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Chromonic liquid crystals: properties and applications as functional materials

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Chromonic liquid crystals (or chromonics) are formed by the self-organization of aromatic compounds with ionic or hydrophilic groups in aqueous solutions. This review summarizes the research on chromonic liquid crystals in the last two decades. The research embraced the studies of commercially available chromonic dyes and drugs, the syntheses and investigations of molecularly designed mesogens, the invention of novel processes for aligning chromonic liquid crystals, and the development of new applications as functional materials and biosensors.

Introduction

The study of non-covalent interactions has become an important area of research because of their significance in biological functions, drug actions, materials properties, and the fabrication of devices. Supramolecular assemblies of complex architectures have been formed, in natural and artificial systems, as a result of multiple non-covalent interactions among small structural motifs and molecular sub-units.[1] Within this broad area of supramolecular science, research on the properties and applications of chromonic liquid crystals (or chromonics) have gained increasing attention in the last two decades.[2,3]

Liquid crystal (LC) is a mesophase in which molecules possess short-range, crystal-like order and yet retain liquid-like mobility.[4] There are two main types of liquid crystals—thermotropic (temperature-dependent) and lyotropic (both temperature- and solvent-dependent) liquid crystals. Chromonic liquid crystals belong to a class of lyotropic liquid crystals.[2,3] In contrast to amphiphilic mesogens (LC-prone molecules) of conventional lyotropic liquid crystals which are flexible, rod-shaped aliphatic chains with ionic groups at one end of the molecule,[4] chromonic mesogens generally have rigid, plank-shaped or blade-like aromatic systems that are functionalized at the periphery with ionic or hydrophilic groups for solubility in aqueous media (Fig. 1).[2,3]

The history of chromonic systems has been delineated in detail by Lydon.[2] In 1915, Sandquist provided the first description of a system (**1** in aqueous solution) that showed chromonic liquid-crystalline properties.[5] More descriptions of chromonic mesophases of individual systems, mainly commercially available dyes and drugs, were found in later years.[2,3] However, chromonics were not recognized as a distinct family of lyotropic liquid crystals until Lydon and Attwood and co-workers[2,6,7] drew attention to the distinctions of these systems from conventional amphiphilic lyotropic liquid crystals. One of the most extensively studied chromonic mesogens is disodium cromoglycate (**2**), an antiasthmatic drug marketed under the trade name "INTAL". It was examined initially by Woodard and co-workers in the 1970s,[8] investigated more extensively later by Lydon and co-workers,[9] and studied further by others in recent years.[10–18] It is now recognized that chromonics embrace not only dyes and drugs (Fig. 1),[2–29] but also nucleic acids.[30] The name "chromonic" was first used by Lydon co-workers because it has the connotations of both color and chromosomes.[2,3,6,7]

Earlier studies of chromonics and their distinctions from conventional lyotropic LC were discussed by Lydon in two excellent reviews in 1998.[2,3] Since then, chromonic mesogens designed for specific applications were synthesized (Fig. 2),[31–39] structure–property relationships of chromonic mesogens were investigated, novel processes for aligning chromonic liquid crystals were invented, and new applications as functional materials and biosensors were reported. In this

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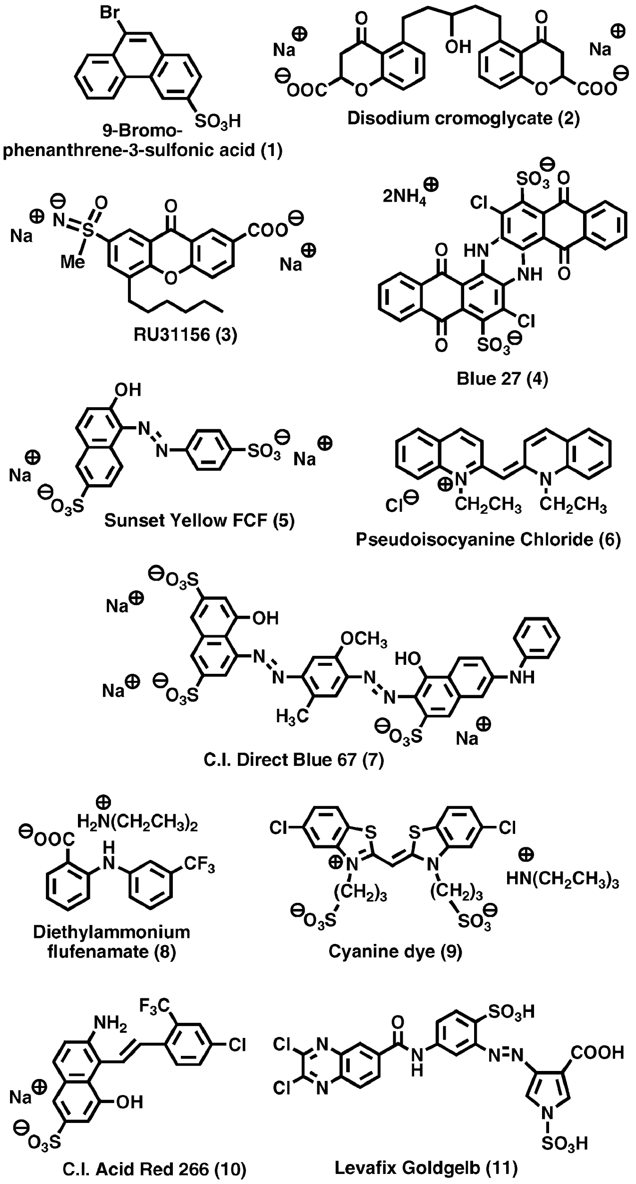


Fig. 1 Examples of dyes and drugs reported to exhibit chromonic liquid-crystalline properties.

review, we focus on the studies of chromonics in the last two decades and their potential applications. It should be mentioned that chromonic LC in organic solvents such as dimethyl formamide (DMF) and methanol[38] have been reported. This review will focus on chromonic phases in aqueous solutions only.

Phase properties of chromonic liquid crystals

Chromonic liquid-crystalline phases

Unlike conventional amphiphilic, lyotropic mesogens that form micellar or lamellar aggregates,[4] molecules in the chromonic liquid-crystalline phases form stacks of some kind.[2,3] The chromonic liquid-crystalline phases commonly observed are the nematic (N) phase and the hexagonal (M) phase.[5–9,19,20,31–38] In the N phase, molecules stack to form columnar aggregates (not necessarily simple one-molecule-wide columns). The long aggregates align parallel to each other but there is no long-range positional order among the columns. In the M phase, molecules stack into columns and the columns arrange in a hexagonal array. In both the N and M phases, the director is perpendicular to the molecular planes (*i.e.* parallel to the column axes.)[2,3,5–9] Both one- and two-phase regions were observed for chromonic liquid crystals.

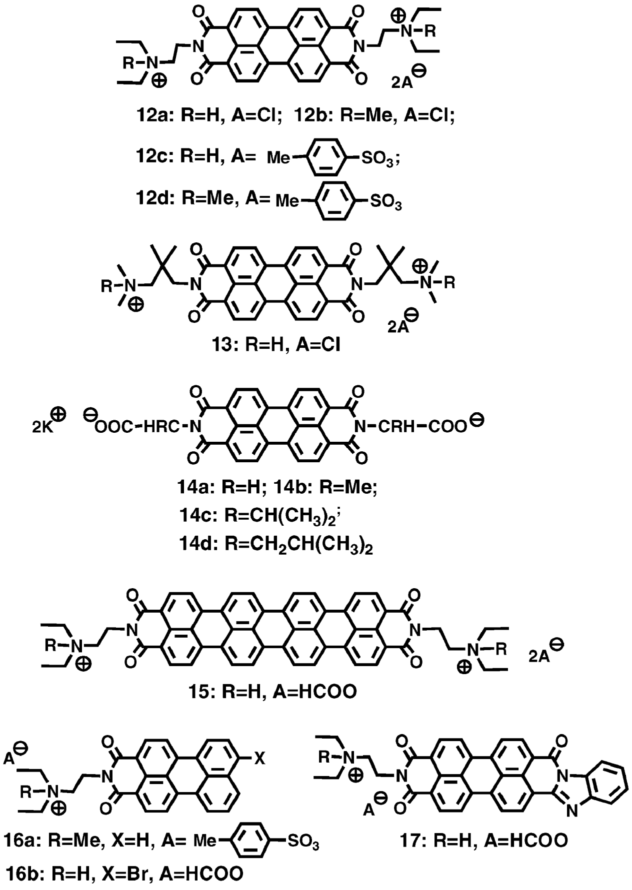


Fig. 2 Examples of molecularly designed chromonic mesogens.[31–39]

A lamellar phase in which the molecules stack to form lamellar brick-wall structures was reported for diethylammonium flufenamate (**8**)[21] and a cyanine dye **9**.[22] In the lamellar phase, the director is parallel to the molecular plane.

A chiral phase is formed by the helical stacking of chiral mesogens (*e.g.*, **14c,d**).[39] A chiral phase can also be attained by doping a chromonic N phase with a chiral dopant, such as doping a solution of disodium cromoglycate (**2**) with alanine, proline and D-glucose, or doping the N phase of RU31156 (**3**) with methylene blue.[10,11] In addition to these phases, more complex hollow column structures have also been proposed.[22,23]

The phase properties of chromonic liquid crystals are influenced by many factors that include the structure and concentration of the mesogen, temperature, ionic strength, and the presence of additives, surfactants and salts. Techniques commonly used to characterize chromonic liquid crystals include polarized optical microscopy, small-angle X-ray diffractometry, and ^{2}H, ^{23}Na and ^{35}Cl NMR spectroscopy. Other techniques such as FTIR, static and dynamic light scattering, X-ray scattering, small-angle neutron scattering (SANS), cryo-transmission electron microscopy (cryo-TEM) and rheology have also been used to examine the properties of the aggregates.

Optical textures of chromonic liquid-crystalline phases

Studies of chromonic liquid crystals by polarized optical microscopy indicated that different optical textures can be observed depending on the type of liquid-crystalline phase and how the liquid-crystalline phase was attained (by concentration or dilution, or by heating or cooling).[2,31–33] Under polarized optical microscope, nematic droplets (Fig. 3(a)) and reticulated texture have been observed for a two-phase N + I region.[2,31–33] The N phase assumes the characteristic nematic Schlieren texture (Fig. 3(b) and (c))[31–33] and occasionally a 'tiger skin' texture.[2]

The M phase shows a more grainy texture than the N phase (Fig. 3(d)).[2,31–33] When the M phase is developed by evaporation of solvent from the N phase, a herringbone texture can result (Fig. 3(e)).[31–33] Grainy M droplet textures, grainy reticulated textures and M ribbons (Fig. 3(f) and (g)) have been observed for a two-phase M + I region.[2,34,38]

Characteristic cholesteric and fingerprint textures (where the spacing of the bands corresponds to half of the pitch) are shown by high pitch chiral N phases where the pitch is larger than 1 μm (Fig. 3(h) and (i)).[2,10,11,39]

Small-angle X-ray diffraction analysis of chromonic phases

Small-angle X-ray diffraction is an important technique for differentiating chromonic phases. A 3.4 Å spacing, characteristic of face-to-face aromatic stacks, is generally observed for the N and M phases.[6–9,12,13,19,20,26] The N phase shows a continuous range of inter-column spacing that varies with the concentration of the samples. While the identification of lamellar phase by polarized optical microscopy is difficult (and the M phase had been mistaken as the lamellar phase), unequivocal distinction of the lamellar phase from the M phase was achieved by small-angle X-ray diffraction analysis.[22] The lamellar phase shows a series of reflections that correspond to spacings in the ratio of $1 : 1/2 : 1/3 : 1/4$, while the spacings of the M phase are in the ratio of $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7} : 1/\sqrt{9}$.[6–9,20–22] Using X-ray diffraction analysis, Tiddy *et al.* provided evidence for the lamellar phase of the cyanine dye **9** in which the molecules are packed with their long axes parallel to the layer plane.[22]

Evidence for the presence of columnar structures more complex than columns of unimolecular stacks was also provided by X-ray diffraction studies. For instance, analysis of C. I. Acid Red 266 (**10**) indicated a column area of ~665 Å^2, much larger than the molecular area of ~114 Å^2, that suggested a multimolecular-wide column.[22,23]

Determination of phase transition and order parameter

The concentration- and temperature-dependent phase transitions of chromonics can be determined by analyzing the optical textures observed under polarized light microscope, the small-angle X-ray diffraction patterns, or the splitting of the ^{2}H resonance peak in ^{2}H NMR spectroscopy.[11–13,33] The ^{2}H nucleus has a spin quantum number $I = 1$ and thus possesses an electric quadrupole moment. The deuterium resonance appears as a single peak in an isotropic medium. However, in an anisotropic (direction-dependent) environment such as that in a liquid-crystalline phase, the quadrupole moment interacts with the electric field gradients and the deuterium resonance splits into two peaks ($2I$ peaks).[11,13] Using ^2H_2O as solvent and then analyzing the deuterium peaks of ^2H_2O by ^{2}H NMR spectroscopy, the concentration and temperature at which transition from an isotropic phase to a chromonic liquid-crystalline phase occurs can be determined. Similar studies using ^{23}Na and ^{35}Cl NMR spectroscopy were performed on chromonic liquid-crystalline systems that contained Na$^+$ or Cl$^-$ as counterions.[12]

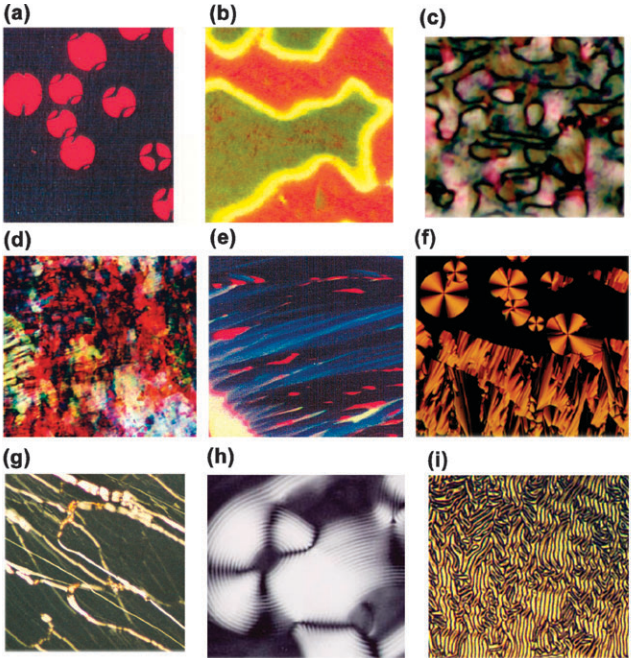


Fig. 3 Representative optical textures observed for different chromonic LC phases when viewed between crossed polarizers of an optical microscope. Optical micrographs showing (a) nematic droplets developed from an isotropic solution of **12a**;[31–33] (b) the Schlieren texture for **12a** in the N phase;[31–33] (c) the optical texture for the N phase of **13**;[38] (d) the grainy texture of the M phase of **12a**; (e) the herringbone texture for the M phase developed from the N phase of **12a**; (f) ribbons (M) developed from an I phase of **12d**;[34,38] (g) the ribbon phase of **16b** coexisting with the isotropic phase;[39] (h) the cholesteric (fingerprint) texture for a chiral N phase of **14d**;[39] and (i) the cholesteric texture for a chiral phase of **14c**.[39]

The order parameters of liquid-crystalline samples can be determined by NMR spectroscopy and optical techniques. The order parameter is a normalized parameter that indicates the degree of order of a system.[4] An order parameter of zero indicates disorder; the absolute value in the ordered state is one. The order parameter (S) of the particular C–^{2}H bond vector can be related to the quadrupole splitting (ν_Q^D) for that deuteron by eqn (1).[13]

$$\nu_Q^D = (3/8)kS \tag{1}$$

where k is the static quadrupole splitting constant of the C–^{2}H bond. Using a splitting constant equal to 183 kHz for Ar–^{2}H bonds, Goldfarb *et al.*[13] determined the effects of concentration and temperature on the order parameter of deuterated disodium cromoglycate (**2**) in the chromonic liquid-crystalline phase in water. Very high order parameters that ranged from 0.76 ± 0.08 for a 4 wt% solution of **2** in the N phase to 0.97 ± 0.1 for a 29 wt% solution in the M phase were determined.[13]

Polarized FTIR spectroscopy and polarized UV-Vis spectroscopy were also used to determine the order parameters of aligned nematic phase. The order parameters of individual vibrational bands of **2** in magnetically aligned nematic phase were analyzed by polarized FTIR.[14] The order parameter S was deduced according to eqn (2) from the IR absorbances parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the optical axis or nematic director. The values determined for most bands were negative suggesting that the molecular plane of **2** was perpendicular to the nematic director.[14]

$$S = (A_\parallel - A_\perp)/(A_\parallel + 2A_\perp) \qquad (2)$$

The order parameter of Sunset Yellow FCF (**5**) in the aligned nematic phase was determined from the polarized light absorptions ($A_\parallel$ and $A_\perp$) and direction-dependent refractive indices ($n_\parallel$ and $n_\perp$) according to eqn (3).[29]

$$S = (n_\parallel A_\parallel - n_\perp A_\perp)/(n_\parallel A_\parallel + 2n_\perp A_\perp) \qquad (3)$$

A 1.25 M solution of **5** was aligned by allowing it to flow into a space (0.01 mm) between two pieces of rubbed glass or rubbed polyimide coated glass. The order parameter of the aggregate of **5** was determined to be about 0.75 at 20 °C, and it decreased to about 0.6 at 70 °C. The order parameter of the N=N bond was negative, suggesting that this bond was perpendicular to the nematic director.[29]

Lavrentovich and co-workers also employed visible light absorption anisotropy to determine the scalar order parameter of the N phase of Blue 27 (**4**) aligned on buffed polyimide alignment layer.[17] At N–I transition, S was determined to be 0.73 ± 0.01. Higher order parameter was obtained at temperatures lower than the N–I transition temperature.

Aggregation behavior of chromonic mesogens and salt effects

Unlike surfactants and lipids that form conventional lyotropic LC due to hydrophobic interactions (entropy-driven),[4] it is generally believed that chromonic mesogens self-organize in solutions into liquid-crystalline phases mainly as a result of intermolecular interactions of the aromatic rings (enthalpy-driven).[2,3] The intermolecular interactions are presumably a combination of van der Waals forces and electrostatic attractions which constitute the so-called "π–π interactions". As reported by many researchers, the aggregation of chromonic mesogens is isodesmic: there is no optimum aggregation size and no critical concentration for the formation of aggregates.[2,3,16,29]

Although the structure of aggregates and the driving force for the formation of chromonic LC are not known with certainty, there is ample evidence for the isodesmic aggregation and the existence of large aggregates even in the isotropic phase, before liquid-crystalline optical properties are manifested.[16,23–27,29] Furthermore, it is known that the size of aggregates, I–N transition temperature, and the optical texture of M phase are influenced by the presence of salts.[7,10,16,18]

The aggregate size of disodium cromoglycate (**2**) in a 14 wt% solution at the I–N transition was determined by light scattering and shear viscosity measurements.[16] The aggregate column was estimated to have a diameter of ~2 nm (about the size of one molecule) and an average length of ~20 nm at the I–N transition. The length of the **2** increased from about 25 molecular units at 39 °C to about 50 molecular units at 32 °C.[16] These results are consistent with the data obtained by X-ray diffraction experiments.[7,13]

There were several reports on the effect of salts on the phase behavior of **2**. The transition temperatures from the N phase to the N + I phase and from the N + I phase to the I phase were raised in the presence of NaCl and KCl. The salt effect observed was attributed to a decrease in electrostatic repulsion between the charged aggregates.[10,15] Furthermore, a herringbone optical texture was observed for the M phase formed by peripheral evaporation of the N phase of **2** in the absence of NaCl, while a grainy texture was obtained in the presence of 1% NaCl.[6]

More systematic studies of salt effects were performed by Raghavan and co-workers.[18] It was demonstrated that anions had negligible effect on the phase transition temperature of **2**, while cations had variable effects. Monovalent cations Na^+, K^+, Li^+ and $NH_4{}^+$ raised the transition temperatures and viscosity of the solutions. The effect was in the order of $Na^+ > K^+ > Li^+ > NH_4{}^+$. Tetraalkylammonium ions (*e.g.*, Et_4N^+ and Bu_4N^+) caused the opposite effect. Raghavan and co-workers proposed that the alkali metal cations, especially Na^+, formed salt bridges between adjacent cromoglycate and promoted the growth of the aggregates. The larger cations Et_4N^+ and Bu_4N^+ were presumably too large to fit well in the aggregate structure and suppressed the growth of the aggregates.[18]

Studies of pseudoisocyanine chloride (**6**) in aqueous solution suggested that the size of aggregates can be much larger than dimers.[24–26] At the clearing temperature (temperature at which transition from the liquid-crystalline phase to the isotropic phase occurred), the aggregation number of **6** was determined spectroscopically to be about 40–50.[24] Using cryo-TEM, long fibers (with large aggregation number of at least 3000 and diameter of about 2 nm) of high stiffness was observed for a 1.25×10^{-2} M solution of **6** in the absence of salt.[25] In the presence of salt (200 mM of NaCl), bundles of very long fibers (several hundreds of nanometer) were observed at concentrations as low as 3×10^{-4} M.[26] Static light scattering studies suggested aggregation number of about 4 at a low concentration (0.75×10^{-3} M) of **6** in water.[27] In the presence of 0.01 M NaCl, the aggregation number increased to at least 30. At a higher concentration of **6** (2×10^{-3} M) in the presence of 0.01 N NaCl, the aggregate number was estimated to be at least 1000. The diameter of the aggregates was determined to be at least 2 nm,[27] similar to that determined by cryo-TEM experiments. Large aggregates of several hundred molecules were also reported for Acid Red 266 (**10**).[28]

Evidence for isodesmic aggregation of Sunset Yellow FCF (**5**) was provided by Horowitz *et al.*[29] They examined the dependence of X-ray peak scattering wave vector on the volume fraction of the aggregates. Furthermore, the dependence of absorption coefficient and birefringence on temperature and concentration of **5** were investigated. Their results suggested that the molecules stacked to form one-molecule-wide columns. As mentioned above, the N=N bond of **5** was deduced to be perpendicular to the long axis of the column. There was no optimum aggregation size or critical concentration at which aggregation began to occur. The ''bond'' energy (between the molecules in the aggregate) was estimated to be roughly seven times k_BT.[29]

Experimental results obtained for Blue 27 (**4**) were compared to predictions made using the theoretical model proposed by Onsager.[17] The Onsager theory predicts the orientation order in a nematic system of thin rigid rods (with length-to-diameter ratio generally larger than 10) that do not interact with each other except through the effect of ''excluded volume''.[40] The nematic scalar order parameter of chromonic LC predicted by this theory was in the range of experimental values determined by Lavrentovich and others. However, it was pointed out by Lavrentovich and co-workers that the Onsager theory predicted no temperature dependence of the order parameter while experimental results showed that the order parameter of chromonic LC decreased with temperature. The experimental results may indicate aggregate interactions and/or changes in aggregate length with temperature.[17] Lavrentovich and co-workers proposed that Coulomb interactions, including aggregate–aggregate, aggregate–counterions and counterions–counterions interactions, might play important roles in governing the stability and order of chromonic liquid crystals. Consideration of the finite flexibility and the polydispersity of the aggregates was also suggested by Lavrentovich and co-workers.[17]

In addition to the models for nematic order of ''hard rods'' in solution,[40,41] several models have been proposed in recent years to simulate and predict the behavior of chromonic mesophases. Examples include the theoretical models proposed by Taylor and Herzfeld,[42] Maiti *et al.*,[43] and Mohanty *et al.*[44]

Effects of additives and surfactants on chromonic phase properties

It was shown that additives, including ethylene glycol, glycerol, methanol, ethanol and urea, stabilized the isotropic phase of disodium cromoglycate (**2**) and led to a decrease in the transition temperature for N to I conversion.[18]

A profound effect of surfactants on the chromonic phase properties of C.I. Direct Blue 67 (**7**) was demonstrated by Ichimura and co-workers.[20] The addition of a very small amount of an anionic surfactant (as low as 0.01% by weight) stabilized the N phase (at the expense of the more ordered M phase) over a wide range of concentrations of **7**.[20]

Molecularly designed chromonic mesogens and the effects of structures and counterions on chromonic phase properties

Most studies of chromonic LC were performed on commercially available dyes or drugs of very different structures. The structure–property relationships of chromonic LC are not clearly understood despite the identification of many chromonic mesogens.

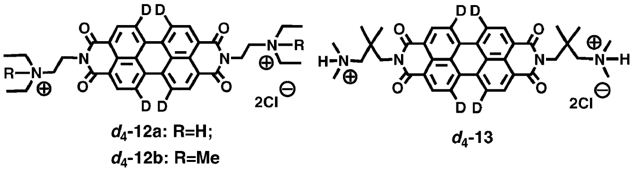


Fig. 4 The structures of ***d*₄-12a**, ***d*₄-12b** and ***d*₄-13**.

Tam-Chang *et al.* designed and synthesized **12–17** (Fig. 2) and demonstrated that chromonic liquid-crystalline properties can be bestowed to rylenebis(dicarboximide)s and rylenedicarboximides by introducing ionic side-chains to these aromatic compounds.[32–39] The effects of the structures of the side-chains, counterions and the aromatic ring systems on the chromonic properties of these compounds were investigated. The order parameters of **12a**, **12b** and **13** were determined by monitoring the splitting of C–^{2}H bonds of ***d*$_4$-12a**, ***d*$_4$-12b** and ***d*$_4$-13** (Fig. 4) in ^1H_2O using ^{2}H NMR spectroscopy.

The studies showed that ionic perylenebis(dicarboximide) **12a** in aqueous solution formed a chromonic N phase at 6–7 wt% at room temperature.[31–33] The order parameter in the N phase increased with the concentration of **12a** and decreased with temperature (Fig. 5). Highly ordered M phase was formed at high concentrations (*e.g.*, 38 wt%). The order of the M phase was rather stable to heating, similar to that observed for **2**.[33]

The effects of counterions and aliphatic side-chains on the chromonic properties of these perylenebis(dicarboximide)s were revealed by comparing the properties of **12–14**. Changing from the protonated ammonium side-chain in **12a** to the methylated ammonium side-chain in **12b** did not cause a significant change to the nematic phase properties or the N–I transition temperature.[45,46] However, replacing the chloride ions by tosylate ions resulted in a dramatic change in phase properties. Compounds **12c** and **12d** with tosylate ions formed ribbon-like liquid crystals dispersed in the isotropic solution (Fig. 3(f)).[38,45,46] The biphasic M + I region persists even at concentrations higher than 30 wt%.[38]

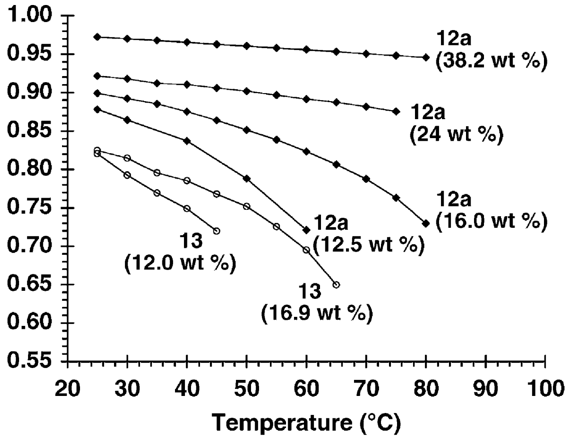


Fig. 5 The effects of concentration and temperature on the order parameter (*S*) of C–^{2}H bonds of ***d*$_4$-12a** and ***d*$_4$-13** in ^1H_2O determined by ^{2}H NMR spectroscopy.

Replacing the side-chains in **12a** and **12b** with the $CH_2CMe_2CH_2NHMe_2$ side-chains in **13** did not change the type of liquid-crystalline phase observed. However, it had a profound effect on the phase transition temperatures. At similar concentrations, the (N to N + I) and the (N + I to I) transition temperatures of **13** were lower than those of **12a** and **12b** by about 15 °C (Fig. 5). In addition, the stability and order parameter of **13** in the N phase were significantly lower than those of **12a** and **12b** at similar concentrations and temperatures.[38,45,46]

The presence of stereogenic centers in the alkyl chains in **14c,d** results in a *chiral* chromonic phase (as indicated by the cholesteric texture in Fig. 3(h) and (i)) presumably due to the formation of a helical twist in the column of molecules.[39] The achiral analogue **14a** showed only Schlieren texture of N phase; no optical texture characteristics of chiral phases was observed.[39]

The effects of the aromatic ring structures were investigated by comparing the properties of **12**, **15** and **16**. As expected, perylenebis(dicarboximide) **12a** and quaterrylenebis(dicarboximide) **15** differed dramatically in solubility and electronic absorption properties.[35,36] Quaterrylenebis(dicarboximide) **15** was soluble in acids (such as HCOOH(aq), CF_3COOH and concentrated H_2SO_4(aq)), but not in water. The λ_{max} of absorption of a dilute solution ($\sim 5 \times 10^{-7}$ M) of **15** in 23.4 M HCOOH(aq) at 85 °C was 830 nm, red-shifted by about 300 nm compared to the λ_{max} of **12a** in water. Despite the difference in solubilities of **12a** and **15**, both compounds form H-aggregates and chromonic N phase.

Changing from perylenebis(dicarboximide) **12** to perylenedicarboximide **16** resulted in a decrease in the charge-to-surface area ratio, and hence lowered the solubility of **16**, compared to that of **12**, in aqueous solutions. Unlike **12d** which was very soluble in water and formed chromonic M ribbons at high concentrations, **16a** was soluble in hot water only and a nematic phase was observed.[39]

At room temperature, anisotropic crystals of **16a** that showed direction-dependent absorption and emission of light were obtained. Single-crystal X-ray diffraction analysis indicated stacking of the perylenemonoimide rings of **16a** in the crystals (Fig. 6), which is presumably driven by strong π-interactions between the rings. The ionic perylenemonomides stacked anti-parallel to each other along a column to minimize repulsion between the quaternized ammonium ions. The crystal packing was stabilized by electrostatic attractions between the ammonium ions and the sulfonate ions. Because of geometric parameters (in addition to intermolecular interactions) that control molecular packing in crystals and the difference in amount of solvent molecules, the molecular packing of **16a** in the crystal will not be the same as that in the chromonic N phase. Nevertheless, the molecular packing in the crystal phase may provide insight into the intermolecular interactions in the chromonic liquid-crystalline phase.

Potential applications

Inspired by natural systems that take advantage of non-covalent interactions in self-assembly and self-organization processes to produce complex biological systems, there is more and more effort being devoted to emulate this strategy in the fabrication of materials and the manufacturing of complex devices. In this arena, the rational design and control of supramolecular entities in chromonic liquid crystals to generate functional materials and devices have gained increased attention in the last decade and are summarized below.[48]

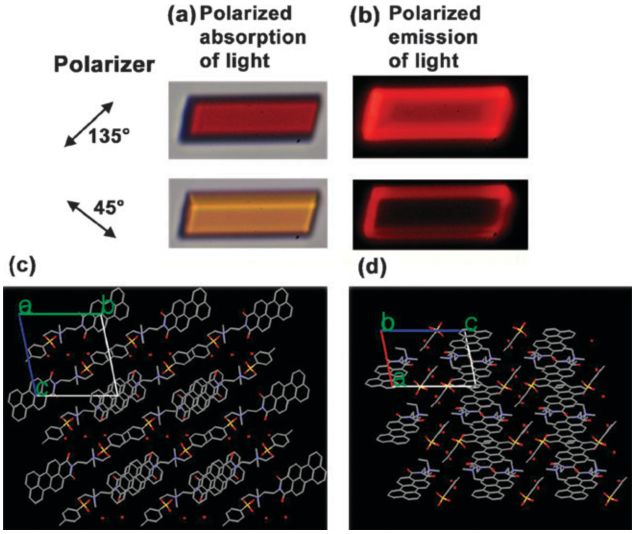


Fig. 6 (a) Optical micrograph showing polarized absorption of visible light by a crystal of **16a**. (b) Optical micrograph showing polarized emission of visible light by a crystal of **16a**. (c, d) The molecular packing, determined by single-crystal X-ray diffraction analysis, of **16a** in a crystal grown from water.[47] In (c), the packing is viewed along the *a*-axis of the unit cell. In (d), it is viewed along the *b*-axis.

Fabrication of oriented films

An important application of chromonic liquid crystals is the fabrication of thin liquid-crystalline films with anisotropic properties. Evaporation of solvent from the aligned LC films gives solid films in which the orientational order of the dichroic mesogens is retained. These liquid-crystalline and solid films have useful properties as linear polarizers, optical compensators, retarders, alignment layers, and color filters.

The alignment of chromonic LC can be achieved by using a strong magnetic field, mechanical shearing, or an alignment layer. An essential criterion for generating high performance films is the self-organization of dichroic dyes into a highly ordered chromonic liquid-crystalline phase.

The first claim of the alignment of chromonics in the nematic state on an alignment layer or in an orienting field to produce polarizer was made by Dreyer in 1946.[49] An oriented surface can be prepared by uniaxially rubbing a substrate surface[17,49,50] or by photoinduced alignment of polymer with photoactive groups such as azobenzene.[51–54]

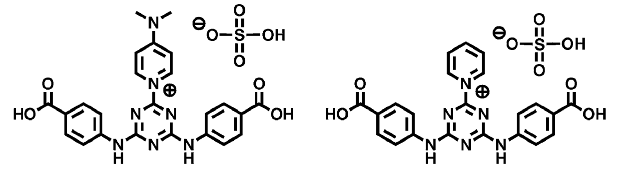
Lavrentovich *et al.* demonstrated that liquid crystal cells with chromonic LC in the planar N phase or the twisted chiral nematic (N*) phase can be used as optical retardation plates with negative birefringence.[50] A planar N phase LC cell was prepared using two glass substrates coated with rubbed polyimide as alignment layers and filled with an aqueous solution of **2** in the N phase. Similarly, a 90° twisted chiral nematic cell was prepared by Lavrentovich *et al.* using an aqueous solution of **2** doped with L-alanine and L-lysine as chiral dopants. It is known that normally black twisted nematic displays (NB TN displays) generally suffer from problems with light leakage in the dark state, chromaticity, and contrast for head-on viewing as a consequence of the positive birefringence of the twisted (thermotropic) nematic LC layer. The incorporation of chromonic LC cells with negative birefringence and twisted optical axis as optical compensators in NB TN displays helped to cancel the birefringence effects of the NB TN cells.[50] The resultant devices provided high head-on contrast, wide viewing angles, and an achromatic dark state.

Ichimura *et al.* prepared an alignment surface by irradiating a film of azobenzene-functionalized polymer with linearly polarized light. After the photoinduced molecular reorientation of the azobenzene groups, an aqueous solution of chromonic mesogens **2**[51] or **7**[52–55] was coated onto the oriented non-ionic polymer surface. The chromonic columnar aggregates were aligned parallel to the azobenzene molecular axis. The addition of a small amount of surfactant to the solution of **7** was important for the formation of the chromonic N phase and a homogeneous layer of the oriented dye on the irradiated polymer surface. The surface-assisted alignment of chromonic liquid crystal of **7** yielded optically anisotropic films of order parameter and degree of polarization as high as 0.89 and 0.95, respectively.[55]

Shear-induced alignment is another important technique for aligning chromonic nematic liquid crystals.[31,32,35,37,56–59] Shear-induced orientation and reorientation of the cyanine dye **9** and C.I. Acid Red 266 (**10**) were examined by Tiddy and co-workers.[56] Shear alignment of (4-dimethylamino-1-[4,6-di(4-carboxyphenylamino)-1,3,5-triazin-2-yl]pyridium sulfate (**18**) and 4,6-di(4-carboxyphenylamino)-1,3,5-triazin-2-yl]pyridium sulfate) (**19**) (shown in Fig. 7) was reported by Sahouani *et al.*[58]

Shear-induced orientation of **12a** in the chromonic N phase followed by evaporation of solvent led to polarizing films of **12a** with dichroic ratio as high as 30 (Fig. 8(a)).[31,32] In addition to polarized absorption of light, these films also showed polarized fluorescent emission.[59] The axis perpendicular to the shearing direction of the film exhibits higher emission intensity than the axis parallel to the shearing direction. The ratio of the emission intensities along the orthogonal directions was as high as 30 at 690 nm, the wavelength of maximum emission intensity.

Using the same approach, unprecedented control of the molecular orientation of quaterrylenebis(dicarboximide) **15** in thin solid films was achieved, producing a novel linear polarizer of light at long wavelengths (Fig. 8(b)).[35] NIR polarizers have applications as optical isolators that are used in conjunction with semiconductor lasers and fiber optics.



(4-dimethylamino-1-[4,6-di(4-carboxyphenyl-amino)-1,3,5-triazin-2-yl]pyridium sulfate
(**18**)

4,6-di(4-carboxyphenylamino)-1,3,5-triazin-2-yl]pyridium sulfate)
(**19**)

Fig. 7 Molecular structures of chromonic mesogens **18** and **19**.[57]

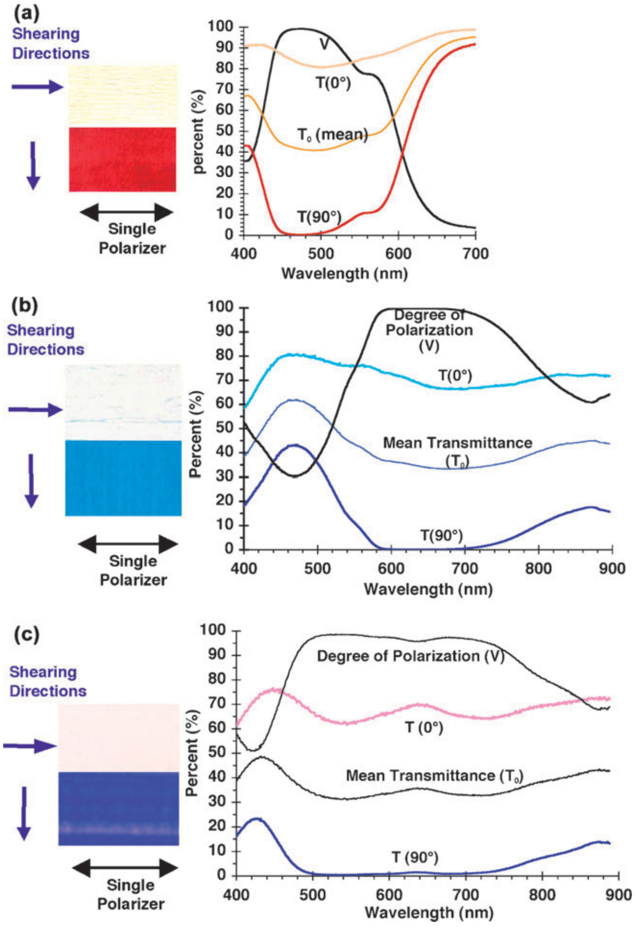


Fig. 8 Optical photomicrographs (left) and visible spectra (right) of the oriented films of (a) **12a**, (b) **15** and (c) mixed aggregates of **15** and **17**. Shearing direction was the direction of the motion of coating rod in the coating process. $T(0^\circ)$ was the transmittance when the aligned film's shearing axis was parallel to the polarization of the incident light. $T(90^\circ)$ was the transmittance when it was orthogonal. Mean transmittance (T_0) was calculated as $[T(0^\circ) + T(90^\circ)]/2$. Degree of polarization was calculated as $[T(0^\circ) - T(90^\circ)]/[T(0^\circ) + T(90^\circ)]$.

Tam-Chang *et al.* further demonstrated the versatility of this approach by preparing broad-spectrum polarizing films that were composed of a mixture of molecularly designed mesogens **15** and **17**. The criteria that enabled the formation of mixed liquid crystals and broad-spectrum polarizing films[37] are listed below. "(1) The surface area of the aromatic region of **17** was not too different from that of **15** to preclude the formation of mixed aggregates of these compounds by solvophobic interactions and π-stacking. The formation of mixed-aggregates (instead of self-aggregates) minimized large regions of inhomogeneous color in the polarizing films. (2) Compound **17** absorbed at different wavelengths compared to **15** so that their mixtures absorbed over a large wavelength range. (3) Both **15** and **17** were dichroic and the principal electronic transition axes aligned with the long molecular axes to ensure that their mixed aggregates and the anisotropic films produced subsequently exhibit direction-dependent optical properties.

(4) Compound **17** displayed chromonic properties under the same conditions as that of **15**. The control of solubilities and chromonic properties of **17** were achieved by adjusting the number of bulky ionic groups attached to the aromatic ring."[37] As shown in Fig. 8(c), the oriented films prepared from the mixed aggregate of **15** and **17** showed polarization properties over a very broad wavelength range ($\sim$500–900 nm).[37]

Polarized transmission IR spectroscopy was used to further elucidate the molecular orientation in the sheared films of **12**, **15** and mixed **15** and **17**.[32,37] The presence of the C–H wagging resonance in the polarized transmission IR spectroscopy and the results of the polarized UV-Vis spectroscopy provided strong evidence that the molecular planes of **12a**, **15** and **17** in the oriented films studied were aligned with the YZ plane and the long molecular axes of the compounds aligned with the Y axis (Fig. 9). The results though cannot exclude the possibility that some molecules were aligned with the XY plane or the long axis of some molecules in the films were aligned with the Z axis.

Monolayer and multilayers of chromonic liquid crystals of **20–23** (Fig. 10) with in-plane orientational order were prepared by using a combination of electrostatic layer-by-layer deposition and shear orientation techniques.[60–62] A glass or mica surface was modified with polycation **20**. An aqueous solution of Violet 20 (**21**) in the chromonic N phase was then coated onto the polycation layer by mechanical shearing. Excess materials were rinsed off to give an oriented monolayer of the anionic mesogen **21** on the polycation layer. Results from atomic force microscopy and X-ray photoelectron spectroscopy indicated that the orientation order of the chromonic stacks was preserved in the dried films.[61] Plausible orientations of **21** relative to the shearing direction and the substrate surface proposed by Lavrentovich and co-workers are shown in Fig. 11(a).[61] Repeated coating of the polycation **20** and shear orientation of the chromonic LC **21** produced multilayers of the oriented mesogens (Fig. 11(b)).[60]

This layer-by-layer shear orientation technique was employed by Boiko *et al.* to prepare films with alternative layers of chromonic mesogens **22** and **23** (Fig. 11(c)).[62] However, no enhancement of anisotropy was observed for these films compared to those of **20** and **21**. It was found that multilayer films with three or more layers of **23** were unstable. Removal of **23** occurred upon gentle washing of the multilayer films.[62]

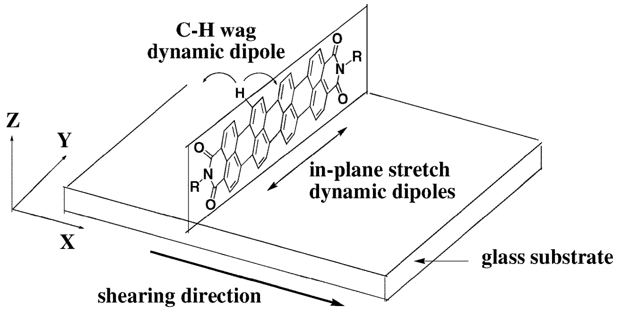


Fig. 9 Schematic diagram showing a possible orientation of a molecule of **15** in a sheared film of **15** on a substrate with the defining axes labelled and the planes of the relevant IR dynamic dipoles of the molecule indicated. Compound **12a** and **17** possesses similar IR dynamic dipoles.

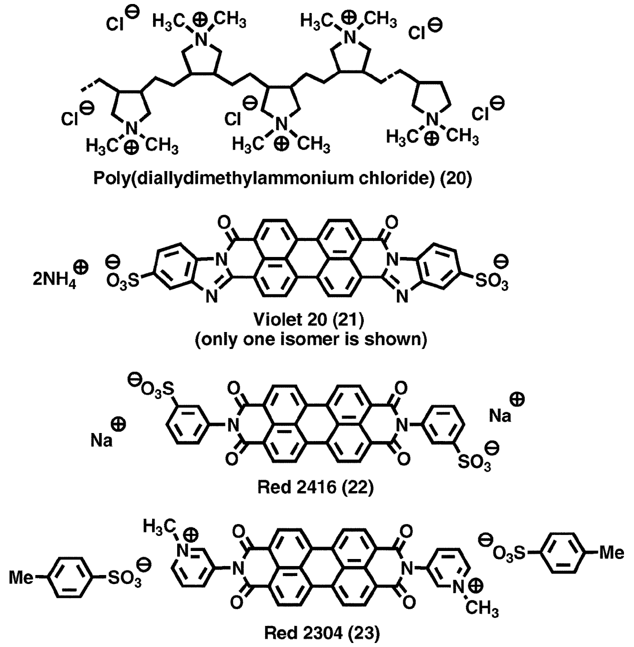


Fig. 10 Structures of polycation **20** and mesogens **21–23** used in the layer-by-layer deposition of chromonic liquid crystals films.

Micropatterned polarizing elements and photoinduced liquid-crystalline gratings

Micro-patterns of anisotropic aromatic materials have also been fabricated by exploiting the self-organization properties of chromonic liquid crystals. Micropatterns of anisotropic aromatic materials have potential applications in the microelectronic fields, as holographic films, as viewing angle-dependent optical materials and in 3D stereoscopic displays.

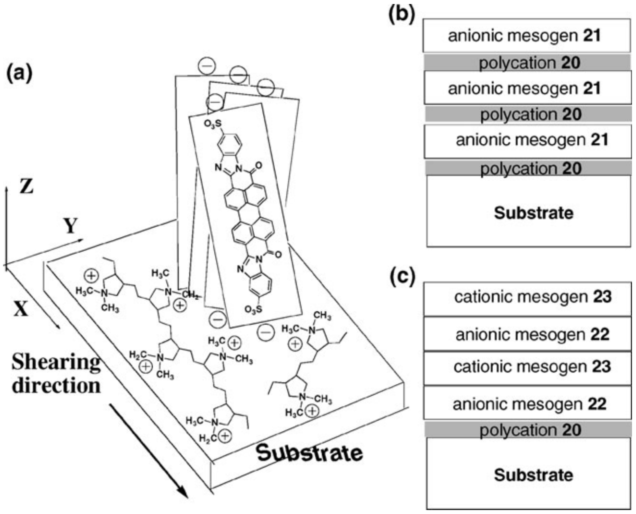


Fig. 11 Schematic diagram showing (a) the plausible orientations of the molecular stacks of **19** in a monolayer of **19** coated onto a layer of polycations **18**; (b) the configuration of a multilayer film of **18** and **19**; and (c) the configuration of a multilayer film of **20** and **21**. The relative thickness of different layers is not drawn to scale.

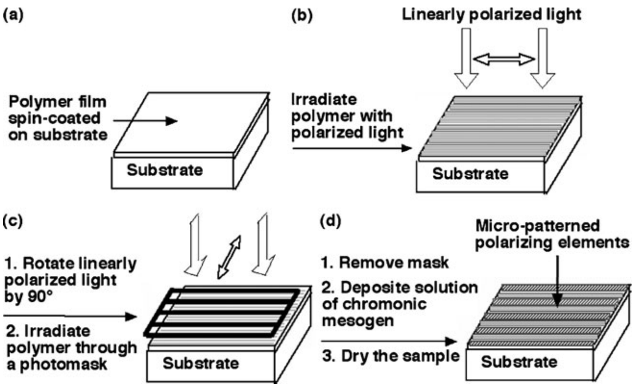


Fig. 12 Schematic diagram that illustrates the procedure invented by Tamaki and co-workers for fabricating micro-patterned polarizing elements. (Redrawn from a figure in ref. 54.)

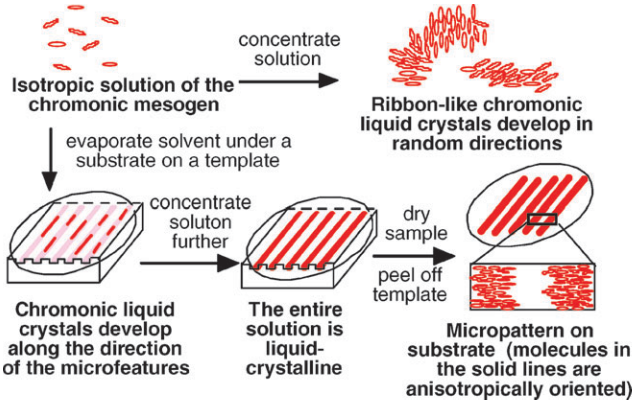


Fig. 13 Schematic representation of the template-guided organization of chromonic liquid crystals leading to a micropattern of anisotropically ordered solid. (Redrawn from a figure in ref. 34.)

A novel technique was developed by Tamaki and co-workers to fabricate micro-patterned polarizing elements for use with LC cells in binocular disparity stereoscopic displays.[54] In this photoalignment technique (outlined in Fig. 12), a polyamide with a photoresponsive dimethylaminoazobenzene substituent was spin-coated on a glass substrate. Linearly polarized light was used to align the polymer. The polarized light was then rotated 90° and the polymer film was irradiated through a photomask to reorient the azobenzene groups in the exposed regions. An aqueous solution of 5 wt% B67 (**7**) and 0.2 wt% of a surfactant was applied on the photoaligned polymer film. Evaporation of solvent resulted in the formation of a chromonic liquid-crystalline phase and subsequently the solid aggregates of **7** on the micro-patterned polymer film. The dichroic ratio, contrast ratio and degree of polarization calculated from the absorption intensities at $\lambda_{\max}$(530 nm) were about 18, 0.85 and 0.91, respectively. These results indicated high orientation order of **7** on the photo-generated polymer pattern. As pointed out by Tamaki *et al.*, this method offers the advantage of direct patterning of multiple orientation of dyes, and hence polarization axis, in a single film.[54]

Wokaun and co-workers used forced Rayleigh scattering to generate holograms from the chromonic liquid-crystalline phases of Levafix Goldgelb (**11**) in a water–methanol mixture. The holographic gratings were generated by photoinduced alignment of optical axes or photoinduced phase transitions of the chromonic liquid crystal.[63]

An alternative approach to generating micro-patterned polarizing elements was developed by Tam-Chang *et al.* This approach exploited the self-organization of dichroic compounds such as **12d** and **16b** into chromonic ribbons on micro-patterned polymer templates (Fig. 13). The self-organization of **12d** on a polymer (PDMS) template produced micropatterns of anisotropically oriented **12d** which were transferable to glass slides (Fig. 14(a)).[34] Control experiments performed using **12a** in the nematic phase showed the formation of grainy materials with no bulk anisotropic order (Fig. 14(b)).[34]

Using this template-guided organization technique, materials with micro-patterned polarizing elements of **16b** were also fabricated.[39] It can be envisioned that sticking two of these patterns together in a such way that the polarization axes are perpendicular to each other will generate more complex polarizing patterns.

Biosensors

Lavrentovich *et al.* explored the use of chromonic LC in biosensors.[64–67] The biosensor was composed of a liquid crystal cell sandwiched between a polarizer and an analyzer which were oriented with their polarization axes orthogonal to each other (Fig. 15). The liquid crystal cell consisted of two glass plates that were coated with rubbed polyimide and separated by a polymer spacer. After the cell was filled with a mixture of **2** in the chromonic N phase, antigen-coated (streptavidin) latex beads (about 0.6 μm in diameter), and antibody (anti-streptavidin), it was sealed with epoxy glue. The specific recognition of the antigen (streptavidin) by the antibody resulted in conglomeration of the latex beads to large particles of diameters larger than 2 μm.[64,65] The transduction mechanism of the sensor was the director distortions of the liquid-crystalline material caused by the presence of large particles, and consequently, light emerging through the analyzer. Microscopic images indicated that the bright areas were much bigger than cross-sectional areas of the conglomerated beads. In the control experiments in which the chromonic liquid-crystalline solution was mixed with the streptavidin-coated latex beads only or the antibody only, no

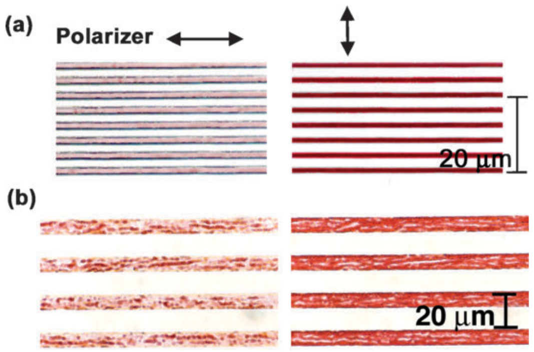


Fig. 14 Optical micrograph showing (a) micro-patterned anisotropic solids of **12d** on a glass surface and (b) grainy textures of solid lines of **12a**.[34]

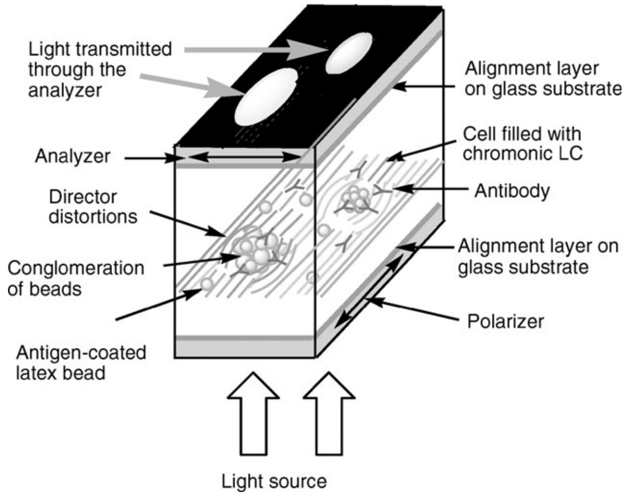


Fig. 15 Schematic representation of a biosensor based on director distortions of chromonic liquid crystals. (Redrawn from a figure in ref. 64.)

conglomeration of the beads occurred, and the amount of light transmitted through the analyzer was insignificant.

To explore the potential use of this sensing platform for detection of microbes, bacterial viability in several chromonic liquid crystals, surfactant-based lyotropic liquid crystals and thermotropic liquid crystals were examined.[66] The prokaryotes studied were: a Gram-positive coccus (*Staphylococcus aureus*), a Gram-negative rod (*Eshcerichai coli*) and a Gram-positive spore-forming rod (*Bacillus atrophaeus*). Among the liquid crystals evaluated, only the chromonic liquid crystals were found to be non-toxic to all three prokaryotes examined.[66]

Director distortions of chromonic LC was used to amplify the recognition and detection of *Bacillus atrophaeus* (BA) spore by anti-BA endospore antibody.[67] The detection sensitivity limit of the sensor approached 10^5 spores mL^{-1}. Currently, applications of this type of biosensors in real-time sensing of microbes are limited by the need to pre-mix the analytes with the chromonic LC before assembling the LC cell and interference from large spherical contaminants and particulates.

Summary

Chromonic liquid crystals hold great promises to useful applications, especially as optical materials and devices in high technology. However, many important questions regarding the structures and properties of these supramolecules still remain unanswered. For example, not all amphiphilic or ionic aromatic compounds display chromonic liquid-crystalline properties in aqueous solution. What are the determining structural factors? Why do some chromonic liquid crystals form lamellar structures and others form columnar aggregates? What structural factors direct the formation of chromonic ribbons (M + I) in preference to nematic phase? Further inquiries on the molecular packing in the aggregates and the driving forces for their formation are necessary. Deeper understanding of the structure–property relationships is important for designing novel mesogens, optimizing properties and developing new applications. The advancement of this field requires continuing efforts of and collaborations among researchers from different science and engineering disciplines to reveal the parameters that govern the properties of chromonics and to develop new applications in high technology.

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References

1 (*a*) J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89; (*b*) G. M. Whitesides, J. P. Mathias and C. T. Seto, *Science*, 1991, **254**, 1312; (*c*) M. C. Fyfe and J. F. Stoddart, *Acc. Chem. Res.*, 1997, **30**, 393; (*d*) J.-M. Lehn, *Science*, 2002, **295**, 2400; (*e*) D. N. Reinhoudt and M. Crego-Calama, *Science*, 2002, **295**, 2403; (*f*) O. Ikkala and G. t. Brinke, *Science*, 2002, **295**, 2407; (*g*) M. D. Hollingsworth, *Science*, 2002, **295**, 2410; (*h*) G. M. Whitesides and B. Grzybowski, *Science*, 2002, **295**, 2418; (*i*) T. Shimizu, M. Masuda and H. Minamikawa, *Chem. Rev.*, 2005, **105**, 1041; (*j*) D. M. Vriezema, M. C. Aragonès, J. A. A. W. Elemans, J. J. L. M. Cornelissen, A. E. Rowan and R. J. M. Nolte, *Chem. Rev.*, 2005, **105**, 1145; (*k*) Y. H. Ko, E. Kim, I. Hwang and K. Kim, *Chem. Commun.*, 2007, 1305; (*l*) F. N. Diederich, *Angew. Chem., Int. Ed.*, 2007, **46**, 68; (*m*) T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int. Ed.*, 2006, **45**, 38; (*n*) X. Zhang, H. Chen and H. Zhang, *Chem. Commun.*, 2007, 1395; (*o*) D. L. Gin, X. Lu, P. R. Nemade and C. S. Pecinovsky, *Adv. Funct. Mater.*, 2006, **16**, 865; (*p*) J. Rebek, Jr, *Chem. Commun.*, 2007, 2777.
2 J. Lydon, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, vol. 2B, p. 981.
3 J. Lydon, *Curr. Opin. Colloid Interface Sci.*, 1998, **3**, 458.
4 (*a*) P. J. Collings and J. S. Patel, *Handbook of Liquid Crystal Research*, Oxford University Press, New York, 1997; (*b*) *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, vol. 3.
5 H. Sandquist, *Ber. Dtsch. Chem. Ges.*, 1915, **48**, 2054.
6 T. K. Attwood, J. E. Lydon and F. Jones, *Liq. Cryst.*, 1986, **1**, 499.
7 T. K. Attwood, J. E. Lydon, C. Hall and G. J. T. Tiddy, *Liq. Cryst.*, 1990, **7**, 657.
8 (*a*) J. S. G. Cox, G. D. Woodard and W. C. McCrone, *J. Pharm. Sci.*, 1971, **60**, 1458; (*b*) N. H. Hartshorne and G. D. Woodard, *Mol. Cryst. Liq. Cryst.*, 1973, **23**, 343.
9 (*a*) J. E. Lydon, *Mol. Cryst. Liq. Cryst. Lett.*, 1980, **64**, 19; (*b*) T. K. Attwood and J. E. Lydon, *Mol. Cryst. Liq. Cryst.*, 1984, **108**, 349; (*c*) J. E. Turner and J. E. Lydon, *Mol. Cryst. Liq. Cryst. Lett.*, 1988, **5**, 93.
10 H. Lee and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, 1982, **84**, 137.
11 D. Goldfarb, M. E. Moseley, M. M. Labes and Z. Luz, *Mol. Cryst. Liq. Cryst.*, 1982, **89**, 119.
12 D. Goldfarb, M. M. Labes, Z. Luz and R. Poupko, *Mol. Cryst. Liq. Cryst.*, 1982, **87**, 259.
13 D. Goldfarb, Z. Luz, N. Spielberg and H. Zimmermann, *Mol. Cryst. Liq. Cryst.*, 1985, **126**, 225.
14 Y. W. Hui and M. M. Labes, *J. Phys. Chem.*, 1986, **90**, 4064.
15 (*a*) L. J. Yu and A. Saupe, *Mol. Cryst. Liq. Cryst.*, 1982, **80**, 129; (*b*) D. Perahia, D. Goldfarb and Z. Luz, *Mol. Cryst. Liq. Cryst.*, 1984, **108**, 107.
16 Y. A. Nastishin, H. Liu, S. V. Shiyanovskii, O. D. Lavrentovich, A. F. Kostko and M. A. Anisimov, *Phys. Rev. E*, 2004, **70**, 051706.

17 Y. A. Nastishin, H. Liu, T. Schneider, V. Nazarenko, R. Vasyuta, S. V. Shiyanovskii and O. D. Lavrentovich, *Phys. Rev. E*, 2005, **72**, 041711.

18 A. F. Kostko, B. H. Cipriano, O. A. Pinchuk, L. Ziserman, M. A. Anisimov, D. Danino and S. R. Raghavan, *J. Phys. Chem. B*, 2005, **109**, 19126.

19 D. E. Sadler, M. D. Shannon, P. Tollin, G. W. Young, M. Edmondson and P. Rainsford, *Liq. Cryst.*, 1986, **1**, 509.

20 C. Ruslim, D. Matsunaga, M. Hashimoto, T. Tamaki and K. Ichimura, *Langmuir*, 2003, **19**, 3686.

21 I. Kustanovitch, R. Poupko, H. Zimmermann, Z. Lux and M. M. Labes, *J. Am. Chem. Soc.*, 1984, **107**, 3494.

22 G. J. T. Tiddy, D. L. Mateer, A. P. Ormerod, W. J. Harrison and D. J. Edwards, *Langmuir*, 1995, **11**, 390.

23 W. J. Harrison, D. L. Mateer and G. J. T. Tiddy, *J. Phys. Chem.*, 1996, **100**, 2310.

24 H. Stegemeyer and F. Stöckel, *Ber. Bunsenges. Phys. Chem.*, 1996, **100**, 9.

25 H. von Berlepsch, C. Böttcher and S. Dähne, *J. Phys. Chem. B*, 2000, **104**, 8792.

26 H. von Berlepsch and C. Böttcher, *J. Phys. Chem. B*, 2002, **106**, 3146.

27 B. Neumann, *J. Phys. Chem. B*, 2001, **105**, 8268.

28 B. Neumann, K. Huber and P. Pollmann, *Phys. Chem. Chem. Phys.*, 2000, **2**, 3687.

29 V. R. Horowitz, L. A. Janowitz, A. L. Modic, P. A. Heiney and P. J. Collings, *Phys. Rev. E*, 2005, **72**, 041710.

30 (*a*) P. Mariani, M. M. De Morais, G. Gottarelli, G. P. Spada, H. Delacroix and L. Tondelli, *Liq. Cryst.*, 1993, **15**, 757; (*b*) G. P. Spada, A. Carcuro, F. P. Colonna, A. Garbesi and G. Gottarelli, *Liq. Cryst.*, 1988, **3**, 651; (*c*) P. Mariani, C. Mazahard, A. Garbesi and G. P. Spada, *J. Am. Chem. Soc.*, 1989, **111**, 6369; (*d*) L. Q. Amaral, R. Itri, P. Mariani and R. Micheletto, *Liq. Cryst.*, 1992, **12**, 913.

31 I. K. Iverson and S.-W. Tam-Chang, *J. Am. Chem. Soc.*, 1999, **121**, 5801.

32 I. K. Iverson, S. M. Casey, W. Seo, S.-W. Tam-Chang and B. A. Pindzola, *Langmuir*, 2002, **18**, 3510.

33 S.-W. Tam-Chang, I. K. Iverson and J. Helbley, *Langmuir*, 2004, **20**, 342.

34 S.-W. Tam-Chang, J. Helbley, T. D. Carson, W. Seo and I. K. Iverson, *Chem. Commun.*, 2006, 503.

35 S.-W. Tam-Chang, W. Seo, I. K. Iverson and S. M. Casey, *Angew. Chem., Int. Ed.*, 2003, **42**, 897.

36 S.-W. Tam-Chang, W. Seo and I. K. Iverson, *J. Org. Chem.*, 2004, **69**, 2719.

37 S.-W. Tam-Chang, W. Seo, R. Kyle and S. M. Casey, *Chem. Mater.*, 2004, **16**, 1832.

38 I. K. Iverson, Dissertation, University of Nevada, Reno, 2000.

39 W. Seo, Dissertation, University of Nevada, Reno, 2004.

40 L. Onsager, *Ann. N. Y. Acad. Sci.*, 1949, **51**, 627.

41 (*a*) S.-D. Lee, *J. Chem. Phys.*, 1987, **87**, 4972; (*b*) J. P. Straley, *Mol. Cryst. Liq. Cryst.*, 1973, **22**, 333.

42 (*a*) M. P. Taylor and J. Herzfeld, *Langmuir*, 1990, **6**, 911; (*b*) M. P. Taylor and J. Herzfeld, *Phys. Rev. A*, 1991, **43**, 1892.

43 P. K. Maiti, Y. Lansac, M. A. Glaser and N. A. Clark, *Liq. Cryst.*, 2002, **29**, 619.

44 S. Mohanty, S.-H. Chou, M. Brostrom and J. Aguilera, *Mol. Simul.*, 2006, **32**, 1179.

45 J. Helbley, PhD Dissertation, Department of Chemistry, University of Nevada, Reno, 2006.

46 S.-W. Tam-Chang, J. Helbley and I. K. Iverson, *Langmuir*, 2008, in press.

47 L. Huang, S.-W. Tam-Chang, W. Seo and K. Rove, *Adv. Mater.*, 2007, **19**, 4149.

48 Several of these applications were also summarized by Lydon in the following review article: J. Lydon, *Curr. Opin. Colloid Interface Sci.*, 2004, **8**, 480.

49 (*a*) J. S. Dreyer, *US Pat.*, 2,400,877, 1946; (*b*) J. S. Dreyer, *US Pat.*, 2,481,830, 1949; (*c*) J. S. Dreyer, *US Pat.*, 2,524,286, 1950; (*d*) J. S. Dreyer, *US Pat.*, 2,544,659, 1951; (*e*) J. F. Dreyer, *J. Phys. Colloid Chem.*, 1948, **52**, 808.

50 (*a*) M. Lavrentovich, T. Sergan and J. Kelly, *Liq. Cryst.*, 2003, **30**, 851; (*b*) M. Lavrentovich, T. Sergan and J. Kelly, *Mol. Cryst. Liq. Cryst.*, 2004, **409**, 21.

51 T. Fujiwara and K. Ichimura, *J. Mater. Chem.*, 2002, **12**, 3387.

52 (*a*) K. Ichimura, *Mol. Cryst. Liq. Cryst.*, 1997, **298**, 221; (*b*) K. Ichimura, M. Momose, K. Kudo and N. Ishizuki, *Langmuir*, 1995, **11**, 2341.

53 K. Ichimura, T. Fujiwara, M. Momose and D. Matsunaga, *J. Mater. Chem.*, 2002, **12**, 3380.

54 D. Matsunaga, T. Tamaki, H. Akiyama and K. Ichimura, *Adv. Mater.*, 2002, **14**, 1477.

55 C. Ruslim, M. Hashimoto, D. Matsunaga, T. Tamaki and K. Ichimura, *Langmuir*, 2004, **20**, 95.

56 T. L. Crowley, C. Bottrill, D. Mateer, W. J. Harrison and G. T. Tiddy, *Colloids Surf., A*, 1997, **129–130**, 95.

57 Y. A. Bobrov, S. M. Casey, L. Y. Ignatov, P. Lazarev, D. Phillips and S.-W. Tam-Chang, in *Flat Panel Display Materials-1998*, ed. G. Parsons, T. S. Fahlen, S. Morozumi, C. Seager and C.-C. Tsai, *Mater. Res. Soc. Proc.*, Warrendale, PA, 1998, p. 225.

58 (*a*) H. Sahouani, K. M. Vogel and M. C. Cliffe, *US Pat.*, 6,395,354, 2002; (*b*) H. Sahouani, K. M. Vogel and M. S. Schaberg, *US Pat.*, 0.066,885, 2002; (*c*) H. Sahouani, K. M. Vogel and M. C. Cliffe, *Int. Pat. Appl.*, WO 01/35161 A1; (*d*) H. Sahouani, K. M. Vogel and M. C. Cliffe, *Int. Pat. Appl.*, WO 01/37038 A1; (*e*) H. Sahouani and K. M. Vogel, *Int. Pat. Appl.*, WO 02/38698 A1.

59 T. D. Carson, W. Seo, S.-W. Tam-Chang and S. M. Casey, *Chem. Mater.*, 2003, **15**, 2292.

60 T. Schneider and O. D. Lavrentovich, *Langmuir*, 2000, **16**, 5227.

61 (*a*) T. Schneider, K. Artyushkova, J. E. Fulghum, L. Broadwater, A. Smith and O. D. Lavrentovich, *Langmuir*, 2005, **21**, 2300; (*b*) T. Schnieder and O. D. Lavrentovich, *US Pat.*, 0,168,511, 2002.

62 O. Boiko, O. Komarov, R. Vasyuta, V. Nazarenko, Yu. Slominskiy and T. Schneider, *Mol. Cryst. Liq. Cryst.*, 2005, **434**, 633.

63 C. Hahn, I. Spring, C. Thunig, G. Platz and A. Wokaun, *Langmuir*, 1998, **14**, 6871.

64 S. V. Shiyanovskii, O. D. Lavrentovich, T. Schneider, T. Ishikawa, I. I. Smalyukh, C. J. Woolverton, G. D. Niehaus and K. J. Doane, *Mol. Cryst. Liq. Cryst.*, 2005, **434**, 587.

65 S. V. Shiyanovskii, T. Schneider, I. I. Smalyukh, T. Ishikawa, G. D. Niehaus, K. J. Doane, C. J. Woolverton and O. D. Lavrentovich, *Phys. Rev. E*, 2005, **71**, 020702R.

66 C. J. Woolverton, E. Gustely, L. Li and O. D. Lavrentovich, *Liq. Cryst.*, 2005, **32**, 417.

67 S. L. Helfinstine, O. D. Lavrentovich and C. J. Woolverton, *Lett. Appl. Microbiol.*, 2006, **43**, 27.