimics a flapping motion.<sup>[11,12]</sup> Other widely reported photo-switches include diarylethenes and spiropyrans, in which conformational changes are accompanied by ring-opening 'twists' or closing 'snap' reactions;<sup>[13–15]</sup> anthracene and coumarin derivatives that reversibly dimerize with one another to 'link and let go';<sup>[10,16]</sup> and overcrowded alkenes, hydrazones, and imines, which can behave as free rotors that revolve and 'spin' about a rigid internal axis.<sup>[17–20]</sup> In principle, the chemist can functionalize each parent photo-switch covalently at secondary locations to tailor and fine-tune optical and mechanical properties to provide a vast library of materials to the engineer to meet various actuation device requirements. Additionally, various non-covalent 'soft' interactions between molecules, such as hydrogen bonding, halogen bonding, or hydrophobic effects, and  $\pi$ - $\pi$  stacking can enable the assembly of dynamic reversible host-guest systems, expanding the versatility of switches via supramolecular self-assembly of two or more components.<sup>[21]</sup> These dynamic molecules represent the smallest building blocks for self-assembly using a bottom-up approach to construct functional mechanical devices that allow controlled motion. While chemically diverse, all these various photo-switch components operate on the principle of microscopic reversibility,<sup>[22]</sup> where the absorption of a photon of specific wavelength drives populations back or forth over the energy barrier between the two non-degenerate states.

An ideal model photo-switch, also the most ubiquitous natural molecule for reversible shape change, and perhaps an inspiration for all artificial bio-mimetic systems, is the rhodopsin/retinal protein/trigger system that enables vision, perhaps the quintessential reversible photo-switch for performance and robustness. In this natural photo-switch, the small retinal



crystal engineering of light-emitting materials.

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molecule embedded in a cage of seven rhodopsin helices isomerizes from a kinked *cis* geometry to a straight *trans* geometry around a C=C double bond with the absorption of just a single photon. This modest shape change of just a few angstroms is then amplified, and triggers a cascade of larger geometric shape and associated chemical changes, eventually culminating in an electrochemical signal of a vision event to the brain, with the energy of the input photon being amplified many thousands of times in the process. Complicated biochemical pathways then revert the straight *trans* isomer back to the bent *cis* geometry, and set the system back up for another domino-like cascade upon receipt of the next incoming photon, for many subsequent vision cycles. The reversion mechanism back to the initial kinked *cis* state is complex and enzymatic; thus, direct application of this retinal/rhodopsin photo-switch to engineering systems is prohibitive. Yet perhaps the leading artificial mimic of this excellent photo-switching effect, however, in terms of reversibility, speed, and simplicity of incorporation, is azobenzene (azo), which has been by far the most successfully incorporated dye into polymers, to provide photo-switchable materials. The fast response (picosecond photo-physics) and absence of side reactions in azo isomerization are also advantageous, so the focus of this review will be mainly the reversible transformation of azos incorporated into various host matrices, such as amorphous polymers, liquid crystalline polymer networks (LCPNs), or liquid crystal elastomers (LCEs). The two energy states of photo-switching molecules exhibit differences in absorbance wavelength and intensity, so there is usually a change of color of such materials upon absorption of light. At the same time, and more usefully, the geometric isomerization between the two energy states brings about micro-motion and conformational change, which while initially modest, can then be carefully engineered and harnessed to produce a secondary shape change or motion, amplifying and magnifying the effect by leveraging a mechanical advantage to drive many useful larger macro-motions.

### 3. Molecular and Macroscopic Motions of Azo Dye Materials

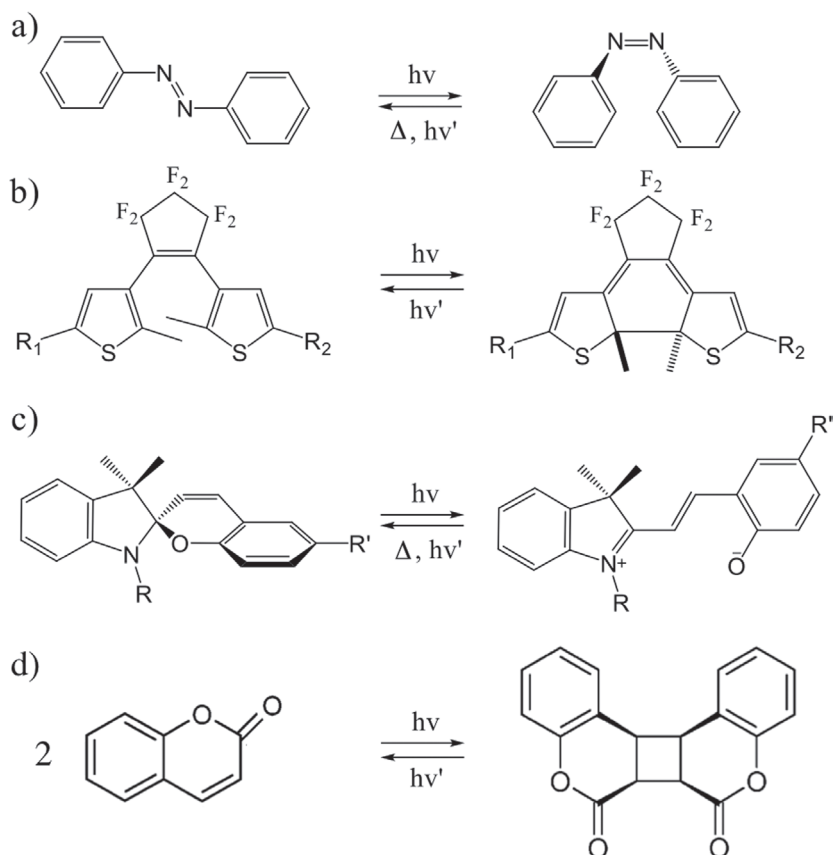
Large geometrical change that occurs in azobenzene molecules upon absorption of light can be measured quite precisely. While the *trans* form of azobenzene is nearly perfectly planar, in *cis*-azobenzene, the two phenyl rings are twisted at 90° relative to the C=N=C plane.<sup>[23,24]</sup> Isomerization reduces the distance between the 4 and 4' positions from 0.99 nm in the *trans* form to 0.55 nm for the *cis* form.<sup>[25–27]</sup> This geometric change also increases the dipole moment, from zero in the *trans* form of parent azobenzene, to 3.1 D in the *cis* form, or even greater differences for 'push-pull' functionalized derivatives.<sup>[28]</sup> The free volume requirement of the *cis* shape can be much larger than the *trans*,<sup>[29]</sup> and the free volume required to *cycle between* these two states can be larger still. It has been estimated that the minimum free volume pocket size required to permit isomerization to proceed through a transition state via the inversion pathway is 0.12 nm<sup>3</sup>,<sup>[12,23,30]</sup> and via a rotation pathway approximately 0.38 nm<sup>3</sup> is required.<sup>[31]</sup> The effects of matrix-free volume constraints on photochemical reactions in general are also

important to consider,<sup>[32]</sup> and overall the geometrical changes in azobenzene are very large by molecular geometric standards; it is thus perhaps no surprise that azo isomerization can influence a wide range of secondary material properties. While the magnitude of the shape change is modest, measurements via high-pressure spectroscopy (10<sup>4</sup>–10<sup>5</sup> atm) of the force applied and of the energy exerted through this isomerization show that azobenzene can perform as an extremely powerful molecular unit,<sup>[33]</sup> which can be employed in carefully engineered actuators to enhance the mechanical advantage provided. Insect wing muscles similarly contract only 1–2%, yet with a force and speed to enable flight. This molecular displacement generates a significant nanoscale force, which has been measured as pN to nN in single-molecule force spectroscopy experiments,<sup>[34,35]</sup> and compared well to theory.<sup>[36]</sup> Harnessing such molecular-scale motions into useful work in a 'device' is of course the next challenging step.

While it is important to study the nanometer-scale azobenzene single molecule conformational changes that can give rise to macroscopic phenomena, by far the most useful applications to mechanical actuation are the reversible changes that can be imparted to bulk phenomena or to macroscopic motion over the micrometer to centimeter size-scale of real materials. Of particular interest to polymer scientists is the immense materials potential that a macromolecular platform can provide to house and organize photo-switch guest molecules, as polymers indeed were the host chosen long ago by natural photochemicals such as retinal/rhodopsin for vision, and chlorophyll for photosynthesis. The first consideration for artificial platforms is perhaps whether or not the host material can contract or expand sufficiently along with the photo-guest, or preferably to even enhance or magnify the mechanical effect. As a first example where measurement was particularly facile, of floating azo monolayer materials at a liquid surface, it was found early on that the larger molecular size of the *cis* shape leads to a corresponding lateral expansion of many tens of percent.<sup>[37]</sup> Another highly visible demonstration of macroscopic motion induced by the isomerization of azobenzene is the mechanical bending and relaxing of a free-standing liquid crystal network (LCN), and a liquid crystal elastomer (LCE) film.<sup>[38,39]</sup> Bending occurs here in these relatively thick films because the free surface (which absorbs the light) contracts, while the interior of the film (which remains dark due to the strong absorbance in the outer part of the film) does not contract. Because polarized light can be used to control the direction of bending, the materials enable multi-directional photo-mechanical control.<sup>[40]</sup> Other examples include expansion-bending of cantilevers coated with an amorphous azobenzene thin film,<sup>[41]</sup> and macroscopic contraction-bending of fibers and cantilevers made of azobenzene LCEs.<sup>[42–47]</sup> One can also invert the coupling of mechanical and optical effects: by stretching elastomeric azo films containing a grating, for example, one can orient the chromophores and take advantage of the associated wavelength-selection properties to guide or filter incoming beams of light, coding information.<sup>[48]</sup>

### 4. Photo-Mechanical Effects

For the first tentative steps towards developing real light-activated devices or even machines, both light input properties



**Figure 1.** Examples of some common molecular isomerizing photo-switches: a) azobenzenes; b) diarylethenes; c) spiropryans. Reproduced with permission.<sup>[9]</sup> Copyright 2017, Royal Society of Chemistry. d) Photodimerization of coumarins. Reproduced with permission.<sup>[10]</sup> Copyright 2004, American Chemical Society.

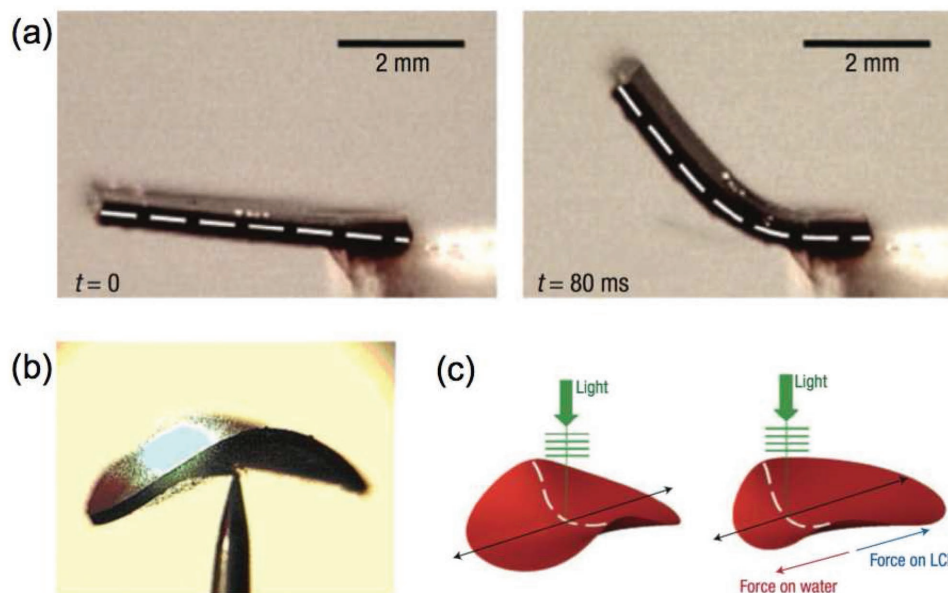
and resulting motion need to be measured, analyzed, and then understood, in order to then be controlled and optimized. The photo-mechanical effect can be defined strictly as a change of shape of a material upon exposure to light (not due simply to heat expansion) and is a phenomenon expressed via the presence of light-switching chromophores in a material.<sup>[49]</sup> Since many azobenzene systems experience significant photo-thermal heating as well, however, from light absorption, for practical applications the overall photo-mechanical effect is the sum of the photo-chemical and photo-thermal contributions where a light-driven component is dominant, though often difficult to de-couple. In its essence, photo-mechanics refers to the direct transformation of light into mechanical motion, and in a crude sense, because everything changes shape somewhat when irradiated, in practice to be useful, the photo-mechanical magnitude should greatly exceed simple thermal expansion. For ease of observation and with the goal of maximizing photo-mechanical efficiency, such materials are generally fabricated into high aspect ratio sheets or needles, forming a thin 2D or 1D actuator. An actuator is an energy transducer that converts an input stimulus into mechanical motion, and in the context here, actuators are the components of a device or machine which convert the input light into mechanical movement. Light-activated photo-reversible actuators in particular can be easily designed and

synthesized, and many are able to undergo large deformations upon relatively low levels of input stimulus.<sup>[50,51]</sup> Photo-mechanical actuation, where light energy is converted into mechanical shape changes of a material, is a particularly promising transducer for small devices due to the possibility for precisely defined, noncontact actions triggered by low-cost light sources or even by sunlight, with little unwanted heating, and where the weight and bulk of wires and batteries is prohibitive.

Azobenzene-based systems are excellent potential candidates for photo-mechanical actuation for many niche applications involving localized actuation, small size, remoteness of the power source, and use in wet environments, so they need to be free from the encumbrance of batteries, wires, electric current, and internal moving parts. A simple and convincing demonstration of azo isomerization causing macroscopic motion is the mechanical bending and unbending of free-standing azo polymer thin films.<sup>[38,39]</sup> As the direction of light polarization can be used to control the bending direction, the polymer materials enable fully directional photo-mechanical control,<sup>[40]</sup> and have been used to drive the macroscopic motion of a ‘swimming’ floating film (Figure 2).<sup>[52]</sup> For such thin films floating on the surface of water, a contraction in the direction of polarized light was observed for LC materials, whereas an expansion was witnessed for amorphous materials.<sup>[53]</sup> A related amplification of azo micro-motion to macroscopic motion is the photo-induced bending of a micro-cantilever coated with an azobenzene dye.<sup>[41]</sup> Other clear examples include the macroscopic bending and three-dimensional control of fibers made of azobenzene liquid crystalline elastomers,<sup>[42–44]</sup> light-driven micro valves,<sup>[54]</sup> and full plastic motors.<sup>[55]</sup> In the following sections three summaries of various manifestations of the photo-mechanical effect leading to macroscale actuation with azobenzene will be described, grouping together the achievements firstly of simple bending or actuation, then of more complex and combined motions, and then lastly what we will term real devices, as they integrate the photo-responsive material into a multi-component structure, and perform more sophisticated tasks beyond simple actuation.

#### 4.1. Basic Bending and Actuation

Photo-mechanical effects in azobenzene dye materials were first noted more than 50 years ago. This early head-start is another reason for the now-ubiquitous use of azo transducers. Merian can be credited with the first observation of the photo-mechanical effect in textile fibres colored with small amounts of orange azo dye, when in 1966 he observed with impressive care and patience that these azo-nylon filaments shrank slightly during



**Figure 2.** a) Photo-mechanical response of a dye-doped LCE sample. The dashed white line shows the orientation of the nematic director. b) The shape deformation of the dye-doped LCE sample. The film is supported by a pin and the illumination is centered on the pin. c) Illustration of the mechanism underlying the locomotion of the LCE sample and interaction with the fluid below it. The black arrows show the axis of the bend. Reproduced with permission.<sup>[52]</sup> Copyright 2004, Nature Publishing Group.

dry processing upon irradiation with a Xe daylight lamp.<sup>[56]</sup> From this literal ‘watching-paint-dry’ experiment and first report in the *Textile Research Journal*, the relatively unimpressive overall contraction of under 0.1% of the original length and complexity of the sample meant that it was not until twenty years later that anyone took much notice of this curious effect. However, in the 1980s, Eisenbach prepared poly(ethyl acrylate) networks cross-linked with a similar azobenzene chromophore,<sup>[57]</sup> and these samples exhibited similar photo-induced contraction of around 0.2% upon irradiation with UV light, and corresponding expansion after visible light irradiation. In further investigations around the same time, Matejka et al. reported that upon an increase of loading of azobenzene into the material above 5%, a greatly increased photo-induced contraction of nearly 1% could then be achieved, paving the way for significant azo actuation by increasing dye loading levels.<sup>[58–60]</sup>

Thin film polymer actuators capable of responding to external stimuli are most desirable for many practical applications, either amorphous, or organized (such as liquid crystalline). Photo-induced reversible changes in the elasticity of azo-containing semi-interpenetrating network films were achieved by UV and visible light irradiation.<sup>[62]</sup> These network films exhibited reversible shape deformation by switching the UV light on and then off, and the photo-mechanical effects were attributed to the reversible change between highly aggregated and dissociated states of the azobenzene groups.<sup>[61–63]</sup> In other studies, similar films of azobenzene-containing vinyl ether films with polycaprolactone had achieved (then) “rapid” (a few seconds) anisotropic shape deformation and recovery. The films, placed under a constant tensile stress, were stretched either perpendicular to, or parallel to, the tensile stress before irradiation. Photo-isomerization of these films resulted in contraction of the film when stretching parallel to the tensile

stress, and film elongation when stretching perpendicular to the tensile stress. The photo-mechanical response was observed to increase with film stretching extent, and was speculated to arise from an anisotropic response effected by the isomerization-induced vibration of azobenzene units, which decreased the modulus of the amorphous area being deformed.<sup>[64]</sup> Other polymer film systems that exhibited large bending angles (90°), and high bending intensities have since been also reported.<sup>[65]</sup>

#### 4.2. Beyond Bending: More Complex Mechanics

Control over molecular alignment can be a powerful tool for amplifying and optimizing large-scale photo-mechanical effects, so photo-mechanical levers for more complex systems are often fabricated from liquid-crystalline polymers (LCPs). In simple amorphous azobenzene-containing polymers, photo-induced dimensional changes in the range of only 1–2% maximum can usually be achieved, and in general they photo-expand with light. In LC polymers and elastomers, however, reversible uniaxial photo-contraction may reach 15–20%,<sup>[66–68]</sup> and in general these systems photo-contract. The light-induced forces are brought about by surface strains in three-dimensionally deformed films,<sup>[69]</sup> and can be large enough to do significant work against an external load, being able to fuel, for example, some real light-powered devices such as the plastic motors,<sup>[55]</sup> robotic-arms,<sup>[70]</sup> and catapult ‘devices’<sup>[71]</sup> that will be described in detail in the next section. Very often then, LC systems are chosen when speed and magnitude are a priority, and amorphous systems when power and robustness are of paramount design importance.

The reason for superiority in some aspects of mechanical control of LC systems over amorphous systems lies in an

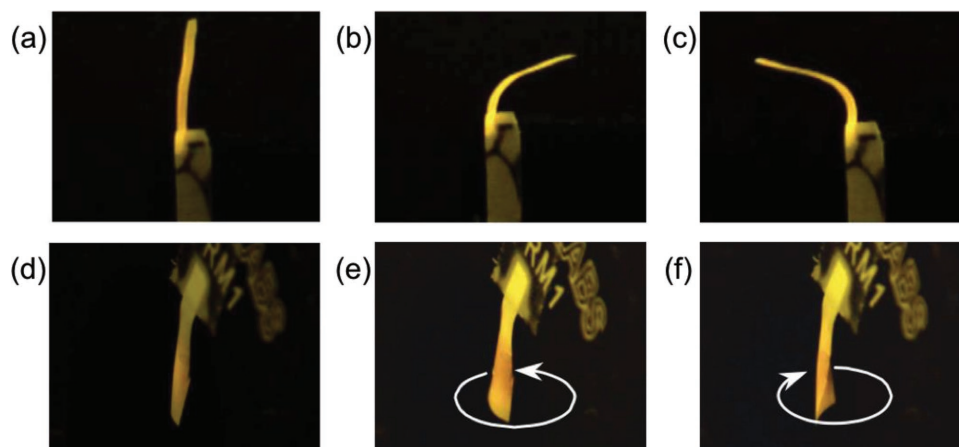
orientation enhancement aspect of the actuation mechanism. In amorphous polymers, the photo-mechanical deformations occur in an isotropic and uniform way, that is, there is no preferential direction for deformation. Anisotropic materials, however, such as LC materials, provide the opportunity for light-direction control over the mechanical response. Efficient photo-induced actuation is particularly strong in liquid-crystalline polymer networks (LCNs) and elastomers (LCEs). LCEs are lightly crosslinked polymers in which the high mesogen order alignment can be coupled with motion of a highly elastic polymer network, giving rise to various unique mechanical properties of the host LCEs. Upon heating, the alignment order decreases, and when the transition temperature between the LC–isotropic phases is exceeded, the films exhibit a contraction along the mesogen alignment direction. Such anisotropic deformation can be significant, and along with the reversibility of the process (upon cooling, LCE films revert back to their original size), and many versatile mechanical properties of the polymer network, LCE systems thus show great potential and promise as artificial muscles.<sup>[72–77]</sup>

The directional light-control potential of photo-controlled actuators made from LCEs was first demonstrated when Ikeda et al. reported various photo-induced 3D motions (bending) of azobenzene LC gels and elastomers, controlled with polarization.<sup>[39,78,79]</sup> The bending here was driven by a gradient in the isomerization-induced reduction in the LC alignment order. Reversibility was achieved via UV irradiation, which destroys the mesogen alignment. First, *trans-cis* isomerization causes the sample to bend, then irradiation with light in the visible-green region restores the azobenzenes to the *trans*-form and the film returns to its original unbent state. The direction of the bending can be controlled via the phase structure of the material system. Homogeneously aligned polymer systems always bend along the mesogen alignment direction,<sup>[79]</sup> while the bending direction of polydomain LCEs can be controlled by the direction of linearly polarized light.<sup>[78]</sup> The latter serves as an example for a precisely controlled and repeatable photo-induced

deformation along any chosen direction, enabling a wider photo-mechanical directional control, an important step towards practical applicability of light-driven actuators.

Another example of more complex direction control is provided by artificial muscle-like photo-mechanical fibres, the bending direction of which can be controlled simply by changing the position of the illuminating source.<sup>[80,81]</sup> Conversely, homeotropically aligned, crosslinked LC polymer films in contrast were observed to exhibit a completely different bending behavior; upon UV light exposure they bent *away* from the light source, due to isotropic expansion of the surface upon *trans-cis* isomerization.<sup>[82]</sup> The initial chromophore alignment is not the only way to control the direction of the photo-induced bending: Tabiryan et al. demonstrated that the direction of bending can also be controlled with the direction of polarization of the excitation beam, an effect attributed to light-induced reorientation of the azobenzene groups (**Figure 3**).<sup>[83]</sup> More recently, van Oosten et al. showed that the bending direction can also be controlled by designing the material to house internal composition gradients within the LC polymer network,<sup>[84]</sup> and as the latest example, Shishido et al. showed that the direction of bending can also be dictated by the type of bonding between the azobenzene groups and the crosslinked polymer network.<sup>[85]</sup>

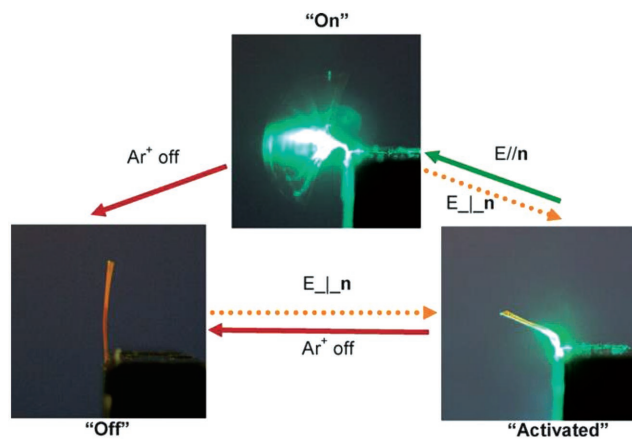
An interesting and important newer development in the design of more complex photo-actuators is the expansion from simple linear contraction and in-plane bending, to out-of-plane twisting and helical motions. An inspiration for increasing the complexity of the photo-induced motion to include twisting perhaps derives from nature: various biological ‘engines’ are built upon such twisting or helical motions,<sup>[86,87]</sup> and many insects combine bending, twisting, and sweeping motions together to generate sufficient power for efficient flight.<sup>[88,89]</sup> White and coworkers at the USAF were the first to emulate and achieve such combined in-plane oscillation and out-of-plane twisting in artificial azo-containing liquid-crystal polymer networks, where oscillation (or bending) coupled with an out-of-plane twisting



**Figure 3.** Photographs of the optically induced deformation of an azo LC polymer film. a) The initial shape of the polymer film. b,c) The polymer is bent away from and towards the laser for beams polarized perpendicular and parallel to the film orientation, respectively. d) The polymer film used for inducing twist deformations with a laser beam of tilted polarization. The film is folded in directions e) counter-clockwise and f) clockwise for  $-45^\circ$  and  $45^\circ$  polarizations, respectively. Reproduced with permission.<sup>[83]</sup> Copyright 2005, The Optical Society.

occurred at intermediate angles, due to combined shear and strain gradients caused by non-uniform light absorption through the thickness of a cantilever.<sup>[90]</sup> The same research team then applied such fast and complex motions as high-frequency photo-driven oscillators,<sup>[42–44,90,91]</sup> capable of achieving frequencies of oscillation as high as 270 Hz and displayed an energy conversion efficiency of 0.1% upon irradiation with a focused blue laser beam, with a wide range of motion close to 180° (Figure 4). Their cantilevers also possessed a significant storage modulus ranging from 1.3 to 1.7 GPa, and were shown to bend faster and attain larger bending angles with a mono-domain orientation, increased azobenzene concentration, and reduced thickness. The bending angles were also dependent upon the incoming light polarization as well as atmospheric pressure. Importantly, these cantilevers were shown to oscillate by flapping through their own shadow repeatedly under a focused beam of only sunlight,<sup>[44]</sup> and thus offer the great potential for remotely triggered photo-actuation under a universally available and free stimulus, which is of interest for independent flight towards the sun or solar energy harvesting with adaptive optics. Such high-frequency solar-powered oscillators could in principle power independent miniaturized micro-opto-mechanical systems, as they contain both the kinematic structure (cantilever), and the force generation component (azobenzene) in a single unit.

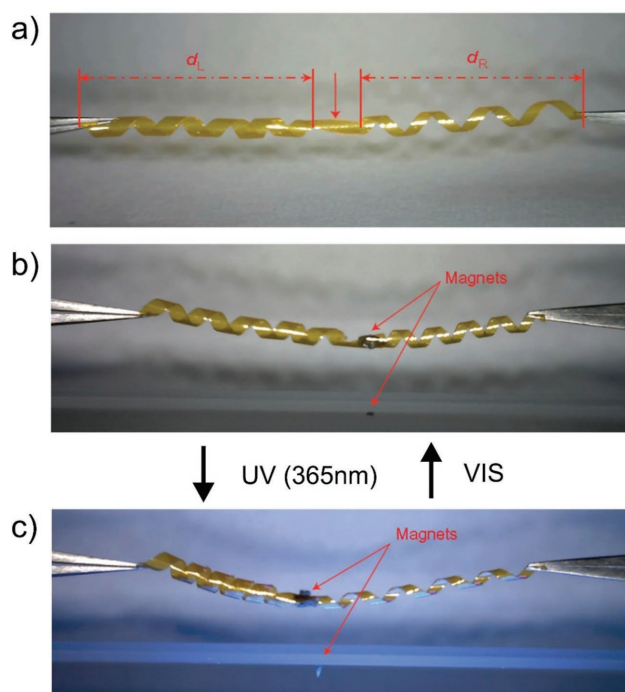
These devices were fabricated from azo-LCNs entirely composed of azobenzene mesogens, so as in such systems, essentially all the incident irradiation is absorbed within the near-surface region of a thickness of 1–2 μm, or even less. As typical thicknesses of the films used are on the order of 10–20 μm, the majority of the azobenzene groups in the bulk of the film thus remain dark and unaffected by incident light. As a result, the efficiency of the photo-mechanical effects generated in such simple uniform azobenzene actuators is far from optimal,



**Figure 4.** The optical protocol for activating a light-powered oscillation of a cantilever. The nematic director ( $n$ ) is positioned parallel to the long axis of the polymer cantilever of dimension 5 mm × 1 mm × 50 mm. When exposed to light polarized orthogonal to  $n$  ( $E \perp n$ ) bending occurs towards the laser source. Cycling the  $Ar^+$  laser from  $E \perp n$  to  $E // n$  can turn the oscillation ‘on’, while blocking the  $Ar^+$  or returning the polarization of the laser beam to  $E \perp n$  turns the oscillation ‘off’. Reproduced with permission.<sup>[42]</sup> Copyright 2008, Royal Society of Chemistry.

both too concentrated at the surface, and absorbed in an inefficient decaying exponential profile so that most of the light energy is lost to internal stress instead of actuation. This first challenge was addressed by Broer et al., who designed actuators fabricated from densely crosslinked high-elastic-modulus polymers with relatively low azobenzene concentration.<sup>[92]</sup> Such twisted-nematic elastomers have proven particularly interesting in terms of their photo-mechanical behavior, as the chirality associated with the twisted molecular alignment may be used to produce a coiling motion of elastomeric cantilevers, which shows uniaxial bending or helical coiling deformation modes after UV irradiation. The initial shape of these twisted-nematic cantilevers can be sensitive to their dimensions: depending on the aspect ratio, they can adopt either helicoidal or spiral shapes.<sup>[93,94]</sup> The light-triggered twisting/coiling motions were further extended by Wie et al., who reported photo-mechanical responses of both twisted-nematic and hybrid-aligned cantilevers.<sup>[91]</sup>

Other approaches to increase the penetration depth of driving light, and thus overall efficiency, were demonstrated by Palfy-Muhoray et al. as early as in 2004, showing that even non-photo-responsive LCEs doped with low concentrations of azobenzene dyes can exhibit remarkable and unprecedented photo-induced deformation behavior.<sup>[52]</sup> In fact, it has been shown recently that the optimum photo-induced response (in terms of the stress generated) is achieved using a moderate concentration of azobenzene, supplemented with higher concentrations of non-photoactive mesogens.<sup>[95]</sup> The largest mechanical force generated by photo-irradiation of the various films was measured as 2.6 MPa. Detailed studies have also been performed on the crosslinker concentration dependence of azo-LCN systems. The crosslinking density alters the elastic modulus and the thermo-mechanical properties of the material system, affecting the mobility of the polymer segments, where, in general, low crosslinker concentration is favorable for optimizing the photo-induced/thermally induced deformation of crosslinked LC polymers, whereas a higher crosslinker concentration (thus higher modulus) is preferable for high photo-induced stress generation.<sup>[76,96,97]</sup> A recent report by Shishido et al. suggests that the photo-induced bending of azo-CLCPs is accompanied by a significant, 2.5-fold decrease in the Young’s modulus upon UV irradiation.<sup>[97]</sup> Such “photo-softening” was observed to be the most pronounced in samples with low crosslinker concentration (and thus low modulus), which also displayed the most efficient photo-induced bending. Upon increasing the crosslinker concentration (and again the modulus), both photo-induced bending and the photo-softening effect was observed to be less efficient, suggesting that there might be a connection between the photo-softening and the photo-mechanical properties of azo-LCNs. In order to explore such connections further, the Broer group offered a route to maximize photo-expansion, and consequently photo-mechanical bending.<sup>[98]</sup> They found that larger expansion was possible upon simultaneous irradiation of an azo-LCN by UV and visible light, stimulating dynamic *trans* ↔ *cis* conversion and enhancing the free volume of a system by a factor of 4. Surface protrusions as high as 12% were achieved on these azo-LNC films compared to just a 3% expansion upon single wavelength irradiation.

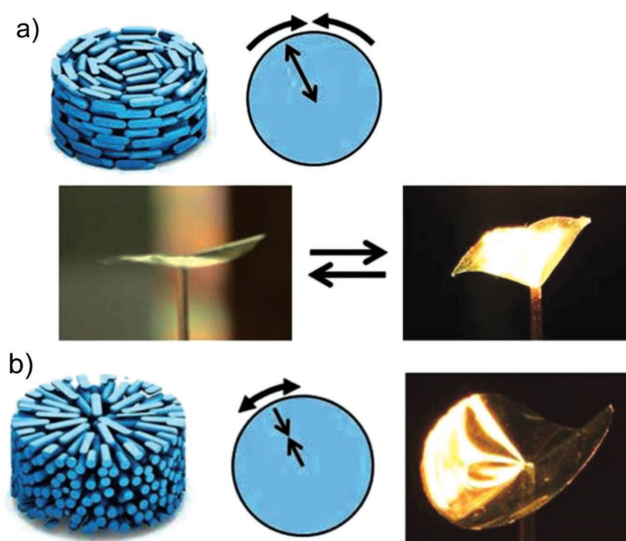


**Figure 5.** The central kink in a mixed helicity ribbon a) incorporating azobenzene chromophores that undergoes a piston-like shuttling motion upon irradiation with b) visible and c) UV light. A magnet is connected to the kink and is transported, and also transmits the push–pull shuttling motion to a second magnet placed 10 mm below. Reproduced with permission.<sup>[99]</sup> Copyright 2014, Nature Publishing Group.

A further step towards biomimicry was recently accomplished by Katsonis et al., who fabricated spring-like photo-actuators that capture some aspects of the extensile function of plant tendrils to demonstrate various types of complex motions such as the winding and unwinding, and even inversion of a helix, all photo-induced as shape changes of azobenzene containing LC polymer films (Figure 5).<sup>[99]</sup> Here, using spring-like polymeric films, molecular movement was converted and amplified into controlled and reversible twisting motions using LC polymer photo-actuators comprised regions that exhibited different dynamic behavior, where these light-induced conformation changes were determined and controlled by their alignment directions. Such motion mimics the movement of plant tendrils such as those found for example in wild cucumbers. The helical deformations were pre-programmed by including chiral azobenzene dopants, and by controlling the relative orientation of the aligned liquid crystals within each spring, respectively. Chiral dopants induce a left-handed or right-handed twist in the liquid crystalline film, and depending on the direction in which such a film is cut, it would either curl, twist, or do both upon irradiation with light. Complex extensile and contractile coiling and twisting helical motions are thus possible, and mechanical energy can be exported from the system by the incorporation of a pair of magnets. Most recently, they reported photo-switching behavior and thermal stability of photo-activated molecular deformation systems on a larger macroscopic scale.<sup>[100]</sup> By employing fluorinated azobenzenes as basic switching elements to slow

the thermal re-conversion from *cis* back to *trans* shapes, the fluorinated switches activated by visible light retained their photo-deformed shape for more than eight days, to build something now approaching ‘real’ light-powered molecular devices photo-switches that can now overcome thermal relaxation on a device-useful timescale. Furthermore, White et al. demonstrated photo-motility of thin strips of azobenzene-functionalized liquid crystalline polymer networks (azo-LCNs).<sup>[101]</sup> By irradiating these polymer films with broadband UV light they revealed that the both directionality and rate of photo-motility are highly dependent on the orientation of the liquid crystalline director.

Other recently notable advances in the field of more advanced mechanical-actuating polymers derive from the use of either complex liquid-crystal order or liquid-crystal elastomer microstructures, and the development of movement patterns that are more complex, designed via lithographic techniques, and respond to a wider range of stimuli, and more exactly, local addressability or spatial precision.<sup>[102–105]</sup> Notably, LC polymer networks that are more complex-ordered and patterned have been most studied by Broer and co-workers,<sup>[104,105]</sup> and engineering of complex molecular ordered and patterned LC polymer networks and elastomers into proof-of-principle real devices has been demonstrated by both the Broer and White groups.<sup>[106]</sup> Here, they used LC cells containing cinnamate-based photo-alignment layers that were irradiated through a photomask with an opening that was wedge-shaped while rotating the cells slowly, using a programming of LCN and LCE materials to localize their mechanical response to generate surface features, or local shape changes. Using these cells for photo-polymerization, various complex-ordered, free-standing films with continuous change of the LC alignment direction were achieved, and most recently, Broer et al. reported a heat-driven mechanical effect of azimuthal and radial-aligned actuator films with an IR lamp (Figure 6).<sup>[104]</sup> By using patterned



**Figure 6.** Actuation behavior of crosslinked LC polymer films with a) azimuthal and b) radial alignment upon heating with an IR lamp. The arrows along the radius and the azimuth indicate the direction of deformation. Reproduced with permission.<sup>[104]</sup> Copyright 2012, Wiley-VCH.

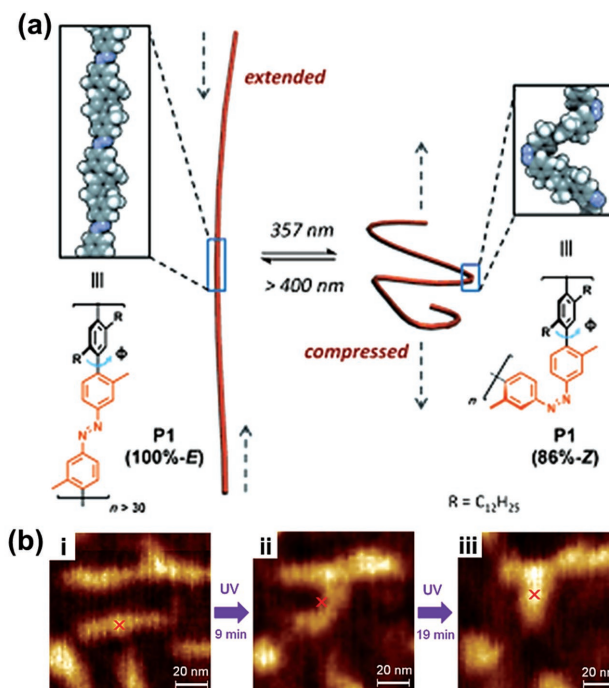


molecular alignment, interesting photo-thermal actuators exhibiting checkerboard patterns upon stimulus were fabricated, and the deformation direction of the actuator films were observed to be different.<sup>[105]</sup>

## 5. Building some 'Real' Light-Powered Molecular Devices

Ultimately, the precise and robust integration of optical actuators into higher dimensional architectures that permit mechanical action to be harnessed by many components working together is essential to span the gap between simple actuating molecular motion, and performing real 'useful' microscopic, mesoscopic, and macroscopic work. 'Useful' in this sense is subjective, yet might include moving linearly along a surface on demand, or other unidirectionally controlled locomotion such as walking, rolling, swimming, flapping, or even flying. This definition might also include performing work on stationary objects, such as shuttling, levering, throwing, or even catapulting. Motors such as tank treads, or belt-and-pulley systems powered by sunlight might also qualify, built from actuator parts driven by reversible molecular shape changes, from the mechanical forces and stresses that can result from irradiation. If cleverly applied, these molecular forces can be amplified into such macroscopic shape-shifting, actuating 'artificial muscles' or true 'molecular devices'.

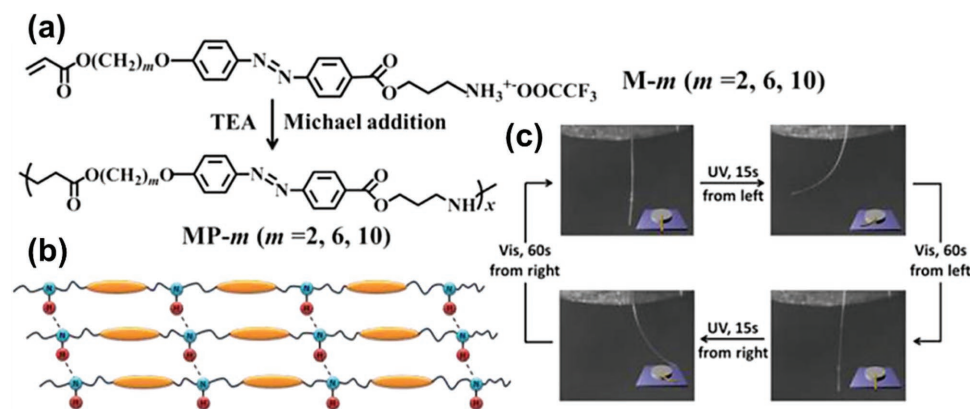
Azobenzene chromophores hold great promise in particular for application as 'artificial muscles' through linear polymerization, placing the azo photo-switch directly into the polymer backbone instead of just the side groups, which invites close comparison to the linear contractile mechanism of real muscle tissue. By incorporating azobenzene within the main chain of a linear assembly, the parallel culmination of modest dimensional changes of just a few Ångströms for each chromophore can amplify in concert, resulting in dramatic changes to the contour length of the polymer. Capitalizing on this strategy, Gaub and co-workers demonstrated the capability of individual polyazobenzene peptides to perform mechanical work by tethering one end of the polymer to a substrate, and binding the other end to a flexible cantilever, allowing one to measure a force exerted by the polymer contracting upon photo-isomerization.<sup>[34]</sup> The extent of this polymer deformation, and thus the usefulness of the peptides for real opto-mechanical applications, depends on both the minimization of the electronic coupling between azobenzene groups, and the conformational rigidity of the backbone.<sup>[107]</sup> The synthesis of rigid-rod azobenzene-containing poly(*para*-phenylene) backbones is one strategy to maximize photo-deformation, enabling accordion-like compression and extension of chains upon cycling with UV and visible light (Figure 7a).<sup>[108]</sup> Lee et al. demonstrated that these single-chain polymeric assemblies may even exhibit crawling movements when deposited onto a graphite surface modified with octadecylamine, and imaged with scanning force microscopy (Figure 7b).<sup>[109]</sup> Chemically or physically cross-linked supramolecular assemblies of these linear photo-mechanical polymers may be envisioned to lift weights, behave as actuators, and to perform other types of directed work with greater resistance against deformation fatigue than individual strands.<sup>[110]</sup> Fang



**Figure 7.** a) Schematic of a main-chain azobenzene-containing polymer (P1;  $R = C_{12}H_{25}$ ) with a poly(*para*-phenylene) backbone. Irradiation with UV or visible light facilitates photo-isomerization of azobenzene and conversion to the compressed and extended conformations, respectively. Reproduced with permission.<sup>[108]</sup> Copyright 2011, Wiley-VCH. b) Scanning force microscopy images of P1 deposited on a modified graphite surface. The polymer crawls along the surface as it contracts upon UV irradiation, demonstrating control over movement direction. The functionalization or tethering of the polymer strands to scaffolds may enable the macromolecules to perform work by lifting weights or transporting cargo. Reproduced with permission.<sup>[109]</sup> Copyright 2014, American Chemical Society.

et al., for example, reported using a simple method of melt spinning to fabricate azobenzene-containing main chain polymers hydrogen-bonded into cross-linked fibers (Figure 8).<sup>[111]</sup> The same authors also reported some photo-induced mechanical properties of the fibers, reporting a maximum stress of 240 kPa generated at 35 °C by a single fiber after UV irradiation. This force reported is similar to the maximum tension forces reported for some chemically cross-linked azobenzene containing polymer fibers, and even to human striated muscles (ca. 300 kPa).<sup>[82]</sup>

With multi-component engineering, such photo-induced deformations (expansion/contraction and bending) can also be harnessed for stationary actuation to design proof-of-principle micro-machines capable of generating continuous mechanical work on constant irradiation. As a first example of such engineering in 2008, Ikeda, with Yamada, Barrett, and co-workers translated the photo-induced deformations of a crosslinked liquid-crystalline polymer film (CLCP) film into rotational motion.<sup>[56]</sup> Here, a laminated film of azobenzene with a thin polyethylene sheet was joined on the two ends of the composite film to create a continuous ring, and then mounted onto a pulley system as a 'belt'. Upon simultaneous irradiation with both UV and visible light at +45 and -45 degrees to each of

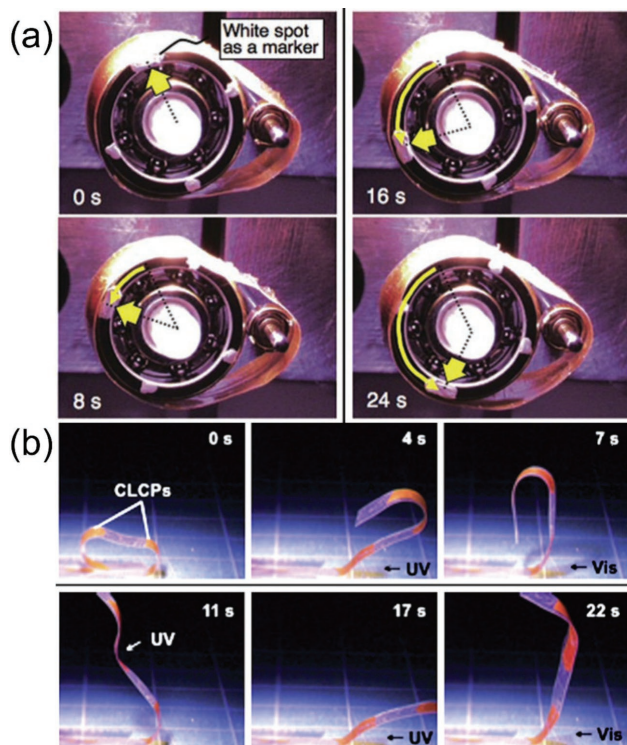


**Figure 8.** a) Synthetic route and chemical structures of acrylate-type azobenzene monomers. b) Supramolecular hydrogen bonding interactions between main-chain polymers to facilitate physical cross-linking. c) Photographs of a polymeric fiber fabricated by simple melt spinning. The fiber reversibly bends upon irradiation with ultraviolet and visible light. The fibers demonstrate robust photo-deformation fatigue resistance and high thermal stability, and show promise for applications as photo-mechanical actuators. Reproduced with permission.<sup>[111]</sup> Copyright 2013, American Chemical Society.

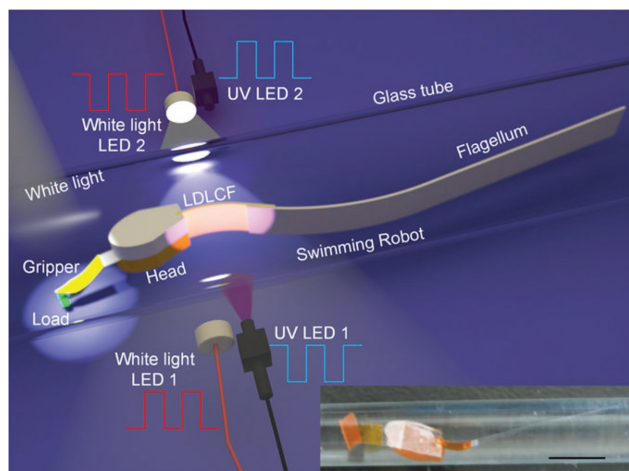
the pulleys to ‘pull’ and ‘push’, the belt was driven continuously in counter-clockwise rotational motion when the light was on (Figure 9a). Other following examples by the same research collaboration included an ‘inchworm’ locomotion achieved by attaching a sheet of azo-LCN on a flexible polyethylene (PE)

substrate with sliding friction that is asymmetric.<sup>[112]</sup> In this application the film undergoes repeated photo-mechanical ‘push-up’ contractions, while the asymmetric end shapes on the PE film edges act like a ratchet, directing a uni-directional motion of the film. Robotic arm-like actuation was also demonstrated by using flexible azo-polymer ‘hinge’ joints (Figure 9b), where specific locations of a PE film were laminated with azo-CLCPs, which provided optical control (expansion or contraction) at various specific individually addressable positions of the film. The light-reversible sections containing the azo-CLCPs thus functioned as hinge joints, acting as ‘arms’ with remote control over the ‘elbows’ and ‘wrists’.

In these various examples of photo-driven actuation, the primary energy source was the combination of UV and visible light sources, which gave rise to locally addressable photo-induced contraction/expansion of the photo-active polymer films. However, UV light is harmful to many living organisms, so it is important to further develop these photo-driven actuators to be powered only by visible light, and ultimately sunlight, for any bio-related applications, and in general there is an advantage to avoiding UV light to lessen material degradation and heating. Some of the first truly sunlight-driven photo-mobile materials, employing photo-responsive azotolane moieties, were developed by Yu et al.,<sup>[113]</sup> who also fabricated visible-light-driven micro-robots that were capable of lifting and moving an object weighing 10 mg, ten times the weight of the robotic arm itself.<sup>[70,114]</sup> This integrated system consisted of several azo-LCN films on PE substrates connected by joints to mimic the wrist, hand, and even fingers. The robotic arm could be manipulated on demand to perform complex movements by addressing individually the various photo-active sections, demonstrating for example that an object could be picked up and then dropped by targeting the ‘fingers’, while the entire arm could be moved by focusing light instead at different ‘elbow’ locations. Following this, White et al. then demonstrated a clever photo-fuelled catapult motion that was capable of launching an object using only moderate-intensity blue-light irradiation to a launch velocity of 0.3 m/s.<sup>[72]</sup> Yu et al. also designed a similar composite material in which up-converting nanophosphors assisted in inducing



**Figure 9.** a) A series of photographs showing the rotation of a light-driven ‘plastic motor’ of LCE laminated film, induced by simultaneous irradiation with UV and visible light. Reproduced with permission.<sup>[55]</sup> Copyright 2008, Wiley-VCH. b) Series of photographs of a 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. Reproduced with permission.<sup>[112]</sup> Copyright 2009, Royal Society of Chemistry.



**Figure 10.** Schematic diagrams of a micro swimming robot and light irradiation system, showing a complex movement actuated and controlled by remote light signals. The bottom insert at the right side of the figure is the actual robot with the load grabbed by gripper with a scale bar of 5 mm. The light beam of controlling the gripper is perpendicular to that of driving the robot to swim. The head of the micro swimming robot has a width of 2 mm, a height of 3 mm, and a length of 5.5 mm; the whole robot has length 26.3 mm and a weight of 31.9 mg. Reproduced with permission.<sup>[118]</sup> Copyright 2015, Nature Publishing Group.

the photo-induced deformation using near-infrared (980 nm) light.<sup>[115]</sup> Moreover, the same group developed a red-light-controllable soft actuator driven by a complex low-power excited triplet-triplet annihilation-based up-conversion luminescence mechanism (TTA-UCL).<sup>[116]</sup> This novel red-light-controllable soft actuator based on TTA-UCL has advantages in potential biological applications, where using red light removes thermal effects entirely, and permits excellent penetration depths into live tissue.

A clever new strategy was reported to manipulate fluid slugs by light-driven tubular micro-actuators fabricated from photo-responsive liquid crystalline polymers.<sup>[117]</sup> Here, photo-responsive asymmetric deformation of the actuator induces capillary forces for liquid propulsion. Several shapes of micro-actuators were fabricated, such as linear, serpentine, helical, and 'Y'-shaped, from a mechanically robust linear liquid crystal polymer. Then, a light-driven, micro swimming 'robot' was created with a gripper based on this new functional material, to realize more complex movements like swimming, grabbing, carrying, and transport, as shown in **Figure 10**.<sup>[118]</sup> These remotely actuated light-driven materials achieve complex driving control of various micro-robotic structures, and as such these materials can be expected to hold great potential for applications such as micro-machines and light-powered robotics.

Newer and more sophisticated examples of photo-mechanical motions and actuators continue to be developed. Zeng et al. demonstrated a light-actuated walking micro-robot based on LCE artificial muscles,<sup>[119]</sup> where the actuator has four conical legs on the LCE body, and can walk via sequential contraction-expansion of the body with a directed 532 nm laser beam. Palagi et al. also demonstrated how soft LCE micro-robots can be driven by structured monochromatic light to perform sophisticated biomimetic motions,<sup>[120]</sup> inspired by the concept

of travelling waves, where complex behaviors can be achieved by directing appropriately-coded structured complex light fields. Rogos and co-workers prepared a natural-scale, soft, caterpillar-like machine,<sup>[121]</sup> where various tasks that the robot performed included walking up a slope, squeezing through a narrow slit, and pushing around objects.

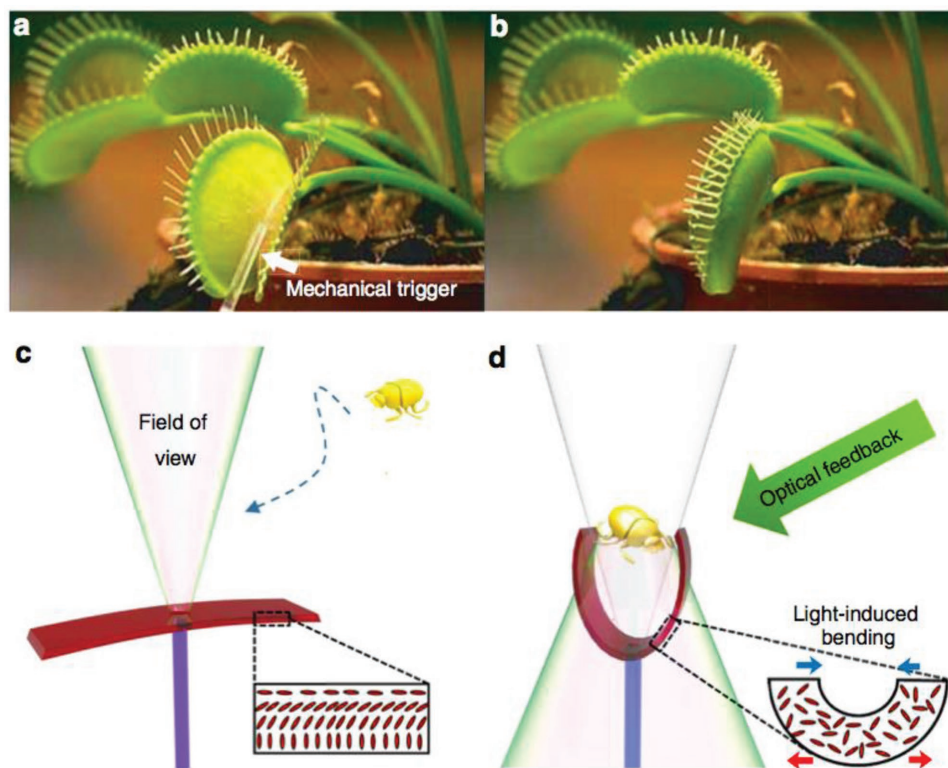
Finally and most recently, a 'predatory' biomimetic micro-robot was proposed by the Priimagi group,<sup>[122]</sup> who constructed a light-driven gripping device they dubbed an 'artificial flytrap', capable of mimicking the capture behavior of a natural Venus Flytrap plant (**Figure 11**). This 'intelligent' LCE micro-actuator was fabricated onto the tip of an optical fibre, which acts as a power source and can also serve as a contactless probe to sense the local environment, allowing the operator to close the grip when an object crosses the field of view, offering some important control and feedback steps towards more autonomous and 'smart' micro-robotics.

## 6. Summary and Outlook

As we hope was demonstrated in this review, reversible photoisomerization of photo-switchable molecules in polymer-based materials can be leveraged to control a wide variety of larger-scale material properties in response to light. Light is an impressively efficient power source for most of these applications, which offers a direct transfer of photonic energy into mechanical motion without requirements for energy converters, amplification, or other subsystems. Light is also an ideal triggering mechanism, since it is highly selective, non-damaging, and can be localized (in time and space) for remote activation and delivery of energy to a system. Thus, for facile and efficient actuation and motion, photo-responsive materials hold great potential. Azobenzene is the current leader amongst the small yet emerging class of photo-reversible molecules, and azo polymers and other supra-molecular azo materials are promising candidates for enabling the potential applications of these systems discussed in this review because of their ease of incorporation, and efficient and robust photo-chemistry. This review described the light-induced effects observed in amorphous polymers, and LCNs and LCEs containing various azo-based photo-reversible dyes. A unifying limitation, however, is that the mechanical forces produced thus far and the efficiency for light energy conversion are still far from optimal. LCEs in particular are promising materials for micro-motors and artificial muscles powered by light, and in these systems, not only two-dimensional but three-dimensional motions have now been achieved, which are competitive and promising for many applications as soft actuators.<sup>[123]</sup> Many general problems also still remain unsolved, however, such as fatigue resistance and improving the bio-compatibility of these materials,<sup>[124]</sup> which are now exciting topics for intensive future research and development.

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**Figure 11.** A Venus Flytrap plant in its a) open stage and b) closed stage. c) Schematic illustration of the light-triggered artificial flytrap in its optically open stage. d) When an object enters into the field of view and produces enough optical feedback (reflected/scattered light), the flytrap mimic closes and captures the object. The insets in (c) and (d) show the schematic molecular orientation in the LCE actuators in the open and closed stages. Reproduced with permission.<sup>[122]</sup> Copyright 2017, Nature Publishing Group.

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actuation, azobenzene, isomerization, molecular machines, photo-mechanics

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