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Azobenzene photomechanics: prospects and potential applications

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Abstract The change in shape inducible in some photo-reversible molecules using light can effect powerful changes to a variety of properties of a host material. This class of reversible light-switchable molecules includes molecules that photodimerize, such as coumarins and anthracenes; those that allow intra-molecular photo-induced bond formation, such as fulgides, spiro-pyrans, and diarylethenes; and those that exhibit photo-isomerization, such as stilbenes, crowded alkenes, and azobenzenes. The most ubiquitous natural molecule for reversible shape change, however, and perhaps the inspiration for all artificial bio-mimics, is the rhodopsin/retinal protein system that enables vision, and this is the quintessential reversible photo-switch for performance and robustness. Here, the small retinal molecule embedded in a cage of rhodopsin helices isomerizes from a *cis* geometry to a *trans* geometry around a C=C double bond with the absorption of just a single photon. The modest shape change of just a few angstroms is quickly amplified and sets off a cascade of larger shape and chemical changes, eventually culminating in an electrical signal to the brain of a vision event, the energy of the input photon amplified many thousands of times in the process. Complicated biochemical pathways then revert the *trans* isomer back to *cis*, and set the system back up for another cascade upon subsequent absorption. The reversibility is complete, and many subsequent cycles are possible. The reversion mechanism back to the initial *cis* state is complex

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and enzymatic, hence direct application of the retinal/rhodopsin photo-switch to engineering systems is difficult. Perhaps the best artificial mimic of this strong photo-switching effect however in terms of reversibility, speed, and simplicity of incorporation, is azobenzene. *Trans* and *cis* states can be switched in microseconds with low-power light, reversibility of 10^5 and 10^6 cycles is routine before chemical fatigue, and a wide variety of molecular architectures is available to the synthetic materials chemist, permitting facile anchoring and compatibility, as well as chemical and physical amplification of the simple geometric change. This review article focuses on photo-mechanical effect taking place in various material systems incorporating azobenzene. The photo-mechanical effect can be defined as reversible change in shape by absorption of light, which results in a significant macroscopic mechanical deformation, and reversible mechanical actuation, of the host material. Thus, we exclude simple thermal expansion effects, reversible but non-mechanical photo-switching or photo-chemistry, as well as the wide range of optical and electro-optical switching effects for which good reviews exist elsewhere. Azobenzene-based material systems are also of great interest for light energy harvesting applications across much of the solar spectrum, yet this emerging field is still in an early enough stage of research output as to not yet warrant review, but we hope that some of the ideas put forward here toward promising future directions of research, will help guide the field.

Keywords Azobenzene · Photomechanics · Thin films · Light harvesting · Liquid crystals · Photochemistry

Introduction

Azobenzene, with two phenyl rings separated by an azo (–N=N–) bond, serves as the parent molecule for a broad class of aromatic azo compounds. These chromophores are versatile molecules, and have received much attention in research areas both fundamental and applied. The strong electronic absorption band can be tailored by ring substitution to fall anywhere from the ultraviolet to red-visible regions, allowing chemical fine-tuning of color. This, combined with the fact that the azo groups are relatively robust and chemically stable, has prompted extensive study of azobenzene-based structures as dyes and colorants. With appropriate electron-donor/acceptor ring substitution, the π-electron delocalization of the extended aromatic structure can yield high optical nonlinearity, and azo chromophores have been extensively studied for nonlinear optical applications as well [1, 2]. One of the most interesting properties of these chromophores, however, and the main subject of this article, is the readily induced and reversible *trans–cis* photoisomerization of the azo bond and the geometric changes that result when azo chromophores are incorporated into polymers and other materials. This light-induced interconversion allows systems incorporating azobenzenes to be used as photo-switches, effecting rapid and reversible control over a variety of chemical, mechanical, electronic, and optical properties.

Examples of azobenzene-based photo-control have been demonstrated in photo-switchable phase changes [3], phase separation (or reversal of phase separation), [4, 5] solubility changes [6, 7], and crystallization [8]. These suggest a highly promising route toward novel functional materials: the incorporation of photo-physical effects into self-assembling systems. The inherent amplification of molecular order to macroscopic material properties can be coupled with molecular-scale photo-switching. For instance, in amphiphilic polypeptide systems, self-assembled micelles were stable in the dark, but could be disaggregated with light irradiation [9]. This construct can act as a transmembrane structure, where the reversible formation and disruption of the aggregate enabled photo-switchable ion transport [10]. In another example, cyclic peptide rings connected by a *trans*-azo unit would hydrogen-bond with their neighbors, forming extended chains. The *cis*-azo analog, formed upon irradiation, participates in intra-molecular hydrogen bonding, forming discrete units, and thereby disrupting the higher-order network [11, 12]. A system of hydrogen-bonding azobenzene rosettes was also found to spontaneously organize into columns, and these columns to assemble into fibers. Upon UV irradiation, this extended ordering was disrupted [13], converting a solid organogel into a fluid. Similarly, large changes in viscosity can be elicited by irradiating a solution of azo polyacrylate associated with the protein–bovine serum albumin [14]. In a liquid crystal systems, light can be used to induce a glass-to-LC phase transition [15, 16]. A wide variety of applications (such as microfluidics) is possible for functional materials that change phase upon light stimulus.

The primary and secondary shapes of azo-containing self-assembled structures in solution can also be controlled with light. Azo block-copolymers can be used to create photo-responsive micelles [17–21], and vesicles [22]. The isomerization-induced change in azo dipole moment plays a critical role in determining the difference between the aggregations in the two states, and can be optimized to produce a highly efficient photo-functional vesicle system [23]. The use of azo photo-isomerization to disrupt self-assembled systems may be particularly valuable when coupled with biological systems. With biomaterials, one can exploit the powerful and efficient biochemistry of natural systems, yet impose the control of photo-activation. The azobenzene unit in particular has been applied to photobiological experiments with considerable success [24, 25]. Order–disorder transitions can also be photo-induced in biopolymers. Azo-modified polypeptides may undergo transitions from ordered chiral helices to disordered solutions [26–28], or even undergo reversible α-helix to β-sheet conversions [29]. In many cases catalytic activity can be regulated due to the presence of the azo group. A cylcodextrin with a histidine and azobenzene pendant, for example, was normally inactive because the *trans*-azobenzene would bind inside the cyclodextrin pocket, whereas the photo-generated *cis*-azobenzene liberated the catalytic site [30]. Thus, the ability to create biomaterials whose biological functions are activated or inhibited on demand via light is of interest for fundamental biological studies, and, possibly, for dynamic biomedical implants [25, 31].

Perhaps ranging as widely as the interesting phenomena displayed by azo aromatic compounds, is the variety of molecular systems into which these chromophores can be incorporated. In addition to liquid-crystalline (LC) media and amorphous glasses, azobenzenes can be incorporated into self-assembled monolayers and superlattices, sol–gel silica glasses, and various biomaterials. The photochromic or photo-switchable nature of azobenzenes can also be used to control the properties of novel small molecules, such as crown-ethers [32], cyclodextrins [33, 34], proteins such as bacteriorhodopsin [35], and 3D polycyclics such as cubane [36], and adamantane [37]. Typically, however, azo chromophores are embedded into a solid matrix for studies and real devices. As a result, matrix effects are inescapable: the behavior of the chromophore is altered due to the matrix, and in turn the chromophore alters the matrix [38, 39]. Although either could be viewed as a hindrance, both can in fact be quite useful: the chromophore can be used as a delicate probe of the matrix (free volume, polarizability, mobility, morphology, viscoelasticity, etc.), and when the matrix couples to chromophore motion, molecular motions can be translated to larger length scales, for example using nanometer "command surfaces" of azo chromophores to re-orient surrounding micron-sized layers of inert liquid crystals [38]. Thus, the incorporation strategy can be extremely valuable for transferring and amplifying azobenzene's photo-reversible effects.

As the above examples illustrate, azobenzene is a unique and powerful molecular switch, the function of which can be amplified such that also larger-scale material properties are switched or altered in response to light. Therefore, azo-containing materials exhibit a number of fascinating photo-mechanical effects. Herein, we present an attempt at a comprehensive review on these photo-mechanical effects in various material systems, and on their exploitation in designing photo-mobile and photo-deformable materials. The motions covered range from 1D motion on flat surfaces and 2D mass transport, to micro- and macro-scale 3D motions and their applications in micro-actuation and robotics.

Azobenzene photochemistry

In this article, we use "azobenzene" and "azo" in a general way: to refer to the class of compounds that exhibit the core azobenzene structure, with different ring substitution patterns (even though, strictly, these compounds should be referred to as "diazenes"). There are many properties common to nearly all azobenzene molecules. The most obvious is the strong electronic absorption of the conjugated π system. This absorption spectrum can be tailored, via ring substitution, to lie anywhere from the ultraviolet to the visible-red region. Based on the absorption spectrum, azobenzenes can be classified into three spectroscopic classes: [40] azobenzene-type molecules, aminoazobenzene-type molecules, and pseudo-stilbenes (Fig. 1). Azobenzene-type molecules exhibit absorption characteristics similar to the unsubstituted azobenzene archetype and a long half-life. Adding ortho- or para- substituents with an electron-donating group (usually an amino, –NH_2), results in a red-shifted absorbance spectrum and a shorter half-life, describing the aminoazobenzene-type spectroscopic class. Substitution of azobenzene at the 4 and $4'$ positions with an electron-donor and -acceptor (such as an amino and a nitro, –NO_2, group) leads to a strongly asymmetric electron distribution (often referred to as a "push/pull" substitution pattern) and defines the third spectroscopic class, the pseudo-stilbenes. Pseudo-stilbenes are significantly red-shifted and have shorter half-lives.

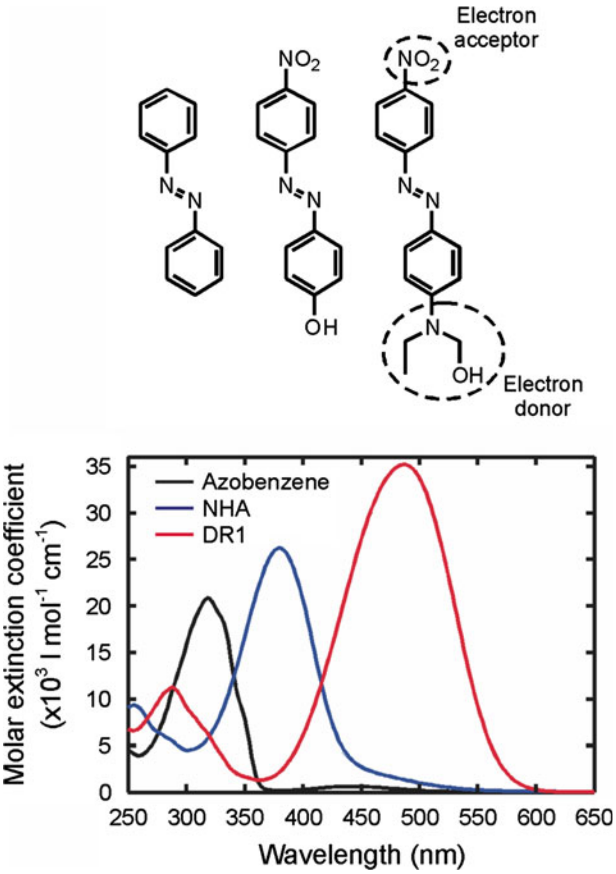

Fig. 1 Examples of azobenzene molecules of azobenzene-type (unsubstituted azobenzene, *upper left*), aminoazobenzene-type (4-nitro-4′-hydroxyazobenzene (NHA), *upper center*), and pseudostilbene-type (Disperse Red 1 (DR1), *upper right*), and their absorption spectra measured from dilute tetrahydrofuran solution. Note that the azobenzene classification rests on the absorption spectrum rather than the chemical structure of the compound. Hence, molecules with weak push-pull character such as NHA can be classified into the aminoazobenzene category

The most startling and intriguing characteristic of the azobenzenes is their highly efficient and fully reversible photo-isomerization. Azobenzenes have two stable geometric isomer states: a thermally stable elongated *trans* configuration, and a meta-stable bent *cis* form. Remarkably, the azo chromophore can interconvert between these two isomers upon absorption of just a single photon, as the quantum yield in many systems approaches unity. For most azobenzenes, the molecule can be optically isomerized from *trans* to *cis* with light anywhere within the broad absorption band in the near UV and Visible, and the molecule will subsequently thermally relax back to the *trans* state on a timescale dictated by the substitution pattern.

Azobenzene photo-isomerization is completely reversible and free from side reactions. The *trans* isomer is more stable by approximately 50–100 kJ/mol

[41, 42], and the energy barrier to the photo-excited state (barrier to isomerization) is on the order of 200 kJ/mol [43]. In the dark, azobenzene molecules will be found initially in the *trans* form. Upon absorption of a photon (with a wavelength in the *trans* absorption band), the azobenzene will convert, with high efficiency, into the *cis* isomer. A second wavelength of light (corresponding to the *cis* absorption band) can cause the back-conversion, and both these forward and reverse photo-isomerizations typically exhibit picosecond timescales [44, 45]. Alternately, azos will thermally reconvert from the *cis* to *trans* state, with a timescale ranging from milliseconds to hours, or even days, depending on the substitution pattern and local environment. More specifically, the lifetimes for azobenzenes, aminoazobenzenes, and pseudo-stilbenes are usually on the order of hours, minutes, and seconds, respectively. The energy barrier for thermal isomerization is on the order of 100–150 kJ/mol [46, 47]. In addition, one can also generate a system that starts in the *cis* state, and where isomerization (in either direction) is completely hindered. For instance, attachment to a surface [48], direct synthesis of ring-like azo molecules [49], and crystallization of the *cis* form [50, 51] can be used to maintain one state, but such systems are not bistable photo-switches, nor are they reversible.

Photostationary states

A bulk azo sample or solution under illumination will reach a photostationary state, with a steady-state *trans*/*cis* composition based on the competing effects of photo-isomerization into the *cis* state, thermal relaxation back to the *trans* state, and *cis* reconversion upon light absorption. The steady-state composition is unique to each system, as it depends on the quantum yields for the two processes (ϕ_{trans} and ϕ_{cis}) and the thermal relaxation rate constant. The composition also thus depends upon irradiation intensity, wavelength, temperature, and the chromophore environment. Azobenzenes are photochromic, since the effective absorption spectrum (a combination of the *trans* and *cis* spectra) changes with light intensity. Thus absorption spectroscopy can be conveniently used to measure the *cis* fraction in the steady-state [52, 53], and the subsequent thermal relaxation to an all-*trans* state [54–57]. NMR spectroscopy can also be used [58]. Under moderate irradiation, the composition of the photostationary state is predominantly *cis* for azobenzenes, mixed for aminoazobenzenes, and predominantly *trans* for pseudo-stilbenes. In the dark, the *cis* fraction is below most detection limits, and the sample can be considered to be in an all-*trans* state. The ring substitution pattern affects both the *trans* and the *cis* absorption spectra, and for certain patterns, the absorption spectra of the two isomers overlap significantly (notably for the pseudo-stilbenes). In these cases, a single wavelength of light activates both the forward and reverse reactions, leading to a mixed stationary state, and continual interconversion of the molecules. For some interesting azobenzene photo-motions, this rapid and efficient cycling of chromophores is advantageous, whereas in cases where the azo chromophore is being used as a switch, it is clearly undesirable.

The mechanism of isomerization has undergone considerable debate [59–63]. Isomerization takes place either through a rotation about the activated N–N single bond, with rupture of the π bond, or through inversion, with a semi-linear and hybridized transition state, where the π-bond remains intact. The thermal back-relaxation is generally agreed to proceed via rotation, whereas for the photochemical isomerization, both mechanisms appear viable with a different one dominating depending on the particular chromophore and environment [64]. Furthermore, ab initio and density functional theory calculations indicate that both pathways are energetically accessible, although inversion is preferred [65, 66]. The availability of the inversion mechanism explains how azos are able to isomerize easily even in rigid matrices, such as glassy polymers, since the inversion mechanism usually has a much smaller free volume requirement than the rotation.

Photoinduced motions and movements

Light irradiation produces geometric changes in azobenzenes, and under appropriate conditions, these changes can translate into larger-scale motions and even macroscopic movements of the material system. These motions can take place at various size scales [67], but as the motion on any size-scale invariably affects (and is affected by) other scales, clear divisions do not exist, and these effects are often concurrent and inter-dependent. The most relevant motion to eventual actuation applications is expansion and contraction due to the photo-mechanical effect and this effect will be highlighted in this review. The related effect of all-optical surface patterning (“photo-morphing”), which occurs when an azo-polymer film is exposed to a light intensity gradient, will also be reviewed and discussed [1, 67–69].

Molecular motion

The root fundamental molecular photo-motion in azobenzenes is the geometrical change that occurs upon absorption of light. In *cis*-azobenzene, the phenyl rings are twisted at 90° relative to the C–N=N–C plane [60, 70]. Isomerization reduces the distance between the 4 and 4′ positions from 0.99 nm in the *trans* state to 0.55 nm for the *cis* state [71–73]. This geometric change creates or increases the dipole moment: whereas the *trans* form has no dipole moment in parent azobenzene, the *cis* form has a dipole moment of 3.1 D [50]. The free volume requirement of the *cis* can be much larger than the *trans* [74], and the free volume required to “cycle between” these two states larger still. It has been estimated that the minimum free volume pocket required to allow isomerization to proceed through a transition state via the inversion pathway is 0.12 nm^3 [60, 75], and via the rotation pathway approximately 0.38 nm^3 [76]. The effects of matrix free volume constraints on photochemical reactions in general have been considered [77]. The geometrical changes in azobenzene are very large, by molecular standards, and it is thus no surprise that isomerization modifies a wide host of material properties. More recent measurements via high-pressure spectroscopy (10^4–10^5 atm) on the force applied and energy exerted through this isomerization suggest that azobenzene is indeed an extremely powerful little artificial muscle, and application optimization for actuators depends largely on clever engineering of the mechanical advantage provided, and is not inherently materials-limited.

This molecular shape change generates a significant nanoscale force, which has been measured in single-molecule force spectroscopy experiments [78, 79], and compared well to theory [80]. In these experiments, illumination causes contraction of an azobenzene-polymer, showing that each chromophore can exert pN to nN molecular forces on demand. This force can be further engineered into an on-off or "ratchet motion" switch bridging the gap between force and simple machinery, such as that demonstrated by an ingenious two-state pseudo-rotaxane that could be reversibly threaded–dethreaded using light which Stoddart and co-workers [81, 82] called an "artificial molecular-level machine". The ability to activate and power molecular-level devices using light is of course attractive in many applications, since it circumvents the limitations inherent to diffusion or wiring, and permits a remote (or even quite distant) power supply. The fast response and lack of waste products in azo isomerization are also advantageous. Coupling these molecular-scale motions to do actual human-scale useful work is of course the next challenging step. Encouraging progress in this direction is evident, however, from a wide variety of molecular switches that have been synthesized. For example, an azo linking two porphyrin rings enabled photo-control of electron transfer [83], and in another example, dramatically different hydrogen-bonding networks (intermolecular and intramolecular) could be favored based on the isomeric state of the azo group linking two cyclic peptides [11, 12]. Other recently reported examples include osmotic pressure pumps [84], created by the photo-controlled solubility of azobenzene, analytical columns that increase the effluent rate of developing solvents [85], reversible light-controlled conductance switching [86], and photoresponsive gold nanoparticle solvation [87], and network formation [88].

Macroscopic motion

While it is important to study the nm-scale azobenzene molecular conformational changes that give rise to macroscopic phenomena, by far the most useful applications to actuation are the reversible changes that can result macroscopic motions over the μm to cm size-scale. The first consideration is perhaps whether the host material can expand or contract to an appreciable extent. In floating monolayers at a liquid surface, it is well-established that the larger molecular size of the *cis* isomer leads to a corresponding lateral expansion of tens of percent [89], which can modify other bulk properties. For instance, this allows photo-modulation of a monolayer's water contact angle [90], or surface potential [91]. Using fluorinated azo-polymers, good photo-control over photo-patterning [92, 93], and wettability has been demonstrated [94–96]. A monolayer of azo-modified calixarene, when irradiated with a light gradient, produced a gradient in surface energy sufficient to move a macroscopic oil droplet [97]. In more recent work surfactants of azobenzene were used to create a liquid–liquid interface between oleic acid droplets in an aqueous solution [98]. Photoisomerization of the azobenzene surfactant created a wavelength-dependent interfacial tension capable of inducing interfacial flow, and this interfacial flow then generated large-scale droplet motion in a direction opposite to the gradient. The photo-controlled droplet motion was thus used to direct droplets into various trajectories. It also suggests possible applications of the above materials to microfluidics. Modest photo-induced contact angle changes for thin polymer films have also been reported [99]. Recently an azobenzene copolymer assembled into polyelectrolyte multilayer showed a modest 2° change in contact angle with UV light irradiation. However, when the same copolymer was assembled onto a patterned substrate, the change in contact angle upon irradiation was enhanced to 70° [96]. The fact that surface roughness plays a role in contact angle is well-established, and shows that many systems can be optimized to give rise to a large change in surface properties through clever amplification.

In layered inorganic systems with intercalated azobenzenes, reversible photoinduced changes in the basal spacing (on the order of 4 %) can be achieved [100, 101]. In polymer films, there is evidence that the film thickness increases, as measured by in situ single-wavelength ellipsometry, atomic force microscopy (AFM), and in situ neutron reflectometry [102–104]. Photo-contraction for semicrystalline main-chain azos has been measured, [105, 106] where the extent and direction (expansion or contraction) of photo-mechanical change can be tuned by using ambient temperature as demonstrated by variable-temperature neutron reflectometry experiments. The experiments demonstrated unambiguously that both photo-expansion and photo-contraction could be optimized in a single azo-material merely by varying the dominance of these two competing effects with low and high extremes of temperature, respectively.

The most convincing demonstration of macroscopic motion due to azo isomerization is the mechanical bending and unbending of a free-standing LC polymer film [107, 108]. The macroscopic bending direction may be selected either with polarized light, or by homogeneously aligning the mesogens within the polymer network. Bending occurs in these relatively thick films because the free surface (which absorbs light) contracts, whereas the interior of the film (which is not irradiated owing to the strong absorption of the upper part of the film) does not contract. Because the direction of bending can be controlled with polarized light, the materials enable full directional photomechanical control [109]. One can also invert the coupling of mechanical and optical effects: by stretching an elastomeric azo film containing a grating, one can affect its wavelength-selection properties and orient chromophores [110]. Much of this bending and related motion at the macroscale are invariably related to or have possible applications in actuation and will be discussed further later in the review.

Photo-patterning and -morphing

In 1995, an unexpected and unprecedented optical effect was discovered in polymer thin films. The Natansohn/Rochon research team [111], and the Tripathy/Kumar collaboration [112], simultaneously and independently discovered a large-scale surface mass transport when the films were irradiated with a light interference pattern. The mass transport takes place when two coherent laser beams, with a wavelength within the azo absorption band, are intersected at the sample surface. The sample usually consists of a thin spin-cast film (10–1,000 nm) of an amorphous azo-polymer on a transparent substrate. The sinusoidal light interference pattern at the sample surface leads to a sinusoidal surface pattern, often referred to in the

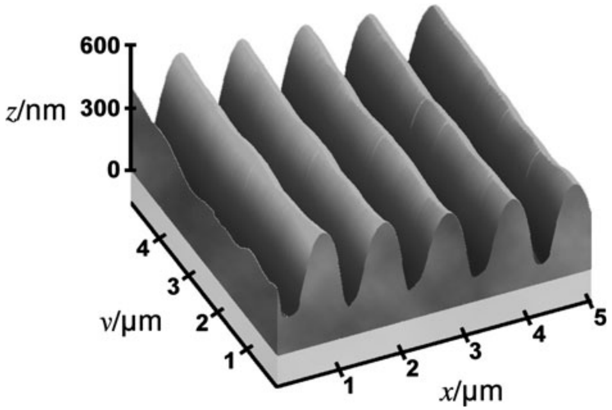

Fig. 2 AFM image of a typical surface relief grating (SRG) optically inscribed into an azo-polymer film. Grating amplitudes of hundreds of nanometers, on the order of the original film thickness, are easily obtained. In this image, the approximate location of the film-substrate interface has been set to $z = 0$, based on knowledge of the film thickness

literature as a surface relief grating (SRG), However, the azo-initiated surface mass transport is not limited to just gratings and can produce arbitrary structures, dictated by the spatial intensity and polarization pattern of the incident light. Hence, the phenomenon might more accurately and generally be called photo-patterning, -transport, or -morphing. The SRGs were found to be extremely large, up to hundreds of nanometers, as confirmed by AFM (Fig. 2), suggesting that light triggers the polymer chains to "walk" across the substrate surface over a distance of hundreds of nm. The SRGs diffract light very cleanly and efficiently, and in retrospect it is clear that many reports of large diffraction efficiency prior to 1995, attributed to birefringence, were in fact due to surface gratings unbeknownst to the experimenters. The process occurs readily at room temperature (well below the T_g of the amorphous polymers used) with moderate irradiation (1–100 mW/cm^2) over seconds to minutes. The phenomenon is caused by reversible mass transport, not irreversible material ablation, since a flat film with the original thickness is recovered upon heating above T_g. Importantly, the photo-patterning of amorphous azo-polymers is strongly polarization-dependent: efficient gratings are formed when an interference pattern formed by two *p*-polarized or counter-circularly polarized light beams, whereas *s*-polarized beams produce essentially no grating [68]. This evidences that neither thermal effects nor photodegradation play a significant role in the light-induced mass transport, and that what appears to be essential for efficient surface patterning is an "electric-field gradient" in the direction of the grating vector [113, 114].

The all-optical patterning unique to azobenzenes has been studied intensively since its discovery and many reviews of the remarkable body of experimental results are available [1, 67, 69, 115]. Critically, it requires the presence and isomerization of azobenzene chromophores, as other absorbing but non-isomerizing chromophores do not produce SRGs. Concomitant with the inscription of a surface relief is a photo-orientation of the azo chromophores, which depends on the polarization of the incident beam(s). The chromophore orientation has been measured using polarized Raman confocal microspectrometry [116–118], and the strong surface orientation has been confirmed by photoelectron spectroscopy [119]. It is found is that the chromophores orient perpendicular to the local polarization vector of the impinging interference pattern. Thus, for a (+45°, −45°) two-beam interference: in the valleys ($x = 0$) the electric field is aligned in the y-direction (see Fig. 2 for the coordinate axes), so the chromophores orient in the x-direction; in the peaks ($x = \Lambda/2$) the chromophores orient in the y-direction; in the slope regions ($x = \Lambda/4$) the electric field is circularly polarized and thus the chromophore distribution are nearly in-plane isotropic. For a (p, p) two-beam interference, the chromophores are primarily oriented in the y-direction everywhere, since the impinging light pattern is always linearly polarized in the x-direction. Recent theoretical studies concerning the origin of the SRG formation relate the photo-orientation and the resultant entropy decrease to the photoinduced deformation of the polymer system [120, 121]. Recent experiments, on the other hand, seem to suggest that efficient photo-orientation is not a prerequisite for efficient mass transport, and that collaborative effects can suppress the SRG formation on azo-polymer films [122].

The anisotropy grating that is submerged below a surface relief grating apparently also leads to the formation of a density grating under appropriate conditions. It was found that upon annealing, which erases the surface grating and restores a flat film surface, a density grating began growing beneath the surface (and into the film bulk) [123, 124]. This density grating only develops where the SRG was originally inscribed, and it appears that the photo-orientation and mass transport leads to the nucleation of “seeding aggregates” that are thermally grown into larger-scale density variations. The thermal erasure of the SRG, with concomitant growth of the density grating, has been both measured [125], and modeled [126].

It was recognized early on that the gratings do not form in systems of small molecules (for instance, comparing unreacted monomers to their corresponding polymers). The polymer molecular weight (M_W), however, must not be too large [127]. Presumably a large M_W eventually introduces entanglements, which act as crosslinks, hindering polymer motion. Thus, intermediate molecular weight polymers ($M_W \sim 10^3$, arguably oligomers) are optimal [128]. That having been said, there are many noteworthy counter-examples. Weak SRGs can be formed in polyelectrolyte multilayers, which are essentially crosslinked polymer systems [118, 129–131], and efficient SRGs have been inscribed in high-molecular-weight azobenzene-polyelectrolyte complexes [132]. Efficient grating formation has also been demonstrated using an azo-cellulose with ultra-high molecular weight ($M_W \sim 10^7$) [133, 134]. In a high molecular weight polypeptide ($M_W \sim 10^5$), gratings could be formed but the grating amplitude-depended strongly on the polymer conformation [135], and restricted conformations (α-helices and β-sheets) hindered SRG formation. More recently, high-modulation-depth surface patterns have been inscribed in amorphous azobenzene molecular glasses [136, 137], and polymer systems employing spiropyran photochromic compounds [138, 139]. These observations serve to highlight that the fundamental mechanism of this complex photomechanical effect is not comprehensively understood up to date.

Nanofabrication applications of photo-patterning

The rapid, facile, reversible, and single-step all-optical surface patterning effect discovered in a wide variety of azobenzene systems has been suggested as the basis for numerous applications. The surface structures are erasable, but on the other hand, one may use a system where crosslinking enables permanent fixation of the surface patterns [140, 141]. It is also possible to remove the azobenzene moieties from the material system after the grating inscription, resulting in thermally stable colorless gratings with unaltered periodicity but somewhat lowered grating modulation depth [142, 143]. Many proposed applications are optical, and fit well with azobenzene's already extensive list of optical capabilities. The gratings have been demonstrated as optical polarizers [144], angular or wavelength filters [145–147], and couplers for optical devices [148]. They have also been suggested as photonic bandgap materials [149], and have been used to create polymeric lasers where emission wavelength is tunable via grating pitch [150–152]. The process has also been suggested as an optical data storage and holographic recording mechanism [153, 154]. The high-speed and single-step holographic recording has been suggested to enable "instant holography" [155], with obvious applications for industry or end consumers. Since the hologram is topographical, it can easily be used as a master to create replicas via molding. This technique has been recently employed to enhance the light trapping, and hence to improve the device efficiency, of polymeric solar cells [156]. The surface patterning also allows multiple holograms to be superimposed into hierarchical structures. This has been used to create multilayered structures [157], with phase correlation between layers of the active azobenzene and an alternating spacer layer, to form 3D linear, tetragonal, and hexagonal relief gratings with a hierarchical structure. Another suggestion is to use the holographic patterning for rapid prototyping of optical elements [158]. Optical elements could be generated or modified quickly and during device operation. They could thereafter be replaced with permanent components, if required.

The physical structure of the surface relief can be exploited to organize other systems. For instance, it can act as a command layer, aligning neighboring liquid crystal phases [159–163]. The grating can be formed after the LC cell has been assembled, and can be subsequently erased and rewritten. The surface relief can also be used to organize fluorophores into various 2D micropatterns [164, 165]. Colloids can also be arranged into the grooves of an SRG, thereby templating higher-order structures [166, 167], and these lines of colloids can then be sintered to form wires [168]. Another advantage of holographic patterning is that there is guaranteed registry between features over macroscopic distances. This is especially attractive as technologies move toward wiring nanometer-sized components. Examples in this direction involved evaporating metal onto an SRG, and then annealing. This formed a large number of very long (several mm) but extremely thin (200 nm) parallel metal wires [169]. More recently, similar concept was applied for fabricating well-ordered TiO_2 nanowire arrays and nanostructures [170]. Lastly, SRGs can be used to optically control the alignment of cylindrical nanodomains in block copolymer thin films. Uniquely, such "optically directed self-assembly" provides both in-plane and

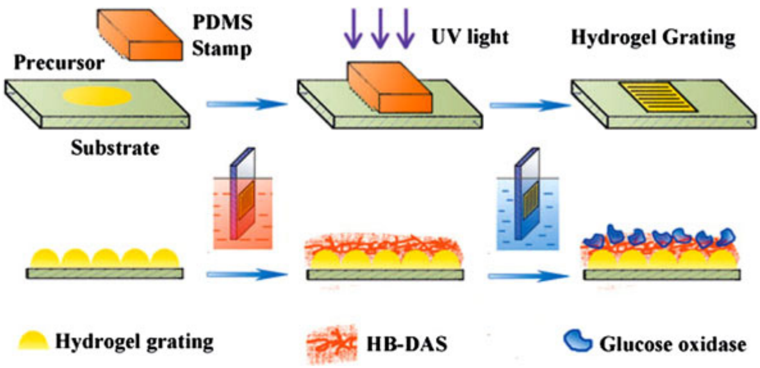

Fig. 3 Schematic of the fabrication of the glucose-sensing hydrogel gratings [173]

out-of-plane control of the micro-phase separated nanostructure without any modification of the substrate or mechanical manipulation [171].

The photoinduced surface structuring renders azo-polymers amenable to a variety of optical-lithography patterning schemes. Soft-lithographic approaches of replica molding using PDMS stamps to reproduce the gratings on a variety of substrates [172] and have been used to fabricate analyte sensors. These sensors were based upon the observed change in the diffraction efficiency of a grating upon analyte absorption. In a recent example [173], diffraction grating on an azobenzene-based material was transferred onto a stimuli responsive hydrogel functionalized with glucose oxidase and has been used to demonstrate glucose sensors capable of quantitative and continuous measurements in solution (see Fig. 3). Another recent example, referred to as "directional photofluidization lithography", employs micromolding for the fabrication of pristine 1D or 2D azo-polymer patterns, which are then post-modified using light-induced azo-polymer movement [174, 175]. By properly optimizing the irradiation conditions, this technique allows fabricating circular, ellipsoidal, and even rectangular nanostructures with feature sizes as small as 30 nm. As the latest example, SRGs have been used as masks for fabricating large-area silicon nanostructures [176]. They provide an intriguing alternative for conventional PMMA-based photoresists, and silicon nanopillar arrays of various shape and with feature size as small as 65 nm have been successfully fabricated (Fig. 4). Similarly, surface patterning can be used to immobilize various compounds, themselves acting as a mask. In a recent example, a tobacco mosaic virus was used as such a mask by placing it on an azobenzene surface. Subsequent irradiation resulted in virus immobilization by the formation of complementary grooves [177].

Of interest for next-generation patterning techniques is the fact that the azo surface modification is amenable to near-field patterning, which enables high-resolution nanopatterning by circumventing the usual diffraction limit of far-field optical systems. Proof of principle was demonstrated by irradiating through polystyrene spheres assembled on the surface of an azo film. The results in a polarization-dependent surface topography pattern [178], and a corresponding surface density pattern [179]. Using this technique, resolution on the order of 20 nm

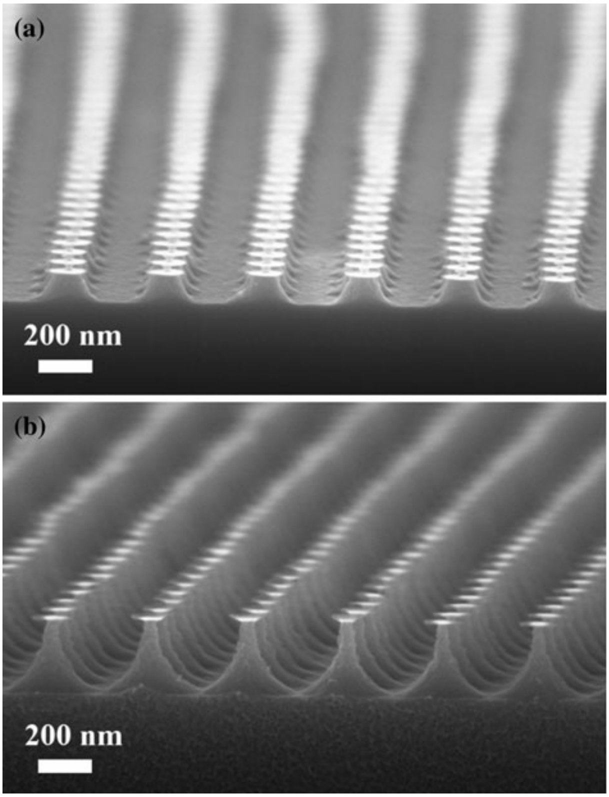

Fig. 4 SEM images of straight-walled (**a** *upper*) and mushroom-shaped (**b** *lower*) silicon nanopillar arrays. The structures are fabricated by reactive ion etching through a mask fabricated using azo-polymer surface deformation, and changing the etching parameters can control the shape of the pillars [176]

was achieved [180]. This process appears to be enhanced by the presence of gold nano-islands [181]. It was also shown that volume is not strictly conserved in these surface deformations [182]. In addition to being useful as a sub-diffraction limit patterning technique, it has been shown that the azo-polymer surface deformation is also a useful technique for photochemical imaging the near-field of various optical interactions [183], especially in mapping the hot spots of plasmonic nanostructures [184, 185].

Photomechanical actuation

If an actuator is defined as an energy transducer converting an input energy into mechanical motion, then azobenzene-based systems are excellent candidates for photo-mechanical actuation for many niche applications involving small size, localized actuation, remoteness of the power source, and freedom from the encumbrance of batteries, electrons, and internal moving parts, where advantageous. The most convincing demonstration of macroscopic motion due to azo isomerization is the mechanical bending and unbending of a free-standing polymer thin film [107, 108]. Bending occurs in these films through surface contraction while the thick inner layer does not contract as it is not irradiated. As the direction of bending can be controlled via the polarization of the light, the materials enable full directional photomechanical control [107, 109], and have been used to drive macroscopic motion of a floating film [186]. The contraction of these materials (as opposed to expansion) appears again to be related to the main-chain azo groups, and may also be related to the LC nature of the crosslinked gels. For a thin film floating on a water surface, a contraction in the direction of polarized light was seen for LC materials, whereas an expansion was seen for amorphous materials [187]. A related amplification of azo motion to macroscopic motion is the photo-induced bending of cantilevers coated with an azobenzene monolayer [188]. Other examples include macroscopic bending and three dimensional control of cantilevers made of azobenzene liquid-crystalline elastomers [189–191], light-driven microvalves [192], and full plastic motors [193]. In this section, a survey summary of various manifestations of the photomechanical effect leading to macroscale actuation with various azobenzene-based materials will be described.

Photo-actuation in monolayers and interfacial films

Monolayers of azobenzene polymers are easily prepared at the air/water interface, and much of the earliest work focussed on these simple systems. In the monolayer state, changes in the molecular shape and orientation can be directly related to the film properties such as film area and surface pressure, providing further ease of direct molecular interpretation of results. Thus, azobenzene monolayer films are ideal for studying macroscopic deformations in terms of molecular-level processes. When azo-polymer monolayers are prepared at interfaces, the motion of azobenzene moieties occurring at a molecular level is transferred directly and efficiently, and can be readily amplified to a macroscopic material. Photomechanical effects of a monolayer consisting of polyamides with azobenzene moieties in the main chain were first reported by Blair et al. in 1980 [194, 195]. At the air/water interface, a decrease in stress was observed upon UV light irradiation of the monolayer, indicating a contraction of the monolayer. In the dark, the stress increased again, and the cycle could be repeated many times. For these main-chain type monolayers, the azobenzene moieties were considered to lie flat on the water surface. The photomechanical effects were then simply attributed to the *trans–cis* isomerization of the azobenzene moieties, which occupy a larger area at the interface when they are in the more linear *trans* form than in the *cis* form. Polypeptide monolayers of two α-helical poly(α-methyl L-glutamate) rods linked by an azobenzene moiety were prepared by Higuchi et al. [89]. The *trans–cis* photoisomerization and the consequent change in geometry of the azobenzene produced a 140° bending of the main chain of the molecule, and a decrease in the limiting area per molecule. An important finding here was that the photoinduced changes in the area of the monolayer occurred more slowly than the spectral changes of the azobenzene moieties, and that the photoinduced changes in the surface area may arise from the rearrangement of the bent molecules, induced by photoisomerization of the azobenzene moieties in the main chain. The intermolecular interaction in the condensed monolayer may have served to slow down the rate of their rearrangement process.

In monolayers of side-chain type polymers, photo-mechanical effects of related azobenzene-containing polypeptides were also investigated by Menzel et al. [196]. They prepared poly(L-glutamate)s with azobenzene groups in the side chains coupled to the backbone via alkyl spacers. The resulting monolayers showed a photoresponsive behavior that was opposite to the above-mentioned systems, however, as they *expanded* when exposed to UV light, and *shrank* when exposed to visible light. This was perhaps the first observation of curious opposite expansion/contraction behavior from the same class of chromophores. The *trans–cis* photoisomerization of the azobenzene moiety upon UV light irradiation in this study led to a large increase in the dipole moment of this unit, however, and this gain in affinity to a water surface was proposed to be responsible for the net contraction [197]. In perhaps the first set of studies into quantifying the effect generally, and optimizing some photo-mechanical systems, Seki et al. prepared poly(vinyl alcohol)s-containing azobenzene side chains and observed photoinduced changes in areas on a water surface in an excellent series of papers beginning in 1993 [198–207]. These monolayers at the air/water interface exhibited a three-fold expansion in area upon UV light irradiation and reversibly shrunk by visible-light irradiation. The mechanism of the photoinduced changes in area was interpreted in terms of the change in polarity of the azobenzene moiety: the *trans–cis* photoisomerization led to an increase in dipole moment, bringing about a higher affinity of the *cis*-azobenzene to the water surface and the expansion of the monolayers. *Cis–trans* back isomerization by visible-light irradiation then gave rise to a recovery of the monolayers to the initial structure. By analyzing the XRD data, it was shown that the thickness of the monolayer becomes larger for the *trans* form than the *cis* form. The resulting change in the thickness by 0.2–0.3 nm due to the *trans–cis* isomerization in the hydrophobic side chain was then directly observed in situ on the water surface [204]. These results with azo monolayers indicate that the photoinduced deformations of the azobenzene-containing monolayers can depend strongly on the location of the azobenzene moieties in the dark: when the azobenzenes are on or in the water subphase, the structural response of the monolayers is determined by the geometrical change of the photochromic units. On the other hand, the change in polarity of the azobenzene moieties is more important when they are away from the water subphase in the dark. The potential of azobenzene monolayers for actuation based applications has been demonstrated by Ji et al. [188] through the amplification of azo motion in monolayers to macroscopic motion. A monolayer of thiol-terminated azobenzene derivative was deposited onto a gold-coated microcantilver, and exposure to UV-light resulted in the reversible deflection of the microcantilever due to molecular repulsion in the monolayer. Other examples of systems composed of azobenzene self-assembled monolayers of planar and curved inorganic surfaces has been excellently presented in a recent review by Klajn [208].

Photo-actuation in amorphous thin films

Azo-polymers offer advantages over azo monolayers as superior materials in view of higher processability, the ability to form good free-standing films with a variety of thicknesses from nanometer to centimeter scales, in addition to flexibility in molecular design, and precisely controlled synthesis. Hence, azo-polymers have emerged as the azo material of choice for most applications. From this point of view, polymer actuators capable of responding to external stimuli and deforming are most desirable for practical applications, either amorphous or organized (such as liquid crystalline). Various chemical and physical stimuli have been applied such as temperature [209], electric field [210, 211], and solvent composition [212], to induce deformation of polymer actuators.

The use of structural changes of photoisomerizable chromophores for a macroscopic change in size of polymers was first proposed by Merian in 1966 [213], when he observed that a nylon filament fabric dyed with an azobenzene derivative shrank upon photoirradiation. This effect was postulated to involve the photochemical structural change of the azobenzene group absorbed on the nylon fibers, yet these fibrous systems were sufficiently complex that the real mechanism could only be speculated upon. The observed shrinkage was also quite small, only about 0.1 %, which made it further difficult to draw firm conclusions. Following this interesting study, however, much effort was made to find new photomechanical systems with an enhanced efficiency [105, 214, 215]. Matejka et al. for example, synthesized several types of photochromic polymers based on a copolymer of maleic anhydride with styrene-containing azobenzene moieties both in the side chains and in the crosslinks of the polymer network [216–218]. The photomechanical effect observed here was enhanced with an increase in the content of photochromic groups, and for a polymer with 5.4 mol% of the azobenzene moieties, a photoinduced contraction of the sample of 1 % was achieved. Most recently, the photoinduced expansion of thin films of acrylate polymers-containing azobenzene chromophores was tracked directly in real time by Barrett and co-workers [102, 103, 219] using a variety of techniques including in situ single-wavelength ellipsometry, AFM, and in situ neutron reflectometry. An initial expansion of the azobenzene-polymer films was found to be irreversible with an extent of relative expansion observed of 1.5–4 % in films of thickness ranging from 25 to 140 nm, then a subsequent and reversible expansion was observed with repeated irradiation cycles, achieving a relative extent of expansion of 0.6–1.6 %. The extent and direction (expansion or contraction) of photo-mechanical change could be tuned for the first time just by using ambient temperature, suggesting that competing dynamic effects exist during isomerization. These variable-temperature neutron reflectometry experiments demonstrated unambiguously that both photo-expansion and -contraction could be induced in a single azo-material merely by varying the dominance of these two competing effects by changing the temperature. This implicates a fundamental competition of mechanisms, and helps unify both the photo-contraction and -expansion literature. In particular, it now appears that most azo materials exhibit photo-expansion below a well-defined cross-over temperature, and photo-contraction above this temperature.

Highly mobile materials will thus be above their cross-over temperature at ambient conditions, whereas rigid materials will be below.

As another technique to measure the photomechanical effect directly, recent developments of single-molecule force spectroscopy by AFM have enabled one quite successfully to measure mechanical force produced at a molecular level. Gaub and co-workers [78, 79] for example synthesized a polymer with azobenzene moieties in its main chain, then coupled the ends of the polymer covalently to the AFM tip and a supporting glass substrate by heterobifunctional methods to insure stable attachment, and investigated the force (pN) and extension (nm) produced in a single polymer in total internal reflection geometry using the slide glass as a wave guide. This clever excitation geometry proved very useful to avoid thermo-mechanical effects on the cantilever. They were thus able to photochemically lengthen and contract individual polymer chains by switching the azobenzene moieties between their *trans* and *cis* forms by irradiation with UV (365 nm) and visible (420 nm) light, respectively. The mechanical work executed by the azobenzene-polymer strand by *trans–cis* photo-isomerization could then be estimated directly as $W \approx 4.5 \times 10^{-20}$ J. This mechanical work observed at the molecular level resulted from a macroscopic photo-excitation, and the real quantum efficiency of the photomechanical work for the given cycle in their AFM setup was only on the order of 10^{-18}. However, a theoretical maximum efficiency of the photomechanical energy conversion at a molecular level can be estimated as 0.1, if it is assumed that each switching of a single azobenzene unit is initiated by a single photon carrying an energy of 5.5×10^{-19} J [78, 79].

Photoinduced reversible changes in elasticity of semi-interpenetrating network films bearing azobenzene moieties were achieved recently by UV and Vis light irradiation [220]. These network films were prepared by cationic copolymerization of azobenzene-containing vinyl ethers in a linear polycarbonate matrix. The network film showed reversible deformation by switching the UV light on and off, and the photomechanical effect was attributed to a reversible change between the highly aggregated and dissociated state of the azobenzene groups [220–222]. In other studies similar films of azobenzene-containing vinyl ethers films with polycaprolactone have achieved rapid (0.1 min) anisotropic deformation and recovery. The films, placed under constant tensile stress were stretched perpendicular and parallel to the tensile stress before irradiation. Photoismerization of these films resulted in film contraction for stretching parallel to the tensile stress and film elongation for stretching perpendicular to the tensile stress. The photomechanical response was observed to increase with film stretching and speculated to arise from anisotropic responses caused by the isomerization-induced vibration of azobenzene molecules which decreases the modulus of the deformed amorphous area [223]. Other polymer films that exhibit high bending intensity and large bending angles (90°) have also been reported [224].

The photomechanical expansion of azobenzene has been used to create a simple UV sensor [225, 226], and has been proposed for applications in mechanically tunable filters and switching devices. The sensor, based upon a fiber bragg grating coated with an azobenzene polymer, measured UV-light intensity by monitoring the center wavelength shift in the fiber bragg grating. Upon photoismerization (proportional to incoming UV light) the encapsulating azobenzene material applied a photomechanical axial strain upon the fiber bragg grating proportionally shifting its center wavelength. Another interesting and similar mode of deformation of polymer colloidal particles by light was reported by Wang et al. [17, 227–231]. They observed that spherical polymer particles-containing azobenzene moieties changed their shape from a sphere to an ellipsoid upon exposure to interfering linearly polarized laser beams, and the elongation of the particles was induced along the polarization direction of the incident laser beam. They also reported the deformation of the micellar structure between spherical and rod-like particles under alternating UV and visible-light irradiation. Gels of polymer films containing azobenzenes are also potential materials for applications, however, in general the gels reported have a disadvantage in that the response is slow, and the degree of deformation of the polymer films is too small to be practically utilized. It is generally agreed now that it is crucial to develop only photomechanical systems that can undergo fast and large deformations.

Photo-actuation in liquid-crystalline polymers

The previously described monolayer, gel, and amorphous polymer films are generally without microscopic or macroscopic order. Hence the photo-mechanical deformations mostly occur in an isotropic and uniform way, i.e., there is no preferential direction for deformation. If materials with anisotropic physical properties are instead used, the mechanical power produced can increase significantly, and more control can be realized. A particularly promising class of materials for efficient photoinduced actuation is liquid-crystalline elastomers (LCEs). LCEs are lightly crosslinked polymers in which the high alignment order of the mesogens can be coupled with the motions of the highly elastic polymer network. This coupling gives rise to many characteristic properties of LCEs. Upon heating, the alignment order of the LCE films decreases, and when the LC–isotropic phase transition temperature is exceeded, the films exhibit a contraction along the mesogen alignment direction. Such anisotropic deformation can be very large, and along with the versatile mechanical properties of the polymer network and the reversibility of the process (upon cooling, LCE films revert back to their original size), LCEs show great potential as artificial muscles [232–237].

Incorporation of photochromic moieties into LCEs allows one to trigger the reduction in the LC alignment order, and in an extreme case to induce the LC-isotropic phase transition, with light. The photoinduced contraction of LCE films was first demonstrated by Finkelmann et al. who observed a 20 % contraction in monodomain nematic LCEs consisting of a polysiloxane main chain and azobenzene crosslinks by irradiating the samples with UV light [238]. From the viewpoint of the photomechanical effect, the subtle variation in nematic order by *trans–cis* isomerization causes a significant uniaxial deformation of LCs along the director axis, if the LC molecules are strongly associated by covalent crosslinking to form a 3D polymer network. Terentjev and co-workers [239, 240] have incorporated a wide range of azobenzene derivatives into LCEs as photoresponsive triggers, examined their deformation behavior upon exposure to UV light, and performed detailed analysis on the photomechanical effects taking place. Furthermore, Keller and

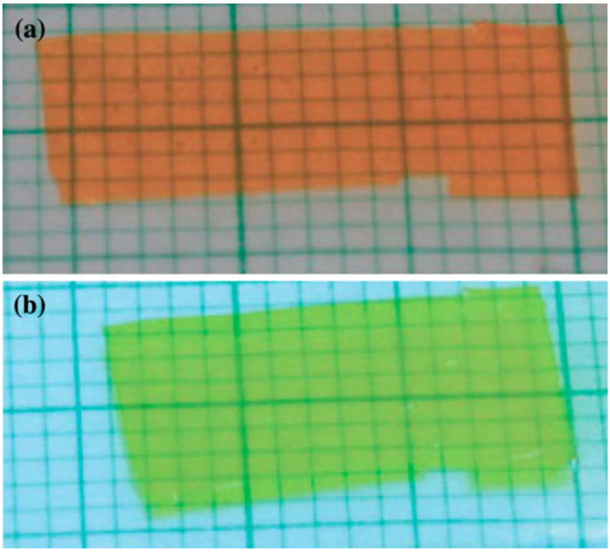

Fig. 5 Photographs of the photodeformation of Keller's azobenzene-containing LCE before (**a**) and under (**b**) UV light irradiation, demonstrating a clear change in shape inducible [241]

co-workers [241] developed monodomain nematic side-on elastomers with large (up to 18 %) and rapid (<1 min) contraction upon UV irradiation as illustrated in Fig. 5.

The large-amplitude actuation controlled by external stimulus in room temperature was obviously highly intriguing from the viewpoint of, e.g., micro-pumps and artificial muscles. The application potential of photocontrolled actuators was further promoted when Ikeda and co-workers [107, 108, 242] reported on photoinduced 3D motions (bending) of azobenzene LC gels and elastomers. The bending is driven by gradient in the isomerization-induced reduction in the LC alignment order: majority of the incident UV irradiation is absorbed within a relatively thin surface layer of the film, which generates asymmetric strain and subsequent deformation. The process is reversible: UV irradiation destructs the mesogen alignment through *trans–cis* isomerization and causes the sample to bend, whereas irradiation with visible-green light restores the azobenzenes to the *trans*-form and the film regains its original unbent state. The nature of bending depends strongly on the details of the material system. Homogeneously aligned polymer systems bend in the mesogen alignment direction [242], whereas the bending direction of polydomain LCEs can be controlled by linearly polarized light (Fig. 6) [107]. The latter serves as an example for repeatable and precisely controlled photoinduced deformation along any chosen direction, enabling full photo-mechanical directional control. It is an important step toward practical applicability of light-driven actuators. Another example of direction control is provided by artificial muscle-like photochromic fibers, the bending direction of which can be controlled by changing the location of the illuminating source [243, 244]. Conversely, homeotropically aligned crosslinked

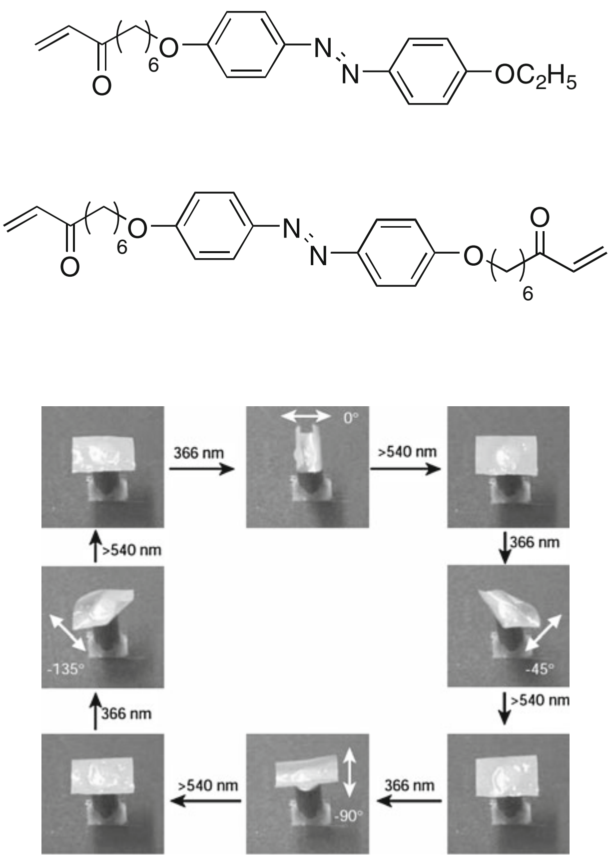

Fig. 6 Precise control of the bending direction of a film by linearly polarized light. Chemical structures of the LC monomer and crosslinker (*top*) used for preparation of the film, and photographic frames of the film in different directions in response to irradiation by linearly polarized light of different polarization directions (*white arrows*) at 366 nm, and bending flattened again by visible light longer than 540 nm [107]

LC polymer films were observed to exhibit a completely different bending behavior; upon exposure to UV light they bent away from the actinic light source, due to isotropic expansion of the sample surface upon *trans–cis* isomerization [245]. The initial chromophore alignment is not the only way to control the directionality of the photoinduced bending: Tabiryan et al. [246] demonstrated that the bending direction can be controlled with the polarization direction of the excitation beam, which was attributed to light-induced reorientation of the azobenzene moieties. More recently, van Oosten et al. [247] showed that the bending direction can be controlled by designing the material to bear internal composition gradients within the LC polymer network, and as the latest example, Shishido and co-workers [248] showed that the bending direction can also be dictated by the nature of bonding between the azobenzene moieties and the crosslinked polymer network.

The above-mentioned studies employed azo-containing crosslinked LC polymers (azo-CLCPs) consisting of azobenzene mesogens only. In such systems, practically all of the incident irradiation is absorbed within the surface region with a thickness of 1–2 μm. As typical film thicknesses used are in the order of 10–20 μm, majority of the azobenzene moieties in the bulk of the film remain unaffected by incident light. As a result, the efficiency of the photomechanical effect generated in such plain-azobenzene actuators is far from optimal. This was first addressed by Broer and co-workers [249] who designed densely crosslinked high-elastic-modulus polymer actuators with relatively low azobenzene concentration. Indeed, as shown by Palffy-Muhoray and co-workers [186] as early as in 2004, even nonphotoresponsive LCEs doped with low concentration of azobenzene dyes can exhibit remarkable and unprecedented photoinduced deformation behavior. In fact, it has been recently shown that the optimum photoinduced response (in terms of the stress generated) is achieved using moderate concentration of azobenzene moieties, supplemented with higher concentration of nonphotoactive mesogens [250]. The largest mechanical force generated by photoirradiation of the various films was measured as 2.6 MPa. Detailed studies have also been performed on the crosslinker concentration dependence of low-azo-concentration CLCPs. The crosslinking density changes the elastic modulus and the thermomechanical properties of the material system in a delicate manner, playing an important role in the mobility of the polymer segments, and in general, low crosslinker concentration is favorable for optimizing the photoinduced/thermally induced deformation of crosslinked LC polymers whereas high crosslinker concentration (high modulus) is preferable for high photoinduced stress generation [236, 251, 252]. Lastly, a recent observation of Shishido and co-workers [252] suggests that the photoinduced bending of azo-CLCPs is accompanied by a significant, 2.5-fold, decrease in the Young's modulus of the sample upon UV irradiation (Fig. 7). Such "photosoftening" was observed to be the most pronounced in a low-crosslinker-concentration (and low modulus) sample, which also exhibited the most efficient photoinduced bending. Upon increasing the crosslinker concentration (and the modulus), both photoinduced bending and the photosoftening effect became less efficient, indicating that there might be a profound connection between the "photosoftening" and the photomechanical properties and azo-CLCPs.

Applications in robotics and micromechanics

Azobenzene-containing LC polymers are ideal candidates for photo-robotics applications as they are capable of strong and efficient mechanical actuation powered remotely by light energy, without the need for additional components such as batteries or wires. They also possess the additional advantages of high processability, easy fabrication, relatively low weight density, low cost as well as low environmental impact of polymeric materials [253, 254]. With appropriate engineering, the photo-induced deformations (expansion/contraction and bending) can be translated into "real-life" actuation, to design proof-of-principle micromachines capable of producing applicable work. As the first example of such

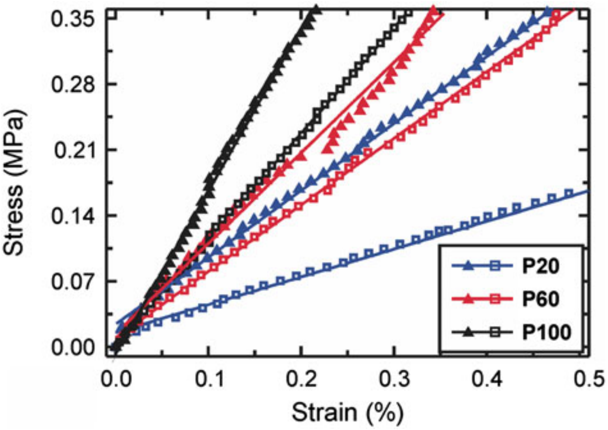

Fig. 7 Stress–strain curves for nonexposed (*filled triangles*) and UV-irradiated (*empty squares*; 5 min irradiation, 365 nm, 10 mW/cm^2) films of three azo-CLCPs, denoted P20, P60, and P100. Each sample bears a modest (5 mol%) azobenzene concentration, whereas their overall crosslinker concentrations are 20, 60, and 100, respectively. The *solid lines* are linear fits to the experimental data, the slope of which are used to determine the Young's moduli of the samples [252]

engineering, Ikeda with Barrett, and co-workers [193] translated the photoinduced deformations of an azo-CLCP film into rotational motion. They laminated the azobenzene film with a thin polyethylene sheet, joined two ends of the laminated film to create a continuous ring, and mounted it onto a pulley system. The belt was then simultaneously irradiated with both UV and visible light (Fig. 8a), which drove the pulleys into counter-clockwise rotational motion, as shown in Fig. 8b. As the azobenzene mesogens were aligned parallel to the long axis of the belt, such simultaneous irradiation caused both the local contraction and the expansion forces, the combination of which gave rise to the observed photoinduced motion. The rotation then exposed new (yet unirradiated) sections of the belt to irradiation, continuing the photo-contraction and -expansion and thus resulting in continuous rotation of the pulleys. This was the first demonstration of a light-fuelled motor.

Other recent examples by the same research group include an “inchworm” locomotion achieved by attaching a sheet of azo-CLCP on a flexible polyethylene (PE) substrate with asymmetric sliding friction [255]. In this application the film undergoes photomechanical contraction while the asymmetric end shapes on the PE films act as a ratchet, directing the motion of the film. Robotic arm-like actuation of flexible PE sheets was also demonstrated by using azo-polymer hinges (Fig. 9). Different sections of a flexible PE film were laminated with azo-CLCPs, which enabled-specific optical control (expansion or contraction) at various individually addressable positions of the film. The sections containing the azo-CLCPs thus acted as hinge joints, acting as “arms” with remote control over “elbows”, and “wrists”. The latest advancement addressed an important problem inherent to the laminated azo-CLCP films: even if their mechanical strength is improved by the flexible polymer substrate, the adhesive between the two layers prevents efficient deformation transfer from the photoactive layer to the polymer substrate. This can be

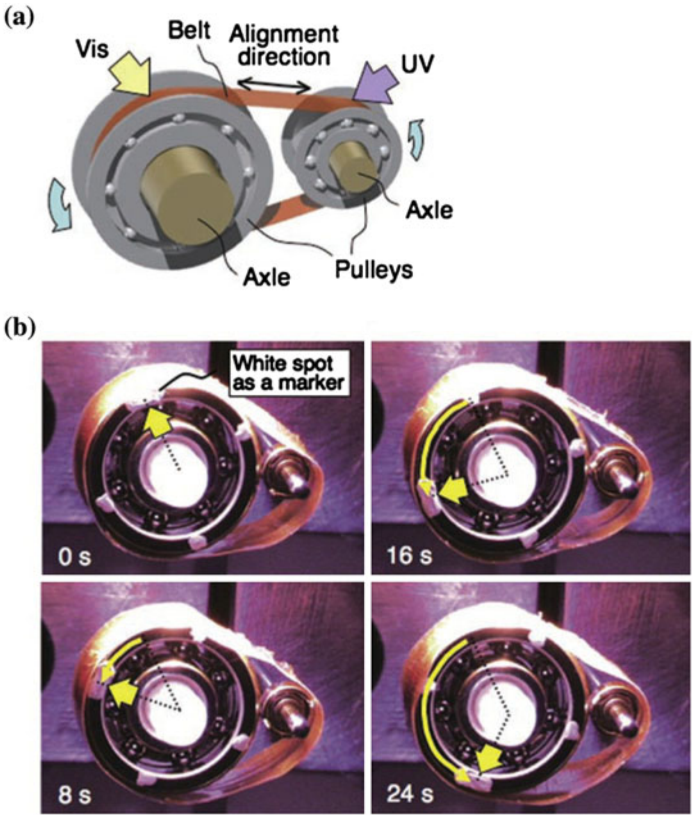

Fig. 8 A light-driven plastic motor using the laminated azo-CLCP film. **a** Schematic illustration of a light-driven plastic motor system, showing the relationship between light irradiation positions and a rotation direction. **b** Series of photographs showing time profiles of the rotation of the light-driven plastic motor with the LCE laminated film induced by simultaneous irradiation with UV (366 nm, 240 mW cm^{-2}) and visible light (>540 nm, 120 mWcm^{-2}) at room temperature. Diameter of pulleys: 10 mm (*left*), 3 mm (*right*). Size of the belt: 36 × 5.5 mm^2. Thickness of the layers of the belt: PE, 50 mm; LCE, 18 mm. Reproduced from Ikeda et al. [193]

overcome by connecting the active and passive layers by chemical bonding (using e-beam crosslinking) [256]. The durability of such adhesive-free bilayer structures was significantly improved as compared to adhesive-containing laminated films, and they might provide a route toward increasing the optical–mechanical energy conversion efficiency of the light-driven motors.

In the previous examples of photo-driven motions, the primary energy source was the combination of UV and visible-light sources, which gave rise to locally addressable photoinduced contraction/expansion of the photoactive polymer films. UV light is harmful to many living organisms, thus it is important to develop photodriven actuators driven by visible light, and ultimately sunlight. The first sunlight-driven photomobile materials, employing photoresponsive azotolane moieties, were developed by Yu et al. [257], who also fabricated visible-light-driven microrobots capable of lifting up and moving an object weighing 10 mg, ten times the

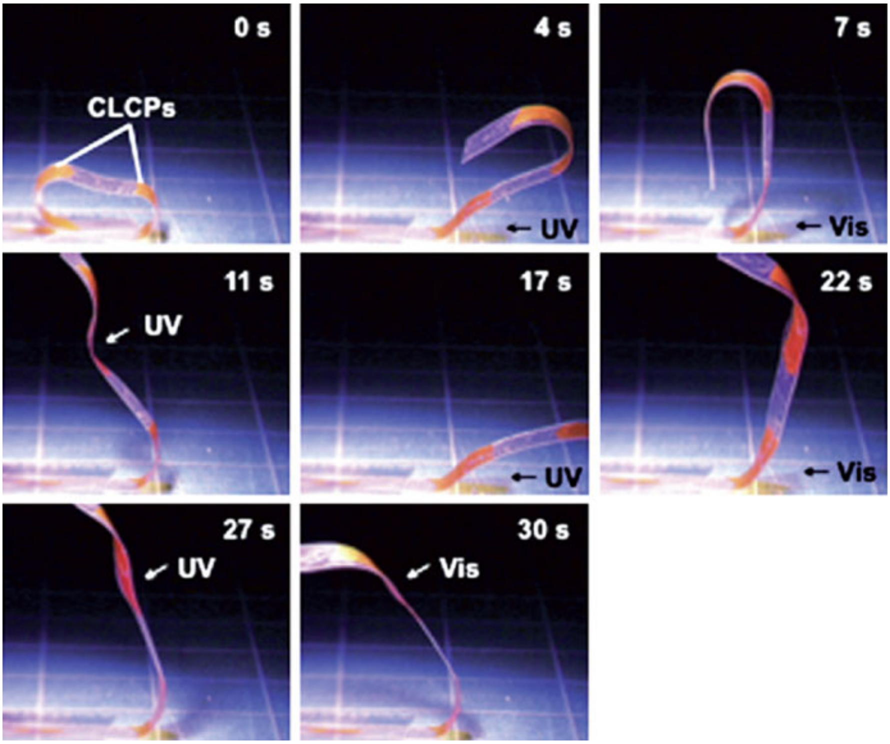

Fig. 9 Series of photographs showing time profiles of the flexible robotic arm motion of a laminated azo-CLCP film, induced by irradiation with UV (366 nm, 240 mW cm^{-2}) and visible light (>540 nm, 120 mW cm^{-2}) at room temperature. *Arrows* indicate the direction of light irradiation. Reproduced from Ikeda et al. [255]

weight of the robotic arm itself [258, 259]. This robot consisted of several azo-CLCP films on PE substrates connected by joints to mimic the arm, wrist, hand and even fingers of the human arm. The robotic arm could be bent and manipulated to perform complex actions by individually addressing the various photoactive sections, for instance an object could be picked up or dropped by addressing the fingers, while the entire arm could be moved by addressing it at different locations. Later on, White and co-workers [260] demonstrated photo-fuelled catapult motion, capable of launching an object at a rate of 0.3 m/s using moderate-intensity blue-light irradiation, and as the most recent advancement, Yu and co-workers [261] designed a clever composite material, in which upconverting nanophosphors allowed inducing the photoinduced deformation using near-infrared (980 nm) light.

White, Bunning, and co-workers [189–191] have designed ingenious high-frequency photo-driven oscillators. They designed LC azo-polymer cantilevers capable of achieving oscillation frequencies as high as 270 Hz and an energy conversion efficiency of 0.1 % upon irradiation with focused blue laser beam, with a range of motion close to 180° (Fig. 10). The cantilevers possessed a storage modulus ranging from 1.3 to 1.7 GPa and were shown to bend faster and attain

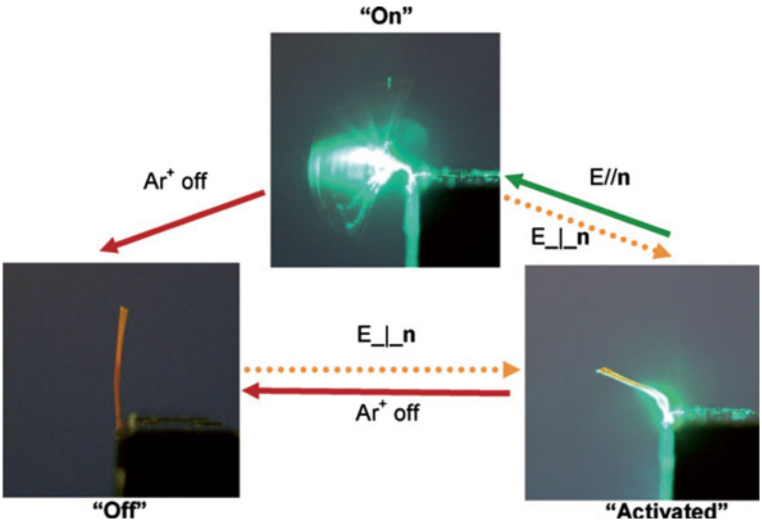

Fig. 10 The optical protocol for activating the light powered oscillation of a cantilever. The nematic director (n) is positioned parallel to the long axis of the polymer cantilever of dimension $5 \times 1 \times 50$ mm^3. When exposed to light polarized orthogonal to n ($E \perp n$) bending occurs toward the laser source. Cycling the Ar$^+$ laser from $E \perp n$ to $E//n$ can turn oscillation ''on'', while blocking the Ar+ or returning the polarization of the laser beam to $E \perp n$ turns the oscillation ''off''. Reproduced from Bunning et al [189]

larger bending angles with monodomain orientation, increasing azobenzene concentration, and reduced thickness. The bending angle was also dependent upon the polarization of incoming light as well as atmospheric pressure. These azo-polymer cantilevers also exhibited oscillation under a focused beam of sunlight [191], and thus offer the potential for remotely triggered photoactuation, adaptive optics, and most importantly energy harvesting. Such high-frequency oscillator could power a miniaturized micro-opto-mechanical system as it contains both the force generation component (azobenzene) and the kinematic structure (cantilever) in a single unit.

Other important proof-of-principle applications of azo-CLCPs include the design and fabrication of microvalves [192], and micropumps [262]. The microvalves were created by fitting a CLCP film over an inlet valve in a sealed valve chamber, where the film in this state completely blocks the inlet preventing flow [263]. Upon irradiation, the bending of the film results in unblocking of the inlet valve as well as a concave cavity under the bent film that allows solution to flow from the inlet to the nearby outlet. In the case of micropumps [262], the CLCP film is placed on the outside of a membrane covering a sealed cavity. Upon irradiation the CLCP film bends, forcing the membrane downwards, reducing cavity volume and increasing the cavity pressure. Thus, fluid flows out through the outlet valve. Upon film contraction, the membrane is pulled upwards increasing the cavity volume, decreasing cavity pressure and forcing fluid inflow through the inlet valve. Related to possible microfluidic applications, van Oosten et al. [264] have reported the design and construction of bio-inspired artificial cilia for microfluidic pumping and mixing applications. Using commercial inkjet printing technology, droplets of reactive azo LC monomers were deposited onto a film of poly vinyl alcohol (PVA) and a thin layer of rubbed polyamide for LC alignment. After self-assembly and crosslinking of the LC monomers another layer of the same or different azobenzene monomer-based ink is added to create mono or bicomponent cilia capable of responding to different wavelengths of light. Dissolving the PVA releases the cilia, which are capable of intensity-dependent upward bending when irradiated with UV light from above. The bicomponent cilia were capable of different bending properties due to their separately addressable sections, and the activation of these two components in sequence with different wavelengths of light would thus imply a non-reciprocal motion, permitting the cilia to pump fluids [265].

While most azobenzene photomechanical systems are based upon amorphous or liquid-crystalline polymers there are also some very recent reports of photomechanical crystals of azobenzene in the literature. There have been reports of numerous solid-state reactions in molecular crystals [266, 267], and of these, crystalline photo-reactions are especially interesting as they are often accompanied by molecular motion and morphological changes at the crystal surfaces [268–271]. Irie and co-workers [272, 273] were among the first to report on these crystalline photoreactions in diarylethene microcrystals accompanied by a rapid, reversible shape change of the crystal under alternating UV- and visible-light irradiation. In contrast to the diarylethene derivatives, the photoisomerization of azobenzene, requiring a larger free volume, is hindered in the bulk crystal. An early AFM study demonstrated the reversible alteration of the layered structure of an azobenzene crystal under UV- and visible-light suggesting that the topmost bilayers of the azobenzene crystal are capable of isomerization [274]. Conclusive evidence of reversible photoismerization in azobenzene crystals has only been recently reported through a reversible 3.5 % reduction in particle size of azobenzene crystals dispersed in water [275], and the fraction of the *cis* isomer was determined to level off at 30 % in the photostationary state. In further work, photoinduced particle size deformation of crystalline azobenzene and silica nano-hybrids fabricated by dry grinding was also reported [276].

In other examples, photoisomerization in crystalline azobenzene was demonstrated by the formation of a surface relief grating upon single crystal azobenzene derivatives [277–279], and the observation of photoinduced vitrification near the surfaces of the single crystals of azobenzene-based molecular materials possessing a glass-forming ability [280]. In further work [281], the reversible mechanical bending of plate-like microcrystals of azobenzene derivatives has been reported. Here, photoisomerization of the *trans* azobenzene molecules on the (001) crystal surface elongates the unit cell length near the (001) surface giving rise to uneven features. As the inner unit cells do not undergo photoisomerization their dimensions remain constant and thus, result in crystal bending. More recently, Kyu and co-workers [282] have observed variously the “swimming”, sinking and stationary floating of azobenzene crystals in a triacrylate solution (TA). The authors explain such motion through the creation of concentration/surface tension gradients formed around the liquid crystal interface by the rejection of TA solvent from the growing crystal fronts. When these gradients act on different facets in an unbalanced manner the crystal is propelled forward and "swims". Solvent rejection in the vertical direction causes crystal flotation while balanced forces on all facets results in stationary crystal growth. In addition, stationary rhomboidal crystals of azobenzene were shown to swim (move away from the UV-light source) upon irradiation. This has been attributed by the authors to the generation of a mechanical torque within the crystal by higher isomerisation rates in the sections closer to the UV light. In addition, isomerisation-induced changes in the polarity and thus solubility of the azobenzene crystals could result in system instability, driving phase segregation, and greater solvent rejection rates from the crystal front closer to the UV light.

Conclusions and outlook

The azobenzene chromophore is a unique and powerful molecular switch, exhibiting a clean and reversible photo-isomerization that induces a reversible change in geometry. This motion can be exploited directly as a photo-switch, and can also be further amplified so that larger-scale material properties are switched or altered in response to light. Thus, azo materials offer a promising potential as photo-mechanical materials. Light is an efficient power source for many of these applications, a direct transfer of photonic energy into mechanical motion with no moving parts, and light is also an ideal triggering mechanism, since it can be localized (in time and space), selective, non-damaging, and allows for remote activation and remote delivery of energy to a system. Thus for sensing, actuation, and motion, photo-functional materials are of great interest. Azo materials have demonstrated a wide variety of switching behavior, from altering optical properties, to surface energy changes, to even eliciting bulk material phase changes. Azobenzene is the arguable leader amongst the small class of photo-reversible molecules, and soft azo-polymers can be considered promising materials for next-generation photo-mechanical applications because of their ease of incorporation, and efficient and robust photochemistry. Herein we have described the photomechanical effects observed in monolayers, thin films, gels, crystals, amorphous polymers, and crosslinked liquid-crystalline polymers-containing azobenzene. In various systems, full macroscopic light-driven actuation has been achieved; however, the mechanical forces produced thus far energy conversion efficiency are still far from optimal. Crosslinked liquid-crystalline polymers in particular are promising materials for artificial muscles and motors driven by light, and in these systems not only two-dimensional but 3D motions have now been achieved, which are competitive and promising for many applications as soft actuators. Many problems also still remain unsolved, however, such as fatigue resistance and biocompatibility of these materials, which need further intensive investigation.

Overall, azobenzene materials might still be viewed more as "solutions in need of a problem to solve", as material development has far outpaced useful applications. For the field to progress now, it requires creative and inspired engineering, continuing on from this body of excellent and successful science, to identify the major unique niches in actuation where azobenzene-based materials and photo-actuation in general are capable of becoming a competitive solution. This review has identified various strengths, properties, and possibilities that azobenzene-based systems are capable of as well as the ability to incorporate azobenzene into various materials and systems. It still, however, lacks unifying problems or application areas where it can display its inherent advantages and potential, such as in energy harvesting and storage. Indeed, these azo materials have been seldom investigated for solar energy conversion and storage applications, despite an inherent strong potential interaction with sunlight. The *trans* to *cis* conversion is exceptionally high quantum yield, and the energy harvested can be more than 50 kJ/mol. Unlike most fast relaxations too after absorption, this energy-rich *cis* form persists, for hours or even days, offering a tantalizing opportunity for scientists and engineers to seize advantage of this harvested sunlight, and transduce or store it, even just thermally. The few recent "proof-of-principle" applications described in the last section, however, have provided much encouragement and confidence, however, as the first important steps toward the ability of azobenzene-based materials to fabricate real macro- and micro-scale robots amenable to remote operation and control, as well as the advantages offered in design simplification and scale-down afforded by the replacement of electrons by photons. Driving actuation with light by this powerful emerging class of photo-energy harvesting materials can offer important and significant advantages that warrant much further study of these materials into their full potential.

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