Liquid Crystal Polymer-Based Soft Robots

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Soft robots outperform the conventional robots on enhanced safety for human–machine interaction, environmental adaptability, and continuous deformation. In this blooming area of fundamental and technological importance, liquid crystal polymer networks and liquid crystal elastomers (referred to as LCNs) have emerged as one of the most valuable candidates for soft robots due to their complex, large, and reversible shape change capabilities. To date, much research effort, mainly regarding chemical synthesis, fabrication technologies and soft robot design, has been dedicated to LC robotic systems to endow them with versatile and complex actions controlled by various stimuli. Herein, starting with the principle that governs the stimuli-responsiveness of LCNs, recent progress made in LCN soft robots is summarized while focusing on different robotic motions, such as grasping, walking, swimming, and oscillation. Especially, novel LCNs with intelligent functions such as reprocessability, reconfigurability, self-regulating behavior and associative learning capability, are highlighted. This article aims to provide significant insights into the design and development of LCN-based soft robots.

1. Introduction

Robots are artificial intelligent machines capable of carrying out complex actions automatically according to human’s command or preprogrammed programs, which have made a great contribution to industrial development. In general, constructed from rigid metal or resin, robots have poor environmental adaptability, low safety for interaction with humans, and lack of freedom for smooth and continuous actuation. Inspired by creatures in nature, scientists have begun to explore soft-robotic systems, whose joints and body are made from soft and pliable materials similar to biological tissues. Due to the flexible joints and body, soft robots can easily handle objects and structures that are soft, delicate, and sophisticated in shape with no need for complex control algorithm. In terms of safety and security, a soft body is less likely to hurt people during the human–machine interaction, and can absorb most impact energy through deformation to avoid damage to the robot itself. Due to these characteristics, recently developed soft robots are able to perform various tasks in complex spaces, grip arbitrary-shaped objects, mimic biological behaviors, and thus provide potential applications for various disciplines such as biomedicine, bionics engineering, lab-on-chip chemistry, micromanipulation, and aeronautics.

Recent research results indicate that stimuli-responsive soft matters are excellent candidates for making soft robotics, because they offer great potential to integrate sensors, actuators, and control systems into the millimeter- or even micrometer-scale soft supportive bodies. Among the variety of soft materials explored so far, liquid crystal polymers, in the form of liquid crystal networks or elastomers (abbreviated as LCNs hereafter) have gained much attention for flexible actuator and soft robotic applications thanks to their unique properties such as rapid stimuli responsiveness, anisotropic deformation, excellent elasticity and flexibility as well as order–disorder phase-transition-induced shape change. LCNs are usually prepared by first aligning the rod-like mesogens uniaxially or organizing the LC director orientation into specific 2D or 3D profiles, through mechanical stretching, surface effects, and electric or magnetic fields, and then carrying out polymer chain crosslinking to retain the shape of LCN in the oriented state. Upon the order–disorder phase transition induced by external stimuli (such as temperature, light, pH, moisture, electric or magnetic fields), anisotropic LCNs can exhibit large and reversible shape change with fast response speed. Depending on the arrangement and orientation state of mesogens within polymer networks, monolithic LCNs can display various predesignated deformations including bending, rolling, twisting, walking, and oscillating. The achievable actuation complexity can be further extended by other means, such as spatial/temporary modulation of stimuli or patterned bi-/multi-layer structures. As a result, versatile modes of actuation and sensing have led to many breakthroughs in the research and development of the soft robotic systems based on LCNs.

The goal of this review is to provide an overview of mechanisms and working principles of LCN soft robotic systems. The review is organized as follows. First, the principle and methods of applying different stimuli to achieve versatile reversible shape change of LCNs are summarized and discussed. Second, LCN soft robots capable of doing mechanical work or mimicking locomotion are classified and elaborated according to their applications. Finally, we focus on the potential of developing

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the next-generation LCN soft robots enabled by materials innovation, advanced processing technologies, and ingenious structural/functional design. We hope this article can provide some guidance and help people who are interested in LCN materials and soft robots and can stimulate more creative work in this field.

2. Actuation Stimuli

LCNs can respond to a variety of stimuli, such as heat, light, humidity, etc., and, as a result, undergo a shape change. The shape-changing of liquid crystal elastomers (LCEs) is associated with stimuli-induced order–disorder phase transition of the mesogens and the concomitant polymer chain conformational change. As the stimulus response of LCNs is the basis for the complex deformations and motions of all LCN robots, we will briefly introduce the main shape-changing mechanisms and representative examples of LCNs under the stimulation of the most used stimuli.

2.1. Temperature-Responsiveness and Deformation Modes of LCNs

All LCNs are thermoresponsive because the reversible order–disorder phase transition of the mesogens, between an LC phase and the isotropic state, can be induced by heating and cooling. This motion of molecules is translated into a macroscopic shape change. In the simplest case of an LCN strip with a uniaxial orientation of mesogens, as shown in Figure 1A, once heated above the order–disorder phase-transition temperature ($T_{lc-is}$), the mesogen alignment is lost, which imposes the random coil conformation for polymer chains. As a result, the LCE strip exhibits contraction along the alignment direction and expansion in the lateral direction. On subsequent cooling to the LC phase, the LCN recovers the ordered state and, due to the memory effect from polymer chain crosslinking, returns to the original shape.\cite{26,38} All in all, fulfilling two conditions—alignment of mesogens and polymer chain crosslinking—thermally induced mechanical responses can be observed in LCNs. Controlling these two factors during the processing or fabrication process of LCN actuators can effectively customize their resultant shape changes and actuation behaviors.

By spatially configuring mesogen orientation state, LCNs can achieve complex and precise thermally induced reversible deformations. As shown in Figure 1B, the LCN strip with splay alignment (containing a homeotropic side and a homogeneous side) can display bending– unbending deformation due to the coexistence of an extensional force and a contraction force arising from the vertical alignment side and the parallel alignment side, respectively, upon order–disorder phase transition.\cite{23,39,40}

Typically, the splay alignment is obtained using reactive mesogens (mesogenic monomers); when the polymerization temperature is above room temperature, the film may exhibit an initial curvature toward the homeotropic side due to the increased order on cooling to room temperature. On subsequent heating to the isotropic phase, the bent strip can be unbent or even further bends toward the homeotropic side. In contrast, if the mesogens are arranged to adopt a twist orientation, the monolithic LCN film can transform into saddle geometry upon heating as the two sides are subjected to orthogonal contraction forces. Likewise, if the orientation of mesogens is offset to the principal axes of an LCN ribbon, the thermal response can generate torsion, yielding helicoidal or spiral shape.

Patterned crosslinking of LCNs with uniaxial mesogen alignment is another effective method to program complex 3D shape from a flat sheet. In this way, crosslinking is made to occur only in selected area, uniaxially aligned LCNs contain spatially distributed crosslinked and uncrosslinked regions; the former is actuation domain that is responsible for the reversible shape changes associated with the LCE-isotropic transition, whereas the latter has no actuation response (nonactuation domains). Thus, when heating above or cooling below the $T_{lc-is}$, the actuation and nonactuation domains within a single film will generate unbalanced contraction/extension force field throughout the film, leading to the targeted complex shape morphing. Using this approach, our group synthesized a liquid crystal polyester containing photodi- merizable cinnamic acid moieties for photo-crosslinking.\cite{23} As shown Figure 1C, by adjusting irradiating time or using customized photomasks, the depths, sizes, or shapes of the crosslinking regions of the uniaxially oriented LCN sample can be controlled. Upon LC–isotropic phase transition, the nonuniform optical inscripion LCN film can lead to versatile 2D-to-3D shape transformations (such as rolling, helix, and so on).

2.2. Light-Controlled LCNs

Light is a clean and versatile energy source with high temporal and spatial control capabilities. As a stimulus, it allows remote, instant, precise, and contactless control of soft robots. In addition, the intensity, wavelength, and polarization of light can be adjusted or optimized for specific needs of the practical applications.\cite{41,42} Hence, light has aroused great interest and emerged as a particularly widely used energy source in soft-robot applications. Thanks to these features, the use of light to drive soft robotic motions also enables miniaturization, simplified design, rapid response, multifaceted controllability, and even the self-regulation of soft robots. Optical remote and wireless control helps the robot to get rid of the electric power, sensing and control systems, reduce the threshold power-to-weight ratio, and achieve miniaturization of soft robots. In addition, light not only provides energy but also time-varying and localized mechanical responses (through light scanning and/or structured light fields), which enables complex and flexible motion based on simplified design. Many LCNs exhibit fast optical response that facilitates real-time control of deformation and movement. Furthermore, light allows multi-facet controllability; for example, selectively addressing various regions of a soft robot using light of different wavelengths, tuning the magnitude of the response through changing light intensity, and directing the bending direction of LCNs by polarization direction of light. More interestingly, the directionality of light field can provide opportunities for active light–matter interactions for autonomous and self-regulating behaviors.

In general, photoresponsive LCNs can be driven photochemically or photothermally. Photochemical mechanisms mainly involve azobenzene (AZO) derivatives as mesogens that can undergo $trans\rightarrow cis$ photosomerization to reversibly control the LC order in LCNs. Under ultraviolet (UV) irradiation, AZO
Figure 1. A) Schematic illustration of temperature-responsive reversible elongation-contraction of LCNs with uniaxial alignment. B) Schematic illustration of reversible bending/unbending of LCNs with splay and twisted alignment caused by order–disorder phase transition. Reproduced with permission. Copyright 2015, Springer Nature. C) Schematic of the photo-patterning strategy for optical inscription of complex actuation modes in LCNs with uniaxial LC alignment (top) and photographs showing examples of shape morphing (down). Note that the light used here is for material preparation, while the obtained LCNs are actuated via temperature changes. Schematic illustration of photo-responsive LCNs based on D) photochemical mechanism and E) photothermal mechanism. Schematic illustration showing the mechanism of humidity-responsiveness based on F) a hygroscopic polymer salt or G) a hydrophobic LCNs. Schematic illustration of electromechanical effects based on H) molecular reorientation in a LCN gel, and I) electrothermally driven molecular order change. (C) Reproduced with permission. Copyright 2017, Wiley-VCH. (G) Reproduced with permission. Copyright 2017, Wiley-VCH.
mesogens in the trans form are converted to the cis isomer, accompanied by a molecular configuration change from a “rod-like” shape that is compatible with ordered LC phase to a bent shape that tends to disrupt LC order (Figure 1D). This can lead to order–disorder transition and free volume change. In addition, the decrease in the molecular length of the AZO from 9 Å (trans-AZO) to 5.5 Å (cis-AZO) induces network stresses determined by cis-AZO content. Due to the high molar extinction coefficient for AZO absorption, usually the photochemically induced order–disorder transition occurs in the surface region, which results in bending motion of the AZO–LCN film. The trans form can then be recovered upon visible light absorption or heating, restoring the LCN to its original shape. Due to the adverse health effects of UV light, AZO derivatives with trans–cis photoisomerization driven by visible light have been developed to address the wavelength issue.

Photothermal effect is also highly efficient to trigger the order–disorder phase transition of LCNs and thus their photoactuation behaviors. Commonly used photothermal agents in LCNs include gold nanoparticles or nanorods, carbon nanotubes (CNTs), graphene, organic dyes, and conjugated polymers. These components can effectively absorb visible light and/or near infrared (NIR) light and convert optical energy into thermal energy, releasing heat that increases the LCN temperature above \( T_{LC-isom} \) and initiates mechanical deformation. Compared with direct heating, the optical heating conserves all the appealing features of light stimulus, i.e., enabling localized and remote stimulation, and thus provides great convenience for achieving light-driven locomotion of soft robots. Localized contraction/extension of an LCN strip occurs upon photothermally induced order–disorder transition if the optical heating is uniform throughout the region exposed to light. In reality, a temperature gradient is often formed along the strip thickness direction with imbalanced contraction forces on the two sides, which results in bending as shown in Figure 1E. It is also worth noting that although in most cases photothermal agents are loaded in LCNs, it is possible to chemically incorporate dye moieties with high quantum yield of optical–thermal energy conversion into the polymer structure. In fact, many reports indicate that both photochemical and photothermal effects contribute to the photoactuation of LCN soft robots containing AZO derivatives.

With different photoactuation mechanisms, the applications of optically driven LCN soft robots are different. Although photothermal effect-based actuation behavior can be used to achieve locomotion in the air, photochemically driven deformation, which requires relatively low light intensities, is more suitable for locomotion in water when heat loss is significant. Compared with LCNs involving photochemical mechanisms, the preparation of photothermal LCNs is easier and more versatile typically. Also, it is facile to adjust the wavelength used, ranging from UV to NIR light which facilitates the applications. Photothermal mechanisms allow for fast and reversible actuation, as well as actuation of thick actuators via heat transfer.

### 2.3. Humidity-Responsive LCNs

Among the stimuli known for actuator, the use of moisture or water has the advantages of being green, inexpensive, and actuating under mild or moderate conditions. In this regard, humidity-responsive LCNs have been demonstrated by incorporating hydrophilic hydrogen-bonded carboxylic acid dimers. After being treated with alkaline solution, the LCN film with uniaxial orientation can convert to hydroscopic polymer salt, which can absorb water and swell mostly perpendicular to the alignment director. Such humidity-responsive actuator with bending behavior can be prepared by bringing only one side of LCN film in contact with basic solution. When the base-treated side faces the humidity, the anisotropic swelling of the base-treated side causes bending of the film toward the untreated side (Figure 1F). Controlling the base-treated areas and LC director field of the LCN, more complex shape-changing behavior, such as folding and curling, can be achieved. In contrast to most humidity-responsive LCNs containing salt units, Yu and coworkers demonstrated humidity-responsive behavior on a hydrophobic LCN (water contact angle: 91.5°).

### 2.4. Electro-Responsive LCNs

Electrical energy is another highly controllable stimulus in addition to light, which can be programmed in terms of magnitude, frequency, and phase before being applied. Electrical-actuation of LCNs can be realized based on different mechanisms. Direct electromechanical effects can be generated via the molecular (or nanofillers) reorientation in a strong electric field, based on the inherent molecular dielectric anisotropy of LCNs, or the polarization of the LCNs or LCN nanocomposites. Based on the same mechanism, low-modulus LC gels (LCGs) could allow larger strain with lower electric field strength, because of the reduced intermolecular friction and easier rotation of the mesogens. On the other hand, as soft and elastomeric materials, LCNs could also be actuated via other classical mechanisms, similar to those of dielectric elastomers and ionic electroactive polymers. In particular, the programmable mechanical anisotropy of the LCNs based on their molecular alignments can be combined with these mechanisms to achieve complex shape changes.

Among the electrically driven systems based on LCNs, electrothermal LCNs relying on Joule heating effect can produce quick response and large deformation in dry materials with low electric current or voltage input, and thus are very promising for soft robotic applications. As an indirect heating strategy, electrothermal LCNs enable local and efficient temperature control over the order–disorder phase transition of mesogens that trigger the reversible shape change or motion. Compared with the photoinduced actuation of LCNs where light penetration depth is
limited, the electric energy can be used to heat a thick LCN film uniformly. In addition, selective and sequential actuation of robot body parts driven by electric energy can also be achieved based on the configuration or patterning of implemented heating elements.

Indeed, to construct LCN-based electrothermal soft robots, the incorporation of heating elements into LCNs, such as deformable heaters or conductive nano-/macro-fillers, is essential. Contraction/extension can be realized through a conductive LCN composite or an LCN with thin and flexible heaters (Figure 1H). Bending motion can be implemented through LCN-based bilayer or multi-layer actuators with sandwiched heaters. Twisting and many other shape morphs driven by electric power are also achievable using LCNs. For example, Schuhladen et al. fabricated a 0.3 mm thick, radially oriented LCN iris embedded with stretchable heaters in a radial magnetic field. This LCN can realize electrically driven radial contraction/expansion, similar to the opening/closing of the human iris. Using LCN-based electrothermal actuators as active hinges, sophisticated architectures such as soft airplane and Miura-Ori structures were constructed. Yu and coworkers demonstrated complex shape evolutions of an electrothermal actuator by locally activating and sequentially addressing its multiple sets of independent heating elements. Recently, Majidi and coworkers reported an electrothermal LCN composite with dispersed liquid metal (LM) microdroplets. Unlike the previous LCN composites with rigid components, the liquid state of LM allows the LCN to maintain its mechanical compliance even with up to 50 vol% of LM. The high content of LM in the LCN improves the thermal and electrical conductivity of the material, which ensures large reversible deformation at relatively low voltage. Furthermore, this LCN composite allows for the autonomous reconstruction of the conductive traces after mechanical damage, thus showing robust electronic connectivity.

3. LCN Robots Doing Mechanical Work and Moving

The reversible shape change of LCN under various stimuli, if judiciously designed and engineered, can serve the purpose of performing mechanical work in various forms, for example, grasping/manipulating objects, translating and transporting, acting as smart switches or energy converters. For different application purposes encompassing a range of motion modes and degrees of freedom control, the corresponding requirements of material properties, stimulation control, and engineering design are different. For example, the reversible shape change of the actuator (usually fixed) that interacts with a target object is responsible for object grasping and releasing, whereas the dynamic interaction between the deforming actuator and environment can drive the locomotion of the actuator. Here, we review and discuss LCN actuators functioning in several major applications.

3.1. Artificial Muscles

As one promising candidate for artificial muscles, LCNs, especially those with a uniaxial LC orientation, can exert muscle-like contractile motion with high strains (up to 400%) and considerable actuation stress. Typically, LCN actuators exhibit a weight-lifting ratio, which is defined as the ratio of the weight of the load to the weight of the actuator, ranging from hundreds to thousands. The contraction force induced by the stimuli contributes to the load lifting, which, upon the removal of the stimuli or application of another stimulation, recovers to stress-free state and lowers down the loads, completing a lifting and lowering down cycle.

It should be noted that, accompanying the order–disorder transition, not only the stored free energy can be released but also the material undergoes significant changes in mechanical properties. Specifically, due to the disrupted intermolecular interactions upon the LC–isotropic phase transition, LCNs become very soft (elastic modulus 0.1–1 MPa compared to 10–60 MPa of skeletal muscles), thus they are incapable to produce satisfactory force at this stage. To address this problem, Yang and co-workers developed an ultra-strong interpenetrating LCN, in which loosely crosslinked main-chain LCN network contributes to the essential actuation function while highly crosslinked thermoset LCN network serves as a framework to retain chain anisotropy and good mechanical strength to a certain extent beyond the Tc [17]. By virtue of such material design, as shown in Figure 2A, the IPN–LC can lift up a load (≈605.02 g) 30 100 times heavier than itself over 40% strain, and achieves the highest records of LCNs in terms of actuation blocking stress (2.53 MPa), actuation work capacity (1267.7 kJ m⁻³), breaking strength (7.9 MPa), and elastic modulus (10.4 MPa), which make the material a very promising candidate for artificial skeletal muscles.

In addition to the tensile actuators based on the in-plane contraction/extension, LCNs with out-of-plane bending or complex deformation that forms multiple supporting points can generate displacement relative to the material thickness and act as weightlifters. White and co-workers reported a flat LCN film with an array of azimuthal +1 topological defects that can transform into a multi-cone 3D shape upon heating, pushing up a plate 147 times heavier than itself to a height that is ≈3000% of the initial film thickness (50 μm). Moreover, laminating multiple layers of LCN films can greatly improve the actuation force and work capacity of the LCN weightlifter without sacrificing its large stroke.

3.2. Gripper

Compared with rigid robotic grippers, there are many advantages of using soft materials to build grippers: handling safely delicate and fragile objects, providing shape adaptability when in contact with objects, realizing flexible control with high motion freedom through simple control inputs, reducing the complexity and cost of the system, and facilitating device miniaturization. Among various soft grippers, LCN-based grippers have some significant features. First, the setup involved is simplified (e.g., for light-controlled grippers), so that LCN grippers can be miniaturized to centimeter or even micrometer scales for manipulating tiny objects such as powders. Second, LCN grippers can be easily integrated with other small-scale actuators to obtain soft robots of multifunctionalities (e.g., controlled lifting and transporting).
Moreover, LCNs allow the reconfiguration of grippers and even can be further devised to intelligently “recognize” and capture different objects (see Section 4.3). To catch static objects, the reversible shape change of the actuator-bending (in most cases) or twisting deformation of LCN strips as well as expansion/contraction of LCN tubes—can be exploited.

The simplest and most common type is constructing a hand-like device containing two or more bendable LCN-based strips, which can be controlled by external stimuli to close/open for grabbing/releasing motion, respectively. When gripped, the contact of the LCN strips with the object provides a static friction force high enough to overcome the gravitational force of the object, allowing it to be lifted/transfered. It should be noted that maintaining stable closure state of the gripper requires either continuous energy input or not. For example, Priimagi and co-workers developed a gripper which, on the one hand, can catch and release the object upon red light on/off based on only photothermal effect; or, on the other hand, catch and hold the object stably upon red light on/off when extra photoinduced stress is pre-stored via UV-induced trans–cis isomerization of AZO mesogens before being photothermally released (Figure 2B). The stability of the gripping state is inherently proportional to the lifetime of the cis-azobenzene.[78]

Taking advantage of the bistable-state actuation mechanism, self-locking grippers, i.e., those that can hold the gripping state in the absence of continuous energy supply, can also be achieved by utilizing the initial shape (stimuli-off state) of the gripper to grasp the objects. An example demonstrated by our group is a self-locking gripper exploiting the power-off state to grab, lift, and secure objects (Figure 2C).[79]
of the reprogramability of our LCN actuator, an electrothermal soft gripping device assembled from a bi-coil shaped “hand” and a helical “arm” was fabricated. Sequentially powering on/off, the two parts can induce a series of actions including “hand” open, “arm” stretching, “hand” closing and “arm” retrieving, which enable gripping and lifting of the object. Specifically, a 72 mg gripper grasped and lifted a 252 mg object and held it at a height of 1.3 cm from the surface. In virtue of the power-off shape of the actuator, the gripper can stably hold and lift the object for a long time (at least a few days), before lowering down and releasing the objects are needed. In practical applications, self-locking grippers could be more appealing because they can grab objects without energy consumption and make the manipulating process easier.

Assembled gripping devices allow for object manipulation in addition to its catching/releasing. When integrated with an “arm” capable of contraction/extension or winding/unwinding, the gripped objects can be moved up and down, accompanied by a rotational movement in the latter case. When integrated with multiple individually addressable segments that can bend/unbend, grippers with movements of higher degree of freedom can be prepared. For example, Yu and co-workers utilized bilayer actuators containing azotolane-LCN and polyethylene (PE) to construct a visible-light-controlled gripping device. The gripper consists of three parts: a “hand” for picking the object, an “arm”, and a “wrist” that can bend independently and oppositely for moving the object both horizontally and vertically and placing it in a container. Coating a small magnetic iron-containing layer to the center of the splay-aligned LCN, Schenning and co-workers demonstrated a gripper with photo-controlled cargo gripping/releasing and magnetically guided locomotion. The gripping system holding a 1.1 times heavier object can translate and rotate flexibly due to the magnetic field induced force (Figure 2D). Other soft robots that assemble gripping and locomotive components to achieve both cargo grabbing and transportation functionalities are discussed later. The added mobility of the devices could free the grippers from the necessity of manual operation.

3.3. Walker, Roller, and Jumper

Soft organisms and insects such as caterpillars, inchworms, snails, and earthworms can deform their bodies to navigate in complex 3D environments. They display diversified locomotion manners, such as walking, climbing, rolling, crawling, jumping and creeping, providing numerous inspirations for researchers to develop locomotive soft robots. With a soft body, these locomotive systems can execute motions with high degree of freedom under simple control signals and modify their body deformation adapt to the surroundings, such as squeezing through a narrow space, and even scaling down to micrometer sizes. For a soft robot to successfully move from one place to another, the main problem and consideration is to effectively transform its reversible shape change into controllable and directional displacement. In general, the deformation of LCN-based soft robot produces a spatiotemporally varying interaction between the soft robot and the surface of the environment. During one reversible deformation cycle, the asymmetry in the forces being imposed on the soft robot is required to create a net position shift in a specific direction. Asymmetric factors can be imposed on the soft robot itself to generate asymmetric friction between the soft body and interfaces, e.g., reducing friction by introducing rigid segments and vice versa, or by changing the contact end shape. Or, asymmetric friction can also be produced through nonuniform stimulation on a uniform soft robot, such as spatially/temporally modulated illumination (scanned laser beam).

The most common type of soft walkers is inspired by caterpillars and inchworms. In the case of bending-based locomotion of a simple strip-shaped walker on a flat surface, the stride/drag (for unbending/bending) or drag/push (for bending/unbending) processes complete one motion step. In this process, if bending and unbending are induced by a uniform stimulation (such as uniform light exposure), the contact between the material and the surface is mainly focused on its two ends; thus, using the asymmetric contact shapes can effectively convert the reversible deformation into a directional displacement. Ikeda and co-workers reported a bilayer actuator with a LCN strip laminated on a longer low-density PE film with one end flat and the other having a sharp point (Figure 3A). The original curled film flatens upon UV irradiation and extends forward with the sharp edge acting as the stationary point; while, under visible light, the film recurls and drags the rear part of the film forward using the flat edge as the stationary point. Consequently, the film advances toward the flat edge side under alternating UV/visible light irradiation. Ideally (without slipping), the maximum step length equals to the length difference of the projections of the curved and flattened states in locomotion direction. The step frequency depends on the mechanical response rate of the soft walker and the operation time required for applying external stimuli. By adjusting the power intensity and frequency at the same time, step length and step frequency can be optimized to obtain higher walking speed.

Without asymmetrical factors (e.g., geometries or material) on the robot itself, the symmetrical actuator can achieve locomotion by using nonuniform light irradiation conditions to break its symmetry. This is very common in scanning light-enabled LCN peristaltic robots. Peristaltic motion can be commonly found in organisms such as earthworms, nematodes, and gastropods. This kind of motion, in general, relies on the generation of a traveling deformation guided by scanning light on a uniform and continuously addressable soft robot. The traveling motion along the soft robot itself can cause asymmetry and generate net displacement. More importantly, as the lighting conditions can be applied in the opposite way, the locomotion direction of the same actuator can be simply reversed. As shown in Figure 3B, Wasyłczyk and co-workers developed a light-driven caterpillar robot of natural scale. Leveraging the alternately patterned LC alignments, the LCN strip can change into a wave-like shape upon phase transition. With a scanning beam, the local and real-time wave forming and ceasing create traveling wave deformation on the original straight film to enable directional locomotion, with average speed between 0.41 and 2.1 body length min−1. Wang and co-workers reported on an earthworm-like robot made of an LCN capillary containing mesogens oriented along the capillary axis. The sequential contraction/expansion of the LCN capillary caused by a moving heat source from left to right generates dynamic segmental blockage/release.
in the glass tube, resulting in peristaltic crawling toward left. By reversing the moving direction of the heat source, the LCN capillary crawls toward right instead. Recently, inspired by the adhesive locomotion of snails (gastropods), Wasylczyk and co-workers showed a millimeter-scale robot that can effectively move in multiple configurations. In addition to using scanning laser to induce the traveling deformation along the monodomain LCN strip, they also introduced slippery mucus (glycerin) between the LCN and the substrate. Combining the pedal waves-like deformation of gastropods as well as the adhesive locomotion mechanism, their soft robot can move on smooth and rough surfaces, vertical and upside-down surfaces, and overcome a rod-shaped obstacle.

Rolling is an effective in-plane locomotive mode because the rolling friction is significantly lower than the sliding friction. Recently, our groups prepared a rolling soft robot with bilayer strip comprising mechanically stretched AZO–LCN film and passive polypropylene (PP). For wheel-like robot with LCN as outside layer, upon UV light irradiation from right, the curvature of irradiation area decreases and bend toward the outer LCN layer, whereas the unexposed left side of the wheel retains its original shape (Figure 3C). This asymmetric change shifts the gravity center of the wheel from right to left resulting in rolling of the robot away from the light source. The rolling direction can be determined by the location of the LCE film. When the stretched LCN film is set as the inner layer, the soft robot will roll toward the light beam under the same irradiation condition. In addition, the rolling speed can be controlled by adjusting the amount of stored energy in the LCE film that is proportional to the elongation degree. A high rolling speed of ≈1 cm s⁻¹ was achieved using a wheel (diameter 27.07 mm) made with a 200% pre-strained LCN layer.

Jumping has been recognized as an efficient locomotion mode for small organisms to overcome obstacles and achieve sudden
movements, but this is extremely challenging for LCN soft robots due to their insufficient actuation force. By adopting the power amplification strategy, the elastic energy can be stored and suddenly released to realize the jumping of the LCN soft robot. Cai and co-workers prepared a soft robot consisting of only an arch-shaped monodomain LCN and CNT composite film with its two ends attached to small magnets (Figure 3D).[86] Under the visible light irradiation, the photothermal effect of CNT heats up the film and establishes a temperature gradient through its thickness, resulting in bending deformation of the film. The arched film can be photo-induced to form a closed loop that is stably bonded by magnetic force. On this basis, further photo-induced bending deformation that tends to open the loop is prohibited. Thus, elastic energy was stored until reaching a critical value to suddenly open the loop and abruptly release elastic energy, giving rise to rapid jumping motion. The measured jumping height and distance are around 5 and 8 times its body height, respectively.

Figure 4. A) Schematic and photographs of electrically-driven “Janus” soft robot that can execute human-like walking and pushing an object forward by alternating activation of its two “legs”. Reproduced with permission.[79] Copyright 2019, Wiley-VCH. B) Schematic and photographs of light-fueled soft transporter robot with multidirectional locomotion and untethered cargo-handling capability. Reproduced with permission.[90] Copyright 2020, Wiley-VCH. C) Schematic and photographs of parallel parking of an LCN walker robot guided by light with three different wavelengths. Reproduced under the terms of the CC-BY 4.0 License.[91] Copyright 2019, The Author(s), published by Springer Nature.
serpentine leg tends to straighten and strikes backward when powered on, the robot pushes the load forward. Meanwhile, the straightening process also lifts the robot’s body, facilitating the other straightened leg to retrieve and recover to the original serpentine shape with low resistance. On this basis, complex two-/multi-leg cooperative movements were readily realized with simple electrical control.

In addition to forward and/or backward unidirectional motion modes, the ability for soft robots to change their motion direction as demanded is important. To modify the locomotion direction of the same device, a good strategy is to make use of the adjustable external stimuli, e.g., the highly controllable light irradiation. By changing the laser scanning manner, a soft crawler that can move straight and turn in a wanted direction was demonstrated by our group.[92] The initial arc-shaped LCN doped with NIR dyes can bend/unbend based on photothermal effect. Due to the different shapes of the soft crawler’s two ends, it can move straight by scanning symmetrically along the principle axis of the crawler with a speed up to 4 body length min⁻¹. Interestingly, scanning asymmetrically along the crawler’s long axis produces additional asymmetric deformation along its width, leading to deflection of the motion such as light-guided 90 degrees turn to right or left. A soft robot capable of orchestrated movement, multidirectional locomotion and gripping function driven entirely by blue light was demonstrated by Schenning and co-workers (Figure 4B).[90] Their soft robot consists of four LCN “legs” doped with photoswitch A1 and two LCN “arms” and an LCN gripper doped with photoswitch A2. Different photoswitches were used to enable independent control of locomotion and gripping functions, while requiring no finely focused light source. Consequently, this integrated soft robot can accomplish orchestrated motion to move in any direction by modulating blue-light illumination on its four legs; as well as cargo picking, transferring, and delivering by controlling the whole system using blue light. Yang and co-workers incorporated three photothermal dyes into the LCN strips separately and obtained a vehicle-like walker by assembling the three actuating parts that can be independently modulated by three-wavelength of light. [91] With this design, light-guided parallel parking of the LCN robot involving multidirectional motion and complex trajectory was accomplished (Figure 4C).

It should be emphasized that, for a given soft walker, changing the stimulation conditions causes different shape evolution of the robot body, which not only can adjust the locomotion speed and direction but also provides a way to change the motion mode or gait. Thus, multi-mode locomotion based on a single soft robot is possible. For example, varying light irradiation conditions (e.g., power, scanning speed/frequency) leads to different heat distribution in the soft robot; thus the same robot can perform crawling, squeezing and jumping movements,[86] or in another report, the same LCN robot can walk, climb, squeeze through gaps and push objects.[84]

3.4. Swimmer

Swimming of aquatic animals relies on different propulsion mechanisms, such as flapping, undulation, peristalsis and lateral bending, to name a few. The essential feature is the periodic deformations of their bodies, such as reversible bending/unbending or traveling-wave motion, which are commonly utilized in LCN-based swimmers. In particular, using light-stimulated LCN, it is easy to spatiotemporally control the body curvature to replicate complex swimming motion in nature on a simple and untethered LCN. Compared with the air medium, the movement of the LCN robot in the liquid medium is more challenging. On the one hand, the motion resistance is high, especially in liquids with high surface tension where the fluidic drag becomes greater, which restricts the actuation and swimming speed. On the other hand, for soft robots based on direct or indirect thermal actuation, due to the high heat dissipation in liquid (e.g., water with a high heat-transfer coefficient), the energy conversion efficiency is low and the actuation is impeded. Therefore, a higher external energy output (e.g., a 20 times greater light intensity than that for in-air actuation) is required to reach the actuation temperature, or the LCN is required to have a lower transition temperature.[93] In contrast, LCN robots that are not depending on thermal actuation can achieve athermal actuation in liquids. For example, LCN robots based on photochemical mechanisms allow for locomotion inside liquid or on the liquid surface at relatively low light intensity.[45]

In a recent study, an LCN was plasticized by 4-cyano-4’-pentylbiphenyl (5CB, a nematic liquid crystal) to form an LCG that has a low T_{LC\rightarrow iso} over a narrow temperature range and reduced material stiffness (Figure 5A).[93] The photothermally induced shape change of the LCG in water is more significant and rapid compared with the original LCN. On this basis, the LCG can be optically controlled to realize underwater crawling and walking, jumping and upward swimming. For example, in the saltwater providing higher buoyancy, an LCG soft robot can swim upward through cyclic arrhythmic stroke (light-induced downward bending, stroking speed is ≈0.3 body length s⁻¹) and relaxation (unbending after removal of the light).

LCN-based actuators that can bend/unbend reversibly can emulate “tails” or “fins” to propel the swimmer by periodically beating the liquid. Cai and co-workers demonstrated a NIR-controlled soft robotic fish whose active “caudal fin” was made of an LCN with one side coated with polydopamine (PDA) (Figure 5B).[94] The average speed of the swimmer is around 1 mm s⁻¹. Considering that a robot can perform a “swimming stroke” through asymmetric bending/unbending behaviors of the LCN, Yu and co-workers reported a bilayer structure, composed of a polydomain LCN-containing AZO and a Kapton layer, that can bend as a result of UV-induced volume expansion of LCN layer at room temperature, and return to flat once ceasing UV light.[95] By irradiating one side of a square propeller, the exposed side beats the liquid rhythmically to propel the swimmer away from light, with a speed of 1.25 body length s⁻¹ when the light intensity is 150 mW cm⁻² (Figure 5C). In addition, focusing UV light on a quarter of a rectangular strip makes it rotate. Combining the fast swimming of the square propeller and the rotary motion of the strip, on-demand direction control and cargo transportation at the liquid/air interface were achieved with an assembled soft robot.

Another type of swimming relies on the formation of traveling waves through the soft robot. Huang et al. fabricated a light-driven micro-robot that can swim toward an object and grab it, followed by transporting and releasing it as needed.[97] Containing AZO photoswitches, the robotic body can swing
Figure 5. A) A liquid crystal polymer gel (LCG) with reduced phase-transition temperature (left) and its upward swimming motions based on light-modulated arrhythmic stroke and relaxation cycles (right). Reproduced with permission.© 2020, The Author(s), published by USA National Academy of Sciences. B) Schematic of NIR-controlled bending/unbending motion that drives a soft robotic fish (up) and swimming of the soft robotic fish near the air–water interface (down). Reproduced with permission.© 2018, American Chemical Society. C) Schematic and photographs of bilayer-structured LCN soft robot with UV-controlled swimming motion at the liquid/air interface. Reproduced with permission.© 2019, Wiley-VCH. D) A dynamic, structured light field commanded traveling-wave deformation on a cylindrical LCN soft robot and the resultant propulsion of the material in liquid. Reproduced with permission.© 2016, Nature Publishing Group.
periodically and perform wave-like swimming motion upon alternative UV/vis light irradiation to both sides of the LCN film. As mentioned earlier, a symmetrical and uniform LCN robot can be triggered in an asymmetric manner to achieve translational motion and direction control. Using structured monochromatic light to scan a monodomain LCN cylinder with fast and reversible mechanical response, periodic traveling waves along its length can be generated to propel the LCN forward or backward in liquid (0.10–0.14 body length min⁻¹), depending on the scanning direction (Figure 5D). Similarly, by changing the pattern and scanning direction of structured light, flexible in-plane control of a LCN disc with homeotropic alignment, allowing translational motion along a square path and in-plane rotation, was demonstrated. This example proves that sophisticated spatiotemporal coordination on a uniform LCN can be achieved via light control, which also allows for various motion directions and gaits of a single material.

3.5. Self-Sustained Motion

Self-sustained motion, such as pulsation, heart-beating, wing-flapping and leaf-fluttering, are autonomous and periodic movements under a constant and continuous energy source. Mimicking this important feature commonly found in nature, self-sustained robotic systems based on LCNs have been realized, including self-oscillation and autonomous locomotion, mostly triggered by light. The fascinating part of such motion is that, when a constant stimulus (such as light) is applied, continuous oscillation or movement, instead of static shape changes, are initiated. Such continuous motion processes achieved without relying on human interference (such as switching on/off light) shows the autonomous characteristics.

Due to the directionality of light, the actual light irradiated area depends on the deformed geometry of the material. Therefore, if the irradiation conditions (e.g., position and intensity of a constant light beam) are appropriately adjusted so that the photo-induced deformation and deformation-dependent light reception form a positive feedback loop, then the asynchronous and interdependent light-intensity oscillations (or the resulting thermal oscillations) and mechanical oscillations can be established, allowing for light-fueled self-oscillating behavior. The most typical self-oscillator is LCN cantilevers with bending-based self-oscillation. When irradiated by light with intensity above a certain threshold, the LCN cantilever deflects over 90 degrees, so that the front surface is shadowed while the back surface becomes the new irradiated side. Subsequently, the contraction on the back surface reverses the bending direction and brings the front surface back into light exposure. As such, a new cycle begins, and the LCN film continuously oscillates. This self-oscillation strategy was first realized by Bunning and co-workers in 2008 through the photochemical effect of monodomain AZO-containing LCN cantilever (Figure 6A). Subsequently, by optimizing the laser intensity, strip size, thickness, and polarization direction, an oscillation frequency of 271 Hz and an oscillation amplitude of 170 degrees were achieved, respectively. Similar bending self-oscillation behaviors, based on photothermal actuation mechanism, were also demonstrated by Gelebart et al. using splay-aligned LCN strips doped with a series of photostabilizers and dyes. Relying only on the photothermal effect to realize the self-oscillation of LCN is a more general approach which also allows the use of more favorable light sources, such as visible light, NIR/IR light, and even sunlight. From a design point of view, a cantilever that includes an active area serving as a hinge and an inert tip for self-shadowing effect is an effective structure to achieve self-oscillation. The active and nonactive components can be programmed in a single film by many means, such as encoding the material with LC ordered/isotropic phases or locally introducing photothermal agents. For example, as the photothermal component PDA can be facilely dip-coated and also easily removed via alkaline washing, Yang and co-workers endowed a splay-aligned LCN film with predefined and reprogrammable self-oscillation behavior by tuning the PDA coatings. The film swinging with amplitude of 4.8 mm and frequency of 5.4 Hz was changed to oscillating 2.6 mm at 9.6 Hz when the PDA dip-coating time was changed from 20 to 40 h.

Self-oscillating soft robots are not limited to in-plane bending, but can also implement (3D) twisting deformation, thereby showing higher dimensionalities of movement, agility, and flexibility. Apart from creating feedback loops (as in the case of bending self-oscillation), another key factor in achieving this periodic torsional movement is to establish a stimuli-induced shear gradient through the LCN thickness. One method of preparing twisting self-oscillators is offsetting the LC alignment direction of the original bendable LCN cantilever along its long axis. By this means, the direction of contractile strain deviates from the long axis of the cantilever, causing the film to shrink more along one of its diagonals than the other direction and producing an intrinsic torsional motion. Based on this mechanism, White and co-workers reported a monodomain LCN-containing AZO which, by tilting the nematic director at an intermediate angle (e.g., 15 degrees) relative to the sample’s long axis, displays 3D oscillating motions encompassing both in-plane bending and out-of-plane twisting deformation (Figure 6B). Note that as light irradiation mainly acts on the surface of the film, the monodomain LCN displays bending/ unbending motion, rather than contracting/extending as when it is evenly triggered. Another way to fabricate twisting self-oscillating soft robot is by offsetting the incident light relative to the long axis of the bendable LCN. Our group reported a dye-doped robotic arm consisting of a monodomain (actuation) side and a polydomain (nonactuation) side, which can execute versatile self-sustained motions by adjusting the direction of the constant incident laser (Figure 6C). On the one hand, when a laser beam is applied to the polydomain side along the long axis of the strip at a grazing angle of 15 degrees, autonomous bending oscillations are elicited. In this case, photo-generated heat on the upper surface first causes upward bending. As the heat accumulates and propagates to the bottom monodomain side that can produce stronger contraction, downward bending and deviation of the LCN from the laser path take place. The shadowed strip cools and then bends upward to complete a bending oscillation cycle. On this basis, deflecting the laser beam from the long axis by 15 degrees while maintaining the same grazing angle, part of the LCN in the oblique direction can be selectively irradiated. The resulting asymmetric stresses generated in both the width and thickness directions result in twisting-based arm-like motion.
More interesting systems are known. As shown in Figure 6D (top), a self-oscillator based on 1D contraction and extension of the LCN was recently achieved by Zeng et al. They focused the laser vertically on the tip of a microscopic LCN fiber with uniaxial LC orientation. Due to the photothermal effect, contraction occurs causing the tip to move away from the laser spot.
Subsequently, the contracted tip cools down followed by the restoration of LC order and the extension of the tip, re-exposing the tip under the laser spot. As such, continuous contraction-extension behavior was generated. Furthermore, by suspending a monodomain LCN strip with large deformability in the air, they demonstrated freestyle self-oscillation with multiple degrees of freedom (Figure 6D, down). By adjusting the irradiation position on the sample, various stable oscillation modes based on bending and/or twisting and/or contraction-extension were achieved. Self-evolution between different modes upon a constant light irradiation was also observed.

A sustainable wave propagation along the LCN axis was reported by Broer and co-workers. The splay-aligned LCN-containing AZO derivatives with short lifetime of cis isomers can be photo-actuated and relaxed rapidly when light is removed.\textsuperscript{101} As shown in Figure 6E, fixing the two ends of the film with a pre-formed bent bump between them, continuous traveling wave was formed under an oblique-incidence light source. With the homeotropic or planar side facing up, the wave traveled toward and away from the light source, respectively. The formation of the propagating wave is based on a self-shadowing mechanism as well as the LC alignment-determined mechanical deformation.

As shown in the reports mentioned earlier, for the realization of steady self-oscillations, the light beam used should be positioned specifically to meet the critical conditions. This limits their practical applications. Schenning and co-workers demonstrated continuous chaotic oscillations under ambient sunlight (>35 mW cm\textsuperscript{-2}) using a splay-oriented LCN-containing visible light-responsive fluorinated AZO.\textsuperscript{102} Although the achieved angle fluctuation of the LCN is small and exhibits no fixed frequency, the continuous oscillation is driven by nonconcentrated sunlight and is independent of the position of light source; both of which are advantageous and highly desired for practical applications.

The oscillation frequency and amplitude are used to describe the self-oscillation of LCNs. Theoretically, the natural resonance frequency of a nondamped cantilever depends on its geometry as well as material rigidity and density. The calculated natural frequency can be used to describe the frequency of bending oscillation of LCN cantilevers. For contracting and twisting self-oscillations, however, Zeng et al. observed much lower frequency than the calculated one, for which they point out that the time delay of the mechanical response serves as the dominating factor in these cases.\textsuperscript{100} On the other hand, the oscillation amplitude increases as the light intensity and/or temperature increases. However, amplitude increasing is accompanied by a significant increase in air drag, leading to amplitude saturation. Reducing air pressure from 1 to 0.03 atm, Bunning and co-workers observed a large amplitude increase from 110 to 250 degrees due to the reduced hydrodynamic loss.\textsuperscript{98}

Conventionally, a walking robot system carrying its own power and control systems allows for convenient, autonomous, and long-distance translation. However, it is appealing to get rid of these on-board systems and simply initiate the automatic and continuous locomotion of a small polymer robot by switching on a simple, external, and unchanging stimulus. Unlike the conventional LCN-based soft locomotors and swimmers as mentioned earlier, the remarkable and prominent feature of LCN-based autonomous locomotive robots is that continuous translation is allowed without dynamic control of stimuli and/or spatially structured stimuli. An early example of autonomous locomotion is achieved using a monodomain nematic LCN disc doped with AZO dyes.\textsuperscript{103} The LCN exhibits fast and large optomechanical response to green light (0.32 mm thick film bends along the LC director toward the light). When irradiating a floating LCN disc from above, the generated peristaltic motion due to position-dependent shape changes pushes water toward the light so that the LCN disc swims rapidly into dark (Figure 6F).

Recently, an important achievement in this area is a light-powered self-walking device propelled by continuous photomechanical waves.\textsuperscript{104} As shown in Figure 6G, turning on an oblique incident light, the prebuckled AZO-LCN (with splay-alignment) fixed on a plastic frame can generate continuous mechanical waves along the principal axis of the LCN, with the wave-traveling direction controlled by the LC orientation of the exposed surface. Therefore, self-walking toward or against light source was enabled based on the interaction between the wave propagation and the substrate.

In addition to the aforementioned self-walking motion, self-rolling soft robots were also achieved. White and co-workers reported a monolithic AZO-LCN with a twisted-nematic orientation.\textsuperscript{101} Upon 320–500 nm light irradiation, the flat film transforms into a helix and then rolls or climbs on a slope continuously under unchanged homogeneous irradiation (Figure 6H). The direction and velocity of locomotion depend on the direction of the LC alignment relative to the long axis of the LCN and light intensity. Interestingly, Cai and co-workers realized self-rolling, autonomous climbing, and self-spinning (when deliberately restricted from translation) with a surprisingly simple setup: a slightly curved monodomain LCN rod on a hot plate or, after doping CNTs into the LCN, under uniform light irradiation.\textsuperscript{104} The initial curvature of the rod prepared by the processing methods is essential for the initiation of autonomous motions, whereas the geometric asymmetry and the temperature gradient established determine the rolling direction (Figure 6I). Furthermore, the simple setup and robust self-rolling motion allow for assembling and combining these LCN rods to construct multifunctional vehicles or conveyors.

4. Next-Generation LCN Soft Robots: Structured Body and Intelligence

Although accumulative understanding of biology and recent advances in novel materials have led to fast development in creating functional LCN soft robots, they still lack configuration complexity of their soft bodies, adaptivity and intelligence in their actuation behaviors. Nature presents various life forms which exhibit bodies of different shapes and various deformations based on them. To manufacture an advanced soft robot, first, the structure of the soft body should be further upgraded to meet the complexity of their natural counterparts. Concomitantly, 3D-distributed mechanical responses are programmed into the soft robot to generate prespecified complex motions. More importantly, a soft robot that can be freely changed to execute various actuation functions can adapt to different applications. In terms of actuation, to date, for most LCN soft robots, one needs to manually control the stimulus source during their
motion process. With a piece of polymer material lacking biological sensing and controlling, it is a huge challenge to create a “thinking” soft robot that can analyze the environment and respond to stimuli autonomously as intelligent life. Fortunately, many LCN-based soft robots that can replicate certain intelligent actions in nature have been discovered in recent years, which is an important step toward intelligent LCNs soft robots.

4.1. Structured Soft Body and Mechanical Response Inscription

The different body deformations of living creatures are controlled by their brain and nerve, giving them the necessary ability for basic life activity. Therefore, designing and fabricating sophisticated soft body for intelligent biomimetic robots is of primary importance. Although substantial progress has been made in the development of traditional LCNs in terms of actuation performance as discussed in previous sections, current LCN soft robots are often simple in structure (usually thin films or strips), resulting in relatively small forces, and at the same time the actuation behavior achieved is limited to certain extent. The main reason, first, is that most LCN actuators require photo-crosslinking or photo-polymerization during the preparation or processing method. Because of the poor penetration of light due to absorption of photoreactive species, LCN actuators have to be prepared as 2D thin films for the sake of complete cross-linking or polymerization. The LC alignment method also impose constrains on the attainable forms of the LCN soft robots. For example, LCNs prepared with the aid of surface alignment layers are typically films having a thickness of about tens of micrometers.[108] More importantly, similar to thermosetting polymers and elastomers that are insoluble and infusible, most LCNs films, once crosslinked, are difficult to be reshaped into another form.

To obtain LCN with complex soft body, the most exploited approach is to replace covalent bonds by dynamic bonds for chain crosslinking in LCNs to improve their reshaping capability and reprocessability.[109] In 2014, a moldable LCN actuator was first reported by Ji and co-workers based on thermal-sensitive exchangeable epoxy-acid bonds. In their works, the LCNs can be reprocessed into targeted geometries with corresponding mesogen orientation by remolding/stretching the materials at high temperature (via direct heating or photothermal effect) to induce network rearrangement by the transesterification exchange reaction with the aid of catalysts.[110–112] Upon cooling to room temperature, the rearranged network with fixed LC orientation can realize designated actuation behaviors. Ikeda and co-workers further reported a photosensitive AZO-LCN with catalyst-free exchangeable phenol-hydroxyl bonds to enable reprogrammability.[113] After stretching and then twisting at 120 °C, the LCN sample was reshaped into a helicoid actuator through the rearrangement of network topology. Upon the order–disorder phase transition under UV light irradiation, the helicoid can bend toward the light source (Figure 7A). Using the same method, the sample can be reprocessed into spiral shape and the corresponding photosensitive actuation can be achieved. In addition, light-triggered bond exchange reaction has also been utilized for preparing reprocessable LCNs, allowing network rearrangement to occur below \( T_{\text{LC, iso}} \). Bowman and co-workers realized fast reshaping of LCNs within several minutes based on allyl sulfide exchange reaction at 30–40 °C.[116] Recently, researchers also exploited dynamic exchangeable bonds to allow various LCN actuators with different components and/or LC alignments to be welded/assembled into one system to fabricate complex soft robots.[117,118]

Compared to exchangeable bonds where the bond number remains constant during material reprocessing, dissociative dynamic bonds, e.g., Diels–Alder (DA) bonds, can undergo dissociation and reformation upon stimulation.[119] Therefore, LCNs based on dissociative dynamic bonds can be transformed into thermoplastic polymers upon the bond breakage and return to the crosslinked state upon bond reformation by external factors. This feature can impart the LCNs with new programming possibilities as well as solution reprocessability. For example, our group reported new liquid crystal Diels–Alder networks (LCDANs) that can be used to manufacture thick and bulk 3D actuators, which is difficult to achieve with other LCN materials.[114] By heating the LCDANs to 125 °C for 3 min, the original DA-bonded network can be de-crosslinked through reverse DA reaction. Upon cooling, this material can remain de-crosslinked/slightly crosslinked state for long time due to the gradual and slow reformation of the DA-bonds, enabling facile reprogramming of the actuator with sophisticated shapes at room temperature. After 6 h at room temperature without any post treatment, the alignment of mesogens and the programmed shape can be self-locked by the reformation of DA bonds. Leveraging this mechanism, we were able to convert, in a controllable manner, a single 2D LCDAN sheet into a series of actuators with arbitrary shapes, such as multi-dome shapes and various origami architectures. Each programmed shape can generate specific reversible deformation. More importantly, the ease of reshaping and self-locking capability of the actuators makes the fabrication of various solid 3D geometries via the same bulk material possible. For example, a cuboid LCDAN can be facilely reprogrammed, such as playing with playdough, into a sphere, a star, a pie, and a parallelepiped after DA bond dissociation. The obtained self-locked solid actuators can realize reversible 3D-to-3D transformation upon thermal-induced phase transition (Figure 7B). Moreover, LCDANs can be processed directly from melt and from solution into, for example, fibers and tubes. Such excellent reprocessability is hard to achieve using LCNs constructed by exchangeable covalent bonds.

Apart from increasing the reprocessability of LCNs, another way to design and prepare complex 3D soft body is by applying 3D/4D printing technology. 4D printing refers to the 3D printing of smart materials that are capable of shape-changing and dynamic motions in response to certain stimulus.[120] As the process of design, control, and material printing can be aided by application softwares, 4D-printed LCN soft-robots can be fabricated into complex microstructures with high resolution.[121,122] Recently, Lewis and co-workers have used hot direct ink writing (HOT-DIW) to form 3D LCN geometries with patterned molecular order.[115] This method utilizes the shear forces imposed on main-chain LC oligomer inks during printing to align the mesogens along the print path. This alignment is subsequently locked into networks via UV-initiated radical polymerization and crosslinking. The resulting multilayer 3D structures, shown in Figure 7C, can morph between two different 3D shapes. More
complex 3D LCN geometries such as cylinder, helix, and honeycomb, and light-fueled microscopic walkers were also fabricated by 4D printing technology. Moreover, by optimizing the viscosity of the LC ink, Zhang et al. have demonstrated a new approach for easily fabricating LCN actuators by directly printing a linear liquid crystal polymer in its isotropic state followed by crosslinking.\[123\]

Although 3D/4D printing of LCN soft robots is still in the early stage, we believe this technology is an effective and promising tool to enhance the processing of advanced LCN soft robots, especially with further development of additive manufacturing techniques and new LC materials as printing inks.

4.2. Reconfigurable LCNs for Changeable Soft Robots

Animals always have more than one motion behaviors for various life activities and can easily change their motion to adapt to different environment. However, most LCNs are permanently cross-linked networks and display one actuation mode once fabricated. Therefore, it is of great interest to develop the ability of reconfiguring a same piece of LCN to change its actuation or motion behavior on-demand. This challenge has been addressed in some recent researches. An effective method is to directly adjust the properties of the mesogens. For example, Primagi...
and co-workers demonstrated a light-reconfigurable AZO-LCN actuator, which can change its shape via photochemically patterned isomerization of AZO mesogens and photothermally induced stress release.\(^{[78]}\) First, programming of the actuation response is conducted via locally modulating the cis-isomer content in an LCN strip by UV light irradiation. Consequently, the inhomogeneous cis-AZO distribution dictates the shape change activated photothermally using red light. By converting the cis-isomers back to trans-form through blue-light irradiation, new patterns can be created by UV irradiation and thus new actuation behaviors can be produced, enabling a single LCN specimen to be reconfigured into a series of shape changes (Figure 8A). On the other hand, a pH-rewritable and reconfigurable LCN film that can generate diverse shape changes upon light irradiation was reported by Broer’s and co-workers.\(^{[124]}\) The splay-aligned LCNs contain azomerocyanine (1-AM) that can be locally converted into the hydroxyazopyridinium (1-HAP) by acid and changed back into original 1-AM by base. Therefore, the same piece of LCN strip can be written, erased, and rewritten with different 1-AM/1-HAP patterns through pH treatment. As the two molecular species absorb light of different wavelengths, two distinct actuation modes can be achieved for each patterned configuration by exciting one of the two chromophores during actuation with suitable light wavelength (Figure 8B).

Another straightforward approach for changing actuation behavior of fabricated LCN film is adjusting polymer chain-crosslinking. To this regard, our group developed an LCN that can change its shape transformations or even locomotion behavior on demand.\(^{[125]}\) The LCN actuator contains anthracene moieties that can undergo reversible dimerization (for crosslinking) and cleavage (for de-crosslinking) upon absorption of UV light at two different wavelengths. A given uniformly cross-linked monodomain LCN shows reversible contraction and elongation upon heating/cooling cycle. Stepwise de-crosslinking in selected areas produces patterned cross-linked areas (actuation domains) and de-crosslinked areas (nonactuation domains) in the LCN. Thus, the same sample can be photo-reconfigured to execute reversible 3D-to-2D transformations upon phase transition. More interestingly, reconfigurable light-fueled micro-robots can be built with loaded photothermal agents. After the first reconfiguring process, a caterpillar-like microrobot that can walk along the laser scanning direction was obtained. This microrobot can be subsequently reconfigured by further de-crosslinking selected regions to generate a wrinkle-shaped

**Figure 8.** A) Reconfigurable shape-morphing: schematic of mask patterns for UV reconfiguration and optical image of the actuator induced by photothermal effect. Reproduced under the terms of the CC-BY 4.0 License.\(^{[78]}\) Copyright 2018, The Author(s), published by Springer Nature. B) pH-induced converting between 1-AM and 1-HAP (top) and pH re writable LCN actuator (down). Reproduced with permission.\(^{[124]}\) Copyright 2017, Wiley-VCH. C) Optically reconfigurable locomotion of a light-fueled microwalker prepared by a dye-doped LCN actuator: the walking by reversible flattening/arching along the laser scanning direction being reconfigured into the crawling by wrinkling/flattening against the laser scanning direction. Reproduced with permission.\(^{[125]}\) Copyright 2019, Wiley-VCH.
4.3. Self-Regulation LCNs for Soft Robot Automation

Living organisms are capable of sensing their environment and executing a specific action through neural reflex-driven pathways. The grand challenge for mimicking such natural intelligence in miniature robots lies in achieving highly integrated body functionality, actuation, and sensing mechanisms. In recent years, a number of LCN soft actuators with simple structure and millimeter sizes have been demonstrated to be able to mimic this natural intelligence, that is, self-regulation and autonomous action to adapt to environmental changes. Self-regulation LCNs represent a potential building block for self-responsive soft robotics. Exploiting LCNs’ properties and devices that autonomously “decide” when to start a specific action in response to a changing environment without external control or intervention, has been demonstrated and reported in a few recent works. For example, sensing and modulating of the environmental light were realized through an LCN-based artificial iris as shown in Figure 9A. The LCN with radially arranged splayed alignment was fabricated via photoalignment approach.\textsuperscript{126} Due to anisotropic thermal expansion on the planar side and the homeotropic side, the iris spontaneously adopts a flower-like shape with a central hole surrounded by twelve identical petals. Upon light irradiation, the initial curled petals unbend to block the incident beam and reduces the light transmittance from 70% (open state) to 30% (closed state), with an adjustable power range of 200 mW. This iris-like light exposure tuning capability can be used as light-controlled adjustable soft optics. In this case, the progressive shape evolving as a function of increasing light power is crucial to the gradual self-regulation of the device.

Moving toward a more sophisticated artificial “intelligence” in soft robotics, autonomously recognize, distinguish, and interact with target objects were demonstrated. An artificial LCN flytrap reported by Priimagi and co-workers is a good example of these self-regulation smart devices, which can recognize different targets by light reflection and automatically grip it only when certain conditions are met (Figure 9B).\textsuperscript{127} The gripper was prepared by integrating a splay-aligned LCN film with photothermal dye at one extremity of an optical fiber, and a constant 488 nm light source was applied in front of this device. When a reflective object entered inside the field of view, light is reflected back to the LCN film and provokes a bending response to grab the...
object. In this case, the optical feedback is based on reflected light intensity determined by the optical property of the object, and only when a certain power-density threshold is exceeded, can the flytrap identify and catch the object. Increasing the optical power to about 300 mW can reduce the response time of the device to 0.2 s. Wiersma and co-workers further demonstrated a LCN microhand that “recognizes” objects with different colors: it captures the black and purple objects while showing no action for yellow and white elements, as shown in Figure 9C. The mechanism is that materials of dark colors, such as black and purple, can absorb the light and produce enough heat to induce the LCN deformation when they are close to the microhand. Based on the same principle, this device has also been exploited for recognizing and selectively gripping particles of different gray levels. Therefore, these works prove that LCNs can be made to act intelligently by identifying objects based on their light reflection or absorption differences and respond accordingly.

4.4. Associative Learning LCNs for Self-Studying Soft Robots

For biology and robotics, intelligence refers to the ability to both respond to external stimuli and learn new (or modify existing) behaviors. Could artificial LCN soft robots behave even smarter such that they can learn interactive and adaptive behavior by conditioning training? Recently, the associative learning LCNs, also termed as Pavlovian materials, that “learn” to respond to an initially neutral stimulus only after being trained by an independent stimulus were designed by Priimagi and co-workers, providing unforeseen routes toward self-studying soft robots. The principle of a Pavlovian material is shown in Figure 10A. Initially, the material is insensitive to stimulus 2 but responds to stimulus 1. After exposed to stimuli 1 and 2 simultaneously (association process), the conditioned material can be “trained” to adopt a response to stimulus 2. As shown in Figure 10B, this associative learning function was realized by coating a thin photothermal dye layer on the homeotropic side of a splay-aligned LCN film. Upon heating (acting as stimulus 1), the order parameter reduces, and the film bends. When exposed to light (acting as stimulus 2), the insufficient heat generated by the sparsely distributed photothermal dyes on the surface layer causes no mechanical response. Interestingly, during conditioning, that is, applying light and heat simultaneously on the LCN film, the higher temperature produced allows the dye to diffuse into the matrix from the surface, resulting in enhanced optical absorption and photothermal effect. The conditioning process thus turns light into a conditioned stimulus and endows the LCN with new responsiveness that is initially not allowed. This material was further devised as a micro-walker that can realize light-fueled locomotion upon the association process (Figure 10C). Moreover, inspired by the classical conditioning experiment, an artificial Pavlov’s dog showing conditioned salivation was constructed by the associative learning LCN and a hydrogel, where the melting hydrogel serves as the reservoir of saliva and the LCN as the dog’s jaw (Figure 10D). In this case,
heating corresponds to the food for the artificial dog and the light irradiation corresponds to the bell. From this new development, it can be envisioned that research in this field will eventually seek to realize self-studying soft robots that can self-adapt, learn, and perform complex robotic actions.

5. Perspective

In this review, we have summarized the recent progress in the field of LCN-based soft robotics, including stimulus response principles, materials innovation, structural design, motion mechanisms as well as robotic implementations. Good mechanical and actuation performance, high freedom degree of their motion as well as their versatile responsiveness are indicative of a bright future of LCN soft robots. However, LCN-based soft robots still need to be further developed to meet the ever-increasing requirements of actuation performance and further enhance their adaptability to various complex conditions in practical applications.

The first consideration for their application is to address the limitations caused by their relatively low actuation stress stemmed from their soft nature. Although their reversible deformation could be large and complex enough for most applications, insufficient actuation stress could result in low load-bearing capability. New material systems (such as IPNs) can be developed to obtain materials with favorable actuation stress and fast reversible deformation.[132,133] Another solution is to adopt a hybrid structure composed of both stiff and soft components.[134]

Second, for most cases where the actuation is essentially thermally stimulated, the mechanical response of an LCN-based soft robot is related to its phase-transition behavior and the temperature-switching approach. The actuation temperature depending on \( T_{\text{LC-isoc}} \) should meet the application requirements and can be tuned by chemical components of LCN materials. A broad or sharp phase-transition temperature range also affects actuation behaviors. The former contributes to dose-dependent mechanical deformation[135] and the latter leads to rapid actuation,[136] thus serving different application contexts. On the other hand, the temperature change rate of the material, in practice, could dominate the reversible deformation speed and thus determine the achievable step frequency, as the disruption of the LC order and the reorientation of the mesogens are rapid at the appropriate temperature. In view of this, highly controllable stimuli (e.g., light, electric, and magnetic fields) can be used for indirect heating to achieve high stimulation frequency. Typically, the same actuation temperature can be achieved within shorter time by increasing the power of the stimulation. Therefore, with high-power stimuli of short-duration, the heating process and the corresponding shape change can be accelerated to a certain extent. However, in most cases, the low thermal conductivity and slow passive cooling process of LCNs during in-air actuation greatly limit the shape recovery speed, thereby making high-frequency actuation challenging (especially for thick actuators). Addressing this problem, the internal and active cooling mechanism has been developed by Cai and co-workers. For example, they prepared a fluid-driven LCN actuator (1.2 mm thick) with internal microfluidic channels. By alternatively injecting hot and cold water into the fluidic channels of the actuator to speed up the temperature-switching processes, rapid cyclic actuation with 1 Hz frequency and 10% actuation strain can be achieved.[136,137] Third, new structural design and engineering of LCN-based soft robots could be developed to enhance the output of useful mechanical work. For example, by increasing the effective contact and friction between the LCN-based gripper and the cargo, the attainable weight-carrying ratio and the reliability of grabbing can be improved. In the scenario of locomotion, ineffective slipping often occurs in the stepping cycle, resulting in shorter step length and unstable movements compared to those of natural creatures of the same size. Therefore, developing LCN-based soft locomotive systems capable of dynamic gripping/friction control and modulation could be a solution.[138] Although challenging, introducing such mechanisms into LCN-based soft robots can increase the step length and locomotion speed, and hopefully, improve locomotion adaptability on various surfaces and provide direction or gait control.

Although multimode motion, multidirectional locomotion and multifunctionality of LCN-based soft robots have been achieved separately, combining these capabilities in one system is necessary for future advanced soft robots. Current researches rely on stimulus control to regulate the actions of a given structure. However, relying solely on stimulus control may complicate the operation and generate interfering actuation behaviors. Therefore, the complexity of LC director layout, network reprogramming and reconstruction, and stimulus modulation can act synergistically to further enhance the agility and adjustability of the robotic motion.

Toward practical applications, the less dependence on the human judgment and intervention during actuation, the more intelligent the soft robot. As demonstrated on LCN-based soft robots, continuous and adaptable motion can be initiated by just turning on a light source, which is a significant progress in imitating the intelligent motion of natural organisms. Intelligent functions such as autonomous motion, self-sensing, self-regulation, and self-learning capabilities should be further advanced. Progresses regarding these functions, especially those that can function steadily and robustly and achieve high motion diversity and reduced requirements for stimuli, can greatly promote their applications as next-generation smart soft robots.

In addition, to improve actuation performance, versatile motion control, and intelligence, the ease of programming and processing the LCN-based soft robots is critical for their industrialization. In this regard, reprogrammable and reproducible LCN soft robots as well as 3D printing technology can be very meaningful research areas for the facile fabrication of soft robots with arbitrary shapes, dimensions, and designated LC orientation profiles. Moreover, assembling multiple actuation parts that can function independently and synergistically is a good way to achieve sophisticated and flexible motions on one system. Therefore, the facile, robust and even seamless assembly strategy is also important for constructing strong and entirely soft robotic systems.[137]

Last but not least, despite the impressive advancements of LCN-based soft robots on all fronts, the research field actually is still at its infancy. All achievements reported in the literature are kind of proof-of-concept or proof-of-principle studies. None of the numerous LCN actuators and robots is even close to any kind of practical applications. It is likely that for a quite long time...
to come, the research effort will still focus on the discovery of new means or the improvement in known methods to make LCN-based soft robots that exhibit enhanced functions, intelligence, and the ability to execute specific tasks. At some point, by accumulating the body of knowledge, it will be important to identify some specific applications for which LCN-based soft robots are particularly promising due to their advantageous over robots built up with other soft materials such as hydrogels. Future research can then address the specific requirements in those applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

intelligent functions, liquid crystal networks, liquid crystal polymers, soft actuators, soft robots

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