

Hydrogen-Bonded Supramolecular Liquid Crystal Polymers: Smart Materials with Stimuli-Responsive, Self-Healing, and Recyclable Properties

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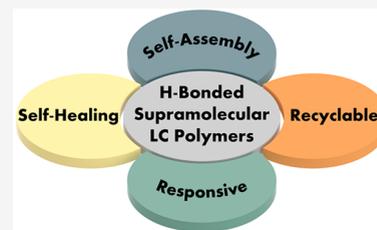
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ABSTRACT: Hydrogen-bonded liquid crystalline polymers have emerged as promising “smart” supramolecular functional materials with stimuli-responsive, self-healing, and recyclable properties. The hydrogen bonds can either be used as chemically responsive (i.e., pH-responsive) or as dynamic structural (i.e., temperature-responsive) moieties. Responsiveness can be manifested as changes in shape, color, or porosity and as selective binding. The liquid crystalline self-organization gives the materials their unique responsive nanostructures. Typically, the materials used for actuators or optical materials are constructed using linear calamitic (rod-shaped) hydrogen-bonded complexes, while nanoporous materials are constructed from either calamitic or discotic (disk-shaped) complexes. The dynamic structural character of the hydrogen bond moieties can be used to construct self-healing and recyclable supramolecular materials. In this review, recent findings are summarized, and potential future applications are discussed.



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1. INTRODUCTION

Stimuli-responsive polymer materials have attracted significant attention for developing materials that respond to external triggers. These materials are designed to change their properties when exposed to a stimulus, including heat, light, pH, solvents, and chemicals. Over the past few decades, the field of research developing “smart” polymer materials has been established as an important topic within polymer science.^{1–4}

The self-assembly and molecular order of liquid crystals (LC) are attractive for fabricating stimuli-responsive materials where changes in nanostructure will alter the properties of the material such as shape, color, or porosity. As a result, LC polymers have emerged as promising smart, functional materials due to their

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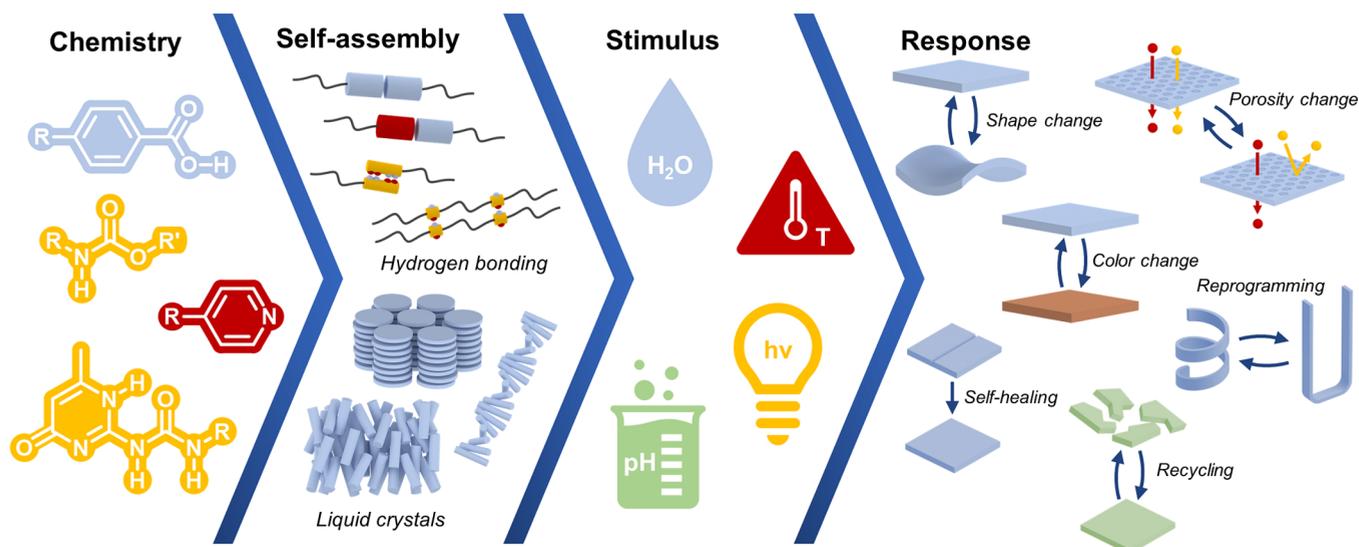


Figure 1. Conceptual steps involved in the fabrication of hydrogen-bonded supramolecular liquid crystal polymer materials with stimuli-responsive, self-healing, reprogrammable, and recyclable properties.

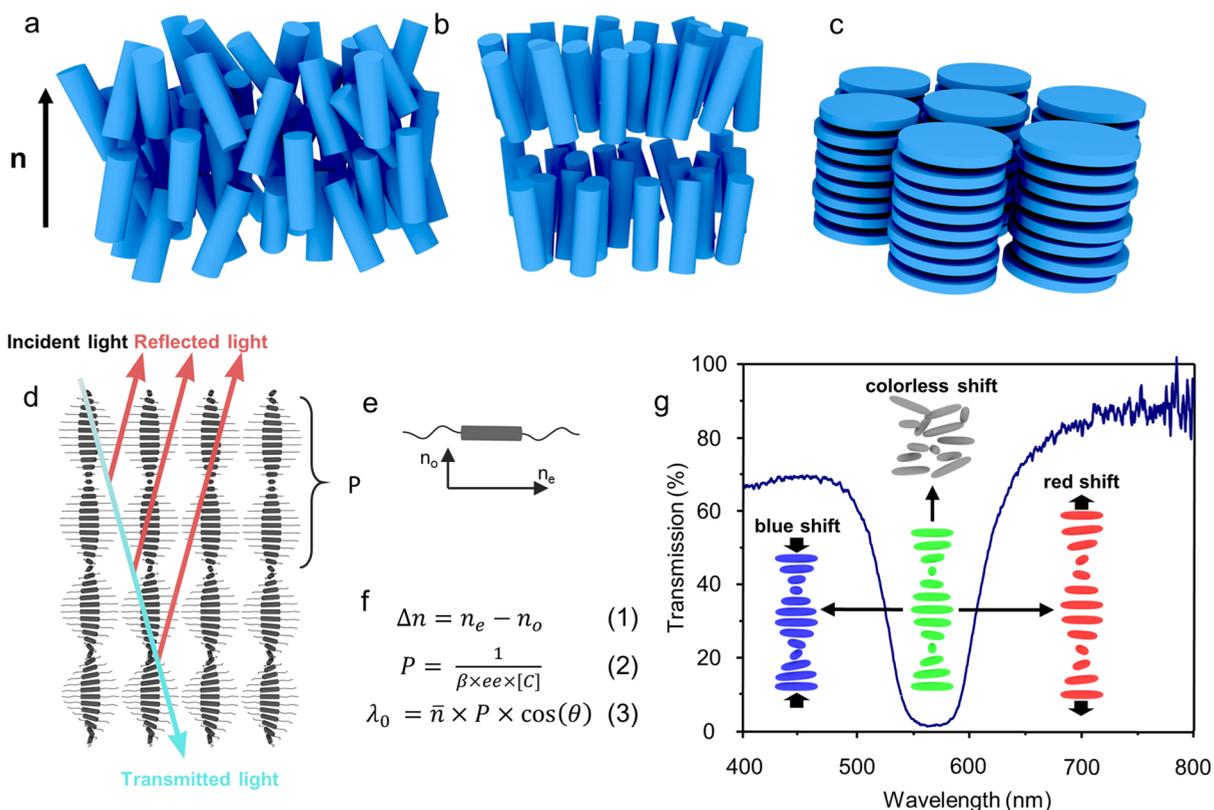


Figure 2. Examples of liquid crystalline phases. (a) Nematic mesophase with the molecular director \mathbf{n} , (b) smectic mesophase, and (c) columnar discotic mesophase. (d) Selective reflection of a chiral (cholesteric) nematic LC. (e) The ordinary and extraordinary optical axes of a calamitic LC and their refractive indices (n_o and n_e , respectively). (f) Definition of birefringence Δn (1), helical pitch P (2), and selective reflection wavelength λ_0 (3). (g) Circularly polarized transmission spectrum of a chiral nematic liquid crystal.

stimuli-responsive anisotropic properties and control over the nanostructure by supramolecular organization.^{5–9} Exciting advancements in polymeric LC materials have highlighted the potential of these materials in various applications such as soft robotics,^{10,11} smart textiles,^{12,13} deployable soft actuating devices,^{14,15} adsorbents,¹⁶ responsive pigments,¹⁷ and sensors.^{18–22}

Hydrogen-bonding interactions are valuable for controlling the supramolecular organization in LC materials and enhancing the stability of polymers and/or as the active trigger endowing the materials with responsive behaviors. Hydrogen bonds are ideal noncovalent interactions to fabricate supramolecular materials because they are highly selective, directional, and dynamic.²³ The hydrogen-bonding interactions in LC materials

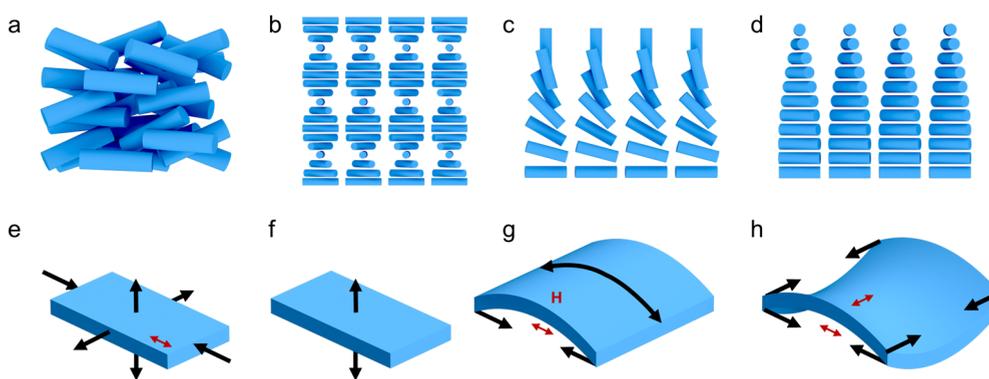


Figure 3. Representation of the director profiles and dimension changes in LC networks or elastomers on exposure to an order-lowering stimulus. (a) Planar uniaxial, (b) chiral nematic, (c) splay, and (d) twisted nematic director profiles, and (e–g) their deformations, corresponding to a decrease in the order parameter.

position molecules in specific, well-defined arrangements, as illustrated in pioneering work by Kato, Fréchet, and co-workers.^{24–27} Hydrogen bonds are formed when a donor with an available hydrogen atom interacts with an acceptor carrying nonbonding electron lone pairs. The strength of hydrogen bond interactions depends on its chemical surroundings (e.g., solvent), the number of hydrogen bonds, and temperature, making them attractive molecular triggers for smart materials that respond to humidity, pH, and heat, for example. The dynamic behavior of hydrogen bonds offers unique opportunities for developing circular polymers with, for example, self-healing and recyclable properties.

This review reports recent progress and demonstrates that hydrogen-bonding LCs can be applied in soft actuators, optical materials, and nanoporous polymers. We discuss the recent findings regarding the chemistry, LC self-organization, and describe potential future applications utilizing humidity, heat, light, and chemicals as environmentally present stimuli (Figure 1). Although magnetic and electric fields have been reported for use as stimuli, especially for robotics, these are beyond the scope of this review because it is predominantly required that the user be in direct control to operate the device, and the device is not autonomous. We restrict our focus to LC polymers containing hydrogen bonding units. Other supramolecular interactions such as ionic interactions and stimuli-responsive polymers like hydrogels will not be considered in this work. Additionally, this review provides an overview for using hydrogen-bonding motifs to construct self-healing and recyclable stimuli-responsive materials and discusses their potential applications along with the challenges that still must be overcome to achieve these goals. To fully understand the subject of hydrogen-bonded stimuli-responsive LC polymers, we will first discuss the basics of stimuli-responsive hydrogen-bonded LC polymer materials.

1.1. Background

1.1.1. Liquid Crystals.

A LC phase is a state of matter between the liquid and the solid phases, also referred to as mesophase. Typically, LCs are divided into two subclasses: (1) lyotropic and (2) thermotropic. In the first class, a mesophase is induced by adding a solvent, whereas the second forms a mesophase without solvent. In this review, we focus on polymer materials based on thermotropic LCs.

Typically, stimuli-responsive LC polymer materials are either constructed from calamitic (rod-shaped) or discotic (disk-shaped) molecules (Figure 2). The lowest order mesophase for calamitic LCs is the nematic phase (Figure 2a). In the nematic

phase, there is only long-range order of the molecular orientation; all the long axes of the molecules point in a common direction. The molecular director \mathbf{n} describes this orientation of the LC molecules. The smectic mesophase is a higher-order phase, where, in addition to orientation, there is also positional order of the molecules, which results in a lamellar organization (Figure 2b).

When a chiral compound (dopant) is added to a nematic LC, helical twisting of the molecular director can be induced, leading to a chiral nematic or “cholesteric” liquid crystalline (CLC) phase (Figure 2d–g).²⁸ The ability of a chiral dopant to induce a twist in the nematic phase is quantified by its helical twisting power (β , see Figure 2f), enantiomeric purity (ee), and concentration ($[C]$). In the CLC, the two optical axes (Figure 2e) of the LC moiety twist continuously through the layer, resulting in a periodic alteration of the anisotropic refractive index throughout the material, resulting in a one-dimensional (1D) photonic material. The length of the helix required for the molecular director to rotate 2π is called the cholesteric pitch (P , Figure 2d). When light travels through such a medium, Bragg reflection of a specific wavelength of light via constructive interference determined by the CLC pitch results in structural color, as seen in Figure 2g.

Discotic LCs consist of a rigid, disk-like core with multiple flexible tails and exhibit both nematic and columnar phases. The nematic mesophase is similar to the calamitic LCs, having only orientational order. In the columnar phase, positional order is also present, as in the smectic calamitic LCs. The disk-shaped LCs self-assemble on top of each other, forming columns that can further assemble into columnar phases (Figure 2c).

1.1.2. Stimuli-responsive Liquid Crystalline Polymers and Networks.

Polymeric materials exhibiting LC order can be obtained in a variety of ways.⁹ The polymeric materials discussed in the review can be broadly categorized into two groups: (1) chemically cross-linked networks and elastomers and (2) physically, supramolecularly cross-linked polymers.

The best-known method of preparing chemically cross-linked networks is by using reactive mesogens; that is, utilizing LC molecules with polymerizable groups such as vinyl ethers,²⁹ (meth)acrylates,³⁰ epoxides,³¹ or oxetanes.³¹ For the preparation of stimuli-responsive LC materials, it is important to achieve control over the molecular director throughout the whole material (alignment, *vide infra*). During fabrication, the molecular director in the mesophase can be readily controlled through a variety of alignment techniques (e.g., a polyimide

alignment layer) and subsequently fixed by in situ (photo)-polymerization into a mechanically stable polymer network.³⁰ Similarly to the reactive mesogens, loosely cross-linked LC elastomers are prepared by (photo) cross-linking longer LC oligomers: the products of chain extending bisacrylic reactive mesogens using amines³² or dithiols.³³

In the second category, physically cross-linked LC polymers, the supramolecular cross-links are achieved by hydrogen bonding.^{34–37} Long-chain LC oligomers and polymers require an alternative approach to realize alignment, and the preferred method of programming the molecular director is by applying strain or shear to the polymer material. By properly formulating the LC monomer mixture, the eventual properties of the material can be tuned to be suitable for different processing techniques, including coating,^{38,39} (photo-) lithography,⁴⁰ and (inkjet or 3D) printing,^{40–44} generating additional opportunities for hierarchically structured materials.

Cross-linked polymer networks display similar molecular order to their monomeric counterparts. They cannot undergo the subsequent phase transitions as their monomers could, however. When triggered by an externally applied stimulus, the cross-linked LC polymer materials undergo a deformation induced by a reduction in molecular order. In the case of highly cross-linked LCs, only a slight decrease in order can be achieved, while for weakly cross-linked LC elastomers, much greater order losses are possible.

The LC alignment determines the nature of the mechanical deformation of the LC polymer, depending on whether the molecular alignment is uniform or nonuniform throughout the depth or in the plane of the material (Figure 3). In the simplest case, uniform planar or “uniaxially” aligned LC polymers exhibit simple expansion perpendicular and contraction parallel to the molecular director in response to a stimulus (Figure 3a,e). Alternatively, when using a planar chiral nematic LC polymer (Figure 3b), only an expansion of the material can be observed in the direction of the helix. While the shape-change (Figure 3f) is somewhat difficult to observe by eye, the characteristic reflection band shift is quite visible. More complex deformations can be realized by using nonuniform alignment profiles. For example, a splay alignment is obtained when one side of the material, let us say the bottom, has a planar alignment, and the other side, the top, has a vertical or “homeotropic” alignment (H, Figure 3c). The bottom of the material will expand in one direction and contract in the other, while the top will expand uniformly. This leads to a net bending deformation toward the bottom (Figure 3g). A twisted nematic alignment is obtained when the LC molecular directors on top and bottom surfaces of the material are angularly offset from each other (e.g., 90°, Figure 3d). Typically, when using orthogonal alignment, a saddle-shape deformation is obtained (Figure 3h). However, when the material is not square but rectangular shaped, the deformation over one axis is suppressed, and bending or twisting deformations are observed.⁴⁵

As mentioned earlier, a nonuniform alignment can also be obtained in the plane of the material. This is typically achieved by using a photoalignment layer⁴⁶ or 3D printing techniques.^{41–44} The integration of a complex director profile in the plane of a polymeric LC film allowed for unprecedented deformations into cone and anticone shapes, for example.^{46,47}

The molecular order in stimuli-responsive LC polymers can be reduced by simply heating the material; thus, temperature always plays a role even in materials designed to respond to other stimuli such as pH or light. Other approaches include the

incorporated molecular triggers such as photoswitchable molecules.⁴⁸ Azobenzene derivatives are the most reported photoswitches in the field of stimuli-responsive LC polymers. Their typical linear structure allows for the incorporation in a LC polymer without disturbing the molecular organization. Upon irradiation with UV light, azobenzenes can undergo *E* (*trans*) → *Z* (*cis*) isomerization and isomerize back (*Z* → *E*) upon exposure to visible light or heat. On one hand, the *Z*-isomer has a kinked shape and exerts stress on the polymer.^{49,50} This results in a reduction in order, and thus a shape change, a photomechanical response. On the other hand, the isomerization is an equilibrium reaction; during UV illumination, the azobenzene moieties shuffle continuously between the *E*- and *Z*-isomers. This process induces heat, which in its turn induces a reduction in order, a photothermal response.⁵¹ Because the latter response relies on the generation of heat, it can also be achieved using other photothermal additives such as dyes⁵² and nanoparticles.^{53,54}

Many materials discussed in the review make use of hydrogen bonds involving carboxylic acid groups. When a material composed of these bonds is exposed to, for example, a diluted potassium hydroxide solution, the hydrogen-bonding interactions are disrupted, and a potassium carboxylate salt is formed. In the first place, this treatment leads to a reduction of the LC order and, second, increased hydrophilicity. In literature, this procedure is often called the “activation” step^{55–57} because after this treatment, the material will become highly sensitive to water/humidity^{55,56} and other polar solvents like alcohols.^{58,59} Now, upon exposure to, e.g., water, a strong anisotropic shape change will occur due to swelling of the LC polymer.

Hydrogen-bonded LC polymers can also be employed to make nanostructured and nanoporous materials. The general approach for fabricating these materials is using highly ordered smectic and discotic (disk-shaped) LCs with hydrogen-bonded mesogenic units, which can be disrupted after polymerization.⁶⁰ When the hydrogen-bonded template molecule is not cross-linked, it may be extracted from the network, yielding nanoporous systems with either two-dimensional (2D) or one-dimensional (1D) pores.

Calamitic mesogens typically consist of reactive hydrogen-bonded benzoic acid dimers that can be fixed in the desired mesophase upon (photo)polymerization, as discussed earlier. After treatment with an alkaline solution, the hydrogen bonds between the benzoic acid dimers are broken, resulting in a 2D nanoporous polymer network with ionic channels. This approach has resulted in pH-responsive adsorbents,^{61–63} membranes,⁵⁷ and optically active^{64,65} and proton conductive materials.^{66,67}

In contrast to calamitic LCs, discotic LCs use a different architectural design in which a template molecule is hydrogen-bonded with three or more reactive gallic acid derivatives containing flexible alkyl tails, affording disk-shaped mesogens. The attractive interactions between the planar aromatic core in these molecules govern the hierarchical self-assembly of the hydrogen-bonded complex, contributing to the discotic columnar mesophase formation. After photopolymerization, the LC morphology is fixed and selective removal of the template molecule with an organic solvent or alkaline treatment yields 1D nanoporous materials with cylindrical pores. This approach has been utilized to fabricate size-selective adsorbents for ions⁶⁸ and small organic molecules,^{69–72} guest–host recognition,^{73–77} and optically active materials.⁷⁷

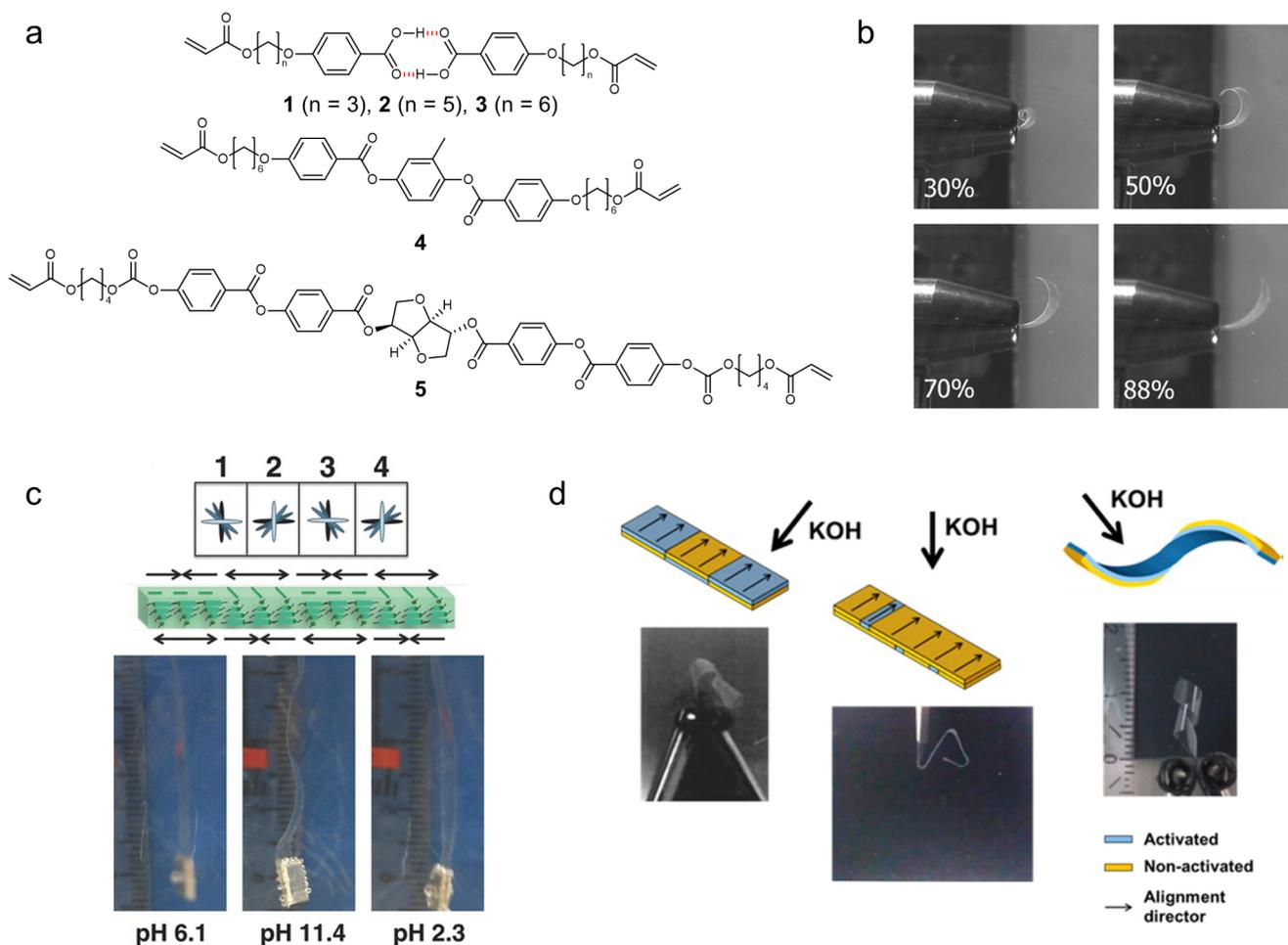


Figure 4. Humidity- and pH-responsive actuators. (a) The chemical structures of the benzoic acid hydrogen-bonded dimers, covalent cross-linker, and chiral dopant used to create the polymer network. (b) Shape changes of an LC polymer film with twisted nematic director configuration under different relative humidity conditions. Reproduced with permission from ref 55. Copyright 2005 American Chemical Society. (c) 3D alignment pattern of the accordion-shaped actuator and the deformation of the material in response to pH changes. Adapted with permission from ref 88. Copyright 2013 Wiley-VCH. (d) Folding and curling deformations of humidity-responsive actuators with localized activation of the polymer films. Activated parts (blue) respond to changes in uniform humidity and show bending and folding or curling, depending on the molecular director, whereas the nonactivated regions (yellow) remained unchanged. Arrows indicate the director alignment. Adapted with permission from ref 89. Copyright 2014 American Chemical Society.

1.1.3. Smart Materials with Stimuli-responsive, Self-healing, and Recyclable Properties. Stimuli-responsive polymers are primarily based on permanent, fixed networks that are typically neither self-healing nor recyclable due to the chemical cross-linking. The supramolecular motifs in these polymers have been mainly used for achieving a stimuli-driven response. However, the field of stimuli-responsive LC polymers is evolving toward smart materials with self-healable or recyclable properties. In recent years, the polymer community has witnessed rapid advancement of sustainable and circular polymers to realize a more sustainable future.⁷⁸ Consequently, functional polymer materials offering dynamic properties are being explored as potential smart materials that could satisfy the demand for sustainable polymers. One approach to achieving dynamic structural character employs supramolecular motifs to form physical junctions between polymer chains rather than irreversible bonding, resulting in a reversible, noncovalently cross-linked network. Among the many supramolecular interaction options, hydrogen bonds have emerged as one of the motifs of choice for construction of physically cross-linked polymers due to their simplicity, specificity, and architecture

tunability.^{79–81} Moreover, the dynamic structural character of hydrogen-bonding moieties allows construction of supramolecular materials exhibiting dynamic self-healing, recycling, and reprocessing properties (vide infra). Combining hydrogen-bonding cross-links with stimuli-responsive LC polymers has the potential to endow the smart, functional materials with both stimuli-driven responses and dynamic properties (Figure 1). In this approach, the responsive and structural characters should be orthogonal rather than interconnected to ensure a robust and reversible system is obtained. The supramolecularly cross-linked network should exhibit sufficient structural and mechanical stabilities reminiscent of classic covalently cross-linked stimuli-responsive polymers while simultaneously preserving the stimuli-responsive and dynamic characters. Hence, upon inducing a stimuli-driven response (to temperature, for example), the hydrogen-bonding interactions should normally remain intact, ensuring the supramolecular polymer network remains physically cross-linked, and only under specific conditions (higher temperatures) should it be that the hydrogen bonds are compromised, enabling the self-healing and recyclable properties to manifest themselves.

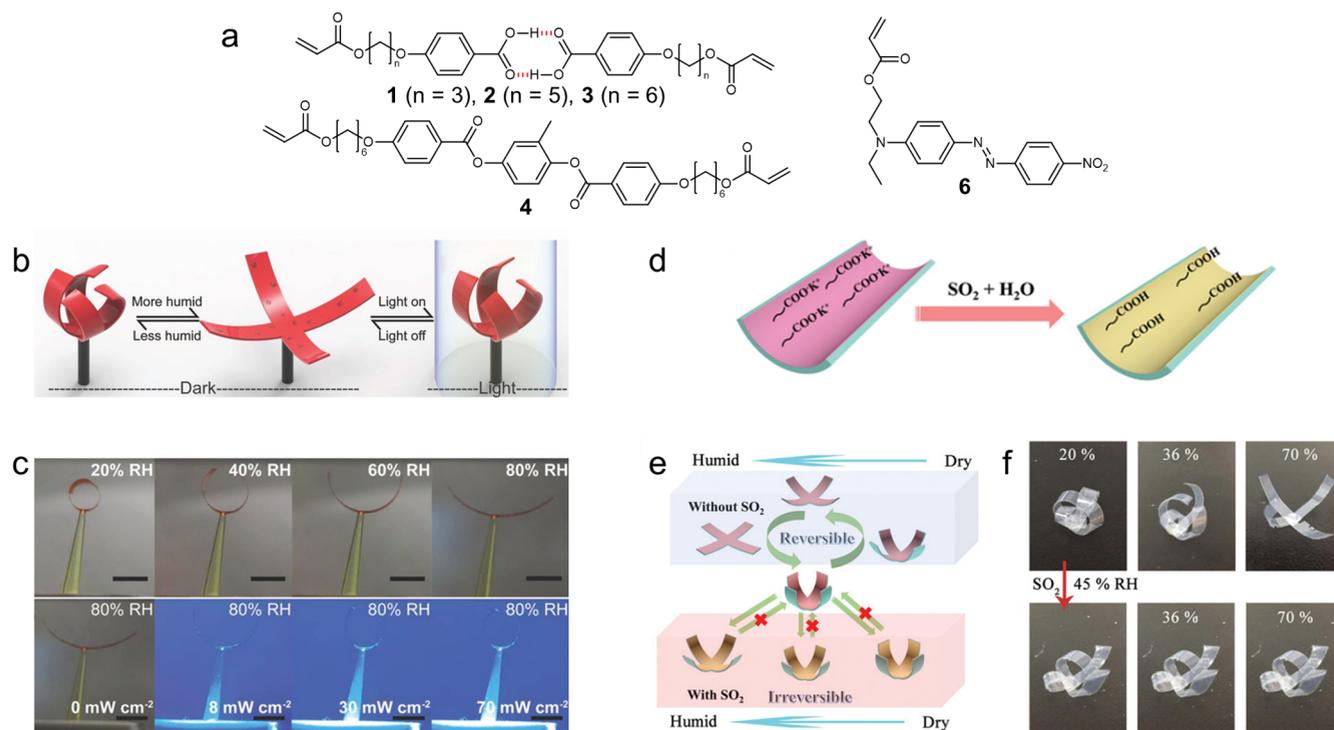


Figure 5. Dual-responsive actuators. (a) The molecular structures of the LCs and dye used to prepare the LC polymer network-based actuators. (b) Schematic representation of the nocturnal actuator opening and closing under dark conditions in response to humidity changes and the humidity-gated actuation in response to light. Adapted with permission from ref 90. Copyright 2018 Wiley-VCH. (c) Curvature changes of the LC polymer network strip upon increasing the relative humidity under dark conditions and upon illumination with light at high relative humidity. The scale bar corresponds to 5 mm. Adapted with permission from ref 90. Copyright 2018 Wiley-VCH. (d) Schematic illustration of the SO₂-induced change. Adapted with permission from ref 91. Copyright 2019 Wiley-VCH. (e) The reversible and irreversible response gated by SO₂. Adapted with permission from ref 91. Copyright 2019 Wiley-VCH. (f) Images of the active flower reversibly opening and closing in response to a change in relative environmental humidity. When exposed to SO₂ gas, the flower becomes inactive showing irreversible motion. Adapted with permission from ref 91. Copyright 2019 Wiley-VCH.

2. SHAPE CHANGING MATERIALS

2.1. pH- and Humidity-responsive Shape Changing Polymers

Shape changing polymer materials with pH and humidity responses can be prepared from dimerized rod-shaped mesogens, which typically have a hydrogen-bonded carboxylic acid core surrounded by aliphatic chains and reactive end groups. In this type of molecule, the hydrogen-bonding interactions between the carboxylic acid moieties govern the self-assembly of the rigid nematic core and stabilize the resulting mesogenic phase,^{82,83} while the network is permanently fixed by chemically cross-linked end groups.^{30,84} Hydrogen bonds are susceptible to the polarity of the environment, and thus actuators can be prepared that reversibly change their shape in response to environmental changes such as pH and humidity. The formation of LC soft actuators is generated by the combination of stability and responsiveness introduced by the hydrogen-bonded mesogens. Utilizing this supramolecular structure, a single-layer pH- and humidity-responsive actuator based on hydrogen-bonded benzoic acid mesogens has been prepared.^{55,85} The benzoic acid derivatives formed dimerized, rod-shaped monomers driven by self-assembly through the hydrogen-bonding interactions. A mixture containing the hydrogen-bonded LC monomers 1–3 and additional diacrylate chemical cross-linker 4 were aligned in either unidirectional or twisted configurations within the nematic mesophase and

subsequently photopolymerized to obtain a covalently cross-linked network (Figure 4a).

To exhibit deformations in response to changes in pH and humidity, a fraction of the carboxylic acid groups was converted to potassium carboxylate groups through alkaline treatment of the hydrogen-bonded network, forming a hygroscopic polymer salt. The activated LC polymer films readily absorb water, leading to anisotropic swelling mainly perpendicular to the alignment director due to an accompanying decrease in order of the material. Complete immersion of a uniaxially aligned activated network in water resulted in reversible expansion, whereas when exposed to water vapor, the film absorbs water primarily from one side, resulting in the film bending away from the vapor source. Similar films with twisted molecular alignments showed strong curling about one of the two axes when immersed in water, while when subjected to a homogeneous humidity change, the material exhibited a strong, reversibly anisotropic response over the whole humidity range (Figure 4b). Furthermore, the LC polymer films also showed reversible actuation as a response to environmental changes in pH and nature of the solvent. In the presence of strong polar solvents, interestingly, the network swells due to the hydrophilic nature of the salt network and forces it to bend in one direction. In contrast, less polar solvents extract water from the film, resulting in anisotropic contraction of the network forcing bending in the opposite direction.⁸⁶

A similar LC mixture containing dimerized benzoic acid monomers has been used to make hydrogel films that exhibit

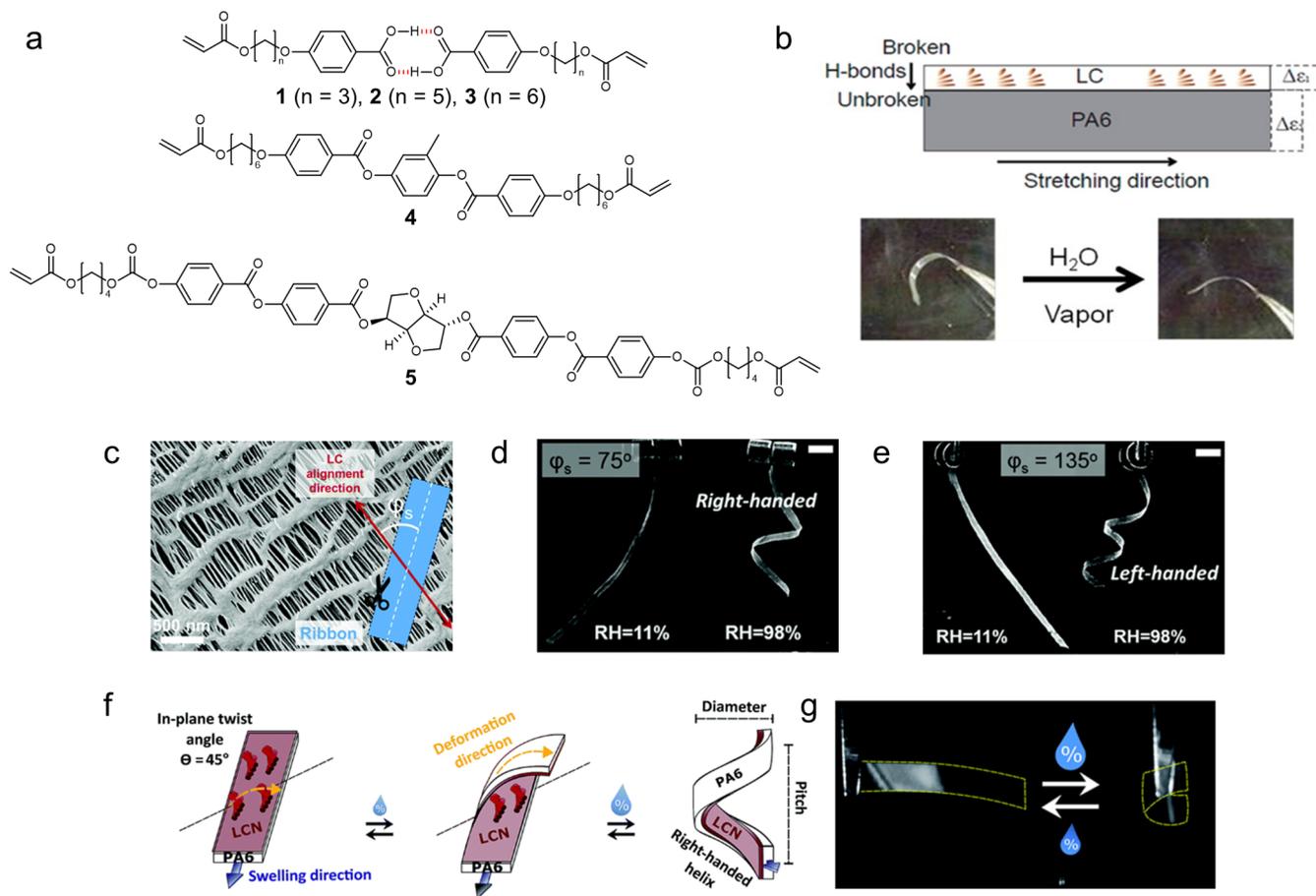


Figure 6. Bilayer and composite actuators. (a) Monomers used for the LC polymer actuator preparation. (b) Schematic representation of the humidity-responsive bilayer film and response to humidity changes. The splay-aligned bilayer film exhibits a hydrogen bond gradient throughout the thickness of the film, which results in anisotropic expansion of the LC layer. The LC layer exhibits a larger expansion ($\Delta\epsilon_1$) than the polyamide layer (PA6, $\Delta\epsilon_2$), yielding bending of the bilayer actuator. Adapted with permission from ref 92. Copyright 2013 American Chemical Society. (c) SEM image of the porous polymer composite. Adapted with permission from ref 93. Copyright 2017 The Royal Society of Chemistry. Ribbons cut at angles (φ_s) of (d) 75° and (e) 135° with humidity-induced shape changes when increasing the relative humidity from 11% to 98%. Adapted with permission from ref 93. Copyright 2017 The Royal Society of Chemistry. (f) Schematic illustrations showing the reversible deformation of the bilayer actuator in response to humidity changes. Adapted with permission from ref 94. Copyright 2018 The Royal Society of Chemistry. (g) Macroscopic deformation of the bilayer actuators at high relative humidity levels forming a right-handing helix. Reproduced with permission from ref 94. Copyright 2018 The Royal Society of Chemistry.

anisotropic expansion.⁸⁷ In this work, the hydrogen-bonded moieties formed a smectic mesophase that was copolymerized with covalent cross-linker mesogens, and after breaking the hydrogen bonds with an alkaline solution, a smectic ordered hydrogel was obtained. During activation, the material readily absorbs water and expands around 50% perpendicular to the alignment director while only minimally along the director. After alkaline treatment, the hygroscopic polymer salt exhibits reversible expansion and contraction up to 20% in response to a change in pH.

LC polymer actuators with unidirectional or asymmetric alignment throughout the thickness of the LC polymer film results in relatively simple macroscopic deformations that reversibly contract, bend, or curl upon applying a stimulus. More complex reversible deformations were created by using LC polymer films with three-dimensional patterned structures.⁸⁸ Using a hydrogen-bonded LC monomer mixture based on the reactive dimers 1–3 and cross-linker 4 in combination with chiral dopant 5 (Figure 4a), LC polymer actuators were developed with twisted nematic alignment and alternating orientation between programmed domains. In this way, a pH-

responsive actuator was obtained that showed an accordion-like deformation due to the opposite response of the distinct domains (Figure 4c).

The responsive LC polymers discussed above exhibit a shape change due to localized exposure to a stimulus or asymmetry in the molecular orientation. Humidity-responsive actuators could also be prepared based on asymmetry in the responsive molecular trigger instead, through localization of the activated areas.⁸⁹ Using this approach, soft actuators that bend, fold, and curl have been made from the same polymer film that responds to a uniform humidity change (Figure 4d). Uniaxially aligned polymer films were prepared with the same LC monomer mixture as highlighted before.^{55,85,86}

It was recently shown that a similar LC mixture of monomers 1–4 with selective activation of the polymer network could be used to mimic a nocturnal flower opening and closing in response to a change in ambient humidity under dark conditions (Figure 5a–c).⁹⁰ Furthermore, the incorporation of photo-thermal dye 6 allowed for humidity-gated photoactuation of the developed “flower”. The absorption of incident light by a photothermal dye induces heating of the material, reducing

molecular order and finally leading to macroscopic deformation. This development demonstrates that different stimuli and trigger molecules can be combined to make multiresponsive bioinspired actuators.

Dual-responsive single-layer actuators have also been made of hydrogen-bonded LC polymers in which the humidity response was gated by exposing the material to SO₂ gas.⁹¹ A monomer mixture consisting of compounds 3 and 4 was used to obtain humidity-responsive polymer actuators by selectively converting one side of the film to the carboxylate salt (Figure 5a).^{89,90} Interestingly, when the activated films were treated with SO₂ gas, the hygroscopic carboxylic salt at the surface is converted back into carboxylic acid through acidification by sulfurous acid, produced by combining SO₂ and water vapor (Figure 5d). As a result, the reversible humidity-induced deformation of the LC polymer films deactivates because the main driver for humidity response, the carboxylate salt, is lost (Figure 5e,f). The response time of the SO₂ gated behavior depends on the relative environmental humidity and could be tuned over a wide range of 20–70%.

In general, alignment of the LCs is obtained by using alignment cells. However, using cells is limiting and not readily scalable, hindering potential applications. Therefore, bilayer actuators have been fabricated by spray-coating the surface of a uniaxially oriented polyamide layer with a mixture of dimerized benzoic acid-derived mesogens 1–3 and cross-linker 4 (Figure 6a).⁹² In this way, it was possible to fabricate anisotropic bilayer actuators with well-aligned LCs in a more straightforward manner than LC cells. The spray-applied LC monomers self-organize on the oriented polyamide substrate with planar alignment at the substrate that rotates to homeotropic alignment at the air interface, resulting in a splayed configuration (Figure 6b). Photopolymerizing resulted in a prebent bilayer exhibiting an inverse curvature radius (1/*r*), with the LC coating on the inside of the curvature due to both polymerization shrinkage and increasing order of the LC network upon cooling to room temperature. The polymer bilayer was activated under alkaline conditions, resulting in a carboxylic salt gradient through the film depth due to the polyamide layer restricting diffusion of the alkaline solution from one side. The bilayer actuator showed humidity-responsive deformation in which increasing the humidity results in expansion of the LC layer and unbending of the prebent bilayer actuator (Figure 6b).

An LC polymer actuator was prepared by utilizing the self-organization of LCs guided by an oriented porous polypropylene structure.⁹³ The LC mixture based on hydrogen-bonded benzoic acid moieties 1–3 and 4 infiltrates into the porous polymer through capillary forces and spontaneously aligns within the pores (Figure 6a), which, after fixation by photopolymerization of the nematic phase, yields an anisotropic composite material with enhanced mechanical properties and stability compared to single-layer LC polymer networks. The orienting propylene scaffold provides improved physical characteristics. Humidity response was induced by the standard activation method.⁸⁹ Depending on the angle at which the films are cut with respect to their alignment (Figure 6c), humidity-driven bending, twisting, or curling deformations were obtained (Figure 6d,e). By constructing bilayer composite films with orthogonal orientation of the alignment directors, a double-layered actuator was generated, exhibiting curling with inverting handedness at approximately 40% relative humidity.

Another appealing, elegant way to prepare bilayer actuators is by using humidity-sensitive polymer substrates with an LC

coating directing the macroscopic response. The bilayers were developed by spray-coating an oriented polyamide film with a photopolymerizable LC mixture composed of benzoic acid moieties 1–3, cross-linker 4, and a small quantity of chiral dopant 5 (Figure 6a).⁹⁴ The self-assembled hydrogen-bonded dimers stabilize the chiral nematic mesophase aligned by the polyamide substrate, forming a twist-aligned LC polymer layer immobilized by photopolymerization. In contrast to previously discussed work,⁹² the hydrogen-bonded LC polymer layer is not converted into a hygroscopic polymer salt. Rather, the polyamide substrate layer itself reversibly absorbs and desorbs water in response to changes in environmental humidity, resulting in a bilayer that bends or curls dependent on the in-plane twist angle of the LC polymer, determined by the initial chiral dopant content. Upon increasing humidity, 0° and 90° twists of the LC director through the film depth result in simple bending bilayer actuators, while intermediate twist angles induce helical twisting motions instead (Figure 6f,g). Recently, using a similar approach, dual-responsive bilayer actuators could be prepared based on a humidity-responsive polymer substrate and a temperature-responsive LC-coating.⁹⁵ Their fabrication and demonstration of stimulus-sensitive bilayer actuators has potential for the development of smart breathable textile using stretched polyamide fibers.

2.2. Temperature-responsive Shape Changing Polymers

Supramolecular polymeric LC materials exploiting hydrogen bonding can also be used to make temperature-responsive actuators. In these polymers, hydrogen bonds play an important role in the construction and stabilization of mesogenic structures and LC phases through self-assembly. Shape memory polymers (SMPs), defined as materials that show recovery of a temporary state to its initial shape, have been widely exploited.^{96,97} Thermal shape memory allows for programming an object or surface via first mechanically deforming the polymer above its glass transition temperature and then cooling the material, “locking” the induced deformation. A reversion to the original shape occurs after exposure of the deformed SMP to a temperature around or above its glass transition temperature.

Two different approaches have been used to develop thermally responsive SMPs, each using carboxylic acid-derived moieties and a polymer matrix, forming phase-separated LC polymeric composites. The first is based on a physical mixture of self-assembled hydrogen-bonded LC dimer moieties and a polymer matrix, yielding LC polymer composites. These LC SMP composites showed triple shape memory effects arising from the multiple thermal phase transitions of the polymer matrix and self-assembled LC phases.^{98–101} Interestingly, these materials also show self-healing properties due to temperature-induced recrystallization of the LC molecules.¹⁰² The second method utilizes a pyridine containing SMP and carboxylic acid monomers that form a supramolecular LC complex through hydrogen-bonding interactions. In this LC polymeric complex, a two-phase separated structure is obtained, comprising a polymer matrix and tethered hydrogen-bonded supramolecular LC structures rather than a simple physical mixture. In contrast to the preparation of other SMP systems based on pyridine-derived mesogens,¹⁰³ the intrinsic LC properties of this supramolecular complex were maintained. The hydrogen-bonded SMP complexes have multishape memory properties exhibiting triple¹⁰⁴ and quadruple¹⁰⁵ shape memory effects.

More recently, in contrast to the LC actuators that exhibit only one-way shape recovery, thermally responsive supra-

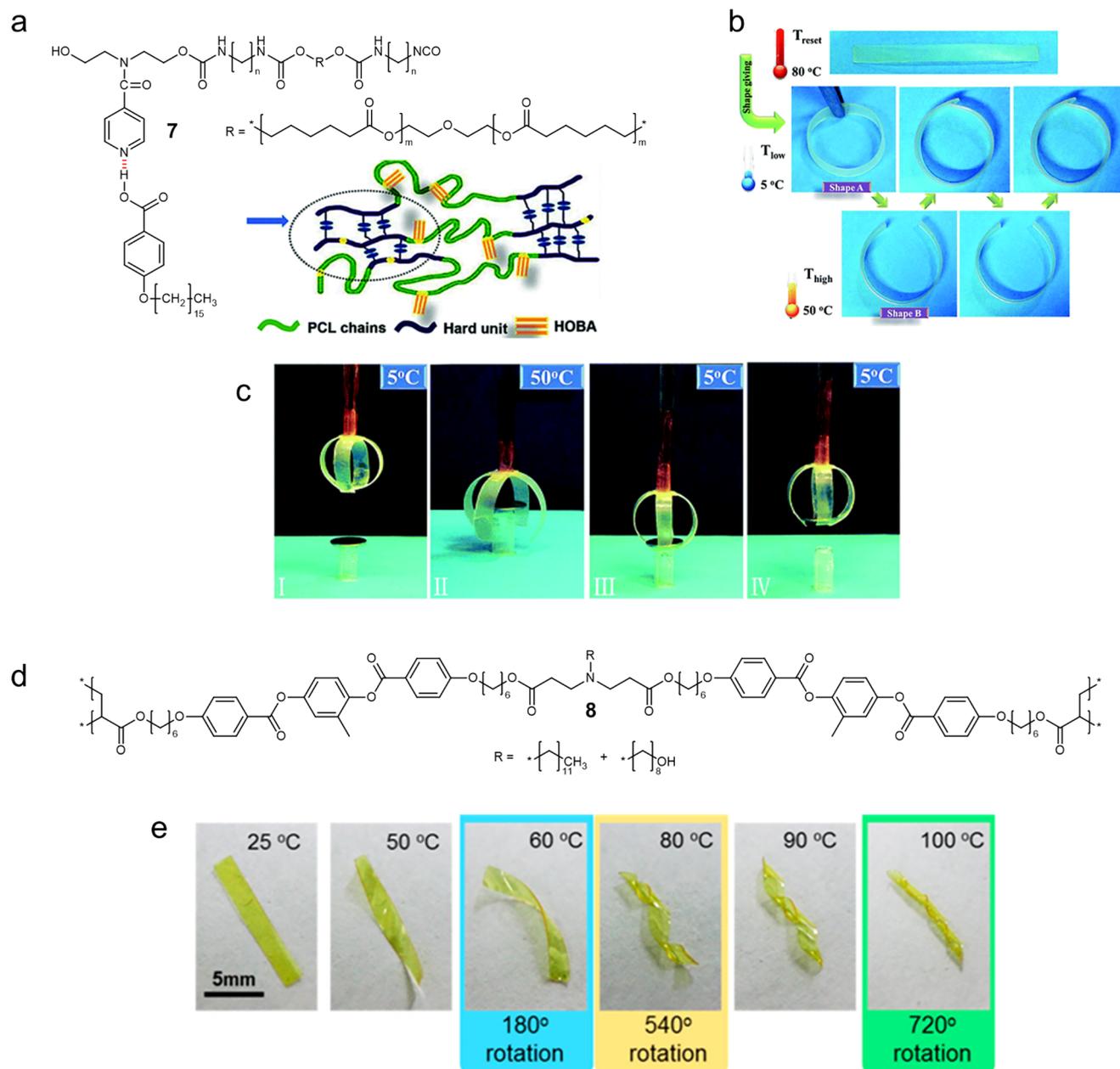


Figure 7. Temperature-responsive actuators. (a) Chemical structures and schematic representation of the LC supramolecular hydrogen-bonded polymer composed of pyridine containing polyurethane and benzoic acid derived moieties. Adapted with permission from ref 34. Copyright 2019 The Royal Society of Chemistry. (b) Images showing the programming of ring-like shapes at T_{reset} and fixing the structure at T_{low} yielding actuators that reversibly change their shape when cycled between T_{low} and T_{high} . Adapted with permission from ref 34. Copyright 2019 The Royal Society of Chemistry. (c) Demonstration of a gripper device capable of reversible catching and releasing a coin. Adapted with permission from ref 34. Copyright 2019 The Royal Society of Chemistry. (d) Molecular structure of the LC polymer with hydroxyl functionalized chain extender. (e) Images of thermal-induced helical twisting motions of twisted nematic aligned LCs in the polymer rotating up to 720° . Adapted with permission from ref 106. Copyright 2018 American Chemical Society.

molecular SMP **7** exhibiting reversible shape memory effects based on hydrogen-bonding complexes between benzoic acid-derived moieties and SMPs with pyridine pendant groups has been reported (Figure 7a).³⁴ LC properties and physical cross-linking of the material were introduced through the formation of supramolecular hydrogen bonds in the urethane hard segments. Polymer films were programmed into ring-like shapes by deforming the material at the shape-forming temperature and subsequently fixed by lowering the temperature below the melting temperature of the polycaprolactone soft segment

(Figure 7b). The resulting actuator exhibits reversible shape memory properties upon heating and cooling: at low temperatures, the ring shape is closed, whereas at higher temperatures it is open. To demonstrate this material's potential, an actuator assembly was fabricated to form a gripper that can pick up and release a load (Figure 7c). This development has highlighted the potential of thermal-responsive supramolecular LC polymers as soft actuators for soft robotic devices.

Temperature-responsive actuators have also been made of LC elastomers with mechanical properties enhanced by introducing

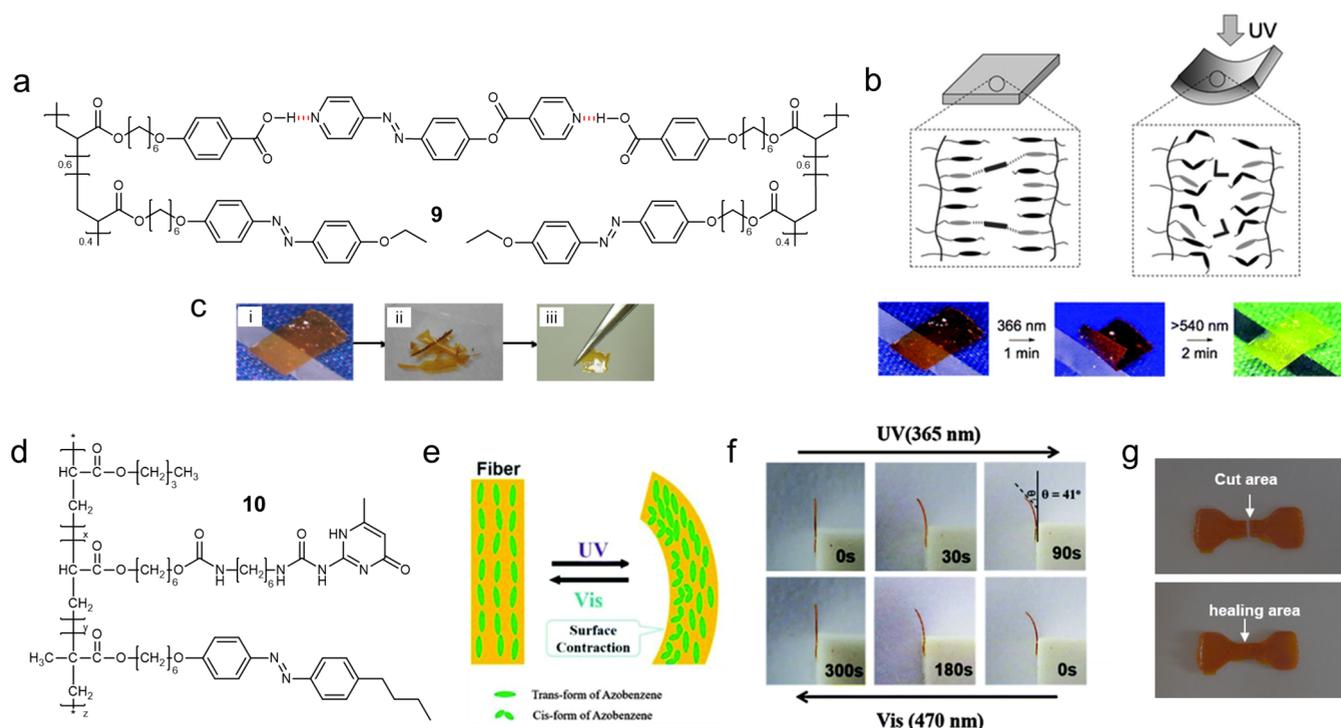


Figure 8. Light-responsive supramolecular cross-linked actuators. (a) Chemical structures of the hydrogen-bonded LC polymer network. (b) Schematic representation showing the photoinduced bending mechanism and macroscopic deformation of the actuator when exposed to UV light (366 nm), bending toward the light source, whereas it is recovered to its initial state upon using visible light (>540 nm). Adapted with permission from ref 112. Copyright 2008 The Royal Society of Chemistry. (c) Recycle process of the hydrogen-bonded LC film: (i) the pristine LC film, (ii) cut into pieces, and (iii) recycled LC film. Adapted with permission from ref 112. Copyright 2008 The Royal Society of Chemistry. (d) Chemical structures of the LC polymer containing azobenzene and self-complementary quadruple hydrogen-bonding side groups. (e) Schematic representation and (f) images of photoinduced bending and unbending of the polymer fiber. Adapted with permission from ref 115. Copyright 2016 The Royal Society of Chemistry. (g) Self-healing of a cut sample into its original shape. Adapted with permission from ref 115. Copyright 2016 The Royal Society of Chemistry.

hydrogen-bonding interactions.¹⁰⁶ Oligomers with reactive end groups were prepared composed of LCs and a hydroxyl-functionalized amine chain extender and photopolymerized into **8**, an LC elastomer with uniaxial alignment (Figure 7d). The incorporated hydroxyl moieties act as physical cross-linkers between the LC polymer chains through intermolecular hydrogen bonding, providing increased toughness and greater elongation compared to polymer materials without hydroxyl end groups. The LC polymer film undergoes reversible actuation upon heating and cooling arising from the nematic–isotropic phase transition. The formation of hydrogen bonds led to an increase in actuation strain, while the actuation temperature is actually decreased. When polymerized in the twisted nematic phase, thermal-induced helical twisting motions are observed upon heating, causing the film to rotate up to 720° (Figure 7e).

2.3. Light-responsive Shape Changing Polymers

Light-driven LC polymer materials containing molecular photoswitches are capable of transducing absorbed light energy directly into mechanical work and have become an emerging research area, offering remotely and precisely controllable actuation methods that can be applied in devices such as untethered soft robotics.^{107–109} Among different photosensitive molecules, azobenzene derivatives have emerged as a particularly attractive photoswitch, arising from its straightforward incorporation of the rod-like *trans*-azobenzene, which can stabilize the mesogenic phase without disrupting the alignment.^{110,111} Upon undergoing *trans*–*cis* isomerization via

absorption of light, the bent *cis* azobenzene disrupts the molecular order, leading to contraction along the molecular director and expansion perpendicular, resulting in macroscopic, anisotropic shape changes. The reverse *cis*–*trans* isomerization is initiated by either heating or light exposure, returning to the initial molecular alignment, leading to reversible macroscopic deformation.

These selective and reversible light-driven deformations are especially interesting as LC polymer actuators for soft robotics. Most light-driven actuators consist of chemically cross-linked systems. However, light-responsive LC polymer actuators based on hydrogen-bonded supramolecular interactions without chemical cross-linking were also prepared.¹¹² These materials combine a LC polymer containing azobenzene and benzoic acid side groups with azobenzene bispyridyl derivatives as cross-linker, forming the hydrogen-bonded complex **9** (Figure 8a). The hydrogen-bonding between the carboxylic acid side groups of the LC polymer and the cross-linker pyridyl governs the self-assembly, yielding freestanding supramolecular cross-linked LC polymer films with a stabilized mesophase. Irradiating the LC polymer film with UV light drives macroscopic bending arising from the generated *cis*–*trans* gradient through the LC polymer film with higher *cis*-azobenzene concentration at the exposed side, causing asymmetric contraction along the alignment director and bending toward the light source (Figure 8b). Unbending of the polymer film toward its initial flat state occurs when exposed to visible light due to the reverted *cis*–*trans*

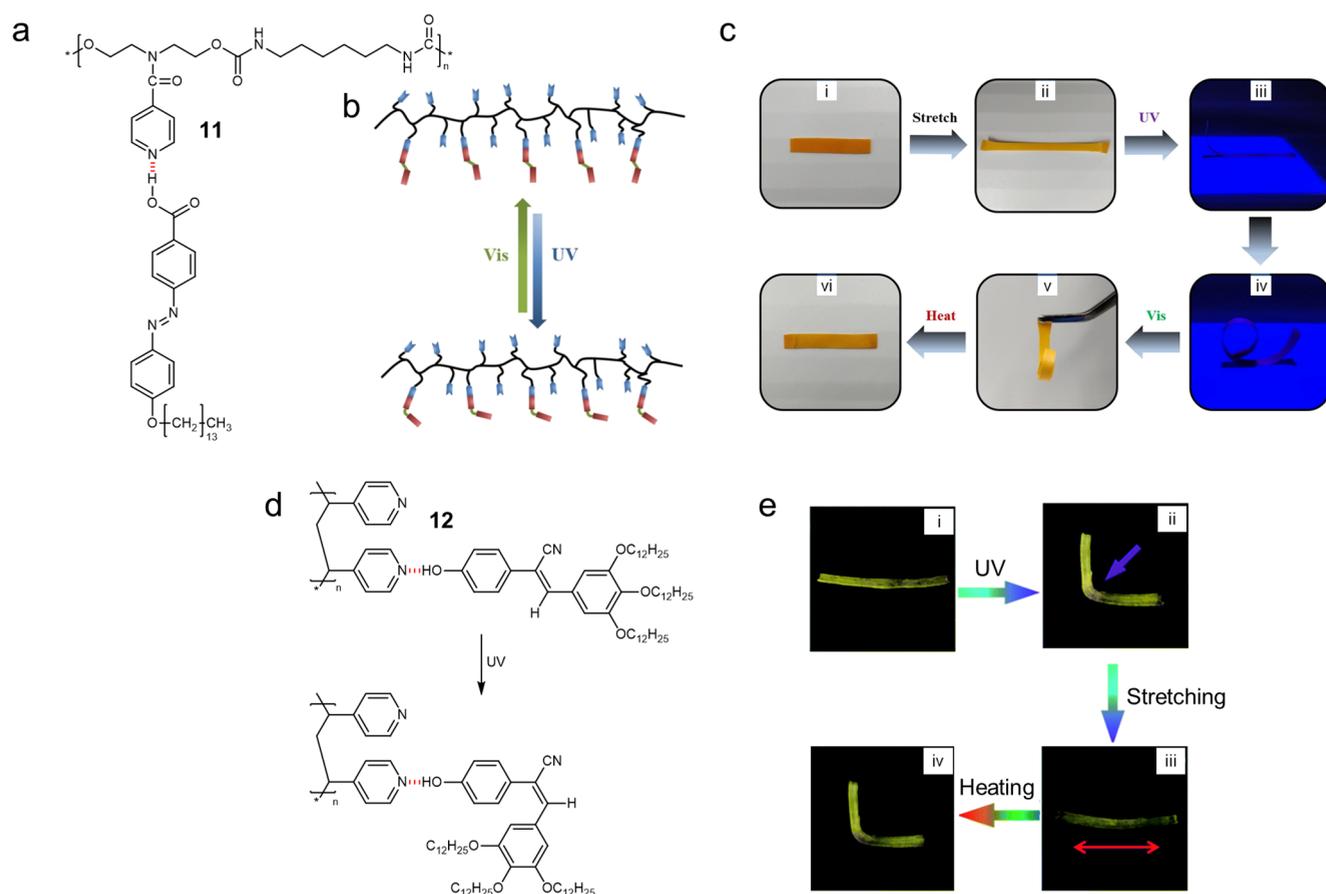


Figure 9. Photoresponsive side-chain LC polymer actuators. (a) Chemical structure and (b) schematic illustration of the light-induced conformational changes of the supramolecular LC polymer complex. Adapted with permission from ref 35. Copyright 2019 Elsevier Ltd. (c) Images of the original shape (i), temporary shape programming (ii), curling induced by photoisomerization (iii,iv), stable fixed shape at room temperature (v), and recovery to its original shape upon heating (vi). Adapted with permission from ref 35. Copyright 2019 Elsevier Ltd. (d) Chemical structure of hydrogen-bonded supramolecular polymer containing poly(vinylpyridine) and α -cyanostilbene derivative. (e) Macroscopic bending of the initial shape (i) upon illumination with UV light (ii), eliminating the light-induced deformation by stretching (iii), and recovery to the bent state upon heating the material (iv). Adapted with permission from ref 117. Copyright 2019 The Royal Society of Chemistry.

isomerization. Interestingly, these supramolecular cross-linked materials can be recycled and used for reconstructing light-responsive actuators in contrast to chemically cross-linked LC polymer films (Figure 8c). Through utilizing the dynamic structural character of the hydrogen bonding moieties, recyclable supramolecular materials were obtained, providing a promising approach toward smart circular polymer materials.

Photoresponsive actuators with enhanced mechanical properties have been made using single-walled carbon nanotubes (SWNTs) in combination with a supramolecular hydrogen-bonded polymer film.¹¹³ The SWNTs were chemically modified, bearing carboxylic acid groups that self-assembled into hydrogen-bonding complexes with the azobenzene LC copolymer containing benzoic acid moieties. The light-responsive composite actuator bends and unbends upon illumination with UV and visible lights, respectively. However, bending of the composite was less pronounced than the same LC polymer without SWNTs. Moreover, the mechanical properties of the composite polymer were improved by incorporating SWNTs arising from the supramolecular hydrogen-bonding interactions.

Photoresponsive LC materials may also be made of side chain polymers with cross-linking induced by hydrogen bonding between pendant groups without using low-molecular-weight

molecule cross-linkers. LC polymers have been prepared based on azobenzene pendant groups with amide linkages forming hydrogen-bonding moieties with the polymer side chain, crucial for forming and stabilizing the smectic mesophase.¹¹⁴ Another example is the use of multivalent hydrogen bonds for the formation of supramolecular cross-linked LC polymers. By using photoresponsive polymer 10 consisting of azobenzene moieties and quadruple hydrogen-bonding side chains (Figure 8d),¹¹⁵ supramolecular cross-linked LC polymers were obtained through the formation of strong noncovalent interactions between self-complementary quadruple hydrogen-bonding moieties. These materials show reversible bending and unbending deformations in response to light arising from the isomerization of azobenzene (Figure 8e,f). Owing to their dynamic reversibility, the introduction of supramolecular hydrogen-bonding interactions into the polymer side chain allowed for self-healing and shaping capabilities, in contrast to covalently bonded LC polymers (Figure 8g). This capability to self-heal via the multivalent hydrogen bonds functioning as physical cross-links offers inspiration for constructing sustainable supramolecular materials.

Other functional LC polymers have been prepared by attachment of photoresponsive mesogens as side chain

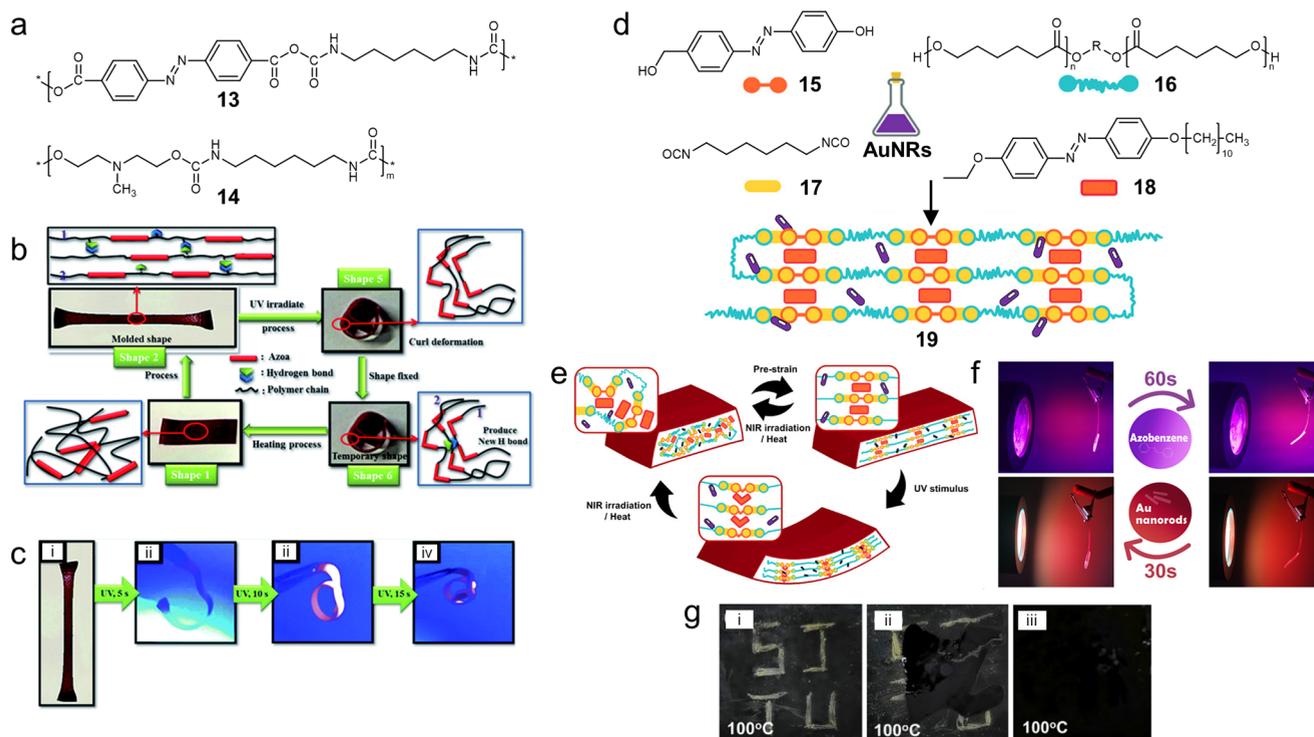


Figure 10. Photoresponsive LC polyurethane actuators. (a) Chemical structures of main-chain LC polymer consisting of an azobenzene soft segment and a hard segment. (b) Schematic illustration and images of the light-induced deformation and shape-memory effect. Adapted with permission from ref 37. Copyright 2017 The Royal Society of Chemistry. (c) The original shape (i), photoinduced deformation (ii,iii), and stable deformed shape under visible light (iv). Adapted with permission from ref 37. Copyright 2017 The Royal Society of Chemistry. (d) Chemical structures and schematic representation of the polyurethane composite. Adapted with permission from ref 122. Copyright 2021 American Chemical Society. (e) Schematic illustration of the multiresponsive shape memory behavior showing the reversible cycle. Adapted with permission from ref 122. Copyright 2021 American Chemical Society. (f) Shape memory performance in response to UV (365 nm) and near-infrared (800–900 nm) irradiation. Reproduced with permission from ref 122. Copyright 2021 American Chemical Society. (g) Self-healing behavior of a scratched surface at 100 °C: (i) the scratched state, (ii) healing state, (iii,iv) original healed state. Adapted with permission from ref 122. Copyright 2021 American Chemical Society.

structures through hydrogen bonds: pyridine-containing backbones linked with azophenol moieties were elaborated for photo deformation.¹¹⁶ The supramolecular polymer consist of a complex with a smectic LC phase. When exposed to UV light, polymer films with temporary programmed shapes could be selectively returned to their initial and permanent state via photothermally driven *trans*–*cis* photoisomerization of the azobenzene pendant groups. Photoresponsive shape memory polymer **11** was also prepared by using polyurethane containing pyridine groups and carboxylic acid functionalized azobenzene (Figure 9a).³⁵ The mixture of these compounds formed supramolecular complexes arising from the hydrogen-bonding abilities of the pyridine and carboxyl groups. The resulting LC polymer showed multishape memory behavior in response to light and could be recovered to its initial shape through heating (Figure 9b,c).

Recently, light-triggered supramolecular LC polymers based on photoswitches other than azobenzene derivatives have been prepared. Hydrogen-bonded supramolecular complexes exploiting interactions between α -cyanostilbene LC monomers bearing phenol groups and pyridine containing poly(vinylpyridine) yielded side-chain polymer **12**, which exhibits photoinduced deformation (Figure 9d).¹¹⁷ The *trans*–*cis* isomerization disrupts the molecular order and pulls on the polymer backbone similar to azobenzene derivatives, causing anisotropic expansion/contraction (Figure 9e). Macroscopic bending of the films is observed as absorption primarily occurs at the illuminated

side, which induces a strain gradient throughout the material. The resulting light-induced deformation can be eliminated by subsequently mechanically stretching the material. Bending of the LC polymer is recovered by heating the material due to the stability of the *E*-cyanostilbene isomer. Later work developed side chain LCEs with covalently attached α -cyanostilbene derivatives and quadruple hydrogen-bonding moieties,^{118,119} the latter allowing for the formation of physically cross-linked supramolecular structures through multivalent hydrogen-bonding interactions. Uniaxially oriented LC elastomers were obtained through melt drawing and demonstrated photo-induced deformation. Moreover, because the prepared polymers are based on physically cross-linked supramolecular hydrogen-bonding moieties, the dynamic material is both recyclable and reprocessable and promising for achieving polymer materials with both sustainable and circular properties.

Main chain polymers have emerged as another method to prepare photoresponsive LC polymer actuators in which supramolecular cross-linking was obtained by hydrogen bonds. Azobenzene LC monomers with acrylate and amine end groups were polymerized to form a hydrogen-bonded main chain LC polymer.¹²⁰ Secondary amino groups in the polymer backbone act as physical cross-linkers between individual polymer chains, yielding supramolecular cross-linked networks. The dynamic reversibility of the hydrogen bonds allowed for the preparation of aligned samples by drawing fibers from the polymer melt: the molecular order was maintained in the cooled material. These

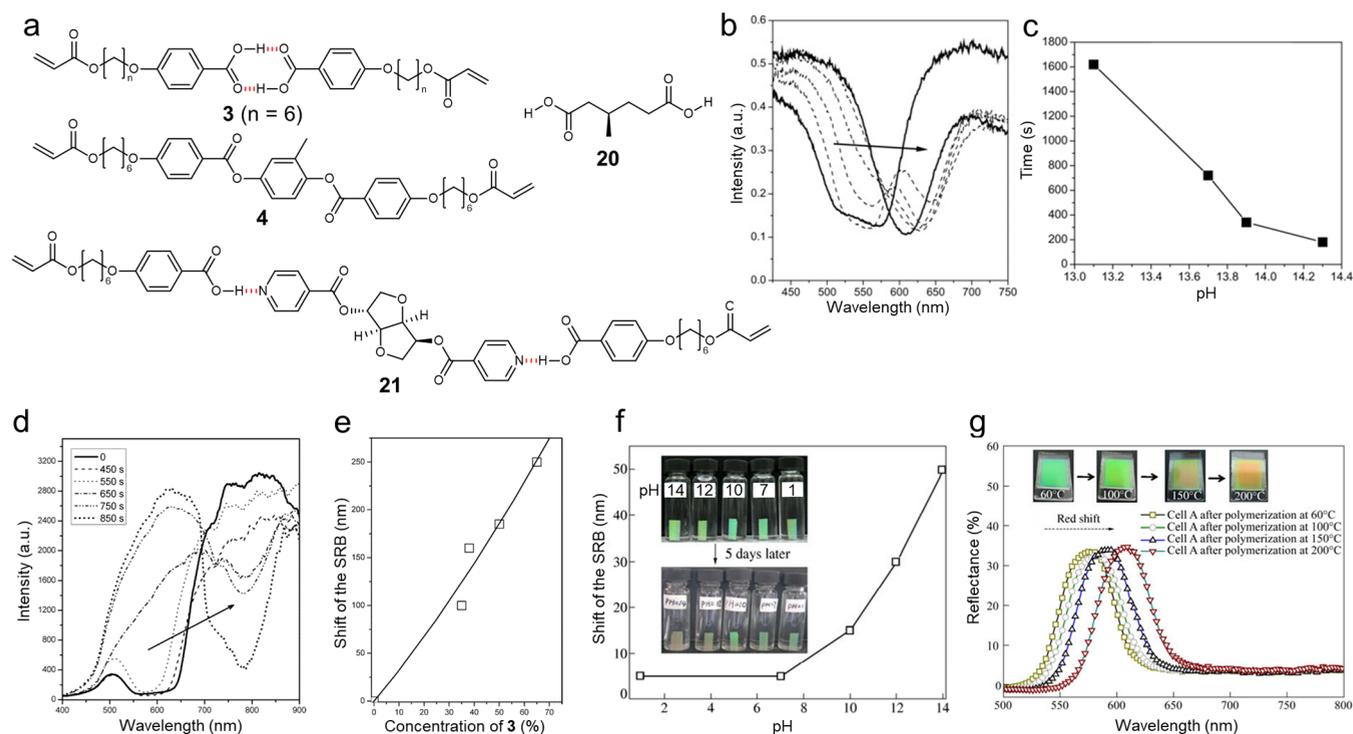


Figure 11. Hydrogen-bonded chiral dopants in photonic materials. (a) The chemical structures of monomers used to prepare the cholesteric films. (b) Shift of the selective reflection band in responsive chiral polymers with 26% of monomer 3 before and during the treatment in 5% KOH solution. Reproduced with permission from ref 127. Copyright 2010 Taylor and Francis. (c) Time needed to shift the selective reflection band as a function of pH. Reproduced with permission from ref 127. Copyright 2010 Taylor and Francis. (d) UV-vis spectra of the film with the hydrogen-bonded chiral dopant immersed in a 10% aqueous solution of arginine as a function of time (left-handed circularly polarized light). Reproduced with permission from ref 128. Copyright 2006 American Chemical Society. (e) Shift of the SRB in the samples with an increasing concentration of the benzoic acid derivative 3. Adapted with permission from ref 128. Copyright 2006 American Chemical Society. (f) Shift of the SRB of the film after treatment in aqueous solutions with different pH values for 5 days. Reproduced with permission from ref 129. Copyright 2013 Springer Nature. The insets are the corresponding photos of the initiative films and the films after 5 days of treatment. (g) Reflection spectra of the film at temperatures between 60 and 200 °C. The insets are the images of the film at the corresponding temperature. Reproduced with permission from ref 129. Copyright 2013 Springer Nature.

materials exhibit bending through exposure to UV light with complete reversibility to their initial state due to the supramolecular cross-links. Secondary amide linkages introduced in the backbone resulted in the formation of main chain LC polymers with enhanced tensile strength and faster light-induced bending.¹²¹

Light-responsive shape changing polyurethanes bearing azobenzene-derived hard segment 13 and soft segment 14 that are physically cross-linked through supramolecular hydrogen bonds between urethane linkages have also been prepared (Figure 10a).³⁷ Molecular orientation was induced by stretching the material while heated and subsequently fixed by cooling, governed by the dynamic reversibility of the hydrogen-bonding interactions (Figure 10b). When the oriented film was exposed to UV light, *trans*–*cis* isomerization of the azobenzene occurred and led to strong curling deformations that persisted after the UV light had been switched off (Figure 10c). Remarkably, the light-induced *cis* state increased the hydrogen-bonded cross-links between the polymer chains, causing the glass transition temperature to exceed room temperature and fix the curled shape, even when exposed to visible light. Heating the temporary shape of the polymer material weakened the hydrogen-bonding interactions, resulting in recovery of the initial shape.

To circumvent contact-induced actuation in devices such as untethered robots, multifunctional polyurethane composite 19 was developed, composed of 15–17 in which azobenzene LC

moiety 18 and gold nanorods were introduced, providing a dual-responsive behavior to UV and near-infrared light (NIR) with reversible cycles (Figure 10d).¹²² The formation of hydrogen bonds between the linear chains and π – π interactions between the benzene rings of the azobenzenes yielded supramolecular cross-linking points in the system. It is worth noting that the mechanical properties of pure polyurethane without physically mixed azobenzene and gold nanorods were insufficient to support themselves. Oriented temporary shapes were obtained by prestraining the polyurethane composite (Figure 10e). When exposed to UV light, the oriented sample macroscopically bends toward to light source due to the photoisomerization of the azobenzene moieties (Figure 10f). After subsequent switching the light source to NIR light, the sample recovered to its initial state, affording a reversible shape change. The recovery process is triggered by the transformation of NIR light energy into thermal energy, thereby raising the sample's temperature, increasing the mobility of the system, and allowing it to recover. This three-step (draw, UV, NIR) multiple stimuli-response cycle was performed 10 times, demonstrating the photoinduced actuation behavior and performance. However, the composite requires preorientation before every cycle. Intriguingly, the composite material exhibited self-healing abilities based on the dynamic properties arising from the physical cross-linking interactions (Figure 10g), again showing how using hydrogen bonding interactions as physical cross-links with a dynamic

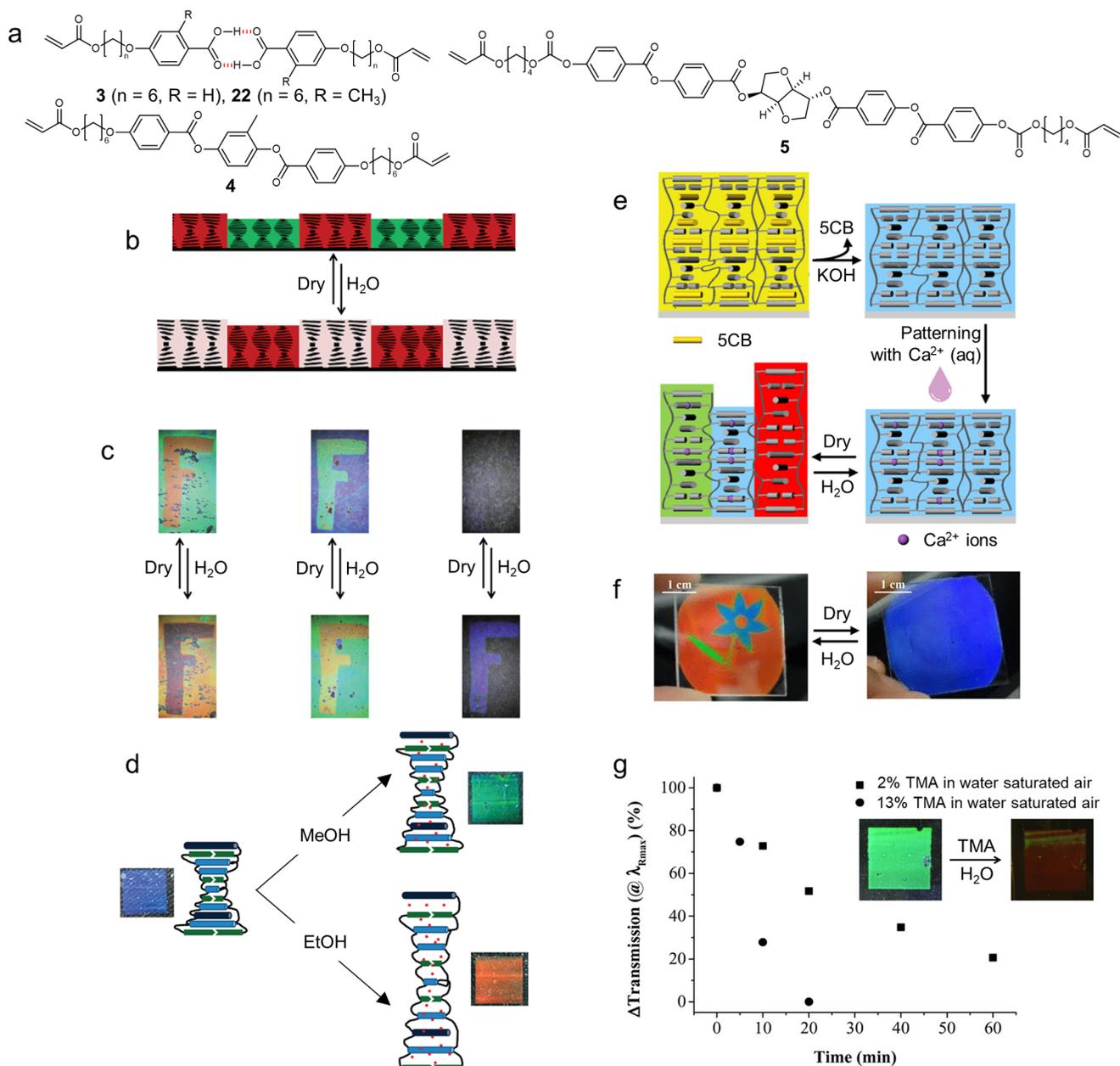


Figure 12. Water, solvent, and vapor responsive photonic coatings. (a) Molecular structures of the components used to fabricate hydrogen-bonded cholesteric LC polymer films. (b) Reversible dual color change of the CLC polymer coating. Adapted with permission from ref 56. Copyright 2015 The Royal Society of Chemistry. (c) Optical images showing three different polymer salt coatings patterned with the letter “F” in ambient conditions (dry) and wet state (H_2O), demonstrating the versatility possible through variations in the mixture composition. Adapted with permission from ref 56. Copyright 2015 The Royal Society of Chemistry. (d) CLC polymer exposed to methanol and ethanol molecules, demonstrating the difference in color change due to their distinct molecular polarities. Reproduced with permission from ref 57. Copyright 2012 American Chemical Society. (e) Schematic of the working principle of the Ca^{2+} patterning in a CLC polymer coating by local exposure to an aqueous solution containing Ca^{2+} ions. Reproduced with permission from ref 130. Copyright 2018 American Chemical Society. (f) The full-color pattern appeared in the wet state due to the difference in Ca^{2+} concentration and corresponding swelling of the CLC coating. In contrast, in the dry state, the patterned regions were indistinguishable, showing a blue-colored state. Reproduced with permission from ref 130. Copyright 2018 American Chemical Society. (g) Transmission intensity change at maximum SRB ($\lambda_{R_{max}}$) of CLC films exposed to 2% (SRB = 513 nm) and 13% (SRB = 524 nm) trimethylamine for different exposure times in water-saturated nitrogen as the carrier gas. Adapted with permission from ref 132. Copyright 2014 Wiley-VCH.

character is a promising approach for constructing sustainable supramolecular materials.

Typical photosensitive azobenzene molecules exhibit relaxation times on the time scale of hours. Azobenzene containing LC polymers showing fast thermal relaxation within seconds after

photoisomerization have been reported using intermolecular hydrogen-bonding and can be used to obtain fast photo-responsive actuators. The *cis*–*trans* thermal isomerization of azobenzene in a LC polymer was drastically increased by using azophenols instead of acetylated azobenzene moieties.¹²³ The

phenolic azobenzene can form hydrogen-bonding interactions with the nitrogen double bond, in contrast to the acetylated groups, promoting the azo-hydrazone tautomerism.¹²⁴ Accompanying the tautomerizable azohydrazone formation, a very rapid (<1 s) thermal back reaction is observed. Another approach consists of using “push–pull” azobenzene derivatives bearing electron-donating/withdrawing groups inducing electron delocalization to afford faster thermal relaxation times. Incorporated azopyridines formed hydrogen-bonding interactions with benzoic acid moieties to induce fast *cis–trans* thermal relaxation after illumination with UV light.¹²⁵ These LC polymers exhibit continuous light-driven, wave-like macroscopic motion upon exposure to constant light arising from self-shadowing and have potential applications in light-driven locomotion and self-cleaning surfaces.

3. COLOR CHANGING MATERIALS

3.1. pH- and Humidity-responsive Color Changing Polymers

Hydrogen-bonded molecules have been used to introduce responsivity and influence structural properties, including alignment, interhelical order, modulus, and phase behavior of structurally colored LC polymer films.¹²⁶ The stimuli-response of these LC polymer materials is often based on coordination of hydrogen bonds and absorbing of solvent molecules, resulting in a photonic shift through volumetric collapse or expansion of the LC polymer network. Photonic “selective reflection band” (SRB) LC polymer coatings are typically made from mesogens doped with a chiral dopant, affording the cholesteric mesophase. As commonly encountered in this text, pH and humidity responses can be enabled by incorporating dimerized benzoic acid-derived rod-shaped mesogens.

Early work demonstrated a change of the reflection color in response to pH. A mixture of reactive benzoic acid LC **3**, cross-linker **4**, and a nonpolymerizable acid **20** as a chiral dopant was used to prepare the cholesteric polymer (Figure 11a).¹²⁷ The chiral dopant forms a hydrogen-bonded complex with the LC, creating a structurally colored film responsive toward aqueous solutions of inorganic bases (KOH, NaOH, CsOH) and amino acids, as they disrupt the hydrogen bonding to form a hygroscopic salt. Again, the carboxylate salt increases the hydrophilicity of the system and allows the uptake and accumulation of water inside the film, resulting in volumetric swelling, increasing the helical pitch of the cholesteric helix and the reflection color to longer wavelengths (Figure 11b,c).

Hygroscopic carboxylate salt formation can also be employed to detect alkaline amino acids in an aqueous solution.¹²⁸ Like inorganic bases, alkaline amino acids can disrupt the hydrogen bonds and form corresponding carboxylate salts in situ, resulting in swelling of the CLC polymer network. The swelling of the polymer increases as a function of time and is accompanied by a ~ 170 nm red-shift of the SRB within 15 min (Figure 11d). The kinetics of the swelling depends on the pK_a and molecular volume of the alkaline moieties used, allowing distinguishing between different amino acids through the distinct SRB color shifts. Furthermore, the degree of swelling is determined by the concentration of benzoic-derived monomer **3** in the polymer, which can thus be used to tune the SRB shift by adjusting the composition of the mixture (Figure 11e).

A similar approach established pH- and temperature responses for CLC polymer materials using hydrogen-bonded assemblies of chiral dopant and polymer. A variation on the

previously discussed systems^{127,128} incorporated chiral dopant **21** based on an isosorbide isonicotinate moiety, with both pyridine ends promoting hydrogen-bonded assembly with the benzoic acid LCs (Figure 11a).¹²⁹ The resulting hydrogen-bonded polymers showed a pH-dependent red-shift of the reflected wavelength when exposed to alkaline solution (Figure 11f). Additionally, a reversible temperature-sensitive red-shift from 60 to 200 °C was demonstrated (Figure 11g). This phenomenon was ascribed to the temperature-dependent weakening of the H-bonds in the chiral dopant assembly.

The introduction of a methylated benzoic acid LC derivative increases the temperature range of the cholesteric phase and allows for the formation of hydrogen-bonded dimers with the nonmethylated benzoic acids. The photonic polymers consisting of reactive carboxylic acid derivatives **3** and **22**, diacrylate LC cross-linker **4**, and polymerizable LC chiral dopant **5** have become a typical system to create pH or humidity responsivity via swelling of the photonic material (Figure 12a),⁵⁶ similar to the humidity-responsive actuators discussed in section 2.1. Because the pitch naturally increases with temperature (Figure 3f), patterned cholesteric LC coatings can be made by photopolymerizing the monomer mixture through a photomask at different temperatures, yielding regions with different pitch lengths (Figure 12b). After activation, swelling of the polymer network results in an increased helical pitch, inducing a red-shift of the reflected wavelength, affording a cholesteric polymer coating with a dual-color change. Interestingly, by changing the amount of chiral dopant in the monomeric mixture, dual-colored coatings with different color-reflecting regions were realized, indicating the versatility of this approach (Figure 12c).

To create a film capable of distinguishing between solvents, a LC polymer network with a similar composition based on nonmethylated **3** and methylated **22** carboxylic acid derivatives and a polymerizable (diacrylate) LC chiral dopant **5**, is incorporated with a nonreactive LC compound acting as a porogen (Figure 12a).^{58,59} After polymerization, the porogen is washed out of the cholesteric film, resulting in a collapsed cholesteric structure with a blue-shift of the reflected wavelength. Subsequently, the cholesteric polymer network is activated by aqueous KOH to form the carboxylate salt in situ. The resulting film exhibits differences in the swelling induced by methanol and ethanol. This difference in swelling was correlated to the molecular affinity, based on the polarity, between the solvent and the carboxylate salt, allowing for the differentiation between alcohol molecules. Specifically, it was demonstrated that the hydrogen-bonded CLC network exposed to ethanol shows a greater red-shift than those exposed to methanol (Figure 12d). Hence this photonic film can distinguish between ethanol and methanol and potentially be used to detect either counterfeit or methanol-contaminated alcoholic drinks.

Cholesteric polymer materials that make use of non-polymerizable LC porogens display a large swelling capacity, permitting a structural color shift over the entire visible spectrum. A printable photonic polymer has been prepared of dimerized benzoic acid LC monomers **3** and **22**, diacrylate dopant **5**, and a porogen (Figure 12a).¹³⁰ The swelling capacity of the material was locally restricted by introducing a bivalent cation that forms bivalent metal-carboxylate complexes, preventing hygroscopic swelling (Figure 12e). After polymerization and formation of the carboxylic salt, ion exchange through local exposure of the coating to an aqueous salt solution containing calcium results in cross-linking through the formation of a Ca^{2+} -carboxylate complex, so hygroscopic

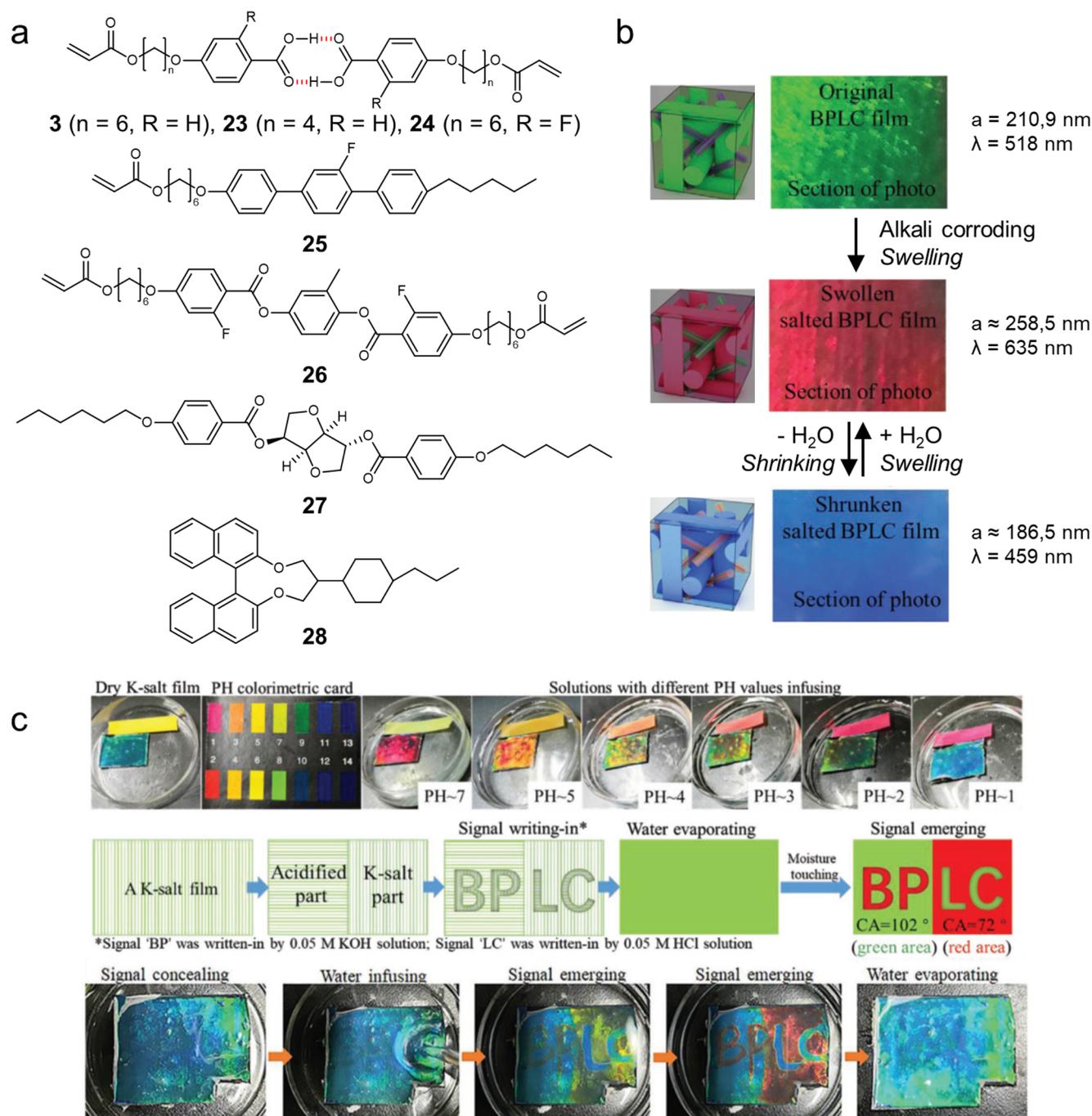


Figure 13. Humidity- and pH-responsive blue-phase LC film. (a) Chemical structures of the monomers used to prepare a blue-phase LC polymer. (b) Images showing the activation and humidity-response in a fully reversible way. Adapted with permission from ref 133. Copyright 2020 Wiley-VCH. (c) Images of the color change in response to solutions with different pH values (top). Schematic illustration (middle) and images (bottom) of the patterned coatings. Reproduced with permission from ref 133. Copyright 2020 Wiley-VCH.

swelling is controlled locally, and a hidden pattern can be exposed after water absorption (Figure 12f). The swell-reducing effect of the ion exchange can also be applied as a sensor to detect Ca^{2+} in serum using a photonic polymer coating with nonreactive moiety **20** simultaneously acting as chiral dopant and porogen, which may be extracted by evaporation after polymerization.¹³¹ This responsive optical material holds promise in the fabrication of inexpensive, easy-to-use, battery-free metal ion sensors for clinical diagnostics.

The swelling behavior of the CLC polymer network can also be modified for use as an indirect gas sensor. A cholesteric mixture composed of nonmethylated and methylated carboxylic acid derivative **3** and **22**, LC diacrylate cross-linker **4**, and the benzoic acid-based chiral dopant **20** was used for inkjet printing cholesteric LC films (Figure 12a).¹³² In this system, chiral dopant **20** is not extracted, in contrast to previously discussed systems. By exposing the film to an amine gas such as trimethylamine, the hygroscopic salt is formed in situ because the amine compound can act as a base and disrupt the hydrogen

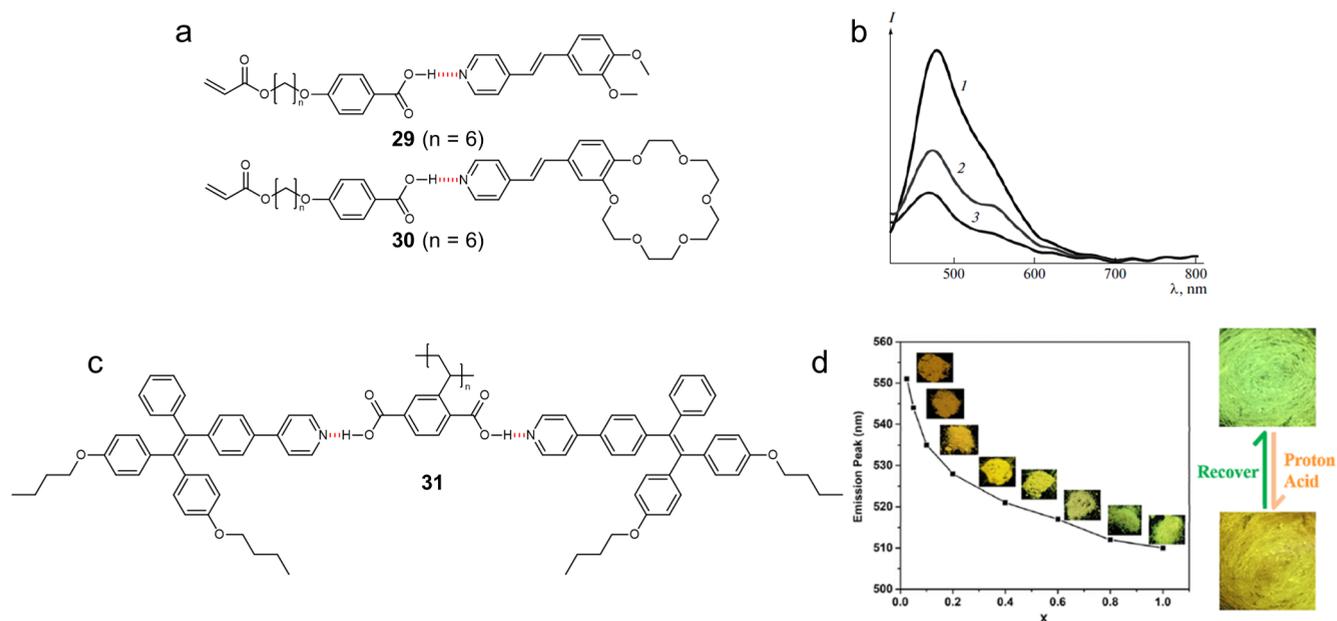


Figure 14. Fluorescent hydrogen-bonded optical materials. (a) The hydrogen-bonded complexes of carboxylic acid-derived monomer **3** and stilbazole molecules. (b) Decreased fluorescence intensity for crown-ether-containing polymer **30** in response to potassium ions (0.01 M KClO₄) after 0 min (1), 2 min (2), and 5 min (3). Reproduced with permission from ref 134. Copyright 2011 Springer Nature. (c) Chemical structures of the discotic hydrogen-bonded complex. (d) The relationship between the emission peak and molar ratio x of the pyridine containing LC groups and reversible fluorescence switching under strong proton acid vapor due to the protonation effect. Adapted with permission from ref 135. Copyright 2019 American Chemical Society.

bonds between the carboxylic acid dimers, allowing the coating to swell through the absorption of water in a humid air environment. Hence, the degree of swelling is an indirect indicator of amine gas concentration (Figure 12g). It was demonstrated that volatile amines produced by a decaying fish could be detected using CLC films as optical sensors, making them interesting for smart food packaging.

Recently, the formation of carboxylate salts has been applied within a LC polymer exhibiting a blue phase, i.e., 3D photonic chiral LC state. Benzoic acid derivatives **3** and **23** and chiral dopants **27** and **28** were combined with novel fluorinated mesogens **24**–**26** to broaden the temperature window of the LC blue phase (Figure 13a).¹³³ Within this tailored mixture, fluorinated monomer **25** was demonstrated to be the main contribution to the enhanced temperature window via synergistic self-assembly into 3D nanostructures through the formation of hydrogen bonds. After fabrication of the photonic blue-phase LC polymer film, the classic base treatment creates the carboxylate salt to enable hygroscopic swelling of the LC polymer network, affording a reversible humidity- and pH-responsive behavior through a color change (Figure 13b,c). Again, patterning of the material is possible by local acidic treatment that neutralizes the hygroscopic carboxylate salt through protonation, resulting in restoration of the original state of the blue-phase LC film (Figure 13c).

Fluorescent hydrogen-bonded LC polymer coatings have also been reported. The reversible transfer of hydrogen atoms facilitates the protonation of stilbazole molecules in the excited state by using the typical carboxylic acid LC derivative **3**, affording hydrogen-bonded complex **29** and **30** (Figure 14a),¹³⁴ resulting in a difference in fluorescence properties and phase behavior. This can be exploited to create a higher sensitivity in fluorescent sensors. One example enabling a type of metal ion sensor is incorporating crown ethers (**30**) that demonstrate a

response to potassium ions by decreasing fluorescence intensity (Figure 14b).

Another pH-responsive fluorescent LC is based on the columnar stacking of discotic molecules. In an example of a color-tunable side chain LC coating, hydrogen bonds are used to attach luminescent LCs made using vinyl terephthalic acid backbones with pyridine-containing LCs as side chain structures, yielding hydrogen-bonded complex **31** (Figure 14c).¹³⁵ The columnar stacking between the pendant LCs allowed for the fabrication of luminescent LC polymers due to aggregation-induced emission of the luminogenic moieties. The emission behavior of the LC polymers exhibited molar ratio dependence as a function of the luminogenic LCs (Figure 14d). Interestingly, fluorescence switching of the LC polymer coating occurred when exposed to strong acidic vapor and was reversible upon evaporation of the strong proton acid (Figure 14d). This reversible color transformation, induced with various acidic vapors, arises from the reversible protonation of the pyridine-containing LC moieties in the LC side chain structure.

3.2. Temperature-responsive Color Changing Polymers

The incorporation of hydrogen bonds can also afford thermal-responsive color changing LC polymers with reversible and irreversible responses. The approach to prepare materials with a reversible response resembles the humidity-responsive systems discussed in section 3.1. The monomer mixture comprises nonmethylated and methylated carboxylic acid derivatives **3** and **22**, LC cross-linker **4**, and diacrylate chiral LC dopant **5** (Figure 15a).¹³⁶ After polymerization and subsequent activation, absorbed water can be removed through evaporation in a dry environment or a temperature difference between the coating and the environment. Hence, the cholesteric LC polymer coating could be used as a humidity sensor and time-temperature integrator due to a change in the pitch length of the cholesteric material that is reflected by a change in reflection

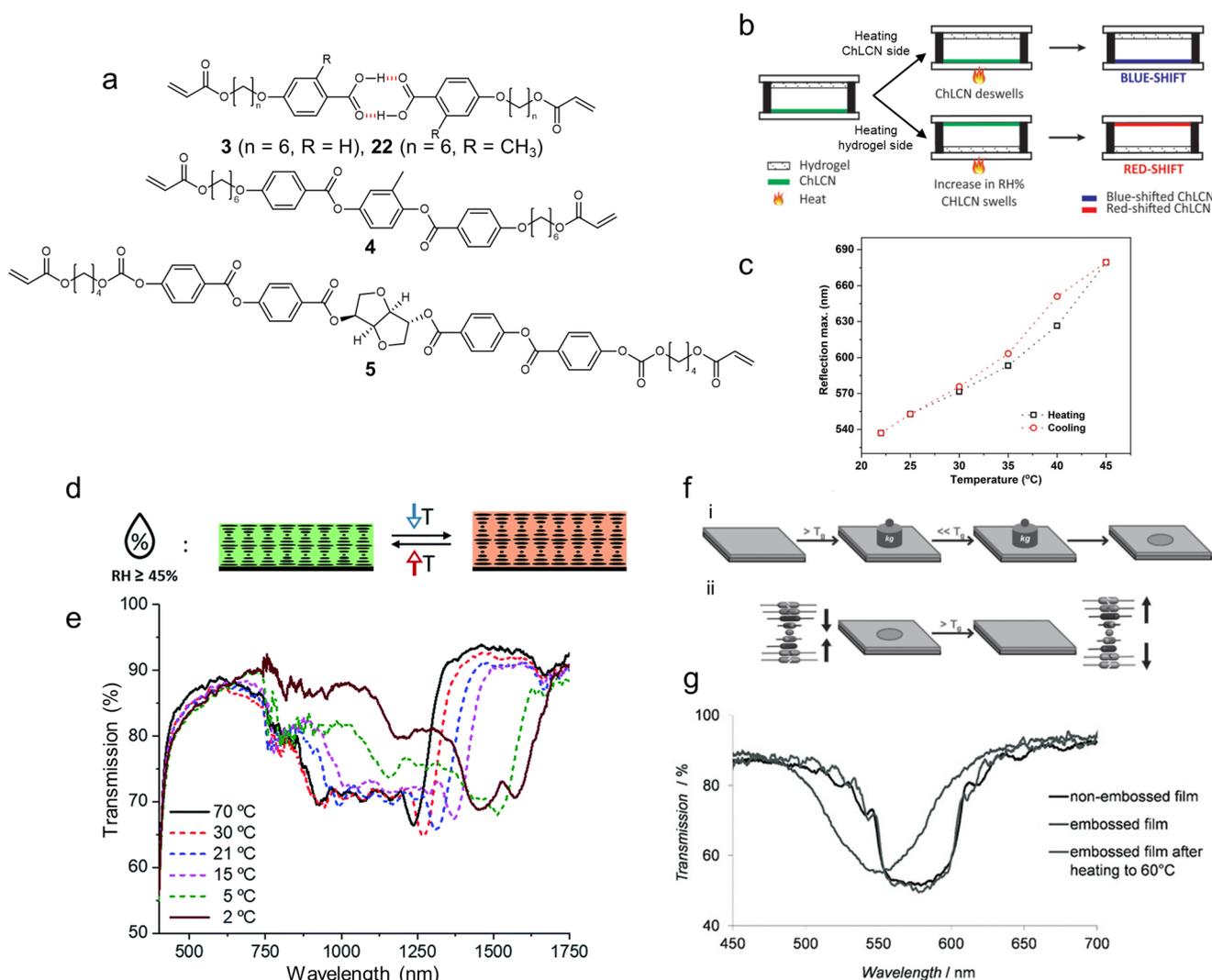


Figure 15. Temperature-responsive optical changing materials. (a) Chemical structures of molecules comprising the humidity- and temperature-responsive cholesteric LC polymers. (b) The working principle of the temperature-responsive device. Reproduced with permission from ref 137. Copyright 2020 The Royal Society of Chemistry. (c) Shift in the reflection peak by heating and cooling from the hydrogel side. Reproduced with permission from ref 137. Copyright 2020 The Royal Society of Chemistry. (d) schematic illustration of the temperature-responsive mechanism. Adapted with permission from ref 138. Copyright 2019 The Royal Society of Chemistry. (e) Transmission spectrum of the broadband Ch-LC coating at 75% RH and various temperatures. Adapted from ref 138. with permission from The Royal Society of Chemistry. (f) Schematic representation of the CLC coating demonstrating (i) the embossing mechanism and (ii) the shape memory temperature response upon heating the material. Adapted with permission from ref 139. Copyright 2013 Wiley-VCH. (g) The reflection band shift upon embossing the film and subsequently heating it to 60 °C. Adapted with permission from ref 139. Copyright 2013 Wiley-VCH.

color. This concept was incorporated in a closed system containing a cholesteric LC polymer coating to generate the stimulus-response and a hydrogel as a water buffer to regulate the humidity (Figure 15b).¹³⁷ Heating the cholesteric LC polymer leads to deswelling and a concurrent blue-shift in selective reflection. In contrast, by heating the hydrogel side, water is released, increasing the humidity of the system, resulting in swelling of the cholesteric coating and thus a red-shift in the reflection peak. As such, the uptake and release of water can be used as a temperature indicator through the temperature-controlled reversible 100 nm shift in reflection over a 12 °C temperature change within a time scale of a few minutes (Figure 15c).

Typical cholesteric reflectors are limited to a ~75 nm reflection bandwidth in the visible spectrum. A broadband

infrared reflective coating with a bandwidth of around 400 nm was fabricated, demonstrating a reversible temperature-response through a humidity-gated shift of the reflected light. These photonic coatings are composed of 3, 4, 5, and 22 and a surfactant to support alignment at the air interface (Figure 15a).¹³⁸ The obtained broadband reflective coating can be converted to a humidity-responsive system after base treatment of the carboxylic acid derivatives, where in high humidity, increasing temperature results in water being desorbed from the coating, decreasing the helical pitch, accompanied by a blue reflection band shift (Figure 15d,e). When the cholesteric coating is cooled, the material reabsorbs water, increasing the helical pitch, leading to a red-shift of the reflected wavelength. Because the humidity-gated, temperature-responsive broadband infrared reflective coating is transparent to the visible spectrum,

this technology becomes interesting for deployment as smart windows for automotive, buildings, and greenhouses.

One approach to design irreversible temperature sensors is by making use of shape memory in cholesteric LC polymers. Irreversible temperature sensors can display the history of exposure even when the external stimulus is no longer present, for example, in food packaging. A chiral-nematic LC polymer network is prepared by photopolymerizing a monomer mixture of **3**, **4**, **5**, and **22** (Figure 15a), which incorporates the supramolecular hydrogen-bonding interactions to enhance the structural properties, such as stabilizing the deformed organization of the polymer chains.¹³⁹ In the cholesteric LC coating obtained, an indentation in the material results in local compression of the cholesteric helix that is fixed upon cooling, leading to a blue-shift of the reflected light in the embossed regions (Figure 15f), stabilized by the supramolecular hydrogen-bonded benzoic acid dimers. Heating the CLC network above the glass transition temperature results in a large, irreversible mechanical response accompanied by a permanent red-shifted color change (Figure 15g).

An alternative approach to obtain an irreversible temperature response is incorporating a noncovalently bonded dicarboxylic porogen which also acts as the chiral dopant in the LC coating. A planarly aligned CLC polymer coating was prepared by photopolymerizing a mixture based on dimerized rod-shaped mesogens **3** and **22** and chiral dopant **20**.¹⁴⁰ After polymerization, evaporation of the hydrogen-bonded porogen causes the structure to collapse, decreasing the helical pitch that results in a blue-shift of the reflection band. By locally heating the polymer, localized evaporation takes place, allowing patterning of the material. This phenomenon was used to fabricate writable photonic polymer paper.

Another recent irreversible temperature sensor displays cholesteric order loss during exposure to temperatures above the polymeric isotropic temperature. This polymer coating is constructed from a mixture of benzoic acid derivatives **3** and **22** and monoacrylate chiral dopant **32**: the acid groups provide supramolecular cross-linking between the cholesteric helices (Figure 16a).¹⁴¹ Because no chemical cross-linker is present, the hydrogen bonds present within the dimerized benzoic acid monomers are fundamental to the structural stability and thermal response of the system. The temperature-dependent dimer–monomer equilibrium of the acid moieties in the supramolecular network determines the stability of the cholesteric order (Figure 16b,c). Exposing the photonic polymer to temperatures above the isotropic transition yields a disordered state; the resulting coating is scattering as it reflects the full-wave spectrum because of the lack of order in the nematic phase. The hydrogen-bonding equilibrium between helices is even more disrupted in the presence of water, enabling a more rapid loss of order. Such a dual-responsive system is potentially attractive as a steam sterilization sensor in which the color loss is accelerated by steam.

4. NANOPOROSITY CHANGING MATERIALS

4.1. pH-responsive Polymers That Change Porosity

pH-responsive nanoporous materials have been constructed from hydrogen-bonded LC polymers using calamitic LCs. Disrupting the hydrogen bonds between the dimerized mesogens of a smectic LC network based on a photopolymerized reactive hydrogen-bonded benzoic acid mesogen **3** and a diacrylate LC cross-linker **33** by a basic solution resulted

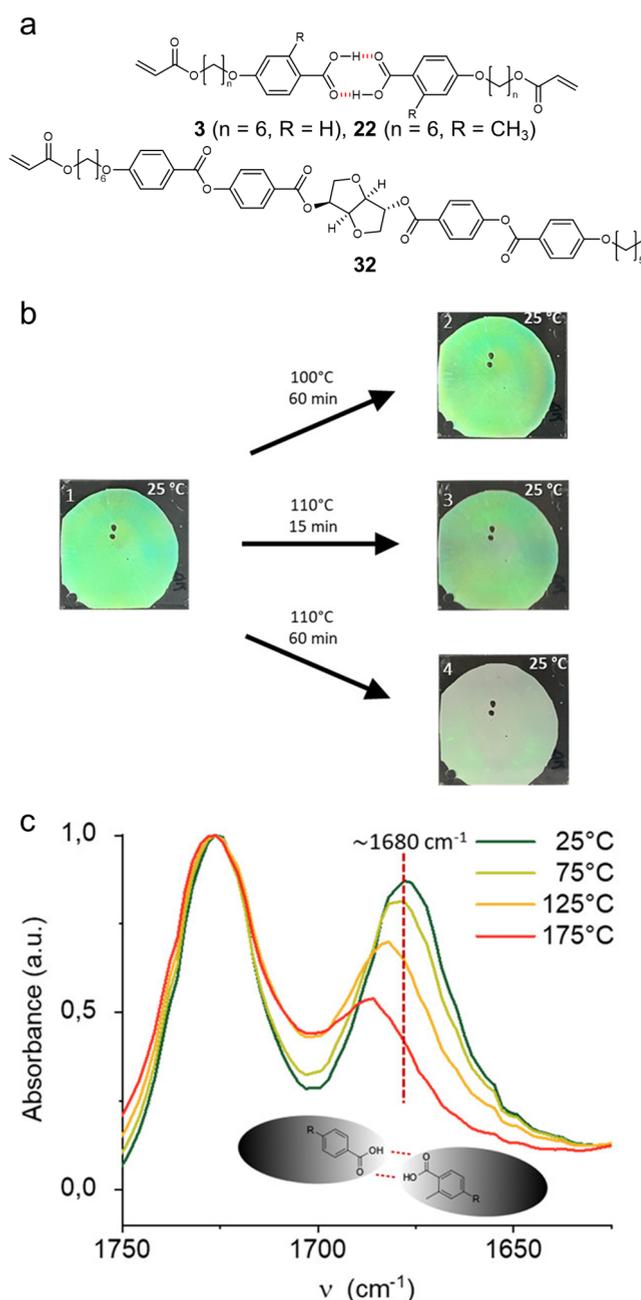


Figure 16. Dual-responsive supramolecular cross-linked color changing polymer. (a) Chemical structures of the monomers used to make a cholesteric hydrogen-bonded film without covalent cross-links. (b) Response to temperature exposure demonstrating color loss after heating above the polymeric isotropic transition temperature. Reproduced with permission from ref 141. Copyright 2020 American Chemical Society. (c) FT-IR spectrum showing the dynamic equilibrium between dimerized and free carboxylic acid as a function of temperature. Adapted with permission from ref 141. Copyright 2020 American Chemical Society.

in a nanoporous network with ionic 2D nanopores; the cross-linker was used to provide mechanical integrity (Figure 17a).¹⁴² Interestingly, the breaking of hydrogen bonds was reversible upon decreasing the pH or increasing temperature: the nanoporous membrane could be switched between open and closed states (Figure 17b). The reversibility of the acid–base treatment on the anisotropic swelling of the system was further

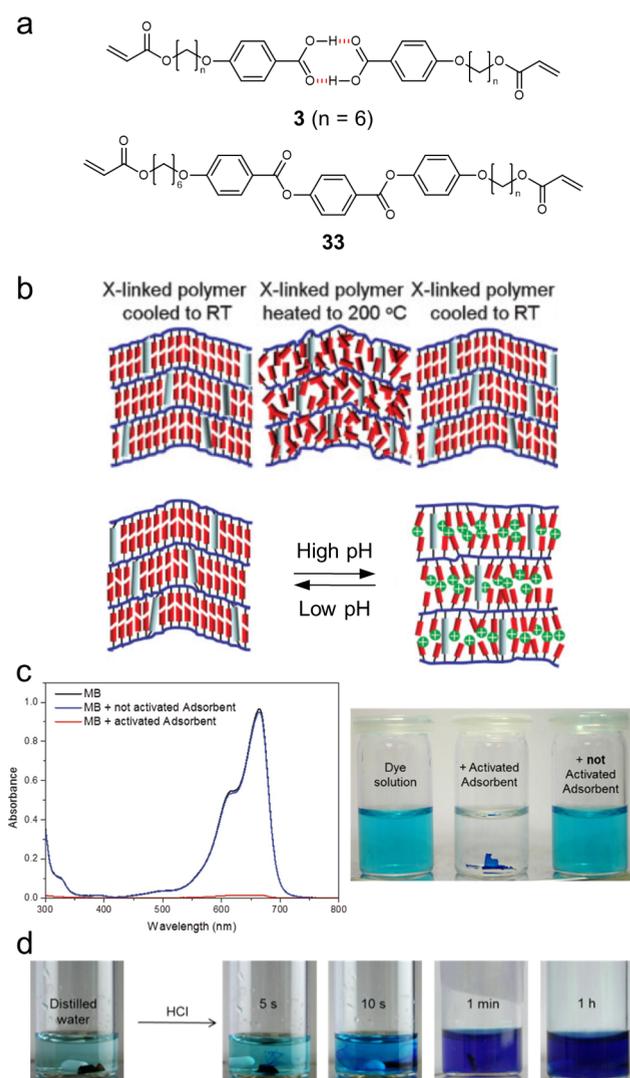


Figure 17. pH-responsive nanoporous materials. (a) Chemical structures comprising the nanoporous materials. (b) Temperature and pH reversible response of the nanoporous system. Adapted with permission from ref 142. Copyright 2008 Wiley-VCH. (c) The absorption process of the dye into the nanoporous LCN. Reproduced with permission from ref 62. Copyright 2014 Wiley-VCH. (d) Release of the dye in an acidic solution. Adapted with permission from ref 62. Copyright 2014 Wiley-VCH.

investigated (vide supra), demonstrating the importance of the ratio of benzoic acid mesogens to cross-linker.⁸⁷

The reversible breaking of hydrogen bonds in a LC polymer network has also been used to prepare a pH-responsive adsorbent for small cationic dyes.⁶² Smectic hydrogen-bonded films were constructed using a hydrogen-bonded LC monomer mixture with polymerizable benzoic acid derivative **3** and reactive cross-linker **33** (Figure 17a). A basic solution was used to open the pores so the carboxylate groups become accessible to cations. In the ionic state, the 2D nanoporous film could be fully saturated with the cationic dye methylene blue, a model compound for small organic cationic pollutants (Figure 17c). Subsequent acidic treatment of the saturated nanoporous film resulted in the near-complete release of the cationic dye and the reformation of closed pores (Figure 17d). The pH-response arises from the protonation of the carboxylate moieties in the

material and the accompanying formation of the hydrogen-bonded network. After exposure to an alkaline solution, the material was again able to reabsorb the dye. The consecutive absorption and release of the dye were repeated for several cycles, demonstrating reversible pH-response and reusability of the material.

Recently, the reversible cationic dye binder concept was applied in a nanoporous composite membrane to remove cationic pollutants from a solution and improve the reusability of the membrane.⁵⁷ By combining the LC polymer network based on reactive benzoic acid dimer **3** and cross-linker **33** with a porous anisotropic scaffold, a composite film was produced in which the LC network layer penetrated the scaffold. The membrane was able to reject various anionic solutes based on charge selective exclusion, whereas small cationic solutes were adsorbed by the negatively charged membrane, resulting in blocking of the pores (Figure 18a). By exposing the membrane to an acidic solution, the carboxylate moieties were converted back to the corresponding carboxylic acid, resulting in a release of the pollutants and closing of the porous structure. Subsequent treatment with an alkaline solution reformed the carboxylate and porous structure, which had the same chemical and physical properties before the fouling (Figure 18b). A similar method based on an orienting scaffold was demonstrated for humidity-responsive actuators (vide supra).⁹³

LC polymer networks based on hydrogen-bonded benzoic acid-derived dimers are not limited to flat films. Using suspension polymerization, broadly dispersed single domain nanoporous particles with an average size of 1.4 μm were fabricated from an LC mixture composed of benzoic acid derivatives **1–3** and cross-linker **33**.⁶¹ The particles had planarly aligned smectic mesogens and concentric lamellar pores, yielding particles with an onion-like layered morphology. After base treatment, the particles showed selective adsorption of the methylene blue dye at high pH and desorption at low pH (Figure 18c). The pH response arises from the deprotonation and protonation of the carboxylic acid groups by changing the pH. The fast adsorption kinetics of this system is attributed to the high surface area of the particles. Furthermore, the polymer LC particles were able to be recovered, allowing for reuse of the material.

4.2. Chemo- and Ion-responsive Nanoporous Materials

In pH-responsive systems, a dye can be released by protonating the carboxylate moieties. Alternatively, the interaction between carboxylates and divalent cations has been exploited to prepare responsive nanoporous materials. Recent work showed the fabrication of responsive monodisperse particles based on hydrogen-bonded benzoic acid mesogen **3** and cross-linker **33**, which used CaCl_2 as a responsive trigger for the release of dye molecules.⁶³ Similar to the work in section 3.1, hydrogen bonds in the particles could be disrupted by exposure to basic solutions, resulting in nanoporous structures. However, in contrast to the pH-responsive systems, the release of the dye is triggered by exposing the saturated particles to a CaCl_2 solution: the carboxylate groups prefer to bind to Ca^{2+} ions, forming chemical cross-links between two carboxylate groups, allowing the cationic dye to be released.

The molecules that trigger a response in nanoporous materials are often tailor-made using the intended guest molecules as a template during fabrication. Examples of this molecular imprinting approach are melamine and tris(triazolyl)triazine derivatives combined with three gallic acid derivatives to make

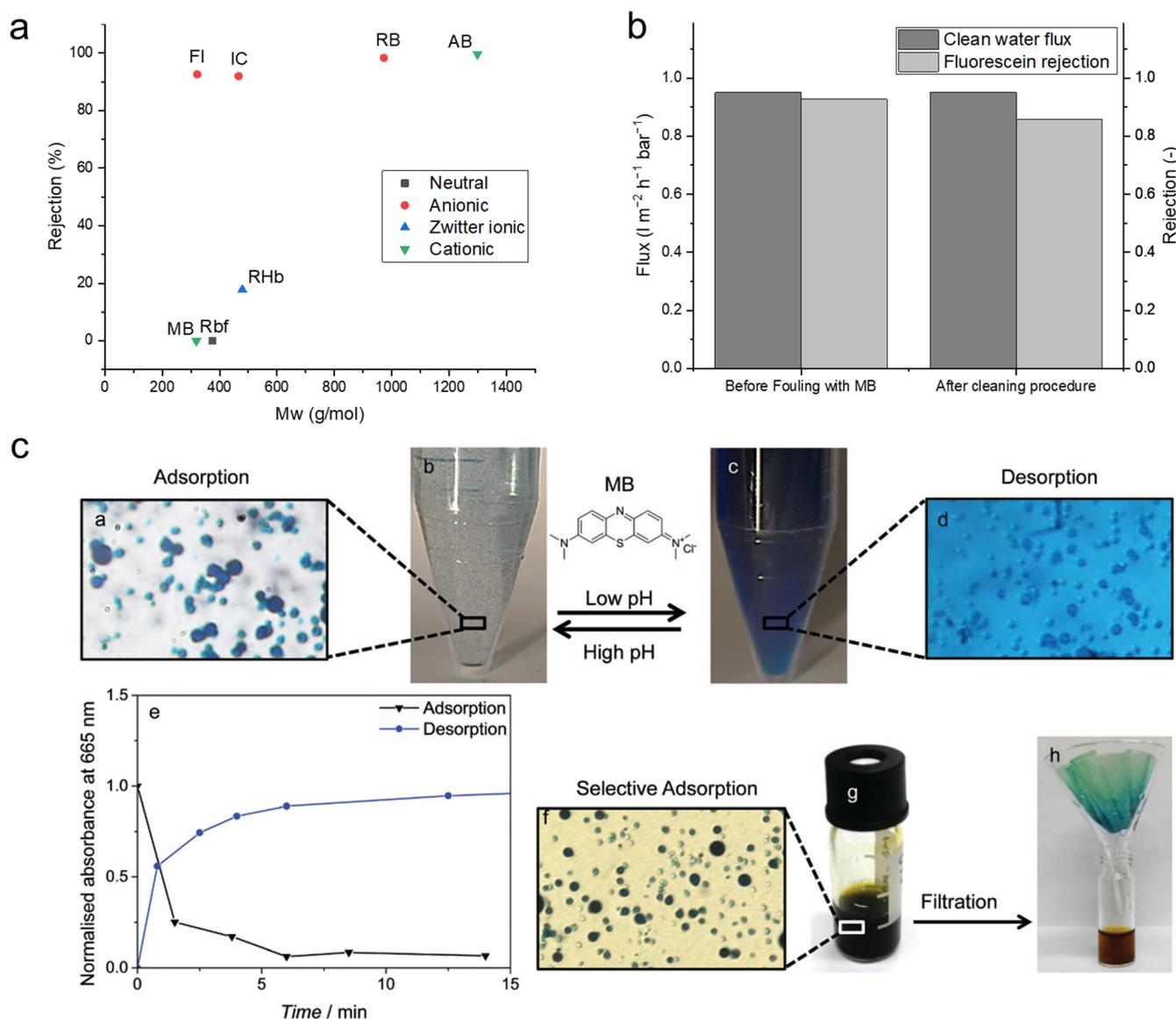


Figure 18. pH-responsive nanoporous composite materials and polymer particles. (a) Rejection behavior of the nanoporous membrane. Adapted with permission from ref 57. Copyright 2021 American Chemical Society. (b) Clean water flux and rejection of a small dye before and after the membrane was fouled and cleaned via a response to an acidic and alkaline environment. Adapted with permission from ref 57. Copyright 2021 American Chemical Society. (c) Selective methylene blue adsorption and desorption via a response to low and high pH. Reproduced with permission from ref 61. Copyright 2016 The Royal Society of Chemistry.

1D nanoporous films.⁶⁹ Novel polymerization techniques were demonstrated, involving a [2 + 2] cycloaddition of coumarin end groups on gallic acid derivatives. The hydrogen-bonded melamine 34 and tris(triazolyl) triazine-derived 35 discotic units self-assembled into a columnar mesophase (Figure 19a). Subsequent polymerization of the material and extraction of the core unit led to freestanding nanoporous films with different pore sizes depending on the core unit used. When the functional groups inside the pores were kept in their protonated carboxylic acid form, a high selectivity was found for the imprinted core molecule, demonstrating the guest–host recognition concept of this system. When the nanoporous films were treated with a basic potassium hydroxide solution, leading to a conversion in the potassium salt form, the system was able to absorb various cationic species. The subsequent release of the cationic species was achieved with acidic and basic washing steps, which were

repeated for several cycles demonstrating the recyclability of the system (Figure 19b,c). In addition, in the protonated state, the material could absorb and desorb small anionic species.

Thus far, the approaches discussed have used benzoic or gallic acid derivatives to generate hydrogen-bonding moieties with two hydrogen bonds at each binding site. The use of thymine-derived side units resulted in the formation of complex 36 with triple hydrogen bonds, leading to higher selectivity toward the templated core molecule (Figure 19d).⁷⁰ The complex consisting of melamine and three thymine acrylate functionalized derivatives resulted in a hexagonal columnar mesophase. Subsequent photopolymerization and removal of the melamine template core resulted in nanoporous melamine imprinted channels. The nanoporous structure selectively absorbs melamine from a solution containing additional small molecules (primary amines) due to the specific size and location of

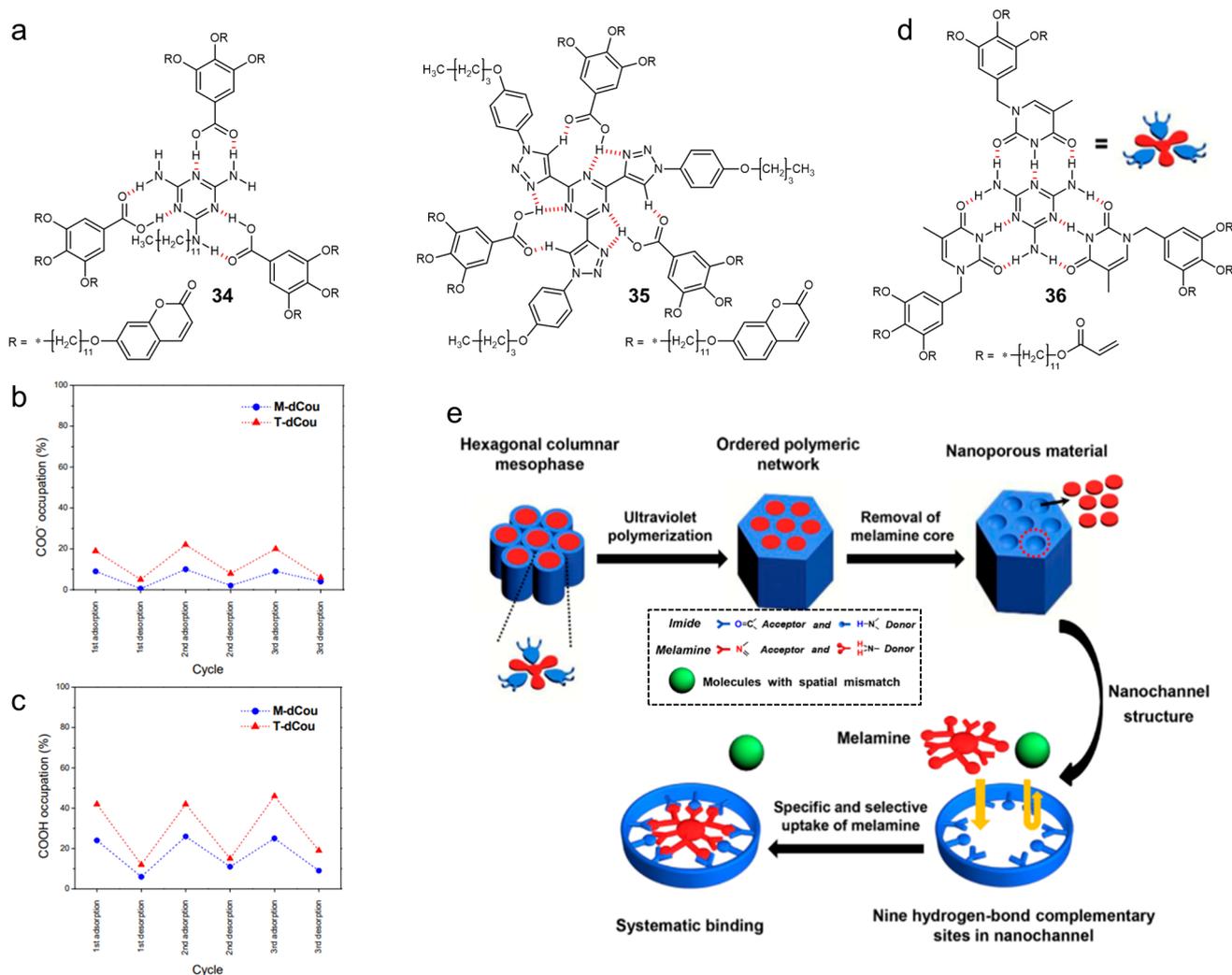


Figure 19. Chemo- and ion-responsive nanoporous materials. (a) Chemical structures of the carboxylic acid-derived coumarin moieties and templates. Occupation degree of the (b) carboxylate and (c) carboxylic acid sites during three repeating adsorption–desorption cycles. Reproduced with permission from ref 69. Copyright 2018 American Chemical Society. (d) Chemical structure of the melamine-thymine-functionalized gallic acid hydrogen-bonded complex. Adapted with permission from ref 70. Copyright 2020 American Chemical Society. (e) Schematic representation of the self-assembly into the columnar phase, polymerization, and removal of the thymine core resulting in a 1D nanostructured material with high selectivity toward the original host. Adapted with permission from ref 70. Copyright 2020 American Chemical Society.

hydrogen-bonding sites in the nanochannel (Figure 19e). The recyclability of the system was demonstrated by performing multiple rounds of adsorbing and removing the melamine, making this material interesting for the removal of melamine in pet foods and milk products.

Dynamic morphology of 1D nanoporous polymer structures was demonstrated in a disk-shaped hydrogen-bonded complex.¹⁴³ A reactive gallic acid derivative was complexed with a tris-benzimidazole template into the discotic moiety 37, affording a polymer film with a columnar mesophase (Figure 20a). The gallic acid contained an additional 4-hydroxybenzoic acid group attached to the carboxylic acid, introducing a cleavable ester linkage, allowing for postmodification of the porous structure (Figure 20b). Hence, four distinct types of nanoporous polymers were prepared with and without the additional moiety with either neutral carboxylic acid or anionic carboxylate pore interior. Interestingly, when the 4-hydroxybenzoic acid was removed, the anionic nanopores were able to

adjust their pore size depending on the available guest molecule while keeping their macrostructure unaffected.

In contrast to most work focusing on the formation of 3:1 hydrogen-bonded complexes, 1:1 complex 38 containing a chiral 2-amino alcohol core unit was also developed to prepare porous materials (Figure 20c).^{75,76} A library of hydrogen-bonded complexes between chiral 2-amino-alcohols derivatives and a gallic acid moiety has been investigated. The complexes that formed a columnar LC phase through hydrogen bonds were subsequently photopolymerized, resulting in nanoporous structures after removing the amino alcohol template. Methylated derivatives of 2-amino alcohol resulted in an unstable columnar LC phase, demonstrating the importance of hydrogen-bonding interactions in this system. The materials exhibited enantioselective absorption of the hydrogen-bonded guest molecules, indicating the potential for separating racemic mixtures by this type of nanoporous LC networks.⁷⁵ Morphological studies showed that desorption of the original guest molecule resulted in an amorphous structure, which was

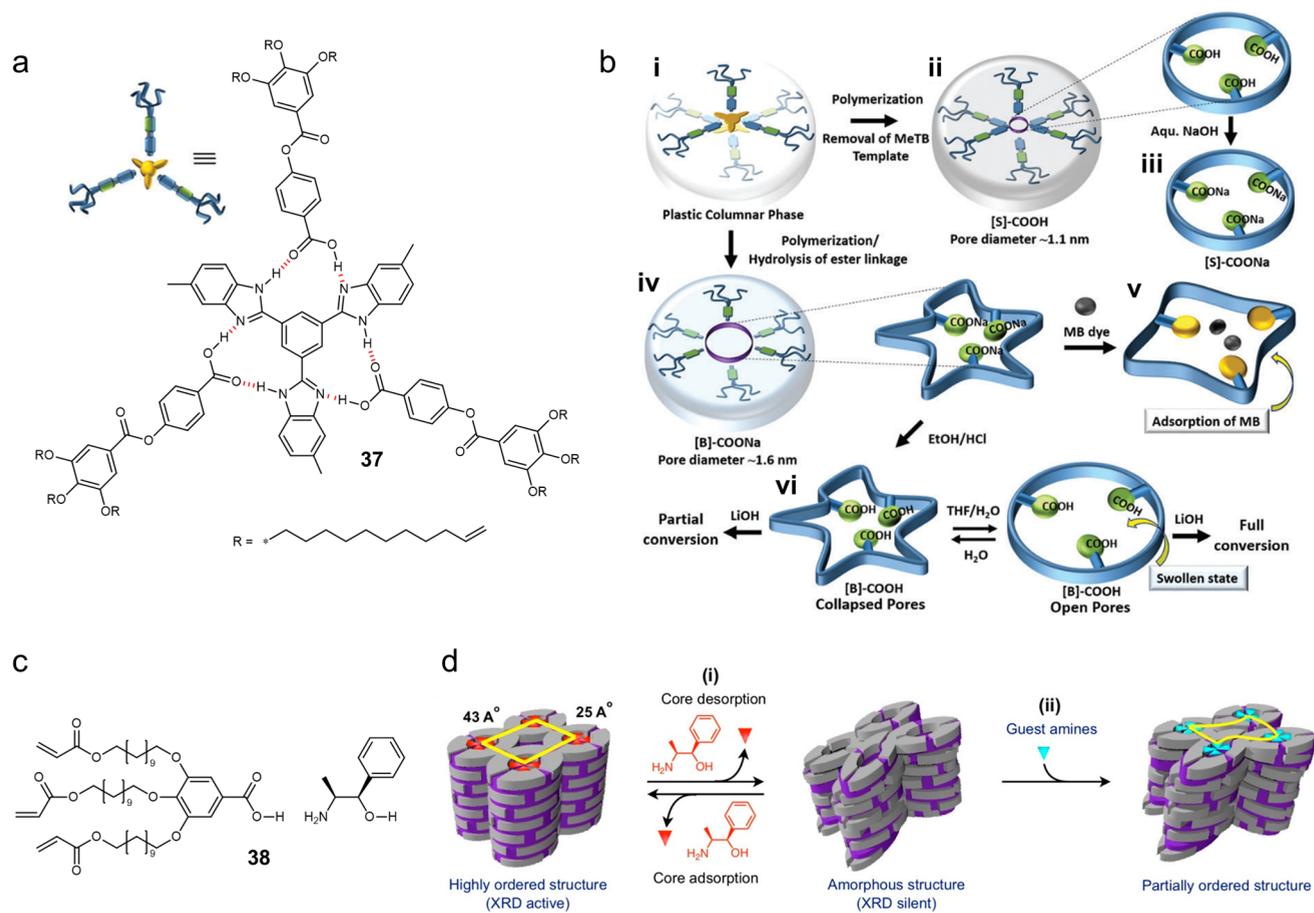


Figure 20. Dynamic nanoporous materials. (a) Chemical structures of the hydrogen-bonded disk-shaped complex. Adapted with permission from ref 143. Copyright 2018 The Royal Society of Chemistry. (b) Schematic representation of the columnar mesophase (i) and postmodification by treating it with DMSO (ii), subsequent reaction with aqueous NaOH (iii), and hydrolysis of the cleavable ester linkage (iv). The anionic pores could absorb the cationic dye methylene blue (v) or switch between collapsed and open pores (vi). Adapted with permission from ref 143. Copyright 2018 The Royal Society of Chemistry. (c) Chemical structure of the 1:1 hydrogen-bonded complex. (d) Schematic illustration of the columnar LC complex demonstrating structural switching upon desorption and adsorption of the core and guest amino alcohols. Adapted with permission from ref 144. Copyright 2020 American Chemical Society.

so-called XRD silent (Figure 20d). Resorption of the guest molecule resulted in the recovery of the original structure. Other chiral amino alcohols could also be absorbed in the porous structure, resulting in minor structural changes. When exposing the material to mixtures of various chiral amino alcohols, there was a preference for the original guest.^{73,75}

4.3. Light-responsive Nanoporous Materials

While exposing nanoporous materials to light sounds trivial, designing effective, responsive systems remains challenging. In the case of actuators, azobenzene moieties are readily incorporated to allow light-driven deformations (vide supra), whereas this is uncommon in nanoporous materials. A light-responsive nanoporous LC polymer network was obtained by using hydrogen-bonded benzoic acid-derived LC monomer 3 and an azobenzene derivative 39 as a chemical cross-linker (Figure 21a).¹⁴⁵ The reactive LC mixture formed a smectic mesophase that was polymerized to obtain free-standing polymer films with planar alignment. Upon illuminating the film with UV light, the photoresponsive azobenzene moieties undergo a *trans*–*cis* isomerization, inducing structural changes in the nanoporous LC material. The dipole moment of the azobenzene derivative changes upon isomerization, leading to a change in the p*K*_a of the benzoic acid moieties, resulting in

selective breakage of the hydrogen bonds within the LC polymer network when illuminated with UV light at pH 9.5, allowing the adsorption of methylene blue (Figure 21b,c). Illumination resulted in a lamellar spacing shrinkage of 0.2 nm, decreasing the availability of active binding sites. With this mechanism, a cationic dye could be locally adsorbed by the UV light illuminated regions of the polymer film (Figure 21d).

Similar advances were recently achieved in discotic LC systems with photoswitchable nanopores based on a hydrogen-bonded complex. Polymerizing complex 40 consisting of azobenzoic acid derivatives and a tris-benzimidazole template core unit yielded the formation of a photoresponsive polymeric film with a columnar LC phase (Figure 21e).⁷² After removing the template molecule, the resulting nanoporous channels were able to absorb the cationic dye Rhodamine 6G with a relatively low uptake rate (Figure 21f). In the porous state, the azobenzene moieties can be isomerized from their rod-like *trans* state to their bent *cis* isomer upon illumination with UV light, resulting in larger pores with greater polarity: the absorption of the cationic dye in the *cis*-enriched nanoporous film increased up to a factor two (Figure 21g). The Rhodamine 6G uptake of original films and irradiated films after relaxation were similar, demonstrating the reversibility of the absorption rates.

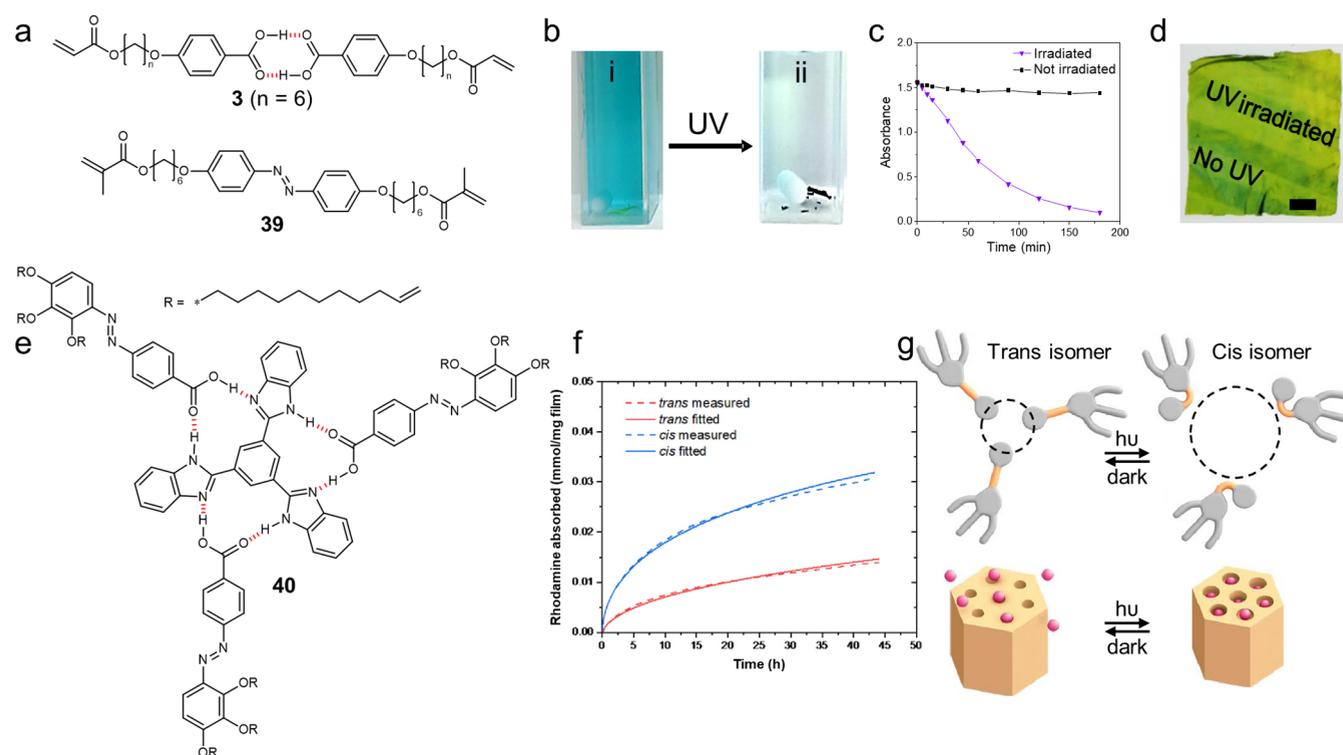


Figure 21. Light-responsive nanoporous materials. (a) Chemical structures of the light-responsive nanoporous material. (b) Images and (c) absorbance of the photoresponsive adsorbent in a methylene blue solution upon exposure to UV light showing the adsorption of the dye due to isomerization from *trans* to *cis*. Adapted with permission from ref 145. Copyright 2015 American Chemical Society. (d) Selectively irradiated film showing adsorption only at the exposed areas. Adapted with permission from ref 145. Copyright 2015 American Chemical Society. (e) Chemical structure of the hydrogen-bonded discotic liquid crystal based on azobenzoic acid derivatives. (f) Graph with absorption kinetics and fitted Fickian equation for both *cis* and *trans* state of the azobenzene moiety. Adapted with permission from ref 72. Copyright 2021 American Chemical Society. (g) Schematic illustration of the *trans*-*cis* isomerization and adsorption of rhodamine 6G. Adapted with permission from ref 72. Copyright 2021 American Chemical Society.

5. CONCLUSION AND OUTLOOK

This review demonstrates hydrogen bonds as a valuable supramolecular interaction for making stimuli-responsive LC polymers with outlook toward self-healable and recyclable futures. Hydrogen bonding directs network construction at the nanoscale and simultaneously serves as dynamic moieties for generating or enhancing the materials' responsive character as well as introducing dynamic and circular properties. Typically, actuators and optical materials are constructed using linear calamitic hydrogen-bonded complexes, while responsive nanoporous materials are constructed from either calamitic or discotic complexes.

When monomeric complexes are used, orientation may be induced using a variety of alignment techniques making a wide range of director profiles possible. For actuators, these director profiles enable complex deformation modes. The twisted chiral nematic or double twisted blue phases in stimuli-responsive photonic and optical materials are obtained either by addition of chiral monomers or (hydrogen-bonded) dopants. Two-dimensional structured nanoporous materials are generally fabricated using hydrogen-bonded benzoic acid derivatives, but in this case the monomer mixture has a smectic (layered) LC phase. One-dimensional nanoporous materials are typically prepared using a template inducing a columnar discotic phase while using an amino-alcohol template is sufficient to obtain a discotic monomer complex in other cases.

In comparing how the hydrogen bonds are utilized in the various applications, there is a clear overlap in the motifs used to fabricate the polymeric LC materials. The incorporation of hydrogen bonds is most often established by using reactive benzoic acid moieties. Typically, single- or two-fold hydrogen bonding provides sufficient thermal stability to construct the material while maintaining the possibility of later breaking the bonds, either thermally or chemically. Overall, hydrogen-bonded benzoic acid-derived moieties are still the golden standard. However, pyridine-benzoic acid type hydrogen bonds are also used, and in a few cases, the four-fold¹¹⁵ or many-fold^{34,35,37} hydrogen bonds are exploited. By using the directionality of hydrogen bonds, the symmetry and geometry of the hydrogen-bonded complexes (e.g., using a template) can be tuned in either calamitic or discotic LC phases.

By using materials that are both LC and hydrogen-bonded, actuators with larger physical motions responsive to a wider variety of stimuli can be achieved. In all cases, the responsive behaviors are attributed to anisotropic deformations of the materials, induced by reducing LC order. In actuators, reducing order leads to complex deformations determined by the director profile of the material. In photonic materials, expansion or contraction of the helical twist of the chiral nematic nanostructure driven by disorder results in red- or blue-shifting of the wavelengths reflected, respectively. Here, an expansion or contraction of 10% or greater is needed to obtain structural color changes. In nanoporous materials, reduction in order generally

alters the porosity or selectivity of the material; however, the macroscopic dimensional changes of the macrostructure commonly seen in the actuators and photonic materials are often not desirable.

All the applications covered in this review show substantial overlap in stimuli. For instance, pH-change has been applied as a trigger in all applications discussed in this work. Some triggers have not been explored for all applications. For instance, light responsiveness was demonstrated for actuators and nanoporous materials but not for optical materials. However, light responsivity could be of great interest in photonic LC polymers as a time-integrating UV exposure sensor, for example.¹⁴⁶ Finally, as seen in nanoporous LC materials, molecular recognition could be of interest in the field of photonic and actuating LC materials; by binding a particular guest, the material could provide visual or mechanical feedback, potentially leading to sensors with enhanced selectivity.

Like all polymer materials, stimuli-responsive polymers should become recyclable or reusable. Considering the dynamic character of hydrogen bonds, self-healing and recyclable materials should both be readily accessible. However, this topic has only been explored a limited number of times for LC polymer actuators^{36,147–151} and not at all for stimuli-responsive optical and nanoporous materials. Recent work in the field of (supramolecular) polymer chemistry has demonstrated various approaches to introducing self-healing through hydrogen bonds.^{152,153} Although these advances are promising, translating them to stimuli-responsive materials brings additional challenges because hydrogen bonds are required for both defining the (micro) structure and the responsiveness of the material. This self-healing could potentially be achieved by using orthogonal hydrogen bonding, for example, involving both acid or basic hydrogen bonds (e.g., benzoic acid or pyridine) and nonresponsive hydrogen bonds (e.g., UPy, amides, ureas, or urethanes).

Smart, functional polymers offer an excellent platform for materials and systems that integrate stimuli-responsive motives to obtain life-like and intelligent materials with dynamically adaptive and interactive functions. This emergent behavior is highlighted in interactive materials that can communicate with biology and implement feedback loops with the promise to realize intelligent materials toward the next-generation systems.^{154–156} Within the scope of this review, sensing and actuation hold potential for interactive materials in which one responsive motive responds to an external stimulus in the environment and subsequently triggers the other response. Dynamic interactive behaviors such as these offer unique and complex phenomena, allowing researchers to gain further insight into adaptive and interactive materials and systems.

In this review, we have discussed stimuli-responsive liquid crystalline polymers employing supramolecular hydrogen-bonded interactions. We have presented the basic principles and challenges in developing these materials, while we also showed the latest breakthroughs that can serve as an inspiration for sparking new ideas. We hope that it also became clear that these supramolecular materials have great potential in meeting social challenges in the fields of soft robotics, water management, sustainable energy, and health.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Technology, in which he studied mechano-optical strain sensors in drawn polyethylene fibers under the supervision of Dr. Cees Bastiaansen in the Stimuli-responsive Functional Materials and Devices Group of Prof. Dr. Albert Schenning, who also supervises him during his Ph.D. research. His Ph.D. research focuses on functionalized composites of anisotropic commodity polymers, focusing on highly ordered nanoporous liquid crystalline polymers.

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