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Smart Materials

Functional Organic Materials Based on Polymerized Liquid-Crystal Monomers: Supramolecular Hydrogen-Bonded Systems

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actuators · functional organic materials · hydrogen bonding · liquid crystals · nanoporous membranes

Dedicated to Prof. Francois Diederich on the occasion of his 60th birthday

Functional organic materials are of great interest for a variety of applications. To obtain precise functional properties, well-defined hierarchically ordered supramolecular materials are crucial. The self-assembly of liquid crystals has proven to be an extremely useful tool in the development of well-defined nanostructured materials. We have chosen the illustrative example of photopolymerizable hydrogen-bonding mesogens to show that a wide variety of functional materials can be made from a relatively simple set of building blocks. Upon mixing these compounds with other reactive mesogens, nematic, chiral nematic, and smectic or columnar liquid-crystalline phases can be formed that can be applied as actuators, sensors and responsive reflectors, and nanoporous membranes, respectively.

1. Introduction

Functional organic materials are of great interest for optoelectronic devices, microelectromechanical systems (MEMS), nanoporous molecular release systems, and sensors.[1] To generate precise functional properties, well-defined hierarchically ordered supramolecular materials are crucial. Over the past few decades, the self-assembly of liquid crystals has proven to be an extremely useful tool in the development of well-defined nanostructured materials.[2,3]

Hydrogen bonds (H-bonds) are ideal noncovalent interactions for the construction of supramolecular architectures since they are highly selective and directional.[4–9] H-bonds are formed when a donor with an available acidic hydrogen atom interacts with an acceptor carrying a nonbonding lone pair of electrons. The strength of the H-bond depends on the solvent and temperature, which makes H-bonding units attractive molecular triggers responsive to humidity and heat. Furthermore, H-bonding interactions are able to position molecules in a specific arrangement within nanostructured materials.[4–9]

Liquid crystals (LCs) can exist in different phases such as smectic and nematic phases, each differing in the degree of lateral orientational and rotational order of the molecules (Figure 1). Furthermore, the self-assembly of these materials on the nanometer scale can be manipulated by using, for example, alignment layers, resulting in materials with a monolithic structure on macroscopic length scales that can be produced on a large scale with low cost. The generation of such defect-free nanostructured materials is comparatively straightforward, in contrast to the preparation of other nanometer-scaled self-assembly systems.[3] In the case of reactive liquid-crystalline molecules, each possible liquid-crystalline phase can be fixed by polymerization, resulting in a wide variety of highly ordered supramolecular materials.[10,11] Furthermore, multicomponent mixtures can be used to adjust the properties of the materials. The monomeric character of reactive mesogens makes these materials compatible with classical top-down structuring techniques such as (photo-) lithography and (inkjet) printing, which generate additional opportunities for combining self-assembled nano-

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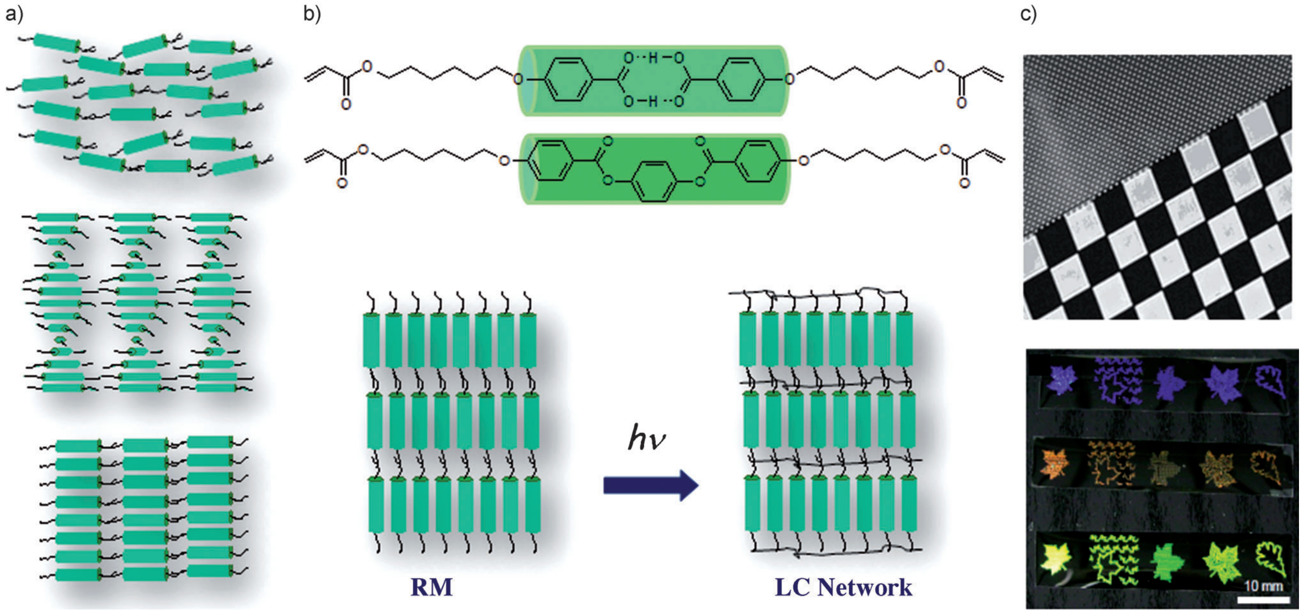

Figure 1. a) Schematic representation of nematic (top), chiral nematic (middle), and smectic A (bottom) LC phases. b) A monodomain can be created by alignment of appropriate monomers (bottom-up approach) and reactive mesogens (RMs) can be photopolymerized to construct polymer materials. c) These systems can be structured by photopatterning and inkjet printing (top-down approach).

structures with structuring on a larger scale (Figure 1).[3] The optical properties of the ordered LC polymerized materials are quite similar to those of the monomers although the mechanical properties change. Interestingly the orientational order of the molecular building blocks in the material results in anisotropic mechanical properties.

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In this Minireview we will give examples illustrating how functional organic materials can be made from polymerized thermotropic liquid crystals. The use of polymerized lyotropic liquid-crystalline systems is beyond the scope of this Minireview.[30] We have focused on photopolymerizable hydrogen-bonding mesogens to show that a wide variety of functional materials can be made from a relatively simple set of building blocks. Pioneering work in this field which greatly influenced current research was carried out by Kato, Fréchet, and co-workers in the 1980s and 1990s.[5–8] This Minireview reports recent progress and shows that upon mixing H-bonding liquid crystals with other reactive mesogens, nematic, chiral nematic (cholesteric), and smectic or columnar liquid-crystalline phases can be formed that can be applied as actuators,[12,13] sensors and responsive reflectors,[18] and nanoporous membranes,[29,30] respectively.

2. Actuators Based on Nematic Liquid Crystals

Polymeric liquid-crystalline materials can undergo mechanical deformation by an external stimulus.[12,13] For densely cross-linked networks, this actuation process is caused by a small revisable change of the local molecular order, that is, by a change in the order parameter. In the case of planar and uniaxial ligand configurations, swelling and shrinkage will occur, while in twisted nematic and splayed director configurations, bending occurs when molecular order in the materials is decreased. A change of the molecular order can be induced simply by increasing the temperature. Light has also been employed to make light-responsive actuators.[13] As an example, a photochromic azo dye is incorporated in a material and upon exposure to light it undergoes a *trans–cis* isomerization. This conformational change causes a reduction in the molecular order in the polymeric liquid-crystalline material. Polymer LC actuators are interesting materials for a wide variety of low-cost applications ranging from micromechanical systems such as valves to propulsion materials inspired by cilia and smart surfaces.[12,13]

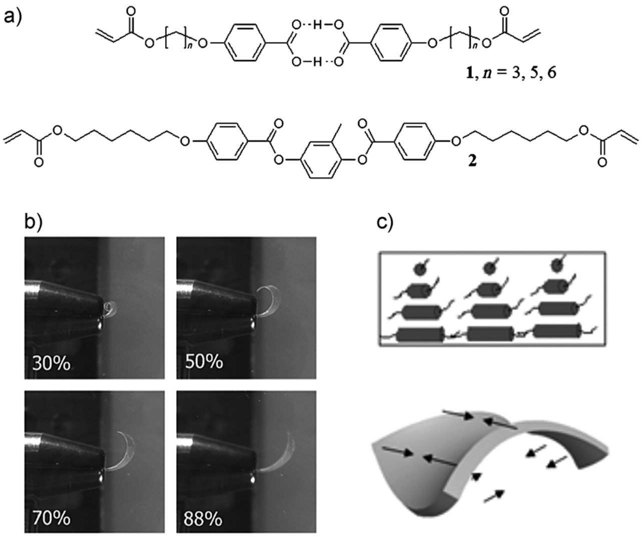

Figure 2. a) Chemical structures of the benzoic acid derivative **1** and the cross-linker **2**. b) Images of the actuator behavior of a twisted nematic film composed of **1** and **2** under different relative humidity conditions. c) Schematic representation of the molecular order in a twisted nematic film and its corresponding deformation upon decreasing the molecular order. Adapted with permission from reference [14]. Copyright American Chemical Society.

Since hydrogen bonds are sensitive to solvent polarity, this interaction can be used to make pH- and humidity-responsive actuators. Our group has used a twisted nematic phase to construct such actuators (Figure 2).[14] A mixture of reactive hydrogen-bonded dimers based on benzoic acid **1** was used to decrease the crystallization temperature, to broaden the temperature range of the liquid-crystalline phase, and to suppress the formation of smectic phases while the chemical cross-linker **2** was added to increase the mechanic stability (vide infra). After photopolymerization at 60 °C the twisted nematic order is maintained in the polymer.[15] Subsequently, the film was treated with KOH to convert a fraction of the carboxylic acid groups into potassium carboxylate groups, forming a hygroscopic network. Interestingly, after this activation step the films exhibit a strongly anisotropic response upon exposure to homogeneously humid air (Figure 2) over the entire range of humidity, while after full immersion in water the films show strong curling about one of the two axes. The actuators also respond to pH changes and to changes in the solvent environment. In the latter case strongly polar solvent easily swells the network forcing binding in one direction while the less polar solvent extracts water to force bending in the opposite direction.[16]

Ikeda and co-workers have shown that chemical cross-linking is not necessary to construct actuators.[17] Freestanding films have been made by self-assembly using polymer **3**, which contains benzoic acid and photochromic azobenzene units, in combination with the azobenzene-based physical cross-linker **4** (Figure 3). The cross-linker is capable of making H-bonds with carboxylic acids at both pyridyl ends. The complex of **3** and **4** forms freestanding films that show optical anisotropy, indicating that the azobenzenes are preferentially aligned. When exposed to UV light the polymer films bend towards the light source along the alignment direction of the mesogens. The bending occurs through the *trans–cis* photoisomerization of the photochromic dyes; this causes a change in alignment and as a result, contraction of the film. Because

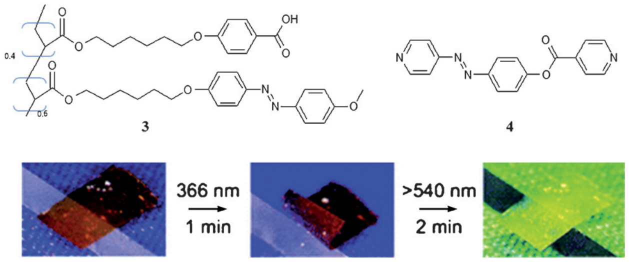

Figure 3. Chemical structures of the polymer **3** and azobenzene-based H-bonded acceptor **4**. The photoresponsive polymer actuator based on **3** and **4** bends and unbends when exposed to UV and visible light. Reproduced with permission from reference [17]. Copyright Royal Society of Chemistry.

of the high amount of azobenzene dye in the polymer, a UV-intensity gradient is present in the films, leading to a higher degree of photoisomerization at the side of the polymer film exposed to the light source. When visible light with wavelengths greater than 450 nm is used, *cis–trans* isomerization takes place causing unbending and straightening of the film (Figure 3). This is the first example of a supramolecular H-bonded polymer film without chemical cross-links that is capable of converting light energy directly into mechanical work.

3. Sensors and Responsive Reflectors Based on Chiral Nematic Liquid Crystals

Cholesteric liquid crystals (CLC), also known as chiral nematic LCs, are a special class of liquid crystals that are able to reflect circularly polarized light as a result of their self-organizing molecular helices. Depending on the handedness of the pitch, left- or right-handed circularly polarized light is reflected (Figure 4b). Furthermore, the pitch of the helix in these networks determines the wavelength of reflection and can be modified in response to the environment, resulting in a color change.[18,19] In this way cheap, battery-free optical sensors and reflectors can be made; these appealing smart materials will find wide applications in the built environment, the packaging industry, and health care.

Shibaev and co-workers have constructed H-bonded CLC polymers based on the reactive cross-linker **9**, the cyclohexanoic acid derivative **7**, and the chiral dopant methyladipic acid **5** (Figure 4a).[20] The reflection band of the polymer films could be positioned in the visible region by adjusting the amount of chiral dopant in the mixture. When the films were treated with organic solvents, the free molecules **5** and **7** were removed, leading to destruction of the cholesteric structure of the material. Interestingly, when exposed to alkaline water solutions, the cholesteric structure remains and the reflection band shifts to longer wavelengths (Figure 4c). The shift of the reflection band depends on the pH and it is proposed that the alkaline solutions disrupt the H-bonding in the polymer film leading to leakage of the non-chemically cross-linked molecules **5** and **7**. During leakage the mechanical properties of the

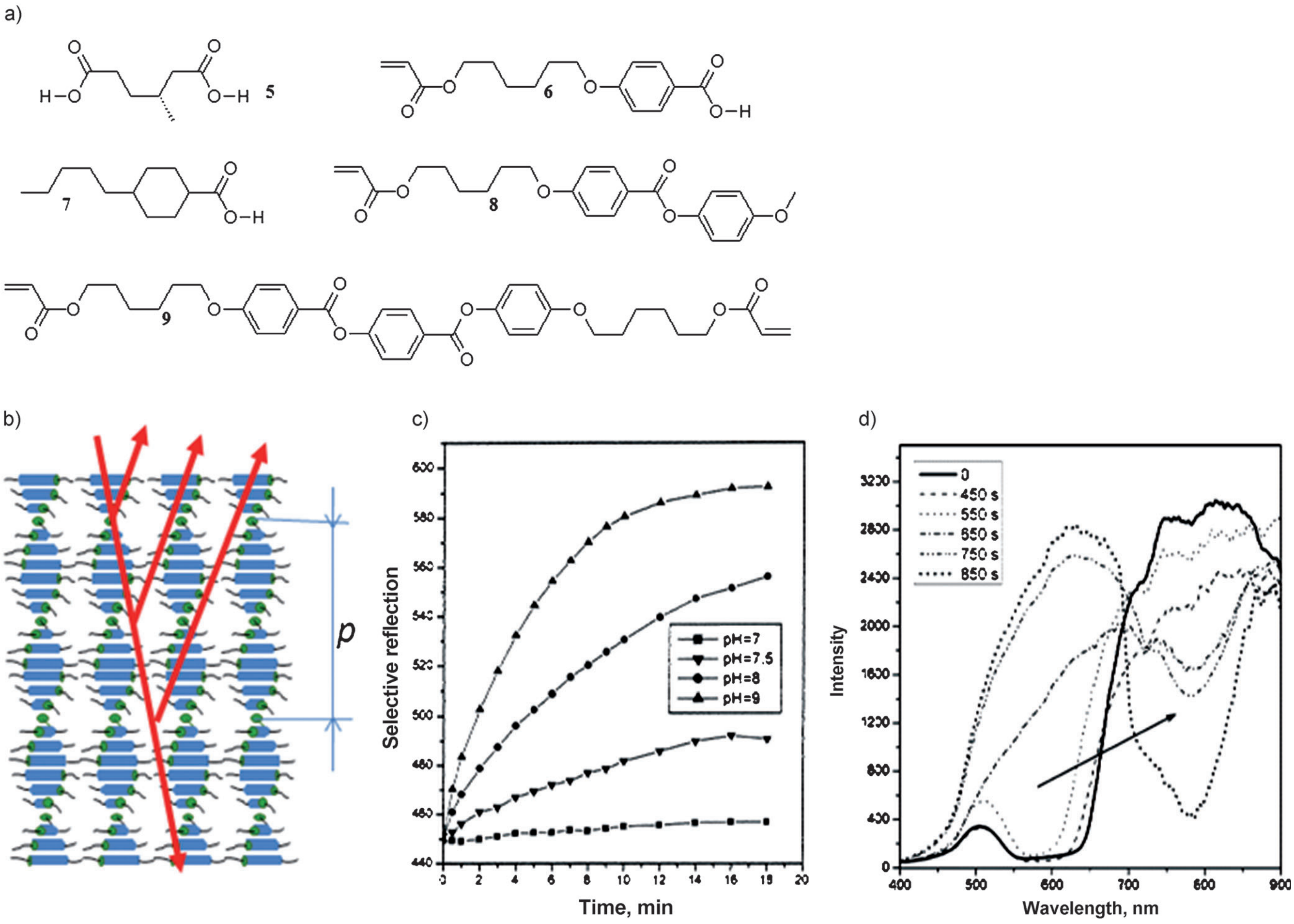

Figure 4. a) Chemical structure of the components (**5**–**9**) used to make H-bonded cholesteric polymer films. b) Schematic representation of a cholesteric liquid-crystalline phase. The cholesteric pitch *p*, which determines the wavelength of the reflection band, can be changed in response to changes in the environment resulting in a color change. c) The shift of the wavelength of the reflection band as function of time at different pH values for polymer films based on **5**, **7**, and **9**. d) Change of the reflection band of polymer films based on **5**, **6**, **8**, and **9** immersed in a 10% aqueous solution of arginine as function of time (c). Plots in (c) and (d) reproduced with permission from references [20] and [22]. Copyright Amercian Chemical Society.

polymer film change resulting in a change in pitch. To avoid leakage, polymers have also been made that contain the reactive H-bonded mesogen **6**. These cholesteric films composed of **5**, **6**, **8**, and **9** act also as pH sensors.[21] Films that contain more H-bonding units respond faster and a larger shift of the reflection band is observed. Most likely the alkaline solution breaks up the hydrogen bonds leading to aqueous swelling of the films. This swelling results in an increase of the pitch and subsequently in a change of the reflection color. Interestingly, these polymer films also respond to concentrated solutions of amino acids like arginine, lysine, and histidine (Figure 4 d).[22] Possibly, the amino acids diffuse into the polymer matrix to bind to the carboxylic acid groups leading to an increased diffusion of water and swelling of the films. These findings open new possibilities for the construction of biosensors based on CLC polymer films.

Thermally controllable reflective films have been made based on the rupture and recovery of H-bond interactions in CLC polymers.[23] Yang and co-workers have made CLC mixtures composed of a cholesteryl ester mixture and the H-bonded chiral dopant complex **10** (Figure 5). These CLC mixtures have a selective red reflection band that shifts to the blue after the sample has been heated to 60 °C. This blue reflection color is a result of an increase in the helical twisting power of the cholesteryl ester mixture and the disruption of H-bonded complex **10**; two new chiral dopants result that change the pitch length greatly. Interestingly, when a small amount of cross-linker **2** was added, so-called polymer walls could be introduced to prevent diffusion in the composite. In this way it was possible to make thermally controllable reflective color paper. A blue letter "T" could be thermally written on a red background using a hot pen; the image was stable for over 3 days at room temperature before it automatically returned to the initial state as a result of recovery of the H-bonded complex **10** (Figure 5).

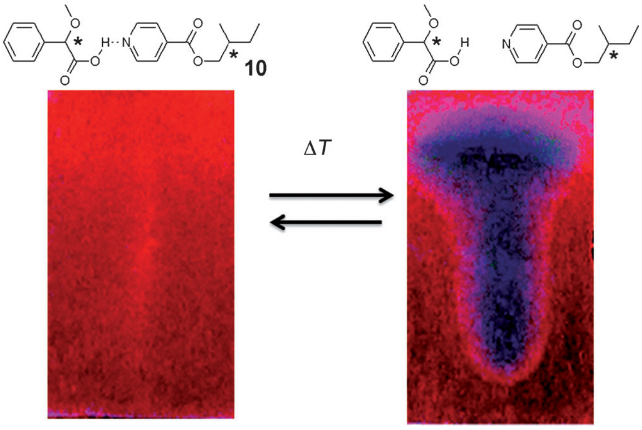

Figure 5. Photographs of a CLC sample containing the H-bonded complex **10** in which thermally the letter "T" has been written. Reproduced with permission from reference [23]. Copyright American Chemical Society.

Wei and co-workers have also made thermally responsive reflective color films based on chiral H-bonding complexes.[24] Single-layer films were constructed containing both right- and left-handed CLC ("double-handed") structures by utilizing an imprinted right-handed helical polymer template (Figure 6 a). This template was made by photopolymerizing a nonreactive CLC mixture in which the reactive mesogen **2** had been dispersed; **2** initially defined the pitch but was subsequently removed. After this film had been refilled with a CLC mixture composed of a H-bonded complex of chiral pyridine derivative **11** and 4-hexyloxybenzoic acid forming a left-handed helix, a double-handed helical structure was obtained. The pitch of this supramolecular mixture is temperature sensitive. Interestingly, when this mixture was heated to 165 °C, the reflection intensity approached 100 % meaning that both left- and right-handed circularly polarized light is reflected within the same reflection band (Figure 6 c). When the temperature was increased, two reflection bands were observed, one of which correspond to the pitch of the polymer template and the other one to the temperature-sensitive H-bonded complex. These results show that it is possible to construct temperature-tunable, multicolored, double-handed light reflection bands.

Recently, a H-bonded complex between the photopolymerizable benzoic acid **6** and the chiral pyridine derivative **11** was applied for electrothermal switching in such films.[25] The H-bonded complex exhibited strong temperature sensitivity with a blue shift from 780 to 540 nm over a temperature range of 25–75 °C. The reflection wavelength could also be electrically switched through tilting the helices axis by applying a voltage. Novel photopolymerizable chiral H-bonded complexes between the reactive benzoic acid **6** and variety of pyridine-equipped chiral dopants **12**–**15** have also recently been constructed (Figure 6 b).[26] These photopolymerized CLC polymers exhibit a thermosensitive reflection band that shifts to the red upon heating. Thermally addressed color paper could be made with heat-written images that are stable for about 3 h at room temperature.

Broadband reflection bands have also been made of CLC polymers in which a pitch gradient was induced by H-bonding.[27] Yang and co-workers UV photopolymerized a mixture of reactive benzoic acid **6**, the chiral pyridine dopant **11**, and the reactive cross-linker **2** to form a H-bonded complex. By the addition of a small amount of a UV-absorbing dye in the mixture, a gradient of UV light intensity was achieved over the thickness of cell during the cross-linking process. This led to an enrichment of the more reactive diacrylate cross-linker **2** at the upper part of the film and an enrichment of the chiral H-bonded complex at the lower part, forming a pitch gradient in the film.[28] As a result, a reflection film with a wider reflection band is obtained that can find many applications in areas such as infrared reflectors.

4. Nanoporous Membranes Based on Columnar and Smectic Liquid Crystals

Nanoporous membranes are of great current interest on account of their applications in filtration, separation, and catalysis.[29,30] Because of the small pore size in these materials, discrimination between molecules and ions based on size and shape is possible while the confined environment

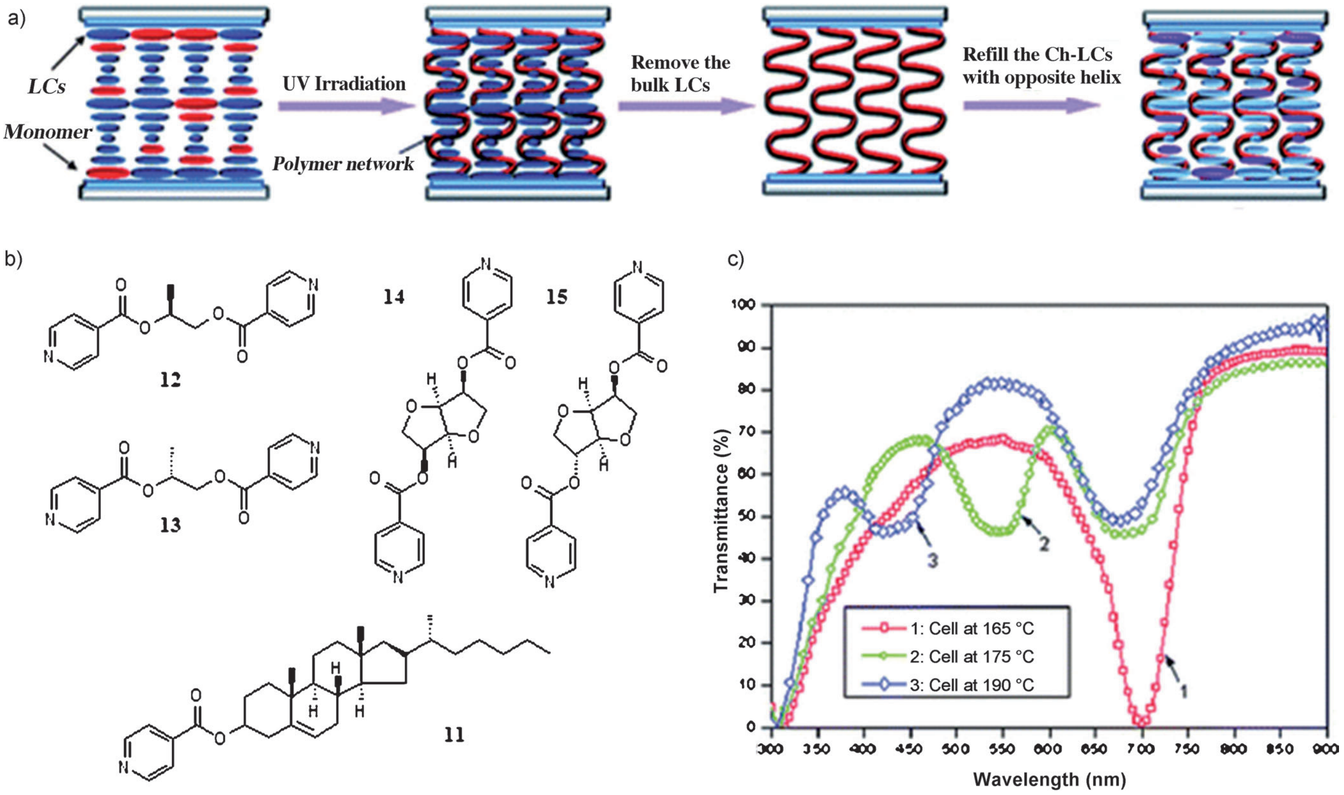

Figure 6. a) Schematic illustration of the fabrication process for making double-handed cholesteric films. b) Chemical structures of the pyridine-based chiral dopants **11**–**15**. c) Temperature dependence of the transmission spectra of the double handed H-bonded CLC film (bottom). Adapted with permission from reference [24]. Copyright Royal Society of Chemistry.

enhances chemical reactions. For making small pores, the self-organization of liquid crystals and their polymers is very appealing. In this context, thermotropic hexagonal columnar and smectic phases can be used to prepare nanoporous membranes.

An elegant way to prepare nanoporous organic materials is the use of H-bonded liquid-crystalline polymers. Kim and co-workers have prepared a hexagonal columnar polymer film consisting of a benzotri(imidazole) **17** core and photopolymerizable trialkoxybenzoic acid acrylate **16** that form a 1:3 supramolecular complex through hydrogen-bonding (Figure 7a).[31] After photopolymerization, the hexagonal columnar LC phase was fixed in a cross-linked polymer film. Interestingly, treatment of the polymer film with acidified methanol resulted in removal of the benzotri(imidazole) core and produced a nanoporous hexagonal film (Figure 7b). Preliminary gas-permeability measurements demonstrated the porous nature of the material.

In a similar approach, Saigo, Ishida, and co-workers have prepared a host–guest complex based on benzoic acid **17** that is H-bonded to chiral amino alcohol **18** (Figure 7a,c) and forms chiral columnar liquid-crystal structures.[32] After photopolymerization, the rectangular columnar structure was maintained in the film.[33] The amino alcohol was desorbed by treatment with an acidic aqueous solution resulting in a loss of the columnar structure in the film. Interestingly, upon readsorption of the amino alcohol, the rectangular columnar structure reappeared.[34] These results show that molecular imprinting can be used to make membranes that bind molecules selectively. Recent detailed studies have shown that modification of the polymer porous material has large effects on properties such as structural order, guest recognition and release, and its repetitive switching.[35,36]

The advantage of a hexagonal columnar structure is that after removal of the template molecule, the pore size is maintained thanks to the rigidity of the polymerized, laterally connected honeycomb structures. A similar procedure cannot be used for smectic LC materials; the molecular organization would be disrupted after removal of the template since the polymerized regions exist in sheets that are not interconnected.

Our group has prepared nanoporous membranes based on a smectic liquid-crystalline network composed of the photopolymerizable benzoic acid **6** and cross-linker **19** (Figure 8a).[37] After photopolymerizaiton, the smectic supramolecular organization in the material is locked. The H-bonded carboxylic acid groups can be opened by treating the film with an alkaline solution. The pores have a two-dimensional geometry and the integrity of the film is maintained by the presence of a small concentration of the covalent smectic cross-linker **19**. Low-temperature transmission electron microscopy revealed that the width of the pores is around 1 nm (Figure 8a). Interestingly, the periodic lateral pores containing carboxylate groups can be filled with cations and cationic dyes.

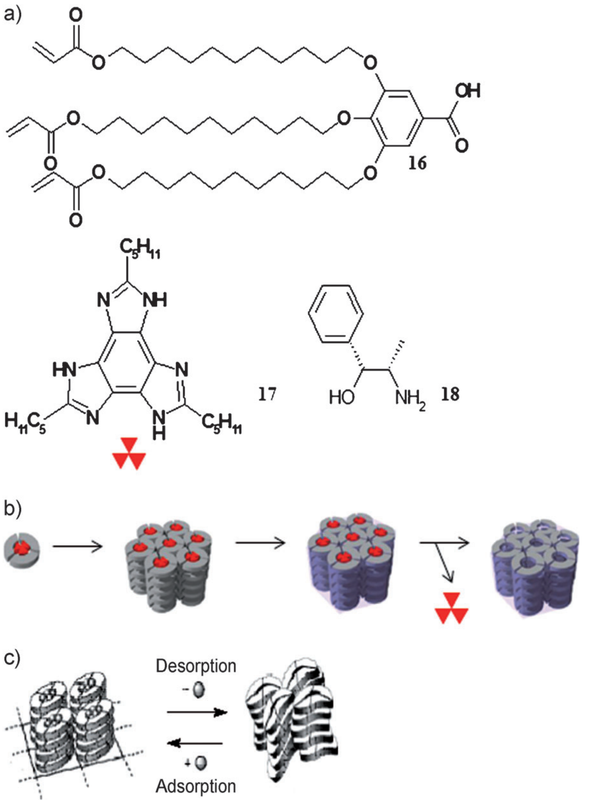

Figure 7. a) Chemical structures of **16**–**18**. b) Schematic representation of the synthesis of a nanoporous polymer with hexagonal columnar channels from a H-bonded complex between **16** and **17**. c) Schematic representation of desorption and adsorption of **18** in the nanoporous columnar liquid-crystalline polymer film based on **16**. Reproduced with permission from references [31] and [36]. Copyright Wiley-VCH.

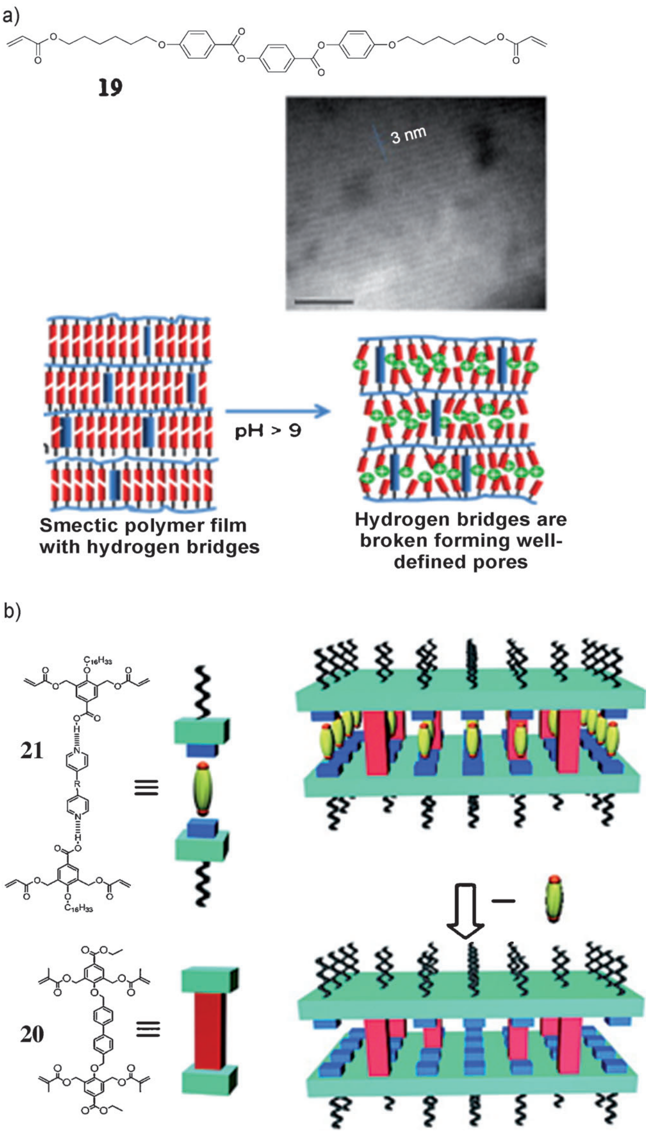

Figure 8. a) Top: Chemical structure of **19**; middle: low-temperature TEM cross-section of a nanoporous membrane film based on **6** and **19** filled with barium ions (white scale bar: 3 nm, black scale bar: 20 nm); bottom: schematic representation of the construction the porous layered films in which the blue bars represent cross-linker **19** and red bars the H-bonded dimer of **6**. B) Chemical structure and schematic representation of the H-bonded complex **21**, the cross-linker **20**, and the construction of nanoporous layered polymers. Reproduced with permission from references [37] and [38]. Copyright Wiley-VCH and Royal Society of Chemistry.

Kishikawa and co-workers have prepared a nanoporous layered material consisting of the reactive cross-linker **20** and building block **21**, which contains a rodlike dipyridine template molecule H-bonded to two polymerizable benzoic acid derivatives (Figure 8b).[38] Mixtures of **20**, template, and **21** form a smectic liquid-crystal phase that was fixed by photopolymerization. After removal of the template, nanoporous layered structures were obtained that are held together by the rigid cross-linker and do not collapse (Figure 8b).

5. Conclusions and Outlook

This Minireview shows that a large variety of functional organic materials can be prepared from a relatively simple set of reactive H-bonding mesogens. For example, from a single reactive benzoic acid moiety, humidity sensors, actuators or nanoporous membranes can be constructed just by tweaking the properties of the liquid-crystal phase. The reported water-responsive actuators might be interesting for the construction of drug-delivery vehicles,[39] while battery-free optical biosensors have been constructed that detect amino acids in water. Well-structured nanoporous polymers have also been prepared which could potentially be used in device architectures for nanofiltration and separation. These illustrative examples demonstrate the enormous potential of using reactive mesogens to construct functional organic materials. The H-bonding units in the polymers provide specificity in both triggering and response, while the ordered LC structure leads to an amplified and cooperative material response.

Research on functional materials based on liquid-crystalline polymers is still in its infancy and a large number of possibilities have yet to be explored. The toolbox of chemical compounds is still very limited and often restricted to what has been commercially available. H-bonding units used in LC-based materials are in most cases carboxylic acid units. Alternative H-bonding units could, for example, change the responsiveness of the actuators and sensors. In the case of membranes, the pores are based on negatively charged carboxylates. The preparation of positively charged nanoporous membranes would dramatically broadened the set of molecules and ions that can be separated. For the most part, the creation of mechanical stability has relied on a single type of linker molecule. One can imagine that by using alternative, functional linkers the response of the polymer materials can be tuned. Therefore, there is a need to extend the toolbox of available reactive mesogens in order to produce functional organic materials with new properties and enhanced responses. Combining different triggers in LC materials could also be interesting in this respect. For example, an H-bonding unit combined with photochromic dyes could lead to light controlled-release systems.

The fabrication of functional organic materials requires complete knowledge of the approach from synthesis to device fabrication as it becomes increasingly important to integrate the materials effectively in device architectures. This issue has not yet been widely addressed. In this context, the possibilities of inkjet printing and photopatterning reactive mesogen mixtures have not been fully explored.[40]

It is clear that the application of reactive mesogens goes far beyond their traditional use in flat panel displays.[2,3] This Minireview shows that functional organic materials based on liquid-crystalline polymers have many very appealing properties and hold great promise in, for example, actuators, sensors, and membranes.

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