Invited article for Spotlight on Applications

Design, Regulation, and Applications of Soft Actuators Based on Liquid-Crystalline Polymers and Their Composites

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ABSTRACT: Soft actuators designed from stimuli-responsive polymers often possess a certain amount of bionic functionality because of their versatile deformation. Liquid-crystalline polymers (LCPs) and their composites are among the most fascinating materials for soft actuators due to their great advantages of flexible structure design and easy regulation. In this Spotlight on Applications, we mainly focus on our group's latest research progress in soft actuators based on LCPs and their composites. Some representative research findings from other groups are also included for better understanding this research field. Above all, the essential principles for the responsive behavior and reconfigurable performance of the soft actuators are discussed, from the perspective of materials' morphology and structure design. Further on, we analyze recent work on how to precisely regulate the responsive modes and quantify the operating parameters of soft actuators. Finally, some application examples are given to demonstrate well-designed soft actuators with different functions under varied working environments, which is expected to provide inspiration for future research in developing more intelligent and multi-functional integrated soft actuators.

1. Introduction

When we mention soft actuators, some high-frequency words come along, and one group of those words are bionic, biomimetic or bio-inspired. Humans have always been good at observing and exploring laws in nature, no matter from themselves or other creatures. These findings are then applied to different levels of biomimetic applications, including mechanics, information, control and mimicry bionics, etc. In today's world, new materials, supercomputers, life science and other science and technology fields are developing rapidly. From metallic robots to fully bionic humans, it may not be too long before we see fully artificial life entities with artificial intelligence like that shown in science fiction movies. The potential achievements will not only benefit mankind, but also change the way humans perceive ethics. To achieve the goals of biomimetic applications, the selection, design and preparation of novel materials are extremely important.

Naturally, the constituent parts of living body are often in soft and flexible forms, apart from skeletons or protective shells of creatures. In fact, many vital movements couldn't be carried out without the bursting forces of soft tissues, such as the contraction/relaxation of muscles and the signaling of nerve fibers. Some advanced functions from nature creatures have been imitated by materials scientists using soft materials, and the typical examples are the self-adjustment of the iris under different intensities of light,[1] and the automatic adaptation of finger joints to grasp objects.[2] The above functions can be realized by different categories of soft materials, like liquid-crystalline polymers (LCPs),[3,4] hydrogels,[5] shape memory polymers (SMPs),[2] natural materials,[6] hybrid materials,[7] electro-chemo-mechanical materials[8] and so on.

Due to their unique features, LCPs have advantages over other soft materials for fabrication of actuators.[9] Generally, LCPs can respond to diverse stimuli like light,[1] heat,[3] electric field,[10] magnetic field[11] and humidity,[4] etc., separately or simultaneously, which is originated from the diversity and compatibility of LCP family. As shown in

Figure 1, the LCP materials can be divided into crosslinked liquid-crystalline polymers (CLCPs)[12] and linear liquid-crystalline polymers (LLCPs).[13] Furthermore, CLCPs contain liquid-crystalline elastomers (LCEs)[14] and liquid-crystalline networks (LCNs),[12] differentiated by the main-chain flexibility, crosslinking degree and glass transition temperature (Tg). It is worth noting that not only covalent bonds[15] but also supramolecular interactions[16] can achieve the chemically-crosslinking effect. Usually, the crosslinking plays an important role in the reversibility and repeatability of the LCP actuators.

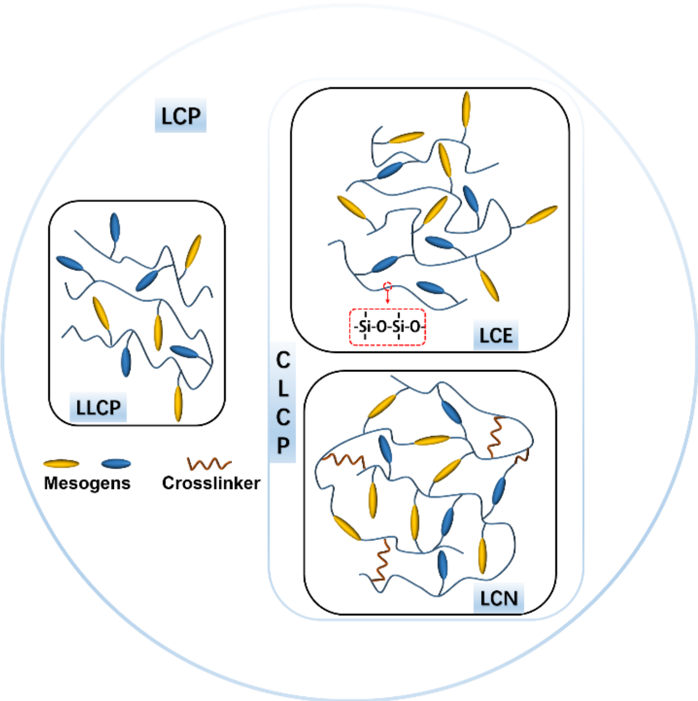

Figure 1. Plausible schematic of LCP family.

For the LCP system, its molecular chain segments contain abundant mesogenic units, which can be manually interfered to achieve well orientation. The classical orientation methods are LC cell methods[17] (Figure 2) and Finkelmann's two-step crosslinking methods.[18] The mesogenic orientation can also be achieved by extrude molding,[19] stretching,[20] and melt-drawing.[15] LCPs prepared by the above processing methods are usually in the form of thin films or fibers. The most interested LCP systems are parallel orientation LCPs (Figure 2a),[21] splayed-aligned LCPs (Figure 2b),[22] and twisted-nematic LCPs (Figure 2c),[23] which show different mechanical properties and initial shapes. Under a certain stimulus, the LC phase often shows an order-to-disorder phase transition, which can be amplified by the polymer matrix (Figure 3), no matter for fiber actuators or film actuators, and thus behaving as a macroscopic deformation, such as contraction, bending, curling, spiral, torsion and so on.

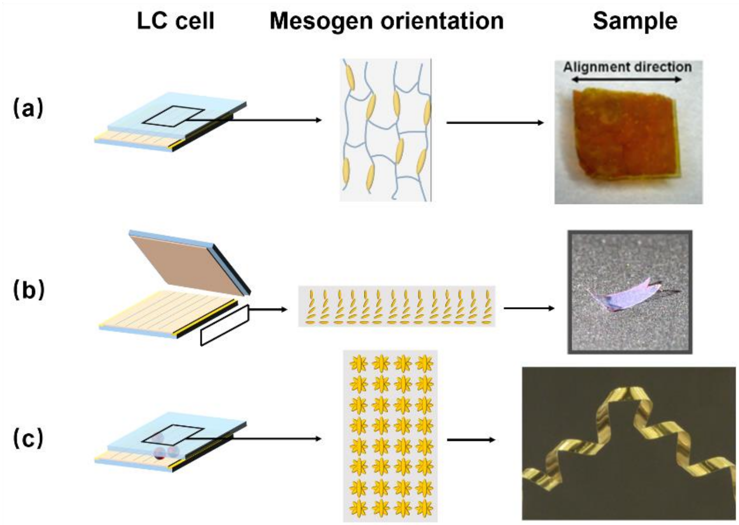

Figure 2. Fabrication of freestanding LCP film by polymerization of LC monomers in one LC cell. (a) The parallel orientated LCP film is obtained by rubbing the orientation inducer layer on the glass substrate. Reproduced from ref. 21. Copyright 2013 American Chemical Society. (b) Splayed-aligned LCP film is obtained by rubbing orientation inducer layer on the bottom glass substrate and coating vertical orientation inducer layer on the upper cover. Adapted with permission from ref. 22. Copyright 2019 Elsevier. (c) The reactant mixed with a chiral reagent gives twisted-nematic LCP film. Adapted from ref. 23. Copyright 2019 American Chemical Society.

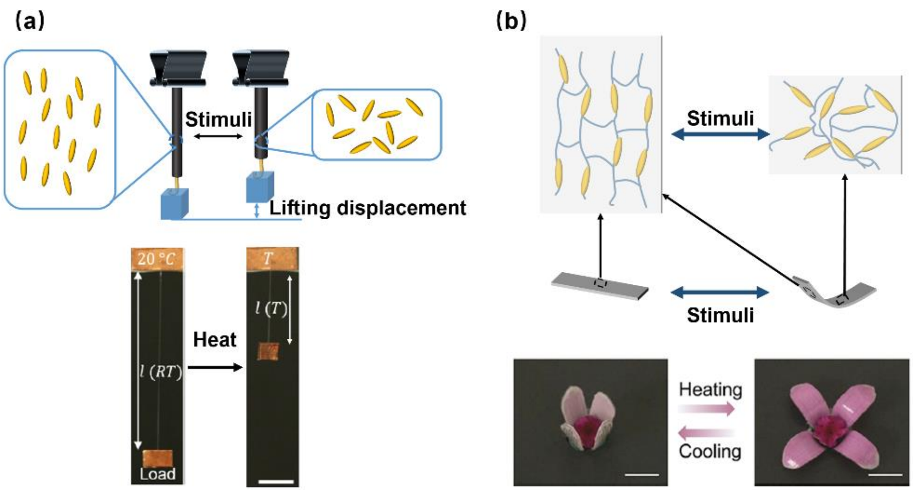

Figure 3. Schematics and experimental pictures show the deformation mechanism of LCP-based soft actuators. (a) Fiber actuator can lift cargo due to the nematic to isotropic phase transition upon exposure to stimuli such as heat or light. Adapted with permission from ref. 24. Copyright 2021 The American Association for the Advancement of Science. (b) Under stimuli such as heat, a volume change gradient occurs perpendicular to the LCP orientation plane in the film actuator, as a result it bends. Reproduced from ref. 25. Copyright 2021 American Chemical Society.

The driving force for LCP actuator is the disturbance from external energy, the simplest form of which is heat.[3] However, at a certain developing stage of LCPs, the function of these materials alone is limited, which cannot meet with the requirement for advanced functional applications. Thanks to the compatibility of LCPs, their competence can be expanded by compositing with other materials. By introducing chromophores, such as photoresponsive azobenzenes,[26] or photothermal agents like carbon nanotubes, graphene, and gold nanorods to the LCP systems,[27,28] the driving force of phase change becomes light energy. Similarly, the introduction of hydrophilic groups into the LCP system and the combination of LCP with conductive/magnetic substances will change the inducement of phase transition into humidity[4] and electric[10]/magnetic field,[11] respectively.

We have carried out a series of research in combining LCPs with other materials to acquire novel functions in broader application areas. Our group's latest research progress of soft actuators based on LCPs[15] and their composites[12,29] will be discussed. Obviously, no matter what the final function of the soft actuator is, it is inseparable from the initial materials design. Hence, this spotlight puts emphasis on discussing the design of materials structure, including the shape (fiber or film), hierarchical structure (monolithic or multi-layer), and the processing characteristics of the materials like reconfigurable, self-healing and other properties. Then, the regulation of the soft actuators will be discussed, including how to achieve different responsive modes, how to achieve quantitative control, how to adapt to their respective working environments, and how to introduce logic and even intelligence to the LCP systems. Finally, some typical utilization examples are given, which are expected to provide inspirations for the advanced requirements of bionic and intelligent soft actuators.

2. Design strategies of soft actuators based on LCPs and their composites

The basic capability of all soft actuators is to sense, analyze external stimuli and respond in a manner of deformation, which should be derived from the composition and characteristic structures of materials. As mentioned above, soft actuators based on LCPs and their composites are often in the form of fibers or films. Fiber actuator usually owns micron or millimeter diameter, great aspect ratio and a certain rigidity.[24] It generally exhibits larger strain and stronger stress under stimuli, but fewer response modes. Film actuator owns micron or millimeter thickness and a relatively larger area.

It lacks some explosive power relative to fiber actuator, but possesses more composability and functions.[30] In this part, we will discuss the design strategies of different LCP actuators separately.

2.1. Fiber actuators

In plants and animals, fiber plays an important role in maintaining tissues' morphologies. Human daily activities are inseparable from the joint movement caused by muscle contraction pulling on bones, and muscle tissue is made up of muscle cells. Muscle cells are often called muscle fibers because they are slender and fibrous in shape. Artificial muscles are being developed to mimic the behavior of muscle fibers, and LCP fiber actuators are making progress in this area, as shown in Figure 3a and Table 1.

Table 1. Typical examples of fiber actuators.

Fabrication method	Responsiveness	Performance	Reference
1: Melt-drawing the LC random copolymer 2: Post-crosslinking by soaking in a crosslinking agent	UV light	Photophobic bending	Ref[15]
1: Electrospinning microfibers 2: Apply load	Heat	Contraction	Ref[24]
1: Polymerization in a PTFE tube (inner diameter: 0.5 or 1 mm) 2: Demolding and stretching	532 nm laser	Lifting objects	Ref[20]

Our group has ever found the abnormal photophobic bending phenomenon of an azobenzene-containing LCN fiber (Figure 4), [15] which was prepared by melt-drawing and post-crosslinking. We discussed the relationship between macroscopic photomechanical motion and microcosmic mesogen location or crosslinking densities, and found that the unusual deformation was caused by the increased molecular free volume upon irradiation of actinic light. These results can help expand the response modes of fiber actuators. Very recently, Cai's group fabricated a series of LCE microfibers with diameters ranging from 10 to 100 μm with the method of electrospinning and post-stretching.[24] These LCE microfiber actuators were thermally controlled, undergoing a nematic to isotropic phase transition to achieve contraction, which exhibits large actuation strain, fast responsive speed, and a high-power density (Figure 3a).

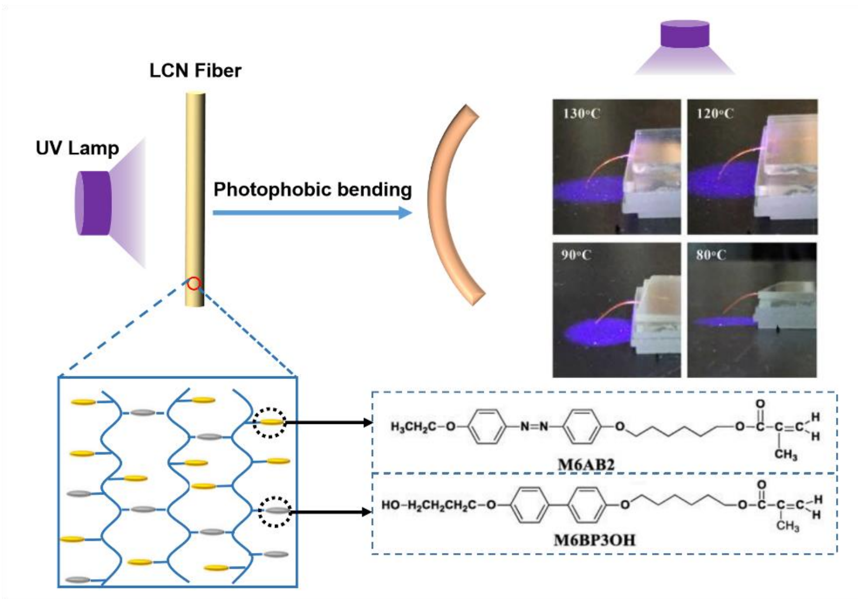

Figure 4. Schematic and experimental pictures of LCN fiber bending away from light stimulus. Adapted from ref. 15. Copyright 2017 American Chemical Society.

Digging deeper into the nature of muscle fiber activity, it can be found that the movement of muscle is controlled by the nervous system, which relies on ion transport to transmit electrical signals. Although ionic conductor materials seem to be more suitable for simulating ion transport, the conductivity of existing materials is not sensitive enough to strain, and there is still a gap between the performance of ionic conducting materials and the requirements of flexible electronics. Therefore, the LCE with alternate rigid mesogenic units and soft chain spacers as matrix would be one of the choices for being synergized by the ionic liquid. By combining the strain-electrical signal conversion capability of the LCE fiber with its thermally-actuated contraction capability, a feedback loop can be formed to act as self-perception.[20]

As for the fiber actuators, its maximum contraction strain is a concerned performance index. Utilizing one ultrahigh molecular-weight LLCP containing azobenzene in a long flexible side chain, a fiber actuator was fabricated by melted-stretching method.[13] Then, the strain energy was stored in the fiber after cooling and the shape was fixed at the same time. Finally, the pre-stored strain energy could be released through the photo-isomerization of azobenzene. Meanwhile, the fiber actuator performed an ultra-large photoinduced contraction, and the contraction rate was as high as 81%.[13]

2.2. Film actuators

2.2.1. Monolithic actuators

Monolithic LCP actuators have been able to achieve a variety of deformation modes and functions by adjusting the chain group species, the position of the mesogenic moieties in main/side chain, the crosslinking density, or by doping functional components while maintaining the stability of LCP matrix. Now, more and more emphases have been placed on the discovery of novel phenomena and the improvement of processing methods. For example, Zhao's group found that a type of side-chain LCE exhibited an anomalous shape change when heated up to phase transition temperature, that was, unlike the normal LCE materials which contract in the stretching direction and expand in the direction vertical to stretching direction under thermal stimulus, as shown in Figure 5. This is originated from the interaction between the main-chain backbone and the side-chain mesogens.[31]

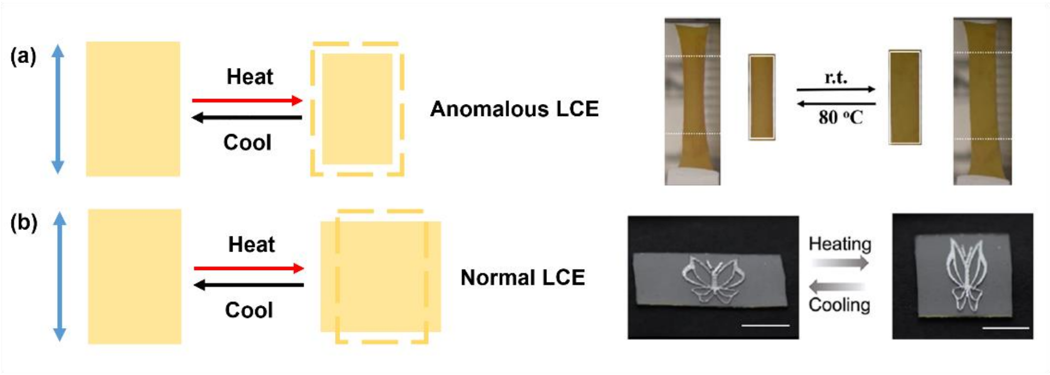

Figure 5. Schematic illustration and experimental pictures of LCP deformation behaviors. (a) Anomalous LCE film. The blue double arrows represent the stretching direction during materials preparation. Reproduced with permission from ref. 31. Copyright 2020 Wiley-VCH. (b) Normal LCE film. Reproduced from ref. 25. Copyright 2021 American Chemical Society.

With the development of 3D and 4D printing technology, the processing methods of preparing oriented LCP materials are widely broadened. In one study, two commercially available components for amine-acrylate aza-Michael addition were used as precursors in the printing ink. The mesogenic orientation was realized once after extrusion molding, due to the huge dynamic difference of the hydrogen addition reaction from the amines group to acrylate.[32] Another advantage of 3D printing for LCE actuators is the flexible design of any initial shapes. For instance, Kim et al. prepared dimethylamino-functionalized LCEs by UV assisted direct ink writing-based 3D printing. The printed LCEs was sensitive to humidity after acidic solution, and then a series of hygroscopic LCE actuators with complex structures were successfully obtained.[19] In another study, LCEs coupled with resistive elements which can enable Joule (resistive) heating on demand was developed by 3D printing. In this work, a specially designed double-nozzles were used to print electrically-controlled actuators with LCE ink as shell layer and liquid metal (LM) as an inner core.[33] The printed core-shell fiber combined the regulatable properties of both LCEs and LM, demonstrating programmable actuation and closed-loop control.

2.2.2. Hierarchical structures

In general, one regularly-oriented LCP actuator only shows intrinsically thermo-responsiveness. To acquire other stimulus responsiveness or multi-stimuli responsiveness, it is necessary to introduce corresponding functional groups or doping related functional substances into the LCP matrix. However, the introduction of stimuli-sensitive functional groups will increase the complexity of chemistry synthesis, while the doping of functional substances may lead to matrix phase separation due to the possible immiscibility. From this point of view, it is an easy way to combine the LCP layer with other stimuli-sensitive materials by bilayer or multi-layer processing fabrication. The potential problem, however, is that the layer-to-layer delamination should be avoided by adjusting proper bonding. Table 2 presents some actuators with hierarchical structures, which can be prepared by coating,[30] adhesion,[34] or molding in a gradient template.[35]

Table 2. Typical examples of hierarchical film actuator.

Layer composition	Responsiveness	Applications	Reference
1: Azobenzene or azopyridine-containing LCP 2: Kapton film	UV and visible light	Bionic leaf or swimmer Oscillators	Ref[12,30,36,37]
1: Azobenzene-containing LCP film 2: Kapton nanofibers	UV	Bionic dragonfly wing	Ref[29]
1: NIR dye-doped LCE 2: NIR dye-free LCE	NIR	Möbius rotator	Ref[34]
1: Splayed-aligned azobenzene-LCN films 2: Patterned polydopamine (PDA) coating	1. UV 2. NIR	Walkers with two modes	Ref[38]
1: Azobenzene-containing LCP without template 2: Azobenzene-containing LCP with SiO_2 opal template	1. Solvent 2. Heat 3. UV	Roller, lifter or walker in liquid or at air/liquid interface	Ref[35]
1: Silicone capsulation 2: LM circuit in the laser patterned grooves	1. Heat 2. Voltage	1. Gripper 2. Spring-like actuator	Ref[25]

Our group has carried out a series of research on the composite films of photoresponsive LCP and polyimide (or commercial name Kapton). The volume of azobenzene-containing LCP expands under irradiation of actinic light due to the change in free volume of azobenzene moieties. As shown in Figure 6a, a bilayer actuator was prepared by coating a layer of azobenzene-containing LCP onto Kapton film.[30] Hereinto, Kapton was chosen due to its suitable elastic modulus. The introduction of Kapton substrate not only amplifies the microscopic volume change of LCPs, but also ensures the reversible bending deformation of the whole system.[12,30] Besides, continuous oscillating motion with tunable frequency and amplitude was also realized by adjusting the composition of monomers or changing the stimulation conditions.[36,37] Recently, we have also applied electrospinning Kapton nanofibers as substrate to reinforce the photo-responsivity of LCP.[29] Hydroxy groups were introduced to the side chain of LCPs to enhance the interfacial strength between LCPs and the highly oriented Kapton nanofibers, thus the mechanical properties of the composites were greatly improved, as shown in Figure 6c. The composite system of LCP and Kapton has the advantage of simple preparation, no need for extra molding or stretching operation, convenient programmability, which provides a potential fabrication path for mass production of soft actuators.

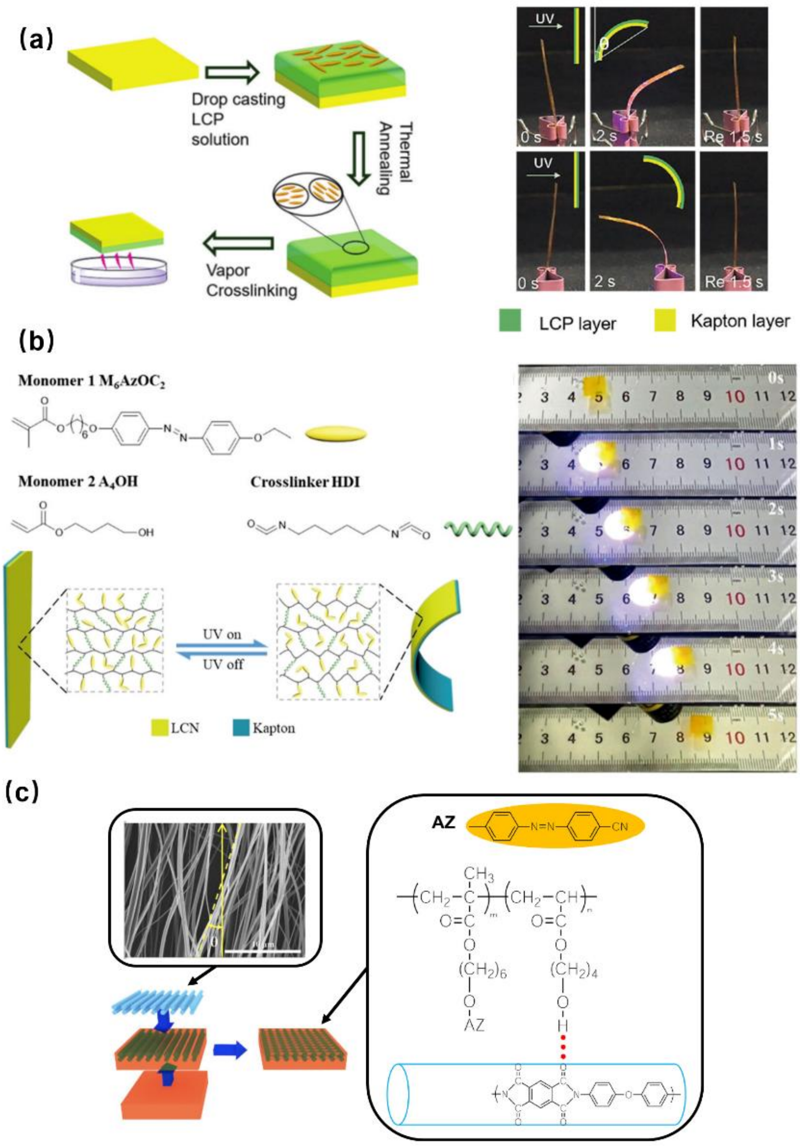

Figure 6. Schematics and experimental pictures of LCP/Kapton composites. (a) A routine for fabricating LCP/Kapton composites and its photoresponsive performance. Adapted with permission from ref. 30. Copyright 2019 The Royal Society of Chemistry. (b) The deformation mechanism of LCP/Kapton composites and swimming under light. Adapted with permission from ref. 12. Copyright 2019 Wiley-VCH. (c) The structure schematic for LCP/Kapton fiber composites. Adapted with permission from ref. 29. Copyright 2021 Elsevier.

Soft actuators with multi-stimuli responsiveness can be adapted to wide range of operating environments. For example, SiO_2 opals were used as the template for LC cells, and then azobenzene-containing LCP precursor was filled in the cell to obtain a

Janus structured actuator that can respond to solvent, heat and light stimulus.[35] The mesogenic orientation degree of the two layers in Janus structure was quite different. Hence, it only bent towards the reverse direction of the opal template under different stimuli. These actuators can rotate or crawl in the liquid or at the interface between the liquid and air.[35] Even if the actuator can only respond to one kind of stimulus, such as an optically controlled actuator, due to the wide range of light wavelengths, it still has chance for adjustment. For example, a photochemically and photothermally controllable soft walker was prepared by selectively coating a polydopamine (PDA) layer onto an azobenzene-containing LCN film. The dual-responsive actuator can be manipulated both by NIR (photothermal PDA) and UV (uncoated area), which enables the actuator to display a variety of driving modes like the car engaging a gear.[38]

In addition, two LCE layers with exactly the same composition were bonded, except that one layer contained photothermal dye and was pre-stretched. The resulting bilayer structure was connected in the way of Möbius rings so as to achieve continuous rotating motion.[34] Moreover, there are also some studies devoted to combining liquid metal (LM) with LCEs,[25] since LM has the advantages of high electric conductivity, high thermal conductivity, and non-toxicity. In a recent work, LM mixed with 5wt% Ni microparticles was first magnetic printed onto LCE surface with the assistance of a laser patterned tape mask and a magnetic field, followed by casting a silicone layer on top of the LCE for encapsulating.[25] The LM-LCE soft actuator combined the electrothermal and mechano-sensing properties of LM with the thermo-responsiveness of LCE. Finally, the morphology-sensitive resistance of LM layer endowed the composite actuator with a pressure-electrical feedback loop, which introduces intelligence to the actuator control.[25]

2.2.3. Reprogrammable actuators

Figure 7 summarizes different types of film actuators with various deformation modes. Some actuators perform one-off deformation (Figure 7b),[39] namely, the deformation will not disappear after removing the stimulus. These actuators are suitable for processing and molding.[13] Another type of soft actuator deforms under one stimulus and keeps the deformation. It can return to its initial shape only under another stimulus, which is similar to the shape memory effect (Figure 7c).[39,40] Then, other deformation modes can occur after a new cycle of stimulation. Obviously, it has both the shape change reversibility and shape retention ability, which can be used in writable and erasable information storage devices.[40] For most soft actuators, once the initial shape is set, the deformation mode is fixed. Undoubtedly, the system with reprogrammable capability[41](Figure 7d) will enhance the utilization of materials and expand its functions. Table 3 summarizes some reconfigurable materials related to LCPs.

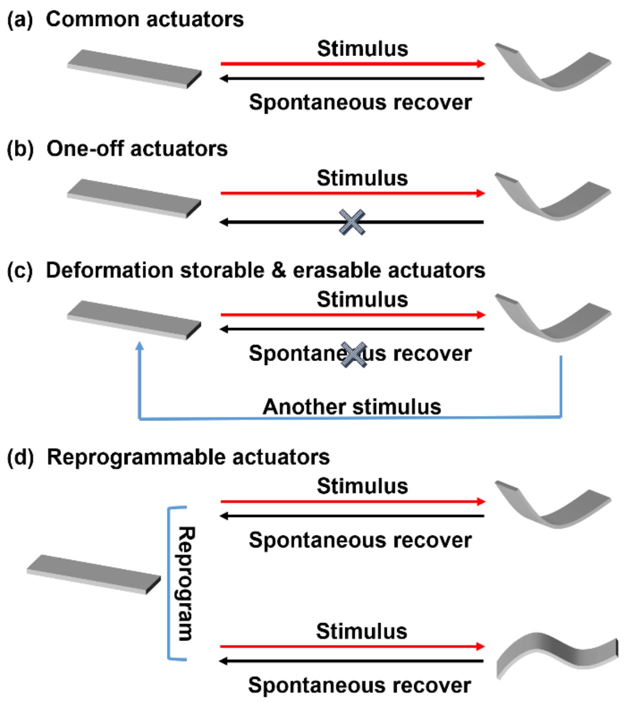

Figure 7. Different types of film actuators. (a) Common actuators deform under stimulus and recover spontaneously. (b) One-off actuators can't recover to initial state.[39] (c) Deformation storable

& erasable actuators keep the changed shape after receiving stimulus and recover only under another specific stimulus.[40] (d) The deformation modes of reprogrammable actuators are variable.[38]

Table 3. Reprogrammable soft actuator examples.

Key component	Performance	Applications	Reference
Main-chain LCPs with furan side groups and bismaleimide for Diels–Alder bonds	Reshaping into any 3D structures (tube, origami, etc.) at room temperature	Lifter Crawler Rotator	Ref[42]
Spray-coating LCN on thermoplastic polyethylene terephthalate (PET)	Arbitrary initial shape by shape molding over PET Tg	Actuator in air or water	Ref[43]
Siloxane LCEs with anionic catalysts by swelling	Switching on/off thermal reprogrammability	3D complex motions	Ref[44]
LCE containing diselenide bond	Self-welding Recycling Reshaping	Multi-dimensional motions	Ref[45]
LCE synthesized by quadruple hydrogen bonds, furan-maleimide Diels–Alder adducts and azobenzene	Shape-switching by UV shape setting and heat erasing	Braille-like actuator	Ref[40]

The reprocessing performance of LLCPs is relatively good since they are often dissolvable in organic solvents,[13] while CLCPs are restricted by the chemically covalent crosslinking, which is not conducive to the recycling of materials. By introducing dynamic covalent bonds such as Diels-Alder bonds,[42] diselenide bonds,[45] disulfide bonds,[46] transesterification,[47] tetraarylsuccinonitrile,[48] or supramolecular bonds like hydrogen bonds[40] into the LCP system, the microcosmic crosslinking networks can be reconstructed and the macroscopic shape of the materials can be rebuilt as well. By this way, the LCP system exhibits incomparable advantages such as self-healing,[48] self-welding[45] and reconfiguration.[46] If we do not rely on supramolecular or dynamic covalent bonds, we can also entrust LCE to thermoplastic substrate materials, by utilizing the shape remodeling property of the substrate to get the initial shape of LCE arbitrarily, and thus acquiring a variety of actuating modes.[43]

The surface of the LCP matrix can also be coated with a stimulus responsive substance that is easy to be eliminated, so that the specific deformation mode can be obtained by directly patterned coating, as shown in Figure 8.[38] Moreover, the functional substances can be got rid of after using, and the coating area can be redesigned to achieve another type of deformation function. Furthermore, if the reconfiguration itself is also in control, that is, it can be reshaped only when it needs to be reshaped, the materials will be provided with more functions. This expectation is realized in a siloxane-based LCE system containing anionic catalysts, which displays switchable thermal reprogrammability.[44]

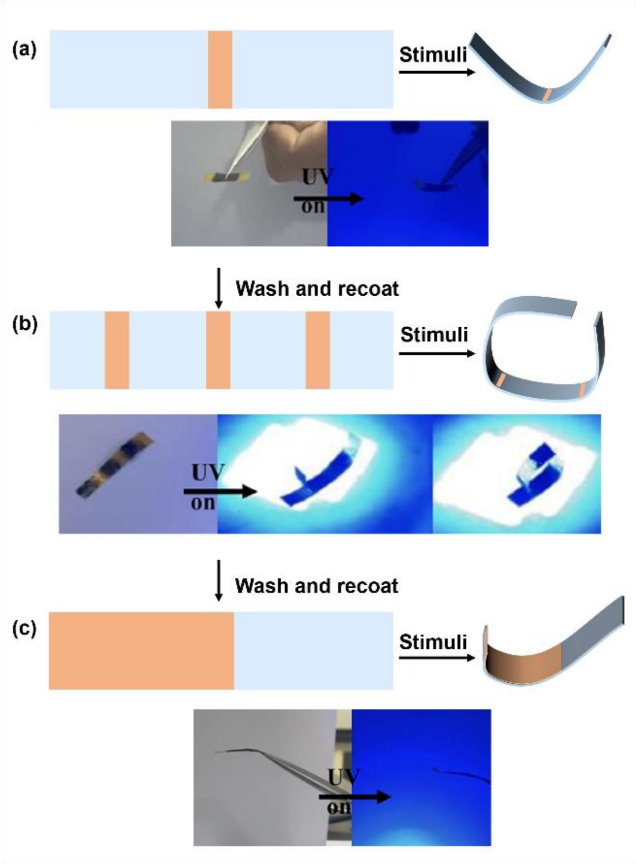

Figure 8. Schematics and experimental pictures of a reprogrammable actuator. (a), (b), (c) The stimulus-responsive coating is applied to the LCN substrate, and the patterned coating can be washed off and redesigned to produce different responsive modes. Orange: stimulus-responsive coating, Blue: LCN substrate. Adapted from ref. 38. Copyright 2021 American Chemical Society.

Our group has also made some progress in the recyclability of photomechanical materials. A bilayer photomechanical actuator was fabricated by combining a small-molecular photo-liquefiable azobenzene derivative with a commercially-available low-density polyethylene (LDPE) film.[49] Although no chemical crosslinking existed at the interface between the small azobenzene molecules and LDPE layer, these film actuators still showed quickly and reversibly photomechanical deformation upon UV irradiation. Due to the good solubility of small molecules in organic solvents, the actuator materials can be recycled by separating the LDPE film and the functional coating in the selective solvent, as shown in Figure 9. In future, we hope to extend this recyclability to LCP composites.

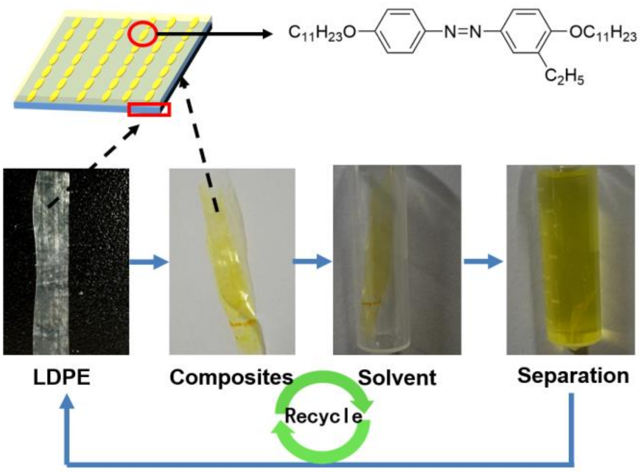

Figure 9. Recyclability of the composite film. The transparency film is the pure LDPE substrate. The yellow coating is azobenzene derivative. Adapted with permission from ref. 49. Copyright 2018 The Royal Society of Chemistry.

3. Regulation methods of the soft actuators based on LCPs and their composites

With the development of LCP soft actuator's design strategy and fabrication technology, it is not difficult to realize simple deformations like bending and torsion, or functions like grasping and crawling. However, researchers are no longer content to perform just basic things with soft actuators. Our group has tried to control the responsive time, actinic light wavelength, deformation amplitude, and other parameters of optical actuators based on LCPs and their composites.[30,50,51] For actuators to eventually be used in micromechanical systems or human-computer interaction scenarios, on one hand, their motions need to be controlled precisely.[12,52] On the other hand, it's better to integrate as many functions as possible in one system.[53] Some progress have already been made in the research of regulating soft actuators.[29,37]

In nature, some insects or reptiles have the ability to change color automatically according to environmental changes. The soft actuator itself is to imitate the movement of these animals, but if we can introduce the color-changing behavior into the materials system, it will undoubtedly improve the system's ability to complete synergistic work. By covalently bonding LCEs with terminally functionalized aggregation-induced-emission (AIE) active tetraphenylethene derivatives and photochromic spiropyran moieties, the fabricated actuator can not only perform complicated motions but also camouflage itself due to photochromic luminescence (Figure 10). The above processes were all achieved by selectively applying different wavelengths of the light stimulus.[54] Another group of researchers doped the moisture-sensitive AIE molecules into the hydrophilic layer, which was then combined with LCE layer. The bilayer actuator showed the ability of simultaneous deformation and color change while changing the environmental humidity.[55] Moreover, one cholesteric LC derivative was used as the monomer for the preparation of LCE,[56] and the LCE film can realize temperature-sensitive deformation and color change concurrently. Interestingly, the materials exhibited switchable hyper-reflectivity for left-polarized and right-polarized light during heating.[56]

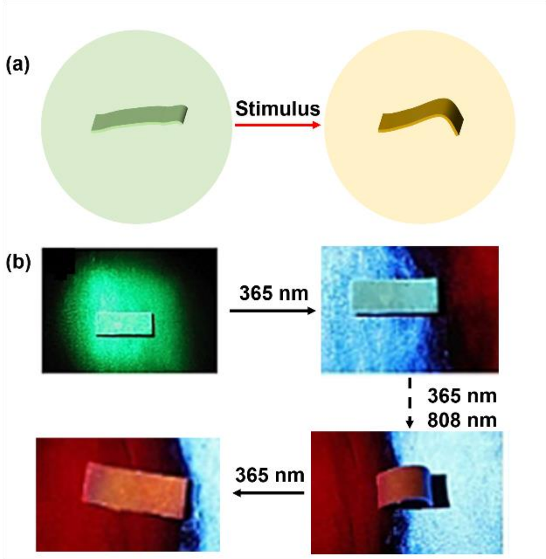

Figure 10. Schematic illustrations (a) and experimental pictures (b) of multi-functional integrated actuator that can deform and change color adapted to environment concurrently. Adapted with permission from ref. 54. Copyright 2021 Wiley-VCH.

Controlling the soft actuator with only one variable usually obtains linearly responsive results, such as the deformation amplitude increases with the intensifying of light intensity or humidity. Although this linear relationship also reflects the accuracy of actuator regulation, it still lacks logic or interrelation. Recently, one multilayer LCE actuator was fabricated by mixing three kinds of photosensitive dyes into the LCE matrix, respectively.[57] Then three wavelengths of light were respectively used to drive the actuator, which can realize the precise control of the actuator's actuating modes and motion directions, thus enabling the actuator to be used as the control unit of the logic circuit.[57] Luo's group used two variables, that is, light polarization angle and intensity, to control the actuator together, and obtained an actuator whose oscillation frequency can be precisely regulated.[58] The actuator was then further developed into the photo-controllable windmill or mimicking the dog tail's wagging behavior. Obviously, adding a regulatory dimension helps to precisely control the actuating performance and deformation modes.[58] Inspired by insect aggregation behavior on water surface, researchers put some small-sized actuators on water surface irregularly, and then utilized light-induced capillary force to control the assembling ways of actuators, achieving a variety of large-scale patterned structures.[59]

Oscillation is a kind of continuous motion, and many important life activities depend on it. For example, birds fly by the vibration of their wings, and fish swim by the swing of their fins. Recently, we achieved highly regulated oscillatory motion by LCP/Kapton bilayer composites. Tunable oscillation frequency and amplitude were acquired successfully.[36,37] There are also many other reports proving that LCP-based soft actuators can achieve oscillation, and most of them are mainly controlled by collimating parallel light, because the intensity distribution of actinic light in the whole operating environment of the actuator is not uniform. As a result, the materials are easy to own self-shielding effect, forming a deformation and recovery loop, maintaining the oscillating motion.

Some researchers have noticed that the movement trajectory of birds' wings is non-reciprocal, so as to achieve effective displacement. Focusing on this, a series of non-reciprocal actuators were developed, which were modulated by three-wavelength, two-wavelength, and single-wavelength, respectively. When it finally decreased to zero wavelength modulation, the non-reciprocal motion of the actuator was self-oscillation.[60] The common LCP-based actuator has only one oscillation mode. Inspired by plant tendrils, one spring-like actuator that possessed tilt, up-and-down, and rotational oscillation modes were created by adding load and changing the light position.[61] Not content with merely getting oscillation based on LCP system, scientist studied a pair of connected oscillators and found that the two oscillators were coupled, like the metronome or pendula with Huygens' synchrony, which had implications for the study of information interaction among multiple actuators.[62]

4. Applications of the soft actuators based on LCPs and their composites

Generally, a soft actuator made of stimulus-responsive materials mainly completes two aspects of applications. One is sensing detection, measuring the temperature, humidity, and other parameters of the working environment. The other is to perform the mechanical motion, such as grasping or lifting objects, transporting objects, completing position displacement, etc. When using one specific stimulus to control the actuator, there are both advantages and disadvantages. For example, light is a kind of non-contact, remotely controllable, and clean energy source, but there must be no high extinction obstruction in the path of light. Another example is, electrically actuated devices often need extra circuits. Although it is convenient to connect electric actuators with other electrical signal conversion equipment, the miniaturized actuator cannot move with complete freedom due to the extra mass of the power supply. If the actuator can respond to multiple stimuli at the same time,[63] it will be closer to the goals of miniaturization and multifunctional integration. Furthermore, it’s important to improve the self-adjustment and self-learning ability of the actuator to increase the intelligence of the system,[22] so that the soft actuator can better adapt to different working environments.

When working as an independent device, the soft actuator can operate in a variety of narrow, rugged environments due to its advantages of softness and small size. For instance, a serpentine locomotive actuator was successfully fabricated using LCEs, which can move effectively in complicated operating environment, due to the strong adaptability of snake crawling.[64] In another study of electrical actuators, the cylindrical LCE actuator had a patterned conductive coating of carbon black on the outside. Instead of connecting directly to a wire, it was in contact with an external copper conductive track, so that the resulting actuator moved like a train along the track.[65]

Our group has been committed to the research of optically-actuated composite materials based on LCPs and their composites, and has made continuous progress in the applications of soft actuators. Earlier, we combined one azobenzene-containing LCP with commercial low-density polyethylene (LDPE) membrane to create a double-layer cantilever that exhibited periodic deformations under proper photo-irradiation conditions.[66] A photo-mechano-electric conversion device was successfully fabricated, in which the cantilever loaded with a copper coil cut the magnetic induction line back and forth in one magnetic field, complying the law of Faraday electromagnetic induction, as shown in Figure 11a.[66] Interestingly, continuous electrical output was elegantly achieved, and the output electricity was proportional to the changing rate of the magnetic flux, which was greatly influenced by light intensity, film thickness, and sample size. This simple and convenient strategy may expand applications of photoactive materials in the capture and storage of light energy.

Recently, we have found that the modulus of LCP and Kapton film are relatively matched, and the binding force between them is strong enough for the fabrication of bimorph actuators. More interestingly, the photomechanical deformation of the LCP/Kapton bilayer system showed a pre-designed motion direction, i.e., it always bends towards the Kapton side independent of the direction of the incident light. This enables us to conveniently manipulate the photoinduced movement for some bionic applications. For example, by observing the leaf structure of a plant, we found that the circadian rhythm of the leaf was caused by the change of the multi-layer tissues in response to environmental changes, and our LCP/Kapton composite materials just met this change rule. This unique feature enables us to simulate the law of blade opening during the day and closing at night using a bilayer film actuator (Figure 11b).[30] In addition, when the LCP/Kapton bilayer film is placed on the surface of the water/ethanol mixture, we are surprised to find that the system displayed the behavior of slapping the liquid under continuous light irradiation, realizing the bionic self-propelled swimming like a dolphin. The remotely controlled light-driven "swimmer" can transport a certain weight thing like a cargo ship, as shown in Figure 11c.[12]

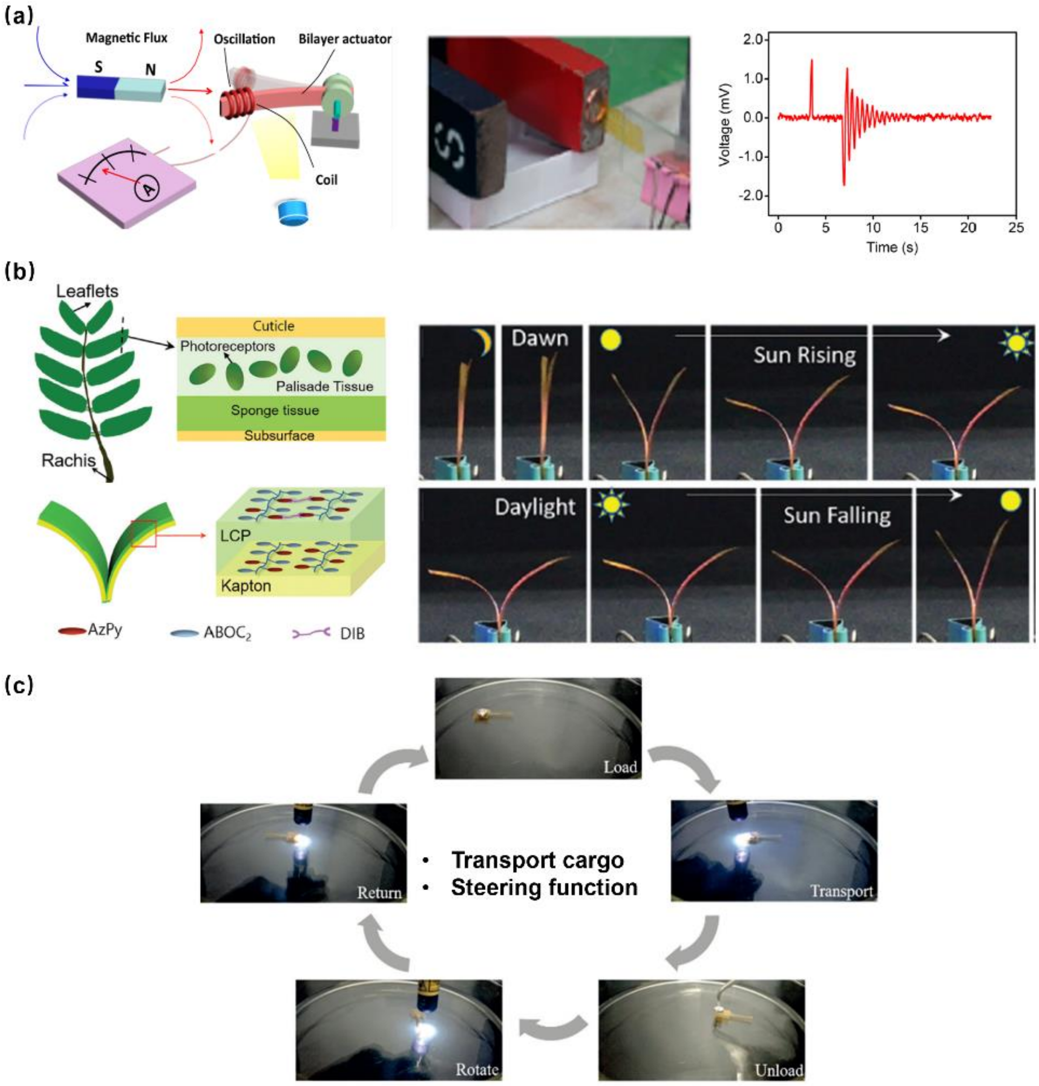

Figure 11. Applications of bilayer actuators. (a) Optical pendulum generator based on LCP composites. Adapted from ref. 66. Copyright 2015 American Chemical Society. (b) Biomimetic circadian rhythms of *Albizia* julibrissin leaves based on LCP composites. Adapted with permission from ref. 30. Copyright 2019 The Royal Society of Chemistry. (c) Bionic swimming based on LCP composites. Adapted with permission from ref. 12. Copyright 2019 Wiley-VCH.

The operating environment of LCE-based soft actuators is not limited to land, but also continues to expand to the liquid surface and even below the liquid surface, or into the sky. Recently, we successfully developed a series of composite materials which could swim on the water surface.[12,67] The self-propelled swimming robot based on LCP/Kapton composites showed an extremely high swimming speed and direction controllability.[12] We even developed a self-actuated boat totally fueled by sunlight with high regulation accuracy.[67] Fish swim not only relying on the swing of fins, but also on the buoyancy of the swim bladder condition, to achieve the adjustment of the swimming depth in the water. Recently, one typical 4-cyano-4'-n-pentylbiphenyl (5CB) liquid crystal was added into LCN,[68] and the volume of the fabricated materials changed greatly before and after illumination, so the buoyancy was adjustable. As a result, the actuator based on 5CB-LCN composites can dive and swim up/below the surface of the water easily.

Inspired by the fluttering wings of birds or insects, the oscillating motion of actuators is expected to achieve flight goals, which is the dream of mankind. Recently, our group has made a series of progress in realizing oscillating motion of soft actuators based on photo-controlled LCP composites. By designing the supramolecular interaction (Figure 12) in the liquid-crystalline copolymer and adjusting the illumination conditions, both chaotic oscillation (Figure 12c)[36] and regular oscillation[37] can be realized with the LCP/Kapton bimorph materials. The chaotic oscillation was realized under continuous illumination conditions. The regular oscillations showed well adjustability relying on the light intensity, wavelength, and other conditions, and were further developed into a charge detecting device (Figure 12e). In another work of our group, the hierarchical nanofiber-reinforced structure of the dragonfly wings was simulated (Figure 13a). The photoresponsive LCP was hot-pressed into composite films by using Kapton nanofiber film as the reinforcing template (Figure 6c). Then the composite film performed a cyclic float and dive motion under continuous light illumination (Figure 13b), which may act as the wings of an aircraft. As a result, the dragonfly dive motion was successfully mimicked, as shown in Figure 13c.[29]

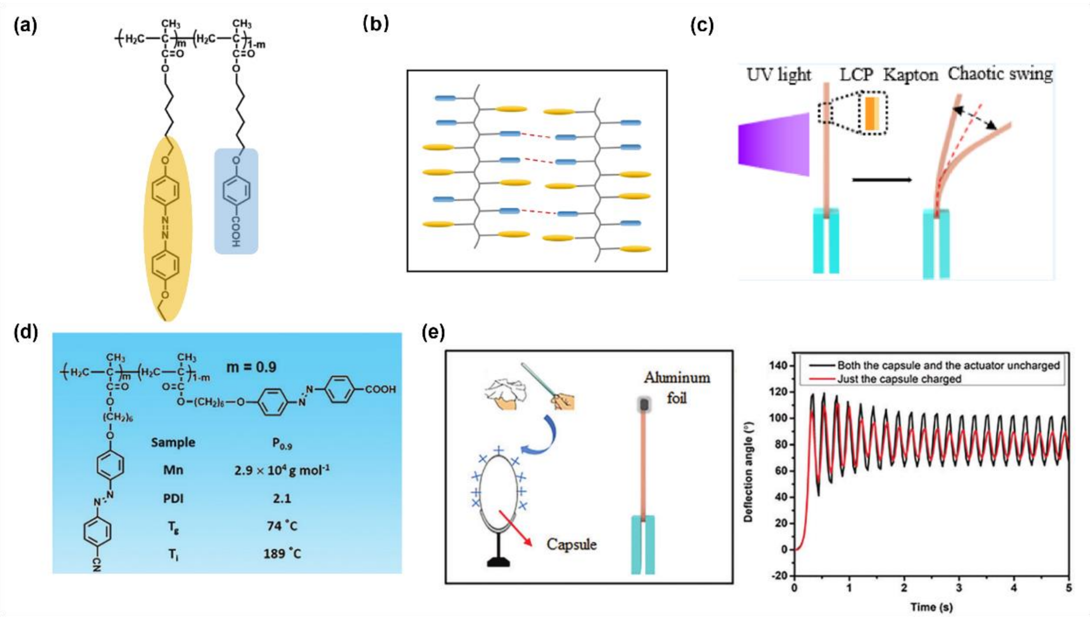

Figure 12. Oscillators enabled by LCP/Kapton bimorph. (a) Molecular structural formula and (b) Possible schematic of hydrogen bond of LCP layer related to chaotic oscillation bimorph. (c) Schematic of chaotic oscillation by LCP/Kapton composites. (a-c) Adapted from ref. 36. Copyright 2021 American Chemical Society. (d) Molecular structural formula of LCP layer related to regular oscillation bimorph. (e) Oscillator detecting charge based on LCP composites. (d, e) Reproduced with permission from ref. 37. Copyright 2021 The Royal Society of Chemistry.

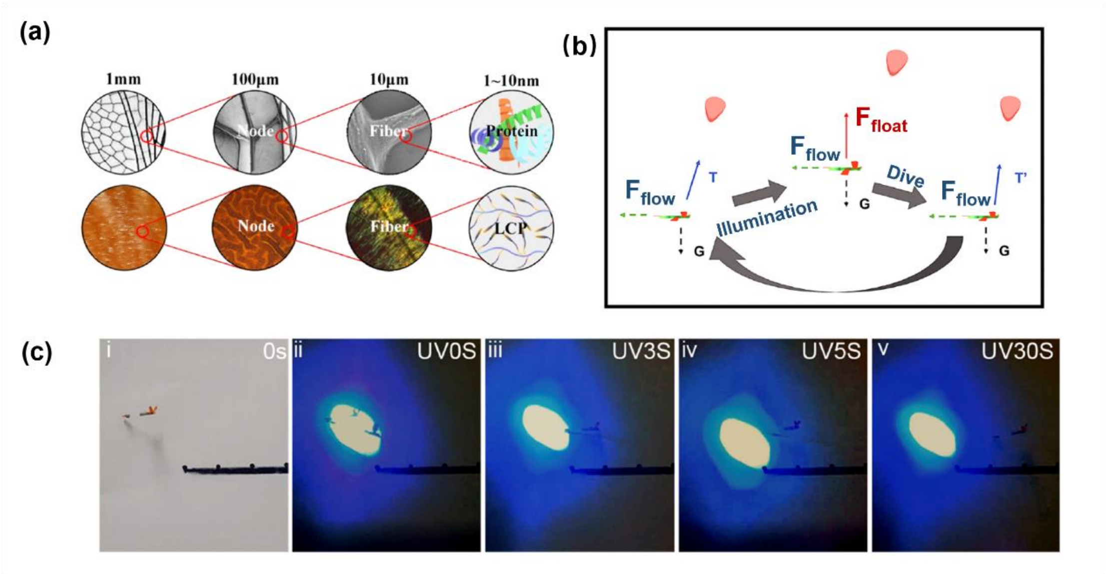

Figure 13. Bionic dragonfly wings enabled by LCP/Kapton composites. (a) Analogous hierarchical structure of dragonfly wing (upper row) and LCP layer (bottom row). (b) Schematic of soft actuator's motion under illumination. (c) Soft actuator mimicked flying of dragonfly in the air. Adapted with permission from ref. 29. Copyright 2021 Elsevier.

5. Conclusions and Outlooks

In this Spotlight on Applications, our group's latest research progress of soft actuators based on LCPs and their composites is throughout every part, and especially the photo-actuated bilayer composites of LCP and Kapton may offer limitless possibility for the design and regulation of soft actuators. It has been about twenty years since the nematic-LCE was found to be capable of stimulus-responsive deformation. LCE materials were originally intended to be used as artificial muscles, and already evolved to perform many other bionic functions. The concentration of researchers has always been on how to design and prepare materials, regulate their responsive behaviors, and develop practical functions.[69] At present, there are already many methods for orientation of mesogens in LCP materials, and it is not very difficult to prepare small test samples of soft actuators, but how to achieve large-scale production rather than manual workshop production remains to be solved. At the same time, from the perspective of environmentally friendly and reusable materials, the reconfigurable, reprocessing performance and self-repairing ability of LCP-based actuators also need to be pushed forward.

The stimuli-responsiveness or the deformation of soft actuators relies on the selection of microscopic components and structural design of materials. However, it is not the final research destination that the LCP-based actuator deforms upon exposure to stimuli. How to control its responsive behavior quantitatively and accurately, and improve its working efficiency is still being underway. More importantly, as the highly concerned intelligent materials, soft actuators should have the ability of self-diagnosis, self-regulation, self-learning, and other advanced properties. How to regulate the responsive path of materials to form a feedback loop is the key to solve the problem. Last but not least, in order to achieve the goal of miniaturization and multifunctional integration, the construction of multi-stimuli responsive LCP actuator, or the combination of LCP with other soft materials, is expected to expand its function and improve the universality of its working environment.

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Notes

The authors declare no competing financial interest.

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