# Liquid Crystal Networks Meet Water: It's Complicated!

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Soft robots are composed of compliant materials that facilitate high degrees of freedom, shape-change adaptability, and safer interaction with humans. An attractive choice of material for soft robotics is crosslinked networks of liquid crystal polymers (LCNs), as they are responsive to a wide variety of external stimuli and capable of undergoing fast, programmable, complex shape morphing, which allows for their use in a wide range of soft robotic applications. However, unlike hydrogels, another popular material in soft robotics, LCNs have limited applicability in flooded or aquatic environments. This can be attributed not only to the poor efficiency of common LCN actuation methods underwater but also to the complicated relationship between LCNs and water. In this review, the relationship between water and LCNs is elaborated and the existing body of literature is surveyed where LCNs, both hygroscopic and non-hygroscopic, are utilized in aquatic soft robotic applications. Then the challenges LCNs face in widespread adaptation to aquatic soft robotic applications are discussed and, finally, possible paths forward for their successful use in aquatic environments are envisaged.

## 1. Introduction

Robotics has played a major role in shifting technological paradigms over the last several decades. The common premise in the design and manufacturing of all robots has been essentially emulating human or animal forms, bodies, and functions and elevating them beyond natural capacities. With the advent of robots as auxiliary machines, a variety of industrial tasks requiring high force, speed, and spatiotemporal precisions became attainable, which would have been inefficient or even impossible otherwise. Hard robots, traditionally, are mechanical machines made of multiple rigid sensing, actuating, and computational components that, together, perform various tasks. Decades of progress have yielded hard robots with remarkably complex motions, control, and functions. However, the noncompliant nature of their building blocks limits their dexterity where safe interaction with humans and soft or fragile objects is indispensable. Hard robots also have difficulty adapting to different shapes and performing tasks in natural environments that at times are cluttered, confined, uneven, and filled with fluids. Designing smaller robots or those with a larger number of miniaturized components and joints, although portray some solutions, ultimately makes hard robots thermodynamically inefficient and costly. Soft robotics is an emerging field in which the challenges hard robots face can be remedied.[1–3]

In soft robotics, the mimicry of human and animal bodies, forms, and functions evolves into the assimilation of soft tissues and organisms, such as muscles and cells.[4,5] Similar to all biological creatures, soft robots are either partially or entirely made of compliant materials, as actuators, that facilitate higher degrees of freedom, adaptability, and safer interaction with humans.[6,7] Countless recipes for the design of soft materials, from molecular to macroscopic levels, have provided a vast repertoire of actuators made from either inherently passive or active materials.[8] Thanks to such diversity in design, not only do soft robots enhance the function and performance of their hard cousins, but they also introduce completely unprecedented capabilities.[9] For instance, soft robots made from biocompatible materials can be utilized in various healthcare technologies ranging from sensing to remote communication and control.[10,11] Small-scale soft robots, particularly, promise minimally invasive medical procedures in confined, complex, and flooded media similar to the human body.[12,13]

The field of soft robotics, in general, and small-scale soft robotics, in particular, have introduced new challenges for materials scientists and chemists in developing novel materials with built-in sensing, actuation, and computational abilities that can operate in complex environments.[14,15] Among the plethora of soft robotic materials with such capabilities, cross-linked networks of liquid crystal polymers (called LCNs hereafter) and

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hydrogels have been the subject of extensive study for their many interesting characteristics.[16,17] For instance, the responsiveness of a great number of LCNs and hydrogels to external stimuli, such as heat, light, chemicals, and magnetic fields, allows for their remote control in untethered robotic applications. However, the stark dichotomy between LCNs and hydrogels in their chemistry, biocompatibility, and more importantly, interaction with water has led the majority of scientists to favor hydrogels in developing soft actuators, robots, and devices that are sought to function in aqueous media (called "aquatic soft robotic" hereafter). The affinity of small-scale soft robots with surrounding aquatic media becomes essential in order for them to be utilized in medical procedures where the workspace is usually confined and filled with liquids, like mucus, blood, and vitreous humor.

In this review, we first elaborate on the dichotomy between hydrogels and LCNs and discuss possible solutions to reconcile their differences. Then we will dissect the complicated relationship between LCNs and water, which should be taken into account in the design of aquatic, LCN-based soft robots. We also review the existing body of literature where LCNs, whether hygroscopic or not, have been utilized in aquatic soft robotic applications and discuss the challenges faced therein. Finally, we portray an outlook and paths forward for the widespread utility of LCNs in aquatic soft robotic applications.

## 2. Hydrogels versus Liquid Crystal Networks

In order to understand the dichotomy between LCNs and hydrogels it is essential to step back and scrutinize their molecular and physicochemical characteristics that pertain to soft robotics. Aside from describing the differences between LCNs and hydrogels, we should also point out a class of materials where LCNs and hydrogels seemingly confluence, namely lyotropic liquid crystal hydrogels.[18] The stark differences between the applicability of hydrogels and LCNs as soft actuators have recently stimulated research on lyotropic liquid crystals in new directions. Biocompatible lyotropic liquid crystal hydrogels, particularly, might be deemed as a class of materials that hand in the best of both LCNs' and hydrogels' worlds. This being said, the research in this field is still in its infancy and many technical challenges need to be solved before the true potential of this class of materials is revealed.
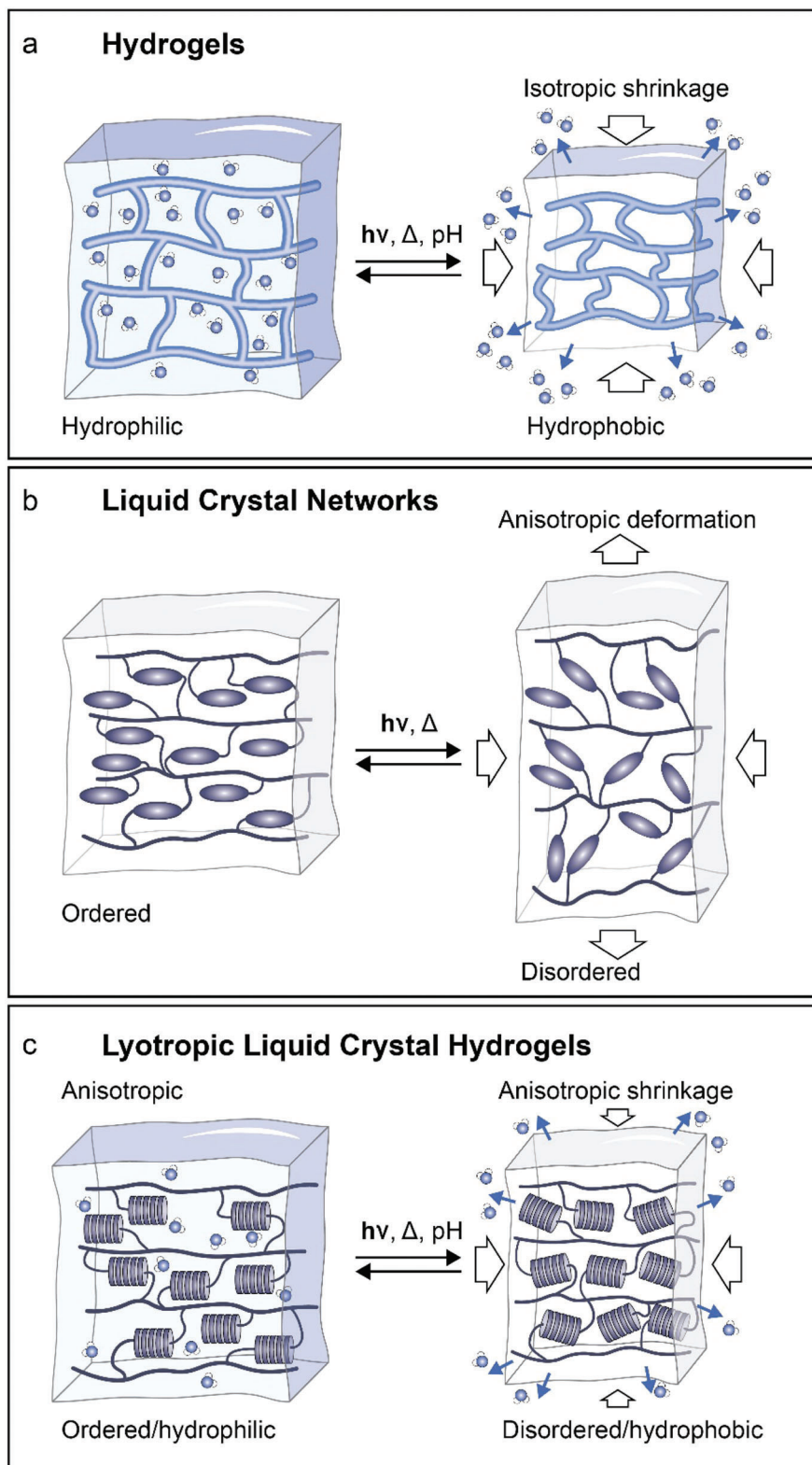
### 2.1. Hydrogels

Hydrogels are soft materials that contain a significant amount of water and are composed of hydrophilic polymer chains crosslinked into 3D networks via different chemical or physical interactions.[19–21] The bioaffinity and substantial water content provide hydrogels with properties comparable to biological tissues, making them appealing for biomedical applications.[22–25] As such, hydrogels have been used in a variety of biomedical applications including biosensors, scaffolds, medical microrobots, and drug delivery systems.[26–30] Many hydrogels can absorb or lose water through a change in hydrophilicity in response to various external cues such as temperature, pH, light, electric field, or chemicals. The molecular-scale hydrophilicity change can trigger coil-to-globule transitions, resulting in reversible macroscopic deformation in the form of swelling and shrinkage (**Figure 1**a). Such an actuation mechanism is driven by water uptake/release, which depends on the diffusion of water molecules into or out of the hydrogel network. In the majority of cases, hydrogel actuation is isotropic, which limits their widespread use in soft robotic applications where asymmetric shape transformations form the basis for locomotion and function. Anisotropic shape changes of hydrogels, hitherto, have been achieved via two dominant approaches.[17,19,31] First, isotropic hydrogels exposed to nonuniform external stimuli such as patterned electric or light fields, show nonuniform shape transformations.[32] In this approach, the mechanism of shape morphing at the microscale is still isotropic and the spatiotemporal control of the applied nonuniform external stimuli with high precision and resolution is challenging.[33,34] The second approach is to prepare hydrogels with intrinsic microscale anisotropy by introducing nonuniformity, heterogeneity, or gradients into their micro- and macrostructures.[35–38] These approaches can result in relatively complex deformations of hydrogels. However, the diffusion-based shape-transformation of hydrogels is inherently slow and the obtained output work is small, presenting major roadblocks for aquatic soft robotic applications requiring fast shape changes.[19,39–42]

### 2.2. Liquid Crystal Networks

Thermotropic liquid crystals (LCs) are molecules with anisotropic, typically rod-like, shapes that contain a relatively rigid core and flexible peripheral alkyl tails. The rigid core enables ordered crystalline packing which diminishes upon heating, as facilitated by the flexible tails. At a certain temperature range, the LC molecules (mesogens) can flow like liquids but have some level of orientational and/or translational order like solids.[43] The anisotropic molecular order gives rise to anisotropic physicochemical properties, such as viscosity, refractive index, dielectric constant, and magnetic susceptibility. Liquid crystal networks (LCNs) are LC-containing polymers crosslinked into three-dimensional networks. Based on their crosslinking density, LCNs can be classified into lightly crosslinked liquid crystalline elastomers (LCEs) or highly crosslinked glassy networks. Throughout this work, we use the general term LCN.[44] Crosslinking arrests the local mesogen alignment and imparts the network with anisotropic mechanical properties and response to external stimuli. Exposure to heat disturbs the arrested LC order and can lead to (in the case of LCEs) a transition between liquid crystalline and isotropic phases. For mesogens aligned in a certain direction (the director), such order–disorder transition manifests in anisotropic macroscopic shape change, which is reversible thanks to the elasticity of the polymer network.[45] Uniformly aligned domains of LCNs typically contract along their director and expand perpendicular to it (Figure 1b). Accordingly, the shape change of two- or three-dimensional LCN constructs can be programmed by encoding predetermined director fields into LCN pixels or voxels through various techniques, such as surface alignment,[46–49] photoalignment,[50–58] strain,[59–63] and the use of external magnetic or electric fields.[64–70]

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**Figure 1.** a–c) Shape-change mechanisms. a) Hydrogels: External stimuli such as light, change in temperature, or change in pH causes the hydrogel network to become hydrophobic and water molecules move out of the hydrogel, resulting in isotropic shrinkage. b) LCNs: External stimuli such as light or heat cause a reduction in the molecular order, resulting in anisotropic deformation. c) Lyotropic LC hydrogels: A loss of water is triggered by external stimuli such as light, change in temperature, or change in pH, resulting in both shrinkage as well as a reduction in the LC order, leading to anisotropic shrinkage.

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The chemical structure of mesogens, their position inside the network, and the degree of crosslinking affect the physicomechanical and actuation properties of LCNs.[45,71,72] LCNs generally outperform hydrogels in programmability, the complexity of shape morphing, response time, and output work. Moreover, in contrast to hydrogels which are predominantly used in water, LCNs are usually utilized in dry conditions due to their limited affinity to water and the inefficiency of thermal actuation under water. LCNs have not been widely regarded as biocompatible materials, which limits their potential in biomedical applications. But, recently, a number of reports investigated their cytocompatibility,[45,73–76] as well as in vivo animal studies.[77] For instance, Shaha et al. implanted LCN constructs mimicking intervertebral discs in rats. Their histological analysis showed that LCN implants caused the development of a fibrous capsule but no obvious inflammatory response or noticeable swelling on the animal.[77] There is still a need for longitudinal studies on their effect on the human body.

### 2.3. Lyotropic Liquid Crystal Hydrogels

Lyotropic liquid crystals undergo phase transitions due to changes in their concentration in a solvent as well as changes in temperature. A sub-category of lyotropic LCs (LLCs) consists of amphiphilic molecules, such as surfactants, that are flexible and composed of a hydrophilic headgroup and a non-polar tail. The hydrophobic effect enables these molecules to self-assemble into highly ordered yet fluidic structures in the presence of a polar solvent such as water. The aliphatic tails of amphiphiles aggregate into fused hydrophobic regions, while the polar or ionic headgroups are found at the LLC–water interface. Amphiphilic LLCs can create disk-shaped or rod-shaped 3D micellar aggregates, which in closely packed configurations form lyotropic nematic phases. Confinement and shear have been utilized to align nematic LLCs, and like in thermotropic LCNs, the order can be frozen upon crosslinking.[18,78]

Another sub-category of LLCs consists of chromonic LCs with flat hydrophobic cores and ionic groups on the molecules' periphery. In water, the flat cores stack face-to-face (Figure 1c) to minimize water interaction, and the polar groups on the periphery provide water solubility. The stacking of chromonic LCs yields anisotropic aggregates which can form LC phases at certain concentrations and temperatures. The control over molecular order of chromonic LCs is possible and desirable director fields have been obtained using techniques such as alignment by shear, chemical surface coatings, surface topographies, and photopatterning.[47,79–82] Shape-morphing hydrogels of chromonic LCs have been reported in recent years with mechanisms rooted in anisotropy of network architecture and mechanical properties.[83–85]

The remarkably low twisting elastic constant and the sensitivity of LLC phases to external cues such as temperature and shear make accurate on-demand molecular alignment control of LLCs and their crosslinking into ordered networks extremely challenging.[86] For these reasons, lyotropic liquid crystal hydrogels have not yet found their way as actuators to mainstream aquatic soft robotics, despite the promise of reconciling between LCNs and hydrogels.

## 3. The Complicated Relationship between LCNs and Water

To our knowledge, there has not been a report that systematically studies, in-depth, the affinity between LCN actuators and water through measurement of surface/interfacial energies, wetting, adhesion, absorption interactions, and static/dynamic contact angle measurement. The scattered knowledge on the subject is perhaps due to the diversity of LCN formulations thus far reported. Our survey of the literature shows that the static contact angle of water on thermotropic LCNs varies between 60° and 100°.[51,87–91] The literature lacks information about dynamic contact angles, especially the receding contact angle, which is a better metric to determine LCNs' hydrophobicity/hydrophilicity.[87] In addition to the water contact angle, the permeability of water (or water vapor) can be used to gauge the level of hygroscopicity. The available data show that the water vapor permeability of typical liquid crystal polymers (LCPs) is significantly lower than other studied polymers, such as Nylon 6, poly(ethylene terephthalate) (PET), and high-density polyethylene with water absorption of less than 0.04%.[92–95] In an older study, blending PET with LCPs reduced water vapor transmission by almost 90% compared to pure PET.[96] The data on the permeability of LCNs is limited.

Our survey suggests that the majority of LCNs used as soft actuators are non-hygroscopic unless certain formulations or microstructures are judiciously selected to bestow them with hydrophilicity or make them hygroscopic. For non-hygroscopic LCNs, water at different temperatures acts only as either a heat source or sink regulating the actuation and relaxation driven by other stimuli, such as heat and light. Moreover, water has no considerable diffusion into or out of the majority of non-hygroscopic LCN networks. For hygroscopic LCNs, in contrast, not only can water regulate the deformation driven by external cues, for example, heat or light, but it can also drive their actuation as a stimulus similar to diffusion-based deformation in hydrogels. The interplay between the diffusion-based and the phase-change-based mechanisms in hygroscopic LCNs adds to the intricacy of their deformation, especially when both mechanisms are in action simultaneously. LCNs, whether hygroscopic or not, have a complicated relationship with water for they display different actuation behaviors when encountering it.

## 4. Non-Hygroscopic LCN Actuators in Contact with Water

The majority of the LCN formulations reported in the literature are non-hygroscopic and the actuation behavior of only a limited number of them is examined in contact with water. It is shown, in all such studies, that the thermodynamic and physical interactions of LCN actuators with water affect their mode, extent, and efficiency of actuation. In some of these studies, water only thermodynamically interacts with LCNs and is essentially a means to deliver or dissipate thermal energy. In some others, the physical interaction of LCNs with water as a medium regulates their soft robotic functionality. For instance, the locomotion (consecutive cycles of actuation and relaxation) of submerged LCNs is affected by volumetric forces, such as drag and hydrodynamic forces, whereas, when the LCN is positioned at the air–water
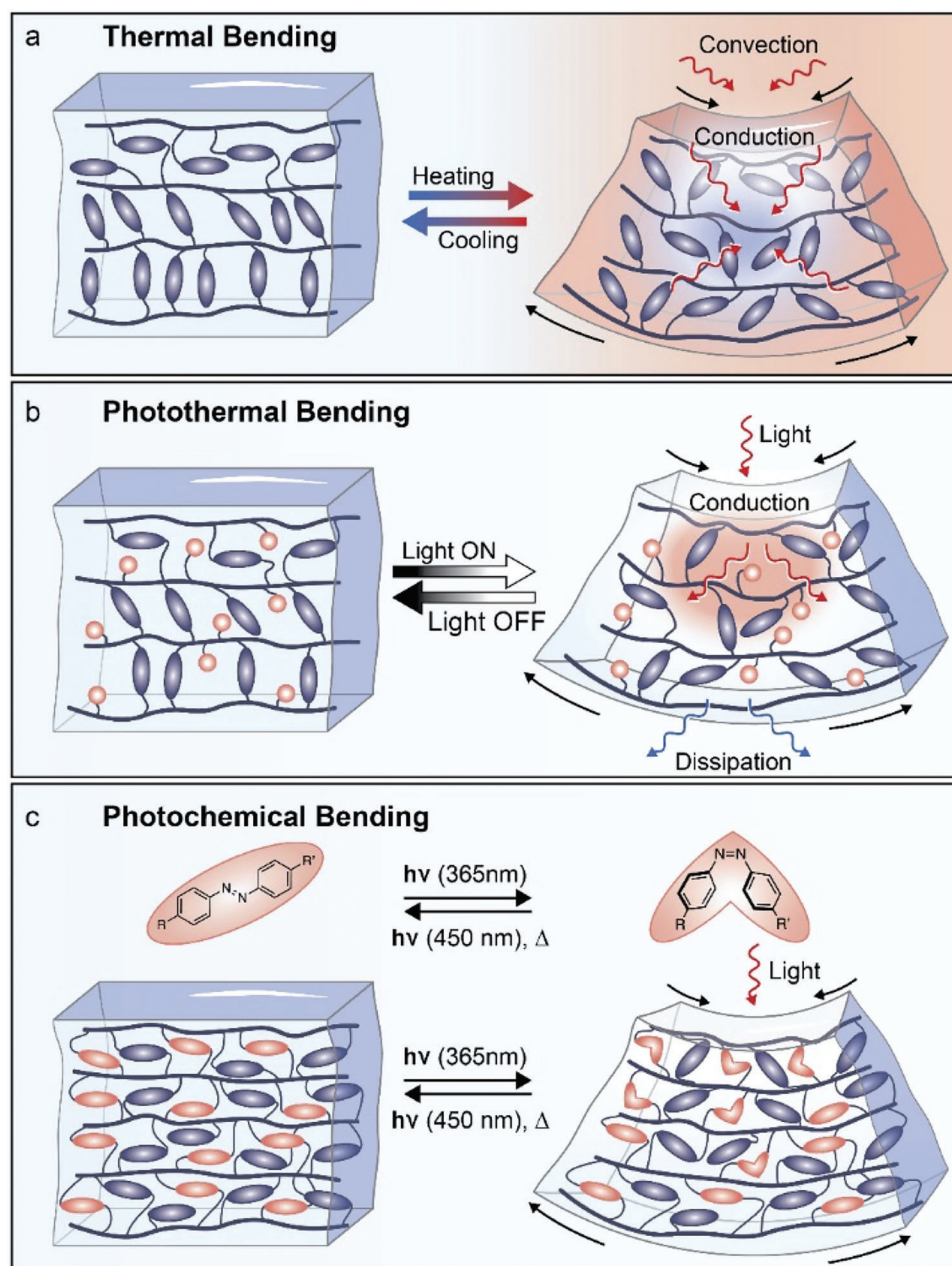
**Figure 2.** Non-hygroscopic LCN actuation mechanisms. a) Thermally induced bending: The surrounding media is heated, typically via a convection mechanism. Conduction heating in splay-aligned LCN causes a reduction in molecular order that is translated to a macroscopic shape change due contraction/expansion at the two film surfaces. When cooled, the LCN regains its original shape. b) Photothermally induced bending: The LCN slab is exposed to light on one side. Photothermal compounds doped into the LCN convert the absorbed light energy into heat. There is conductive heating within the LCN, and the heat generated rapidly dissipates in water. The increased temperature in the LCN causes a reduction in molecular order that causes macroscopic bending. When light exposure is ceased, the LCN rapidly regains its original shape. c) Photochemically induced bending: When exposed to, typically, UV light, azobenzene photoswitches in the LCN isomerize from the rod-like *trans*- to the bent *cis*-isomer. As the light is absorbed by the azobenzenes, the UV irradiation does not penetrate the full depth of the LCN slab. This results in a gradient in *cis*-isomer population and resultant anisotropic strain and macroscopic bending. This mechanism typically does not generate heat within the sample. The blue box around the schematics demonstrates the water environment.

interface, surfaces forces such as capillary become increasingly important.

As shown in **Figure 2**, the common actuation mechanism of almost all LCNs, whether hygroscopic or not, whether submerged or positioned at the air–water interface, is a reduction in molecular order rendered by heat or light.[50,97–101] The heat can be introduced to LCN actuators either directly through high-temperature air or fluid or indirectly through electrical current (or Joule heating) or light. The latter is known as the photothermal mechanism in which LCNs contain chemical dopants that convert absorbed

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light into thermal energy. Reduction of the order at the molecular scale, and shape change at the macroscale, can also be achieved through photochemical mechanisms, using molecular switches undergoing reversible isomerization reactions upon exposure to light of different wavelengths. In this section, we will elaborate on how these actuation mechanisms are affected when LCN actuators are submerged in or floating at the air–water interface.

## 4.1. Thermal Actuation in Water

The actuation behavior of non-hygroscopic LCNs dramatically changes when they encounter water, either submerged in it or positioned at the water–air interface. The overall coefficient of heat transfer of water is immensely larger than that of air. That is, depending on the difference between the surrounding water and phase transition temperatures, warmer water can act as a superior heat source and colder water can act as a superior heat sink compared to air. The heat transfer mechanism in thermal actuation and relaxation of LCNs in dry conditions is facilitated by the typically poor conduction and (free or forced) convection of air. In contrast, water, as a heat source or sink, can trigger or facilitate thermal actuation and relaxation of LCNs by promoting molecular disorder via conformal contact (Figure 2a).

While the majority of non-hygroscopic LCNs covered in this review are light-responsive, some are solely thermally responsive, for which water is used as a heat source or sink. Heating and cooling of water medium are common practices in labs to produce homogeneous temperatures around LCN actuators and visually monitor their thermal deformation or measure parameters such as thermal coefficient of expansion.[52,102,103] Cold water can be used to regulate actuation and relaxation. For example, it has been found that for underwater electrothermal actuation of artificial muscles composed of liquid metal–LCN composites, higher input power is required to achieve the same actuation stroke as in air, but faster cooling in water allowed for faster relaxation.[104] The temperature gradient across a medium of warm water in contact with a cold substrate is also used to drive asymmetric underwater actuation leading to locomotion and load bearing of LCN actuators.[105] Heating and cooling of LCNs by water, although seemingly easy, is impractical for aquatic soft robotic applications. The very same reason, i.e., the high overall heat transfer coefficient of water, makes it virtually impossible to rapidly alternate water temperature, which is necessary for dynamic soft actuation. Indeed, deformation driven by cyclic heating and cooling of water is extremely slow compared to photothermal or photochemical actuation.

## 4.2. Photothermal Actuation in Water

In the photothermal actuation mechanism, light absorbed by photothermal dopants locally generates heat that causes LC molecular disorder and macroscopic actuation (Figure 2b). Once the light source is removed the LCN relaxes back to its original shape through the dissipation of heat to its surroundings. The photothermal mechanism offers high spatiotemporal control in actuation, providing complex deformation profiles thanks to the adjustability of the spatial and temporal properties of the incident light.[50,100,106–108] In the air, photothermal actuation can be

significantly faster than other stimulation methods as it is based on heat conduction within the LCN actuator. However, the heat transfer coefficient of the surroundings dramatically affects the heat dissipation rate and shape relaxation. A crude approximation by Shahsavan et al. shows that the photothermal temperature increase of a slab of LCN upon exposure to known light intensity is much less in quiescent water than in air.[52] Indeed, the greater overall heat transfer coefficient of water makes both rates of energy storage and thermal dissipation from the LCN much faster. Accordingly, the ratio between the stored energy and the energy input, i.e., the energy conversion efficiency, is much lower. Therefore, much higher energy input is required to create a similar photogenerated temperature increase in water than in air.

Photothermal heat generation combined with fast energy dissipation in water has created a host of possibilities to elicit aquatic soft robotic functions from LCNs. In the majority of reports, doping LCNs with organic compounds such as fast-switching azobenzene derivatives like DR1, render photothermal actuation without disturbing the director fields.[51,52,106,109] Also, nanoparticles have been employed as efficient photothermal dopants that deliver selective absorption of light at different wavelengths ranging from visible to infrared. Such nanoparticles include, but are not limited to, carbon nanotubes (CNTs), gold nanorods (GNRs), and graphene.[110–113] A variety of photothermal deformation profiles such as twisting, bending, coiling, and winding, upon NIR irradiation in water, are reported.[113] The use of nanoparticles to induce photothermal actuation underwater, although effective, might disturb the molecular alignment and change the mechanical properties of LCN actuators, which could adversely affect their actuation amplitude and ability to overcome drag during undulating deformations. Instead, improved photothermal functionality can be achieved by coating LCNs with photothermal materials such as polydopamine (PDA), which not only offer photostable performance and strong absorbance in the NIR region but also have negligible effect on the mechanical properties of the LCN.[114,115]

The hydrophobic nature of LCNs can be utilized to create photothermal soft robotic locomotion and function at the air–water interface. One of the first swimming LCNs, reported by Camacho-Lopez et al., was indeed using a hybrid mechanism to slide at the air–water interface. In this seminal work, the LCN flaps deformed photothermally, bulged the capillary line and broke the symmetry. They swam away from constant light through the thermal Marangoni mechanism, in a manner analogous to that of a flatfish (**Figure 3**a).[116] Aside from the thermal Marangoni effect that could facilitate the sliding of photothermal LCNs at the air–water interface, modulation of capillary forces acting on the contact line, although difficult, can create interesting soft robotic scenarios. For instance, the exposure of the air-facing side of LCN actuators to undulating light can be used for free-form locomotion and navigation of LCNs on the water surface (Figure 3b).[117] The capillary bridge in these works is not broken and elastocapillary forces at the interface assist the relaxation stroke and better locomotion. In a recent study, an LCN construct functioned as a clutch within an active gear train at the air–water interface. When exposed to light, the teeth of the LCN clutch bent downward into the water, disengaging from the neighboring gears, and halting the transmission of power on demand (Figure 3c).[51]
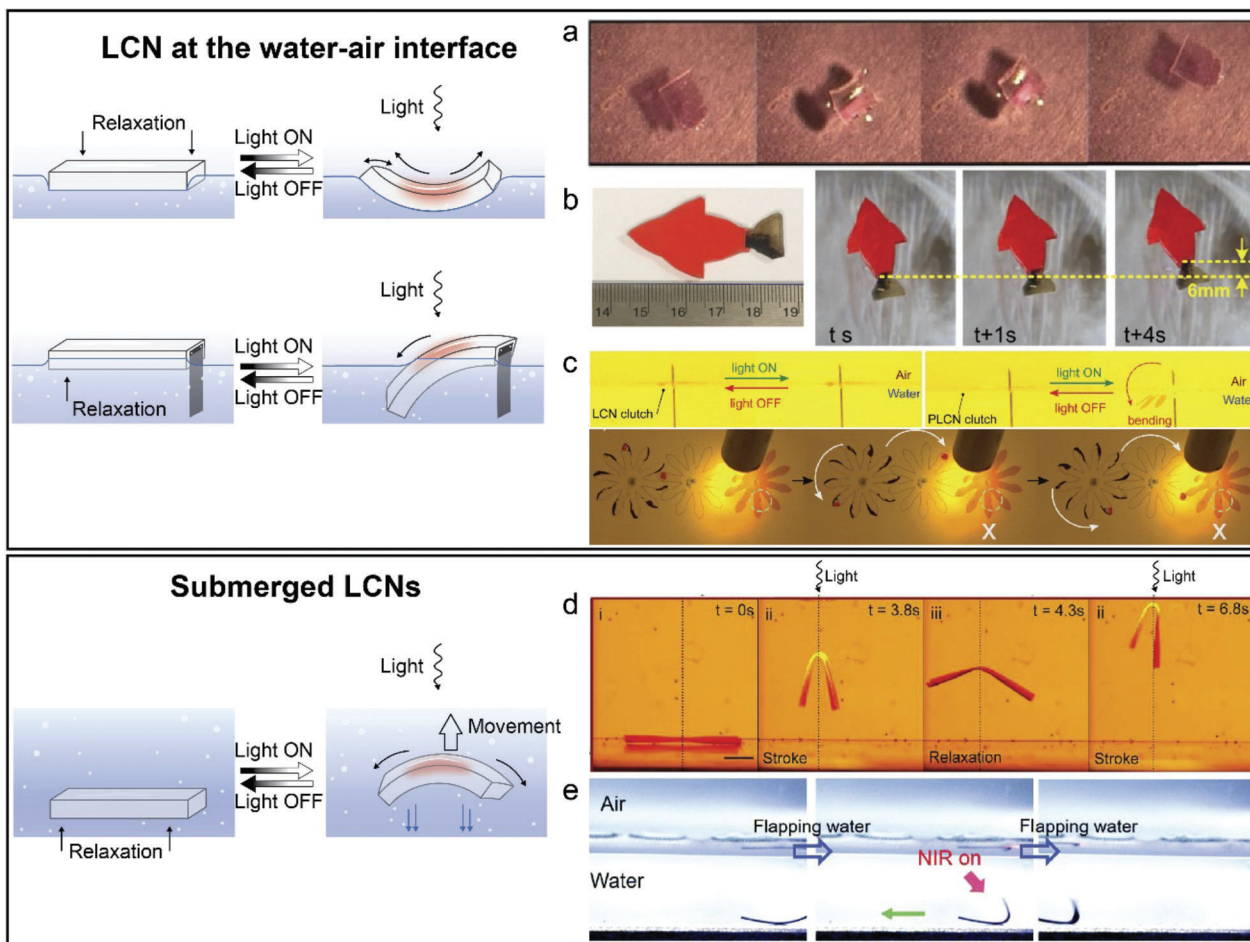
**Figure 3.** Movement of photothermal LCNs at the air–water interface and submerged in water. a) Bending of the LCN is used to manipulate the capillary line, breaking the symmetry and creating a propulsive force through the thermal Marangoni mechanism. Reproduced with permission.[116] Copyright 2004, Springer Nature. b) Repeated actuation without breaking the contact line is used to generate a propulsive force that pushes the swimmer forward. Reproduced with permission.[115] Copyright 2018, American Chemical Society. c) Breaking the contact line by actuating downward into the water is used to control the transmission of power through a gear train. Reproduced with permission.[51] Copyright 2022, Royal Society of Chemistry. d) Repeated rapid bending followed by slower relaxation through the cycling of UV light on and off is used to achieve propulsive force to achieve upward swimming. Reproduced with permission.[52] Copyright 2020, The Authors, published by National Academy of Sciences, USA; e) Repeated actuation of one end of the LCN through NIR light exposure is used to generate a propulsive force that pushes the LCN along a submerged surface. Reproduced with permission.[59] Copyright 2022, Royal Society of Chemistry.

Photothermal soft robotic locomotion and function for LCNs submerged in water present other challenges. Depending on the size of the LCN constructs and the Reynolds number of water surrounding them, hydrostatic pressure and drag forces could suppress the deformation through fast dissipation of energy. One intuitive approach to overcome this problem is to simply increase the intensity of the incident light to create a high local temperature where the robot needs to function. For example, Martella et al. used photothermal LCN-based photonic micro-hands that can selectively grab small particles based on their optical properties.[109] The micro-hand could distinguish between particles of different colors and function selectively based on absorbance at a specific wavelength. The dark objects absorbed the incident laser and increased the local temperature, causing the LCN hand to bend. The light hitting the micro-hand with low-absorbing objects did not create sufficiently large heat to cause bending. As the microhand relaxed faster underwater than in

the air, the excitation power required for actuation was five times higher.

To overcome the limitations imposed by the fast heat dissipation, drag, and hydrostatic pressure underwater, Shahsavan et al. used liquid crystal gels (LCGs) by doping LCNs with extensive amounts of short-chain mesogens like 5CB.[52] LCGs showed significantly reduced stiffness and phase transition temperature, as well as a photoinduced reduction in their density, which collectively resulted in greater actuation at the same light intensity compared to their LCN counterparts. Underwater crawling, walking, and jumping was observed for LCGs under much lower illumination intensities. However, more subtle spatiotemporal control over illumination was required to overcome the drag force and hydrostatic pressure to propel the LCG robot in an upward swimming motion (Figure 3d). Softening, reducing the transition temperature, and fine-tuned spatiotemporal control over the illumination were used to elicit soft robotic functions beyond

locomotion. In another work, LCN films exposed to light contracted along their long axis with a slight upward bending. When the light was off the LCNs recovered to the initial flat shape. By varying the location and the size of the exposed area, different bending patterns were achieved. Cycling the light exposure on and off caused the LCN film to undergo repeated actuation, generating a propulsive force that pushes the film forward inside the water (Figure 3e).[59]

Deng et al. have recently demonstrated autonomous microfluidic pumping, translocation of micro-object through liquid propulsion, and hydrodynamic coupling between two non-equilibrium artificial cilia, all driven by the self-shadowing effect.[100,118] The LCN strips in their report progressively bent with elevating laser intensity in an aqueous environment, and eventually, a self-sustained oscillatory motion was realized. By implementing two orthogonal laser beams on a single specimen, the motion symmetry was broken, and programmable non-reciprocal strokes could be induced, which, in turn, affected the fluidic pumping efficiency.

### 4.3. Photochemical Actuation in Water

The photochemical effect in LCNs is often introduced by azobenzene photoswitches that undergo isomerization and induce macroscopic shape change incorporated into the LCN. Azobenzene derivatives transition from the stable rod-like *trans*-isomer into a metastable bent *cis*-isomer under irradiation with typically near-UV light. The *trans–cis* photoisomerization can disrupt the polymer network and cause a decrease in LC order, which in turn can give rise to macroscopic deformation. The thermodynamically stable *trans*-isomer can be retained either through thermal relaxation or upon exposure to light in the *cis*-isomer's absorption band, typically in the blue–green region of the visible spectrum (Figure 2c).[119] Azobenzene derivatives with long *cis*-lifetimes and those that can be addressed with visible light have also been synthesized, due to their potential in biomedical and photopharmacological applications.[120–123] This allows for an additional level of control over the photochemically driven LCNs compared to their photothermal counterparts as the actuator remains bent for a period set by the *cis*-lifetime once the light has been removed.[124] However, photochemical LCNs with azobenzene derivatives usually rely on UV light for actuation, which limits their potential use, especially in biomedical applications.

Many researchers have circumvented the issue of fast dissipation of photothermal heat in water by using photochemically responsive LCNs. Photochemical actuation, at its best design, is an isothermal process and hence well suited for use in water. The higher heat dissipation in water can extend the lifetime of the meta-stable *cis*-isomer as it reduces potential heat-promoted back relaxation, which in some cases has resulted in marginally larger actuation upon irradiation underwater.[125–127] Photoisomerization of azobenzene derivatives can also result in a reduction of LCN density, which can be a useful attribute when designing aquatic soft robots and locomotors.[54]

Da Cunha et al. systematically studied the contribution and role of photochemical and photothermal mechanisms in the actuation of LCNs in contact with water. LCNs with mono- and bi-

functional azobenzenes with long *cis*-lifetime had different underwater actuation behavior than azobenzenes with shorter *cis*-lifetime, which drive photothermal rather than photochemical actuation. Under identical illumination conditions, the photochemical mechanism resulted in remarkable bending underwater, while the photothermal mechanism led to limited actuation, as expected based on the fast heat dissipation discussed earlier. The fast dissipation of heat in water stymied the relaxation of LCNs which typically rely on thermal back relaxation in photochemical mechanisms. An amphibious walker prepared from photothermal LCNs could consequently move in water at a slower speed.[128]

The slow relaxation of photochemically active LCNs enables on-demand manipulation of the capillary line when they are positioned at the air–water interface. For example, Hu et al. used optocapillarity induced by the deformation of LCNs at the air–water interface to achieve programmable and reconfigurable two-dimensional assemblies.[129] UV irradiation induced directional bending in the film, which was used to obtain curvature of menisci at the edges of the actuators, providing control over the magnitude and direction of the attractive or repulsive capillary forces between the actuators. Different assembly patterns were achieved through different combinations of upward and downward bending of the actuators (**Figure 4**a). Bilayers of LCNs and other materials have also been used to construct soft robots capable of swimming at the air–water interface. Ma et al., for instance, fabricated a bimorph composite swimmer consisting of an LCN film and a Kapton film. The actuation was controlled through exposure to UV, with a fast relaxation when exposure ceased. The deformation was attributed to continuous cycling between the *trans* and *cis* isomers of the azobenzene rather than the *trans–cis* isomer ratio. By cycling the UV light, the swimmer propelled itself forward with downward beats into the water, analogous to how dolphins swim (Figure 4b).[130]

Swimming underwater solely based on the photochemical deformation of LCNs has rarely been reported. To the best of our knowledge, the only successful photochemical swimmer is reported by Huang et al. through operating the swimmer via periodic exposure to UV and white light, creating an artificial flagellum swinging back and forth and pushing the LCN construct forward (Figure 4c). Given the slow nature of photochemical deformation, the speed of locomotion was very low.[131] While photochemical LCNs have not shown much utility as swimmers up to date, their slow actuation and relaxation have been the basis of design for the manipulation of water itself or other objects underwater. Van Oosten's well-known work is an example of photochemically driven LCNs that function like cilia underwater.[132] The photochemically driven artificial cilia were used as mixers or pumps, capable of both forward and backward strokes. Asymmetric movement of the cilia was achieved by using two different azobenzene dyes, varying the composition of the actuator in-plane and allowing for different degrees of bending based on the color composition of light used. Later on, photochemical light tracking fiber assays resembling cilia were reported with the potential for transport of submerged objects.[127,133,] A more sophisticated design inspired by aquatic polyps was later developed by da Cunha et al. using a hybrid construct of photochemical LCNs and passive magnetic elastomers to grasp and release buoyant objects underwater on demand (Figure 4d).[134] In
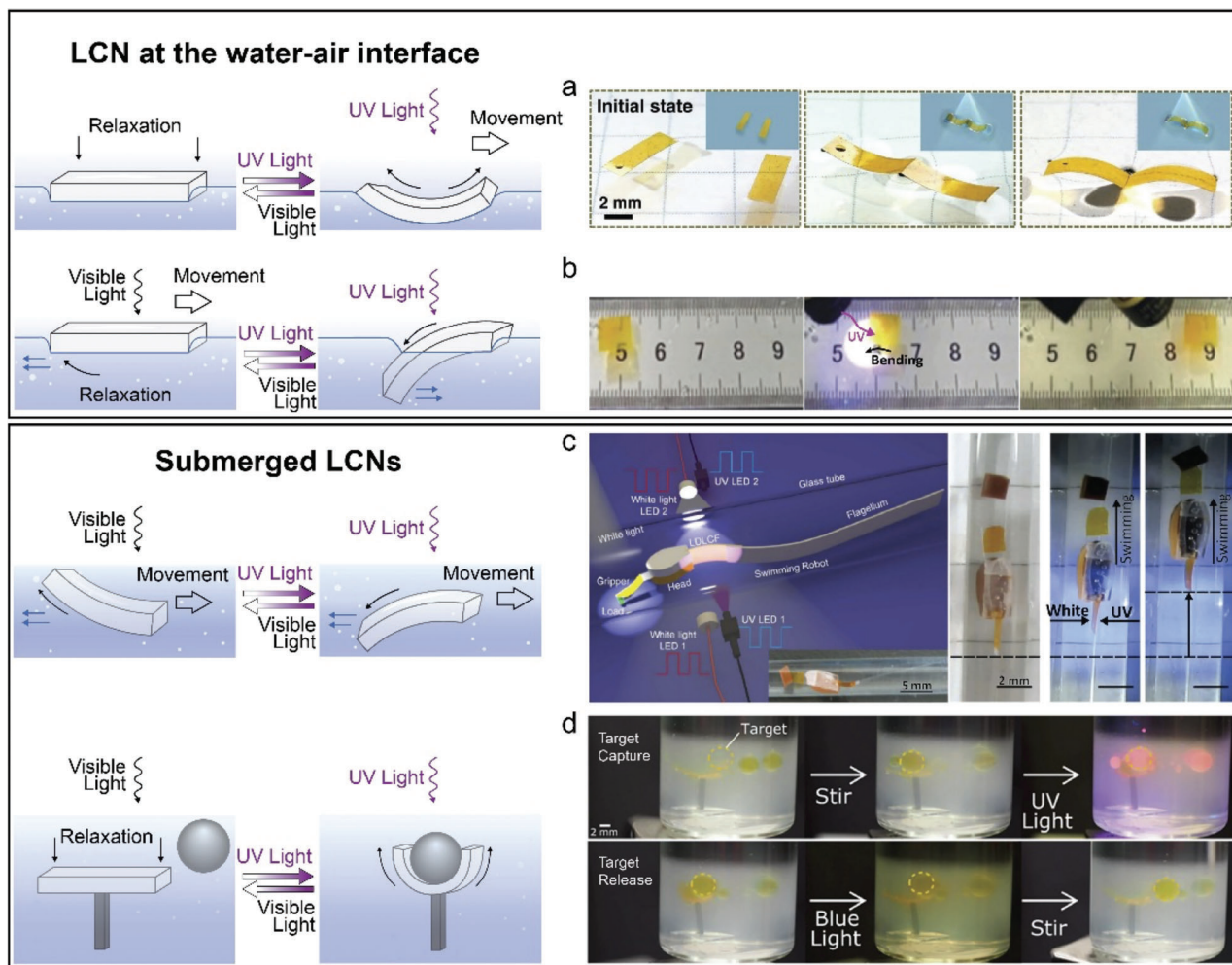
**Figure 4.** Movement of photochemical LCNs at the air–water interface and submerged in water. a) Directional bending of the LCN creates a curvature of the menisci at the edges of the actuators, resulting in controllable attractive or repulsive capillary forces between the actuators. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0).[129] Copyright 2020, The Authors, published by Springer Nature. b) Repeated downward actuation that breaks the capillary line with fast relaxation generates a propulsive force that drives the LCN swimmer forward. Reproduced with permission.[130] Copyright 2019, Wiley-VCH. c) Bending of the LCN through periodic exposure to UV and white light causes an artificial flagellum to swing back and forth, which generates a propulsive force that pushes the swimmer forward. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International license (https://creativecommons.org/licenses/by/4.0).[131] Copyright 2015, Springer Nature. d) LCN grippers bend to grasp and relax to release buoyant targets through exposure to UV and visible light, respectively. Reproduced with permission.[134] Copyright 2020, The Authors, published by National Academy of Sciences.

addition to swimming and cargo transport, photochemical LCNs as confining surrounding media have been used to transport and mix liquids.[135–137]

## 5. Hygroscopic LCN Actuators

Unlike their non-hygroscopic counterparts, hygroscopic LCN actuators have enhanced affinity to water, which resembles, to some extent, the swelling/shrinkage of hydrogels. Such affinity can be obtained by changes in the chemical formulation or microstructure of the LCNs that allow tangible water absorption. Absorption of water (or environmental humidity) by hygroscopic LCNs manifests itself via macroscopic shape-change, which is essentially an actuation method auxiliary to the more common thermal, photothermal, and photochemical actuation mechanisms.

Thus far, several methods have been proposed to make LCNs respond to changes in ambient humidity, including assisted water diffusion, induced hygroscopicity, interpenetrating networks (IPNs), and hybridization (**Figure 5**).[138,139] In this section we will elaborate on such methods and how they could hand in hygroscopic actuators whether they be solely based on bulk LCNs or based on chemical or physical hybrid designs containing LCNs. We will also discuss the application of such actuators in the context of aquatic soft robotics.

### 5.1. Assisted Water Diffusion

Inherently hygroscopic molecules typically contain a sizable amount of polar functional groups (e.g., C–O–C or C=O) or

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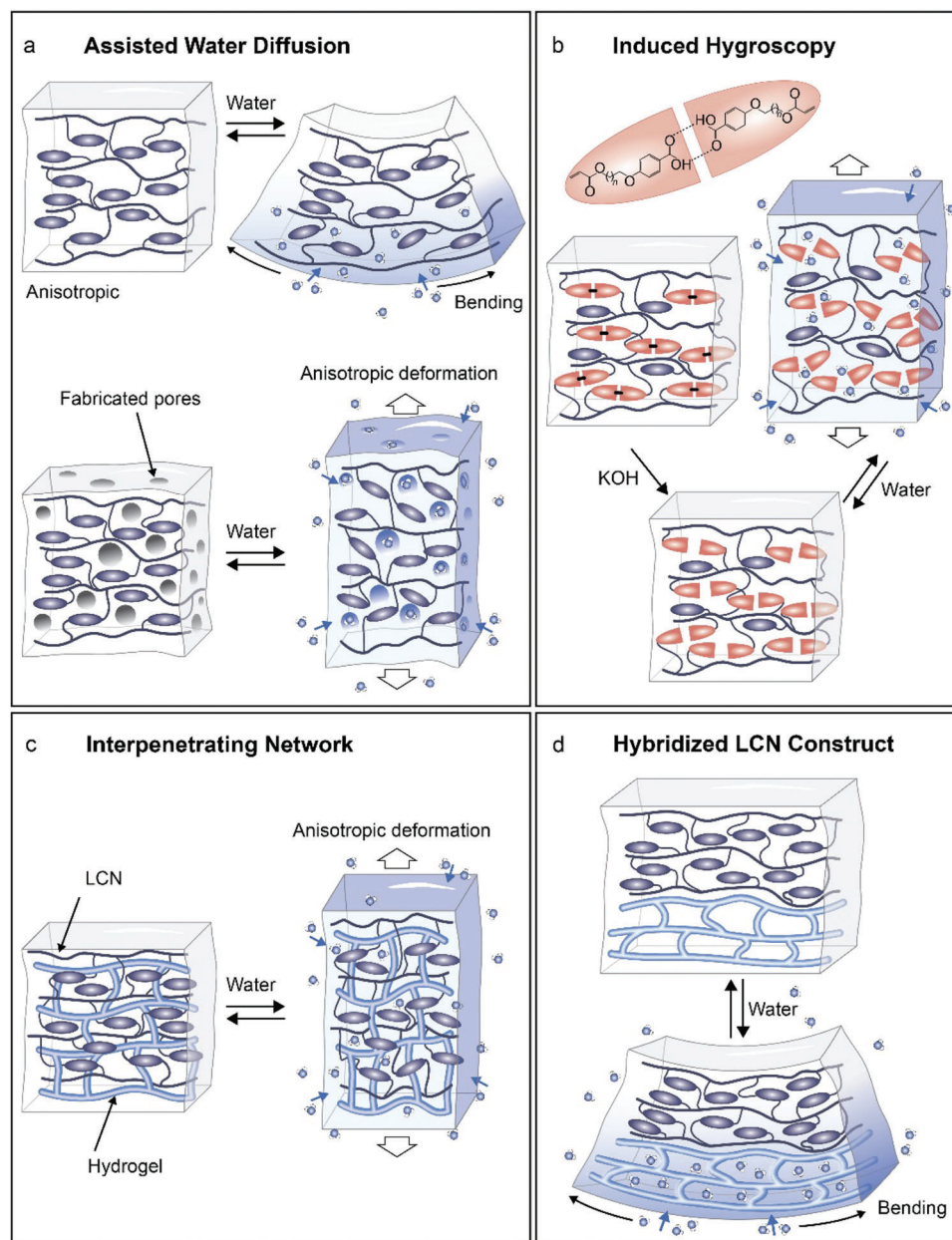
**Figure 5.** Methods to achieve hygroscopic responsiveness in LCNs and their actuation mechanism. a) Assisted water diffusion: The LCN is fabricated to absorb water molecules, by reducing the thickness or introducing pores. When exposed to humidity the LCN absorbs water molecules, which disrupts the molecular ordering of the liquid crystal mesogens. If water is absorbed equally throughout the LCN, this results in anisotropic deformation based on the alignment of the mesogens. If only one side of the LCN is exposed to humidity, there will be a gradient of absorbed water in the LCN, resulting in bending. b) Induced hygroscopicity: Carboxylic-acid-terminated molecules are included in the LCN to form hydrogen bonds. Treatment with a basic solution breaks the hydrogen bonds to form a polymeric, hygroscopic salt. As a result, the LCN will absorb water upon exposure to humidity, which reduces the order of the LC mesogens and results in anisotropic expansion. c) Interpenetrating network (IPN): The LCN is used as a template for the formation of a hydrophilic secondary network. Upon exposure to humidity, the IPN will absorb water, resulting in swelling. This swelling will be anisotropic as dictated by the LCN alignment. d) Hybridized LCN construct: The LCN is hybridized at a macroscopic level through the preparation of multilayer films. Upon exposure to humidity, the hygroscopic layer will expand more than the LCN layer, resulting in bending directed by the alignment of the LC mesogens.

moieties that interact with ambient humidity without additional treatment. Many seemingly non-hygroscopic LCNs indeed have such polar functional groups. In such cases, however, the overall LCN composition is still rich with non-polar groups and the network porosity is too small which impedes the diffusion of water

molecules within the LCN films. In an interesting observation, Liu et al. reported a non-hygroscopic, photoresponsive LCN film that could undergo macroscopic deformation upon exposure to a humidity gradient. The LCN consists of RM257 crosslinker and azobenzene monoacrylate to yield the photochemical response.

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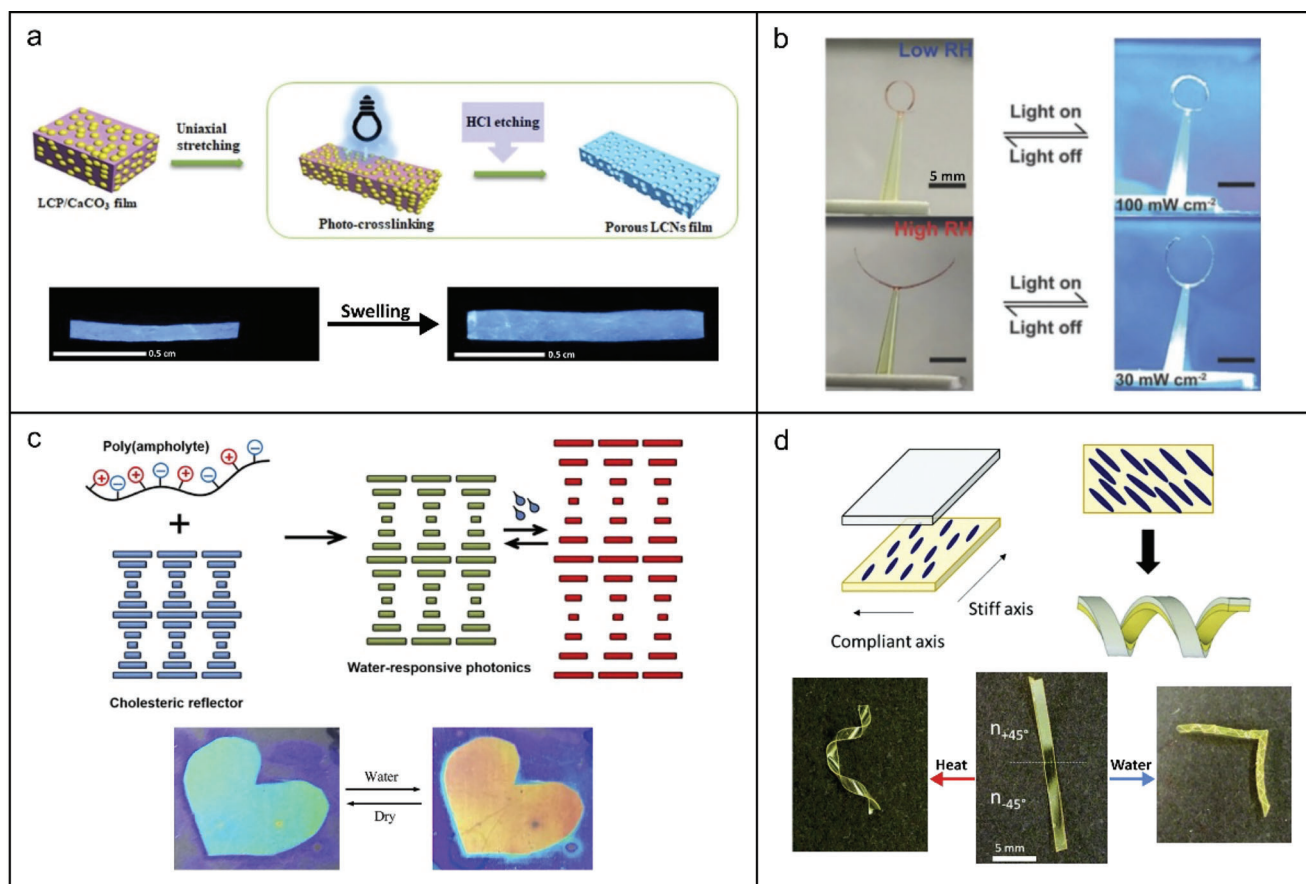
**Figure 6.** Hygroscopic LCNs. a) Assisted water diffusion: Enhanced LCN swelling is achieved through the introduction of porosity. The swelling occurs anisotropically due to the anisotropy in the molecular alignment and mechanical properties of the LCN. Reproduced with permission.[141] Copyright 2022, Wiley-VCH. b) Induced hygroscopicity: Gated humidity-responsive actuation is achieved through a base treatment to establish a gradient of deprotonated carboxylic acid groups, leading to anisotropic swelling upon water intake. Upon photothermal heating, the humidity inside the film both depletes the swelling and decreases the LC alignment. Reproduced with permission.[56] Copyright 2018, Wiley-VCH. c) Interpenetrating networks: An IPN of cholesteric LCNs and poly(ampholyte) networks demonstrates reversible changes in reflective colors upon different humidity content. The hydrophilic network swells when exposed to high ambient humidity, which changes the chiral pitch and therefore the reflection wavelength of the IPN. Reproduced with permission.[150] Copyright 2019, American Chemical Society. d) Hybridized LCN constructs: Modifying the alignment throughout the LCN film in a bilayer LCN–hydrogel actuator results in complex actuation modes upon exposure to heat or humidity. Reproduced with permission.[159] Copyright 2017, Royal Society of Chemistry.

Similar to many other reports, such chemical formulation bears ethers, esters, and acrylates as potential adsorption sites. Herein, however, the used LCN film was relatively thin, 14 μm, in which case even a relatively thin hydrated layer gave rise to significant bending and decreased the alignment of the mesogens. The humidity gradient as a result of heterogeneous water absorption through the film thickness led to the bending of the LCN away from the source of humidity, offering an orthogonal control to UV irradiation, which led to bending to the direction of illumination.[140]

To assist the diffusion of water into LCN films, Jiang et al. developed a fabrication method for porous LCN actuators. The porosity was introduced by adding $CaCO_3$ particles to the LCN precursor and etching them out of the polymerized network after the film fabrication. The introduction of the porous microstructure into the non-hygroscopic LCN dramatically enhanced the LCN swelling by up to an order of magnitude (**Figure 6**a). This was attributed to the presence of large voids that facilitated access to polar sites that are prone to absorb water molecules. Due to the anisotropy in the molecular alignment and mechanical properties of the LCN, the swelling was anisotropic. Complex deformation profiles triggered by heat or light were obtained as a result of the interplay of volume variation due to water absorption and shape changes arising from the reduced molecular alignment of the mesogens. Theoretically, these porous LCNs can also be further functionalized by loading them with functional fillers such as dyes or fluorophores.[141]

## 5.2. Induced Hygroscopicity

Although the natural presence of polar, hydrophilic groups in the LCN may lead to (minor) water absorption, in most cases this does not cause swelling or disruption in the LC alignment sufficient for macroscopic deformation. Post-treatment of LCNs with acids or alkalis can be used to modify their polarity and

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increase their hygroscopicity and, as a result, sensitivity to ambient humidity. Harris et al. reported an LCN composed of monoacrylate molecules terminated with carboxylic acids that could form dimers via hydrogen bonding. Alike common LC crosslinkers, the hydrogen-bonded dimers are essentially bifunctional rod-like mesogens that can form aligned LC phases. Their post-treatment with a basic solution breaks the hydrogen bonds and forms a polymeric salt, which destructs the order of the mesogens. Because of the presence of hygroscopic salt, the post-treated films undergo significant anisotropic swelling in response to ambient humidity, resulting in directed bending/deformation of the film determined by molecular patterning.[142] In a subsequent study, the same authors investigated the response of a series of LCNs to different solvents and solvent mixtures. The alkali-treated and dry films still contained significant amounts of water, so when immersed in water-miscible polar solvents like ethanol or methanol, the water was extracted out of the matrix, resulting in inverse actuation compared to the water-induced actuation.[143]

Building on this method, other techniques and chemical modification routes have been explored to fabricate more sophisticated and complex actuation. For example, de Haan et al. reported an LCN that through localized treatment with basic solution was capable of asymmetric shape changes such as bending, twisting, or curling when exposed to humidity.[144] Kim et al. recently explored inducing hygroscopicity into LCNs made by the Aza-Michael reaction. Treating such LCNs with an acidic solution created hygroscopic ammonium ions from existing dimethyl amino groups. This formulation was used as an ink for the 3D printing of complex architectures with intricate actuation modes.[145]

Post-treatment-induced hygroscopicity of LCNs has created a host of possibilities for programming humidity-responsive shape changes. For example, Wang et al. treated one side of the actuator with a basic solution and then programmed its humidity response by locally decreasing the hygroscopicity via $CaCl_2$ treatment and subsequent use of dipotassium ethylenediamine tetraacetic acid as a chelating ligand to reprogram the actuation.[146] Lan and co-workers elicited a gated response in humidity-responsive, hygroscopic LCNs in an $SO_2$-rich atmosphere. In dry conditions, the presence of $SO_2$ blocked the relaxation of the film through the acidification of carboxylic salt on the film's surface.[147]

Using heat and light as primary and humidity as a secondary mechanism of actuation can hand in gated control over the deformation. Wani et al. made an induced hygroscopic LCN actuator with gated dual responsiveness. By treating one side of a splay-aligned LCN film with KOH solution, a gradient of deprotonated carboxylic acid groups was established, leading to anisotropic swelling upon water intake. Upon photothermal heating, the humidity inside the film both depleted the swelling and decreased the LC alignment. Based on this strategy, an artificial nocturnal flower was fabricated that remained closed under daylight and bloomed only in the dark in the presence of sufficient environmental humidity (Figure 6b).[56] Hu et al. reported the formation of free-standing blue-phase LC films using hydrogen-bonded mesogenic precursors that spontaneously self-assemble into 3D nanostructures without additional orientation treatment. The blue-phase LC films showed reversible humidity- and pH-responsive color change and actuation, which

was rooted in the alteration of the lattice parameters of the nanostructures.[148]

### 5.3. Hygroscopic LCN Interpenetrating Networks and Copolymers

Another method for fabricating humidity-responsive LCN actuators is the use of interpenetrating networks (IPNs) of LCNs and hydrogels.[149,150] In the LCN–hydrogel IPNs the LCN is used as a template for the formation of the secondary network consisting of strongly hydrophilic monomers. This method efficiently combines the alignment introduced by the LCNs and hygroscopicity introduced by the secondary network. To the best of our knowledge, LCN-hydrogel IPNs have not been used as humidity-sensitive actuators. However, their dimensional changes as a result of water uptake have been exploited in photonic applications. For example, researchers have reported IPNs of cholesteric LCNs and hydrophilic polymer networks, including poly(ampholyte) networks that demonstrate reversible changes in reflective colors in environments with different humidity content. The color change in such IPNs is due to the swelling of the hydrophilic network when exposed to high humidity ambient, which changes the chiral pitch and consequently the reflection wavelength (Figure 6c).[149,150] In a similar strategy, but using poly(acrylic acid) as the interpenetrating network inside the cholesteric LCN, Stumpel et al. developed a color-changing system that was responsive to the change of not only humidity but also pH through the protonation and deprotonation of carboxylic acid moieties.[151] Shi and co-workers reported IPNs of cholesteric LCNs and hygroscopic polyampholytes with dual response to humidity and strain. Through localized photopolymerization at different temperatures and patterned incorporation of an ionic compound, they could achieve complex visual effects in response to multiple stimuli.[152]

Copolymerization of hydrophobic mesogens with hydrophilic monomers is another approach tested by several groups to form networks with higher water swelling abilities. Kaneko, Yamakoa, and co-workers published a series of reports on the synthesis of a variety of liquid crystalline hydrogels by the copolymerization of hydrophobic reactive mesogens and acrylic acid and observed liquid crystalline phase formation and anisotropic optical and mechanical properties for the obtained copolymer hydrogel networks.[153–156] The presence of hydrophilic comonomer in these systems drastically enhanced the ability of the network to absorb water and swell, while maintaining the liquid crystalline phase. In a relatively different approach, poly(ethylene glycol) (PEG) derivatives, such as PEG-diacrylate or PEG-dithiol have been used as comonomers in LCN networks to enhance their hygroscopic behavior. Cross-linked copolymers of PEG-dithiol and PEG-diacrylate, as hydrophilic comonomers and reactive mesogens have been shown to form liquid crystalline networks with high water absorption and swelling capability with reversible shape-change in response to both heat and water.[157]

### 5.4. Hybridized LCN Constructs

Besides modifying LCNs at the molecular level, a more direct approach to elicit humidity response is to hybridize them at the

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macroscopic level, e.g., via the preparation of multilayer films. The combination of an oriented LCN film and a hygroscopic film not only maintains the inherent properties of the LCN but also introduces humidity response to the hybrid construct. Similar to a classic Timoshenko bilayer beam, each layer has a distinct coefficient of expansion, which leads to bending of the construct under proper stimulation.[158] The anisotropic mechanical properties of the LCNs in such multilayer designs can guide the bending deformation to a direction dictated by the director field. Based on this strategy, Boothby and co-workers developed a bilayer LCN–hydrogel actuator that deflected upon exposure to humidity due to the swelling of the hydrogel layer. They showed that more complex actuation modes can be programmed by manipulating the alignment throughout the LCN film (Figure 6d). Shape change in response to humidity in this design was reversed upon heating, making it possible to repeatedly switch between flat bilayer and programmed 3D shapes.[159] Presenting a simple and high throughput manufacturing process, Verpaalen et al. developed a spray-coating technique for the fabrication of bilayered actuators. More precisely, they sprayed a cholesteric LC onto a hydrophilic polyamide film, which gave a bias for twisting deformation upon swelling of the polyamide layer. The twist pitch was determined by the amount of chiral dopant in the cholesteric layer, making the shape morphing of the film programmable.[160] Building on this technique, the same group reported a dual-responsive bilayer composite that not only actuates upon swelling but also undergoes humidity-gated, amplified distortion at elevated temperatures.[161]

The hybridization of LCNs with different materials is a powerful tool to impart multi-responsiveness and functionality to a construct. In line with this idea, Lan et al. reported a fluorescent LCN–hydrogel bilayer capable of changing its luminescence color while actuating. They doped a hydrophilic acrylate monomer mixture with an aggregation-induced-emission (AIE) luminogen and polymerized it to a hydrogel layer on top of the LCN film. The employed AIE-luminogen showed humidity-dependent fluorescence emission due to twisted intramolecular charge transfer through interaction with water. Thus, swelling not only caused the bilayer film to bend perpendicular to the LC alignment director but also red-shifted the fluorescence emission by about 50 nm, effectively changing the perceived color from green to yellow.[162]

## 6. LCN Actuators Meet Water: Challenges and Outlook

Hygroscopic or not, LCNs exhibit entirely different actuation behavior in wet and dry conditions. While water appears to be a good heat source, it can be practically utilized in soft robotic applications only as a heat sink as it facilitates the dissipative relaxation of thermally responsive LCNs. Particularly, photothermally driven LCNs, which enjoy precise spatiotemporal control over their actuation, can take advantage of water's high overall coefficient of heat transfer for their rapid relaxation, and as such are far more widely studied. But photothermal actuation underwater or at its interface with air comes at the cost of high energy input for the actuation and low overall energy efficiency. Despite the relatively higher efficiency of the photochemical actuation mechanism in water, photochemically driven LCNs often rely on the

use of UV rather than visible light, limiting their potential applications, especially in biomedical fields. In addition, both photochemical and photothermal actuation of LCNs are significantly affected by capillary, hydrostatic, and drag forces exerted on them by water. For small-scale robotics, the problem of locomotion at low Reynolds numbers also adds up.[163]

In order to be more functional as soft robots, whether inside or outside water, LCNs' initial geometry should be evolved from 2D films to 3D constructs. In the past several years, different additive manufacturing strategies, such as extrusion[164–169] and two-photon polymerization[61,170–173] have been leveraged to realize complex initial geometries and accordingly intricate shape changes either in dry or submerged conditions, which certainly promise more practical soft robotic functionalities for LCNs in the future. Furthermore, decoupling soft robots' locomotion from their function can be a powerful approach to enhance the efficiency of LCNs in aquatic and medical soft robotics. For this, LCNs must be equipped with responses to other stimuli such as magnetic fields. The incorporation of magnetic particles in LCN films has been recently used to achieve their magnetically controlled locomotion which was decoupled from their underwater photochemical or photothermal function.[134,174,175] However, the doping of LCNs with microparticles does interfere with their molecular alignment making necessary a trade-off between LCN performance and particle loading. The addition of magnetic control is a promising direction for gaining finer control of LCN robots, but further research on the topic is required before it can be successfully implemented for real-world applications.

Our survey shows that hygroscopic LCNs have rarely been used in aquatic soft robotics. This is partly due to their mechanism of humidity-sensitive actuation and relaxation, which is based on out-of-equilibrium and generally slow diffusion of water in and out of the network in humid as opposed to flooded conditions. Maintaining such out-of-equilibrium conditions in aquatic soft robotics and flooded conditions is challenging as the hygroscopic LCNs will essentially reach their equilibrium swelling. As such, we believe that hybridized hygroscopic LCNs, LCN–hydrogel IPNs, and chemically activated hygroscopic LCNs containing dynamic crosslinkers have essentially limited applicability in aquatic soft robotics. Indeed, similar to hydrogels, the swelling/deswelling mechanism does not offer rapid underwater actuation for such hygroscopic LCNs.

Photo- and heat-sensitive porous hygroscopic LCNs, reported by Jiang et al., put a path forward to reconcile the differences between hydrogels and LCNs and offer a new material that combines the good properties of both.[141] However, new chemistry and methods are still required for the synthesis and fabrication of porous hygroscopic LCN actuators with fast responses to multiple stimuli. The application of photoswitchable molecules with humidity-sensitive photochemical properties may introduce novel solutions to enhance the applicability of LCNs in aquatic soft robotics. For example, hydroxyazobenzenes spontaneously transform from slow-switching to fast-switching compounds in non-polar versus polar solvents, allowing for thin films with a strongly environment-dependent thermal isomerization rate.[176,177] Hydroxyazobenzene-containing thin polymer films have recently been used in devising novel schemes for monitoring environmental humidity.[178] Their incorporation into (hygroscopic) LCNs can offer interesting routes toward environmentally

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adaptable actuation schemes. Another interesting approach is to utilize chemistries that make hygroscopic LCNs have different physicochemical and mechanical properties in air versus water. Such humidity-dependent properties could be achieved via the incorporation of water-sensitive dynamic covalent bonds or supramolecular crosslinks to LCNs, resulting in their spontaneous softening in aquatic conditions. Soft LCNs typically require less energy input for actuation and relaxation and theoretically offer higher actuation efficiency underwater. The abovementioned strategies may also offer interesting prospects in the development of amphibious soft robots.

To summarize, LCN actuators have shown potential as building blocks of soft and small-scale robots to be operated in flooded terrains, thanks to their inherent programmable, anisotropic, and stimuli-responsive properties, which hydrogels often do not inherently have. As we saw in this review, there exists a considerable body of literature demonstrating proof-of-concept aquatic soft robotic locomotion and functions driven by LCN actuators. However, they have not yet found practical real-world applications. This issue is arguably rooted in the complicated nature of the interaction between LCNs and water, which was the main subject of the current review. We envision that unlocking the mysteries behind such a complicated relationship will pave the road for the widespread application of LCNs in aquatic soft robotics in the future.

## Conflict of Interest

The authors declare no conflict of interest.

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