

Technical Note

# Bio-Inspired Soft Robotics: Tunable Photo-Actuation Behavior of Azo Chromophore Containing Liquid Crystalline Elastomers

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**Featured Application:** Inspired by nature, mechanical and material engineers construct innovative operating robotic models. Bio-inspiration always sparks novel ideas to design smart materials and structures for the development of innovative robots.

**Abstract:** Bio-inspiration relentlessly sparks the novel ideas to develop innovative soft robotic structures from smart materials. The conceptual soft robotic designs inspired by biomimetic routes have resulted in pioneering research contributions based on the understanding of the material selection and actuation properties. In an attempt to overcome the hazardous injuries, soft robotic systems are used subsequently to ensure safe human–robot interaction. In contrast to dielectric elastomer actuators, prolific efforts were made by understanding the photo-actuating properties of liquid crystalline elastomers (LCEs) containing azo-derivatives to construct mechanical structures and tiny portable robots for specific technological applications. The structure and material properties of these stimuli-responsive polymers can skillfully be controlled by light. In this short technical note, we highlight the potential high-tech importance and the photo-actuation behavior of some remarkable LCEs with azobenzene chromophores.

**Keywords:** actuators; azobenzene; bio-inspired; opto-mechanical; photo-actuation; soft robotics



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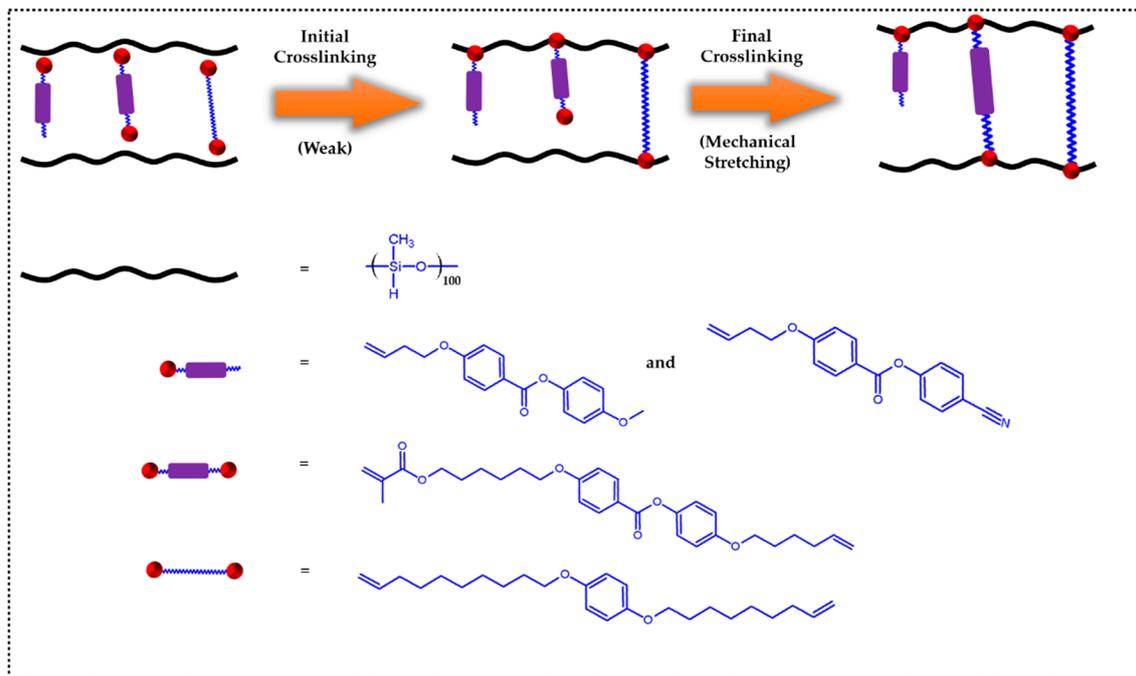


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## 1. Introduction

Liquid crystalline elastomers (LCEs) are a new unique class of material derived from the combination of elasticity properties (like in an elastomer) and orientational order of mesogenic building blocks (liquid crystalline molecular array). Typically, mesogenic units are incorporated as flexible spacers to build linear polymer liquid crystal macromolecules [1–3]. Since the monodomain alignment of mesogenic groups was thermodynamically unstable, due to its spontaneous conversion into polydomain structures, researchers were only synthesizing polydomain side-chain LCEs until the pioneering research works of Küpfer and Finkelmann [4,5]. They introduced new two-step crosslinking conditions to develop monodomain LCEs, where initially a weak crosslinked network was constructed; later, this developed director orientation was replicated by the second crosslinking step via mechanical stretching to induce monodomain [6,7]. Evidently, for LCEs due to the coupling behavior of liquid crystalline order and the polymer backbone, external mechanical stress can considerably influence the state of an order [8,9]. The crosslinking process in different liquid crystalline phases (nematic or isotropic phase) highly influences the orientational distribution and results in different properties [10]. When the crosslinking was done in the nematic phase, the state of order was fixed within the crosslinking zones, leading to ‘frozen-in’ order. This can be achieved by exposing the sample to the applied mechanical stress perpendicular to the original direction of the monodomain [11–13]. The synthetic

strategy proposed by Küpfer and Finkelmann for the preparation of monodomain nematic LCEs was sketched in Figure 1 with chemical structures used.

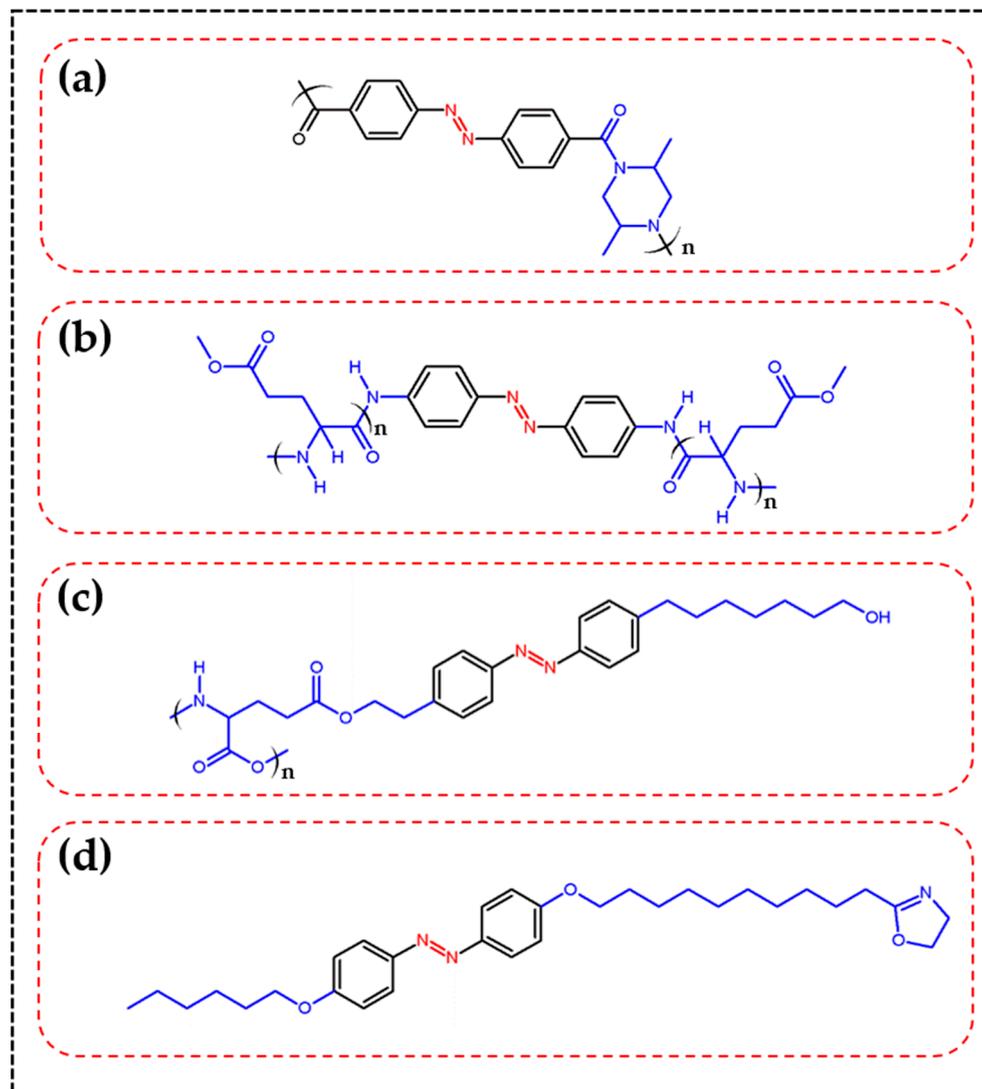


**Figure 1.** Schematic illustration of synthetic strategy with chemical structures, proposed by Küpfer and Finkelmann for the synthesis of monodomain nematic liquid crystalline elastomers (LCEs) [5].

Over the last two decades, the booming progress in designing different types of LCEs with a variety of liquid crystalline phase has been noticed for the fine-tuning of the properties. Researchers investigated a wide variety of LCEs with diverse liquid crystalline phases including nematic, cholesteric (or helical), smectic phases (smectic A, smectic C, and smectic C\*), and discotic and blue phases [14–17]. These LCEs with diversified liquid crystalline phases have been recognized as potentially effective to more technology-related topics, such as adaptive varifocal micro lenses in miniature electronic devices to soft actuator components of artificial muscle along with biomedical and soft robotic applications [18–22].

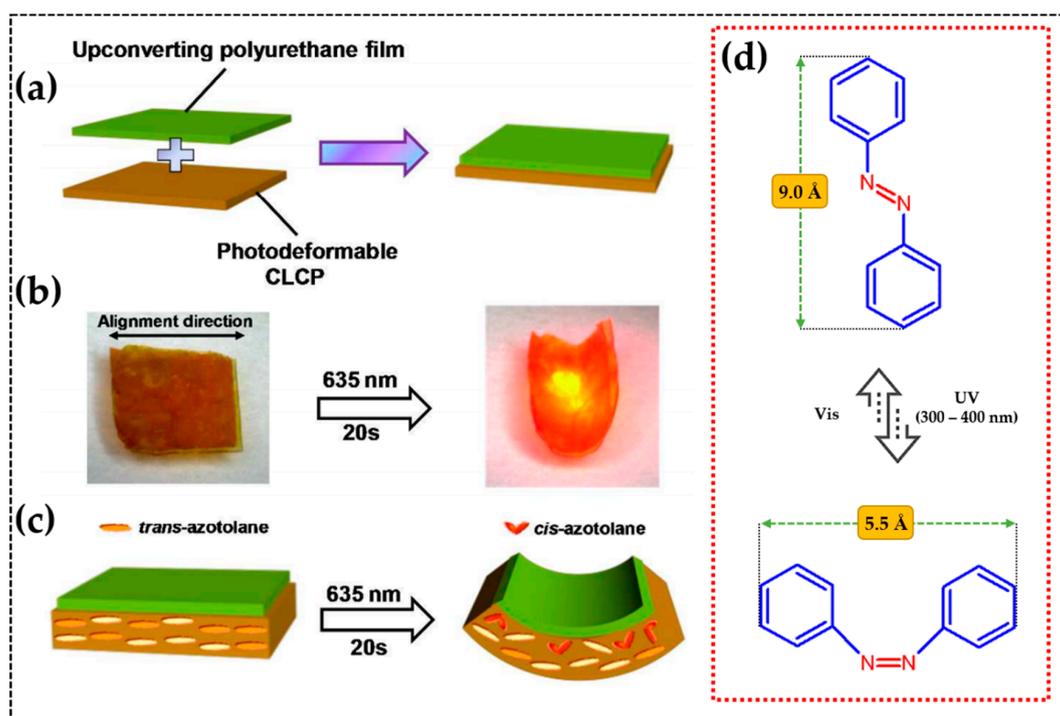
Some of the prominently studied polymers are outlined in Figure 2. The structure presented in Figure 2a comprise polyimides with azobenzene chromophores in the main chain and it was initially reported by Blair et al. [23]. Upon exposure to UV light, at the air/water interface, the stress diminution signpost the contraction of the monolayer. Under the dark condition, the stress increases again resulting in slight expansion of the monolayer. The photomechanical effects are caused by *trans*–*cis* photoisomerization of azobenzene chromophores (are more linear in their *trans* form than *cis* form) that can occupy a large surface area at the interface [23]. The polypeptide monolayers comprising two  $\alpha$ -helical poly( $\gamma$ -methyl L-glutamate) structures connected to azobenzene group prepared by Higuchi et al. [24] demonstrate the geometrical structural discrepancy during *trans*–*cis* photoisomerization resulting in the bending of the main chain (See Figure 2b). Menzel et al. [25] further investigated these photoresponsive behavior associated with polypeptides. The authors modified the structure (See Figure 2c) and introduced alky spacers. These monolayers demonstrated an expansion in UV light and contraction to the visible light. Upon exposure to UV light, the *trans*–*cis* photoisomerization created a huge increase in the dipole moment resulting in high affinity to the water surface [25]. The similar properties were observed by poly(vinyl alcohol)s enclosing azobenzene side chains (for structure, see Figure 2d) developed by Seki et al. [26].

In an effort to examine the structure–property relationships, a variety of symmetrical and unsymmetrical molecules was designed [27–34]. The bent-core (banana shape) mesogenic molecules with azobenzene chromophores are of special interest due to their structure relationships with light-triggered phase transition and photo-actuation properties [35–38]. These azobenzene, bent-core banana molecules were widely studied as intelligent stimuli-responsive materials for technological applications [39–43]. Merging the elastic property of polymeric elastomers and self-organizing properties of liquid crystals, many scientists have reported prospective works on crosslinked liquid crystalline polymers (CLCPs), which exhibit unique macroscopic shape-changing properties such as bending, contraction, and swirling especially under the influence of light. Most importantly, the photochemical phase transition of azobenzene chromophore (azotolane) containing CLCPs has a great influence on the photo-actuation (See Figure 3a–c.) [44–50]. In addition to azotolane moieties in the CLCP film, authors used other components such as platinum(II) tetraphenyltetrabenzoporphyrin (sensitizer) and 9,10-bis(diphenylphosphoryl)anthracene (annihilator) in order to trigger the *trans-cis* photoisomerization with 635-nm laser at a low power density of  $200 \text{ mW cm}^{-2}$ . The actuation performance was driven by low-power excited triplet–triplet annihilation based upconversion luminescence [50].



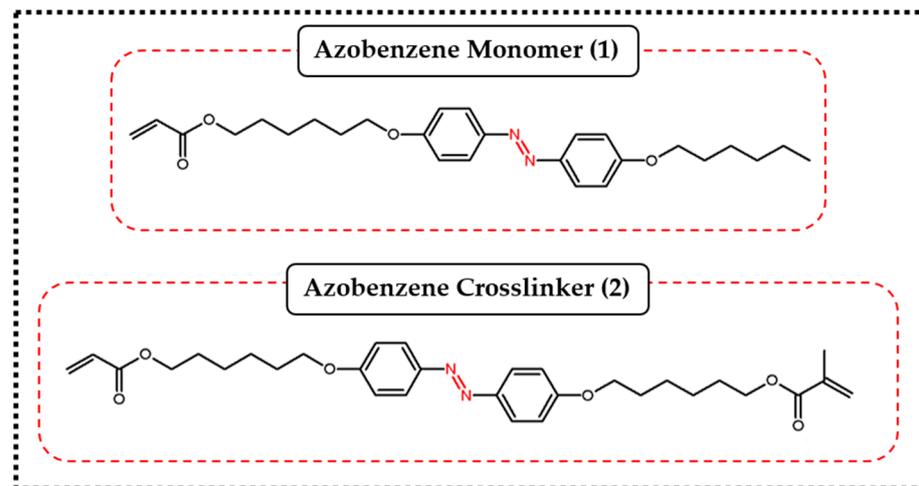
**Figure 2.** The photomechanical effects caused by *trans-cis* photoisomerization in some selected polymer systems developed by (a) Blair et al. [23], (b) Higuchi et al. [24], (c) Menzel et al. [25], and (d) Seki et al. [26].

In brief, photoisomerization is a phenomenon of structural transformation of molecules under photo-excitation. Photoisomerization of azobenzene molecules was demonstrated in Figure 2d. The *trans* form (up) can be converted to the *cis* form (down) using ultra-violet (UV) radiation of wavelength of 300–400 nm. The visible light illumination of *cis* azobenzene at >400 nm can revert the molecule back to *trans* form. By applying heat to *cis* form, the molecule can also be relaxed to stable *trans* form. The photoisomerization process of azobenzene mesogens in CLCPs can result in induced molecular reorientation, and this is the source for photo-actuation [50–54]. The chemical structures of azobenzene chromophores (monomer and crosslinker) used to prepare photo-actuating liquid-crystalline gels (LCGs) by Ikeda et al. are shown in Figure 4 [51].

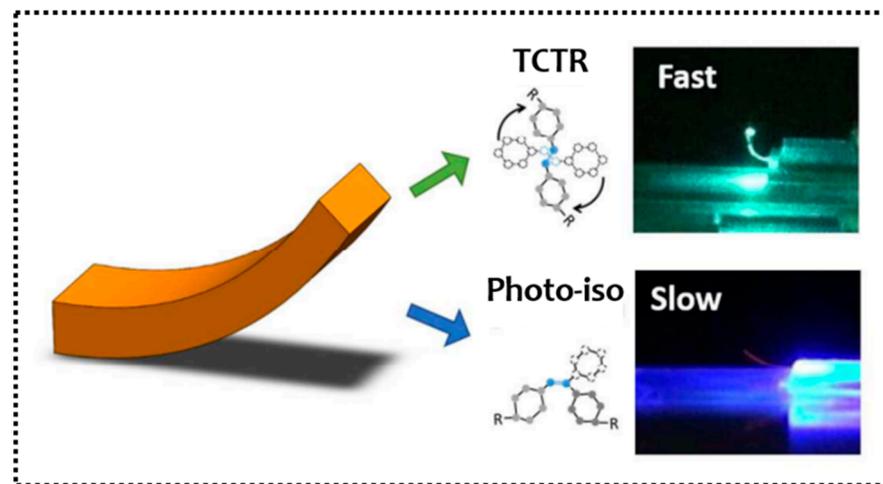


**Figure 3.** (a) Schematic illustration representing preparation of the assembly film composed of azotolane crosslinked liquid crystalline polymers (CLCP) film (b) Photographs of the as-prepared assembly film bending toward the light source along the alignment direction of the mesogens in response to the 635 nm laser with the power density of  $200 \text{ mW cm}^{-2}$  (Thickness of each layer in the assembly film:  $15 \mu\text{m}$  of upconverting film and  $27 \mu\text{m}$  of CLCP) (c) Schematic illustration demonstrating plausible mechanism for the photoinduced deformation of the as-prepared assembly film, Adapted with permission from [50], ACS, 2013. (d) *Trans*–*cis* isomerization of azobenzene molecule.

Yun et al. [52] studied azobenzene-doped liquid-crystal polymer (azo-LCP) prepared by “host-guest” method of fabrication process. 1,4-bis-[4-(3-acryloyloxypropyloxy)benzyloxy]-2-methylbenzene was used as host and 4-4'-bis[6-(acryloxy)hexyloxy]-azobenzene as guest material. The authors proposed that the azobenzene monomers elicit the alignment of the mesogens in two ways: (i) photoisomerization of azobenzene and rotation of azobenzene by means of a *trans*-*cis*-*trans* reorientation (TCTR), the latter was activated at around 365 nm. The authors evidently confirmed that the photo-bending speed of azo-LCP in the TCTR case is always faster than that of photo-isomerization (See Figure 5 for Sketch and bending snapshots of azo-LCP). The materials made of azo-LCP can precisely control the actuation that can advantageously be utilized in photo-driven soft robotics. The contraction of LCP along the major alignment direction of mesogens was favored by transformation of nematic to the isotropic phase of mesogens. Conversely, the shape of LCP is recovered when the mesogens transform from isotropic to the nematic phase. This can be achieved by visible-light irradiation [52].



**Figure 4.** Chemical structures of azobenzene chromophores (monomer and cross-linker) used to prepare liquid-crystalline gels (LCGs) by Ikeda et al. [51].



**Figure 5.** Sketch and bending snapshots of azobenzene-doped liquid-crystal polymer (azo-LCP) at 445 nm (**Fast-Top**) and 365 nm (**Slow-Bottom**), respectively, representing trans-cis-trans reorientation (TCTR) and photoisomerization mechanisms. Adapted with permission from Reference [52], ACS, 2018.

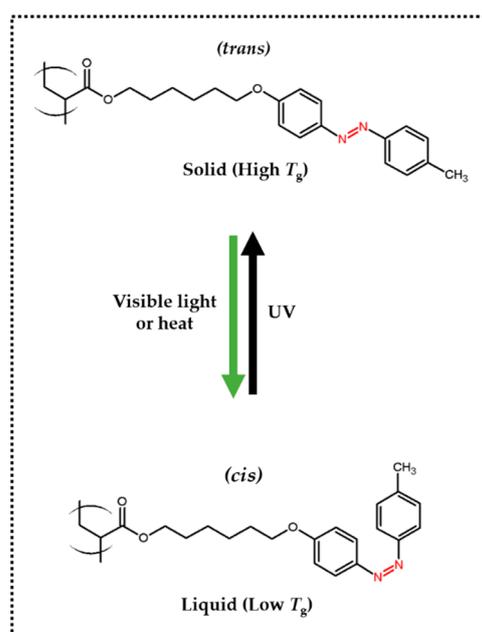
Since many scientific efforts have been put forward to improve the photo-mechanical effect, the research works carried out by Garcia-Amorós et al. [53,54] interestingly studied the effect of different lengths of photo-active crosslinker spacer (4,4'-dialkoxyazobenzenes) on opto-mechanics of light-controlled actuators. The authors also proposed the incorporation of 4-alkoxy-4'-cyanoazobenzene chromophores as side chain monomers to nematic LCEs and obtained characteristic kinetic parameters for the thermal isomerization of this cyano-substituted azo chromophore and the final photo-actuator behavior was explained in detail [54]. The recent passionate growth in soft robotic designs offers new opportunities to construct simpler structures using soft polymeric materials like LCEs and dielectric elastomers. These can be utilized depending on the design objectivity and mechano-compatibility in soft robotics. The diversified approaches show that these stimuli-responsive soft materials have several applicational advantages in the development of artificial muscle-like actuators. Because of the combination of orientational order of liquid crystals and the elasticity of conventional rubbers, these materials can easily implementable in a wide range of technological fields from micromechanical systems to soft robotic haptic interfaces [55–60].

## 2. Light-Induced Response of Azobenzene Chromophores

On exposure to suitable wavelength of light, azobenzene chromophores show rapid response behavior. Due to this characteristic feature, azobenzene derivatives are widely used as photosensitive materials for a broad range of technological applications. In brief, two benzene rings link together with azo ( $-N=N-$ ) functional group to form azobenzene chromophore. Functionalization of benzene ring can be done to prepare a variety of azobenzene derivatives by tuning electron-donating and withdrawing properties to achieve push-pull type azobenzene structures [61].

The fine-tuning of rigidity and flexibility of azobenzene molecules induced to unveil liquid crystalline (LC) behavior, which makes them extremely useful in designing photo-responsive materials. Under photo-excitation, the two isomeric configurations of azobenzene (a thermally stable *trans* state and a meta-stable *cis* form) undergo conversion from *trans* to *cis* state. During conversion, the molecule undergoes systematic geometrical deformation, which will end up with different molecular sizes for *trans* and *cis* forms (As shown in Figure 3d, the distance between reference carbon atoms of aromatic rings decrease from 9.0 Å to 5.5 Å, as the molecules transform from *trans* to *cis* state) [62].

One of the important parameters to consider in technical applications of a polymer is glass transition temperature ( $T_g$ ). For a quick glance,  $T_g$  is a characteristic property of polymer and is related to the temperature where the molecular chains begin to move. The polymers containing azobenzene moieties can have switchable  $T_g$  and can induce reversible *cis-trans* photoisomerization. This photoswitching of  $T_g$  is a topic of scientific curiosity and technical importance. The first report involving  $T_g$  of azobenzene-containing polymers reported by Zhou et al. [63] proposed light-induced reversible solid-to-liquid transitions of the polymers. This strategy can be applied to heal the cracks in high- $T_g$  polymers without harmful plasticizers. The authors also demonstrated that light can switch the  $T_g$  of the polymer, which eventually controls the mechanical properties of the polymers [63]. The polymers with switchable  $T_g$  developed by Zhou et al. are displayed in Figure 6. Since the ultraviolet (UV) irradiation of *trans* polymer powder samples not generated adequate amount of *cis* form, authors dissolved the *trans* polymer in dichloromethane ( $CH_2Cl_2$ ) and stirred it under the illumination of UV light to achieve respective *cis* form. The authors also prepared two control samples to prove the liquefaction was not due to the residual solvents.

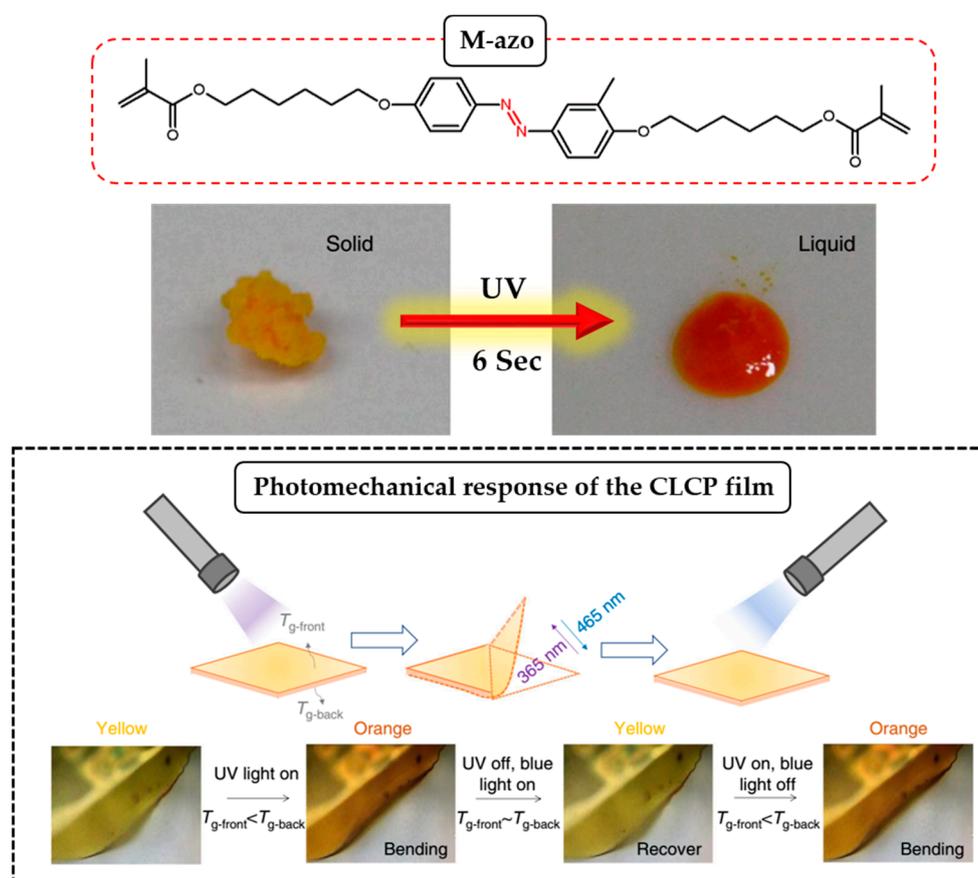


**Figure 6.** Schematic illustration and solid-to-liquid transitions of azobenzene-containing polymers developed by Zhou et al. [63].

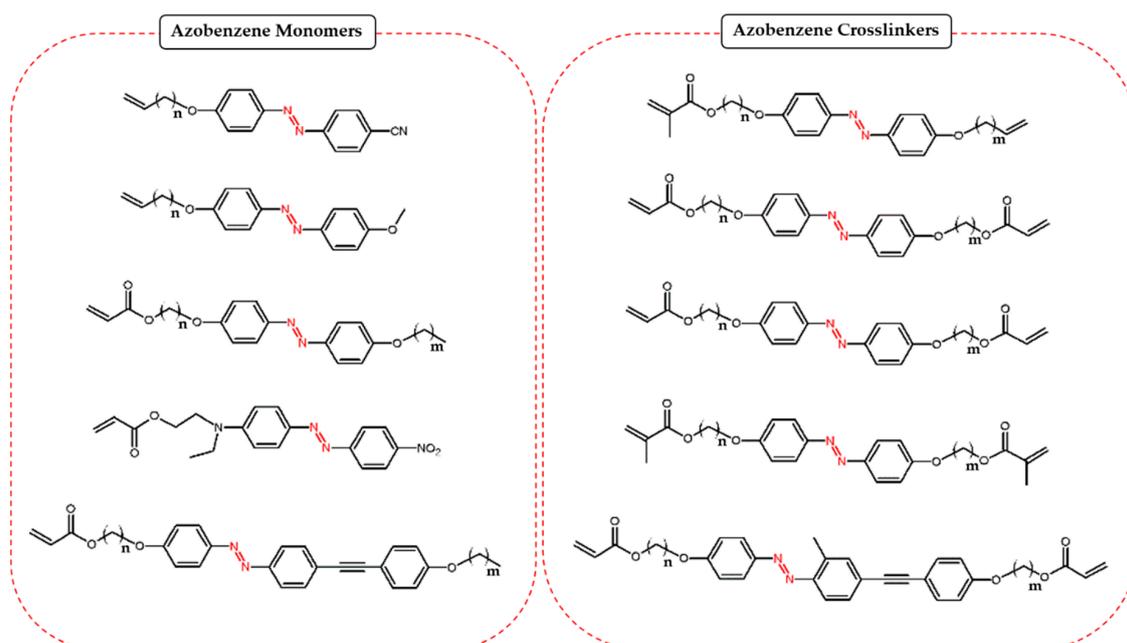
The differential scanning calorimetry (DSC) studies demonstrated that *trans* form showed a  $T_g$  of 48.0 °C and in both the heating curves (first and second), we can notice the two-phase transitions at 94.0 and 108.0 °C. However, for *cis* form, we can observe the  $T_g$  at −10.0 °C with broad exothermic peak at around 94.0 °C. Consequently, the study revealed that  $T_g$  of the polymer decreased with the *cis* content, serving as plasticizer [63].

Considerable attention has been focused on phase transition compounds especially where solid-to-liquid phase change involved. Under the influence of light, the molecular interaction in the solid state weakens to form a liquid state. This “photomelting” behavior of certain materials is of special interest in the material science field for the development of photosensitive materials. Despite diverse functional photomelting compounds are available, fast responsive materials are having superior significance to design bio-inspired robotic structures [64,65]. Based on photoswitchable  $T_g$  and “photomelting” behavior of azobenzene monomer, Yue et al. studied light-induced mechanical response in CLCPs. The photoresponsive moiety used by the authors is *meta*-methylazobenzene (M-azo), it was covalently crosslinked with dodecyl glyceryl itaconate (DGI) to construct CLCP films. The *trans*-to-*cis* photoisomerization of azo groups that CLCP network results in a photoswitchable  $T_g$  and performs reversible photomechanical motions upon exposure to UV/visible light [47]. As shown in Figure 6, the solid M-azo compound changes to liquid state. To trigger the transition, the solid M-azo compound was irradiated with UV light of wavelength 365 nm at an intensity of 125 mW cm<sup>−2</sup> for just 6 s. As the  $T_g$  of the polymer is closely associated with the mechanical properties of the polymers, the high  $T_g$  and storage modulus (140 MPa) was obtained for DGI/M-azo films before UV treatment. The lower Young’s modulus of 65.6 MPa was noticed in DGI/M-azo films after UV irradiation. This is due to the creation of *cis*-form in polymer films, which will reduce the  $T_g$  of the polymer. This photoswitchable  $T_g$  is exceptionally to achieve conspicuous photomechanical actuations of DGI/M-azo films under UV illumination. The authors evidently confirmed that bending and restoration of the films to original position were successfully controlled. This color-changing behavior of the films from orange to yellow was easily recognized (See Figure 7, Section: Photomechanical response of the CLCP film). This photoabsorption process is time-dependent. The irradiated light intensity plays a crucial role in deciding the degree of change in the  $T_g$  as well as response speed. By applying different intensity of irradiated light (3.28 to 45 mW cm<sup>−2</sup>), authors can control the bending speed of the film (0.4 to 2 mm s<sup>−1</sup>) at ambient temperature [47].

As discoursed earlier (in Figure 1), based on the properties of siloxane CLCPs [5,66] and acrylic CLCPs, listed (in Figure 7) azobenzene chromophore containing LC materials will be utilized to fabricate CLCP films from one-step or two-step protocols. The fabricated CLCP films find their major application in the construction of photo-driven micro/macroactuators. Some of the prominent azobenzene-containing liquid crystalline (LC) materials (monomers and crosslinkers) utilized to prepare LCPs with polysiloxane and polyacrylate backbone are shown in Figure 8.

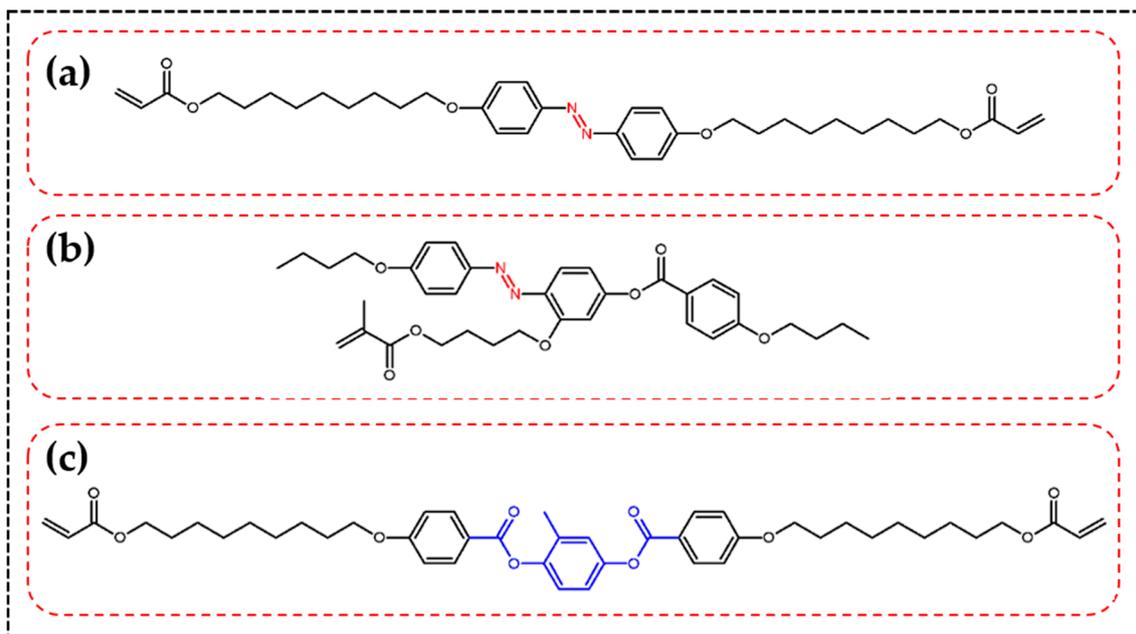


**Figure 7.** Schematic illustration, snapshots of photomelting process of *meta*-methylazobenzene (M-azo) compound and photomechanical response of the crosslinked liquid crystalline polymer (CLCP) film developed by Yue et al., Adapted with permission from [47], Springer Nature, 2018.



**Figure 8.** Partial list of chemical structures of azobenzene chromophore containing liquid crystalline (LC) materials (monomers and crosslinkers) utilized to prepare liquid crystalline polymers (LCPs) with polysiloxane and polyacrylate backbone [60,67–71].

Braun et al. [72] studied the effect of azo crosslinkers on photo-actuation abilities of LCE systems in comparison to non-azo crosslinkers. For the construction of the LCE system, authors utilized varying quantities of azo crosslinkers, non-azo crosslinkers, and azo monomer (For chemical structures, see Figure 9). Since the phase transition of mesogens involved in the construction of LCE system is influenced by variation of applied temperature, the temperature dependency on the photo-actuation of LCE systems was studied. It was reported that an extraordinary robust photo-actuation of up to 34% was achieved using azo-crosslinkers at 70 °C. However weak photo-actuation (change in length) compared to thermal actuation was achieved using non-azo-crosslinkers. Irrespective of azo moieties, higher crosslinking agents are necessary to provide mechanical stability to the LCE systems, which eventually utilized in the mechanical actuation device applications. The mesogenic orientation during photo-actuation also influences the performance of the constructed devices. Therefore, the contribution of azo moieties in monomers and crosslinkers plays a pivotal role in deciding the photo-actuation performances of LCEs. The well-known photoresponsive azo-crosslinker (crystalline 74 °C nematic 91 °C isotropic) used in the work (Figure 9a) mostly performs the dimensional variations to produce bending actuation. The knowledge of optimizing the azo-crosslinkers in LCE films is also important to decide the stiffness and crosslinking structures, which ultimately decide the actuation performances of the LCE system. The authors denoted that even 100 µm thickness LCE film was uniaxially actuated without just bending actuation, perceiving strong photoresponse of 40% under white light (440 nm) illumination [72].

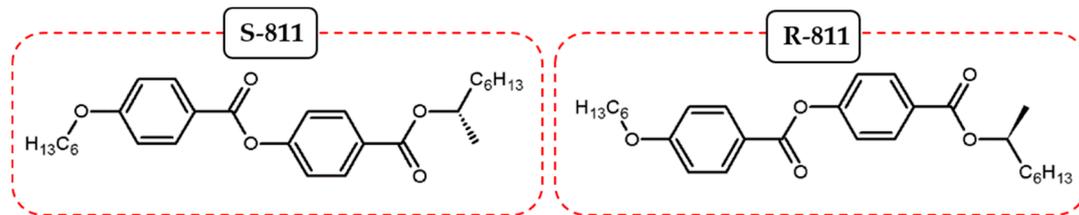


**Figure 9.** Chemical structures of (a) azo-crosslinker (c 74 °C n 91 °C i), (b) azo monomer (c 53 °C n 84 °C i), and (c) non-azo-crosslinker (c 66 °C n 92 °C i) use to construct LCE system by Braun et al. [72]. Note: c = crystalline, n = nematic, and i = isotropic.

### 3. Bio-Inspired Application Prospects

The principle of biomimetics strives us to learn how nature has refined and not necessarily to imitate but redefine the characteristic qualities of natural systems that will be pertinent to designed robotic structures. One such possible way to explore the potential of biological principles present in nature is through their wide application in soft robotics. Currently, we can notice copious research works experiencing the design history approach for the re-examination of nature designs using technological tools. The most recent incarnation of synthetic efforts has been the development of functionally diverse LCPs in order

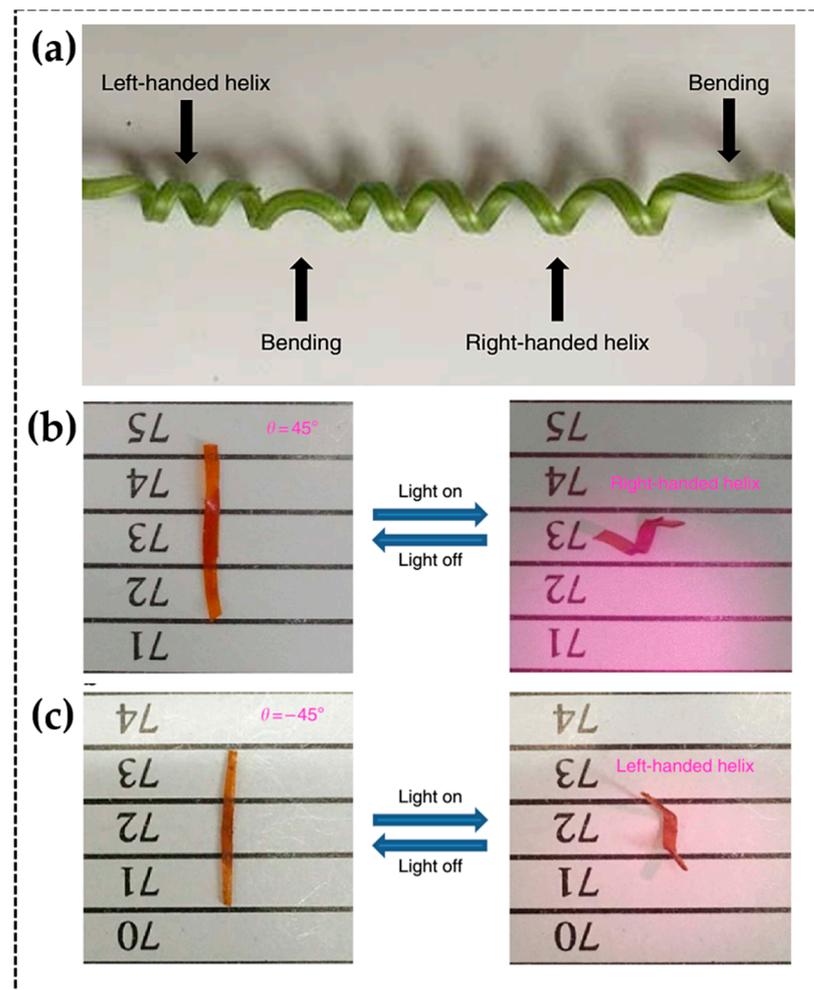
to address customized applications in soft robotics [56,62,73–77]. To accomplish the basic mechanical winding and unwinding motions inspired by plant tendrils, Iamsaard et al. [78] developed the LCPs with azo-crosslinkers. A small quantity of chiral dopants (S-811) fine-tunes the liquid-crystal director to achieve a complex range of dynamic mechanical behavior that mimics plant tendril structures (see Figure 10 for chemical structures of chiral dopants used by Iamsaard et al. in addition to azobenzene monomers/crosslinkers for the preparation of CLCP films, which mimic the plant tendril structures. See Figure 11a for the photograph of a cucumber plant tendril with bending and chiral twisting distortions).



**Figure 10.** The chiral dopants in addition to azobenzene monomers and crosslinkers used by Iamsaard et al. [78] to prepare liquid crystalline polymers (LCPs).

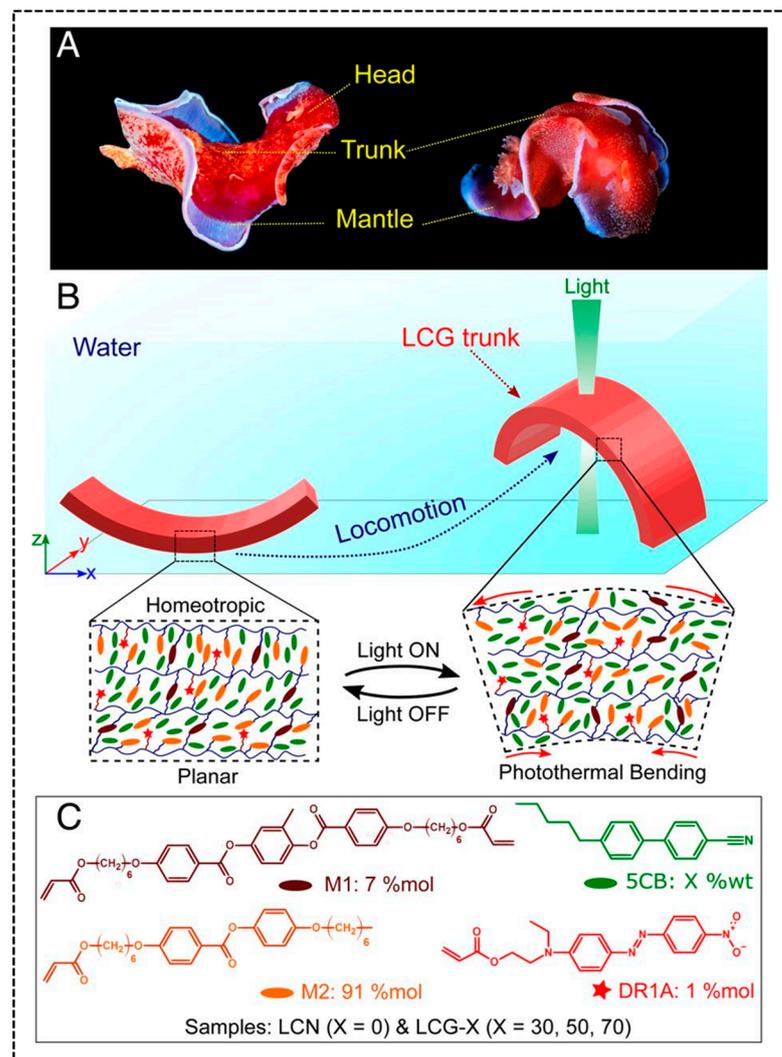
Inspired by the flapping motions of insect wings generating three-dimensional (3-D) motions like bending and twisting for the capability of agile flight, Lee et al. [79] synthesized azobenzene-based uniaxially aligned “monodomain” azo-liquid crystalline network [(azo-LCN) - designated here as MD-20CL]. The developed LC polymer comparatively contains appropriate concentration (~20 wt. %) of azobenzene crosslinker to LC monomer used (Similar chemical structure, as shown in Figure 9a, but with six flexible -CH<sub>2</sub>- spacers on both sides). The oscillatory responses were obtained after exposing MD-20CL cantilevers to 1.0 W cm<sup>-2</sup> of 442 nm. The authors evidently confirm that the dimensionality of the oscillations is strongly influenced by the alignment of nematic director to the cantilever. On exposure to coherent wave laser (442 nm), bending of the sample arise due to the development of non-uniform strain through the sample thickness. Whereas the modifications in the orientation of the nematic director generate a shear gradient that motives the twisting behavior of the cantilever. These flexural torsional oscillations replicate 3-D motions like bending, sweeping, and twisting to generate flapping motions [80]. The authors performed photopolymerization to achieve glassy, high modulus azo-LCN. Because of preferential alignment LC mesogens along the rubbing direction, the modulus of MD-20CL turns into anisotropic. The measured storage modulus measured parallel to nematic director was approximately 1 GPa and 0.6 GPa when measured perpendicular to nematic director [79].

The technical benefit of LCE material developed by Wang et al. [80] is advantageous because of the preparation of comparatively thick films despite LC alignment procedure, which is eventually useful in transmitting heavier loads. Taking the advantage of two-step crosslinking mechanism proposed by Küpfer and Finkelmann, two different pre-crosslinked LCE samples could be impulsively attached together during the second hydrosilylation crosslinking step, without using additional glues. As shown in Figure 11b,c, the LCE ribbons attain helical configurations in 8 s after exposing to near-infrared light source. The ribbons fully recover to their original shapes immediately after removing the light source. The authors concluded that the polysiloxane-based LCE system exhibits an astonishing pro in building multilayer hierarchical structures, which mimic a distinct plant tendril, which can also perform bending and chiral twisting (left-handed and right-handed) operations. Herein, the authors performed near-infrared light (center wavelength: 808 ± 3 nm, output power: 8 W) twisting actuation of the bilayer LCE ribbons. The change in the temperature caused by the heating effect of near-infrared light was prudently recorded using a thermal imager (FLUKE Ti90) to examine the curling behavior of LCE ribbons [76,80].



**Figure 11.** (a) The photograph of a cucumber plant tendril with bending and chiral twisting distortions (b,c). The bilayer LCE ribbon with  $45^\circ$  and  $-45^\circ$ , respectively, angle between the top and bottom layer was irradiated under an 808 nm near-infrared light for 8 s. Adapted with permission from Reference [80], Springer Nature, 2016.

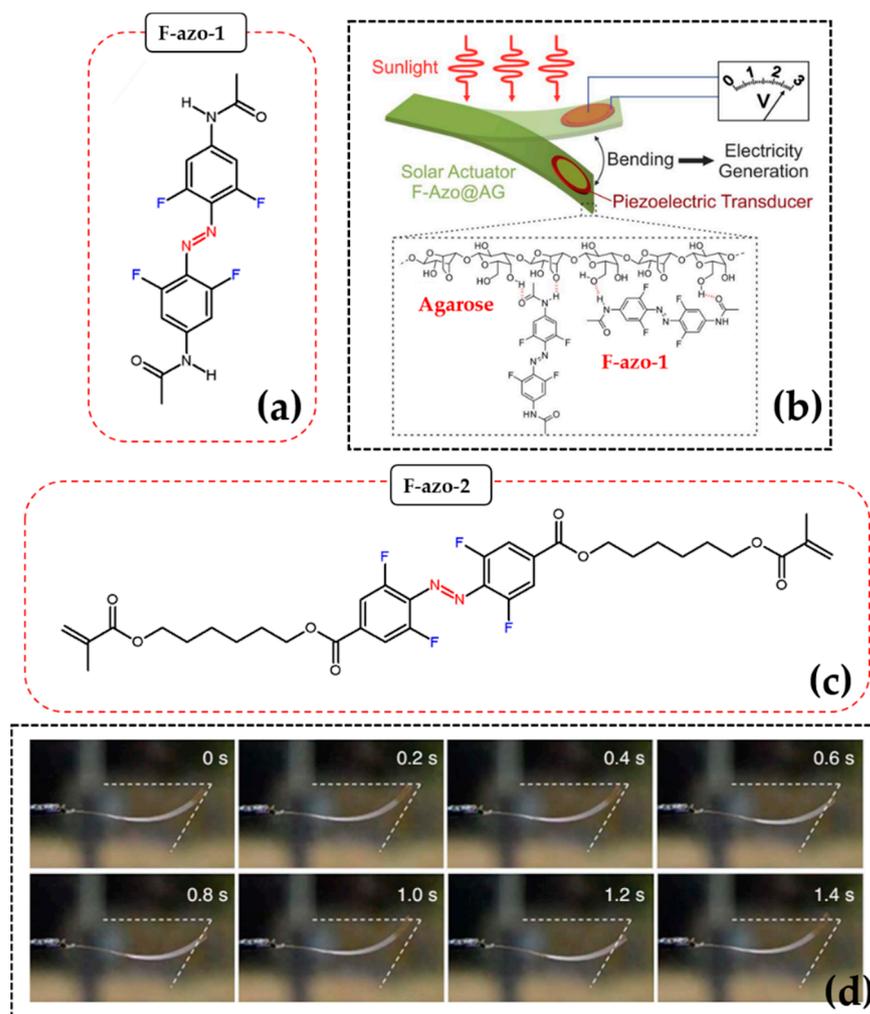
Mimicking underwater soft-bodied sea invertebrate's locomotor movements is challenging. Precisely controlled deformations and physicochemical properties of developed light-driven liquid crystal gels (LCGs) by Shahsavan et al. [81] promisingly control unhindered dynamic shape deformations and having substantial applications in technologies such as soft robots. The authors demonstrated different modes of underwater locomotion, by remotely actuating LCGs. Figure 12A schematically demonstrates the swimming mechanism of *Hexabranchnus sanguineus* (Spanish dancer) based on a large-scale bending undulation along its central trunk. Figure 12B illustrates the schematic hybrid molecular alignment summarizing undulating flexion of the trunk in sea slugs. Figure 12C represents the chemical structure of mesogenic monomers and the photothermal agent used to prepare LCGs by Shahsavan et al. [81]. From thermal actuation investigations and finite-element simulations, the authors predicted huge and fast photothermal actuation of LCG samples in aqua media at ambient conditions ( $23^\circ\text{C}$ ). the underwater bending of LCGs was performed by illuminating a 532-nm laser beam with different input powers. It was observed that the photothermal response of LCG-70 is almost 30 times higher than its pristine form. The studies revealed that the mechanical relaxation times in oscillatory mode is around 0.2 s [81].



**Figure 12.** Shape morphing in a sea slug and artificial monolithic analogs from liquid crystal gels (LCGs). (A) An *Hexabranchus sanguineus* (Spanish dancer) swimming with the bending undulation of its central trunk. (B) Schematic view of an artificial analog of the Spanish dancer's central trunk made from LCG constructs that move by repeating shape morphing. The relaxed state on the left side corresponds to a splay molecular alignment, while the bent state on the right side corresponds to the photothermally deformed LCG construct with disordered molecules. (C) The chemical structure of mesogenic monomers and the photothermal agent used to realize the light-fueled deformation of liquid crystalline networks (LCNs) and liquid crystalline gels (LCGs); X represents the amount of the 5CB added to the original LCN precursor mixture in weight percentage. Adapted with permission from Reference [81], National Academy of Sciences of the United States of America, 2020.

As depicted in Figure 13a,b, Xiong et al. constructed soft photo-actuators based on LCPs driven by sunlight. The authors prepared agarose polymer films with homogeneously dispersed F-azo-1 compound. The films were equipped with piezoelectric transducer is polyvinylidene difluoride (PVDF) at the edge as shown in Figure 13b. When the film was exposed to sunlight, the instantly generated bending movement of the films was transferred to the PVDF generator, resulting in an open-circuit alternating voltage signal. An alternating voltage signal of 0.164 V was generated by this solar actuator (F-azo@AG) for continuous sunlight illumination of 6 s [82]. It was noted that many researchers are actively involved in visible-light responsive azopolymers considering damaging effects of UV radiation. For photo-actuators, various mechanical motions such as twirling, bending, contraction, rotation, twisting, and other motions for photo-actuators can be triggered by

exposing to light. The most commonly observed phototropic plant; sunflower (*Helianthus annuus*) is the best example, which effectually responds to sunlight with mechanical motion [74,75,83]. Concerning the extendable durability, recently fluorinated azobenzene molecules [*ortho*-Fluoroazobenzene-(F-azo)] are synthesized and their remarkable stability was reported [84–86]. Excluding ultraviolet light stimulated photoisomerization, these F-azo compounds tune their transition from *trans* to *cis* form in visible wavelengths. Kumar et al. designed LC soft actuators with appropriate doping of F-azo-2 (Figure 13c) in addition to LC monomers and crosslinkers. The constructed films demonstrated their ability to self-propelling oscillatory motion upon sunlight exposure, as shown in Figure 13d [87].



**Figure 13.** (a–c) Chemical structures of F-azo compounds, (b) Schematic illustration of the conversion of sunlight into electric power by combining a solar actuator made of supramolecular film (composed of F-azo-1, hydrogen bonded with agarose polymer matrix) with a piezoelectric transducer. The piezoelectric transducer is polyvinylidene difluoride (PVDF). The bending of the actuator under solar irradiation leads to bending of the piezoelectric transducer and subsequent generation of electricity. Adapted with permission from Reference [82], The Royal Society of Chemistry, 2018, (d) Series of photos portraying self-oscillatory motion of the liquid crystalline (LC) film (made of F-azo-2 and other LC monomers) during sunlight exposure. Adapted with permission from Reference [87], Springer Nature, 2016.

Designing light-responsive soft actuators is quite challenging because the selection of materials for device applications involves the understanding of the inherent properties of chosen material. Many factors are to be considered for suitable importunities, such as response time, reversibility, cyclic stability, elastic modulus, etc., of used materials.

In addition to LC materials, shape-memory materials (SMMs) and polymer gels plays a significant role in designing light-driven actuators made of soft elastic materials [88]. In order to improve the response time of gel-type actuators driven by light, Tamesue et al. [89] and Takashima et al. [90] reported curdlan polymer gels with host–guest interactions (such as a linear high molecular-weight  $\beta$ -1,3-glucan, decorated with  $\alpha$ -cyclodextrins ( $\alpha$ -CDs) as hosts and a poly(acrylic acid) with azobenzene pendants as guests). The works reported by Harada and coworkers involve the design strategy of covalently crosslinked polyacrylamides decorated with both host  $\alpha$ -CDs and azobenzene moieties [91]. These novel supramolecular gel materials are significant in performing reversible photo-deformation for many successful cycles and with fast response time ( $<1$  s). Consequently, these supramolecular gel-actuators are fascinating and systems thereof suitable for artificial robots that can promisingly perform biomimicking sensitive gesticulations. Apart from azobenzene chromophores, some modified cyanine dyes and coordination complexes thereof can also have light absorption properties [92]. These dye-doped LCE systems can tune the material properties by synergic chemical bond interaction. In the future, the LCE systems with azobenzene monomers/crosslinkers with modified cyanine dyes and supramolecular gel materials decorated with azobenzene pendants can exhibit pronounced light absorption and photothermal properties, which can be useful in building soft robotic structures to perform biomimetic movements.

#### 4. Conclusions

In this short report, we have discussed the latest developments involving azobenzene chromophores based LCEs. There is a consensus view emerging that these azobenzene chromophores incorporated LC elastomeric scaffolds can be distinctively utilized for potential applications in robotic wireless actuators and sensors. Covalent linkages and alignment of azobenzene chromophore mesogens play a pivotal role in the dynamic actuation behavior of elastomers under the influence of light [62]. The tunable photomechanical response of CLCP films under a precise wavelength of light can provide a promising opportunity to develop programmable LCP actuators for robotic tactile sensations [77]. Bio-inspiration striving exciting development of light-responsive LCPs by mimicking dynamic 3D motions existing in nature creation. It seems that certainly there are still many interesting design approaches that are awaiting to develop azobenzene mesogens, and involving them in various supramolecular/macromolecular assemblies, which can dynamically tune its mechanical response triggered by broad wavelength range [93].

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#### References

1. Mayer, S.; Zentel, R. Liquid crystalline polymers and elastomers. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 545–551. [[CrossRef](#)]
2. Ula, S.W.; Traugott, N.A.; Volpe, R.H.; Patel, R.R.; Yu, K.; Yakachi, C.M. Liquid crystal elastomers: An introduction and review of emerging technologies. *Liq. Cryst. Rev.* **2018**, *6*, 78–107. [[CrossRef](#)]
3. Zentel, R. Liquid Crystal Elastomers. *Adv. Mater.* **1989**, *10*, 321–329. [[CrossRef](#)]

4. Küpfer, J.; Finkelmann, H. Liquid crystal elastomers: Influence of the orientational distribution of the crosslinks on the phase behaviour and reorientation processes. *Macromol. Chem. Phys.* **1994**, *195*, 1353–1367. [[CrossRef](#)]
5. Küpfer, J.; Finkelmann, H. Nematic liquid single crystal elastomers. *Die Makromol. Chemie Rapid Commun.* **1991**, *12*, 717–726. [[CrossRef](#)]
6. Bengs, H.; Finkelmann, H.; Küpfer, J.; Ringsdorf, H.; Schuhmacher, P. Highly oriented discotic elastomers. *Die Makromol. Chemie Rapid Commun.* **1993**, *14*, 445–450. [[CrossRef](#)]
7. Kundler, I.; Finkelmann, H. Strain-induced director reorientation in nematic liquid single crystal elastomers. *Macromol. Rapid Commun.* **1995**, *16*, 679–686. [[CrossRef](#)]
8. Finkelmann, H. Liquid single crystal elastomers (LSCE)—Mechanical optical and electric properties. *Macromol. Symp.* **1995**, *98*, 327. [[CrossRef](#)]
9. Brostow, W.; Walasek, J. Statistical thermodynamics of polymer liquid crystals: Competition between energetic and entropic effects. *J. Chem. Phys.* **1996**, *105*, 4367. [[CrossRef](#)]
10. Zubarev, E.R.; Kuptsov, S.A.; Yuranova, T.I.; Talroze, R.V.; Finkelmann, H. Monodomain liquid crystalline networks: Reorientation mechanism from uniform to stripe domains. *Liq. Cryst.* **1996**, *26*, 1531–1540. [[CrossRef](#)]
11. Brand, H.R.; Kawasaki, K. On the macroscopic consequences of frozen order in liquid single crystal elastomers. *Macromol. Rapid Commun.* **1994**, *15*, 251–257. [[CrossRef](#)]
12. Menzel, A.M.; Brand, H.R. Instabilities in nematic elastomers in external electric and magnetic fields. *Eur. Phys. J. E.* **2008**, *26*, 235–249. [[CrossRef](#)] [[PubMed](#)]
13. Brand, H.R.; Pleiner, H.; Martinoty, P. Selected macroscopic properties of liquid crystalline elastomers. *Soft Mater.* **2006**, *2*, 182–189. [[CrossRef](#)] [[PubMed](#)]
14. Krause, S.; Zander, F.; Bergmann, G.; Brandt, H.; Wertmer, H.; Finkelmann, H. Nematic main-chain elastomers: Coupling and orientational behavior. *Comptes Rendus Chimie* **2009**, *12*, 85–104. [[CrossRef](#)]
15. Rousseau, I.A.; Mather, P.T. Shape Memory Effect Exhibited by Smectic-C Liquid Crystalline Elastomers. *J. Am. Chem. Soc.* **2003**, *125*, 15300–15301. [[CrossRef](#)]
16. Lagerwall, J.P.F. An introduction to the physics of liquid crystals. In *Fluids, Colloids and Soft Materials: An Introduction to Soft Matter Physics*; Fernandez-Nieves, A., Puertas, A.M., Eds.; John Wiley & Sons, Inc: Hoboken, NJ, USA, 2016; pp. 307–340. [[CrossRef](#)]
17. Castles, F.; Morris, S.; Hung, J.; Qasim, M.M.; Wright, A.D.; Nosheen, S.; Choi, S.S.; Outram, B.I.; Elston, S.J.; Burgess, C.; et al. Stretchable liquid-crystal blue-phase gels. *Nat. Mater.* **2014**, *13*, 817–821. [[CrossRef](#)]
18. Algorri, J.F.; Zografopoulos, D.C.; Urruchi, V.; Sánchez-Pena, J.M. Recent Advances in Adaptive Liquid Crystal Lenses. *Crystals* **2019**, *9*, 272. [[CrossRef](#)]
19. Ghilardi, M.; Boys, H.; Török, P.; Busfield, J.J.C.; Carpi, F. Smart Lenses with Electrically Tuneable Astigmatism. *Sci. Rep.* **2019**, *9*, 16127. [[CrossRef](#)]
20. Kent, T.A.; Ford, M.J.; Markvicka, E.J.; Majidi, C. Soft actuators using liquid crystal elastomers with encapsulated liquid metal joule heaters. *Multifunct. Mater.* **2020**, *3*, 025003. [[CrossRef](#)]
21. Prévôt, M.E.; Ustunel, S.; Hegmann, E. Liquid Crystal Elastomers—A Path to Biocompatible and Biodegradable 3D-LCE Scaffolds for Tissue Regeneration. *Materials* **2018**, *11*, 377. [[CrossRef](#)]
22. Cladis, P.E. Phase Transitions in Liquid Crystalline Elastomers: A Fundamental Aspect of LCEs as Artificial Muscles. In *Interactive Dynamics of Convection and Solidification*; Ehrhard, P., Riley, D.S., Steen, P.H., Eds.; Springer: Dordrecht, The Netherlands, 2001. [[CrossRef](#)]
23. Blair, H.S.; McArdle, C.B. Photoresponsive polymers: 2. The monolayer behaviour of photochromic polymers containing aromatic azobenzene residues. *Polymer* **1984**, *25*, 1347–1352. [[CrossRef](#)]
24. Higuchi, M.; Minoura, N.; Kinoshita, T. Photo-responsive behavior of a monolayer composed of an azobenzene containing polypeptide in the main chain. *Colloid Polym. Sci.* **1995**, *273*, 1022–1027. [[CrossRef](#)]
25. Menzel, H.; Weichart, B.; Hallensleben, M.L. Langmuir-Blodgett-films of photochromic polyglutamates. *Polym. Bull.* **1992**, *27*, 637–644. [[CrossRef](#)]
26. Seki, T. Dynamic Photoresponsive Functions in Organized Layer Systems Comprised of Azobenzene-containing Polymers. *Polym. J.* **2004**, *36*, 435–454. [[CrossRef](#)]
27. Tschierske, C. Mirror symmetry breaking in liquids and liquid crystals. *Liq. Cryst.* **2018**, *45*, 2221–2252. [[CrossRef](#)]
28. Krasna, M.; Cvetko, M.; Ambrožič, M. Symmetry breaking and structure of a mixture of nematic liquid crystals and anisotropic nanoparticles. *Beilstein J. Org. Chem.* **2010**, *6*, 74. [[CrossRef](#)]
29. Lamy, X. Uniaxial symmetry in nematic liquid crystals. *Annales l'Institut Henri Poincaré (C) Non Linear Anal.* **2015**, *32*, 1125–1144. [[CrossRef](#)]
30. Emsley, J.W.; Lelli, M.; Joy, H.; Tamba, M.-G.; Mehl, G.H. Similarities and differences between molecular order in the nematic and twist-bend nematic phases of a symmetric liquid crystal dimer. *Phys. Chem. Chem. Phys.* **2016**, *18*, 9419–9430. [[CrossRef](#)]
31. Salamończyk, M.; Vaupotič, N.; Pocięcha, D.; Walker, R.; Storey, J.M.D.; Imrie, C.T.; Wang, C.; Zhu, C.; Gorecka, E. Multi-level chirality in liquid crystals formed by achiral molecules. *Nat. Commun.* **2019**, *10*, 1922. [[CrossRef](#)]
32. Shen, T.-Z.; Hong, S.-H.; Lee, J.-H.; Kang, S.-G.; Lee, B.; Whang, D.; Song, J.-K. Molecular Ordering: Selectivity of Threefold Symmetry in Epitaxial Alignment of Liquid Crystal Molecules on Macroscale Single-Crystal Graphene. *Adv. Mater.* **2018**, *30*, 1802441. [[CrossRef](#)]

33. Gallardo, H.; Cristiano, R.; Vieira, A.A.; Filho, R.A.W.N.; Srivastava, R.M.; Bechtold, I.H. Non-symmetrical luminescent 1,2,4-oxadiazole-based liquid crystals. *Liq. Cryst.* **2008**, *35*, 857–863. [CrossRef]
34. Han, J. 1,3,4-Oxadiazole based liquid crystals. *J. Mater. Chem. C* **2013**, *1*, 7779–7797. [CrossRef]
35. Alaasar, M. Azobenzene-containing bent-core liquid crystals: An overview. *Liq. Cryst.* **2016**, *43*, 2208–2243. [CrossRef]
36. Takezoe, H.; Eremin, A. *Bent-Shaped Liquid Crystals: Structure and Physical Properties*; CRC Press: Boca Raton, FL, USA, 2015; pp. 3–62.
37. Gimeno, N.; Pintre, I.; Martinez-Abadia, M.; Serrano, J.L.; Ros, M.B. Bent-core liquid crystal phases promoted by azo-containing molecules: From monomers to side-chain polymers. *RSC Adv.* **2014**, *4*, 19694–19702. [CrossRef]
38. Lu, J.; Zhang, Z.; Yan, D.; Zhang, Z.; Guan, J.; Qiao, J. Synthesis of 4-Chloro-1,3-Diazobenzene Bent-Cores Liquid Crystals and Characterizations of Their Mesogenic Behaviors and Photoisomerization Phenomena. *ChemRxiv* **2020**. preprint. [CrossRef]
39. Begum, N.; Kaur, S.; Xiang, Y.; Yin, H.; Mohiuddin, G.; Rao, N.V.S.; Pai, S.K. Photoswitchable Bent-Core Nematic Liquid Crystals with Methylated Azobenzene Wing Exhibiting Optic-Field-Enhanced Fréedericksz Transition Effect. *J. Phys. Chem. C* **2020**, *124*, 874–885. [CrossRef]
40. Kim, D.-Y.; Jeong, K.-U. Light responsive liquid crystal soft matters: Structures, properties, and applications. *Liq. Cryst. Today* **2019**, *28*, 34–45. [CrossRef]
41. Yang, J.; Zhao, W.; He, W.; Yang, Z.; Wang, D.; Cao, H. Liquid crystalline blue phase materials with three-dimensional nanostructures. *J. Mater. Chem. C* **2019**, *7*, 13352–13366. [CrossRef]
42. Hada, M.; Yamaguchi, D.; Ishikawa, T.; Sawa, T.; Tsuruta, K.; Ishikawa, K.; Koshihara, S.-y.; Hayashi, Y.; Kato, T. Ultrafast isomerization-induced cooperative motions to higher molecular orientation in smectic liquid-crystalline azobenzene molecules. *Nat. Commun.* **2019**, *10*, 4159. [CrossRef]
43. Wang, X.; Li, Z.; Zhao, H.; Chen, S. New azobenzene liquid crystal with dihydropyrazole heterocycle and photoisomerization studies. *R. Soc. Open Sci.* **2020**, *7*, 200474. [CrossRef]
44. Ube, T. Development of novel network structures in crosslinked liquid-crystalline polymers. *Polym. J.* **2019**, *51*, 983–988. [CrossRef]
45. Kondo, M. Photomechanical materials driven by photoisomerization or photodimerization. *Polym. J.* **2020**, *52*, 1027–1034, Early Access. [CrossRef]
46. Bi, M.; He, Y.; Wang, Y.; Yang, W.; Qin, B.; Xu, J.; Wang, X.; Wang, B.; Dong, Y.; Gao, Y.; et al. Photo Actuation Performance of Nanotube Sheet Incorporated Azobenzene Crosslinked Liquid Crystalline Polymer Nanocomposite. *Polymers* **2019**, *11*, 735. [CrossRef] [PubMed]
47. Yue, Y.; Norikane, Y.; Azumi, R.; Koyama, E. Light-induced mechanical response in crosslinked liquid-crystalline polymers with photoswitchable glass transition temperatures. *Nat. Commun.* **2019**, *9*, 3234. [CrossRef]
48. Li, X.; Wen, R.; Zhang, Y.; Zhu, L.; Zhang, B.; Zhang, H. Photoresponsive side-chain liquid crystalline polymers with an easily cross-linkable azobenzene mesogen. *J. Mater. Chem.* **2009**, *19*, 236–245. [CrossRef]
49. Ube, T.; Ikeda, T. Photomobile Polymer Materials with Complex 3D Deformation, Continuous Motions, Self-Regulation, and Enhanced Processability. *Adv. Opt. Mater.* **2019**, *7*, 1900380. [CrossRef]
50. Jiang, Z.; Xu, M.; Li, F.; Yu, Y. Red-light Controllable Liquid-Crystal Soft Actuators via Lowpower Excited Upconversion Based on Triplet-Triplet Annihilation. *J. Am. Chem. Soc.* **2013**, *135*, 16446–16453. [CrossRef]
51. Ikeda, T.; Nakano, M.; Yu, Y.; Tsutsumi, O.; Kanazawa, A. Anisotropic Bending and Unbending Behavior of Azobenzene Liquid-Crystalline Gels by Light Exposure. *Adv. Mater.* **2003**, *15*, 201–205. [CrossRef]
52. Yun, J.-H.; Li, C.; Kim, S.; Cho, M. Comparing Photo-Actuation of Azobenzene-Doped Nematic Liquid-Crystal Polymer Through Its Activation Mechanism: Trans-cis-trans Reorientation and Photoisomerization. *J. Phys. Chem. C* **2018**, *122*, 6310–6317. [CrossRef]
53. Garcia-Amorós, J.; Finkelmann, H.; Velasco, D. Influence of the photo-active azo cross-linker spacer on the opto-mechanics of polysiloxane elastomer actuators. *J. Mater. Chem.* **2011**, *21*, 1094–1101. [CrossRef]
54. Garcia-Amorós, J.; Martínez, M.; Finkelmann, H.; Velasco, D. Photoactuation and thermal isomerisation mechanism of cyanoazobenzene-based liquid crystal elastomers. *Phys. Chem. Chem. Phys.* **2014**, *16*, 8448–8454. [CrossRef] [PubMed]
55. Seankennedy. The Science Creative Quarterly (SCQ). Biomimicry/Bimimetics: General Principles and Practical Examples. Available online: <https://www.scq.ubc.ca/biomimicrybimimetics-general-principles-and-practical-examples/> (accessed on 6 July 2020).
56. Olsen, Z.J. The Design, Modeling, and Optimization of a Biomimetic Soft Robot for Fluid Pumping and Thrust Generation Using Electroactive Polymer Actuators. Master's Thesis, University of Nevada, Las Vegas, NV, USA, 2018. Available online: <https://digitalscholarship.unlv.edu/cgi/viewcontent.cgi?article=4304&context=thesisdissertations> (accessed on 6 July 2020).
57. Marchese, A.D.; Katzschmann, R.K.; Rus, D. A Recipe for Soft Fluidic Elastomer Robots. *Soft Robot.* **2015**, *2*, 7–25. [CrossRef] [PubMed]
58. Jiang, H.; Li, C.; Huang, X. Actuators based on liquid crystalline elastomer materials. *Nanoscale* **2013**, *5*, 5225–5240. [CrossRef] [PubMed]
59. Wen, Z.; Yang, K.; Raquez, J.-M. A Review on Liquid Crystal Polymers in Free-Standing Reversible Shape Memory Materials. *Molecules* **2020**, *25*, 1241. [CrossRef]
60. Ohm, C.; Brehmer, M.; Zentel, R. Liquid Crystalline Elastomers as Actuators and Sensors. *Adv. Mater.* **2010**, *22*, 3366–3387. [CrossRef]

61. Barrett, C.J.; Mamiya, J.-i.; Yager, K.G.; Ikeda, T. Photo-mechanical effects in azobenzene containing soft materials. *Soft Matter* **2007**, *3*, 1249–1261. [[CrossRef](#)]
62. Yu, Y.L.; Nakano, M.; Ikeda, T. Directed bending of a polymer film by light—Miniaturizing a simple photomechanical system could expand its range of applications. *Nature* **2003**, *425*, 145. [[CrossRef](#)]
63. Zhou, H.; Xue, C.; Weis, P.; Suzuki, Y.; Huang, S.; Koynov, K.; Auernhammer, G.K.; Berger, R.; Butt, H.-J.; Wu, S. Photoswitching of glass transition temperatures of azobenzene-containing polymers induces reversible solid-to-liquid transitions. *Nat. Chem.* **2017**, *9*, 145–151. [[CrossRef](#)]
64. Akiyama, H.; Yoshida, M. Photochemically reversible liquefaction and solidification of single compounds based on a sugar alcohol scaffold with multi azo-arms. *Adv. Mater.* **2012**, *24*, 2353–2356. [[CrossRef](#)]
65. Norikane, Y.; Uchida, E.; Tanaka, S.; Fujiwara, K.; Koyama, A.R.; Akiyama, H.; Kihara, H.; Yoshida, M. Photoinduced crystal-to-liquid phase transitions of azobenzene derivatives and their application in photolithography processes through a solid–liquid patterning. *Org. Lett.* **2014**, *16*, 5012–5015. [[CrossRef](#)]
66. Finkelmann, H.; Rehage, G. Investigations on liquid crystalline polysiloxanes, 2. Optical properties of cholesteric phases and influence of the flexible spacer on the mobility of the mesogenic groups. *Die Makromol. Chem. Rapid Commun.* **1980**, *1*, 31. [[CrossRef](#)]
67. White, T.J.; Broer, D.J. Programmable and adaptive mechanics with liquid crystal polymer networks and elastomers. *Nat. Mater.* **2015**, *14*, 1087–1098. [[CrossRef](#)] [[PubMed](#)]
68. Liu, D.Q.; Bastiaansen, C.W.M.; den Toonder, J.M.J.; Broer, D.J. Photo-Switchable Surface Topologies in Chiral Nematic Coatings. *Angew. Chem. Int. Ed.* **2012**, *51*, 892–896. [[CrossRef](#)] [[PubMed](#)]
69. Yamada, M.; Kondo, M.; Mamiya, J.-I.; Yu, Y.; Kinoshita, M.; Barrett, C.J.; Ikeda, T. Photomobile polymer materials: Towards light-driven plastic motors. *Angew. Chem. Int. Ed.* **2008**, *47*, 4986–4988. [[CrossRef](#)]
70. Pang, X.; Lv, J.-a.; Zhu, C.; Qin, L.; Yu, Y. Photodeformable Azobenzene-Containing Liquid Crystal Polymers and Soft Actuators. *Adv. Mater.* **2019**, *31*, 1904224. [[CrossRef](#)]
71. Yu, Y.L.; Nakano, M.; Ikeda, T. Photoinduced bending and unbending behavior of liquid-crystalline gels and elastomers. *Pure Appl. Chem.* **2004**, *76*, 1467. [[CrossRef](#)]
72. Braun, L.B.; Linder, T.G.; Hessberger, T.; Zentel, R. Influence of a Crosslinker Containing an Azo Group on the Actuation Properties of a Photoactuating LCE System. *Polymers* **2016**, *8*, 435. [[CrossRef](#)] [[PubMed](#)]
73. Habib, M.K.; Watanabe, K.; Izumi, K. Biomimetics Robots from Bio-inspiration to Implementation. In Proceedings of the IECON 2007—33rd Annual Conference of the IEEE Industrial Electronics Society, Taipei, Taiwan, 5–8 November 2007; pp. 143–148. [[CrossRef](#)]
74. Mazzolai, B.; Beccai, L.; Mattoli, V. Plants as model in biomimetics and biorobotics: New perspectives. *Front. Bioeng. Biotechnol.* **2014**, *2*, 2. [[CrossRef](#)] [[PubMed](#)]
75. Snell-Rood, E. Interdisciplinarity: Bring biologists into biomimetics. *Nature* **2016**, *529*, 277–278. [[CrossRef](#)] [[PubMed](#)]
76. Cho, K.-J.; Wood, R. Biomimetic Robots (Chapter 23). In *Springer Handbook of Robotics*, 2nd ed.; Springer: Berlin/Heidelberg, Germany, 2008; pp. 543–551.
77. Albu-Schäffer, A.; Bicchi, A. Actuators for Soft Robots (Chapter 21). In *Springer Handbook of Robotics*, 2nd ed.; Springer: Berlin/Heidelberg, Germany, 2008; pp. 499–501.
78. Iamsaard, S.; Aßhoff, S.J.; Matt, B.; Kudernac, T.; Cornelissen, J.J.L.M.; Fletcher, S.P.; Katsonis, N. Conversion of light into macroscopic helical motion. *Nat. Chem.* **2014**, *6*, 229–235. [[CrossRef](#)]
79. Lee, K.M.; Smith, M.L.; Koerner, H.; Tabiryan, N.; Vala, R.A.; Bunning, T.J.; White, T.J. Photodriven, Flexural–Torsional Oscillation of Glassy Azobenzene Liquid Crystal Polymer Networks. *Adv. Funct. Mater.* **2011**, *21*, 2913–2918. [[CrossRef](#)]
80. Wang, M.; Lin, B.-P.; Yang, H. A plant tendril mimic soft actuator with phototunable bending and chiral twisting motion modes. *Nat. Commun.* **2016**, *7*, 13981. [[CrossRef](#)]
81. Shahsavan, H.; Aghakhani, A.; Zeng, H.; Guo, Y.; Davidson, Z.S.; Priimagi, A.; Sitti, M. Bioinspired underwater locomotion of light-driven liquid crystal gels. *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 5125–5133. [[CrossRef](#)] [[PubMed](#)]
82. Xiong, Y.; Zhang, L.; Weis, P.; Naumov, P.; Wu, S. A solar actuator based on hydrogen-bonded azopolymers for electricity generation. *J. Mater. Chem. A* **2018**, *6*, 3361. [[CrossRef](#)]
83. Briggs, W. How do sunflowers follow the Sun—And to what end? *Science* **2016**, *353*, 541–542. [[CrossRef](#)] [[PubMed](#)]
84. Bushuyev, O.S.; Tomberg, A.; Friščić, T.; Barrett, C.J. Shaping crystals with light: Crystal-to-crystal isomerization and photomechanical effect in fluorinated azobenzenes. *J. Am. Chem. Soc.* **2013**, *135*, 12556–12559. [[CrossRef](#)]
85. Bléger, D.; Schwarz, J.; Brouwer, A.M.; Hecht, S. o-Fluoroazobenzenes as readily synthesized photoswitches offering nearly quantitative two-way isomerization with visible light. *J. Am. Chem. Soc.* **2012**, *134*, 20597–20600. [[CrossRef](#)]
86. Knie, C.; Utecht, M.; Zhao, F.; Kulla, H.; Kavalenko, S.; Brouwer, A.M.; Saalfrank, P.; Hecht, S.; Bléger, D. Ortho-fluoroazobenzenes: Visible light switches with very long-lived z isomers. *Chem. Eur. J.* **2014**, *20*, 16492–16501. [[CrossRef](#)]
87. Kumar, K.; Knie, C.; Bléger, D.; Peletier, M.A.; Friedrich, H.; Hecht, S.; Broer, D.J.; Debile, M.G.; Schenning, A.P.H.J. A chaotic self-oscillating sunlight-driven polymer actuator. *Nat. Commun.* **2016**, *7*, 11975. [[CrossRef](#)]
88. Mauro, M. Gel-based soft actuators driven by light. *J. Mater. Chem. B* **2019**, *7*, 4234–4242. [[CrossRef](#)]
89. Tamesue, S.; Takashima, Y.; Yamaguchi, H.; Shinkai, S.; Harada, A. Photoswitchable Supramolecular Hydrogels Formed by Cyclodextrins and Azobenzene Polymers. *Angew. Chem. Int. Ed.* **2010**, *49*, 7461. [[CrossRef](#)]

90. Takashima, Y.; Nakayama, T.; Miyauchi, M.; Kawaguchi, Y.; Yamaguchi, H.; Harada, A. Complex Formation and Gelation between Copolymers Containing Pendant Azobenzene Groups and Cyclodextrin Polymers. *Chem. Lett.* **2004**, *33*, 890. [[CrossRef](#)]
91. Takashima, Y.; Hatanaka, S.; Otsubo, M.; Nakahata, M.; Kakuta, T.; Hashidzume, A.; Yamaguchi, H.; Harada, A. Expansion–contraction of photoresponsive artificial muscle regulated by host–guest interactions. *Nat. Commun.* **2012**, *3*, 1270. [[CrossRef](#)]
92. Qin, B.; Yang, W.; Xu, J.; Wang, X.; Li, X.; Li, C.; Gao, Y.; Wang, Q.-e. Photo-Actuation of Liquid Crystalline Elastomer Materials Doped with Visible Absorber Dyes under Quasi-Daylight. *Polymers* **2020**, *12*, 54. [[CrossRef](#)] [[PubMed](#)]
93. Wie, J.J.; Shankar, M.R.; White, T.J. Photomotility of polymers. *Nat. Commun.* **2016**, *7*, 13260. [[CrossRef](#)] [[PubMed](#)]