Light-Driven Actuation in Synthetic Polymers: A Review from Fundamental Concepts to Applications

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Abstract

Light-driven actuation of synthetic polymers is an emerging field of interest because it offers simple remote addressing without complicated hydraulic, electric or magnetic systems. Reviews on this area predominantly emphasize on the development of mechanical motions like bending, twisting, folding etc. However, the scientific and fundamental aspects of these materials are critical in order to expand applications and industrial relevance. Polymer actuators driven by light, not only comprises soft actuators (large deformations at low stress) but also include stiff actuators (high actuation stress at low strain). Synthetic polymeric materials with photo-responsive additives together with underlying mechanisms, processing parameters and final properties are required to broaden the scope of the field. In particular, parameters like actuation stress, actuation strain and work capacity have been given limited attention in the past and are discussed extensively. This work gives a comprehensive critical review on all light-driven synthetic polymer actuators, their actuating mechanisms and materials. A holistic perspective together with an insight into future prospects can lead academia and industry towards future innovations and applications of these exciting functional materials.

1. Introduction

Actuators which respond to external stimuli have been around for a long time and are used in a wide range of applications. As an example, bimetallic actuators that respond to temperature

are extensively used as thermostats, which control temperature etc. An actuator is capable of harnessing energy from an external source to trigger changes in the internal state of the structure, leading to some sort of mechanical deformation and/or response in terms of actuation stress, strain, work and/or deformation mode (contraction, expansion, bending, twisting).[1]

Over the past few decades, extensive research and innovation have emerged in the field of actuating materials, which respond to a variety of electrical, magnetic, chemical, optical or environmental stimuli. A wide range of organic (polymers) and inorganic (metals, ceramics) materials have been reported as potential actuating materials.[2–7] **Figure 1** represents these two broader classes of actuators subdivided into categories based on the actuation mechanism and materials type.
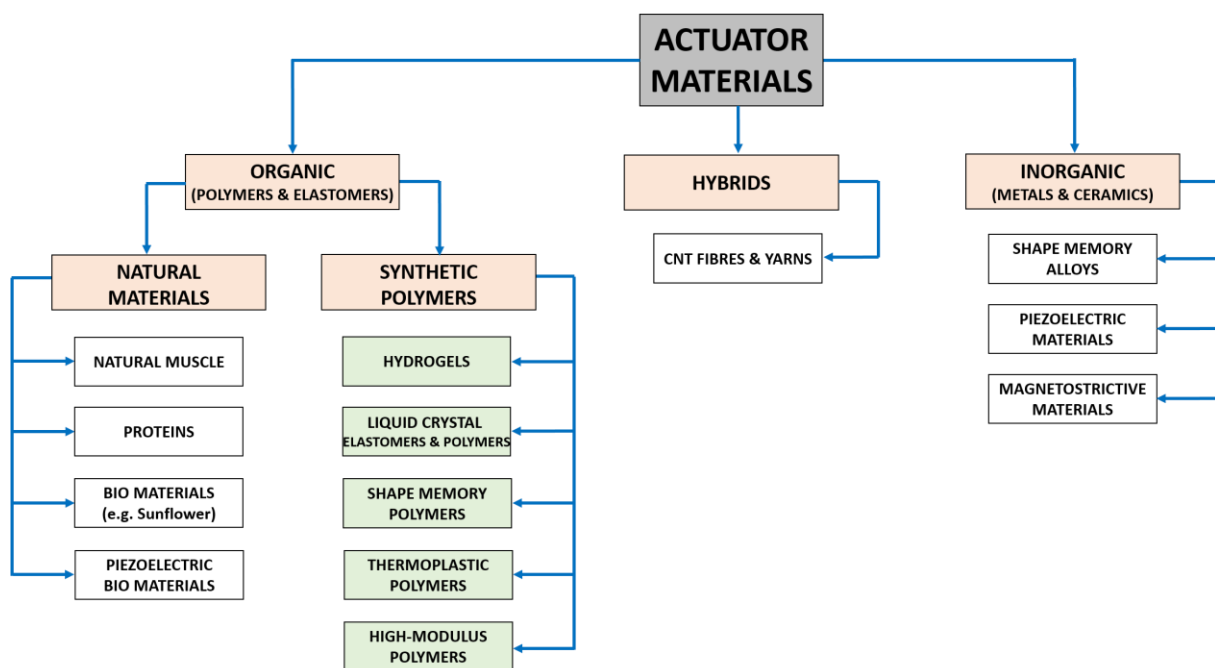

Figure 1: Classification of actuators on the basis of organic and inorganic materials. In terms of photo-actuation, promising material sub-divisions are shown in green.

Table 1: Figure of merit for different types of actuators

Actuator Type	Advantages	Limitations
Electromagnetic (EM) motors	- Probably the first ever known actuators. - Readily available in each size and shape.	- In order to prevent overheating, thermal conductance must be good enough which in turn depends on the surface area. So to achieve higher output, size must be larger. - Motor maximum currents that can be sustained for a given time are thermally limited.
Hydraulic Actuators	- These actuators convert pressurized hydraulic fluid energy into a rotary or linear motion. - Hydraulic actuators are considerably faster than pneumatic actuators since fluid is relatively incompressible. - These actuators generate a stress of 15-20MPa.	- Since hydraulic actuators involve fluid, the problems such as leakage, coupling and routing are associated with the system. - Hydraulic fluid pumps needs to be actuated by a source which usually is an electromagnetic motor or internal combustion engine. - When attempted to get large output, response time also might suffer. - Friction might adhere the process.
Pneumatic Actuators	- Similar in structure and principle to that of hydraulic actuator. - Lighter parts as inflatable elastic tubes or braided mesh bladders are being used instead of pistons. - Maximum output for a pneumatic actuator is about 0.67 MPa. - Pneumatic actuators offer tighter tolerances to leakage and requires fast-acting valves to avoid gas compressibility.	- In order to regulate pressure and air flow, pneumatic servo valve is a necessary evil which ultimately limit the dynamic performance of these actuators. - Air/gas, which is being used as fluid in pneumatic valve actuators, is low in viscosity, highly compressible and offer poor lubrication.
Shape Memory Alloy (SMA) Actuators	- Relative flexibility, electrical resistivity, enormous work density, and high specific power makes them the perfect candidate for many applications. - Widely used in robotics application as artificial muscle actuator.	- Contraction time for SMA actuators is associated with the amplitude of the current passing through it. Since the electrical resistivity increases during phase transition, this is directly related to the heat generated. Although using large currents, contraction time can be reduced. - A continuous flow of coolant over the SMA actuator makes the system expensive and complex. - Cooling cycle (expansion to regain its shape) is relatively longer than the heating cycle (contraction associated with heating). - The ratio of relaxation time to actuation time is still too high.
Contractile Polymer Actuators	- These are considered to be more similar to natural muscles than any other actuator category. - These can convert chemical/electrochemical energy into mechanical energy. - Contractile polymers such as gels can substantially swell or shrinks in a reversible manner using external stimuli such as solvent conditions, pH, electric field, temperature and light. - These are considered to be good in strength, robustness and response rate.	- Contraction of these contractile polymer gels are very slow and often associated with serious fatigue problems. - Expansion (swelling) and response time of these actuators are gel size dependent.

Actuator Type	Advantages	Limitations
Piezoelectric Actuators	- when an electric field is provided to such materials they generate mechanical stress or deformation as a response - Mechanical stress generated by piezoelectric materials are highly anisotropic yet quite large and promising.	- Energy transformation efficiency of piezoelectrics is low. - However, strains generated are too small to be directly useful. - Piezoelectric ceramics materials show substantial hysteresis and therefore require accurate positioning.
Magnetostrictive Actuators	- The promising materials from this class change their dimensions in the presence of a magnetic field. - These materials have a very high energy density as compared to piezoelectrics and therefore preferred for high force applications.	- A particular problem associated with these actuators is the brittleness and low strength which requires them to be kept under permanent compression. - Like piezoelectrics these materials demonstrate low strains and requires amplification. - Large magnetic fields and so the large coils are required to achieve considerable mechanical deformation which cause heating and therefore additionally require water cooled coils. - The whole system quite large, complex and expensive.
Natural Muscle Actuator	- Skeletal muscle fibre is the building block of generating force and creating movements in the body. - It carries a compact and portable power source i.e. body. - It is by far the best and sustainable actuator. - Muscle stiffness is proportional to the force it generates and remarkably constant per unit cross-sectional area at about 0.35MPa.	
Light-driven Actuators	- Rapid transmission of energy from source to the actuator material. - Doesn't require large and complex auxiliaries. - It is particularly intriguing because it allows actuation of materials without any physical contact. - Offers the potential to control the irradiation intensity, wavelength and polarization direction thus offering a controlled and designable actuation response.	- Skin is not transmissive for light. Often that's why we can't replace natural muscle in human body. - A low penetration depth of light (i.e. shadowing effect) within a material can be an essential drawback.

The extensive family of organic and inorganic actuator materials includes: electromagnetic motors, hydraulic and pneumatic actuators, shape memory polymers (SMP),[8–10] liquid crystal elastomers (LCE),[11,12] contractile polymer gels,[13] coiled synthetic fibers,[14] hydrogels,[15] electroactive polymers,[16,17] electrostatics,[18] shape memory alloys (SMA),[19–22]

piezoelectrics,[23,24] magnetostrictive materials,[25] carbon nanotube (CNT) fibers,[26] and yarns.[27] **Table 1** summarizes the pros and cons of some of these actuators type. Although not all have practical industrial applications (e.g. contractile polymer gels, electroactive polymers etc.), some of them have shown useful values for actuation stress (e.g. SMA offers an absolute actuation stress of around 200MPa), others offer actuation in terms of deformation and work (e.g. LCE, CNT fibers etc.) and other compelling attributes such as rapid response rate and reversibility (e.g. piezoelectrics, LCE, coiled synthetic fibers). Moreover, this class of materials also comprises many natural materials and actuators which are important e.g. natural muscle, protein, sunflower and bio-actuators etc.[28–32] In fact, natural materials are often inspire research activities to create synthetic alternatives.[33–37] The intention is to design synthetic actuators either by mimicking nature or to get inspiration from nature to create synthetic alternatives. Nature based actuators is a vast and specialized domain with some excellent reviews available,[28–32] and therefore it was excluded from the review.

In order to realize actuation in aforementioned synthetic polymer materials, which can be referred to as host materials, stimuli are usually indispensable. For fast and easy manipulation of the actuating components, light is often regarded as the most appealing option. Light as an external stimulus offers several advantages over other types of stimuli such as heat, pH and moisture, because the latter stimuli are diffusion based which tends to be slow. Light also has advantages over current or voltage driven electrical devices mainly because of the fast transmission of input energy into the host material, without requiring large and complex auxiliaries e.g. a complex wire system. It is particularly intriguing because it allows actuation of materials without any physical contact and offers the potential to control the light intensity, wavelength and polarization direction thus offering a controlled and designable actuation response. Of course, light can also have limitations in terms of shadowing effects (i.e. light gradient or limited penetration depth) and a careful choice of, for instance, the light source in

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combination with the proper design of light absorption is a critical issue in the design of devices. A high light absorption, for instance, generates a steep light gradient in the cross-section of the sample, causing the sample to bend or impeding in harnessing the potential contraction (i.e. a uniform contraction). On the other hand, shadowing effects can be useful and advantageous sometimes e.g. if bending is required.

Although, many inorganic materials like metals and ceramics are excellent materials for actuators, they usually do not respond to light because they are reflective, scatter light or have a non-tunable and very high absorption or reflection. These materials are hard, often brittle (ceramics in particular) and usually associated with very small mechanical deformations. In addition, the incorporation of light-responsive additives, and modulation of their light absorption for light-driven actuators is challenging or impossible to achieve. Most importantly, the optical characteristics of metals and ceramics are not easily tuned in terms of absorption, reflection and transmission. Also, the polarization state of light cannot be used to control motion because metals and ceramics are often non-dichroic.[38]

Organic materials and in particular synthetic polymer materials, on the other hand are flexible, low-cost, easy to process, can accommodate a wide range of additives and can easily be shaped into a wide variety of objects including films, fibers or complex parts (e.g. molded or 3D printed). However, pure synthetic polymers in general are not good light actuators but can be made so by adding some photo-responsive fillers/additives. Synthetic polymers can often be oriented by stretching, to achieve ultra-high strength and stiffness.[39–50] Potential materials of interest in terms of photo-addressable host materials range from very low moduli (<0.1 GPa) in the case of soft polymers like elastomers or gels, to very high moduli (>100 GPa) in the case of high-performance oriented polymer fibers or films like solution-spun, ultra-drawn polyethylene. **Figure 2** outlines the main classes of synthetic polymeric materials that will be

covered in this review along with their associated mechanisms of actuation. The underlying mechanisms for these host materials to become light-driven actuator materials was classified in two broad categories i.e. photo-isomerization and photo-thermal mechanisms.
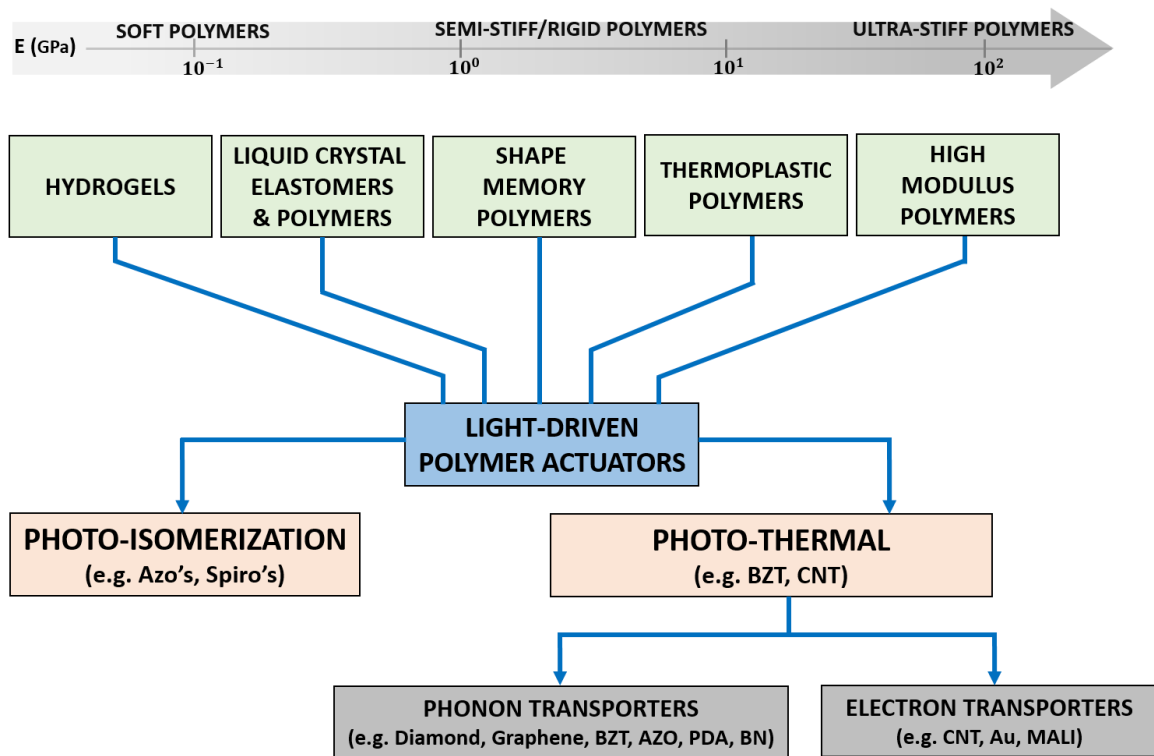
Figure 2: Photo-addressable organic polymer materials classified by potential actuating materials and associated mechanisms.

Additionally, a wide variety of routes are nowadays available to exploit the optical anisotropy of polymers in terms of dichroism and birefringence.[51–57] For example, in anisotropic polymer systems with dichroic photo-responsive additives, actuation can only be achieved if the polarized light is parallel to the orientation direction of these additives. Dichroism refers to the absorption of incident light more strongly in one plane than the other. This is advantageous in order to achieve actuation response in a specific direction. Birefringence is an optical property of anisotropic materials which means exhibiting different refractive indices in a direction parallel and perpendicular to the axis along which the molecular chains are aligned. Uniaxially

aligned LCP, for example are birefringent. Birefringence of the uniaxially aligned LCP films decreases with the order of the system upon heating and vice versa. It is therefore possible to measure order parameter from birefringence value or the birefringence from transmission measurements through uniaxially aligned films (of known film thickness) oriented at 45° to crossed polarizers.[55]

Exposing light responsive substance to infrared (IR), visible (Vis) or ultraviolet (UV) light can be an effective way to convert photons into motion and/or deformation. However, it is only possible if photo-responsive agents are present in the host materials. In the absence of these photo-responsive materials, there will, of course, not be any actuation. This energy transition can be very rapid and sometimes accompanied by a large photo-induced molecular motion, which, if sufficiently high, alter the physical and mechanical properties of the materials in which they are incorporated.

In some flexible polymer material systems (e.g. LCE), such molecular and/or nano-scale motion of the photo-switchable isomers can be transformed into macroscopic deformations in the host molecules. For example, photo-responsive azobenzene units, aligned and polymerized in a densely crosslinked LCE of high modulus (~1GPa), when exposed with UV light undergoes reversible light-induced isomerization accompanied by a photo-induced motion at molecular scale. This nano-scale structural movement of azobenzene molecules induce anisotropic mechanical deformation in the crosslinked host molecules in terms of expansion/contraction and a simple geometrical variation (such as alignment conditions of the nematic units) cause macroscopic deformations such as bending and coiling.[58–60]

A photo-responsive polymer can have light absorbing additives or chemical groups that are linked to the polymer backbone or incorporated as side groups in a chemical network. Light is absorbed in the absorption bands of the photo-absorbing material and can be measured by

recording the absorption spectrum. This light can simply heat the material or initiate an isomerization or combination thereof The rise in temperature of host polymers (as observed through infrared thermal images) is established only in the presence of these photo-responsive additives.[61–63]

Light energy upon absorption causes the transformation of isomeric conformation states of photo-chromophores (attached to host molecules) by overcoming the energy barrier in between these states. For example; azobenzene is a photo-chromic molecule, which upon absorption of a photon within the absorption band undergoes an efficient and reversible photo-isomerization.[64] More specifically, a strong energy absorption occurs in the UV-visible range of the spectrum in the π-conjugated system. Trans-azobenzene shows a strong π–π* transition near 320 nm and a weak n–π* band near 440 nm. Cis-azobenzene on the other hand has a stronger n–π* band near 440 nm and weak transition bands at 280 nm and 250 nm.[65] Because of the planar geometry of the trans conformation, dipole moment is almost zero. The cis isomer, adopts a bent conformation and has a dipole moment of 3 Debye.[65] This actually helps in modifying the dynamics of host polymer molecules followed by the isomerization.

Available heat energy or conformational transformation of functional groups upon light exposure induce mechanical actuation in the host polymer materials.

In case of a photo-activated oriented polymer actuator (either based on photo-isomerization or photo-thermal) the actuating effect is reversible as long as the host material remains in the linear viscoelastic regime. Upon photo-activation host material deforms as a result of contraction due to, for instance, cis-trans isomerization or the negative coefficient of thermal expansion. In the linear viscoelastic regime, the oriented polymer reverts back as soon as the light irradiation is stopped or the source is removed.

According to Beer-Lambert law,[66] light absorption (A) is dependent on the concentration c of the photo-absorbing material, molar attenuation coefficient ε, and the path length d (i.e. film thickness) (**Eq. 1**).

$$A = \varepsilon . c . d \qquad \text{Eq. 1}$$

The transmission of incident light is calculated from the absorption (**Eq. 2**).

$$T = 10^{-A} \qquad \text{Eq. 2}$$

The above relations indicate that the transmission of light through host material depends upon the amount of light being absorbed. A non-uniform and non-optimal photo-thermal effect can be generated by optimizing light absorbance and transmission. A higher photo-absorbance near the exposed side can generate an exponentially decaying light transmission profile (**Figure 3**) towards the back side of the sample. As a result of inhomogeneous internal stresses bending will occur.[67] Moreover, using bi-layer (photo-active and photo-inactive) films,[68,69] and patterned masks,[70–73] various deformations such as twisting, curling and rotation effects can be generated.
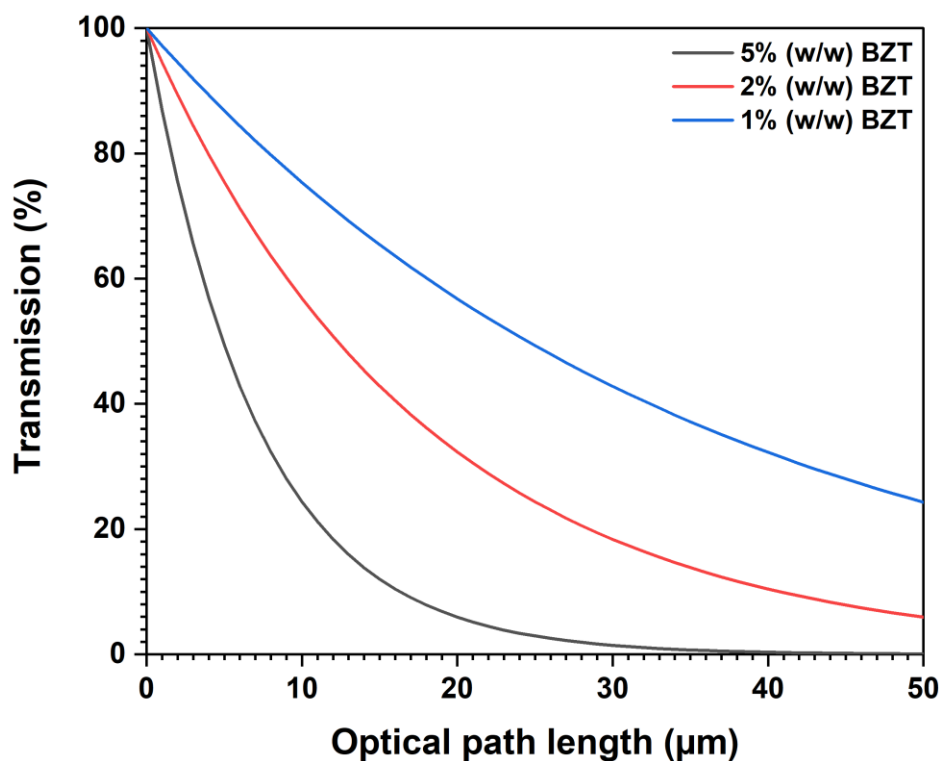
Figure 3: Light transmission profile as a function of optical path length indicating a photo-thermal gradient within the polymer film. Effect of dye concentration and film thickness is also evident.[62] Copyright 2021, American Chemical Society.

Recent reviews on photo-actuation,[59,69,74–80] primarily concentrate on the application side of existing light-driven actuating materials. The current review focusses mainly on the mechanisms and fundamentals of light-driven actuation in various organic polymer materials, including the most recent advancements in the field. However, in order to better understand, these mechanisms are also discussed in context of some applications.

Herein, we present a comprehensive review on the photo-responsive actuation effects in various synthetic polymer systems and their exploitation in designing photo-addressable systems and applications. Section 2 of this review covers the fundamental light-driven mechanisms originated by various photo-responsive additives. Section 3 is categorized on the basis of potential host materials (i.e. synthetic polymers) and highlights recent developments

towards light-driven mechanical actuation. We will focus on composite materials created by combining photo-responsive additives within host materials for light-driven mechanical responses in the form of an actuation stress, strain or deformation. Section 4 discusses the potential of these polymer based light-driven photo-reversible actuators for a variety of applications including robotics, micro-fluidics and medical applications as well as new applications fields (such as functional textiles and 4D printing). In the outlook and prospects section of this review, an overview of light-driven synthetic polymer actuators including quantitative parameters such as additive concentration, light spectrum, irradiation intensity, actuation stress and strain and fundamental mechanism etc. is given. It also discusses future opportunities and current challenges of this field.

2. Light-driven actuation mechanisms in polymers

In recent years, photo-mechanical responses have been demonstrated extensively in various polymeric systems. Common examples include polymers with photo-isomerizable moieties (e.g. azobenzene,[81,82] and spirobenzopyran[83–85]), photo-absorbers (e.g. benzotriazole[86,87] and polydopamine[71,88]) and photo-thermal nano-additives (e.g. polypyrrole nanoparticles,[89] rGO,[68] gold nano rods[90] and CNTs[1,91]). Depending on their chemical nature, the host polymer and the method of incorporation, two mechanisms of photo-actuation are usually dominating; photo-isomerization and photo-thermal effects.

2.1. Photo-isomerization

Photo-isomerization refers to light-activated transitions between conformational isomeric states in organic molecules that are used as additives or are linked to the polymer chains (either as side groups or along the main chain or in chemical networks) through polymerization. These conformational states, when present in soft polymer substrates like hydrogels, and liquid crystal

elastomers, trigger photo-mechanical deformation. These responses are often reversible upon illumination at a different (higher) wavelength.

Photo-isomerization is often accompanied by thermal effects which are highly dependent on heat management (thermally isolating or not) and mobility of the polymer matrices (rubber, crystalline, glassy). The photo-isomerization of light-active moieties involves the conversion of their conformational isomers i.e. from trans to cis state and back. As the two isomers differ significantly in terms of structural conformation, the photo-isomerization is accompanied by a large deformation on molecular scale (depending upon the moduli of the host material).

Azobenzenes, with two phenyl rings separated by an azo (-N=N-) bond, belong to a reversible light-switchable class of compounds that can undergo photo-isomerization.[92,93] The photo-isomers can switch between cis and trans conformation (**Figure 4a**) upon irradiation with light of wavelengths of 365 nm (trans to cis) or 450 nm (cis to trans).[94–96] Fluorinated azo compounds which switch in the visible light region were also reported.[57,78,97,98] The cis to trans (more stable) state is restored by thermal relaxation effect (the time taken by the system to lose heat energy) however it can take a long time span from hours to days to realize the whole transformation.[93,99] The cis-trans recovery is usually accelerated by illumination with a higher wavelength of light.[54,59]

The underlying phenomena of azobenzene was studied both experimentally and through physical and computational modelling. For example; a semi-empirical quantum chemistry Molecular Orbital PACkage (MOPAC) proposed by Armstrong et al. can be followed to determine the normal modes and vibrational energies of azobenzene.[100] Similarly an extensive theoretical study reported by Dokic et al. can be employed to understand azo-derivatives, cis-trans thermal isomerization and the effect of substituents and solvents. [101] Molecular level orientation and reorganization of azobenzene derivatives was proposed by Heinz et al. using a

molecular dynamics (MD) simulation, such that the theoretical results can be compared to experimental data, obtained through X-ray diffraction and UV/vis spectroscopy.[102]
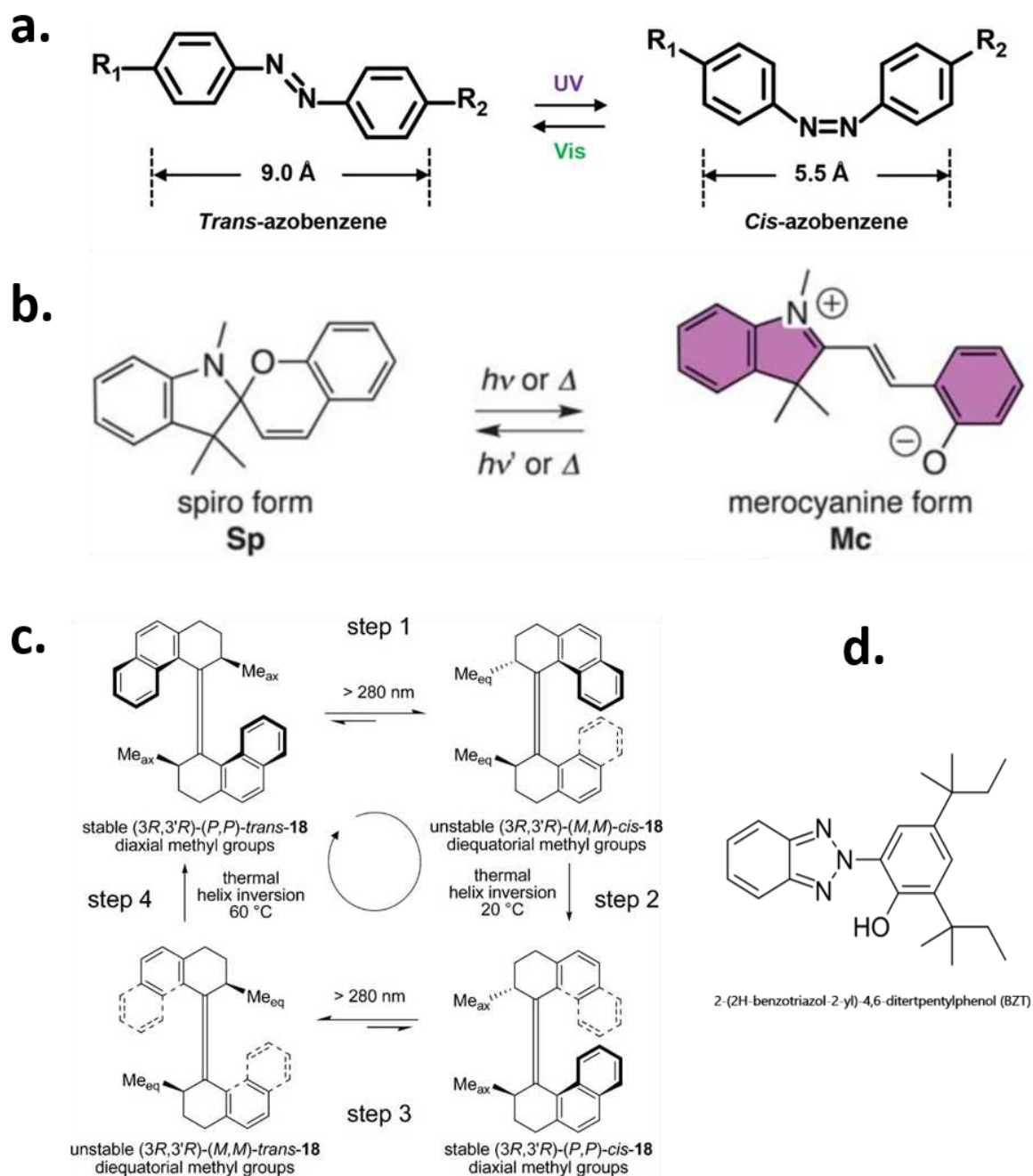
Figure 4: **a.** Reversible trans–cis photo isomerization of azobenzenes. Reproduced with permission.[78] Copyright 2019, Wiley-VCH. **b.** Chemical structures and isomerization of

spirobenzopyran isomers. Reproduced with permission.[103] Copyright 2011, Royal Society of Chemistry. **c.** Photo-isomerization and thermal isomerization processes of a molecular motor. Reproduced with permission.[104] Copyright 2007, American Chemical Society. **d.** Chemical structure of BZT Tinuvin-328 (BASF).

Spirobenzopyrans (SP) are another class of stimuli responsive materials that undergo a reversible optical and structural modification (**Figure 4b**) when irradiated with UV-light (<400 nm) and Vis-light (400-700 nm), respectively.[105] The unique behavior of SP can be attributed to the photo-cleavage of the C–O spiro bond upon light-irradiation allowing a reversible conformational re-arrangement between a closed-colorless spiropyran form and opened-colorful merocyanine form.[106–108]

Molecular motors

Far more complex light driven molecular motion is achieved in so-called molecular motors,[109] which can perform work such as collectively induced controlled motion of much larger objects.[110] "A 'molecular motor' is a molecular machine in which the change in relative position of the components influences a system." When a molecular motor returns to its original state at the end of the motor cycle, as a function of the trajectory of the components, system progressively drive away from equilibrium and the work performed is not undone.[111]

Light as an energy source can translate unidirectional rotary motion into continual rotary function in these molecular motors (**Figure 4c**). By applying light and heat, the unidirectional rotation of a molecular motor can reversibly be controlled. The two reversible photo-isomerization steps converts the stable isomers into unstable isomers, each followed by an irreversible thermal steps converting unstable isomers into stable isomers.[104]

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The rotational properties of these motors were successfully demonstrated in solution.[112] In order to study the behavior and functionality of these motors on a solid surface (apparently flat), scanning tunneling microscopy (STM) studies were performed.[111] Although deposition of single molecule motors on surfaces like copper and gold was successful, no lateral motion could be induced by light or STM tip pushing, indicating a strong interaction between the molecule and the surface.[113] However, lateral studies showed that movement of the motor across the surface could be induced by applying voltage from the STM tip. Although an electric stimuli was used to generate motion instead of the photo irradiation, the authors theorize that the movement in these molecular motors is still the result of the same rotational process.[114]

The remarkable properties of both photo-isomers and molecular micro-/nano motors were extensively demonstrated in solutions, nematic liquids, gels and soft elastomers.[112] It was also shown that the environment has a dominant influence on the kinetics of the transitions.[113] Though, it is uncertain if this motion can be converted into useful functionality outside the solutions. It is beautiful to see these motors in action capable of achieving the motion in solutions. However, when it comes to function on a solid surface, artificial molecular motors currently pale in comparison to the motors found in literature.[115]

2.2. Photo-thermal effect

This photo-actuation approach involves the conversion of photon energy into thermal energy, which can then be used to power an actuation system. In certain cases, the material itself absorbs the electromagnetic radiation, for instance, in the case of partially conjugated systems.[116] In conjugated systems, electrons at ground and excited states are closer in energy as compared to non-conjugated systems. It means a lower energy light (with larger wavelength) is sufficient to excite electrons in such systems. Therefore, conjugated materials (such as polyacetylene) itself absorb the electromagnetic radiation. Usually host polymer materials

require an optical radiation absorbing material, so that it can absorb most of the incident light energy and convert it into heat energy. These radiation absorbing materials can be used as heating elements in light-driven actuators.

In its essence, photo-thermal actuation refers to the direct transformation of light into heat through embedded/coated substances (additives) leading to a certain kind of mechanical deformation (e.g. contraction or expansion or both) within the host polymer material. More complex deformations such as bending and twisting can be achieved by generating a thermal gradient, patterning or by adjusting illumination conditions.[71,72,89,117,118] Aiming at developing a fast response and high sensitivity, the light-responsive additives must possess special optical as well as thermal properties.

As stated previously, thermal effects are nearly always present in photo-addressed systems and sometimes completely dominate. The heating-up and cooling down of a system is influenced by many factors including materials parameters like heat conduction and heat capacity and environmental circumstances (convection, flow etc.). In a light-driven actuation device, heat generated by photo-thermal effect can be transported through the host medium by two fundamentally different mechanisms i.e. either by phonon-transport or by electron-transport depending on the photo-responsive additives.

2.2.1. Phonon-transport

When heat is being transported through an electrically isolating medium the dominant mechanism is often phonon transport.[119] Chain oriented materials with high crystallinity and strong interactions, are expected to have a high phonon transport and a high thermal conductivity. In case of chain orientation, phonon hopping becomes effective and therefore the transportation of thermal energy between the corresponding chains is enhanced.

Benzotriazole 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (BZT) is a yellowish powder (**Figure 4d**) with a distinctive crystal appearance (homogenously dissolves upon melting), which belongs to a class of commercially available UV absorbers. When used as an additive, it absorbs UV irradiated energy at a wavelength of 365 nm more efficiently than the substrate or host material.[120] This absorbed light photon energy is dissipated in the form of phonon heat energy.[86,87]

Dopamine-melanin colloidal nano-spheres are novel photo-thermal agents for cancer therapy. Light-to-heat energy efficiency of these nano-spheres is 100 times higher than that of CNTs.[121] *Polydopamine (PDA)* nano-coatings also serve as an excellent photo-thermal layer even when the coating thickness is less than 50 nm.[71,122,123] Upon illuminating with an IR light source of 808 nm wavelength, PDA nano-coating converts the absorbed light energy into thermal energy (i.e. heat), causing the substrate to heat up to a temperature of around 160 °C in just 20 s.[71]

2.2.2. Electron-transport

When free electrons (and/or holes) cause thermal energy, i.e. heat to be transported through the medium, it is viewed as electron transport as in case of conjugated materials, which are good electron or hole conductors. Electron transport is relatively often more effective than phonon-transportation.[124,125] For instance in the presence of electron transporters such as CNTs (even only in small amounts) in a non-conjugated material like polyethylene, thermal conductivity of the composite enhances many times (providing effective percolation), indicating a rapid and effective transportation of thermal energy through the medium. However, in an electron transport system, we cannot rule out the presence of phonon transport, for instance when there is no conduction path for electron hopping.

CNT, and metallic nanoparticles such as gold, are also acknowledged as radiation sensitive materials.[126] Light (photons) of appropriate energy (depends on wavelength) upon absorption by these additives fills the gap between lower and higher energy states within the atoms of the functional additives, causing the electrons to excite. When present in the host materials, electrons of the photo-responsive additives after excitation, vibrate and collide with the neighbouring atoms of the host material. And thus so light energy is converted into heat energy (through electron transportation) leading to a temperature rise within the host molecules surrounding them. One of the direct implications of exposing these nano-scale substances to light irradiation is photo-mechanical actuation. Their promising features, such as high surface area, excellent mechanical properties and thermal conductivity, have heralded some interesting insights into the possibility of designing photo-induced actuators based on nano photo-sensitive materials.[90,127–131]

Methyl ammonium lead iodide (CH$_3$NH$_3$PbI$_3$), is a unique solar-sensitive material that holds the potential to exhibit an excellent photo-thermal effect by converting solar energy into heat.[72] Methyl ammonium lead iodide (MALI) is a typical organic-inorganic hybrid material. Like CNTs, graphene and gold nanoparticles, black MALI can absorb light and transform light energy into thermal energy upon photo-illumination. MALI is relatively inexpensive ($5/g) and can easily be processed in solutions without aggregation posing significant technological advantages over its competitors (i.e. CNT, graphene and gold).[72]

3. Synthetic polymer materials for photo-actuation

In photon-triggered actuation, light energy conversion is intermediated by a thermal process causing an inherent response in the host material. Materials best suited for light-driven

actuation will have a high coefficient of thermal expansion (CTE). Depending on the nature of actuation, i.e. expansion or contraction, either a high positive or negative CTE is essential. A positive CTE is associated to isotropic polymers while a negative CTE is characteristic for oriented polymer materials. An efficient way to control negative CTE in polymer is by aligning their polymer chains through stretching or drawing processes.

Negative CTE behavior of oriented natural (e.g. silk) and synthetic polymers (e.g. polyethylene and Kevlar fibers), originates from the presence of highly aligned polymer chains, leading to a chain contraction along the orientation direction upon heating.[132–134] Photo-mechanical behavior observed in oriented semi-crystalline polymers is not merely the result of chain contraction in the crystal lattice but also partly an entropic effect related to the oriented amorphous phase i.e. taut-tie molecules that link crystalline lamellae together and permit the load transfer between crystalline regions.[133]

Among various non-organic and organic materials, polymers are by far the most suitable light activated materials for a number of reasons. These exciting new materials are mechanically responsive, i.e. they undergo mechanical deformations in response to photo-irradiation. Moreover, the actuation response of a polymer to light can be modified and improved by optimizing stimulus parameters (e.g. wavelength, intensity, polarization direction etc.) as well as host material parameters (e.g. sample thickness, chain orientation direction, draw-ratio, modulus etc.).

It is worth noting that the relatively low thermal conductivity of polymers may prevent rapid transport of heat, thus impeding the actuation potential in terms of contraction and/or expansion. For polymer films or sheets with high thickness or a high optical density, a thermal gradient is unavoidable and may even be desirable. A low penetration depth of light within a material can be a drawback.[117] For instance, if light only penetrates the surface layer, then only

the surface chromophores that will receive the light and the material will bend rather than contract, which is another form of mechanical actuation. Yet, to achieve contraction rather than bending, the film needs to be sufficiently thin or needs to be exposed to light of high intensity or need a low concentration of chromophores, in order to accumulate enough light energy throughout its cross-section.[72,126,135,136]

The following synthetic polymer materials (as host materials for different photo-responsive additives/moieties) were considered suitable for light-driven actuation and classified with respect to their stiffness. Following sub-sections will discuss the fundamental actuation mechanisms (i.e. photo-isomerization or photo-thermal) in these materials through examples of various combination of these host materials with photo-responsive additives/moieties. The underlying mechanism is highlighted in each particular example.

3.1. Hydrogels based photo-actuators

Photo-responsive hydrogels have received enormous attention owing to their drastic volume change induced by light irradiation and promising applications in biomedical devices and soft robotics.[76,89,137,138] Usually, the physical origin of the contraction and/or expansion is related to upper critical solution temperature (UCST) or lower critical solution temperature (LCST) demixing. Phase separation in hydrogels is related to the macromolecular interactions between polymer chains and water molecules. Heating or cooling the system results in changes in these interactions, which leads to phase transition and macroscopic volume changes.[139–141]

Photo-actuation in hydrogels can be categorized by two approaches: (i) isomerization of light-driven entities upon irradiation, leading to a modification of gel properties such as hydrophilicity, charging state, or crosslinking density,[103,142,143] and (ii) photo-thermal effects induced by a light-responsive agent integrated in the hydrogel, inducing a volume transition of

the hydrogel.[144–146] The synthesis of molecules undergoing photo-isomerization is often complex and laborious. The latter strategy, however, is easy to implement and control with versatile combinations of photo-thermal agents,[98,146,147] including polypyrrole (PPy), graphene oxide (GO), spiropyran and CNTs.

Photo-thermal energy transduction through photo-responsive additives have provided efficient platforms for controlling the volume and shape of hydrogels in response to visible light or near infrared (NIR) radiation.[144,147–153] These composite materials can serve as soft actuators that are able to perform mechanical actions depending on the application. Local or global changes in the volume or shape resulting from swelling/de-swelling of the hydrogels (e.g. LCST) can induce mechanical movement, including bending, twisting, rolling and curling. To be utilized widely, a reversible volume change by the hydrogel in response to light irradiation of modest intensity is typically required.

Anisotropic locomotion was demonstrated (**Figure 5a)** using PPy nanoparticles as photo-thermal nano-transducers, loaded into a gradient porous hydrogel, N-isopropylacrylamide (NIPAm).[89] With pore size modulation and distribution, the thermo-responsive material with pendent hydroxyl groups (PNIPAm-OH) acts as a photo/thermal-responsive composite material responding to NIR laser stimulation (980 nm, 2.5 Wcm^{-2}). A gradient porous structure of the hydrogel provides a higher de-swelling rate at the top surface (being irradiated) than at the bottom causing the hydrogel strip to bend in the direction of the irradiation. Elasticity of the hydrogel brings the strip back to its original shape by swelling when the irradiation stops. These hydrogel motions were highly reversible and repeatable. An actuation stress of ~0.13 kPa was recorded at a strain of around ~90% which illustrates the soft nature of these hydrogels and the corresponding low stresses and high strains.

Based on poly(N-isopropylacrylamide) (PNIPAm) hydrogels incorporating light-responsive reduced graphene-oxide (rGO), a photo-responsive actuator was devised, that showed large volume reductions in response to irradiation by visible light of modest intensity.[68] Exposure to visible light of 41.8 mW/cm^2 for 30 s provided sufficient heat to induce full bending of the bi-layer actuator toward the active layer, PNIPAm/rGO side due to hydrogel shrinkage. Since the passive layer, polyacrylamide (PAAm), retained its equilibrium dimensions, induced stress at the common boundary constrains dimensional changes of the PNIPAm/rGO layer, forcing the bilayer to bend one way. A fully reversible and reproducible bidirectional actuation (**Figure 5b**) was achieved by adjusting the swelling ratio (λ_f) of the hydrogel layer.

Recently, redox-responsive hydrogels based on photo-induced electron transfer processes were employed to actuate materials; an artificial molecular muscle (AMM) was developed by Liles et al.[154] Irradiation of polyethylene glycol (PEG) hydrogel with blue light (~450 nm) resulted in electron transfer from light absorbing photo-redox catalyst [Ru(bpy)$_3$]$^{2+}$ to viologen units incorporated into the hydrogel network. This causes the reduction of polyviologen, which in turn led to a decrease in electrostatic repulsion, loss of the corresponding counter-anions, and intramolecular folding of the polyviologen chains. This process triggered a contraction of the hydrogel approaching ~35% over the course of 5 h.
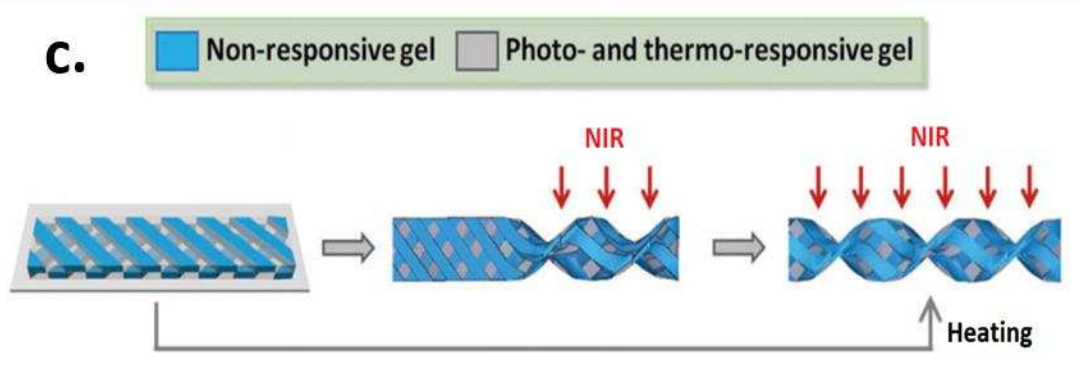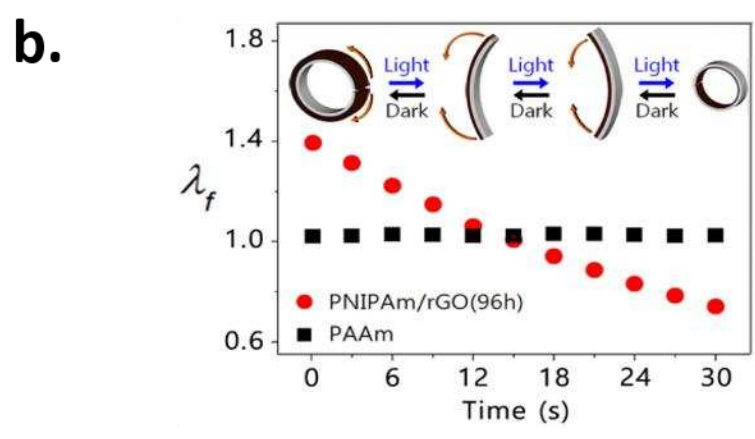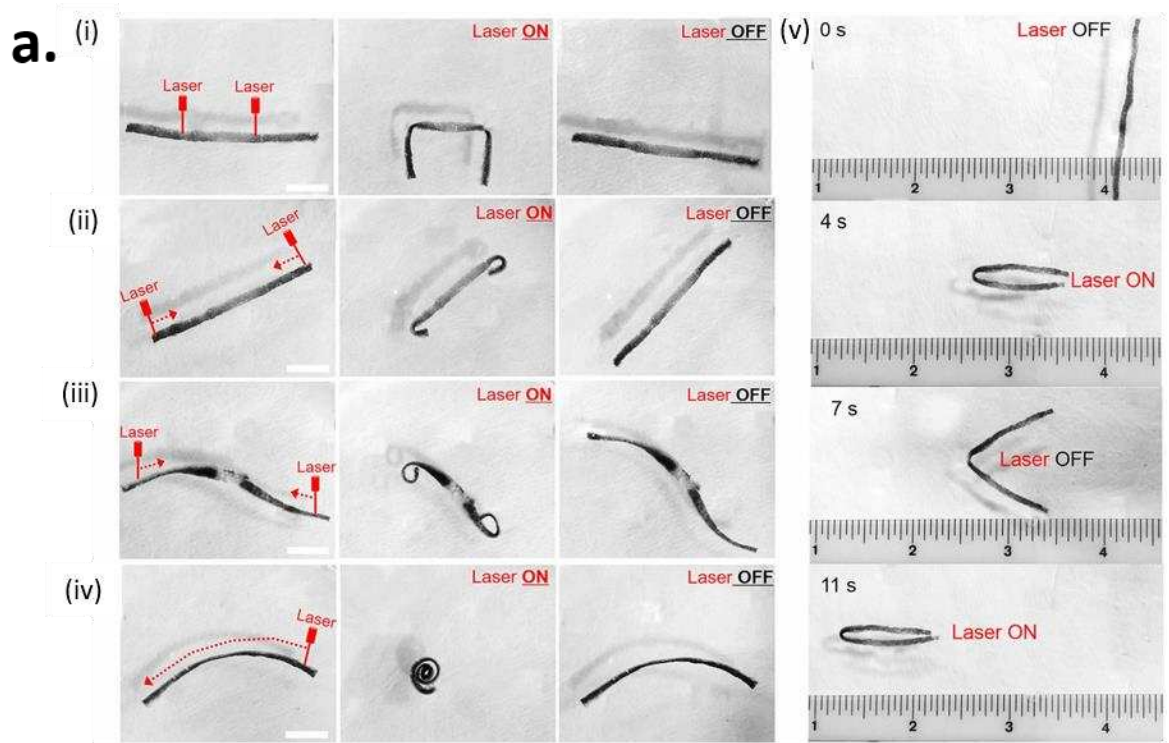
Figure 5: **a.** Laser irradiation to programmable locomotion of hydrogels. **(i, ii)** Folding and curving on both ends of the hydrogel strip in the same directions. **(iii)** Curving on both ends of

a hydrogel strip in opposite directions. **(iv)** Curling the whole hydrogel strip into a spiral pattern by moving the laser in a parallel direction along the hydrogel, the scale bar is 1 cm. **(v)** Optical image series showing the forward-moving hydrogel driven by laser irradiation. Reproduced with permission.[89] Copyright 2015, Wiley-VCH. **b.** λ_f (swelling ratio) for the active and passive layers of a circular actuator (inset: schematic diagram of the bending behavior from ring to reverse ring). Reproduced with permission.[68] Copyright 2016, Springer Nature. **c.** The resultant PAAm/PNIPAm/rGO composite hydrogel showed patterned deformation under the irradiation of NIR light or direct heating. Reproduced with permission.[155] Copyright 2019, Royal Society of Chemistry.

A new strategy wherein programmable deformations activated either by heating or irradiation was proposed.[155] Composite hydrogel structures were prepared by combining spatially distributed thermo- and photo-responsive poly(N-isopropylacrylamide)/reduced graphene oxide (PNIPAm/rGO) gels embedded in a non-responsive polyacrylamide (PAAm) gel. Whereas, rGO was essentially acting as a photo-thermal agent the resultant heterogeneous structure showed patterned bending, folding, and twisting (**Figure 5c**) actuated by either heating or NIR light (5 mW/cm^2) irradiation to build-up internal stress, which induced volume contraction of the PNIPAm/rGO gel. The deformations (**Figure 5c**) were related to the de-swelling mismatches between the responsive and non-responsive gels at elevated temperature. [155]

3.2. Shape memory polymer (SMP) based photo-actuators

Shape memory polymers (SMPs) are an important class of actuating materials.[156–158] In general, these SMPs are irreversible e.g. they respond to a stimulus but do not revert back to their original state upon removal of the stimulus. Presently, the most widely explored SMPs are the thermally responsive. They return to their original shapes upon heating.[10,159] Harnessing

the functionality in SMPs using direct heat is not always practical, especially when electronic devices are involved or a partial shape change is anticipated. Remotely triggered shape change, using light and in particular sunlight, is preferable in order to directly convert photo/solar energy to mechanical work, not to mention that light can easily be modulated precisely and focused as required.[160]

Photo-sensitive additives/fillers/compounds can be introduced into a polymer matrix during synthesis. The photo-response is therefore dependent on the distribution, alignment, dichroism of these moieties as well the chemical structure and composition of the host polymer. However, a muscle-inspired (protein adhesion to natural muscle) photo-sensitive material coated on existing SMPs makes the whole process simple, cost-effective and re-programmable.[88] Li et al.[71] introduced a simple and inexpensive post-synthesis method to endow conventional SMPs with photo-active functionality, using polydopamine (PDA) dip-coating, while keeping their original unique properties. The flexible light-driven shape deformation can easily be applied, patterned and removed (using alkali solution). Even a very thin layer of PDA (~50 nm) can convert light (808 nm IR) into heat energy, significant enough to trigger a phase transition of common SMPs. Actuation stress generation and its dependency on light intensity was also evaluated. A relatively greater response was recorded at higher intensities (~130 kPa at 600 mW/cm^2 for a 150 μm thick PDA-SMP sample).

Yang et al.[72] suggested a similar method of converting a wide range of currently available thermal-responsive SMPs into light-driven SMP actuators by merely coating them with a solar-sensitive material: methyl ammonium lead iodide ($CH_3NH_3PbI_3$) perovskite. This unique material exhibits an excellent photo-thermal effect by converting solar energy (120 mW/cm^2) into heat, causing shape change of SMPs. Most interestingly, such coatings can easily be patterned to make SMPs photo-responsive and photo-inert alternatively or locally. However,

the coating has poor stability (degradation under aqueous conditions) and is only suitable for temporary shape change. Photo-actuation response also depends on coating and sample thickness.

3.3. Liquid crystal based photo-actuators

Liquid-crystalline elastomers (LCEs) are weakly cross-linked elastic polymer networks comprising rigid, anisotropic and directionally ordered units, termed mesogens, coupled to polymer chains. Any change in their orientation will be translated to changes in the mechanical properties of the bulk material.[161] The self-organizing nature of LC networks and the flexibility of the rubber network allow for large and reversible anisotropic dimensional changes in response to applied stimuli.

The alignment order of the LCE films decreases upon heating above the LC isotropic phase transition temperature. The films exhibit an anisotropic contraction along the mesogen alignment direction. Upon cooling, the LCE films revert back to their original size, i.e. by expanding. Such reversible deformations along with the versatile mechanical properties of the polymer network, make LCEs a promising class of materials for efficient actuation as artificial muscles.[55,162–165] Since the underlying mechanism of actuation is the switching between the LC (in most cases nematic) phase and the isotropic phase, in principle, any external source (such as light in this instance) that can activate such a phase transition could be used to trigger the actuation.

3.3.1. Liquid crystal elastomers with azobenzene moieties

Elastomers composed of nematic polymers have remarkable elastic and optical properties. For instance they can change shape mechanically when the degree of ordering is changed from nematic to isotropic state,[166] typically achievable by heating up to a certain temperature.

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However, the said phenomena can also be realized through optical means, i.e. by photo-isomerizing the nematic rods comprising of photo-responsive units such as azo's (**Figure 6a**),[167] which can bend from *trans*- to *cis*-isomers on absorbing a photon.[81,82] Either thermally activated or optically stimulated, a photo-thermal elastic response offers an actuation of up to 400% strain.[168] A reduction in nematic order is considered to be the reason for inducing molecular shape changes within the sample.[169]

This exciting material class eventually recovers back from *cis-trans* over a period of time spanning from several seconds to minutes.[93,99] However, LC order recovery can be accelerated by visible light irradiation, which stimulates the depletion of the cis population.[170] Changes in shape (i.e. expansion or contraction) or properties (i.e. stress or strain) brought about by increasing the temperature of the specimen could also be accounted for by photo-irradiation; these two phenomena are somehow interconnected.

Azo based LCE's are highly dichroic in nature. That means incident light absorption efficiency is orientation-dependent for the trans-azo molecule. In order to achieve an efficient transition of photo-isomers, azo-molecules must be aligned with the light polarization direction.[171] However, photo-induced deformation along a particular direction might not ensure a wider perspective. Directional photo-mechanical actuation may not be useful towards certain applications of light-driven actuators.[172]

Using a splayed or twisted molecular alignment rather than a uniaxial planar alignment significantly improved photo bending of LC actuators.[173] Although in-plane strains are limited, shifting director orientation along the thickness of the film results in a sharp strain gradient, causing tight bending of the actuator. The main source of these differences is believed to be the heating of the film that aids in the bending of both the splay and twisted nematic systems.[174]
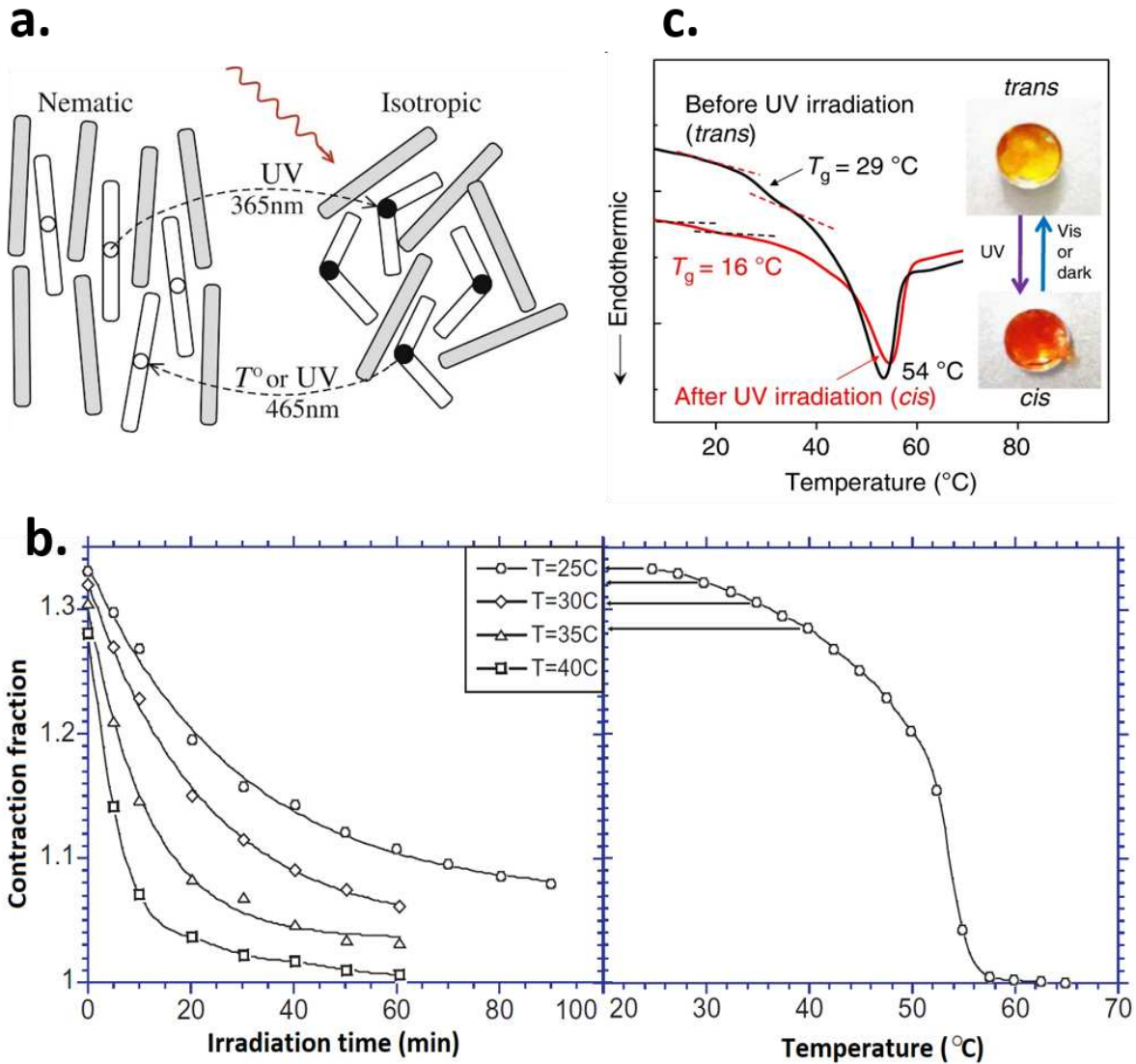
Figure 6: **a.** Dye guest molecules bend and disrupt the nematic order of their hosts. For azo dyes UV light is required. Reversible action is by thermal decay or stimulated decay by light of longer wavelength. Reproduced with permission.[54,167] Copyright 2002, American Physical Society. **b.** Contraction along the director as a function of illumination time for various initial temperatures (left). Contraction along the director as a function of temperature (right). Reproduced with permission.[167] Copyright 2009, Taylor & Francis. **c.** DSC measurements of photo-switchable T_g, owing to UV-irradiation and photo-isomerization of the polymer network in trans-, and cis-form. Reproduced with permission.[175] Copyright 2018, Springer Nature.

Finkelmann et al. demonstrated the light-induced contraction of LCE films for the first time. Nematic LCE films containing azobenzene crosslinks exhibit 20% contraction upon irradiating with UV light.[135] The comparative effect of thermal- and photo-contraction of nematic elastomers incorporated with azo chromophores (**Figure 6b**) was also presented.[167] Photo-irradiation was carried out at several initial temperatures, with samples undergoing higher contractions at higher starting temperatures. It was proposed that in order to optically disrupt the order parameter or to approach the isotropic phase, the nematic-isotropic transition temperature must be reached.

Li et al. developed nematic azo side-on elastomers with relatively rapid (<1 min) contraction fraction of 17% upon UV irradiation (100 mW/cm^2). The significance of the azo concentration on response rate and light intensity on contraction fraction was also demonstrated.[176] Hogan et al. incorporated various azo derivatives as photo-responsive triggers into a wide range of LCEs. The deformation behavior of these moieties was examined upon exposure to UV light. Photo-mechanical effects based on the proportion and positional role of the light-sensitive groups in the cross-linked polymer network, were detailed.[54] A relatively lower contraction effect was observed when the position of the azo group within the corresponding mesogenic moiety was weakly coupled to the polymer backbone by a long spacer, in contrast to, where a strong parallel alignment between the rod and the backbone is induced, even when the proportion of photosensitive moieties are lower. It was proposed that this could result in the kinked cis form of the moiety having less of a destabilizing effect on the backbone anisotropy, and so the elastomer response to UV irradiation is reduced.

In order to examine the conformational changes of polymer chains on a macromolecular scale, polymeric materials based on azobenzene and spiropyran were synthesized owing to their potential photo-isomerization upon exposure to light.[177] However, it was unclear whether the

response was dominated by photo-isomerization of the chromophore or photo-induced heating. A significant temperature increase was also reported under light-irradiation. Liu et al. reported a UV-irradiated (365 nm, 40 mW/cm^2) bending of azo based cross-linked LCP films towards the incidence side.[178] Deformation reverted back immediately upon exposing the films to visible light (530 nm, 60 mW/cm^2).

Ikeda et al. reported similar light-induced bending behavior of azobenzene LCEs and gels.[171,179–181] According to their studies, the majority of the incident light is absorbed within a relatively thin layer of the film towards the irradiated side, leading to an asymmetric contraction through thickness and subsequent bending. The process is reversible and the film reverts back to an unbent state by regaining its *trans* state.

A rather surprising photo-switchable effect was described recently.[175] The azo-chromophores showed reversible photo-isomerization, resulting in a change in glass transition temperature (T_g) of the crosslinked LC polymer network. A lower T_g was recorded for the polymer films under photo-irradiation, owing to the cis-form of cross-linked azo-moieties in the polymer network (**Figure 6c**). According to the study, the photo-switchable T_g contributes to light-induced bending. Polymers that display a low T_g are softer and more flexible at room temperature and thus respond quickly to stimuli, exhibiting mechanical deformation such as bending.

It is interesting to question at this point, whether the observed mechanical effect, i.e. reduction in orientational order, is a consequence of heating from light-absorption or due to photo-isomerization. Actually, both mechanisms are important and could occur simultaneously. The characteristic temperature of a UV photon is roughly 10^4 K; almost 100 times more than a visible light photon.[57] A higher actuation stress using a UV-source (365 nm) was reported as compared to a visible light source (442 nm) at similar light intensity (~220 mW/cm^2) owing to

the observed difference in temperature of the samples upon irradiation.[182] It can be expected that photo-illumination causes significant heating of the network. However, this cannot be realized without the presence of any photo-absorbing chromophores or dyes such as azo's undergoing trans-cis isomerization upon photo-illumination. The transition cycle potentially involves release and absorption of thermal energy.[135]

Contraction or strain is not the only way to record a photo-mechanical response. Cviklinski et al. measured the stress of a clamped nematic elastomer film with pendent azo groups (side-chain).[136] Clamping generates stress in the sample to contrast the tendency to contract upon illumination. The effect of radiation intensity was also validated.

Concentration and position of azo-chromophores define the light-induced deformations in LC polymers. The former affects the degree of isomerization of azobenzene moieties and therefore the macroscopic deformation behavior of the films while the latter determines the contraction and corresponding force, which are found to be more significant when azo-chromophores are positioned at crosslinks rather than at side chains. The maximum actuation stress recorded was 2.6 MPa.[96] High crosslink densities (high modulus) are preferable for high photo-induced stress generation.[55,183,184]

Azobenzene molecules crosslinked within the polymer network of LCEs cause *contraction* upon photo-irradiation because of their alignment with the LC director.[60,185] Hagaman et al., on the contrary, proposed a photo-active shape change phenomena based on *volume change* of linear, printable LCEs that consist of poly(siloxanes) containing pendent azobenzene photo-switchable groups.[182] Irradiating the photo-active and non-active bi-layer films with 365 nm light wavelength cause photo-isomerization, leading to free-volume expansion of the active polymer matrix due to size differences of azobenzene *trans-cis* isomers. The bi-layers exhibited

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rapid actuation, which is reversible in seconds and photo generated stresses ranging from 1.0 to 1.7 MPa.

3.3.2. *Liquid crystal elastomers with CNT fillers*

A promising strategy to add functionality to LCEs can also be attained by embedding functional nanoparticles, ultimately enhancing their performance as actuators.[186] Incorporating carbon nanotubes (CNTs) in LCE is technologically simple as compared to synthesizing photo-isomerizable molecules or molecular chromophores into the LCE network. Moreover, photo-actuation can be induced at a wide range of wavelengths without requiring filtered light to specific wavelengths.[187]

CNTs with their diameter in the nanometric scale, high aspect ratio and large surface area, offer excellent thermal conduction, which is a key element for photo-actuation and photo-mechanical response.[188,189] Especially single-wall carbon nanotubes (SWCNTs), are one of the most effective fillers for LCEs, owing to their strong absorption in the visible and NIR region as a result of band gap transitions.[189]

LCEs incorporating CNTs showed significant photo-thermal actuation when irradiated with light.[56,186,190,191] This interesting class of materials can efficiently absorb and convert photo-energy into thermal-energy, serving as a nano-scale heat source to heat polymer matrices effectively. The available heat is sufficient to induce a nematic-isotropic phase transition in the LCE network, displaying orientational actuation.

CNT concentration in LCE is an important factor that influences the photo-mechanical actuation significantly. Yang et al. observed a faster response and higher actuation strain at 0.2 wt% as compared to 0.1 wt% filler content.[56] Pre-oriented (160%) 0.2 wt% SWCNT/LCE films, showed a contraction of about 30% and a temperature rise of up to 80 °C (an increase of

almost 15 °C) was recorded upon IR photo-irradiation (808 nm, 45 mW/cm^2).[56] The authors proposed that with more SWNTs present in the matrix more heat was produced, resulting in faster actuation and larger axial strains.

Marshal et al. reported that only a small amount (0.1 wt%) of CNTs in LCEs can induce already a reasonable actuation stress (~8 kPa) when irradiated with an IR or visible light source (670 nm, 67 mW/cm^2). The observed mechanical actuation was rapid, reversible and light-intensity dependent.[186] Studies showed that the wavelength of light has little effect on the photo-actuation response,[186] while light intensity plays a vital role towards actuation.[131] The actuation stress for a 0.3 wt% SWCNT/LCE film increased from 55 kPa to 80 kPa when the irradiated IR light intensity was raised from 1.7 W/cm^2 to 3.4 W/cm^2.[131]

With the presence of CNTs, the LCEs could also actuate well below the nematic-isotropic transition. Experimental results showed that the material's nematic–isotropic transition temperature (T_{ni}) was evidently lowered from 82 °C to about 63 °C in presence of CNTs.[131] Nanocomposite films of SWCNT/LCE with a polysiloxane backbone and pre-aligned side-on mesogenic units, were reversibly and rapidly actuated by white light over a large spectrum. Upon irradiation of 413 mW/cm^2, a contraction stress of 75 kPa was also recorded in the 0.3 wt% SWCNT/LCE nanocomposite film, which was close to zero for the reference LCE film.

3.4. Thermoplastic polymer based photo-actuators

Thermoplastic polymers are being widely used in our daily life owing to their low-density, low-cost and ease of manufacturing. Adding functionalities to these common polymers using photo-responsive additives is appealing as also shown by considerable attention gained by the field of light-driven actuation.[62,63,192] Over the last two decades, there have been numerous

reports in the literature on the photo-actuation behavior of some of these promising materials, especially polymer-CNT composites.[53,130,193–195]

A homogeneous dispersion of CNTs in the polymer matrix is crucial to effectively utilize the photo-mechanical actuation potential of these fillers. Solution blending or in-situ polymerization has been demonstrated to be more efficient in dispersing nanoparticles like CNTs, as compared to melt-processing routes.[196] However, improved dispersion can also be achieved using specific compatibilizers.[197] A good dispersion of multi-walled carbon nanotubes (MWCNTs) in ethylene-vinylacetate copolymer (EVA) showed a uniaxial mechanical actuation in braille form elements upon illumination by a visible light source (627 nm). A rather low frequency light source induced a higher and faster response. A maximum deformation change of about 15% was observed using blue light with a maximum actuation stress of 63.8 kPa extrapolated using a Young's modulus value of 0.42 MPa.[197] A further study showed a substantial increase in actuation stress (~165 kPa) when these nanocomposites were pre-stretched (50%) and constrained. Pre-stretching aligned the CNTs in the drawing and chain orientation direction, hence improving the heat conduction. A very high opto-mechanical energy conversion factor of 55 MPa/W containing 0.1 wt% of MWCNTs was reported.[128]

Tunable photo-responsive actuators based on anisotropic CNTs embedded in a paraffin wax layer on a polyimide substrate was also reported.[126] Thin composite films (~23 µm) produced reversible photo-mechanical motion from phototropic/apheliotropic bending to three-dimensional helical transformations depending on the different CNT orientations (**Figure 7**). In addition to substantial photo-absorption (772 nm at 50 mW) and thermal conduction, differences in thermal expansion between paraffin wax and polyimide, and the anisotropic mechanical properties induced by the CNT (greater stiffness along the axial direction),

contributed to the apparent deformation. An improved deformation and faster response was also reported for thinner samples.
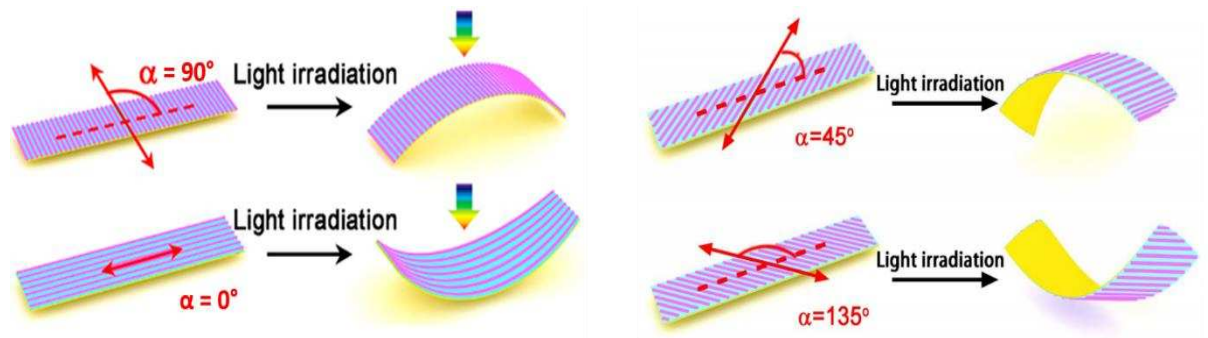
Figure 7: Apheliotropic and phototropic bending of polyimide/paraffin wax composite strips with different aligned CNT orientations. Reproduced with permission.[126] Copyright 2016, American Chemical Society.

A combination of different photo-thermal additives may enhance the actuation effect and does provide actuation over a wide range of incident light wavelengths. Pan et. al.[198] realized this concept by means of solution-casting followed by solid-state drawing. Free-standing anisotropic (drawn) polyethylene (PE) composite films, containing photo-thermal dyes (benzotriazole, graphene nanoparticles and Lumogen IR 788) were prepared. Drawn film samples (~5 µm thick at draw-ratio (λ) 40, and ~8µm thick at $\lambda=30$) were cut at 90° and 45° (with respect to chain-orientation direction) and showed immediate deformations such as bending and curling, owing to their low modulus along these directions. When these deformed samples were exposed to an UV (365 nm) and NIR (780 nm) light source (120 and 90 mW cm^{-2}) simultaneously, unbending occurred. It was proposed that this phenomenon was caused by the induced additive-gradient and asymmetric CTE through film thickness. It was also reported that draw-ratio had a significant impact on the displayed deformations as it was difficult to deform thicker samples.

Light-driven actuators based on stiff polymer with room temperature elastic moduli in the order of 1 GPa was devised by Broer et al.[199] Diacrylate dopants containing azobenzene moieties were blended with liquid crystalline diacrylate hosts and photo-polymerized in a twisted configuration. The resulting twisted networks were densely crosslinked. Anisotropic expansion/contraction was induced in the system when irradiated with UV light (365 nm, 1 W/cm^2), and simple variations in geometry were exploited to generate uniaxial bending or helical coiling deformation modes at 100 mW/cm^2. It was expected that these systems were able to deliver much more work output than current polymer actuator materials since mechanical energy is directly related to elastic modulus.

3.5. High-modulus polymer photo-actuators

Highly oriented polymers can exhibit outstanding mechanical properties, outperforming even metals and ceramics.[200,201] Examples of such materials include carbon fibers, aramid fibers based on intrinsically rigid poly-p-phenylene terephthalamide (PPTA) and fibers based on highly aligned and chain extended flexible chain polymers like polyethylene. Chain extended ultra-high molecular weight polyethylene (UHMWPE), in particular, has gained special attention very recently as a promising candidate for light-driven polymer actuators because of being lightweight, low-cost, superior in mechanical properties and even transparency.[202] Oriented UHMWPE is non-responsive to light in a large portion of the electromagnetic spectrum, however it has been shown that this can be altered by additives.

Highly oriented (draw ratio (λ) = 60) UHMWPE with specially synthesized photo-responsive azobenzene dyes with aliphatic tails was characterized by Verpaalen et al..[203] A fast, reversible, exposure intensity dependent actuation stress (~60 MPa) was generated at a low strain of ~0.06%, regardless of the light source (365 nm or 405 nm) (**Figure 8a**). Although actuation was anticipated through light-induced conformational changes in the azo compound,

the dominant mechanism behind this photo-mechanical response might as well have been a thermally induced entropic effect by the embedded photo-thermal azobenzene agent.
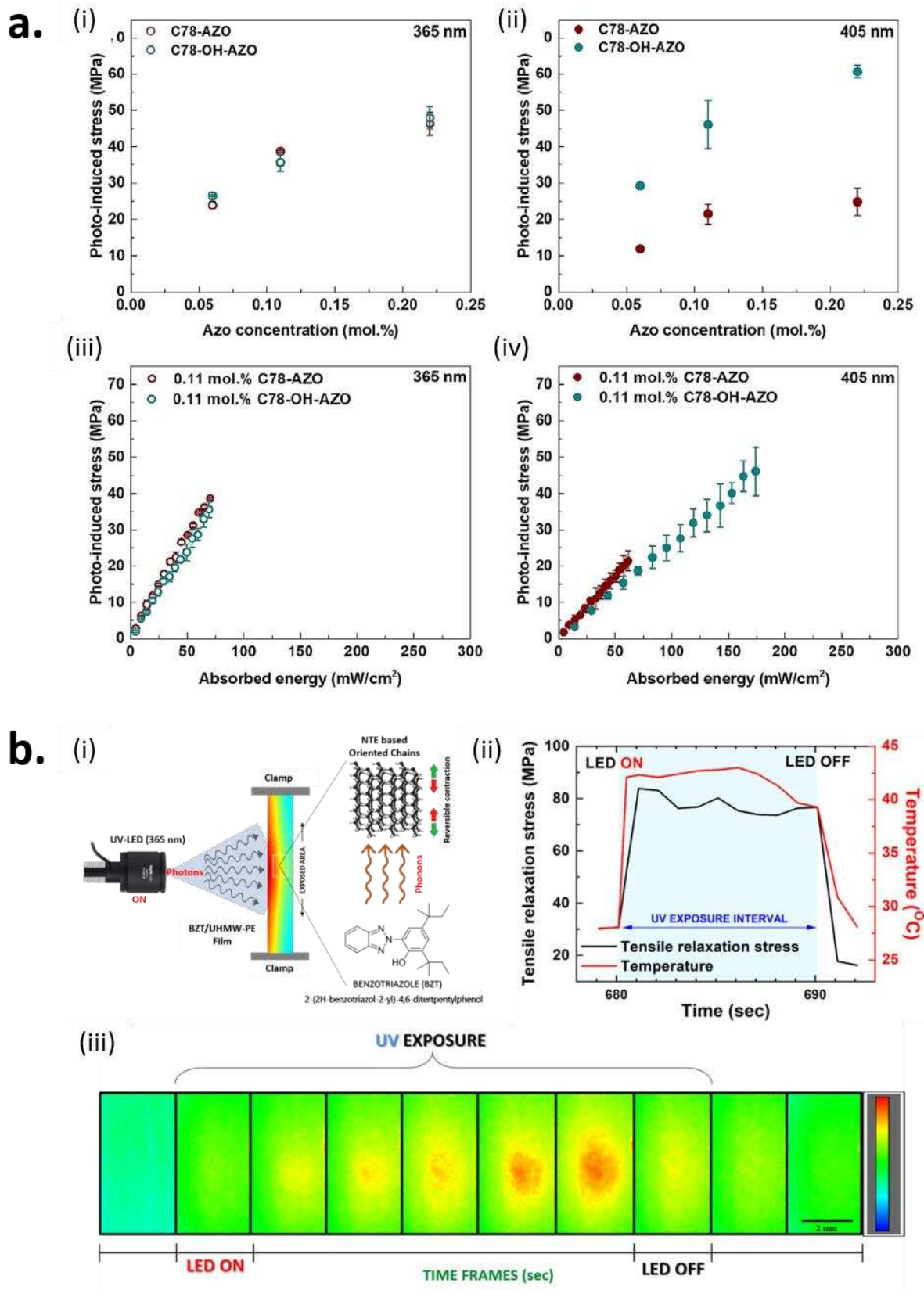
Figure 8: **a.** Stress generation in ultra-drawn, azobenzene-doped ultra-high molecular weight

polyethylene (UHMWPE) composites: **(i)** Photo-induced response of composites exposed to a

365 nm LED. **(ii)** Photo-induced response of composites exposed to a 405 nm LED. **(iii)** Stress response as a function of the absorbed energy employing a 365 nm LED. **(iv)** Stress response as a function of absorbed energy utilizing a 405 nm LED. Error bars correspond to standard deviation. Reproduced with permission.[203] Copyright 2020, Elsevier. **b. (i)** Proposed principal mechanism of photo-actuation behavior of drawn UHMWPE/BZT films upon UV exposure at a wavelength of 365 nm. **(ii)** Photo-thermal response observed upon UV exposure (0.9 A) of a drawn 5 wt % BZT/UHMWPE film, showing a rapid response as heat is generated with light, leading to the generation of an actuation stress (light blue area shows the UV exposure interval). **(iii)** Infrared images of a 1 wt% BZT/UHMWPE film during an UV exposure cycle (10 s interval), showing a rapid thermal response by the embedded BZT within the film in terms of heat signature. Reproduced with permission.[61] Copyright 2020, American Chemical Society.

Recently, our group presented a simple method to fabricate photo-actuators based on transparent, ultra-drawn UHMWPE films using commercially available, low cost additives such as 2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol (BZT).[61] Unlike, most traditional responsive polymer films, there is no need to synthesize complex compounds. The photo-induced (365 nm) thermal response was fast (< 1 sec) and reversible, even at small BZT content (~ 1 wt%) and generated a high specific actuation stress of > 70 MPa at very low (~0.1%) strain, viz. the highest ever reported. Moreover, the photo-mechanical response incurred was purely the result of a thermally induced entropic negative coefficient of thermal expansion (CTE) effect (**Figure 8b**) and not related to transformational changes as in the case with liquid crystal elastomers (LCE) or azobenzene compounds.[203–207]

The aforementioned system is not only limited to UHMWPE but applicable to many other oriented semi-crystalline polymers. For instance, our group has also demonstrated a melt-processed ultra-drawn high-density polyethylene (HDPE) actuator.[63] Actuation was again

triggered by light energy absorbed by the BZT and transferred into heat. The generated heat induced entropy driven contraction of the extended macromolecular chains, and when constrained, resulted in an actuation stress (~20 MPa) at a strain of 0.1%.

A semi-empirical model for predicting the actuation stress in these oriented polymer systems,[62] indicated that the draw ratio (λ) has a minor influence on the maximum attainable photo-actuation stress (**σ**) of a UHMWPE/BZT actuator. Instead the stress is dominated by the temperature increment (ΔT) between the light-on and light-off state (**Eq. 3**).

$$\sigma(\lambda) = \left[\frac{\alpha_h + (\alpha_c - \alpha_h)\frac{3\pi}{4}\lambda^{-3/2}}{E_h^{-1} + (E_c^{-1} - E_h^{-1})\frac{3\pi}{4}\lambda^{-3/2}}\right] \Delta T \qquad \text{Eq. 3}$$

Where as E_h, E_c and α_h, α_c are respectively the Young's modulus and coefficient of thermal expansion of the helix and coil elements in an oriented system.

It might therefore seem obvious to attempt to increase ΔT by further optimizing experimental parameters like photo-thermal additive content, optical path length (i.e. sample thickness, transparency), or light intensity of the light source.

3.6. Other polymer photo-actuation approaches

There are other strategies for polymer actuation, which are less common. One such scenario involves light interacting with the photo-responsive polymer material, triggering photochemical reactions that alter the structure of the crosslinked polymer network and cause subsequent macroscopic deformation. Long et al.,[208,209] incorporated photo-initiator Irgacure-184 along with allyl sulphide in the polymer backbone (pentaerythritol tetra(3-mercaptopropionate) (PETMP) mixed with 2-methylene-propane-1,3-di(thioethylvinylether) (MDTVE) and ethylene glycol di(3-mercaptopropionate (EGDMP)) during network synthesis. The studies suggested that upon UV-irradiation (365 nm, 20 mW/cm^2) the photo-initiator

generates radicals that attack allyl sulphide functionalities along the polymer chains, changing the conformational entropy of the network, which results in macroscopic stress-relaxation.

Molybdenum disulphide (MoS_2) is an excellent candidate for opto-mechanical energy conversion. MoS_2/polydimethylsiloxane (PDMS) polymer composites showed a reversible actuation stress of about 31 kPa at 50% pre-strain and 2 wt% of MoS_2 when irradiated with an 808 nm NIR light source of ~160 mW intensity.[210] PDMS based composites with different photo-responsive agents on similar grounds were also reported in the literature. Examples of photon induced actuation stresses in PDMS based composites are: 21 kPa for 2 wt% carbon black (CB),[210] 11 kPa for 2 wt% graphene oxide (GO),[210] 14 kPa for 2 wt% SWCNTs,[210] 50-60 kPa for 1 wt% MWCNTs,[1,211] 40 kPa for 2 wt% GNPs,[210] 49 kPa for 1 wt% single layer graphene (SLG),[212] and 30 kPa for 0.01 wt% nanotube liquid crystals.[213]

Instead of direct exploitation of light-to-heat conversion, Baglio et al. proposed the use of micro-lenses to obtain localized heating and thus efficient actuation, rather than heating up the whole system, which requires a high irradiation intensity and power.[214] A focused light incident beam on bi-layer cantilevers caused bending due to a difference in CTE of the two layers at a very low power. The proposed strategy is particularly useful in applications such as self-sufficient micro-systems where highly localized power is required for actuation.

Polymer matrices have shown the ability to change the direction of their photo-actuation response from expansion to contraction when a greater imposed pre-strain was applied to the sample. Interestingly, the samples expand at small pre-strains (~10%) and contract at larger pre-strains (10-40%) under identical exposure intensities. It was believed that orientation ordering of the CNTs occurred by uniaxial extension at higher pre-strains, hence inducing contraction along the orientation direction. The aforementioned behavior was reported by Loomis et al.[91] in GNP/PDMS polymer composites (0.1 – 5 wt%) when illuminated with an

IR (808 nm, 500 mW) laser source. It was reported that mechanical response depended on the applied pre-strain, GNP concentration and photo-intensity. At low pre-strains (3-9%), actuators showed reversible expansion while at high pre-strains (15-40%), a reversible contraction was observed. A maximum actuation stress of 50 kPa was obtained at a pre-strain of 40% and a GNP loading of 5 wt%. An optical to mechanical conversion factor of 7-9 MPa/W was also reported.

Despite the vast majority of researchers believing that photo-induced thermal actuation occurs in these CNT-polymer composites, a few contemplate that the effect may be caused by geometrical constraints exerted by the bending of CNTs upon irradiation. Ahir et al.[1] reported photo-induced reversible mechanical actuation in PDMS-CNT composite when exposed to IR radiation (675 nm). A maximum actuation stress of ~50 kPa was reported at a pre-strain of 40% and 1 wt% MWCNT loadings. This was explained by the bending of rod-like MWCNTs upon IR irradiation by photon absorption, thus causing sample contraction over a perfectly aligned composite response.

Photo-induced phase-transition (PIPT) is a phenomenon in crystalline materials stimulated only by light-irradiation. An optically driven actuator can be devised based on such materials and characterized by differences in mechanical properties associated to two distinct phases.[117] For example, polydiacetylene (PDA) substituted with alkyl-urethane exhibits distinct reversible PIPT around 410 K using light irradiation (532 nm) of 2.2-2.8 eV and 2.7-3.5 eV, respectively.[117] Phase change can be characterized by a change in color, which is related to the variation in electronic distribution induced by a conformational change of the side group.[215–219] This study also showed that sample thickness affects significantly strain generation depending on how far the light penetrated through the sample.[117]

Yang et al. recently developed multi-level sulphur-doped molybdenum oxide nano-rings (0.5 nm thick), which when embedded in PDMS displayed strong photo-absorption in both the visible and IR light ranges (808 nm, 1 W/cm^2).[220] These photo-thermal nano-agents can function as highly efficient light-to-heat convertors capable of delivering local temperatures up to 400 °C within 20 s.

4. Application perspective

Polymer photo actuators described above are of interest for a number of fields/applications like fluidics, robotics, medical, textiles etc. Conversion of energy into any sort of mechanical work is of fundamental interest. Within the context of this review, light-activated photo-reversible actuators convert light energy into mechanical movement. These, in essence, simple devices are able to undergo reversible deformation such as contraction, expansion, bending, twisting, rotation, curling etc., using relatively low concentrations of light-responsive substances.

Light-driven actuation is particularly promising for small devices on account of precisely defined, contactless actions triggered by economical light sources or even sunlight, without the need of auxiliary equipment, wires, batteries or chemicals. In the next section, we will discuss the potential of light-driven photo-reversible actuators for a variety of applications.

4.1. Photo-actuators for micro-fluidics

Light transduction can be considered as the simplest approach for actuating fluidic devices. Heat energy produced by photo-responsive additives induces a volumetric expansion in an expandable fluid, which is enclosed in a chamber. The expandable fluid is connected to a flexible diaphragm on one side, causing the actuation (**Figure 9a**). The deflection of the diaphragm caused by the fluid expansion is a function of the change in temperature.

McKenzie et al.[221] developed a light-driven volumetric type thermal actuator using carbon black as a photo-absorber and heating element and air as an actuation fluid enclosed in a silicon cell. The system uses light energy transduction (780 nm at 10 mW power) to change backpressure of an impinging fluid jet, to signal hydraulic or pneumatic elements, potentially in hazardous environments and aerospace.

A similar light-driven volumetric type thermal actuator was reported by Mizoguchi et al.[222] comprising of a piece of carbon wool as photo-absorber and a thermally induced phase change material, Freon-113. Upon irradiation, the phase change material changes from liquid to gas and actuates a pre-stressed membrane diaphragm. The maximum reported actuated displacement was 33 µm at an irradiation power of 11 mW.

Some of the light sensitive materials are very promising to offer direct micro-fluidic actuation upon irradiating with light such as polymer gels.[223–226] Direct transduction of light into mechanical actuation is fascinating as it offers a simpler design and fabrication, comparatively little energy losses and rapid response rate. Photo-responsive polymer gels exhibit reversible volumetric strain by phase change transition upon irradiation by light over a wide range of wavelength (UV,[223] visible,[224,225] or IR[226]) and intensity. It was reported, that irradiation causes the temperature of the gel to rise, which leads to a volumetric contraction, a maximum of which being observed at phase change temperature.

Ikehara et al.[117] reported a photo-induced phase-transition (PIPT) polymer actuator. The polymer (PDA-4U3) showed a phase change when illuminated by light or at a temperature of 125 °C. The two phases differ in mechanical properties causing an actuation strain in the material at phase change temperature. The material exhibits a rapid response rate (<5 ms) at a high strain (1.2%), and a deflection of 2 µm which was maintained for >60 min. Microspheres containing gold nanoparticles (AuNPs) dispersed in thermally phase change polyethylene

glycol (PEG) wax demonstrated a peak actuation displacement of 110μm upon irradiation with a visible light (532 nm, 36 mW) source. The AuNPs upon irradiation, generated thermal energy from optical energy, causing the PEG wax to melt, expand and displace a thin silicon membrane in a micro-actuator fluidic device (**Figure 9b**).[127]

Novel ionic liquid polymer gels (ionogels) containing photo-responsive benzospiropyran units and phosphonium-based ionic liquids can act as photo-actuated valves in channels of a micro-fluidic device.[227] The valves are actuated by simply applying localized white light irradiation (1 mW/cm^2) with the ionogels reducing in volume due to merocyanine–spiropyran switching, and associated loss of water from the polymer.[228] By using different ionic liquid components within the gels, it is possible to tune the valve actuation time, facilitating sequential actuation events.

Van Oosten *et al*. integrated photo-responsive azo dyes crosslinked with LCPs into a microsystem.[70] Photo-responsive actuators in the form of artificial cilia were printed using reactive liquid crystal monomer inks. The ink-jetted cantilevers consisted of two different crosslinked azo-LCPs arranged in tandem with a splayed orientation (**Figure 9c**), each one of them was sensitive to a different wavelength of light source i.e. UV (280-390 nm, 9 mW/cm^2) and Vis (455nm, 9 mW/cm^2), allowing two differentiated bending motions (**Figure 9c**). The micro-actuators mimic the motion of natural cilia. This can potentially be useful for flow and mixing in microfluidic systems.

a.

ACTUATION

DEFLECTED DIAGHRAM

FLEXIBLE DIAGHRAM

FLEXIBLE DIAGHRAM

EXPANDABLE FLUID CHAMBER

EXPANDABLE FLUID CHAMBER

PHOTO-ILLUMINATION

b.

(i)

flexible membrane

rigid substrate

Au NP-PEGDA composite

PEG wax

reservoir cap

reservoir

(ii)

membrane

rigid substrate

$h_{actuator}$

$D_{orifice}$

$V_{wax + microspheres}$

$D_{reservoir}$

532 nm laser

c.

(i)

(ii)

Flow

10–50 μm

(iii)

Ultraviolet on

Light off

Ultraviolet + Visible on

Visible on

(iv)

hv

(v)

Start

Visible light

Ultraviolet + visible light
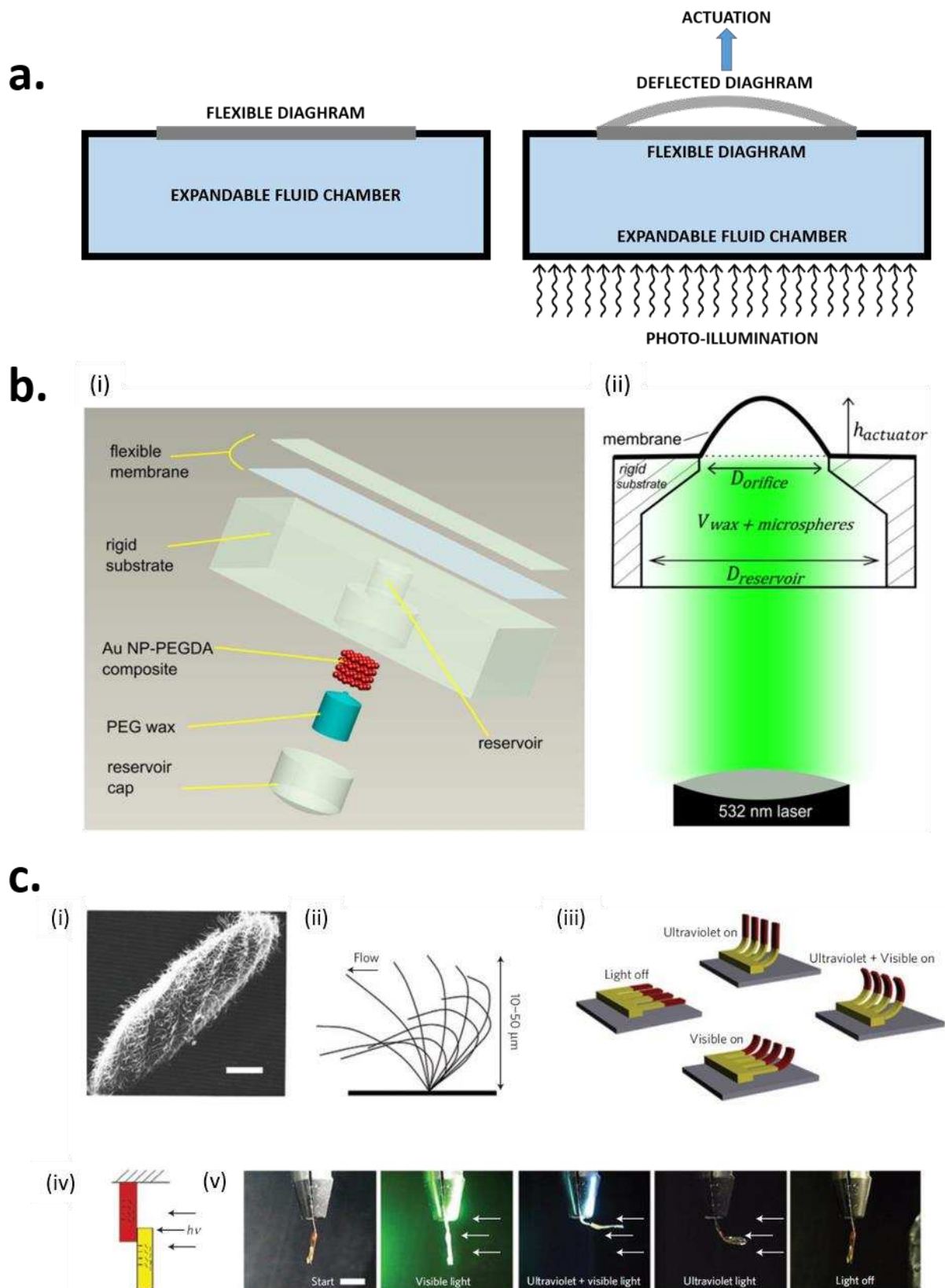
Ultraviolet light

Light off

Figure 9: **a.** Schematic illustration of an actuating diaphragm based fluidic device. **b. (i)** Exploded view of the micro-actuator. **(ii)** Schematic of remote activation of the actuator by a

48

532 nm laser source. Upon irradiation, the wax/microsphere composite in the reservoir melts, deforming a thin elastomer membrane to form a structure with a height $h_{actuator}$. Reproduced with permission.[127] Copyright 2013, IOP Publishing Ltd. **c. (i)** Natural cilia that can be found on several microorganisms, such as paramecia (scale bar 20 µm). **(ii)** A paramecium uses the beating motion of the cilia, characterized by different forward and backward strokes, for self-propulsion. **(iii)** Artificial, light-driven cilia produce an asymmetric motion controlled by the spectral composition of the light. **(iv)** Schematic representation of the macroscopic set-up, showing the orientation of the molecules. **(v)** Steady-state responses of a 10 μm thick, 3 mm wide and 10 mm long modular liquid-crystal network actuator to different colors of light (scale bar 5 mm). Reproduced with permission.[70] Copyright 2009, Springer Nature.

4.2. Photo-actuators for robotics

In terms of actuation, not only a high stress value by the actuator is important but also the maximum strain and work it can offer. Although many actuators offer a variety of properties, they still need to be integrated into a device or application. In order to be able to find their potential use in robotics, sufficient mechanical motion (e.g. sliding, bending, twisting and folding) is crucial. The mechanism should be reversible, rapid, and repeatable over a large number of cycles.

4.2.1. *Photo-mechanical deformation*

A typical robot should have independent 3D structural support and actuation functions, with the former being static and the latter being active.[138] However, Jin et al, devised a strategy to create a single-component polymeric robot.[229] A programmable thin film crystalline SMP network (nitro-cinnamic acid functionalized polycaprolactone) with thermo- and photo-reversible covalent bonds was proposed. Within the same material, thermo-reversible bonds

ensure a 3D structural support via plasticity-based origami techniques,[158] and photo-reversible bonds, activated in a spatio-selective manner to create network anisotropy, leading to precisely controlled local actuation via a reversible shape memory mechanism.[9,230]

Li et al.[71] proposed a post-synthesis method to develop photo-active SMPs using polydopamine (PDA) dip-coating. Ease of application makes it possible to realize light-controlled shape programming through surface pattering (**Figure 10a**).

Yang et al.[72] suggested a similar approach to develop light-driven SMP actuator films capable of undergoing reversible deformations (**Figure 10b**) by merely coating them with a solar-sensitive material such as methyl ammonium lead iodide ($CH_3NH_3PbI_3$).

Ikeda et al.[231] reported photo-induced anisotropic bending of azobenzenes liquid-crystalline gels (LCG). These gels are anisotropically bendable upon photo-illumination at 366 nm towards the irradiation direction and reversible upon photo-illumination at 450 nm. Response time is very low (~20 s) and the system essentially requires the azo-LCG to be immersed in a good solvent (such as chloroform or toluene) at room temperature or in air at 90 °C (i.e. above T_g of the polymer).

It is possible to fabricate reusable and reprogrammable photo-responsive polymer actuators upon incorporation of a pH-sensitive photochromic azo dye (azomerocyanine (AM) that can be locally converted to the hydroxyazopyridinium (HAP) form by an acid in a liquid crystalline network.[73] A variety of patterned polymer films able to deform/bend at different wavelengths of light (530 nm and 405 nm, respectively) were generated (**Figure 10c**). The acidic patterning is reversible and allows to erase and rewrite new patterns in the polymer film, giving access to re-useable, adjustable soft polymer actuators.
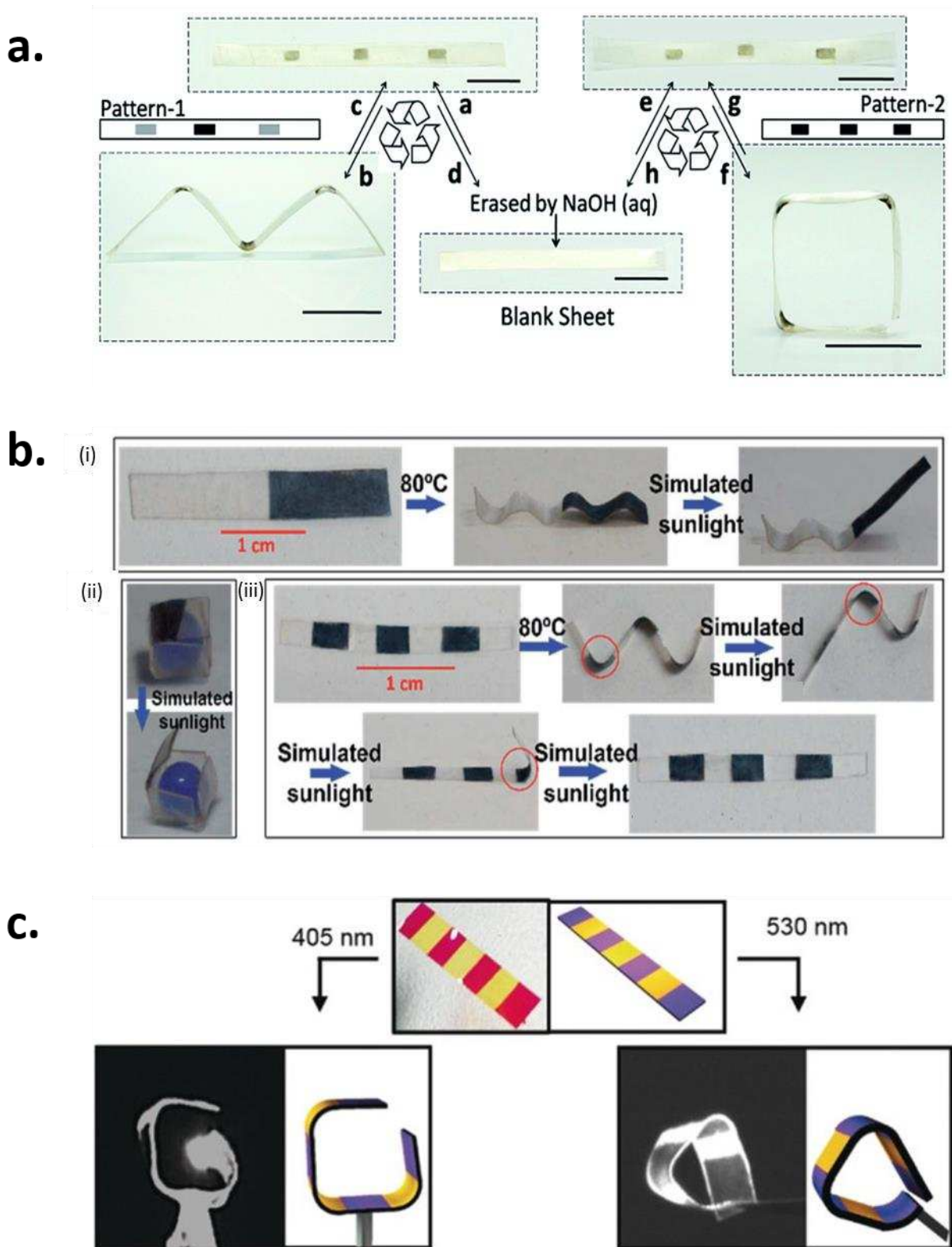
Figure 10: **a.** Shape-reprogramming. **(i)** Blank SMP was stretched to ε = 100% at 120 °C and

then patterned with pattern-1 in dopamine solution (the black rectangle represents the top side

and the gray rectangle represents the bottom side). **(ii)** Irradiation of the patterned sample for

15 s. **(iii)** Heating for 15 s at 120 °C while stretching to recover the flat shape. **(iv)** Erasing the PDA pattern with 0.1 M NaOH aqueous solution. **(v)** Patterned with pattern-2 in dopamine solution. **(vi)** Irradiation of the patterned sample for 15 s. **(vii)** Heating for 20 s at 120 °C while stretching to recover the flat shape. **(viii)** Erasing the PDA pattern with 0.1 M NaOH aqueous solution and back to the blank sheet. Light intensity: 1.4 W/cm^2. Scale bars: 0.5 cm. Reproduced with permission.[71] Copyright 2016, Royal Society of Chemistry. **b. (i)** Simulated light triggered shape recovery of a film partially coated with $CH_3NH_3PbI_3$. **(ii)** Opening a box by light. The upper side of the box opens by simulated sunlight while the other sides remain unchanged. **(iii)** Spatial control of shape recovery by patterning the $CH_3NH_3PbI_3$ coating. Light is focused on the circled area each time. The light intensity in all the above cases is 120 mW/cm^2. Reproduced with permission.[72] Copyright 2017, Royal Society of Chemistry. **c.** Specific bending of a patterned film. The same film is exposed with 405 nm (left) and 530 nm (right) light. The film specifically bends at the yellow region (HAP form) when exposed to 405 nm and at the magenta region (AM form) when exposed with 530 nm. When switching off the light, the film unbends to the flat state. At the right side of each image a schematic of the patterned film and its bending behavior is shown. Reproduced with permission.[73] Copyright 2017, Wiley-VCH.

The actuation behavior of a light-driven LCE-CNT composite was employed in a reversible tactile application in the form of a braille display. CNTs incorporated into LCE films shaped as braille dots were designed (**Figure 11a**) that can reversibly undergo a light induced (658 nm, 60 mW/cm^2) contraction with deformations up to 40 μm (or ~10%) of their initial height in less than 6 s without degradation.[129]
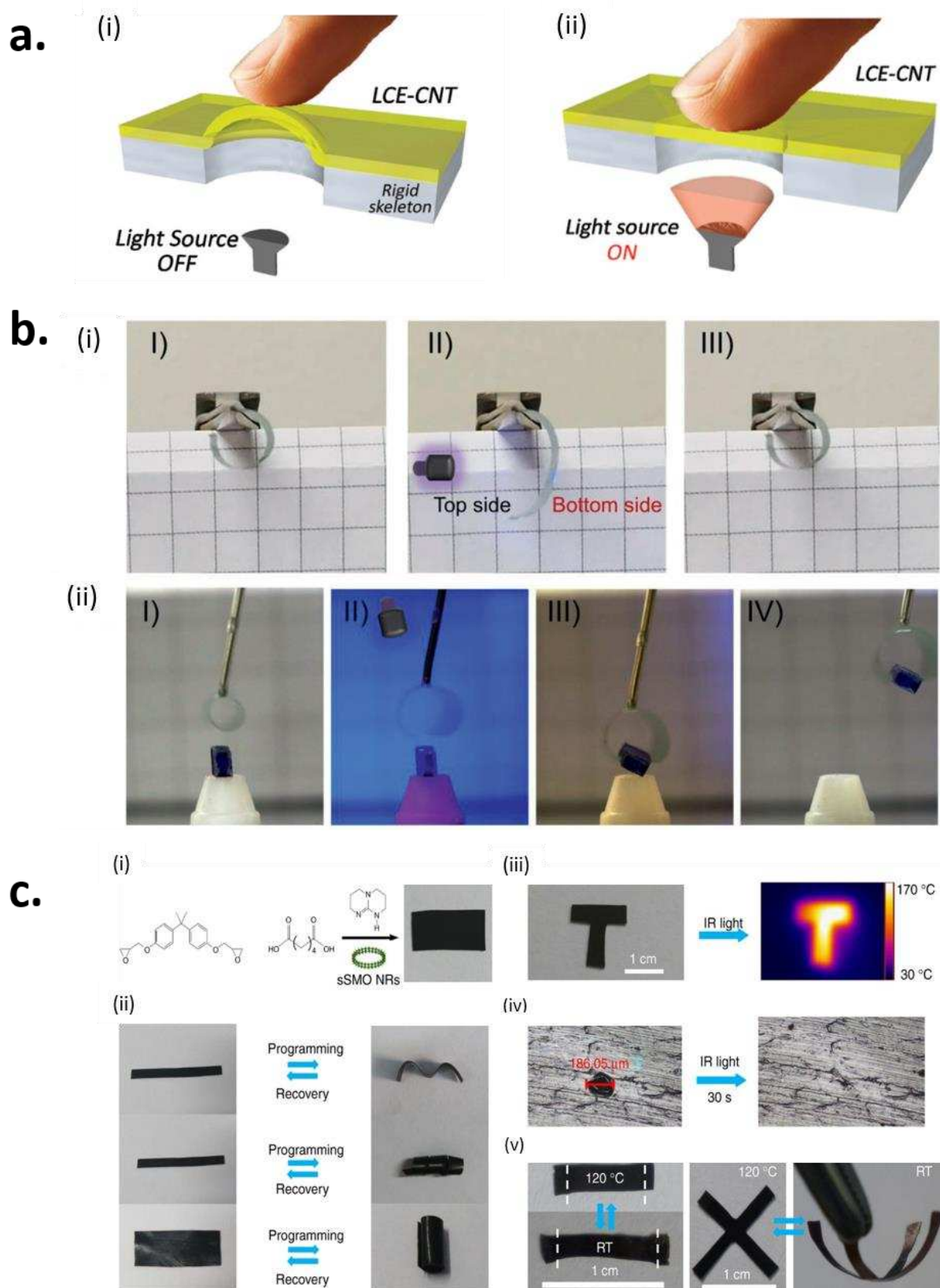
Figure 11: **a.** Schematics of LCE/CNT blisters. **(i)** Ambient state, light source is OFF. **(ii)** Actuated state—blister contracts—when it is light-actuated (ON). Reproduced with

permission.[129] Copyright 2012, IOP Publishing Ltd. **b. (i)** UV–NIR response of drawn PE-BZT-GN-NIR films exposed to light (incident light from the right, I-II-III: light off-on-off). **(ii)** Light responsive PE-BZT-GN-NIR gripper using UV–NIR light (I-II-III-IV: light on-on-off-off). Here, the intensities of UV (365 nm) and NIR (780 nm) light are approximately 120 and 90 mW/cm^2, respectively. The size of the composite film is approximately 1.5 × 1.5 cm^2 and the thickness is about 8 µm with a draw ratio of ~30. Reproduced with permission.[198] Copyright 2021, Wiley-VCH. **c.** Light-activated performance of the SMONRs-epoxy composite. **(i)** Synthesis of SMONRs-virimer. **(ii)** Demonstration of the shape memory effect of SMONRs-virimer under visible light. **(iii)** Photo-thermal image of SMONRs-virimer; photo-thermal image of the letter T under IR irradiation (808 nm, 1.0 W/cm^2). **(iv)** Self-healing measurements under IR irradiation. **(v)** Reversible actuation and dynamic structures of SMONRs-xLCEs by IR irradiation. Reproduced with permission.[220] Copyright 2017, Springer Nature.

Recently, soft actuator and robotic devices were presented using a commodity polymer (PE) incorporating more than one photo-thermal additive (BZT, GN and Lumogen IR 788).[198] The bending/unbending deformation of these composite films were used to fabricate a light-driven gripper (**Figure 11b**). The gripper opens under light-irradiation (either UV or NIR), holds an object upon switching-off the light and can lift an object 20-times its own weight. The effect was shown to be rapid and reversible.

More recently a new design based on the sulphur-doped molybdenum oxide nano-rings (SMONRs) was proposed.[220] This nano-photo-thermal agent can be employed as a photo-initiator to various prospects such as remotely induced visible-light shape memory response, self-healing, reshaping performance and reversible actuation of dynamic three-dimensional structures (**Figure 11c**).

4.2.2. Light-activated robots

A two-axis nano-positioner (~100 µm/axis) with 120 nm resolution and ~5 µm/s actuation speed based on a GNP/PDMS photo-actuator was also devised (**Figure 12a**).[232] Efficient light absorption was induced by the embedded GNPs and subsequent energy transduction to the surrounding polymer chains. Precise and controllable mechanical motion was produced through entropic elasticity of the pre-strained graphene/elastomer composite. The system can potentially be integrated in optical microscopes or probe stations as an opto-mechanical nano-positioner.

In the presence of a photo-chromic molecule, hydrogels are able to reversibly shrink and swell in an aqueous environment upon photo-irradiation. An arc-shaped hydrogel walker based on N-isopropylacrylamide-co-acrylated spiropyran-co-acrylic acid p(NIPAAm-co-SP-co-AA) was demonstrated.[83] Spiropyran, caused the hydrogels to contract reversibly when exposed to a white light source at an intensity of about ~305 kLux from 1-2 cm. The hydrogel walker in deionized water was able to exhibit a unidirectional locomotion on a ratcheted surface (**Figure 12b**).

Inspired by natural heliotropism phenomena, an artificial device actuated by sunlight was realized by Li et al..[233] Utilizing a polyurethane fiber-network reinforced SWCNT/LCE composite films, an artificial heliotropism actuator with an altitude angle of 60° and an azimuth angle of 180° was achieved. As a result, a significant increase in photo-current output was observed from the solar cells captive in the artificial heliotropic actuating device (**Figure 12c**).

By fabricating the light-responsive polymer film on top of a piezoelectric poly(vinylidene difluoride) (PVDF) film, electrical energy as a result of photo-mechanical actuation under NIR excitation could be harnessed (**Figure 12d**).[234]

A bent-beam micro-gripper was devised by Elbuken et al. using a mechanically rigid and chemically stable SU-8 polymeric material which was characterized by a very high CTE.[235] Irradiation of light (630 nm) provided the required heat (14 K) to thermally expand the material, and micro-actuation in terms of finger-opening (20-50 µm) was demonstrated (**Figure 12e**) at an incident power of 50 mW. Being non-contact, electrically isolating and operating at low temperatures, the proposed photo-thermal micro-actuator could be integrated in micro-electro-mechanical systems (MEMS) devices.
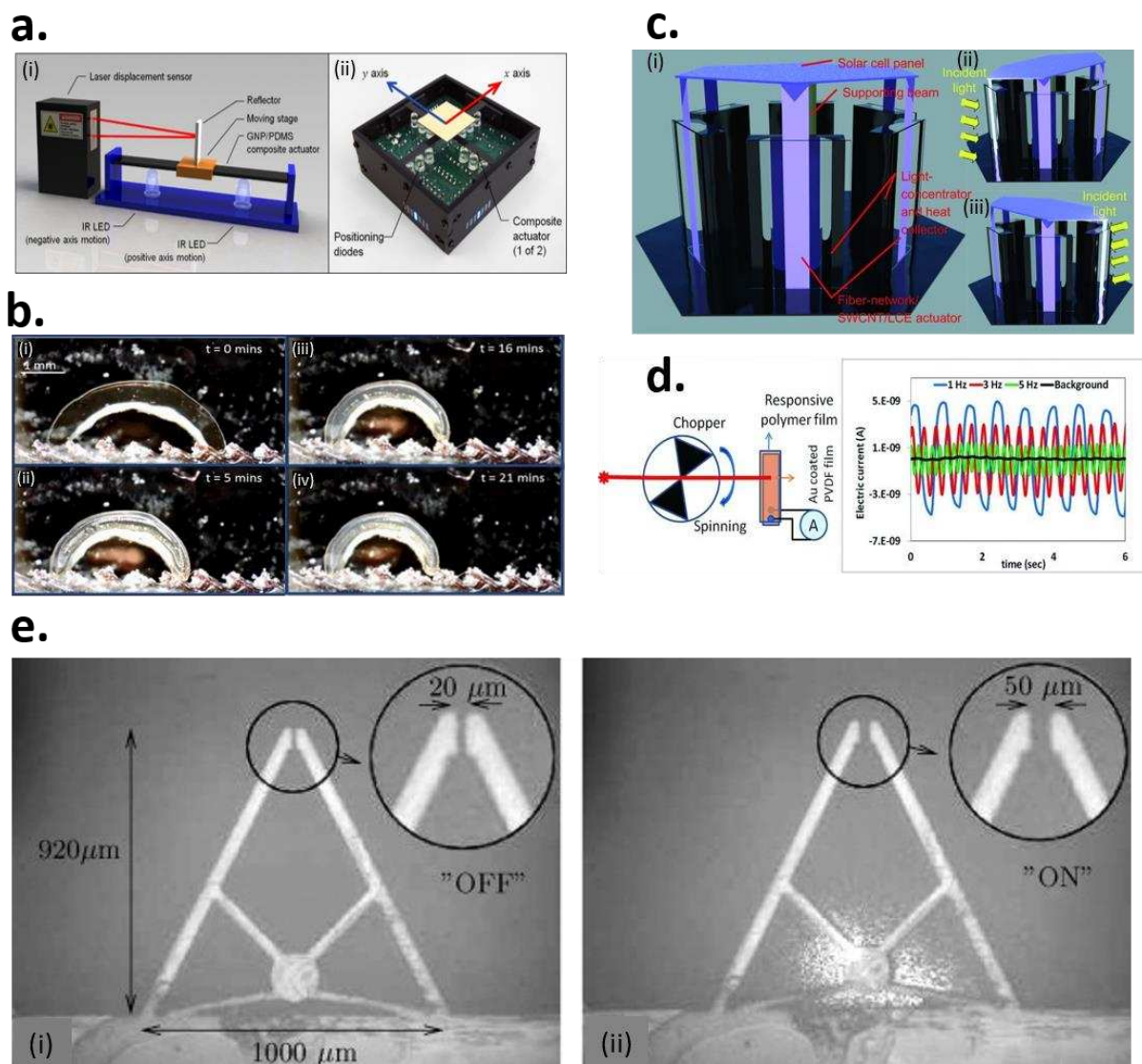

Figure 12: **a. (i)** Simplified single-axis nano-positioner layout. A laser displacement sensor is used to measure stage position. Independently controlled diodes on either side of the stage

allows for differential positive or negative axis stage motion. **(ii)** Nano-positioner with cover plate removed, showing positioning diodes and dual GNP/PDMS composite actuators. Reproduced with permission.[232] Copyright 2013, Springer Nature. **b.** Series of snapshots showing the effect of light irradiation on the hydrogel walker. **(i)** Light irradiation is initiated. **(ii-iv)** Gradual reduction of inter-leg distance results in the trailing leg (right) being "dragged" over the bevel of the ratchet step. Reproduced with permission.[83] Copyright 2017, Elsevier. **c.** Concept of the artificial heliotropism. **(i)** 3D schematic of the system. **(ii, iii)** 3D schematic of the heliotropic behavior. The actuator(s) facing the sun contracts, tilting the solar cell towards the sunlight. Reproduced with permission.[233] Copyright 2012, Wiley-VCH. **d.** Optical apparatus to characterize the NIR response of films. Current outputs generated by the system with the processed film on top of a PVDF/gold film were recorded in response to the 785 nm light source radiation with frequencies of 1 Hz (blue), 3 Hz (red), 5 Hz (green) and 1 Hz background (black). Reproduced with permission.[234] Copyright 2012, Wiley-VCH. **e.** Optical images of the SU-8 micro-gripper: **(i)** fingers are closed with 20 µm gap, **(ii)** fingers are opened with 50 µm gap when laser is illuminated. Reproduced with permission.[235] Copyright 2008, Elsevier.

Eelkema et al.[110] demonstrated microscopic movements induced by changes in helicity of a molecular motor. The reversible rotation of the surface texture of a LC film and microscopic objects placed on top of this film was achieved using a molecular motor. The photo-isomerization results in a change in helical chirality of the motor molecules used as dopant, which in turn reflects directly as the reorganization of the polygonal liquid crystal texture. The rotational change in surface relief upon irradiation with UV light (365 nm) generates sufficient torque to rotate a microscale (5 x 28 µm) glass rod placed on top of the LC film (**Figure 13a**). A subsequent thermal isomerization of the motor molecules in the LC matrix results in reverse rotation of the glass rod.[104]

a.

(i) Molecule 1
Rotor
Axle
Stator

(ii)

(iii) 24 nm
0 nm

(iv)

b.

CH₃

(i) hν
Point A

(ii)
Point A

(iii)
Point A

(iv)
Point A

c.

(i) Meso-(R,S-R,S) isomer
III
C₆H₁₃
(R)
(S)
C₆H₁₃
C₆H₁₃
(R)
(S)
C₆H₁₃

(ii) Side view

d.

(i) Vis   Belt   Alignment direction   UV
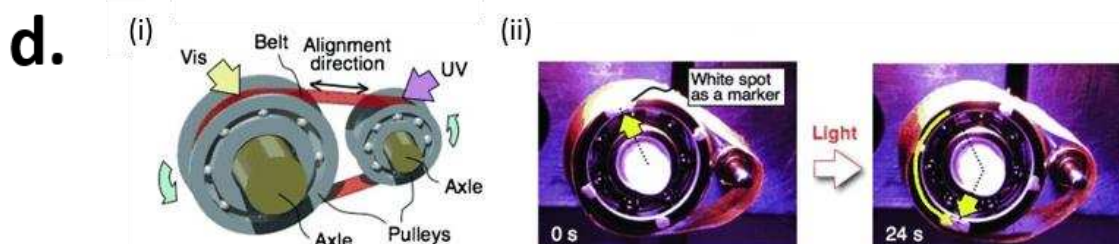Axle
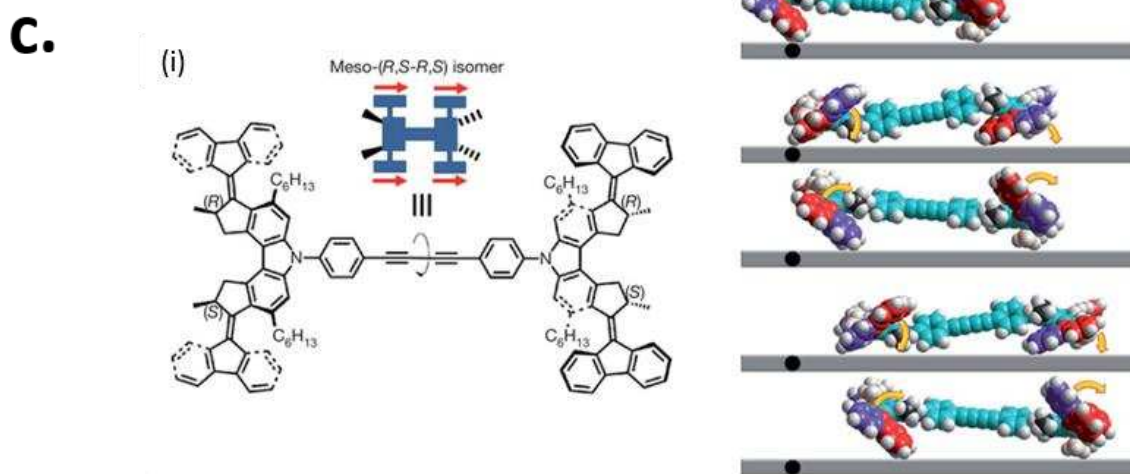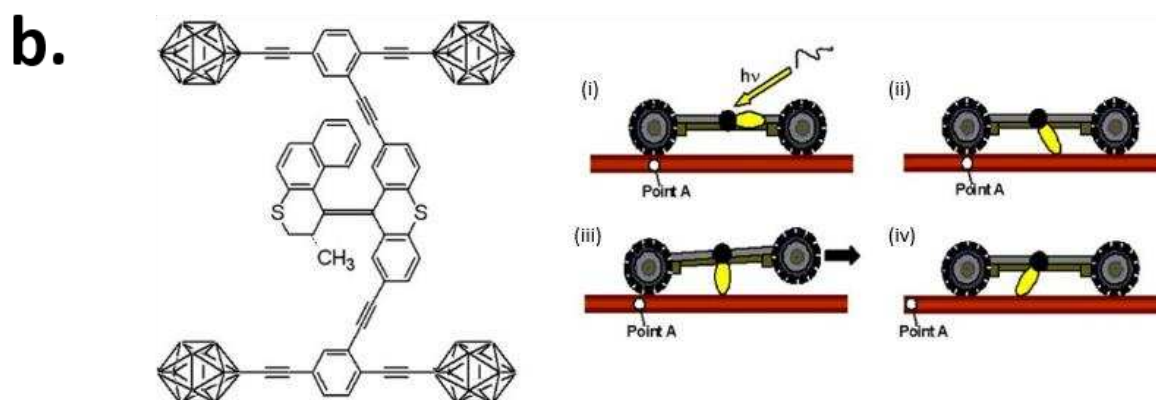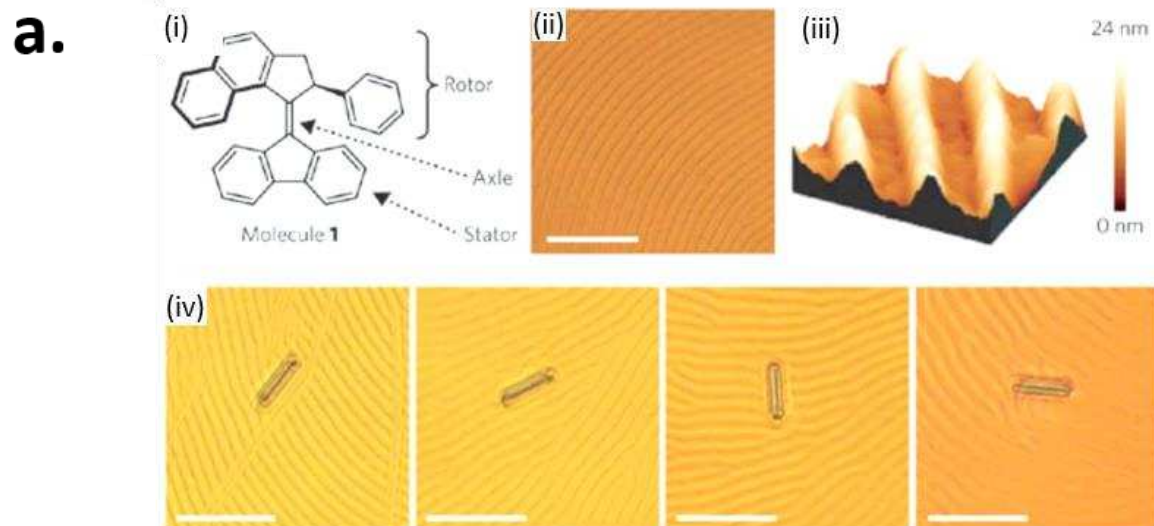Axle   Pulleys

(ii) White spot as a marker
Light
0 s   24 s

Figure 13: **a. (i)** Structure of the molecular motor (molecule **1**). Bonds in bold point out of the page. **(ii)** Polygonal texture of a liquid-crystal film doped with molecule **1** (1 wt%). **(iii)** Glass rod rotating on the liquid crystal during irradiation with UV light. Frames (from left) were taken at 15 s intervals and show clockwise rotations of 28° (frame 2), 141° (frame 3) and 226° (frame 4) of the rod relative to the position in frame 1. Scale bars, 50 µm. **(iv)** Surface structure of the liquid-crystal film (atomic force microscopy image; 15 µm^2). Reproduced with permission.[110] Copyright 2006, Springer Nature. **b.** Structure and proposed propulsion scheme for the motorized nano car. Reproduced with permission.[113] Copyright 2020, American Chemical Society. **c. (i)** Structural representation of the meso-(R,S-R,S) isomer. **(ii)** Molecular model representation (side view) of the paddlewheel-like motion of the four-wheeled molecule. Reproduced with permission.[111,114] Copyright 2017, Royal Society of Chemistry. **d.** A light-driven plastic motor with the LCE laminated film. **(i)** Schematic illustration of a light-driven plastic motor system. **(ii)** Series of photographs showing time profiles of the rotation of the light-driven plastic motor. Reproduced with permission.[115] Copyright 2008, Wiley-VCH.

Tour and co-workers demonstrated a nano car which bears a light-activated unidirectional molecular motor, an oligo(phenylene ethynylene) chassis and axle system with four carboranes to serve as the wheels.[113] Kinetics studies in solution show that an overcrowded alkene based rotary motor indeed rotates upon irradiation with UV light (365 nm), and the fullerene-free carborane wheel system is an essential design feature for motor operation (**Figure 13b**). Although, it was anticipated that the motor might work as a type of propeller, the proposed nano car showed no movement on a copper surface in the presence of light, owing to a strong interaction with the surface.

Though electrically driven instead of light, Feringa and co-workers were able to demonstrate the first motorized nano car capable of directional motion across a surface.[114] By placing the

STM tip directly above the centre of an individual nano car, a voltage could be applied and movement was induced on a copper surface. The design of Feringa's nano car is based on a flat, aromatic chassis, connected with four molecular motors functioning as the wheels of the car (**Figure 13c**). These motors act as paddlewheels, propelling the structure forward.

Apart from molecular motors which are either photo-functional only in solutions, or require an electric field to actuate outside the solutions, Ikeda and co-workers devise a contactless light-driven motor.[115] A light-driven plastic belt based on an azo containing LCE film (18 µm) laminated on the both sides of the PE film (50 µm) was used to drive the motor. Upon irradiating the belt with UV light (366 nm, 240 mW/cm^2) from the top right and visible light (>500 nm, 120 mW/cm^2) from top left simultaneously, a light induced rotation of the belt generates causing the two pulleys of the motor to rotate in counter clockwise direction at room temperature (**Figure 13d**). The belt part irradiated with UV light tends to contract along the alignment direction of azobenzene mesogens while expand at part irradiated with visible light. These contraction and expansion forces produced simultaneously at different parts of the belt induce rotation of the belt and the pulleys in the same direction. The rotation of the belt then brings new parts to be exposed to UV and to visible light, enabling the motor to rotate continuously.

4.3. Photo-actuators for medical devices

The use of light as a stimulus is particularly attractive in the field of medical devices since the mechanism to induce the actuating response is non-invasive and especially in the case of NIR (650-1350 nm) minimally absorbed by tissue or organs, and thus maximally by the material. Light is a promising stimulus for medical devices as it can be directly used at the polymer surface or can be delivered locally using optical fibers. [236,237]

Ideally, the wavelength of the laser is tuned to the so-called biologically 'friendly' window of human tissues. The majority of light-responsive chemical moieties are responsive in the UV and Vis spectral range, which is generally not limiting in an in-vitro environment, and may be sufficient for many applications. However, systems that would be desirable for translation to an in-vivo setting are limited to NIR spectral range in which light is not harmful and has deeper penetration through tissue as compared to UV and visible light.[238] The NIR window is ideally suited for *in-vivo* actuation because of minimal light absorption by hemoglobin (<650 nm) and water (>900 nm).[239]

Typically, photo-responsive polymers are characterized by the presence of photoactive groups such as azobenzene, spirobenzopyran, triphenylmethane or cinnamonyl along the polymer backbone, or by side chains that are able to undergo reversible structural changes under light irradiation.[236] However, photo-actuation is not limited only to photoactive moieties and can also be activated through composite systems such as carbon and gold based nanomaterials in which a light-responsive material is suspended within the host polymer network, though not covalently attached.[240,241]

The role of light-activated materials is more likely to be considered as energy transducers to transform photonic energy to heat, to trigger biomedical "treatments". Photo-responsive bio-actuators can effectively and functionally transform environmental stimuli (i.e. light) into controlled mechanical responses that can be used for the development of smart drug delivery systems, biomimetic microfluidic components such as micro-valves or micro-pumps, and medical devices, such as blood vessel opener.

Shimoboji et al. proposed photo-responsive polymer enzyme switches based on copolymers of DMA with azophenyl-containing monomers and endoglucanase 12A (EG 12A).[242] In order to switch the polymer–enzyme conjugates on and off, photo-responsive polymer material serve

jointly as antennae and actuators that reversibly respond to distinct optical signals (wavelengths of light). The enzyme switches work efficiently when the enzymes are free in solution or when immobilized on magnetic beads, showing excellent reversibility and time responses. This approach might also be used to retain the enzymes turned off in pro-drug therapeutic applications until they reach their target, where the target could be activated using optical fiber technology.

Aneurysms, which are abnormal localized dilation or bulging of a portion of a blood vessel, is a significant cause of ischemic strokes. Maitland et al. presented a promising approach consists of a photo-thermally activated shape memory polyurethane (incorporating 0.06 wt% green dye Ryvec-518) based device which can be introduced into the thrombus in a rod-like shape via a catheter.[243] When activated photo-thermally by a laser (operating at 810 nm at 0.1-1.5 W for 0.1-2.0 s) incorporated in the device, it attains a coil- or umbrella-like shape in as little as one second (**Figure 14a**). As the laser heats the SMP above its transition temperature (55 °C), the device expands, releasing the coil, capable of trapping the clot, before contracting again when the temperature drops. This way, the blood clot can be mechanically removed from the artery, together with the device.

Photo-thermally responsive polymer hydrogel films as stimuli-activated gates to control release of drug were reported by Yavuz et al.[244] A copolymer of poly(N-isopropylacrylamide (PNIPAm) and polyacrylamide (pAAm) was covalently attached to gold nano-cages via thiolate linkages. A photo-thermal effect of the gold nano-cages caused the PNIPAm-co-pAAm to undergo reversible conformational changes resulting in an on–off gating of the pores. Upon exposure to a NIR laser (Ti: sapphire, ~800 nm, 10 mW/cm^2), the light is absorbed by the nano-cages and converted into heat, triggering the smart polymer to collapse and thus release the pre-loaded drug (**Figure 14b**). When the laser is turned off, the polymer chains relax back to

their extended hydrophilic conformation and terminate the release. In response to temperature variation upon irradiation, the diameter shrank by 13% on heating to 41°C and increased back to its original value on cooling to 37°C. The controlled release of doxorubicin (DOX) a drug widely used in chemotherapy and lysozyme drugs was reported in the study. Upon exposure with IR light for 5 min, in-vitro experiments respectively showed 80% bioavailability of the enzyme and a significant decrease in cell viability.
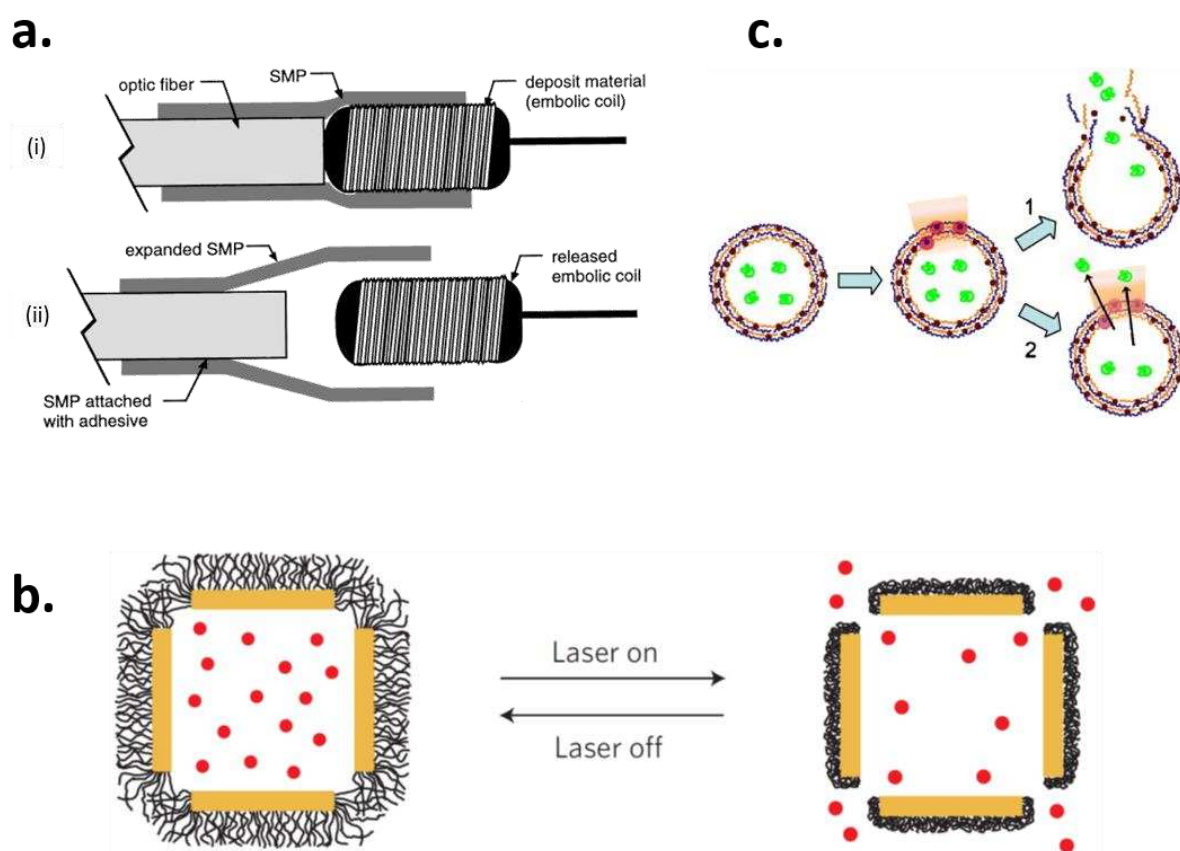
Figure 14: **a.** Schematic representation of an embolic coil release micro gripper. **(i)** The delivery device with the coil loaded and ready for deployment. **(ii)** The delivery device after the SMP has been heated above its transition temperature. Reproduced with permission.[243] Copyright 2002, Wiley-VCH. **b.** Schematic illustrating side view of the Au nano-cage upon reversible photo-actuation and release of drug. Reproduced with permission.[244] Copyright 2009, Springer Nature. **c.** Schematic of two possible release scenarios of encapsulated material

by laser nanoparticle interaction. **(1)** Upon illumination, the nanoparticles produce a large amount of heat that breaks the capsule wall open. **(2)** During illumination, the nanoparticles produce a small quantity of heat sufficient to exceed the glass transition of the polymer capsule, decreasing the shell's permeability until illumination is stopped. The increased permeability allows for the encapsulated material to be released from the capsules without the shell being damaged. Reproduced with permission.[245] Copyright 2010, Elsevier.

A vast amount of work associated to controlled release of encapsulated drugs from photo-responsive polymeric microcapsules was reported by Sukhorukov and co-workers [241,245–248] One such example proposed smart capsules comprising mesh like photo-absorbing gold NP aggregates within the polymeric capsules wall.[246] Poly(diallyldimethyl- ammonium chloride) (PDADMAC) and poly(styrenesulfonate) (PSS) based layer-by-layer assembled capsules were filled with Alexa Fluor 555 dextran (10 kDa) drug for an in-vitro study. Since, gold NPs do not possess near-IR absorption, an NIR absorption peak (700-900 nm) was formed by aggregating them in NaCl salt ions.[249,250] When irradiated with infrared laser (~850 nm, 10-60 mW/cm^2), the NP absorbs light and converts it to heat, which dissipates to the polymer network around it. As a result, it either breaks the wall or takes it above T_g to make it permeable (**Figure 14c**), the latter being reversible,[245] and in both cases leading to the release of encapsulated drug. As soon as the irradiation halts, the NP stops producing heat and the polymeric complex around the NP rapidly cools, returning to its impermeable state. Depending on the irradiation intensity and exposure time used, controlled (either partial or complete) release of drug can be ensured.

4.4. Photo-actuators for textiles

Polymer fibers are typically bundled into yarns, which can then be interlooped or interlaced into textile fabrics. The employment of actuators in various textile forms helps to realize simple to complex movements. For example, a single fiber actuator can exhibit linear motion. Yarn

actuators can demonstrate contraction, expansion and relaxation while fabric actuators can result in relatively high displacements and forces with potential applications in smart textiles and clothing.[251]

The actuation mechanism of fiber actuators is mainly associated to a change in material properties. This includes a change in the fiber's molecular order, volume, or distance between constituent fibers in the yarn. We can expect different changes according to the fiber material, geometry and structure. A photo-thermal effect involves light energy being converted into heat, which in turn causes actuation. It is highly likely that if a material can be actuated through heat, it has the potential to be actuated by light using appropriate photo-responsive additives embedded in the fibers. In such cases textile based actuators absorb energy in the form of heat directly or indirectly from light-responsive materials embedded into the textile assemblies (fiber, yarn and/or fabric) to register a response.

Liquid crystals (LCs) are the most common photo responsive materials for light-activated fibers, because of their rapid and reversible deformation, precise positioning and controllability. The actuation principle is based on the light-induced molecular realignment of the polymer network. Photo-responsive fiber arrays (mimicking natural cilia) based on LC main chain polymer crosslinked with azobenzene were developed by Broer et al.[252] The fibers (~70 µm in diameter) are able to bend towards the UV light (365 nm) in a reversible way functionally suitable for efficient transport of objects. When exposed with a complex UV light pattern, photo-responsive behavior of the fibers follows an asymmetric path close to that of natural cilia's motion. The transport of plastic flakes was demonstrated by immersion of the fiber array in a reduced viscosity paraffin oil (**Figure 15a**).
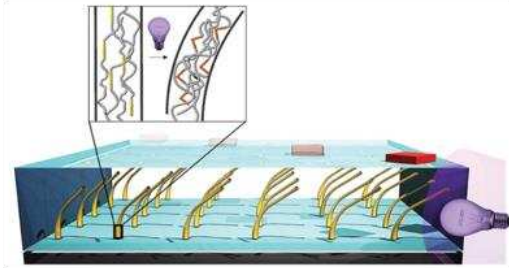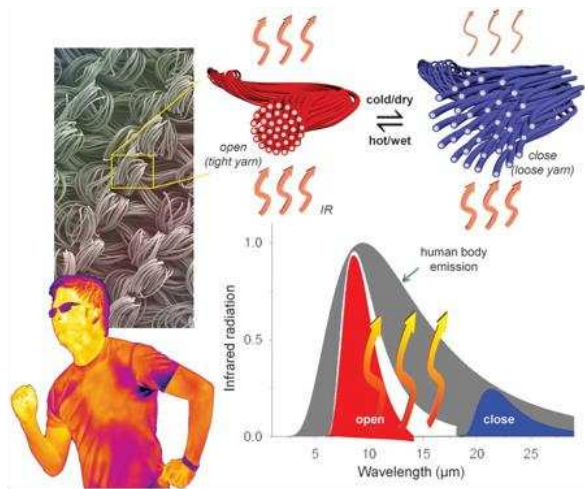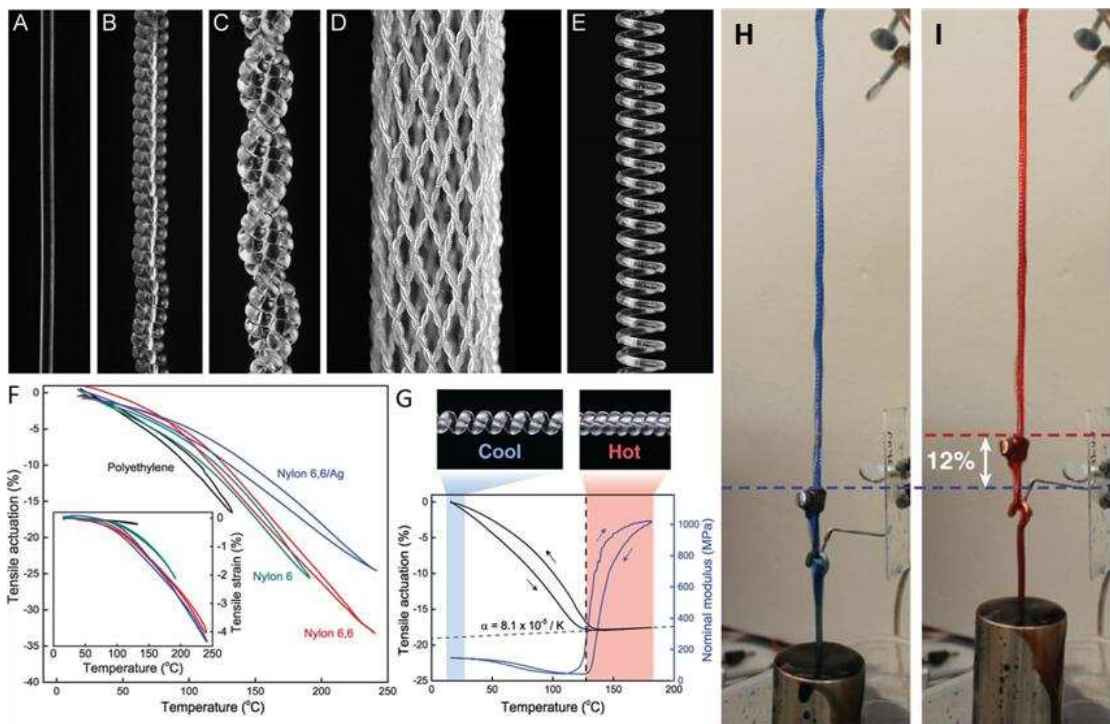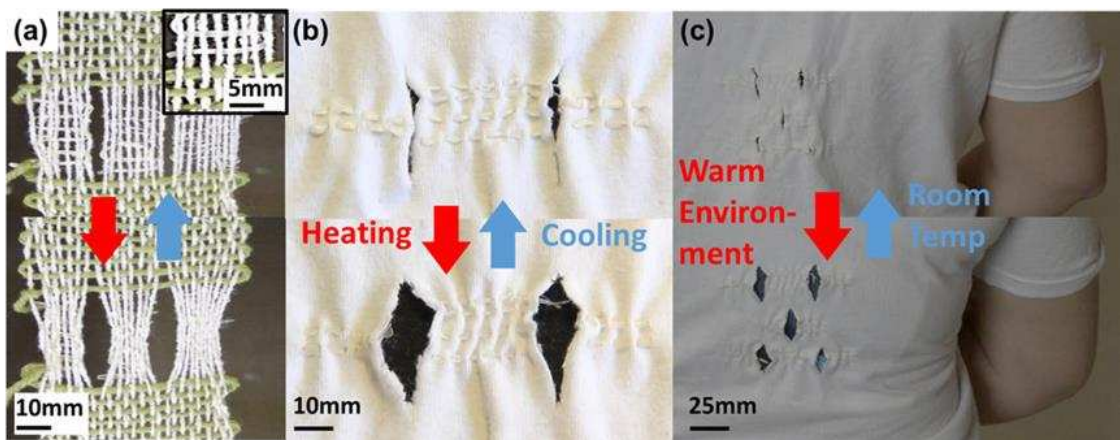
a.

d.

b.

c.

66

Figure 15: **a.** Schematic representation of the collective bending of photo-responsive fibers leading to the transport of floating objects. Reproduced with permission.[252] Copyright 2016, Wiley-VCH. **b.** Optical images of (**i**) a non-twisted 300 μm diameter fiber; (**ii**) the fiber of (i) after coiling by twist insertion; (**iii**) a two-ply artificial muscle formed from the coil in (ii); (**iv**) a braid formed from 32 two-ply, coiled, 102 μm diameter fibers produced as in (iii); (**v**) a 1.55-mm-diameter coil formed by inserting twist in the fiber of (i), coiling it around a mandrel, and then thermally annealing the structure; (**vi**) Comparison of the negative thermal expansion of braided polyethylene, nylon 6 monofilament, nylon 6,6 monofilament, and silver-coated nylon 6,6 multifilament fibers before twisting (inset) and after coiling by twist insertion. (**vii**) Tensile stroke and nominal modulus versus temperature for a coiled, 300 μm-diameter nylon 6,6 monofilament muscle under 7.5 MPa static and 0.5 MPa dynamic load. Optical micrographs (top) are shown of the coils before and after contract. (**viii, ix**) Thermal actuation of a coiled 860 μm diameter nylon 6 fishing line lifting a 500 g load by 12% when heated from ~25 °C (dyed blue) to 95 °C (dyed red). Reproduced with permission.[253] Copyrights 2014, American Association for the Advancement of Science. **c. (i)** Loom woven smart textile using LCE fibers to develop pores upon heating. **(ii)** LCE fibers sewn into a cotton shirt creating pores upon heating. **(iii)** Demonstration of the LCE smart shirt demonstrating pores for improved heat transfer and sweat evaporation during exercise. Reproduced with permission.[254] Copyright 2019, American Chemical Society. **d.** Design principles of an IR gating textile. Reproduced with permission.[255] Copyright 2019, The American Association for the Advancement of Science.

Crosslinked LCP fibers (20 mm x 20 μm) containing azobenzene moiety, when irradiated with UV light source (365 nm, 100 mW/cm^2), bend towards the light along the alignment direction of mesogens in close to 3 s. Photo-deformed fibers recovered their initial state upon exposure

to visible light (540 nm, 120 mW/cm^2) in 9s. An actuation stress (~210 kPa) similar to that of human skeletal muscle was also recorded for these LC polymer fibers.[256]

Without necessitating any light-driven additives, pre-alignment or pre-deformation, crosslinked polyacrylamide (PAM) nanofibers can act as photo-responsive polymer actuators, generating a fast response on their own. This interesting new class of polymer actuator can photo-deform reversibly upon irradiation with NIR light (785 nm, 93 mW with a spot size of 3 mm^2).[234] PAM molecules self-assemble into a fibrillar morphology and the resulting films exhibit a high-degree of optical anisotropy. It was suggested that the actuating response could be entropic recovery of a kinetically trapped state, similar to the one observed in pre-aligned CNTs.[1]

Fiber-based actuators are light, simple, and universal by definition, but the actuation force is small and often unsuitable for real applications. Despite their apparent simplicity, actuating fibers allow for very complex actuation behavior when spun into yarns or woven/knitted into fabrics, indicating a promising strategy for developing novel wearable devices. The order change in the molecular chains in response to light does not involve an exchange of mass or volume change. Volume change is usually caused by mass exchange between fibers and their surroundings, which results in contraction or expansion in all directions. A variation of temperature causes this change due to thermal expansion or phase transitions like melting and crystallization.[251]

Baughman and co-workers proposed numerous twisted yarn actuators as artificial muscles activated by various stimuli including light.[257–263] They proposed that yarns contract and rotate because of the change of gaps between fibers owing to thermal contraction/expansion. When the individual distance changes of numerous aligned fibers in a yarn are added up and magnified, it generates both rotational and translational motion of the yarn.[259]

An elegant approach to tune the stress, strain, stroke and work of actuator based on high modulus fibers was proposed in the literature.[14,253,261,264] Through coiling or twisting, relatively small fiber contractions can be translated into larger macroscopic deformations (**Figure 15b**). Commercially produced low-cost high-strength polymer fibers such as polyethylene and nylon fibers can provide a greatly amplified tensile stroke by inserting twist into these fibers. In a study by Madden et al. it was shown that thermal contraction of twisted nylon 6,6 fibers (**Figure 15b-vi**) can be as large as 34% as compared to 4% for its untwisted counterpart, exceeding the maximum in-vivo stroke of human skeletal muscles (~20%).[265] Moreover, it was reported that the monofilament based coiled structure stiffens with increasing temperature, producing a 24-fold increase in nominal tensile modulus (**Figure 15b-vii**). The maximum specific work during contraction recorded for the coiled nylon 6,6 muscle was 2.48 kJ/kg, which is 64 times that for natural muscle.[265] The ability to generate high torque by reversibly untwisting upon heating makes these structures so special and extraordinary. Both length contraction of these helically configured polymer chains (negative axial expansion) and fiber diameter expansion (positive radial expansion) cause the fiber to untwist.[253]

Thermally responsive LCE fibers were fabricated using direct ink write printing technique. The polymer chains in the fibers were then aligned by mechanical stretching. Following conventional textile manufacturing techniques, these fibers were knit, sewn and woven into a variety of complex patterns. Smart functional textiles were demonstrated to respond to the wearer's increased body temperature and environmental temperature by creating pores adding breathability (**Figure 15c**). LCE fibers constituting these smart materials were able to reversibly contract up to ~51% upon heating.[254]

Infrared radiation emitted and absorbed by human body and trapped by textiles clothing keeps us warm in cold weather. However, this is less desirable in hot weather. A knitted fabric

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composed of triacetate cellulose bimorph fibers, coated with carbon nanotubes (through ~1.8 µg/ml solution dyeing) was produced by Zhang et al.[255] Upon heating, the yarn itself expanded and collapsed, which modify the microstructure of the yarn by altering the inter-fiber spaces. The spun yarn has low density with large inter-fiber spaces. On exposure to high temperature and wet conditions, the yarn collapses into a tight bundle, bringing the neighboring meta-fibers into resonant electromagnetic coupling that shifts the IR emissivity to a state that spectrally overlaps with that of skin. This effectively "opens" the cloth to promote radiative cooling of the human body. When cold and dry, the reverse effect occurs. The IR "open" state here corresponds at the yarn level to a collapsed (i.e., smaller inter-fiber spacing) structure but with larger pores between yarns at the fabric level (**Figure 15d**). The self-adjustment of the textile structure could improve wear comfort through thermal management, as well as expanding our ability to adapt to demanding environments.

In a nutshell, integration of fiber/yarn/fabric based actuators in wearable textile applications is highly desirable yet challenging. The structural arrangement of the light sensitive fibers in different yarn and fabric configurations allows to amplify or engineer the response of the fiber based actuator to warrant a response which can be employed in potential industrial and consumer applications. The integration of photo-thermal actuation in textile manufacturing techniques is critical to develop scalable industrially relevant solutions. Furthermore, the wearability, durability, washability, compatibility and affinity to skin is important to be explored further for repeated use of these materials in everyday applications. However, recent developments in this area of application are quite promising.[251,266,267]

4.5. 4D printed photo-actuators

While three-dimensional (3D) printing of traditional materials results in static structures, four-dimensional (4D) printing of responsive materials adds another dimension in play by creating

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dynamic architectures using additive manufacturing techniques that can alter shape over time in response to a suitable stimuli.[268–270] Due to their adoptability with respect to printing, responsive polymers such as shape memory polymers,[271–273] hydrogels,[274–277] and liquid crystalline elastomers (LCEs).[270,278] are acknowledged as suitable candidates for 4D printed photo-actuation. As a matter of fact, 4D printed light-activated materials actually often use heat from a light source to activate shape change properties.[279]

Liu et al. developed a self-folding approach based on localised light actuation. A single layer of pre-strained polystyrene has been patterned with black ink using a desktop printer and then exposed to infrared (IR) light, resulting in a local increase of temperature on these patterned black lines and folding of the layer (**Figure 16a**).[280] A black ink pattern is printed on the polymer sheet, providing a local absorption of light, which heat up the "hinge" to temperature above its glass transition (105°C). At this temperature, the predefined inked patterned regions relax and shrink, a stress gradient is obtained locally, and the bending moment is generated. Using this technique, the heat diffuses through the thickness and reaches a temperature higher than the T_g of the polymer, while the rest of the layer, without any pattern, stays under the transition temperature. It is also possible to pattern both sides of the polymer layer in order to be able to fold in two different directions, mountain, and valley folds. A similar self-folding method, devised by the same group, induced actuation by the absorbance of patterned light from a laser, using the same pre-strained polymer layer. The laser beam locally heats the polymer layer and reaches a temperature above its glass transition temperature.[281]

Another approach is based on programming the diffusion rate of a global stimulus in the active material (**Figure 16b**). Grayscale patterns have been printed on SMP and then exposed to an ultraviolet (UV) light, in order to heat up and exceed the glass transition temperature (105°C) of the polymer. The degree of transparency of the line pattern controls the light absorption

(namely different quantities of light energy are transformed into thermal energy), allowing the control of the onset time of the folding of the different printed grayscale lines when T_g (105°C) is reached.[282] A similar method is based on printing different coloured patterns on SMP. The different coloured patterns absorb different spectrums of light, allowing the control of sequential folding (**Figure 16c**).[283]
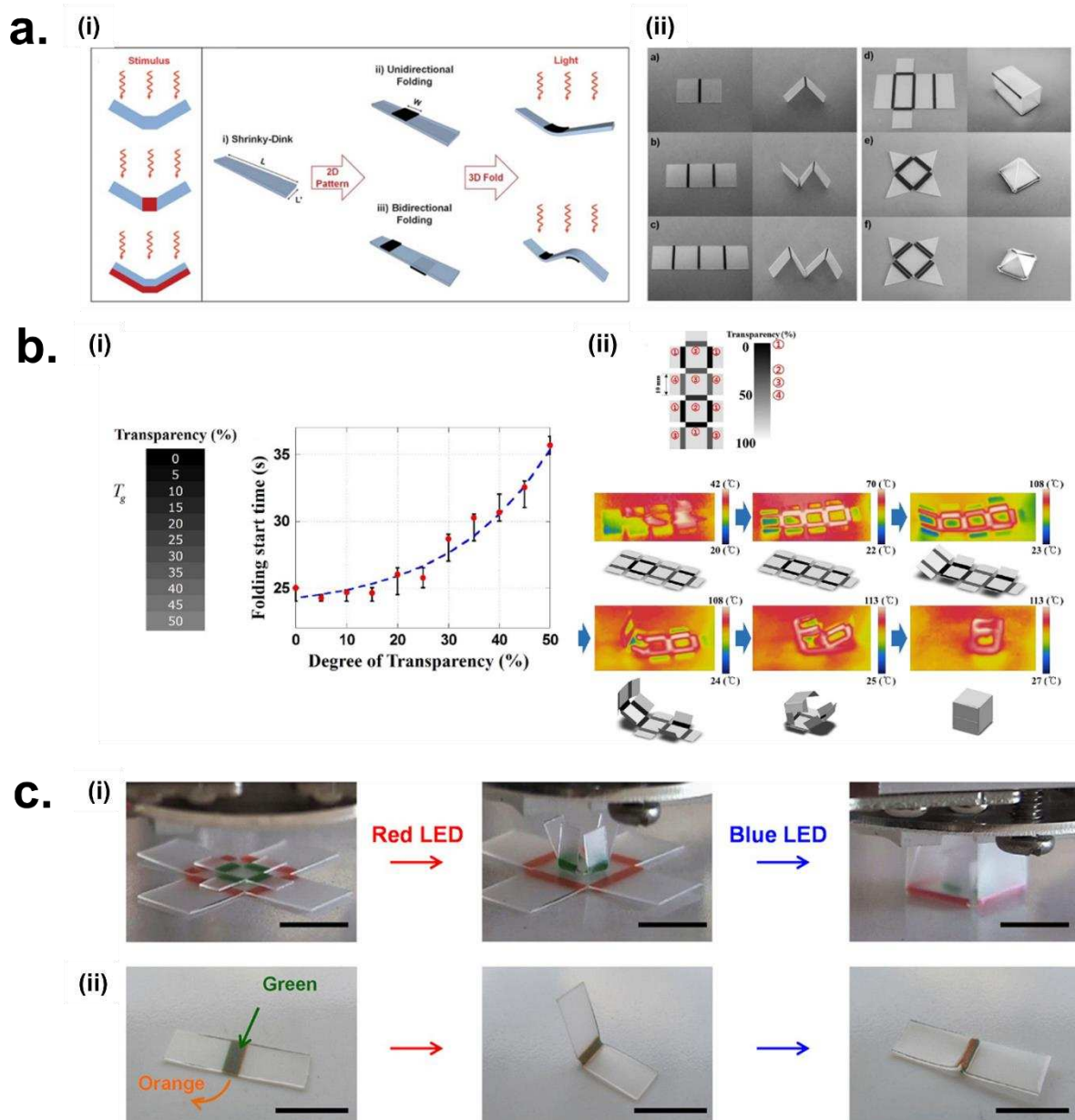

Figure 16: a(i) Schematic of a simple approach to self-folding using printed ink on oriented polymer via light actuation. **(ii)** Photographs of 3D structures created by self-folding of bi-

oriented polystyrene (BOPS) patterned with printed ink.[280] Copyright 2012, The Royal Society of Chemistry. **b(i)** Folding start time as function of line pattern transparency. **(ii)** Pattern of 3D cube using sequential folding based on line transparency (top), thermal image of sequential self-folding cube (bottom).[282] Copyright 2015, Springer Nature. **c)** Images of complex structures formed via sequential folding. (**i**) Nested boxes with a small box with green hinges (5 mm × 5 mm × 5 mm) on top of a large one with orange hinges (10 mm × 10 mm × 10 mm). (**ii**) Unfolding pathway: Folding first occurs toward the top green hinge using a red LED. An orange hinge is patterned on the opposite side of the green hinge. Unfolding occurs by activating the orange hinge using a blue LED.[283] Copyright 2017, American Association for the Advancement of Science.

Ryu et al. proposed a microfabrication technique to design bending hinges of an origami shape (**Figure 17a**) using 4D printing.[284] A polymer sheet (containing 3 wt% Tinuvin 328) was stretched and covered with a photomask and irradiated with light (365 nm, 40 mW/cm^2) on the mask side. Upon exposure, stress relaxation was generated through the thickness of the exposed pre-stretched polymer sheet. Once the photomask and strain was removed the desired product shape was obtained after bending of the sheet at the corners, i.e. at exposed regions in order to reach mechanical equilibrium.

Ceamanos et al. reported 4D printing of azobenzene-containing LCEs.[285] Fast mechanical responses have been observed in these 4D printed LCE strips (90 μm thick) when excited with UV light (365 nm, 200 mW/cm^2). These 4D printed elements can lift objects (1 g) many times heavier than their own weight, demonstrating a capacity to produce effective work (**Figure 17b**).

a.

(i)

Uniaxially strain to $\varepsilon_x = \varepsilon_1$

1a
1b

Irradiate through mask 1a,
Uniaxially strain to $\varepsilon_x = \varepsilon_2 < \varepsilon_1$,
Irradiate through mask 1b

Remove load

Uniaxially strain to $\varepsilon_y = \varepsilon_1$
Irradiate through mask 2

Remove load

Stamp box perimeter

(ii) (iii) (iv) (v)

b.

i) ii) iii) iv)

c.

(i)

Bilayer helix

Static Dynamic

(ii) (iii) (iv)

20 µm 10 µm

(v)

Bilayer   0 s   300 ms   500 ms

10 µm

Monolayer   0 s   300 ms   500 ms

(vi)

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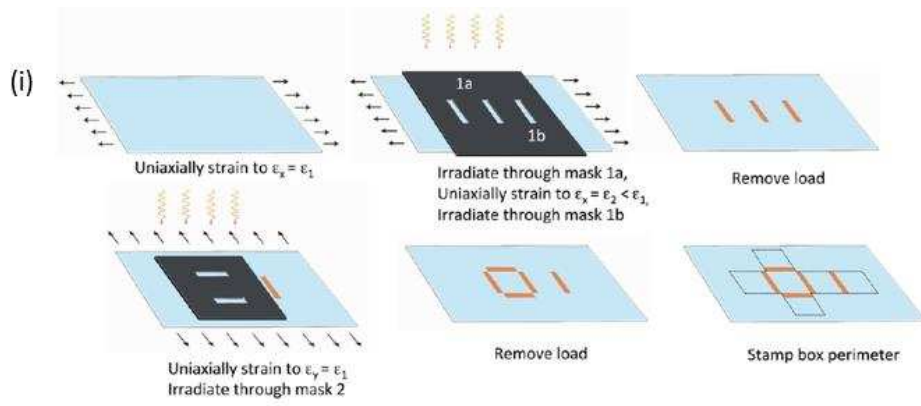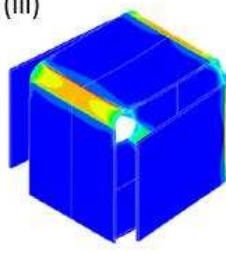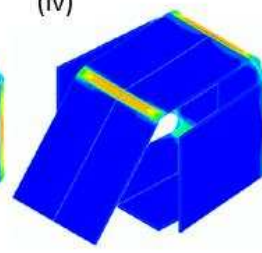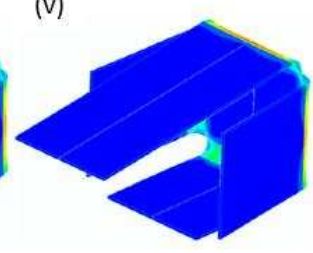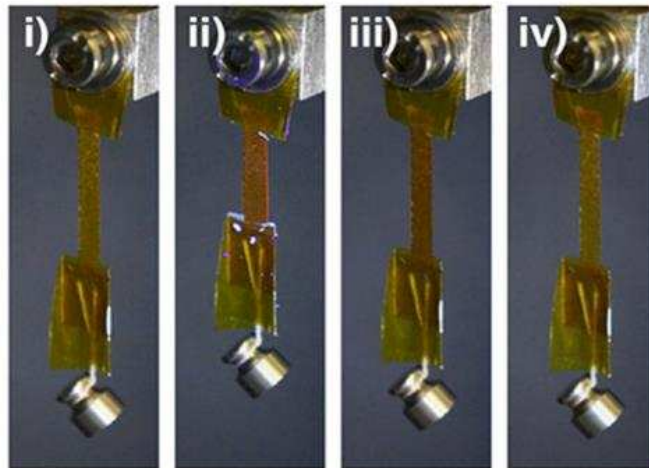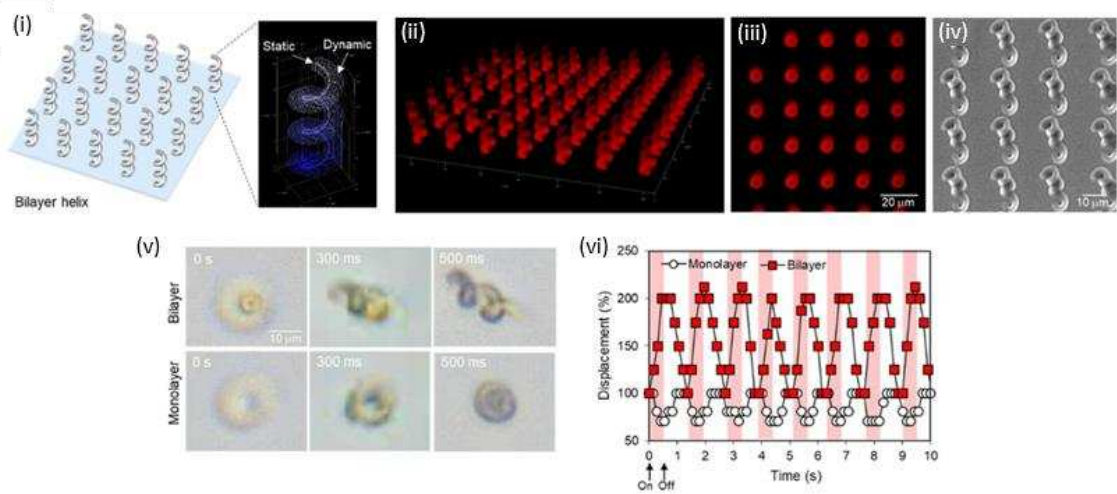
Figure 17: **a.** A six-sided box fabricated by photo-origami that requires multiple hinges created in multiple straining and irradiation steps: **(i)** photo-origami protocol, **(ii)** fabricated closed box, **(iii)** simulated closed box, **(iv)** simulated box with an open top, and **(v)** simulated box with a partially open top. Reproduced with permission.[284] Copyrights 2012, American Institute of Physics. **b.** Photo-response of a rectangular LCE strip with uniaxial orientation of the director along the long axis of the element with UV exposure. A weight of 1 g is attached to the lower extreme of the strip. Images of the LCE element successively acquired **(i)** before UV illumination, **(ii)** after UV illumination (1 min of illumination with 200 mW/cm^2), **(iii)** 2 min after ceasing the UV illumination, and **(iv)** after 30 min of blue light illumination (455 nm, 4 mW/cm^2). Reproduced with permission.[285] Copyright 2020, American Chemical Society. **c.** **(i)** CAD image of the bilayer helix. **(ii, iii)** 3D reconstructed confocal laser scanning microscopy (CLSM) image and **(iv)** field-emission scanning electron microscopy (FESEM) image of bilayer helices. **(v)** Phase-contrast images of the bilayer helix and soft monolayer helix after 300 and 500 ms of laser exposure. **(vi)** Displacement of each helix as a function of time when the laser was turned on at 2 Hz and off at 1 Hz. The displacement was defined as follows (ε (%) = $-(d_0 - d)/d_0 \times 100$, where d_0 is the initial distance from the top edge of the helix to the center of the helix). The cycle of laiver exposure was composed of 500 ms turn on and 1 s turn off. Reproduced with permission.[286] Copyright 2020, American Chemical Society.

Nishiguchi et al. recently printed a 4D soft actuator using multiphoton lithography (MPL) technique for controlled printing density.[286] The nanocomposite hydrogel used composed of thermo-responsive poly(N-isopropylacrylamide) (PNIPAm) and gold nano rods (AuNRs). Light-driven (808 nm) manipulation with AuNRs performed ultrafast, reversible shape morphing based on body deformation (**Figure 17c**). Due to the light-driven thermal response, PNIPAm/AuNR nanocomposite gels undergo non-equilibrium actuation comprising a distinct forward and reverse stroke, leading to an artificial micro swimmer.

4D printing technology is only half a decade old yet already demonstrated great potential in light-driven actuator applications for the future. However, evolution of such a dynamic field requires to overcome challenges being faced today such as high cost of manufacturing, limited potential materials, and undesirable printing quality.[279,287]

5. Outlook and prospects

In this study, light-driven actuation materials ranging from soft to ultra-stiff synthetic polymers were reviewed (**Table 2**). Focus was primarily given to materials and mechanisms of this dynamic and growing area of research. State of the art techniques for the fabrication of novel functional composites and smart devices with advanced performances were also outlined.

This review showcases the considerable progress made in photo-actuation over the last couple of decades. **Figure 18** provides a comprehensive overview of the photo-mechanical actuation performance of state-of-the-art photo-actuators based on various light-absorbing agents incorporated in synthetic polymers. Attributes like actuation stress, strain and work capacity are important from an application point of view. As the illustration implies, photo-responsive synthetic polymer actuators are spanning from large deflections, strokes and strains as high >100% (twice that of natural muscle)[28], to large mechanical forces per unit area (>70 MPa), outperforming many inorganic actuators.[25] These properties suggest a wide potential of these materials for applications ranging from soft yet highly expandable artificial muscles, to ultra-stiff yet flexible actuators.

Table 2: Parameters, actuating performances and mechanism of photo-responsive synthetic polymer actuators with reference to light-absorbing additives and host materials.

Polymer class	Host materials	Light-responsive additives [concentration wt%]	Spectrum [UV/Vis/IR]	Activation wavelength [nm]	Light Intensity [mW/cm^2]	Actuation Stress [MPa]	Actuation Strain [%]	Principle phenomena upon light absorption	Reference
Hydrogels	PNIPAm	PPy	IR	980	2500	~0.00013	90	Photo-thermal differential swelling	[89]
	PNIPAm	rGO	Vis	-	41.8	Photo-mechanical deformation		Photo-thermal differential swelling	[68]
	PEG	[Ru(bpy)$_3$]$^{2+}$	Vis	~450	-	-	35	Photo-induced electron transfer and chain folding	[154]
	PNIPAm + PAAm	rGO	IR	-	5	Photo-mechanical deformation		Photo-thermal differential volume contraction	[118,155]
Liquid crystal elastomers & polymers	Nematic LCE	Azobenzene (1%)	UV	365	-	-	20	Photo-isomerization Opto-thermal disruption of order parameter	[135]
	Nematic LCE	Azobenzene (0.2-1%)	UV	365	100	-	~18	Photo-thermal contraction	[176]
	LCP	Azobenzene	UV	366	25	2.6	~0.3	Photo-isomerization Thermal contraction	[96]
	Poly methyl hydrosiloxane (PHMS)	Azobenzene	UV	365	220	1.7	~0.8	Photo-thermal differential contraction	[182]
	LCE	CNTs (0.1%)	Vis	670	67	~0.008	-	Photo-thermal effect	[186]
	LCE	SWCNTs (0.3%)	IR	808	4500	~0.02	~30	Photo-thermal effect	[56]
	LCE (polysiloxane)	SWCNTs (0.3%)	Vis	-	413	~0.075	~35	Photo-thermal effect	[131]

Polymer class	Host materials	Light-responsive additives [concentration wt%]	Spectrum [UV/Vis/IR]	Activation wavelength [nm]	Light Intensity [mW/cm^2]	Actuation Stress [MPa]	Actuation Strain [%]	Principle phenomena upon light absorption	Reference
Shape memory polymers	SMP	Polydopamine (PDA) (~0.2%)	IR	808	600	~0.13	20	Photo-thermal phase transition	[71]
	Epoxy SMP	methyl ammonium lead iodide (CH$_3$NH$_3$PbI$_3$)	Vis	-	120	Photo-mechanical deformation		Photo-thermal phase transition	[72]
Thermoplastics	EVA	MWCNT (0.1%)	Vis	627	-	~0.0638	15	Photo-thermal effect	[197]
	EVA	MWCNT (0.1%)	Vis	627	-	~0.165	50	Photo-thermal effect	[128]
	Polyimide & paraffin wax	CNT	IR	772	50	Photo-mechanical deformation		Photo-thermal effect Differential thermal expansion	[126]
High-modulus polymers	UHMWPE	Azobenzene	UV-Vis	365	175	~60	~0.06	Photo-thermal effect	[203]
	UHMWPE	BZT (5%)	UV	365	-	~70	~0.1	Entropy driven photo-thermal effect	[61]
	HDPE	BZT (5%)	UV	365	-	~21	~0.1	Entropy driven photo-thermal effect	[63]
Others	PDMS	Carbon black (2%)	NIR	808	160	~0.021	50	Photo-thermal effect	[210]
	PDMS	SWCNT (2%)	NIR	808	160	~0.014	50	Photo-thermal effect	[210]
	PDMS	MWCNT (1%)	NIR	808	160	~0.06	50	Photo-thermal effect	[1,211]
	PDMS	MWCNT (1%)	IR	675	-	~0.05	40	Orientational order disruption by CNT bending	[1]
	PDMS	GNPs (2%)	NIR	808	160	~0.04	50	Photo-thermal effect	[210]

| Polymer class	Host materials	Light-responsive additives [concentration wt%]	Spectrum [UV/Vis/IR]	Activation wavelength [nm]	Light Intensity [mW/cm^2]	Actuation Stress [MPa]	Actuation Strain [%]	Principle phenomena upon light absorption	Reference
	PDMS	GNP (5%)	IR	808	500	~0.05	40	Photo-thermal effect	[210]
	PDMS	Single layer graphene (1%)	NIR	808	160	~0.049	50	Photo-thermal effect	[212]
	PDMS	GO (2%)	NIR	808	160	~0.011	50	Photo-thermal effect	[210]
	Allyl sulphide+ PETMP+MDTVE +EGDMP	Irgacure-184	UV	365	20	Photo-mechanical deformation		Photo-thermal entropic effect	[208,209]
	Polyacrylamide nano-fibers	-	NIR	785	93	Photo-mechanical deformation		Photo-thermal entropic effect	[234]
	PDMS	MoS$_2$ (2%)	NIR	808	160	~0.031	50	Photo-thermal effect	[210]
	PDMS	MoS$_2$ nano-rings	IR	808	1000	Photo-mechanical deformation		Photo-thermal effect	[220]
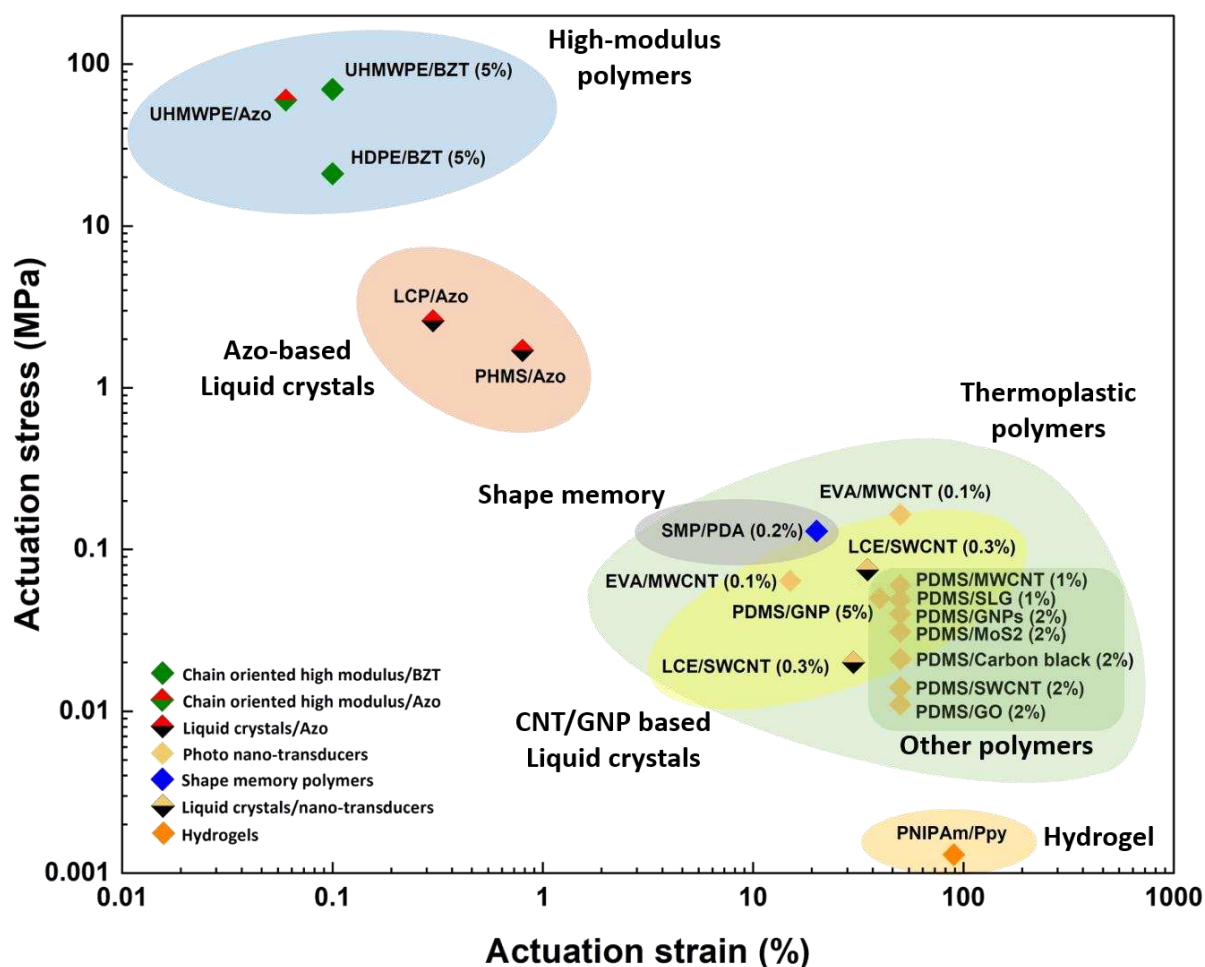
Figure 18: Photo-mechanical actuation performance comparison of state-of-the-art synthetic polymer based photo-actuators based on different light-absorbing agents.

Undoubtedly, new combinations of host materials and photo-absorbers will be discovered and programmed to develop novel and diverse applications, embracing new technologies like artificial muscles, smart textiles and biomedical applications. However, for practical applications of these materials, it will be highly beneficial to have control over its actuation by carefully adjusting the influencing parameters. Such as, it is essential and fundamental to ensure that the addition of functional additives does not interfere with the properties of the host, are physically compatible with each other and offer a quick response. Clearly, the additive content should be optimized,[56,96,176] as a too low photo-active compound content may fail to trigger actuation while a too high content may deteriorate the flexibility and mechanical

properties of the host polymeric material. Dispersion and alignment of light-responsive additives in the polymer matrix is worthy of further attention.[196,197] Better dispersion of additives or fillers such as CNTs or graphene will considerably improve the photo-actuation performance since homogeneous dispersion will lead to more homogeneous heat generation and therefore actuation response.[1,60,96,185] However, in certain cases, an anisotropic dispersion and alignment is crucial but more challenging to achieve and control. Furthermore, alignment of the host material in a certain direction (like in oriented polymers) guides the additives (e.g. graphene) or functional groups (e.g. AZO) in the same direction, achieving an anisotropic actuation response which might be favorable for certain applications. Light modulation, especially polarization direction, wavelength, intensity and exposure duration, is another fundamentally important consideration.[203] Localized actuation is a key requirement in certain applications and can be induced by light polarization.[214] Light irradiation intensity on the other hand improves the response significantly as reported by numerous studies.[71,131,136,176,186]

Actuated systems covered in this review are solely based on light-driven polymer materials. However, polymers systems actuated by thermal energy are not considered out of scope. Normally thermally-driven systems can easily be transferred into light-driven systems by embedding suitable photo-responsive additives in polymers. Basically, heat is being generated through these additives upon absorbing electromagnetic energy from light, which in turn triggers the actuation in such systems.

So far, the photo-actuation of polymeric materials has attracted a lot of attention in the academic community for many decades and even the 2016 Nobel Prize in Chemistry was awarded to the design and production of molecular machines including light-driven molecular motors. Many prototypes of devices have been suggested and the scientific literature is nowadays so abundant that a review on this topic is complicated to say the least. More

importantly, actual commercial applications beyond prototypes in an academic setting are extremely hard to find e.g. the authors of this review struggled to identify any, which is somewhat worrying after such a prolonged academic effort.

For instance, one of the main disadvantage or limitation associated to photo-isomerization is that it only works in soft matter such as soft liquid crystals, soft hydrogels etc. In order to extend the photo-isomerization mechanism to ultra-stiff matter (e.g. engineered polymers), we need to partially heat them into the molten state followed by the photo-isomerization.

Molecular motors are generally remarkable in terms of their functionality. However, these systems only work in solutions, nematic liquids, gels and soft elastomers.[112] Furthermore, kinetics of transitions in these motors are influenced by the environment. It is still uncertain, if these systems can work (even for very small motion) without any solution and be useful in terms of practical functionality.[115]

In case of photo-thermal actuation mechanism, oriented polymers like polyethylene are intrinsically limited by the rather low temperature resistance. For instance, heating-up of the system to temperatures in the vicinity of the α-relaxation temperature, or above inevitably result in loss of its functionality (either because of morphological changes such as partial relaxation of orientation or even complete melting) or reversibility (because of large deviations from linear (visco-)elastic behaviour). In order to build the same functionality in systems with enhanced temperature resistance, it is suggested that ultra-drawn polymers even with a low maximum attainable draw ratio such as nylon, polyester etc. should be exploited.[62]

Moreover, within highly-drawn chain-oriented polymers (such as polyethylene), we can only achieve high actuation stress at low strain. In order to achieve higher strain in such systems, we can design them like coil springs, which will transform small intrinsic deformation in larger macroscopic deformation.[253]

There is no doubt that the light-driven functionality in polymeric materials has emerged as a promising approach towards mechanical actuation. In order for these materials to be utilized in practical devices, new design geometries need to be developed that can provide high mechanical stress together with large strokes for actuation. For example, a multifilament assembly can provide a much higher mechanical force than a monofilament or single fiber. Similarly, a uniaxial (1D) fiber when modified into a twisted or spring-like (3D) configuration that transforms small inter-fiber contractions into large macroscopic deformations and as such enhance the performance window of fiber based actuators or artificial muscles.[253] Nature is full of such bioinspired examples (fish fins, pine cones, wheat awns, tree roots in soil, self-cleaning and anti-reflection surface pattering of insect wings etc.) in which mere design manages to create highly functional structures and complex behaviors using intrinsically simple materials.

One exciting challenge in developing light-actuated polymer based devices is that more careful consideration needs to be given to design criteria. Industrially viable applications of light-driven actuators is still a distant dream. With the goal of optimizing all aspects of actuator performance, new applications can be generated using innovative design concepts.

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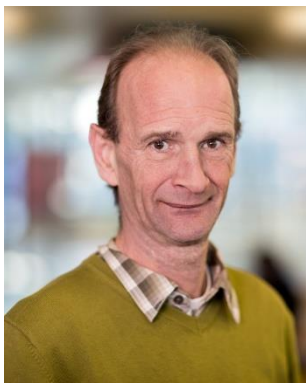
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