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FEATURE ARTICLE

Controlling chirality with helix inversion in cholesteric liquid crystals

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The helical organization of cholesteric liquid crystals is omnipresent in living matter. Achieving control over the structure of the cholesteric helix consequently holds great potential for developing stimuli-responsive materials matching the level of sophistication of biological systems. In particular, inversion of a cholesteric helix is associated with inversion of the circular polarization of the light it reflects. While control over the cholesteric period has been thoroughly investigated, reports on helix inversion are scarcer. Predicting which systems display helix inversion also remains a challenge because of the subtle balance of contributions underlying this phenomenon. Here we provide an overview on recent advances in controlling and understanding helix inversion in cholesteric liquid crystals.

Introduction

Helices are arguably one of the most elegant examples of chiral structures. A helix is characterized by its periodicity (pitch, p) or by its wavenumber $q = 2\pi/p$ and by its handedness, which is defined as positive for a right-handed or clockwise twist and negative for a left-handed or counter-clockwise twist (Fig. 1). Helical macromolecules are typical structural motifs in biology: polynucleotides, proteins and collagen fibers are all right-handed helices.[1] At the supramolecular level, the helical organization of cholesteric liquid crystals is found in a large number of biological materials. Collagen in bone or fish scales,[2] chitin in arthropod shells[3] or cellulose in plant cell walls[4] are all helical architectures in which the cholesteric order is stabilized by locking it into the solid state. While the sense of rotation of these materials is usually constant, a few examples of systems involving cholesteric helix inversion have been reported also.[5,6] Helical biological materials display high levels of performance and complexity and in particular sophisticated optical and mechanical functions.[7] Designing new advanced materials inspired from these biological helical systems requires achievement of reversible, fast and precise control over the structure of the cholesteric helix: its pitch, its orientation and also its handedness.[8,9]

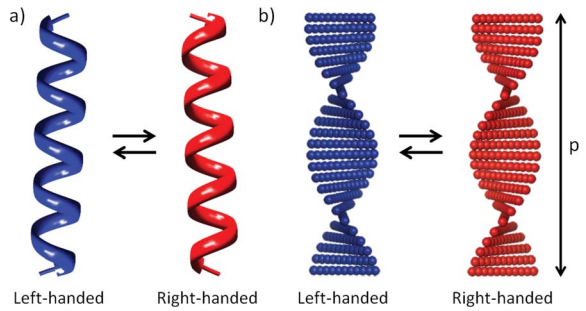

Fig. 1 (a) Twist inversion between a left-handed and a right-handed helix. (b) Schematic representation of helix inversion in a cholesteric liquid crystal. Each rod represents the local director, which is perpendicular to the helix axis; p is the helical pitch.

Inversion of molecular twist is a crucial element for motion of synthetic molecular rotors[10] and other complex molecular machineries.[11] At the macromolecular level, helix inversion has been achieved in helical polymers[12,13] including clickamers,[14] peptides,[15] RNA,[16] and synthetic polymers.[17] Solvent-induced helix inversion in helical polymers organized on a surface was demonstrated also.[18] As our purpose is to focus on supramolecular helix inversion in liquid crystals, helix inversion in macromolecular systems will not be reviewed here. At the supramolecular level, helical organization occurs in chiral smectic and cholesteric liquid crystals. In these liquid crystals the director, *i.e.* the local alignment axis, rotates in space around an axis in a helical fashion, with a pitch that is generally longer than a few hundreds of nanometers in the case of cholesterics. Controlled helix inversion has been reported in chiral smectics.[19] In cholesteric liquid crystals, helical organization is at the origin of unique reflection properties: light is reflected selectively over a narrow range of wavelengths whose central position λ_0 is determined by the pitch p of the helix ($\lambda_0 = np$ at normal incidence, with n the mean refractive index). Selective reflection constitutes the basis for applications where a single color has to match a specific value of the control parameter—color reflectors and filters, tunable lasers or thermal imaging. Another

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remarkable property of cholesteric liquid crystals is that the reflected light is circularly polarized, with the same handedness as the cholesteric helix. Numerous investigations have aimed at controlling the pitch of the cholesteric helix.[20] In contrast, reports on cholesteric helix inversion are still scarce. Based on the large number of technological applications based on pitch modifications, it is likely that controlling helix inversion will constitute a solid basis for future technological applications, in particular optical materials in which reflection of polarized light is involved.

In this feature article, we provide an overview on helix inversion in cholesteric liquid crystals, focussing on recent advances in controlling this phenomenon. The external stimuli which have been used for that purpose include chemical composition, temperature and irradiation with light. The review of experimental findings will be accompanied by an account of theoretical models which have been proposed to achieve a better understanding of the mechanisms of transmission and amplification of chirality, from the molecular to the supramolecular level. We describe examples of helical twist inversion in thermotropic and in lyotropic cholesteric liquid crystals. This overview includes not only synthetic compounds but also biopolymers and viruses.

1. Molecular chirality and handedness of the cholesteric helix

In a nematic liquid crystal the molecules (or mesogens) are preferentially aligned along the director. If there is no enantiomeric excess of chiral species, the free energy minimum corresponds to a uniform director and the mesophase displays a $D_{\infty h}$ symmetry. Alternatively, in the presence of molecular chirality, the director is spontaneously twisted in a helical fashion.[21] According to the elastic continuum theory, if only twist deformations are taken into account the density of elastic energy, f_{el}, can be expressed as:[22]

$$f_{el} = k_2 q + (1/2) K_{22} q^2 \quad (1)$$

where K_{22} is the twist elastic constant and k_2 is the chiral strength. These quantities depend on the chemical composition of the liquid crystalline material and on the thermodynamic parameters (temperature and density). K_{22} is a positive quantity accounting for the energetic cost of twist deformations; typical values of K_{22} are of the order of a few piconewton. The chiral strength k_2 is a pseudoscalar, which has opposite values for enantiomeric systems and vanishes in an achiral nematic phase. By minimization of the elastic energy, the equilibrium pitch is obtained: $p = -2\pi K_{22}/k_2$, which becomes infinitely long in (achiral) nematic liquid crystals.

Unlike the elastic constant, the chiral strength varies greatly from system to system and even when the chemical composition of a sample is known, neither its sign nor its magnitude can be easily predicted. The reason is that the chiral strength bears a subtle dependence on the coupling between molecular chirality and orientational order. This problem was addressed by various theories; their ingredients change with the nature of the systems, therefore models will be recalled later on, when presenting examples. In general, helix inversion requires the competition of different contributions of opposite sign, which may derive from the presence of different chiral species or different molecular conformers of a chiral compound. More subtle effects are amenable to the presence of various kinds of intermolecular interactions, each with its own chiral character, and to the biaxiality of molecular order.† The subtle balance between these competing contributions can be modified either by fine tuning molecular chirality in the sample or by using an external stimulus such as temperature or light.

2. Molecular control over twist inversion

2a. Doping nematic liquid crystals with chiral molecules

More than 80 years ago G. Friedel described the close relationship between the nematic and the cholesteric mesophase.[23] He showed that even a small amount of chiral non-racemic solute transforms a nematic into a cholesteric liquid crystal. The chiral dopant can be mesogenic itself, but not necessarily, and it is enough that it dissolves in the nematic host. The chiral dopant induces a twist distortion, quantified by the helical pitch and handedness, which depends on its chemical structure and absolute configuration in a way which is neither simple nor obvious. At low dopant concentration, the inverse pitch increases proportionally to the amount of enantiomerically pure dopant, and the slope is a specific property of each dopant for a given nematic host. A quantitative description of the cholesteric induction requires the definition of the "helical twisting power" (HTP), which characterizes the ability of a chiral dopant to twist a nematic mesophase:

$$\mathrm{HTP} = \frac{1}{p\, c\, ee} \quad (2)$$

where c is the concentration of the chiral dopant and ee its enantiomeric excess. The sign of HTP is positive for a right-handed cholesteric helix and negative for a left-handed one. In the case of a mixture of dopants, the resulting HTP is the sum of individual contributions:

$$\mathrm{HTP} = \sum_i x_i \ \mathrm{HTP}_i \quad (3)$$

where x_i is the molar fraction of i component ($\sum_i x_i = 1$) and HTP_i is the corresponding helical twisting power. Eqn (3) applies also when a dopant presents different conformers, which can be seen as a special case of a mixture.

Amplification of molecular chirality in doped nematics occurs thanks to the ability of liquid crystals to transmit torques.[22] It provides a unique opportunity to investigate the relationship between the molecular structure, intermolecular interactions and mesoscale organization, but also to achieve molecular control over the structure of the whole cholesteric mesophase. Compared to the cholesteric liquid crystals which are constituted only by chiral mesogens, doped cholesteric liquid crystals offer some major advantages: there is more freedom in the design of the

† Here and in the following when speaking of 'biaxiality' we will refer to molecular order. In general this biaxiality can be related to the lack of axial symmetry in the molecular shape. This should not be confused with the biaxiality of the phase (for a discussion of this difference see *e.g.* D. C. Wright, N. D. Mermin, *Rev. Mod. Phys.*, 1989, **61**, 385–432). In principle the cholesteric phase is biaxial, but this is generally neglected and it is treated as locally uniaxial.

dopant which does not need to fulfil the requirements of a mesogen and pitch and handedness of the material are readily modified by adjusting the concentration of the dopant.[24]

Theories have been developed in order to explain the molecular origin of cholesteric organization in thermotropic liquid crystals. These theories involve chiral interactions between molecules, and different models were proposed, depending on the nature of these interactions. An early contribution by Goossens clarified the relationship between molecular symmetry and formation of the cholesteric mesophase by considering a model system of rigid molecules interacting through dispersion forces.[25] Subsequent developments assuming either dispersion interactions,[26–28] short range intermolecular repulsions[29] or even a combination of both[30] highlighted the prominent role of the coupling between molecular chirality and orientational order in determining the cholesteric organization. This coupling makes it difficult to rationalize the relation between the absolute configuration of the dopant and the handedness of the induced cholesteric helix.

Helical twist inversion, experimentally observed under different conditions, has been a long standing challenge for theoreticians. Theoretically it has been shown that the twisting behavior of thermotropic liquid crystals can be interpreted in terms of molecular geometry and the subtle role of molecular biaxiality in determining the handedness of chiral mesophases induced by molecular dopants has been demonstrated.[27,28,30] This issue deserves some explanation: an elongated molecule will preferentially align its long axis (*a*) to the director, which means that its short axes (*b* and *c*) will tend to lie along the helical axis. Unless the molecule is axially symmetric, the degree of alignment of the axes *b* and *c* will be different. This is meant as biaxiality of molecular order. Its effect on the handedness of the cholesteric helix derives from the fact that, depending on its orientation, a molecular dopant is potentially able to induce opposite phase helicities. Fig. 2 illustrates schematically the relationship between molecular biaxiality and chirality induced by a chiral dopant. In general, due to the partial ordering existing in a liquid crystal, both short axes of a dopant contribute to induced helicity. If the two contributions have different signs, the cholesteric organization will result from the competition between twist distortions in opposite senses. A net small chirality, *i.e.* a large cholesteric pitch, is expected in these systems. In this situation, even small changes in the biaxiality of molecular order, due to slight variations in the dopant structure or in the temperature, are sufficient to change the balance of oppositely handed contributions and thus revert the handedness of the cholesteric helix.

As shown by experiments and demonstrated by theory, cholesteric handedness is reversed if a dopant is replaced by its enantiomer. From application point of view this key property has been successfully applied to the determination of absolute configuration of chiral molecules,[31] or to the determination of enantiomeric excess by using liquid crystalline media.[32] Less obvious is the helix inversion occurring upon small chemical changes in the dopant. Though being structurally similar and homochiral, biphenyl derivatives **3.1** and **3.2** induce oppositely handed cholesteric phases (Fig. 3).[33,34] The simplest reason accounting for opposite handedness in the cholesteric phase formed by these dopants would be the value of their twist angle, ϕ: biphenyl conformations with $\phi = 0°$ or $\phi = 90°$ are achiral, and pairs of molecules with twist angle of opposite sign are enantiomers (Fig. 4), which means that they have opposite HTPs.[27] However, the twist angles of **3.1** and **3.2** are $\phi \approx +65°$ and $\phi \approx +52°$, respectively, which means that this simple explanation must be discarded. In fact, it was shown that the main reason for twisting the director in opposite sense lies in different orientational preferences for **3.1** and **3.2**.[35] To describe these preferences it is convenient to introduce what can be called the 'molecular plane', shown Fig. 4. Biphenyl derivative **3.1** has a disc-like behavior, characterized by the tendency to keep its molecular plane perpendicular to the cholesteric axis. Within this plane the disc-like dopant shows no preference for alignment of the *para* axis. Thus, the helicity induced in the cholesteric phase is that viewed along the axis perpendicular to the molecular plane. In contrast, **3.2** displays a more rod-like behavior because the bromine atoms in *para* position confer an elongated shape to the molecule: it shows a tendency to align its *para* axis along the local director, without any strong preference for keeping the molecular plane perpendicular to the cholesteric axis. As a consequence, the cholesteric helix formed by **3.2** is defined by helicity from directions perpendicular to the *para* axis.

Several other systems display inversion of cholesteric handedness upon small changes in the dopant structure. A remarkable case, clearly showing that substituents may be more important than the presence of some structural helicity, is that of oligonaphthalenes. Configurationally homogeneous (all-S) derivatives of tetra-, hexa-, octa-naphthalene, linked at the 1,4-positions,

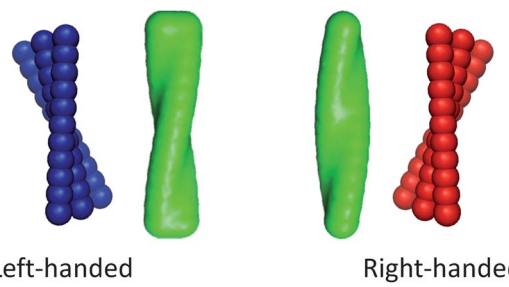

Fig. 2 Schematic representation of the role of biaxiality in determining the handedness of an induced cholesteric helix. Green ribbons (D_{2d} symmetry) represent dopant molecules that are not axially symmetric (in this representation one of their short symmetry axes is perpendicular to the plane of the page). Beside each ribbon, the twist induced in a nematic liquid crystal is shown (each coloured rod represents the director).

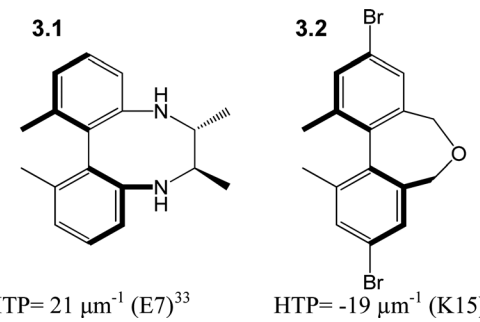

Fig. 3 Structure of biphenyl derivatives **3.1** and **3.2** and their helical twisting powers (HTPs). The nematic host is reported in brackets.

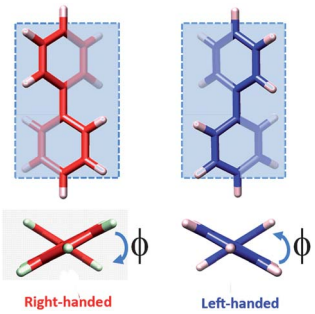

Fig. 4 Biphenyl structures with twist angle ϕ of opposite signs. Top: frontal view. The shaded rectangle represents the 'molecular plane', bisecting the twist angle ϕ between the benzene moieties. Bottom: side view.

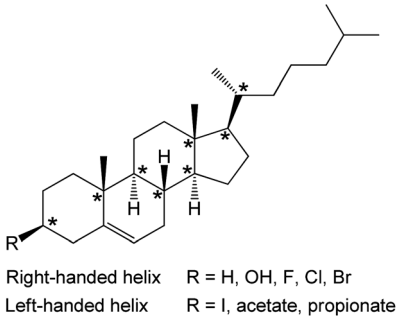

Fig. 5 Cholesteryl derivatives forming cholesteric phases of different handedness. Stars indicate the eight chiral centers.

have the structure of right-handed helices, with the helix axis roughly parallel to the naphthyl–naphthyl bonds. However, somehow counter-intuitively, they were found to induce cholesteric phases with handedness alternating from positive to negative on moving along the series.[36]

The HTP of a given dopant usually changes in magnitude, but not in sign when the nematic host is changed. However, in some cases also inversion of handedness was observed upon changing the solvent.[37,38] This effect was mostly evidenced for dopants with low helical twisting powers. For example, methyl phenyl sulfoxide used as a dopant induces cholesteric phases of opposite handedness in different nematic solvents.[37] Since the chirality of this molecule changes as a function of the rotation around the $C_{(aromatic)}$–S bond, it was speculated that the cholesteric inversion could be traced back to the stabilization of different dopant conformations, depending on the nematic host. However, with the help of NMR experiments it was shown that the main reason for the change of cholesteric handedness from one nematic host to another is the slightly different orientational behavior of the dopant.[39]

Examples where cholesteric inversion is not a consequence of changes in the absolute configuration of the chiral molecule were also reported for micellar systems doped with chiral molecules. Inversion of the helix was observed as a function of the concentration of dopant[40] and of the composition of the non-chiral host.[41,42] With the support of ^{13}C NMR experiments, such changes were explained in terms of conformational changes in the dopant, promoted by the environment.

2b. Chemical substitution in chiral mesogens

Cholesteric phases can be formed by introducing chiral dopants in nematic phases or by using mesogens which are chiral themselves. Indeed, observation of the cholesteric phase of cholesterol is generally recognized as the discovery of liquid crystals.[43] Cholesteryl derivatives gave early examples of helix inversion (Fig. 5). The handedness of their cholesteric phase depends on the substituent at the C3 position (R). Cholest-5-ene (R = H), cholesterol (R = OH) and some halides (R = F, Cl, and Br) form right-handed phases whereas in the presence of bulkier substituents (R = I, acetate, propionate, nonanoate, myristate, …) the phase is left-handed.[44] Interestingly, these changes do not involve the eight chiral centres which have the same absolute configuration for all derivatives and are mostly located in the fused ring core. Binary mixtures of cholesteryl derivatives were shown to follow a linear additive law: upon addition of a derivative inducing opposite twist, the cholesteric helix gradually unwinds and then rewinds in the opposite sense, through a macroscopically achiral organization (compensated nematic phase).[45] Even more surprising was the observation that, when dissolved in a non-chiral nematic host, these derivatives may induce a twist of opposite sense to that observed in their pure cholesteric mesophase, and that helical sense inversion may be induced by a change of concentration in binary mixtures of cholesteryl derivatives and nonchiral mesogens.[46] These phenomena raised a strong interest and were widely investigated, but turned out to be difficult to explain. Early semi-phenomenological models were proposed.[47] Recently, a molecular theory provided a theoretical explanation for these experimental observations, in terms of contributions of different sign of guest–host and guest–guest interactions to the chiral strength of mixtures.[30] Other theoretical calculations evidenced a strong sensitivity of the twisting ability of cholesteryl derivatives to changes in the molecular geometry, which is probably related to the high number of chiral centres in the molecule.[48]

Cholesteric phases formed by cyanobiphenyl derivatives having an asymmetric carbon in their alkyl chain provide another interesting example of helix inversion. These systems exhibit an odd–even effect: for a given absolute configuration of the chiral center, a right-handed or a left-handed cholesteric phase is formed, depending on the position of the chiral carbon (odd or even).[49] An empirical rule was proposed to correlate molecular structure and absolute configuration with cholesteric handedness in these systems, and the underlying reason was devised by the fact that, for the same absolute configuration of the chiral center, the molecular structure exhibits opposite helicity, depending on whether the chiral center is separated from the aromatic ring by an odd or an even number of bonds.[50] A detailed analysis of the twisting ability of cyanobiphenyl derivatives with chiral alkyl and alkyloxy chains showed a complex behavior, with conformer contributions which differ from each other in magnitude and sign.[51] This is a general feature of flexible chiral molecules. Therefore, in a sample containing several conformers, generally there is only a little unbalance in favour of one or the other sign, which makes the cholesteric handedness very sensitive to little chemical variations.

2c. Helical polymers and colloidal suspensions

Lyotropic liquid crystals are solutions of anisotropic molecules in isotropic liquids: most of them are formed by stiff or semi-flexible polymers, both covalent and supramolecular, in water or in organic solvents. Examples of lyotropic cholesteric liquid crystals comprise biopolymers with helical structure, like polypeptides and polynucleotides. Rather counter-intuitively, it is not possible to associate the well-defined molecular helicity of the polymers with the handedness of their cholesteric mesophase. This was recognized early, simply on the basis of packing considerations. According to the Straley model of hard threaded rods, inversion of the cholesteric helix may result from a change in the slope of the thread: right-handed screws with a weak twist (large pitch) pack into a right-handed supramolecular helix, whereas right-handed screws with a tight twist organize into a left-handed helix (Fig. 6).[52] This is only a general consideration; the behavior of real systems is also driven by a variety of interactions, in which the solvent plays an important role.

Inversion of the cholesteric helix was observed for poly(γ-benzyl-L-glutamate), PBLG, in organic solvents (Fig. 7). Despite having an α-helix structure, this polymer forms either a right- or a left-handed cholesteric phase, depending on the solvent.[53] This behavior was explained by a theory based on dispersion interactions between chiral rods in a dielectric medium. Dispersion interactions depend on the relative dielectric constant of rods and solvents and at a certain value of this ratio a change of the chiral strength k_2 in eqn (1) and a subsequent helix inversion were predicted.[54] Further reasons for the cholesteric inversion were suggested by subsequent theoretical developments, including steric rod–rod repulsions[55] and accounting for the polymer flexibility.[56] Theoretically, it was shown that intermolecular dispersion and steric interactions may promote twist distortions in opposite sense.[57] These interactions depend on the conformation of the side chains of PBLG, and NMR experiments revealed that solvent affects these conformations.[58]

Other interesting examples are provided by stacked arrays of nucleobases. Water solutions of 2′-deoxyguanosine-5′-monophosphate d(pG), its dimers d(GpG) and longer oligomers exhibit a hierarchical self-assembly process: planar tetramers of Hoogsteen-bonded guanosines stack on each other to form chiral columns, which above a given concentration organize into a cholesteric phase. It was observed that, although the overall

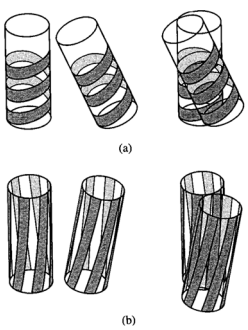

Fig. 6 The Straley model: steric interactions between right-handed screws produce a relative twist that is right-handed for a tight pitch (a) and left-handed for a larger pitch (b). Reproduced from ref. 59. Copyright (1999) by the American Physical Society.

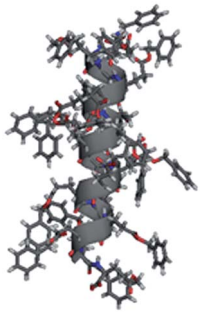

Fig. 7 Segment of poly(γ-benzyl-L-glutamate), PBLG, with ribbon representation of the backbone and stick representation of the side chains.

structure of the columnar aggregates is similar, the cholesteric handedness changes from one system to another.[60] Analogous effects were reported for duplex forming DNA and RNA sequences. B-DNA (≥100 base pairs) was generally found to form a left-handed cholesteric phase;[61] however the twist deformation was reported to invert by changing the solvent[62] and upon binding of drug-like molecules.[63] Very recently it was found that the cholesteric phase formed by oligonucleotides may be right- or left-handed, depending on their sequence and length.[64] For one of the investigated oligomers, a change of handedness with concentration was reported: the left-handed helix was found to gradually unwind with increasing concentration and then to rewind in the opposite sense. Due to the polyelectrolyte nature of polynucleotides, an important role of electrostatic interactions appears reasonable. Based on a detailed model for the screened electrostatic interactions between helical charge distributions,[65] a right-handed phase was predicted for B-DNA, which does not agree with experimental findings; however this model highlighted the subtle dependence of the chiral interactions between the helical polymers upon the details of the charge pattern on their surface.[66] Recently, the delicate relationship between molecular and phase helicity was demonstrated for a model of hard cylinders decorated with a helical charge distribution, interacting through a screened Coulomb (or Yukawa) potential: it was found that the handedness of the cholesteric phase can be tuned by the periodicity of the molecular helix of charges.[67] Another study pointed to the competing effect of steric and electrostatic interactions: while best packing of right-handed B-DNA promotes a right-handed phase organization, the opposite twist is favored by charge repulsions.[68] Within this framework, the twist inversion observed for some oligonucleotides[64] was ascribed to the prevalence of the one or the other interaction, dictated by the inter-axial distance between linear aggregates.[69]

Finally, the intriguing behavior of suspensions of rod-like viruses in water is worth mentioning. M13 and *fd* viruses form left-handed cholesteric phases.[70,71] Results in line with experiment were obtained for M13, modeled as a hard particle, with shape and charge chirality deriving from the helical arrangement of the coat proteins; even in this case, a prevailing contribution of electrostatic interactions was devised.[72] Alternatively, it was proposed that the origin of the phase chirality would be in chiral fluctuations of the virus shape; experimental findings in support of this hypothesis were claimed,[73] but the reason why fluctuations of a given chirality should prevail is not clear. These models are

challenged by the recent discovery of a right-handed cholesteric phase for the *fd* Y21M mutant,[71] which differs from *fd* only for having a methionine in place of a tyrosine as the 21st amino-acid in the coat protein.

3. Temperature-induced helix inversion

As the structure of thermotropic liquid crystals is temperature-dependent by definition, it is not surprising that temperature could be used as an external stimulus to induce helix inversion. While thermal control over the pitch of thermotropic cholesteric liquid crystals has been largely documented and exploited in a variety of applications including forehead thermometers or thermochromic paints,[74] examples of temperature-induced helix inversion remain scarce.

Usually, temperature-induced inversion of cholesteric handedness is indicative of competing contributions that have oppositely handed effects but comparable relative weight. The dominant contribution may change with temperature, leading to inversion of cholesteric handedness. Cholesteric liquid crystals exhibiting temperature-dependent helix inversion are generally characterized by a large pitch, *i.e.* low chirality. Theoretically it has been shown that in the case of flexible molecules the helix inverts because the statistical distribution of molecular conformations, promoting twist distortions of different handedness, changes with temperature.[28,30] To understand this mechanism one should remind the considerations concerning the relation between molecular order and sense of the director twist (Section 2a).

Temperature-controlled helix inversion was observed in a few single component cholesteric liquid crystals in which the mesogens display multiple chiral centers and/or axes. For mesogens bearing two chiral centers such as **8.1** (Fig. 8), the origin of helix inversion was attributed to the competition between chiral centers having opposite effects on the sign, strength and temperature dependence of the twisting power of the whole molecule.[75] This phenomenon was observed also in trioxadecalin **8.2** (Fig. 8) where it was ascribed to a change of the mean alignment axis in the molecule with temperature, due to the different flexibility of the molecular core and the tail.[76] While inversion of the helical twist for mesogens having multiple chiral centers had been known for many years, it was later found that helix twist inversion can also occur in cholesteric liquid crystals composed of mesogens having a single chiral center, such as **8.3** and **8.4** (Fig. 8).[77,78] These chiral mesogens have flexible chains and it has been suggested that the helix inverts because the statistical distribution of molecular conformations promoting twist distortions of different handedness changes with temperature.[79]

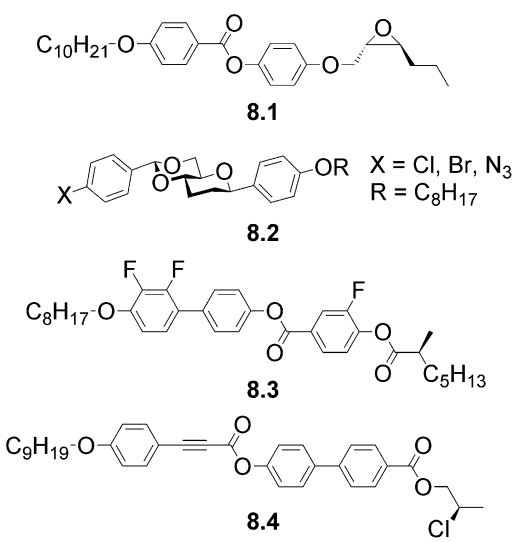

Fig. 8 Examples of thermotropic liquid crystals that undergo inversion of helical twist sense in the cholesteric phase upon changing the temperature. While **8.1** and **8.2** have multiple chiral centers,[75,76] **8.3** and **8.4** have a single chiral center.[77,78]

Mixtures of liquid crystals have been used to adjust the temperature of cholesteric helix inversion. Temperature controlled helix inversion has been exploited to design materials overcoming the 50% reflectance limit of cholesteric liquid crystals.[80,81] This limit derives from the fact that, of the two circularly polarized components of the incident unpolarized light, only the component having the same handedness as the cholesteric helix is reflected. The component with opposite helicity is transmitted. A material overcoming the reflectance limit was obtained by using a cholesteric mixture exhibiting thermally induced helix inversion, in the presence of photopolymerizable monomers. A portion of the material was frozen into a given helicity by curing with UV light at a certain temperature. After polymerisation was finished, the temperature was decreased and helix inversion occurred in the un-polymerized portion of the system. The resulting film showed an increase of reflectance up to 90%.

Temperature-driven helix inversion has been evidenced also in lyotropic cholesteric phases, in particular in concentrated solutions of semiflexible polymers. Different explanations have been proposed, depending on the system. It was ascribed to an order–disorder transition in the triple-helical schizophyllan[82] and to a change of the α-helical screw sense, from right- to left-handed on increasing the temperature, in poly(β-phenethyl-aspartate).[53] However, it was shown that a structural change of the polymer is not a necessary requirement: cholesteric inversion with temperature was observed in solutions of PBLG, despite the persistent right-handed sense of the α-helix of this polypeptide.[83] Proposed explanations lie in the change of polymer–polymer interactions due to changes in the side-chain conformation and/or in the degree of solvation with temperature. Yet different and interesting is the case of polymers derived from hexyl isocyanate with pendant chiral groups.[84] These polymers may have right- and left-handed helical backbones and in a sample both forms are simultaneously present, with the one or the other which prevails, depending on the chemical structure and on the absolute configuration of the pendant groups. A shift of the equilibrium was proposed as the cause for temperature induced inversion of cholesteric handedness in these lyotropic liquid crystals.

4. Light-induced helix inversion

The thermal sensitivity of cholesteric mixtures limits their applicability, in particular because their use prevents working at ambient temperature and because little temperature variations will modify their organization. As an alternative to temperature-controlled helix inversion materials, light-sensitive cholesteric

liquid crystals have been developed where helix inversion can be induced by irradiation with light. The successful strategy to develop these materials consists in making use of photochromic switches as chiral dopants in nematic hosts. Photochromic switches are molecules that can be interconverted reversibly between two (*meta*)-stable states by light.[85] This change is the result of photoisomerization, photocyclization, or a combination of both. As a consequence of the interconversion, the interaction of the switches with the nematic liquid crystal is modified also (Section 2a). Helix inversion will consequently occur upon irradiation if the two states of the photochromic dopant are able to induce opposite cholesteric helices and if the photostationary state is sufficiently in favor of the unstable isomer.

4a. Controlling helix inversion by irradiation with UV light

Interest in stimuli-responsive optical materials has recently triggered attention towards photocontrollable cholesteric mesophases, with possible applications ranging from tunable reflectors and lasing elements to displays or information-storage devices. Photoinduced color changes in cholesteric mesophases were first reported in 1971 by Sackmann, who investigated *cis–trans* isomerization of (achiral) azobenzene dissolved in a (chiral) mixture of cholesterol derivatives.[86] Other authors have reported on photoinduced color changes in cholesteric liquid crystals where all mesogens are chiral photochromic switches.[87] However, the most efficient approach is likely to involve the use of chiral photo-responsive dopants. Numerous investigations based on doping nematic phases with chiral and photo-responsive switch molecules have demonstrated large and controllable pitch modifications in cholesteric liquid crystals.[24,88] Photoinduced broadening of the reflection band can be harnessed in tunable reflectors and lasing elements and has been reported recently in commercial nematic hosts doped with binaphthyl-based azobenzene dopants.[89] The large majority of investigations on photoresponsive cholesterics have focused on phototuning *i.e.* changing the spectral position of the reflection notch upon light exposure.[20] In contrast, reports of chiral switchable dopants inducing the formation of cholesteric helices of opposite sign for the two switching states remain scarce. They would not only modify the spectral position but also the handedness of the circularly polarized light that is reflected.

Overcrowded alkenes are chiral and photo-responsive molecules promoting photo-inversion of the cholesteric helix when used as dopants: the helical twisting powers of their stable form and of their photoisomer have opposite signs, which means that the stable cholesteric helix and the helix at photostationary state will have opposite handednesses (Fig. 9).[90,91] Moreover, overcrowded alkenes usually exhibit high values of helical twisting powers in both isomeric forms, which ensures a large photoinduced pitch variation even at low dopant concentration (Fig. 9b). A large variety of overcrowded alkenes with high helical twisting powers and various photoisomerisation and thermal kinetics has been synthesized and characterized.[90] The unique properties of this class of molecules opened the way to various achievements, including reversible full-range color control of cholesteric liquid-crystalline films by photoirradiation,[92] photoinduced rotation of cholesteric textures where the rotation direction was associated with inversion of cholesteric handedness (Fig. 10),[93,94] and

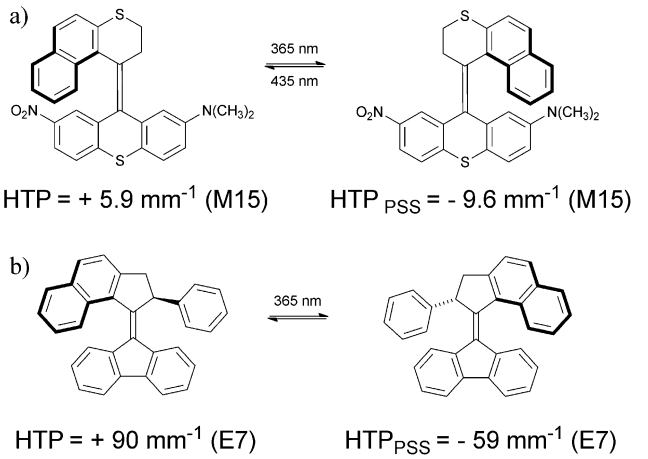

Fig. 9 Examples of overcrowded alkenes promoting photo-induced helix inversion when used as dopants in cholesteric liquid crystals.[24,98] HTP indicates the helical twisting power of the stable form and HTP_{PSS} indicates the helical twisting power at the photostationary state. M15 and E7 are commercially available nematic mixtures.

addressability of the handedness of a helical polymer by irradiation with two different wavelengths.[95] New developments in the future are expected from the exploitation of the coupling between light-induced helix inversion and the special feature of selective reflection of cholesteric mesophases: when the handedness of the helix is reverted, the polarization of the reflected light is also reverted. Inversion of handedness of the reflected light was observed for cholesteric mixtures[96] and in a commercial nematic (achiral) mixture doped with overcrowded alkenes.[97] Albeit relevant for the development of materials involving polarized light, photo-controlling the polarisation of reflected light is seldom reported in literature.

In usual conditions the reorganization of the director under irradiation can be described simply: the process can be seen as helix unwinding under the control of the isomerization process through a sequence of equilibrium states.[98] At a certain stage of the photochemical conversion from one isomer to another, a mixture with a vanishing helical twisting power (HTP = 0 μm^{-1}) and consequently an infinitely long pitch is formed. The inversion point corresponds to the disappearance of the cholesteric texture in optical micrographs under crossed polarizers (Fig. 10b). Under irradiation, the rate of variation of the cholesteric pitch reflects the rate of variation of the mixture's helical twisting power. The helical twisting power resulting from the sum of individual contributions varies with time, in accordance with the evolution in concentration of the two isomers of the dopant, see eqn (2). This evolution instantaneously induces reorganization of the liquid crystal, as can be concluded by considering characteristic times. For a cholesteric liquid crystal, the typical reorganization time is in the order of $\tau_{nem} = D^2\gamma/k_2$ where D is the thickness of the cell, γ is the twist viscosity coefficient and k_2 is the twist elastic constant of the nematic host. For a thickness in the micrometre range, τ_{nem} is of the order of seconds. This typical time is smaller than the characteristic times of photo-isomerization τ_{photo} of most of the photochromic dopants which are currently used ($\tau_{photo} \approx 200$ s for the molecular motor shown in Fig. 9b).[98] Since the whole helix

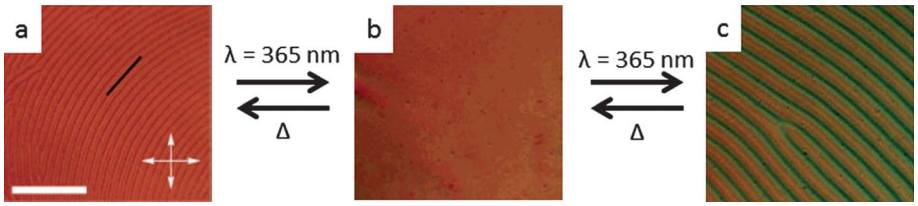

Fig. 10 (a) Photo-controlled modification of the cholesteric texture formed by a thin film of E7 doped with 1 wt% of an overcrowded alkene. The crossed arrows indicate the directions of the crossed polarizers. Scale bar, 50 μm. (b) After 135 s of irradiation with 365 nm light, the inversion point is reached and a non-helical chiral nematic phase (compensated nematic) is formed. (c) Further irradiation induces rewinding of the cholesteric helix with an opposite handedness. Adapted from ref. 94. Copyright (2006) American Chemical Society.

inversion process can be described as a helix unwinding and rewinding under the control of isomerization of the dopants, a proper design of the dopants will allow adjusting the kinetics of helix inversion, both during irradiation and relaxation steps.

The delicate synthesis of optically pure overcrowded alkenes remains a limitation for their use as photo-responsive dopants in cholesteric liquid crystals. Their preparation as enantiopure compounds requires the use of preparative HPLC, which provides little amounts that are not sufficient for potential applications. In order to apply photoinduced cholesteric helix inversion to the creation of new materials and devices, photo-active enantiopure dopants will have to be conveniently accessible in reasonable quantities. Consequently, researchers have investigated the possibility to use other classes of molecules as photoswitchable chiral dopants, most of them based on *cis* → *trans* isomerization (Fig. 11). In 2004, Feringa *et al.*[99] and Spada *et al.*[100] reported light-induced helix inversion in cholesteric mesophases by using a binol-based azobenzene as a dopant. Feringa *et al.* reported that a binaphthyl-based core ensuring chiral induction, symmetrically functionalized by two azobenzene moieties, yields reversible helix-inversion in the commercially available nematic mixture E7 (Fig. 11a).[99] To our knowledge, this result has not been verified in other nematic hosts. Spada *et al.* reported that the HTP of their binaphthyl substituted with one azobenzene (Fig. 11b) reverses sign under UV irradiation in ZLI-2359, a nematic host previously available from Merck.[99] So far, this result is not reproducible in other nematic hosts.[100] Photoinduced cholesteric helix inversion has also been reported in the nematic liquid crystal 5CB doped with derivatives containing chiral α,β-unsaturated ketones, such as the compound shown in Fig. 11c.[101] Reversible helix inversion was recently achieved *via* a combination of photochemical and thermal isomerizations of chiral azobenzenophane derivatives (Fig. 11d) dissolved in 5CB[102] and in other commercially available nematic hosts.[103] However, a drawback of azobenzene derivatives lies in their lack of thermal stability. The search for versatile dopants allowing helix inversion, with high helical twisting powers, remains an ongoing challenge.

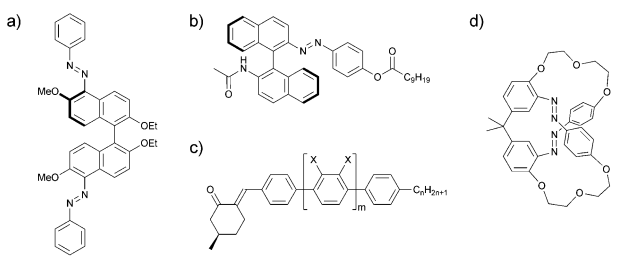

Fig. 11 Examples of photo-responsive dopants promoting helix inversion in cholesteric liquid crystals.[99–103]

4b. Controlling helix inversion with circularly polarized light

A racemic mixture of enantiomers has no resulting helical twisting power. Consequently, a liquid crystal doped with a racemic mixture of enantiomers will form a compensated nematic (or pseudo-nematic) texture, where the pitch is infinite and no chiral character is expressed. This mixture remains pseudo-nematic even under irradiation with non-polarised light, because light has the same effect on dopants with opposite absolute configuration, thus an equal amount of opposite enantiomers is always present in the mixture and the resulting helical twisting power remains zero. However, the use of circularly polarized light allows deracemization of racemic mixtures. Photo-resolution of overcrowded alkenes used as dopants in a nematic liquid crystal by irradiation with circularly polarized light has consequently been used to photoinduce a cholesteric mesophase from a compensated nematic liquid crystal.[104] Reversal of cholesteric handedness by switching polarisation of the incident light appears to be promising for applications.

Conclusion

The systems reviewed here highlight that different external stimuli can be used to induce helix inversion in cholesteric materials, however only a few of them appear really useful in view of potential applications. Control of cholesteric structures with temperature has limitations and allows for only a limited number of applications as it precludes using the materials at room temperature and more generally outside calibrated temperature ranges. Also, cholesteric liquid crystals exhibiting temperature-dependent helix inversion are generally characterized by a large pitch, *i.e.* low chirality. In stark contrast, the use of light as an external stimulus has special advantages, such as being highly orthogonal, quick and easy to apply at room temperature and most importantly it allows precise and reversible control over twist inversion for helices with a large range of helical pitches. We anticipate that the most efficient approach to induce *in situ* helix inversion in future advanced materials will be provided by the use of light as an external stimulus, under the condition that a larger range of efficient dopants are designed and synthesized.

From a fundamental point of view, even the most recent investigations on cholesteric helix inversion demonstrate that predicting which systems will display helix inversion remains a challenge. Even in the simplest systems, oppositely handed contributions are simultaneously present and resulting chirality emerges from a small unbalance between these contributions. Usually, generic models are insufficient to describe these systems and a detailed microscopic analysis is required; on the other hand, this may preclude the use of statistical thermodynamics theories, which are necessarily based on simplified intermolecular potentials, to connect the molecular structure to the mesoscale behaviour. Likewise, this problem cannot be easily addressed by Molecular Dynamics of Monte Carlo simulation techniques. One reason is that accurate atomistic force-fields are needed, together with accurate sampling aimed at reducing the statistical errors, to allow small chiral effects to emerge. Rational design of helix-inversion cholesteric materials will consequently benefit from future theoretical investigations aimed at bridging the gap between molecular chirality and helix inversion in cholesteric liquid crystals.

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