*Encoding smart behavior in chiral
liquid crystal-based materials*

Thesis

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The research described in this thesis was performed within the laboratories of the Biomolecular Nanotechnology (BNT) group, the MESA+ institute for Nanotechnology, and the Department of Science and Technology (TNW) of the University of Twente. This research was supported by the Netherlands Organization for Scientific Research (NWO) and by the European Research Council (ERC).

European Research Council
Established by the European Commission

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Encoding smart behavior in chiral liquid crystal-based materials

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ISBN: 978-90-365-3989-0

DOI: 10.3990/1.9789036539890

Cover image by: Sarah Jane Aßhoff

Printed by: Gildeprint Drukkerijen – The Netherlands

Encoding smart behavior in chiral liquid crystal-based materials

DISSERTATION

to obtain

the degree of doctor at the University of Twente,

on the authority of the rector magnificus

Prof. dr. H. Brinksma,

on account of the decision of the graduation committee,

to be publicly defended

on Thursday November 5, 2015 at 14.45 h

by

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Contents

Chapter 1	Cholesteric liquid crystals - responsive matter for smart materials	
1.1	Introduction to cholesteric liquid crystals	2
1.2	Confinement, textures and polymer stabilization	6
1.3	Properties and their controllability	14
1.4	Conclusion	22
1.5	References	22
Chapter 2	Engineering the cholesteric helix with light	
2.1	Smart thin film reflectors, filters and sensors	26
2.2	Smart thin films for photonic applications	32
2.3	Smart lasers based on photo-responsive cholesteric liquid crystals	36
2.4	Smart polymer films for actuation	41
2.5	Conclusion	47
2.6	References	48

Chapter 3	Time-programmed helix inversion in photo-responsive liquid crystals	
3.1	Photo-induced helix inversion in cholesteric liquid crystals	54
3.2	Results	55
3.3	Conclusions	60
3.4	Methods	60
3.5	Acknowledgments	65
3.6	References	65
 Chapter 4	 Creating and manipulating topological structures with light	
4.1	Introduction	68
4.2	Topological diversity	70
4.3	Opto-molecular control over topological transitions	72
4.4	Discussion	76
4.5	Methods	77
4.6	Acknowledgements	78
4.7	References	79

Chapter 5 Superstructures of cholesteric droplets as all optical switchable distributors of light

5.1	Introduction	84
5.2	Results and Discussion	85
5.3	Conclusion	93
5.4	Methods	93
5.5	Acknowledgments	95
5.6	References	95

Chapter 6 An artificial seed pod from enantiomerically paired networks

6.1	Introduction	97
6.2	Results	101
6.3	Discussion	106
6.4	Methods	107
6.5	Acknowledgments	107
6.6	References	108

Chapter 7

Self-organizing nanoparticles in twisted liquid crystals

7.1	Introduction	110
7.2	Results and Discussion	112
7.3	Methods	122
7.4	Acknowledgments	124
7.5	References	124

Summary 127

Samenvatting 131

Acknowledgments

About the author

Chapter 1

Cholesteric liquid crystals – responsive matter for smart materials

1.1 Introduction

Molecules displaying a liquid crystalline state are characterized by some anisotropy in shape, which accounts for their special properties. Typically, the molecules that display liquid crystallinity have rod-like or disk-like shapes, where one dimension of the molecule is significantly longer or shorter than the other two. In this manuscript rod-like molecules will be discussed exclusively (Figure 1.1). Some rod-like molecules display liquid crystallinity only if they are dissolved in a solvent, usually water. These lyotropic liquid crystals display liquid crystallinity in a specific range of concentrations. Many biological substances are lyotropic liquid crystals, DNA, chitin, cholesterol and some lipids to name but a few. In contrast, the liquid crystals involved in this thesis are thermotropic, which means that they reach the liquid crystalline state within a specific range of temperatures– and secondarily, within a specific range of pressure.

Fig. 1.1: Some usual rod-like thermotropic liquid crystals. E7 is a mixture that was commercialized by Merck, and that displays liquid crystallinity at room temperature. The transition temperatures are in °C [1-4].

1.1.1 Nematic liquid crystals

Rod-like molecules can organise into a variety of liquid crystals, ranging from the achiral nematic and smectic mesophases, to chiral mesophases such as the cholesteric or the chiral smectic mesophases, and including some special transition phases like twist grain boundary and blue phases. These phases are characterised by their order parameter S^{5-7} . Figure 1.2 shows schematic representations for nematic and cholesteric liquid crystals.

Fig 1.2: Schematic representation of a nematic and a cholesteric liquid crystal. The blue rods represent the molecules and the director is depicted as a black arrow.

The research described in this thesis is based on nematic liquid crystals and on their chiral counterparts, cholesteric liquid crystals. In (achiral) nematic liquid crystals the molecules display long range order, because, on average, they are aligned with their long axis pointing in a common direction. This common direction is called the director, and depicted as an arrow (Fig. 1.2). However the molecules do not display any positional order - like stacking for example. The order parameter is $0.3 < S < 0.8$ and can be calculated according to equation 1 with θ being the deviation of a single mesogen axis, compared to the orientation of the director:

$$S = \left\langle \frac{3 \cdot \cos^2 \theta - 1}{2} \right\rangle \quad (1)$$

When considering a cube containing a nematic liquid crystal, and a light beam travelling through this cube, intuitively one understands that the interaction between light and matter will be different, depending on whether the light travels

parallel or perpendicular to the director. This provides liquid crystals with their characteristic birefringence property (Fig. 1.3), an anisotropic, optical property that makes liquid crystals very popular for technological applications such as optical filters, lenses and displays. Strikingly, these properties become even more unusual in their chiral counterparts⁵⁻⁸.

Fig.1.3: How molecular anisotropy is connected to birefringence properties in nematic liquid crystals. The birefringence results from the liquid crystal molecules having two short axes and one long axis. Due to this anisotropy in shape, nematic liquid crystals have different refractive indices in different directions. The refractive indices of two directions are the same $n_{\perp}$ but differ from refractive index in the third dimension $n_{||}$. Therefore, this property of nematic liquid crystals is called "birefringence".

1.1.2 Cholesteric liquid crystals

Cholesteric liquid crystals are the chiral counterparts of nematic liquid crystals. Like nematic liquid crystals, they display positional order: on average, the molecules are oriented with their main axis parallel to each other. Moreover, due to the presence of a few (or more) chiral molecules in the mesophase, cholesteric liquid crystals experience a torque, and, on average, they display a helix-based organisation (Fig. 1.2).

Liquid crystals were found in 1888, when Friedrich Reinitzer discovered that cholesterol shows distinct temperature-dependent colour changes⁸. Cholesterol

Introduction

gave its name to cholesteric liquid crystals. The special optical properties of cholesteric liquid crystals originate from their helical organization, *i.e.* from the cholesteric helix. Circularly polarized light of the same handedness as the cholesteric helix cannot travel along the direction of the helical axis and is reflected instead. Since this only holds for light of a certain wavelength range this leads to the colourful cholesteric reflection that is characterised by iridescent colours. The colour of the reflection depends on the period of the cholesteric helix, which is quantified as the pitch p – the length of a 360° rotation of the director along the helix axis.

Arguably, the most straightforward strategy to prepare cholesteric liquid crystals involves doping a nematic liquid crystal with a few percent of a chiral compound. If the nematic host and the chiral dopant are compatible, then the chirality of the dopant can be amplified at the mesoscopic level of the cholesteric helix. Efficient amplification of chirality can be achieved if the dopant is well soluble in the nematic host and can organize between the liquid crystal molecules in a way that will lead to a tightly twisted cholesteric helix⁹. The ability to induce the twist of the cholesteric helix is called the helical twisting power (HTP). The HTP is specific for each chiral dopant/nematic host pair and follows equation (2):

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

with ee being the enantiomeric excess of the chiral dopant and c the concentration, that can either be the molar fraction or a weight concentration⁸. Importantly, this equation is valid for low concentrations of dopant only. The HTP determines not only the pitch but also the handedness of the cholesteric helix – a negative HTP indicates a left-handed helix and a positive HTP corresponds to a right-handed helix. Notably, there is no direct correlation between the chirality of the dopant and the handedness of the cholesteric helix, and to the best of our knowledge, predicting the sign of the HTP for a given dopant/host pair remains an open challenge. In this thesis I will use the HTP related to the weight percentage (unless otherwise specified).

Fig. 1.4: Some chiral dopants and their helical twisting power in some usual nematic hosts. HTPs are related to wt% of the dopants in the nematic host. Adapted with permission from [9,10] (Copyright 2011 OSA Publishing).

1.2 Confinement, textures and polymer stabilization

1.2.1 Confinement and surface anchoring

Liquid crystals are very sensitive to boundary conditions, *i.e.* the organisation of liquid crystals is influenced by their orientation at interfaces. There are different types of organisation for a nematic liquid crystal in a cell, depending on the alignment that is promoted at the interfaces. Planar organisation is achieved by using glass slides that are spin coated with a polyimide layer and rubbed with a velvet cloth, so that the mesogens are anchored with their long axis parallel to the substrate all pointing in the rubbing direction. Alternatively, perpendicular anchoring at both interfaces will promote a homeotropic organization of the cell. Surfaces promoting perpendicular anchoring include different types of polymer coatings or monolayers of cetyltrimethyl ammonium chloride, phospholipides or similar compounds with long alkyl chains. When one surface promotes planar anchoring, and the other promotes homeotropic anchoring, the liquid crystal undergoes hybrid alignment.

These definitions, where planar alignment corresponds to an alignment that is parallel to the interface, and homeotropic alignment refers to an alignment that is perpendicular to the interphase, is used for other types of liquid crystals also, including cholesteric liquid crystals, and for other geometries of confinement. Chapter 4 and chapter 5 report on the molecular organization and optical properties of cholesteric microspheres submitted to either planar or homeotropic anchoring conditions. Due to the spherical geometry of droplets, the liquid crystals organize into complex supramolecular structures¹¹ that will be discussed in more detail within these chapters.

1.2.2 Textures and polarized optical microscopy

Liquid crystals display special optical properties that can be assessed by simple visual inspection. However, these properties originate at a scale that is much smaller than the resolution of our eyes. Many investigations involving liquid crystals are therefore based on polarised optical microscopy. Polarized optical microscopes are equipped with two linear polarizers that allow determining the direction of alignment of the liquid crystals. The first polarizer is placed between the light source and the sample. Hence the light that hits the sample is plane polarized. The second linear polarizer, commonly named analyser, is placed between the sample and the detector (or the binoculars in the case of a visual inspection). These analysers can usually be rotated from a position parallel to the first polarizer to the crossed position (90° in respect to the polarizer) and further to a parallel position again. Light that has been plane polarized in one direction cannot pass the analyser if this is in crossed position, unless its polarization has been modified by interaction with the sample.

Crystals and liquid crystals are birefringent, which means that these anisotropic materials display different refractive indices for different directions of propagation of light, and depending on its polarisation also. Usually, one specific direction governs the optical anisotropy, whereas all directions perpendicular to the optical axis are equivalent (Fig.1.3, p. 4). Light whose polarization is perpendicular to the optical axis is governed by the so-called “ordinary” refractive index. Light, whose polarization is in the direction of the optical axis, feels the “extraordinary” refractive index.

Plane polarized light can become elliptically polarized after propagating through birefringent materials, and therefore, it can pass the analyser in crossed

position partially. This property of liquid crystals is used to analyse their different phases and phase transitions, alignment orientations and to characterize liquid crystal samples in a more general manner also (their purity for example). Moreover, polarized optical microscopy can provide useful information regarding the reflection properties of chiral liquid crystals, such as the polarization and colour of the light that they reflect. In a recent review, Abbot *et al.* provide a useful introduction to using optical methods for characterizing soft matter¹².

When observed with a polarized optical microscope, liquid crystals generate optical patterns that are called “*textures*”. Each liquid crystalline mesophase displays characteristic textures, depending on the conditions of its confinement. Within textures, the most noticeable features are in areas in which the molecules cannot arrange in their preferred orientation due to geometrical constraints. These points or lines are topological defects, and because they are disorganised they appear dark under a polarised light microscope. Since liquid crystals are fluids, textures are not static signatures of liquid crystal organisation, but they rather change and develop over time, e.g. when defects merge to result in homogeneous areas or to build together a new defect.

In a nematic liquid crystal submitted to planar alignment, light experiences different refractive indices depending on whether it propagates along the optical axis of the sample, or with an angle. Once the light exits the sample the ordinary and extraordinary rays of light recombine to an elliptically polarized beam. This elliptically polarized light can pass the analyser partially, which means that the microscope image becomes bright. Depending on the orientation of the sample, with respect to the direction of planar polarization of the incident light, the brightness and colour of the microscope image change.

If the planar anchoring is non ideal, or if a nematic liquid crystal is inserted in a cell where the glass slides have been covered with a polymer promoting planar anchoring, but not rubbed in a given direction, then the planar alignment of the sample is inhomogeneous: the liquid crystal director is parallel to glass slides but points in different directions. These different orientations generate differences in colour and intensity, the so-called Schlieren textures. Areas of the Schlieren textures where the orientation of the director coincides with the direction of one of the linear polarizers of the microscope are visible as dark brushes. In this texture the points, where two or four brushes meet, correspond to singularities of the director and are called disclinations in the structure⁷.

Introduction

Nematic liquid crystals in a cell with homeotropic alignment cannot be observed under crossed polarizers, since light that travels through a homeotropic nematic sample will not experience any changes in polarisation. Therefore, the light passes the analyser with zero intensity and generates a dark image.

In a cell where the glass slides promote perpendicular anchoring and the thickness is significantly smaller than the pitch of the cholesteric helix, the helix cannot form and the cholesteric film displays a pseudo-nematic texture¹³ (Fig. 1.5). For large cell thicknesses, comparable to the cholesteric pitch or larger, the cholesteric helix forms and cholesteric fingers can be observed under a polarised optical microscope. With further increasing the cell thickness, these fingers evolve until they fill the whole area of the sample. The resulting pattern of alternating dark and bright lines is called fingerprint texture⁶ (Fig. 1.5).

Fig.1.5: Photomicrographs showing the texture observed under crossed polarizers. Left: homeotropic texture of a cholesteric liquid crystal with a pitch that is slightly smaller than the cell gap that shows cholesteric fingers. Right: fingerprint texture of a cholesteric liquid crystal when the pitch is smaller than the cell gap. Scale bars measure 100 μm .

Some cells, instead of being constituted by two parallel glass slides, are made of two glass slides forming a wedge whose thickness increases laterally from zero to several millimetres. These wedge cells are usually treated to induce planar alignment, and their thickness increases laterally, from zero up to several millimetres, depending on the wedge angle and the size of the cell. Wedge cells can be used to determine the pitch of a cholesteric liquid crystal. As with homeotropic boundary conditions, in planar cells there is a critical cell thickness under which a cholesteric helix cannot form. With increasing the cell thickness, the cholesteric helix can form in half-pitch steps with a defect line between areas of

different pitch numbers (Fig. 1.6a). The resulting texture is known as Grandjean-Cano texture, and allows determining the pitch by measuring the distance r_n between two defect lines and inserting in equation (3)

$$(3) \quad p = 2 \cdot r_n \cdot \tan\theta$$

with θ being the angle of the wedge.

Fig. 1.6: Grandjean-Cano texture observed for cholesteric liquid crystals a) in a wedge cell and b) by using a spherical lens. These textures allow measuring the pitch of a cholesteric liquid crystal.

If the cholesteric liquid crystal has been prepared by using a few percent of chiral dopants in a nematic matrix, then knowing the concentration of the chiral dopant, one can also calculate the HTP of a dopant/host pair. However, the handedness of the cholesteric helix has to be determined separately.¹ A similar strategy to determine the pitch of a cholesteric liquid crystal involves a glass slide with planar alignment coating as a substrate and a glass lens as a cover. Since the distance between the lens and the slide also increases gradually from the centre to

¹ Determining the sign of the helical twisting power is usually performed by mixing the unknown liquid crystal with a cholesteric liquid crystal of known handedness.

Introduction

the rim of the lens, a Grandjean-Cano texture forms also (Fig.1.6b). The pitch can be determined by measuring the distance between the circular disclination lines, following equation (4)

$$(4) \quad p = \frac{r_{n+1}^2 - r_n^2}{R_{lens}}$$

where r_n is the radius of the circular disclination lines and R_{lens} is the radius of curvature of the lens^{6,9}.

Fig. 1.7: The oily streak texture and corresponding distribution of the director over the sample. a)-g) Computer simulations and 3D imaging of the director structure of oily streaks. The spatial pattern of the elastic free energy density is calculated and shown by means of the color-coded scale with energy density ranging from that of the minimum-energy uniform cholesteric structure (white) to that of highly distorted regions with highest energy cost (black). (c-e) Computer-simulated cross-sectional images for oily streaks (f,g) Experimental cross-section (h,i) polarized optical microscopy images of cholesteric texture of a planar aligned liquid crystal showing several oily streaks. (a- g) are reproduced with permission from [7] (Copyright 2010 Springer International Publishing AG).

In areas where the thickness of the cell is much larger than the pitch, a cholesteric liquid crystal forms a planar texture that is characterized by several “defect lines”. These lines are actually walls where the supramolecular organization cannot adjust to the preferences of the cholesteric director. The defects are called oily streaks (Fig.1.7) and appear especially when the planar texture gets distorted due to geometrical mismatches or when the system is driven

out of equilibrium by external stimuli. The areas between the oily streaks have usually uniform organization and are called domains⁷.

1.2.3 *In-situ cross-polymerization and preservation of the liquid crystalline order*

Liquid crystals respond to a variety of external stimuli, and by definition, thermotropic liquid crystals respond to changes in temperature primarily. Dependence of liquid crystal order to temperature can be an advantage for applications like sensors that change their colour in response to heat. However, for many applications it is important that the liquid crystalline materials are stable towards variations in temperature. Early studies dating back to the 1980s¹⁴⁻¹⁶ have shown that one strategy to overcome temperature-dependence of liquid crystals consists in fixing liquid crystal organization by using *in-situ* polymerisation of reactive liquid crystal monomers. Commonly, these reactive liquid crystals contain one or two acrylate end groups that are connected via flexible spacers to a rigid core. Provided that a photoinitiator is added to the mixture, these reactive molecules photo-polymerize. The rigid core usually consists of three aromatic rings, while cores containing two aromatic rings or cores that contain cyclohexyl rings are used also. Not all these monomers display liquid crystallinity at room temperature, but even so, some can have a positive influence on the performance of the liquid crystal polymer network that is formed in the end. Another means to tune the properties of this liquid crystal polymer consists in changing the length of the spacer. For synthetic reasons the use of alkyl spacers containing four or five carbons is rather uncommon. Many reactive monomers have alkyl spacers with three or six carbons. Some reactive monomers display even longer spacers, for example alkyl chains with eleven carbon atoms. However, these molecules are often less relevant for the preparation of thin films, since they tend to be more affected by crystallization.¹⁷ Figure 1.8 shows examples of commonly used reactive mesogens.

Fig.1.8: Examples of acrylates and diacrylates used as reactive mesogens to perform *in-situ* polymerization.

In the presence of traces of photo-initiator, the reactive monomers can form networks via light-induced radical polymerization, in the absence of oxygen. The polymer network that will form after cross-polymerization will consequently freeze the liquid crystalline order. The liquid crystal properties that are related to the fluid character will be strongly altered. However many properties that are related to anisotropy and the organization of molecules can be preserved.

In-situ polymerization can yield complex composite materials, when not all liquid crystals are polymerisable, but instead, only a specific percentage of polymerisable liquid crystals are added to classical liquid crystals. Depending on the ratio between liquid crystals and reactive monomers, *in-situ* polymerization can lead to either a polymer network that stabilizes the liquid crystal organisation, or to phase-separation with liquid crystal droplets that are dispersed in a liquid crystal polymer. These two types of liquid-crystal-based materials are called polymer stabilized liquid crystals (PSLCs) and polymer-dispersed liquid crystals (PDLCs), respectively (Fig.1.9). Detailed information about available reactive mesogens, photo-initiators and about the specifics of *in-situ* polymerization has been reported in several books and reviews¹³⁻¹⁸.

Fig.1.9: A thin film of polymer-stabilized cholesteric liquid crystal (left panel). Reproduced from¹⁹ and a thin film of polymer-dispersed liquid crystal (right panel), as observed by scanning electron microscope. Reproduced from²⁰.

Chapter 7 reports on the organization of superparamagnetic nanoparticles in a thin film of polymer-stabilised liquid crystal. In chapter 6, a liquid crystal polymer network is prepared as a self-standing material that can display advanced actuation modes under irradiation with light. In that material, some nematic molecules were added to the liquid crystalline blend in order to optimize the balance between flexibility and robustness of the film.

1.3 Properties and their controllability

1.3.1 Optical properties of cholesteric liquid crystals

Chapter 3 and Chapter 5 report on progress towards the precise, reversible and selective photo-control over the unique optical properties of cholesteric liquid crystals, with a special focus on their selective reflection. Indeed, cholesteric liquid crystals reflect circularly polarized light of a certain wavelength range, selectively, as a result from their overall helical organization⁷. Figure 1.10 represents a cholesteric liquid crystal in a planar cell schematically. Considering that the pitch is $300 \text{ nm} < p < 600 \text{ nm}$ and the cell thickness is $d = 10 p$, the cholesteric helix will be in its relaxed, non-frustrated state with the helix axis oriented perpendicular to the glass slides. Irradiation of such a sample with white light directed parallel to the helix axis leads to a Bragg-like reflection of circular polarized light in a wavelength range centred on λ_0 defined by

$$(5) \lambda_0 = n \cdot p$$

Introduction

with n representing the mean refractive index of the cholesteric liquid crystal. Because of birefringence, the width of the wavelength range $\Delta\lambda$ depends on the value of λ_0 and typically varies between 50 nm and 100 nm in the UV and visible range. The selective reflection of cholesteric liquid crystals is not strictly speaking a Bragg diffraction. Intuitively, selective reflection occurs because the component of the light that is polarized with the same handedness as the cholesteric helix cannot pass through the sample, whereas the part of the light that is polarized with opposite handedness can.

Fig.1.10: Schematic representation of the selective reflection of a cholesteric liquid crystal in a planar cell. (The reflected and transmitted light would only be completely circular if the angle $\theta = 0$. In the scheme above the light should be elliptically polarized)

If selective reflection occurs in the visible range, the sample shows reflection colours that can be detected by visual inspection or under the optical microscope. However, depending on the pitch, selective reflection can occur outside the visible spectrum also, in the UV or near infrared for example. Optical spectroscopy is commonly used to study selective reflection in these wavelength ranges. Figure 1.11 depicts a typical reflection band and a typical circular dichroism spectrum. The latter shows the chirality of the cholesteric by measuring the difference in absorbance of left-handed and right-handed circular polarized light.

If the incident light does not propagate parallel to the helix axis but with an angle θ with respect to the direction of normal incidence, the reflected light is not circularly polarized but instead displays elliptical polarization. Also the wavelength of reflection blue shifts according to equation (6)

$$(6) \lambda_{\theta} = n \cdot p \cdot \cos\theta$$

Nature makes use of the angle-dependence of selective reflection, to produce the iridescent colours of some fruits²¹, shells and beetle cuticles²²⁻²⁵ (Fig.1.12), which has inspired material scientists and engineers in the development of several technological applications.

Fig.1.11: Typical optical spectra for thin films of cholesteric liquid crystals in planar cells. a) Visible spectrum showing a typical cholesteric reflection band and b) circular dichroism spectrum of a cholesteric liquid crystal. The signals being positive and negative show that cholesteric with both handedness's are present in the sample.

Fig.1.12: The surface of an iridescent beetle shell is reminiscent of a stabilised liquid crystal texture (Credit: Zina Deretsky, National Science Foundation).

Since the cholesteric helix determines the reflective properties of cholesteric liquid crystals, any changes in pitch, handedness or orientation of the helix influences the reflection. In display technology the common strategy to achieve this effect consists in manipulating the orientation of the cholesteric helix by using an electric field.²⁶ Because of their dielectric anisotropy, the molecules reorganize under an electric field, and form new textures with different optical properties. Cholesteric liquid crystals with a negative dielectric anisotropy switch from a transparent, well-organized planar state to a scattering state by applying a low frequency electric field. This scattering state can be maintained after removal of the electric field and can be switched back at higher frequencies. Alternatively, the reflection blue-shifts, applying an electric field is parallel to the helical axis of a planar aligned cholesteric liquid crystal with a positive dielectric anisotropy. It is still unknown whether this reflection shift results from either a periodic distortion of the texture or from a field-induced pitch gradient. However, the thermal instability of cholesteric liquid crystals remains a challenge for electronic applications of displays. Indeed, the pitch depends on the helical organization of the liquid crystal, and the order decreases with increasing temperature, which means that the reflection colour of cholesteric liquid crystals usually shifts with small variations of temperature (Fig.1.13)²⁷.

Fig. 1.13: Example of thermochromic effect for a cholesteric liquid crystal. The reflection colour blue-shifts with increasing temperature. Adapted with permission from [28] (Copyright 2008 AIP Publishing LLC).

Photo-controlling the cholesteric helix to achieve pitch-dependent colour changes appears as a very valuable alternative to using temperature. In order to do so, light-responsive liquid crystals can be designed by making use of photo-

responsive molecular switches. Shifting the reflection wavelength was reported at early stages and can be achieved by using azobenzene switches as dopants in cholesteric liquid crystals. Indeed, azobenzenes are characterised by their shape anisotropy in the *trans*-state, which is compatible with liquid crystal ordering, whereas the photo-induced *cis*-isomer is bent and disturbs the liquid crystal order, which leads to a decrease of the nematic–isotropic transition temperature and an increase of the pitch (Fig.1.14).

Fig.1.14: The photo-isomerisation of the azobenzene switch (a) decreases the isotropic transition temperature, when the switch is used as a dopant in a nematic liquid crystal (b). T_{NI} is the nematic–isotropic transition temperature.

Besides photo-controlling the pitch, the use of photo-responsive switches as dopants allows controlling also the handedness of the cholesteric helix, *i.e.* the polarity of the reflection in response to irradiation with light²⁹. Only very few dopants can be used for this purpose however, and among these the most versatile series are the light-driven molecular motors developed by Prof. Feringa at the University of Groningen (Fig.1.15). These motors are overcrowded alkenes that undergo unidirectional rotation around the central C=C bond when irradiated with UV light. Overall, these molecular motors have a helical shape and their helical chirality is amplified by cholesteric liquid crystals efficiently – in other words,

Introduction

molecular motors based on overcrowded alkenes display large helical twisting powers in typical nematic liquid crystals. The sign of their helical twisting power is determined by their molecular handedness, and upon photo-isomerisation, it is known that molecular motors undergo helix inversion³⁰⁻³². While each individual motor undergoes a continuous unidirectional rotation, as long as irradiation with light proceeds, at the ensemble level, the proportion of motor molecules at each of the four positions will reach an equilibrium determined by the kinetics of each step, the intensity of irradiation and the thermal relaxation of the motor. Since each position can have a different HTP, the state of the cholesteric helix and the related optical properties at the photo-equilibrium are determined by the ratio of motor at each position. Once irradiation stops, the cholesteric liquid crystals doped with molecular motors relax to their initial pitch and handedness. This relaxation process is discussed in Chapter 3.

Fig.1.15: An example of light-driven molecular motor from the first generation and its rotation cycle under irradiation with UV light (a). When used as chiral dopant in a liquid crystal, molecular motors allow controlling the period of the cholesteric helix and its handedness, simultaneously (b). Reprinted from [32].

The unique optical properties of liquid crystals were at the origin of their discovery, yet their potential applicability was not clear from the beginning. In particular, their fluid character made it necessary to confine them between solid substrates, such as glass slides. Liquid crystal films were stabilized by *in-situ* polymerization to overcome this issue by creating self-standing materials. However, polymerization can modify the optical properties of liquid crystals considerably. For example, the reflection band of cholesteric liquid crystals usually shifts upon polymerization, because of changes in the refractive index and because of anisotropic shrinkage. In fully polymerised liquid crystal polymers, the optical properties are not responsive anymore towards external fields, temperature and light. In strong contrast, polymer-stabilized liquid crystals display altered optical properties but retain a dynamic behaviour. Depending on the ratio of non-polymerisable liquid crystal over reactive monomers, the materials show properties of a homogeneous phase or properties of both phases. For cholesteric liquid crystals, the latter situation can lead to increased bandwidths of reflection or increased operation voltages and multi-state behaviour for electric field switching. In any case, the polymer network induces a memory effect that can significantly decrease the relaxation times of the system³³⁻³⁵. However, the formation of a polymer network can also induce unwanted effects on the properties of liquid crystals. During *in-situ* polymerization, the liquid crystalline organization can be disturbed and domain sizes can decrease, which can generate a lot of scattering and overall, the transparency and reflection of the film can be damaged³⁶.

1.3.2 Mechanical properties of liquid crystalline elastomers

If the *in-situ* formation of a liquid crystal polymer network does modify the optical properties of a liquid crystal, it can also have considerable effects on the mechanical properties of the material. In self-standing films of liquid crystal polymers, changes in the molecular organization are amplified efficiently and induce macroscopic shape changes. In particular, liquid crystal polymer films do not shrink or swell to the same extend in all directions. Like all structurally determined properties these anisotropic shape changes can be induced by several stimuli of which the most common are: humidity, temperature and light^{37,38}. Shape changes induced by humidity differ from the other two, since in this case they are related to changes in volume. During shrinking or swelling of the material the water molecules will locate between the liquid crystal molecules.

Introduction

In liquid crystal polymers, temperature-induced deformations result from a decrease in liquid crystalline order, similarly to what is described above regarding temperature-induced changes of optical properties. Imagine a cuboid of polymer-stabilised liquid crystal, having a rectangular base. Upon temperature increase the liquid crystal becomes more disordered: the cuboid contracts along the director and expands perpendicular to it until isotropic organisation is reached and the film assumes a more cubical shape. Similarly, liquid crystal elastomers can deform anisotropically when the order decreases during heating. In the literature many examples of temperature induced deformation and resulting motion of films have been demonstrated¹⁷.

Fig.1.16: Schematic representation for the anisotropic deformation of a liquid crystal polymer network containing azobenzene photo-switches, under irradiation with light.

Embedding azobenzene switches in liquid crystal polymer networks allows designing films that show strong deformations in response to light^{39,40} (Fig.1.16). The disordered state is induced by the photo-isomerization of the azobenzene switches and can thermally as well as photonically relax back to the initial ordered state. Since light is a non-contact trigger, the deformation process can be precisely controlled in terms of time and space. Therefore light-controllable liquid crystal polymer films that move due to anisotropic deformations are promising candidates for soft actuators and researchers are constantly working on materials that can show complex movements and show high efficiency in converting the light energy into motion. In a recent publication Broer and co-workers describe the mechanism of a photo-induced anisotropic deformation based on azobenzene containing liquid

crystal polymer films and its effect on the surface morphology⁴¹. Chapter 6 reports on a liquid-crystal-based photo-actuator inspired by the motion of a chiral seedpod.

1.4 Conclusion

The intrinsic anisotropy of nematic and cholesteric liquid crystals is at the origin of special optical and mechanical properties that can be controlled by using external stimuli such as temperature, light or other external fields. One of the major challenges in using these materials for applications consists in stabilizing their structure without forfeiting their responsiveness, which is mostly approached by *in-situ* polymerization. While thin films of liquid crystals have already found a large number of applications, new opportunities emerge from exploiting liquid crystalline materials in the third dimension. Spherical and cylindrical confinements as well as three-dimensional movements offer new topologies and properties, and thereby also new possible applications. At the same time, research is developing towards optimizing the triggering mechanisms and control systems, with light being definitely one of the most promising. Chapter 2 reviews recent achievements in using photo-responsive cholesteric liquid crystals for smart materials and their possible applications beyond displays.

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Chapter 1

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Chapter 2

Engineering the cholesteric helix with light

Nematic liquid crystals and their chiral counterparts have found various applications as dynamic functional materials for information and mass transport, sensing, catalysis, as templates, and in photonics, energy technology and, infamously, in electro-optical displays¹⁻¹¹. In these applications electric fields are used primarily to switch between macroscopic properties. However, electricity as a control system is stretched to its limits, as new technologies ask for faster switching times and for localized, convenient and contact-free stimuli. Light appears as an ideal alternative, and the potential of this approach was highlighted throughout the 2015 “Year of Light”. In this chapter, inspiring examples are discussed, where photo-controllable cholesteric liquid crystals have been used to design technologically-relevant systems.

2.1 *Smart thin film reflectors, filters and sensors*

The selective reflection of cholesteric liquid crystals has been at the origin of the discovery of liquid crystals¹², and since then this property has been investigated thoroughly. Currently, this property is harnessed in filters, reflectors and sensors based on cholesteric liquid crystals.

Photo-responsive cholesteric liquid crystals are able to change their reflection colors upon irradiation with light. The design, development and understanding of light-responsive cholesteric liquid crystals have been reviewed previously¹³. More recently, there is a growing interest in optical materials that adjust not only the wavelength of their reflection but also its polarity, in response to external stimuli. These materials are potentially relevant for applications involving circularly polarized light¹⁴. Photo-responsive cholesteric liquid crystals that switch the handedness of their light reflections must contain a minimal proportion of photo-switchable molecules that can invert the handedness of the cholesteric helix, which determines the polarity of the reflection.

Molecular motors based on overcrowded alkenes invert the handedness of the cholesteric helix, upon proper irradiation with light¹³. These molecular motors, pioneered by the group of Prof. Feringa (see also 1.3.3), consist of an upper half and a lower half connected by a central C=C bond (Fig.2.1). Because of steric hindrance the two halves are tilted towards each other leading to a helical shape. During irradiation with light, a left-handed motor isomerizes to a right-handed isomer that can relax thermally to provide an isomer with the initial handedness. Sequential photo-isomerization and thermal helix inversion of these molecules induces unidirectional rotation around the central C=C double bond, hence these motors are rotary motors.

Fig.2.1: Schematic representation of the unidirectional rotation of molecular motors based on overcrowded alkenes (used in chapter 3). This molecular design was pioneered by the group of Prof. Feringa [15].

Molecular motors based on overcrowded alkenes can be used as dopants in nematic liquid crystal hosts. Overall, the liquid crystal molecules adapt their organization to the 3-dimensional geometry of the motor and amplify its helical shape up to the cholesteric helix. During photo-isomerization, the fraction of photo-isomer increases at expense of the stable isomer that has an opposite handedness, leading to a decrease in the absolute value of the effective HTP. After passing the pseudo-racemic point where the HTP of both populations cancel out, the absolute value of the effective HTP increases again, with the opposite sign. For the cholesteric helix, this translates into a photo-induced unwinding, helix inversion and final rewinding that are accompanied by red-shifting, disappearance, and blue-shifting of the cholesteric reflection, respectively. The inverse behavior is observed during relaxation, in a different time-scale however, as the relaxation is much slower than the photo-step.

Rational design principles have been developed to make molecular motors with desired properties^{16,17}. However, not all molecular motors are well soluble in nematic hosts and even when soluble they do not always display high HTPs in usual hosts^{18,19}. Helix-inverting photochromic cholesteric liquid crystals have been

developed, based on several different nematic hosts and doped with different types of molecular motors¹⁸⁻²⁰. Notably, a few motor/host pairs are characterized by high HTPs, both in the initial stage and at photo-equilibrium. Therefore, the reflection of these materials can be tuned within the entire spectrum of light, from UV to near infrared, and in both circular polarizations²¹. Another advantage of motor-doped cholesteric liquid crystals is that their relaxation times can be engineered to become relatively short compared to other dopants. Many applications including tunable reflectors, light-sensitive sensors and filters can be envisioned but are still somewhat limited by the elaborate synthesis and purification procedures needed to produce the molecular rotors.

Besides molecular motors, azobenzene-based chiral derivatives can also display photo-induced helix inversion, under some conditions, binaphthyl-derivatives^{22,23} and α,β -ketone based dopants in particular (Fig.2.2). Currently, these dopants do not outperform overcrowded alkenes as dopants, and they lack versatility.

Fig.2.2: Chiral azobenzene-based switchable dopants that can invert the cholesteric helix under irradiation with light [22-26].

Recently, helix inversion was also achieved by using as dopants bicyclic azophanes with planar chirality²⁶ (Fig.2.3). However, the HTP of these compounds in their stable all-*trans* form is very low in all three nematic hosts that were investigated. In two of these nematic hosts, Tamaoki and co-workers could achieve inversion of the cholesteric helix and the related inversion of handedness of the cholesteric reflection. With either UV or visible light the all-*trans* compounds isomerize into a *trans-cis* isomer and an all-*cis* isomer as well. Both photo-isomers induce the opposite helix sense compared to the all-*trans* isomer. Depending on the

ratio of the isomers, the dopant mixtures at photo-equilibrium can reach relatively high HTP values. The addressability of these dopants using visible light is an advantage considering the safety risks related to the use of UV light. However, visible light can be rarely used as a trigger without affecting its intended performance. Furthermore, the time that is required to recover the initial reflection is rather long (about 12 h). This relaxation time is too long for fast switching but too short to use it for fixing the photo-state.

Fig.2.3: Bicyclic azophane-based dopants and HTP values in 5CB. Adapted with permission from [26] (Copyright 2009 Royal Society of Chemistry).

A year later Li and co-workers followed up on this work by using light-driven cyclic azobenzenophanes to induce helix inversion in cholesteric liquid crystals (Fig.2.4)²⁵. The dopants that showed axial chirality were mixed into three commercially available nematic hosts and showed low to moderate HTPs. Under irradiation with UV light ($\lambda = 360\text{nm}$) the HTPs can be switched to slightly lower absolute values of the opposite sign. Interestingly, the process can be reversed by irradiation with visible light ($\lambda = 440\text{nm}$), which leads to HTPs close to the initial values. Azobenzenophane-doped cholesterics are therefore interesting for two-way optically switchable materials but the relatively short stability of the photo-equilibrium state would constitute a shortcoming regarding optical data storage and similar applications: 8h are required to relax back thermally from the UV-induced photo-state.

$$n = 3, 5$$

dopant	host NLC	β (wt%) μm^{-1}			$\Delta\beta/\beta$ (%) ^a
		initial	PSS _{UV}	PSS _{vis}	
(R)-1	E7	+40	+7	+30	83
	K15	+50	-10	+43	120
	ZLI-1132	+8	-26	+6	425
(R)-2	E7	+32	-10	+26	131
	K15	+12	-18	+8	250
	ZLI-1132	+32	-16	+24	150

Fig.2.4: Cyclic azobenzenophane-based dopants and HTP values of bicyclic azobenzenophane-based dopants. Adapted with permission from [25] (Copyright 2010 ACS Publications).

Fig.2.5: Dithienylethene based dopant that undergoes a ring-closure reaction under UV light. Used as a dopant in a cholesteric liquid crystal their photo-isomerization can induce helix inversion. The process is reversible using visible light. Adapted with permission from [27] (Copyright 2012 ACS Publications).

Besides photo-switches undergoing *trans*-to-*cis* isomerization, some dopants undergo a photo-induced, reversible transition from an open to a closed form. In 2012 Hayasaka *et al.* reported dithienylethenes derivatives that are characterized by low HTPs but can induce helix inversion under irradiation with $\lambda = 254$ nm. The reverse process was achieved under irradiation with visible light ($\lambda > 400$ nm) (Fig.2.5). As photo-responsive dopants, dithienylethenes show outstanding fatigue resistance, thermal stability and all-optical switching behavior and consequently hold promise for all-optical, flexible displays, optical data storage and asymmetric synthesis of organic molecules and polymers. However, their low helical twisting powers and tuning ranges limit their application prospects¹⁷.

Among dithienylethenes, some chiral derivatives (Fig.2.6) show much higher HTPs, while retaining propensity to induce helix inversion, thermal stability, fatigue resistance and two-way optical switching also using $\lambda=310$ nm and $\lambda=550$ nm¹⁴. Therefore these dopants reported by Li *et al.* show higher applicability for optical data storage. However, the kinetics of the photo-conversions are still in the time scale of several tenth or even hundreds of seconds, which is much slower than needed for such applications.

Careful analysis of the state of the art shows that dynamic wavelength tuning as well as polarity switching has been achieved in light-responsive cholesteric liquid crystals. Consequently, these materials have been recognized as promising candidates for future optical technologies involving reflection. However, these technological applications ask for systems with increased thermal stability, while retaining photo-reversibility. Also, regarding computational and biomedical devices it appears that sensitivity towards irradiation with near IR light remains a major challenge that could be addressed by using azobenzene derivatives²⁸⁻³⁰.

In parallel to improving the performances of molecular photo-switches as dopants, also the stabilization of the liquid crystals by *in-situ* polymerization offers room for improvement as well as unexplored benefits^{31,32}.

Fig.2.6: Dithienylethene-based switchable dopants for photo-responsive cholesteric liquid crystals show high HTP values because of their bridged binaphthalene based substituents. Adapted with permission from [14] (Copyright 2013 John Wiley & Sons, Inc.)

2.2 Smart thin films for photonic applications based on phase transitions

The above-mentioned applications are solely based on adjusting the cholesteric reflection with light. Other photonic applications require designing materials, the optical properties of which can be switched on and off, reversibly. In most displays, on and off switching originates from electric field-induced changes in the liquid crystal order, or in anchoring transitions. With light, similar mechanisms can be implemented by using the photo-induced decrease of anisotropy. This strategy will lead to the development of all-optical systems. As mentioned in section 1.3.1, the liquid crystalline order can be reduced optically and isothermally in azobenzene-doped cholesteric liquid crystals. As a consequence of the photo-induced *cis* to *trans* isomerization, these dopants lose their nematogenic form, which can trigger migration of the dopants towards interfaces, phase segregation, and induce cholesteric-to-isotropic phase transitions. Kundu *et al.* have reported on

an azobenzene-doped cholesteric liquid crystal confined between two indium tin oxide coated glass slides (Fig.2.7) that undergoes a phase transition and an anchoring transition simultaneously. Under irradiation with UV light, the cholesteric film becomes pseudo-nematic and due to migration of the dopant towards the interfaces, the anchoring changes from planar to homeotropic (perpendicular). This photo-induced anchoring transitions is promising for large scale productions, while the irreversibility of the process limits the range of applications related to switchable systems³³.

Fig.2.7: Photo-induced simultaneous anchoring and phase transitions in cholesteric liquid crystals containing azobenzene moieties. Adapted with permission from [33] (Copyright 2013 OSA Publishing).

The complete phase transition from a reflective cholesteric liquid crystal towards the transparent isotropic phase has been reported by Wei *et al.*, also using azobenzene-based molecular switches as dopants (Fig.2.8)³⁴.

Fig.2.8: Cis-trans grating in a film of azobenzene-doped cholesteric liquid crystal. (a) Molecular structure of the azo-dyes undergoing a trans-cis photo-isomerization. (b) Equivalent energy diagram: after photo-excitation, molecules decay to the cis state, which is metastable and transforms back to trans. (c) Pictorial representation of the azo-dye doped cholesteric liquid crystal: the red rods represented the dye in its trans state aligned with the helical structure of the chiral nematic host; in the illuminated region the rods bent into a V-shape (cis form), altering the local order parameter. Adapted with permission from [34] (Copyright 2013 OSA Publishing).

Fig.2.9: Optical aperture based on a photo-controlled isothermal phase transition. Adapted with permission from [35] (Copyright 2014 OSA Publishing).

Moreover, the nematic-to-isotropic phase transition could be photo-induced locally, by using high input power Gaussian beams in a cholesteric liquid crystal doped with the azo-dye methyl red. The isotropic phase was segregated from the nematic phase by an interfacial wall that can be regarded as a photo-controlled optical aperture³⁵ (Fig.2.9).

While all cholesteric liquid crystals doped with azobenzenes can undergo light-triggered phase transitions where the order is decreasing, there are only a few systems in which the liquid crystalline order could be enhanced by irradiation with light. Kurihara *et al* have used spiropyrans to induce an isotropic-to-nematic transition, almost 15 years ago (Fig.2.10)³⁶. Kosa *et al.* have recently demonstrated an isotropic-to-cholesteric transition using naphtopyran switches. Materials like this are promising for photonic lasing, solar energy harvesting or photochromic and polarized variable transmission sunglasses³⁷.

Fig.2.10: Structures and phase transition temperatures of spiropyran-based liquid crystals. Adapted with permission from [36] (Copyright 1991 Royal Society of Chemistry).

Photo-controlling phase transitions and texture transitions in cholesteric liquid crystals show potential towards optical data storage, signaling, sensing and applications in the field of energy technologies. However, current achievements do not include self-standing materials and moreover, the temperature stability and switching kinetics of these materials remain a challenge.

Fig.2.11: Structures and isotropic-to-cholesteric transition temperatures of naphthopyran-based liquid crystals. Adapted with permission from [37] (Copyright 2012 Nature Publishing Group).

2.3 Smart lasers based on photo-responsive cholesteric liquid crystals

Lasers are not only used for research purposes but also in a broad range of applications encompassing communication, industry, medicine, and environmental care also. A majority of lasers are based on photonic bandgap (PBG) materials. In cholesteric liquid crystals, the energy levels of the cholesteric reflection are forbidden to transmit light, and therefore they are considered photonic bandgap materials. Cholesterics are thus used for lasing also, with the advantage of being compact, all-organic, self-assembled materials that are able to emit a quasi-continuous wave multi-directionally and can be tuned within a large spectral range.³⁷ Even though not all these properties have been achieved in one single material so far, liquid crystals lasers³⁹ remain a very contemporary research area and large area holographic laser displays, miniature medical diagnostics and skin treatment are envisioned as applications⁴⁰.

Liquid crystal lasers are currently limited by their lasing threshold, which inhibits the use of low-power and incoherent light sources. In order to compensate for this shortcoming, one option consists in improving their electrical control. Another option involves photo-controllable cholesteric liquid crystals. Most photo-controllable liquid crystal lasers that have been reported are based on the use of azobenzene-based dopants. Under irradiation with UV light, these lasers show either reversible or irreversible wavelength shifting of about 15 nm, and some show wideband wavelength lasing also. An increase of the tuning spectrum was achieved by Chen *et al.* by using a cholesteric liquid crystal with a chiral azobenzene moiety as a photo-responsive PBG material and added quantum dots as a gain material (Fig.2.12)⁴¹. The result was an optically highly stable and flexibly tunable laser that showed a 60 nm emission red-shift under irradiation with UV light and a 40 nm blue-shift under irradiation with blue light. The material was proposed for single photon lasing.

Fig.2.12: Laser based on cholesteric liquid crystals, and doped with quantum dots. The cholesteric containing an azobenzene-based switch shows a pitch increase under UV light. The reverse reaction can be induced with visible light. Depending on the pitch of the helix, the wavelength of laser emission can be tuned. Adapted with permission from [41] (Copyright 2014 Royal Society of Chemistry).

Humar *et al.* have demonstrated a simple way to produce liquid crystal droplets that could be used as low-loss whispering-gallery-mode resonators⁴². The nematic droplets were embedded in a polymer matrix and their lasing properties could be tuned electrically (Fig.2.13). While the method appears straightforward, the droplets were lacking stability and monodispersity. These shortcomings could be addressed by encapsulating cholesteric liquid crystals in spherical polymer shells, using interfacial polymerization to confine a cholesteric liquid crystal in a polyurea shell⁴³. Guo *et al.* show that these cholesteric microcapsules embedded in a polymer film are reflective and that the reflection can be either left-handed circular polarized, right-handed circular polarized, or even a combination of both polarities (Fig.2.14). The authors also demonstrate that the reflection wavelength can be tuned thermally and report on the influence of droplet size monodispersity and shell thickness on the reflection properties. While there is not much information about the textures of the cholesteric microcapsules, the combination of stability and responsiveness seems promising for smart spherical lasers. Even more promising is the approach of Lee *et al.* that encapsulate cholesteric liquid crystals in a hydrogel membrane (Fig.2.15). In this work, monodisperse droplets were generated in a microfluidic device, yielding free-standing microcapsules with a dynamically tunable cholesteric reflection⁴⁴.

Fig.2.13: Spherical liquid crystalline droplets and their potential application to spherical lasers. Adapted with permission from [42] (Copyright 2009 Nature Publishing Group).

Fig.2.14: Film composed by self-standing droplets of cholesteric liquid crystals and schematic representation of their lasing properties. Adapted with permission from [43] (Copyright 2013 Royal Society of Chemistry).

Fig.2.15: Mono-disperse hydrogel capsules filled with a cholesteric liquid crystal, and their reflective properties. Adapted with permission from [44] (Copyright 2015 John Wiley & Sons, Inc.).

The stability of the droplets can be enhanced further by *in-situ* polymerization of the liquid crystal droplets. In particular, Cipparrone *et al.* have created cholesteric polymer beads (Fig. 2.16) and characterized their optical properties by polarized optical microscopy⁴⁵. They claim that the polymer network fixes the optical properties of the cholesteric droplets and envision using similar beads as optical microresonators and lasers. However, the stability of these beads comes at the costs of their dynamic properties. Besides lasers, the authors also suggest using these polymerized cholesteric beads for optical manipulation experiments that involve optical tweezers. Such experiments have attracted much attention recently, and an example involving cholesteric droplets was reported by Brasselet and co-workers⁴⁵. They demonstrated passive optical sorting of chiral material without chiral morphology using cholesteric droplets and circular polarized light sources (Fig. 2.17). The sorting mechanism was based on a spin-dependent optical force and development of more optical sorting strategies based on orbital-dependent optical forces are envisioned.

Fig.2.16: Reflective properties of cholesteric polymer beads. a-f) Optical microscopy images of the chiral microspheres (short pitch). Pictures in the left column are taken in transmission configuration through crossed polarizers, while pictures in the right column were obtained in reflection mode. g) The microparticles after the water evaporation (upper left); the magnification shows the polymerized particles (100 $\times$ objective). Adapted with permission from [45] (Copyright 2011 John Wiley & Sons, Inc.)

A new dimension of opportunities appears to become accessible with exploring materials with 3-dimensional shapes. While research is still focused on thin films of cholesteric liquid crystals primarily, cholesteric liquid crystals confined into 3D shapes like spheres and cylinders trigger a constantly growing interest. Key challenges are the combination of stability and adjustability of the reflection/emission, as well as a high degree of monodispersity. These key challenges might be tackled successfully by using encapsulation techniques for photo-responsive cholesteric liquid crystals, combined with droplet generation in microfluidic systems.

Fig.2.17: Chiral sorting of cholesteric droplets with circularly polarized light. Adapted with permission from [46] (Copyright 2014 Nature Publishing Group).

2.4 Smart polymer thin films for actuation

Optics and photonics are usual fields of applications for liquid crystalline materials, but there is growing interest in their photomechanical properties also. As mentioned in the first chapter briefly, liquid crystal polymer films undergo anisotropic shape changes that can alter surface properties or lead to microscopic and macroscopic motion. Within the last years, liquid crystal polymer films doped

with azobenzenes have become a vivid and quickly growing research field, reviewed in several publications⁴⁷⁻⁵². Most of the early work was focused on nematic films bending under irradiation with UV light. Mostly the motion was induced by irradiation from one side of the film, which leads to anisotropic contraction on this side only, and eventually results in bending towards the light source^{53,54}. Furthermore, researchers studied the influence of the concentration and location of the azobenzene-dyes as well as the use of light of different wavelengths and polarization. Kondo *et al.* demonstrated that the concentration of azobenzenes affects the polymerization degree and the macroscopic deformation while the location of the azobenzenes, meaning the position of the switch within the side chains or as cross-linkers, determines the length and force of contraction (Fig.2.18)⁵⁵. Lee *et al.* studied the photo-induced oscillation of cross-linked glassy cantilevers⁵⁶. Upon irradiation with polarized laser light the cantilevers oscillated at high frequency and with large amplitude, undergoing in-plane bending and simultaneous out-of-plane twisting (Fig.2.19).

Fig.2.18: Effect of concentration and location of azobenzene switches on the photo-mechanical properties of thin films of cholesteric liquid crystal polymers. a) Order parameters S of CLC polymer films prepared from mixtures containing various feed ratios of an azobenzene monomer and an azobenzene crosslinker b) Change in length along the alignment direction of the azobenzene containing CLC polymer film by irradiation with UV light (366 nm, 25 mW cm⁻²) at 30 °C. c) Value of contraction length after irradiation with UV light for 100 s (Δl_{100}) of the CLCP films containing various azobenzene contents. Size of the film: 5 mm × 7 mm × 20 μm. Adapted with permission from [55] (Copyright 2010 Royal Society of Chemistry).

The frequency of oscillation depends on the cantilever aspect ratio while the amplitude depends on the laser intensity and the temperature. This appeared promising with respect to speed of response and motion, but the use of polarized

42

light to guide the movement remains a limitation for applications. Therefore, other studies focus on the triggering of actuation using different wavelengths of light, two-way photo-induced switching (suppressing or accelerating temperature-induced relaxation) and the use of non-polarized light. Yoshino *et al.* have reported a liquid crystalline polymer network doped with azobenzenes, inspired by muscle fibers (Fig.2.20), that bends towards a UV light source and reverses bending under irradiation with visible light⁵⁷.

Fig.2.19: Cantilevers made of liquid cholesteric liquid crystal polymer networks, that oscillate at high frequency and with large amplitude, undergoing in-plane bending and simultaneous out-of-plane twisting. Reproduced with permission from [56] (Copyright 2011 John Wiley & Sons, Inc.).

Developing materials that provide specific mechanical responses to a stimulus can be achieved with polymer networks of photo-responsive liquid crystals, provided the director field, film thickness and surface properties are controlled⁵⁰. In the frame of this strategy, Wie *et al.* have investigated how the photo-actuation of liquid crystal polymer cantilevers depends on the anchoring conditions at the

liquid crystal interfaces (twist nematic or hybrid anchoring)⁵⁸. They have concluded that large-magnitude flexural-torsional responses depended strongly on the alignment of the nematic director field with respect to the film geometry (Fig.2.21).

Fig.2.20: a) Schematic illustration of the experimental setup. b) Snapshots of the cholesteric liquid crystal polymer fiber that exhibits reversible photo-induced bending and unbending behavior upon alternating irradiation with UV light (100 mW cm^{-2}) and visible light (120 mW cm^{-2}). The inset of each photograph is a schematic illustration of the state of the fiber. The size of the fiber is $30 \text{ mm} \times 20 \mu\text{m}$. Adapted with permission from [57] (Copyright 2010 John Wiley & Sons, Inc.)

Wie's studies were inspired by the motions of animals and the authors mention soft robotics as possible applications which is a field that is attracting a lot of attention since Whiteside et al. challenged their peers in a conference paper on the

Faraday Discussions meeting in 2009⁵⁹. Whiteside pointed out that soft robotics show great potential for biomimetic systems and controlled complex movements. Similarly, Sprinks published in 2012 a paper on light-driven muscles emphasizing their unique, fascinating properties like high power to weight ratio, fast response times, high energy conversion efficiency, noiseless operation, excellent fatigue resistance, self-repair and self-sensing properties⁶⁰. Sprinks stresses the hierarchical structure of muscles and how the small contractions of single sarcomeres (250 nm/sarcomere) are accumulated in the bundles of muscle fibers to yield contractions of several millimeters. The author concedes that there are systems that can mimic a few of those properties but there is no artificial system that combines them all. Also, research towards applications should demonstrate real mechanical work for which the actuator must work against an external load. They state that to achieve this, the actuator has to be matched to the expected load. As successful future approaches, Sprinks envisions the design and synthesis of new molecules, but also other approaches such as optimizing the nano-assembly as well as more quantitative studies of work capacity, power output and overall energy conversion efficiency.

Fig.2.21: Illustration of elastic restoration of TN and hybrid liquid crystal network doped with azobenzene, after removal of 445 nm irradiation. All tests employed cantilevers of dimension 6 mm (L) × 0.5 mm (W) × 8 μm (T). F and B indicate front and back surfaces, respectively. Reproduced with permission from [58] (Copyright 2013 Royal Society of Chemistry).

Fig.2.22: a, Upon alternate irradiation with ultraviolet and visible light, the central kink of a mixed-helicity ribbon performs a continuous piston-like motion. **b**, The device displays no sign of fatigue over ten cycles of alternating irradiation. **c**, A magnet connected to the kink ($m \approx 2$ mg) undergoes a push–pull shuttling motion, a motion further transmitted to another magnet placed 10 mm below ($m \approx 0.5$ mg). Reproduced with permission from [61] (Copyright 2014 Nature Publishing Group).

Addressing this challenge, our research team has designed bio-inspired azobenzene-doped polymer springs with different shapes by cutting thin strips out of a thin film with twist alignment⁶¹. Depending on the geometry of the cutting direction and the director field, these strips curl, bend or twist with different handedness. Under UV light winding, unwinding and even helix inversion of the strips could be shown and work of about $3 \text{ J/mol}_{\text{azobenzene}}$ was demonstrated by lifting a small weight. Moreover, a piston like machine was constructed that could move a magnet, which pulled a second magnet at a small height distance back and forth (Fig.2.22). However, for practical application the work efficiency of this system needs still to be improved and improving the resistance of the films will allow carrying higher loads.

In general, developing liquid-crystal based materials that perform work with a high efficiency remains a challenge. At the same time, these materials are especially adapted to actuation involving complex shapes and movements rather than high work output. Just like for optical applications it might be possible to program more complex motions and shapes into the material by exploring the director fields of 3-dimensional confinements like fibers, spheres and core-shell systems. For new designs we can find plenty of inspiration in our natural environment and bio-inspired actuators that can mimic the motion of soft animals or plants can be envisioned for medical applications such as drug delivery as well as in the field of soft robotics. Beyond mimicking nature, artificial systems combining the self-assembling property of the liquid crystals with fabrication strategies like inkjet printing and 3D printing, lithography and holography will give us access to translate, amplify and harness nanoscale properties up to the macro scale.

Practically, material studies might benefit strongly from paying special attention to combining different materials like using interpenetrating polymer networks or working on liquid crystalline composites. So far some work has been done on using liquid crystals as templates to organize metallic nanoparticles in the textures or on studying the influence of nanoparticles on topological defects. However, there are many fascinating properties of nano-sized and micro-sized objects that can still be combined with liquid crystalline self-assembly and other specific properties of liquid crystals.

2.5 Conclusion

Photo-responsive materials based on cholesteric liquid crystals show potential as smart materials in various fields, all-optical technologies, smart lasers and light-controlled actuators constituting a few of them only. Most of these research fields call for new photo-responsive molecules with faster isomerization kinetics or more stable photo-isomers to enable either information storage or faster switching of the material properties. Next to the synthetic challenges, material-related aspects will have to be explored before cholesteric liquid crystals make it to practical applications: controlling the director field by manipulating surface anchoring and supramolecular organization, confinement in three dimensions and stabilization with simultaneous preservation of dynamic properties. To succeed, research can draw inspiration from numerous biological systems, including plants or animals,

and combine these with innovative methods of fabrication and production. In so doing, photo-responsive liquid crystalline materials might be used as frequently in the future as their electrical counterparts currently are.

2.6 References

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Chapter 3

Time-programmed helix inversion in light-responsive liquid crystals

Doping cholesteric liquid crystals with photo-responsive molecular motors or switches allows controlling the color and polarization of the light they reflect, reversibly. However, accelerating the rate of relaxation of these photo-responsive liquid crystals remains challenging. In this chapter, we show that the relaxation rate of the cholesteric helix is fully determined by helix inversion of the molecular dopants.

Part of this chapter has been published as S. J. Aßhoff, S. Iamsaard, A. Bosco, J.J.L.M. Cornelissen, B. L. Feringa and N. Katsonis “Time-Programmed Helix Inversion in Phototunable Liquid Crystals” *Chem. Commun.* **2013**, 49, 4256-4258.

3.1 Photo-induced helix inversion in cholesteric liquid crystals

The development of smart materials has triggered interest towards photo-controllable liquid crystals.^{1,2} Special attention has been directed to photo-controlled cholesteric liquid crystals in view of their unique structural and optical properties: their helical structure reflects light selectively over a narrow range of wavelengths, whose central position λ_0 is determined by the pitch of the cholesteric helix.^{3,4} Using light as an external stimulus allows the position of the reflection band to be adjusted and consequently allows the color that is reflected to be modified.^{5,6}

The most efficient approach towards designing phototunable cholesteric liquid crystals involves chiral and photo-responsive dopants such as azobenzenes,⁷ overcrowded alkenes⁸ or other photochromic molecules.⁹ In addition to modifying the spectral position of reflection upon irradiation with UV light, some photo-responsive dopants promote helix inversion also, thereby modifying the handedness of the circularly polarized light that is reflected.² Dynamic control over these optical properties is determined by the range of the shift in the reflection band that can be achieved, the possibility of helix inversion and the time taken by the material to switch between two states.

Potential applications require materials that can be photo-modulated to an activated state. The stability of the material in the activated state is determined by its reorganization kinetics for relaxation in the dark. Although considerable progress has been made in photo-modulating the pitch over large ranges and inducing helix inversion more efficiently, adjusting the kinetics of both the photo-controlled and the reverse (thermal relaxation) process has received less attention.^{6,10} In particular, a major drawback of a large majority of photo-responsive cholesteric liquid crystals lies in the kinetics of their relaxation step. The thermal relaxation of cholesteric liquid crystals doped with azobenzene compounds has been investigated in view of their potential applications to color-stable materials.¹¹ However, their relaxation is still too fast to be neglected.^{7,12} Alternatively, other applications require color-tunable systems that restore their initial color instantaneously after cessation of irradiation. For those applications liquid crystals doped with overcrowded alkenes seem particularly promising, because these photo-responsive molecules can be designed to display ultrafast

helix inversion. Based on the availability of a large data regarding the kinetics of thermal helix inversion of overcrowded alkenes, we sought to formulate a general paradigm correlating the kinetics of relaxation of the phototunable liquid crystals with the rate of helix inversion of these overcrowded alkenes in an isotropic solution.

Fig. 3.1: Overcrowded alkenes used as dopants. HTP values reported here are measured for the nematic host E7 and expressed as a mole fraction (left panel). The UV/Vis absorption spectra of the stable forms are measured in n-hexane (right panel).

3.2 Results

Achieving control over the rate of winding and unwinding of the cholesteric helix requires an improved understanding of the interplay between isomerization of the photo-responsive dopants (at the molecular level) and the reorganization which occurs at the macroscopic level. Previously it had been demonstrated that the kinetics of photo-induced texture rotation are determined by the dopants (molecular rotary motors), provided that the rate of photo-isomerization of these dopants is significantly slower than the characteristic time of reorganization of the liquid crystal host.^{13,14} In this chapter it is demonstrated that the relaxation of phototunable cholesteric liquid crystals can be time-programmed by judicious choice of the exact structure of the dopant. Moreover, the kinetics of relaxation of cholesteric liquid crystals doped with three different overcrowded alkenes have been investigated and their dynamic behavior has been compared to (i) the

isomerization rate of the dopants in solution and (ii) the typical reorganization times for the nematic liquid crystal used as a host.

Fig. 3.2: Photo-isomerization of a cholesteric liquid crystal (E7 doped with 6 wt% motor **1**), followed by UV/Vis spectroscopy. First, irradiation triggers the unwinding of the cholesteric helix and the reflection color undergoes a red-shift (a). Once the helix is unwound, disruption of the cholesteric order results in diffusion and a corresponding decrease of transmission (b). After helix inversion the helix rewinds with opposite handedness, which results in remission of the diffusion (c) and subsequent blue-shifting close to the initial reflection wavelength (d).

In solution, overcrowded alkenes undergo a cis-trans isomerization around their central double bond upon irradiation with UV light (Fig. 3.1) resulting in an inversion of the helical conformation of the molecules.¹⁶ In a nematic host, overcrowded alkenes show a good propensity to twist the cholesteric helix as evidenced by their large helical twisting powers (HTP). Considering that at the photostationary state (PSS) the dopant is predominantly present in the unstable form and that the induced cholesteric helix is reversed, it is possible to infer that the unstable isomer has an HTP opposite in sign compared to the stable form of the dopant. This was demonstrated previously for motor **1**,¹⁴ by using a simple phenomenological model that quantitatively correlates the HTP of each isomer with its molecular shape.¹⁷ The cholesteric mixtures were loaded into a planar cell with a thickness of 5 μm and the modification of their optical properties was studied *in-situ* by UV/Vis spectroscopy. Structural information on the cholesteric helix is inferred from changes in the selective reflection of the material at a wavelength λ_0 dependent on: $\lambda_0 = n p$, where p is the pitch of the cholesteric helix and n is the refractive index of E7.¹⁸ For low concentrations of dopant, a linear relation is observed between the dopant concentration and the inverse of the pitch: $\text{HTP} = 1/(c \cdot ee \cdot p)$, where c is the concentration of the dopant in the mixture expressed as mole fraction, p the cholesteric pitch and ee the enantiomeric excess of the dopant. We prepared a set of cholesteric liquid crystals that initially reflect

between 350 nm and 400 nm to investigate their phototuning and relaxation behavior over the whole visible range.

Upon irradiation of the cells with UV light, the proportion of stable form of the dopants decreases in favor of the unstable form. This photo-conversion is accompanied by a modification of the resulting helical twisting power, because the HTP of a mixture of dopants is the sum of their individual contributions. The photo-induced process can be followed by means of UV/Vis spectroscopy (Fig. 3.2). The UV/Vis spectra recorded in-situ show a red-shift of the reflection band, which corresponds to an increase of cholesteric pitch, and consequently to unwinding of the cholesteric helix (Fig. 3.2a). At a certain stage of the photochemical conversion from one isomer to the other, a mixture with an effective helical twisting power $HTP = 0 \mu m^{-1}$ and consequently an infinitely long pitch is formed. The inversion point corresponds to disappearance of a cholesteric structure which is accompanied by a disruption of the helical order and induces losses of light through diffusion, which are visible in the decrease of the overall transmittance of the samples (Fig. 3.2b).

Fig. 3.3: CD spectra following the relaxation of the same cholesteric liquid crystal; both helix unwinding (left) and helix rewinding (right) are observed.

After further irradiation, the position of the reflection does not undergo further modification, which means that the cholesteric system has reached the photostationary state (Fig. 3.2c). At the PSS, the reflection band is only slightly red-shifted compared to the initial state, which is in agreement with the PSS of approximately 99% in favor of the unstable form for 1.¹⁴ While the pitch of the cholesteric helix is nearly the same in the initial state and at the PSS, its handedness has been reversed. Photo-induced helix inversion has been evidenced earlier by polarized IR spectroscopy.⁵ Here, we demonstrate helix inversion for

cholesteric liquid crystals doped by molecules **1**, **2** and **3**. Experimental evidence is provided by UV/Vis spectroscopy, where disruption of the cholesteric order observed (Fig. 3.2b,c) and by circular dichroism (Fig. 3.3).

The potential correlation between inversion of the cholesteric helix and the helix inversion which occurs at the molecular level of the dopants, was investigated through the time dependence of the changes in the reflection band during the relaxation process (Fig. 3.4 for the cholesteric helix doped with **1**). In contrast to photo-switching, thermal relaxation is not dependent on the conditions of irradiation. In fact, once the photostationary state has been reached, the relaxation of the system depends only on the thermal isomerization rate of the dopant. A model to account for the kinetics of unwinding and rewinding observed during the relaxation process can be proposed. Based on the assumption of first order kinetics for the isomerization of the dopant, the data was fit using the following equation:

$$\lambda = \frac{n \cdot 10^{-3} / c}{|HTP_P - \Delta HTP \cdot \chi_{M,PSS} \exp(-k_{rel} t)|} \quad (1)$$

where λ is the position of the reflection band (expressed in nm), n is the refractive index, c is the concentration of the dopant, HTP_{st} is the HTP (expressed in μm^{-1}) of the stable form, ΔHTP is the difference of HTPs between the stable and the unstable isomer, $\chi_{unst,PSS}$ is the molar fraction of unstable form at photostationary state, k_{rel} is the rate constant of the dopant relaxation from unstable to stable form and t is the time. The rate constant and HTP were allowed to vary to achieve the best fit to the data, which indicates that the whole system can be modeled in a simple manner (see section 3.4.2 for details of the fitting procedure). In particular, these results demonstrate that anchoring and edge effects can be neglected completely to describe the phenomenon as a whole, despite the fact that thin cells were employed. The uncertainty in the values obtained for dopant **3** are higher than for the other dopants, which we attribute to the fact that its relaxation proceeds the quickest, and hence the error is the largest in the measurement of $\lambda_0 = f(t)$.

Fig. 3.4: Thermal (helix-inverting) relaxation of a cholesteric liquid crystal doped with molecule 1, as followed by UV/Vis spectroscopy. The data points correspond to the right edge of the selective reflection band and were fitted according to Equation 1. The top panel shows the reflection colors and pictograms of the cholesteric helix.

Comparing the rate constants extracted from the fits with the rate constants determined for the dopants in hexane, shows that the relaxation is unperturbed by the liquid crystalline environment. Hence the photo-induced evolution of HTP induces reorganization of the liquid crystal essentially instantaneously, *i.e.* in accordance with typical reorganization times of liquid crystals. For a cholesteric liquid crystal, the typical reorganization time is in the order of $\tau_{\text{nem}} = D^2 \cdot \gamma / k_2$ 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 micron range, τ_{nem} is of the order of seconds. The reorganization time is less than the characteristic relaxation times of most overcrowded alkenes ($\tau_{\text{rel}} \approx 800$ s for **1**, see Table 1).¹⁴ Consequently, the reorganization of the director can be described as helix unwinding and rewinding under the control of helix inversion of the dopants, through a sequence of equilibrium states.¹⁴

Table 3.1: Values extracted from fitting the experimental data.

Dopant	k_{rel} for dopant in solution [s^{-1}] ^a	k_{rel} for cholesteric helix [s^{-1}] ^b	$\chi_{\text{unst PSS}}$ ^b	HTP _{st} [μm^{-1}] ^b
1	$1.18 \cdot 10^{-3}$	$1.27 \cdot 10^{-3}$	0.995	100.5
2	$3.64 \cdot 10^{-3}$	$3.89 \cdot 10^{-3}$	0.993	34.5
3	$7.32 \cdot 10^{-3}$	$1.16 \cdot 10^{-2}$	0.885	48

^a Measured. ^b Values extracted from fits assuming $\text{HTP}_{\text{st}} = -\text{HTP}_{\text{unst}}$.

3.3 Conclusions

We have studied the time-dependence of helix engineering in cholesteric liquid crystals doped with overcrowded alkenes. Helix inversion has been evidenced both by UV/Vis and CD spectroscopy. Moreover, we have shown that the kinetics of relaxation of the cholesteric helix are fully determined by the kinetics of the light-sensitive dopants. As the thermal helix inversion in overcrowded alkenes has been optimized successfully in solution through variations in molecular structure, our results evidence that helix inversion in phototunable liquid crystals can be dramatically accelerated also, and consequently holds great potential towards using new cholesterics for smart materials with sophisticated functions.

3.4 Methods

Phototunable cholesteric liquid crystals were prepared by doping a commercially available nematic liquid crystal (E7, Merck) with a series of overcrowded alkenes synthesized according to literature procedures¹⁵ and purified by Chiral Technologies Europe. The dopants were dissolved in CH_2Cl_2 and mixed with E7 (dopant concentrations in E7: **1** = 5.92 wt%, **2** = 14.9 wt%, **3** = 10 wt%). Then the solvent was evaporated at 40°C and under a N_2 -stream. After evaporating the solvent, the mixture was heated up to 65°C (i.e. above the clearing point) and stirred for 15 min. After cooling down to room temperature the mixtures were introduced in 5 μm glass cells (EHC, Japan). The cells were filled with the cholesteric liquid crystal by capillary forces.

For the UV/Vis-measurements, the cells were irradiated at $\lambda=365$ nm by using a Hönle LED lamp ($600\text{mW}/\text{cm}^2$ at a distance of 5 cm and an angle of 30° related to the cell plane) for 180 sec (mixture doped with molecule **2**) or 210 sec (mixture

doped with molecule **1** and **3**). The UV/Vis-measurements were made using an Ocean Optics USB200+VIS-NIR-ES Spectrometer and a DV-MIDI-2-GS-lamp.

3.4.1 CD spectra

A Jasco J715 was used for CD-measurements. A UV pencil lamp (4.4 mW/cm² in a distance of 5 mm) was used for UV-irradiation. The irradiation times were 4 min to 8 min. After these times the UV-light was switched off and the measurements were started immediately.

3.4.2 Relaxation kinetics

The colour shift during the dark relaxation was followed by determining the wavelengths corresponding to the left edge and the right edge of the reflection band, over time. The fitting was done for both set of values. The mean values for k_{rel} , HTP_{st} and $\chi_{unst,PSS}$ can be found in Table 1. The data have been fitted using a least square minimization procedure with Eq. 1 considering respectively wavelength λ as the dependent variable and time t as the independent variable.

Assuming a first order kinetic for the isomerization process, is it possible to write the time dependence of x_{st} and x_{unst} , the mole fractions of the stable and unstable isomeric forms in which the dopant can be found ($x_{st}+x_{unst}=1$). The mole fraction of the stable isomer can be written as

$$x_{st}(t) = x_{st,eq} + (x_{st,PSS} - x_{st,eq}) \exp(-k_{rel}t)$$

where k_{rel} is the rate constant of the thermal isomerization, $x_{st,PSS}$ and $x_{st,eq}$ are the mole fraction of stable isomer respectively at photostationary state ($t=0$) and at equilibrium ($t \rightarrow \infty$). For the motors under investigation it has been shown that $x_{st,eq} \approx 1$, which means that $x_{st}(t)$ can be rearranged as

$$x_{st}(t) = 1 - x_{unst,PSS} \exp(-k_{rel}t)$$

where $x_{unst,PSS}$ is the molar fraction of the unstable isomer at the photostationary state. The pitch p of the cholesteric helix can be expressed in terms of the HTPs of the two isomers of the motor HTP_{st} and HTP_{unst} , namely

$$p = 1/c(x_{st}HTP_{st} + x_{unst}HTP_{unst})$$

Finally, Eq. 1 can be easily derived by substitution of the previous formula.

Chapter 3

The relaxation rate k_{rel} , the HTP of the stable isomer HTP_{st} , and the product of the difference between the HTPs of the stable isomer and unstable isomer multiplied by the molar fraction of the unstable isomer at the photostationary state $\Delta HTP \chi_{unst,PSS}$, are obtained by numerical minimization of the summed square difference between the experimental and computed wavelength λ at time t with a custom made code written in Mathematica [Wolfram Research, Inc., Mathematica, Version 6.0, Champaign, IL (2007)]. The concentration of the dopant was known.

Table 3.2: Data used for the fits

	1	2	3
Molecular Weight [amu]	406	344	372
Conc. [wt%]	5.92	14.9	10
Conc. [mole fraction]	0.04	0.12	0.075

3.4.2.1 Dopant 1

Left edge

Right edge

Table 3.3: Fitting parameters for 1

	Left edge	Right edge	Average
$k_{rel} [s^{-1}]$	$1.28 \cdot 10^{-3}$	$1.26 \cdot 10^{-3}$	$1.27 \cdot 10^{-3}$
$HTP_{st} [\mu m^{-1}]$	106	95	100.5
$HTP \chi_{unst,PSS} [\mu m^{-1}]$	212	188	200

Table 3.4: Results obtained from the fitting parameters reported in Table 3, assuming $HTP_{st} = -HTP_{unst.}$

	Left edge	Right edge	Average
$x_{unst,PSS}$	0.999	0.990	0.995

3.4.2.2 Dopant 2

Left edge

Right edge

Table 3.5: Fitting parameters for 2.

	Left edge	Right edge	Average
$k_{rel} [s^{-1}]$	$3.80 \cdot 10^{-3}$	$3.98 \cdot 10^{-3}$	$3.89 \cdot 10^{-3}$
$HTP_{st} [\mu m^{-1}]$	37	32	34.5
$HTP_{x_{unst,PSS}} [\mu m^{-1}]$	73.0	63.9	68.5

Table 3.6: Results obtained from the fitting parameters reported in Table 5, assuming $HTP_{st} = -HTP_{unst.}$

	Left edge	Right edge	Average
$x_{unst,PSS}$	0.986	0.999	0.993

3.4.2.3 Dopant 3

Left edge

Right edge

Table 3.7: Fitting parameters for 3.

	Left edge	Right edge	Average
$k_{rel} [s^{-1}]$	$1.16 \cdot 10^{-2}$	$1.15 \cdot 10^{-2}$	$1.155 \cdot 10^{-2}$
$HTP_{st} [\mu m^{-1}]$	51	45	48
$HTP_{x_{unst,PSS}} [\mu m^{-1}]$	90	79	84.5

Table 3.8: Results obtained from the fitting parameters reported in Table 7, assuming $kP_{st} = -kP_{unst}$.

	Left edge	Right edge	Average
$x_{unst,PSS}$	0.88	0.88	0.88

Acknowledgments

Dr. Alessandro Bosco (Elettra-Sincrotrone Trieste, Italy) is acknowledged for the calculations of the motor kinetics. The synthesis of the molecular motors was performed by Supitchaya Iamsaard. Prof. Ben L. Feringa (Stratingh Institute for Chemistry, University of Groningen, The Netherlands) is acknowledged for insights into the synthesis and photochemistry of overcrowded alkene-based molecular motors.

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Chapter 4

Creating and manipulating topological structures with light

Topology refers to spatial properties of materials. This universal concept is encountered in daily life and is known to determine many static and dynamical properties of matter. Achieving control over the topology of materials therefore constitutes a contemporary and interdisciplinary challenge, and harnessing the responsiveness of liquid crystals appears as a relevant strategy to address it. In this chapter, we report on creating topological structures in droplets of cholesteric liquid crystals. Our results are in line with recent theoretical investigations that had predicted the formation of these free-standing and connected topological structures in confined cholesteric liquid crystals. We also demonstrate that light can be used to achieve topological remote-control, which may foster the development of new devices based on the control of topologically structured soft media, such as high-dimensional rewritable topological memories.

Part of this chapter has been published as T. Orlova, S.J. Aßhoff, T. Yamaguchi, N. Katsonis and E. Brasselet “Creation and manipulation of topological states in chiral nematic microspheres” *Nat. Commun.* **2015**, 6, 7603.

4.1 Introduction

Liquid crystals are well-known to exhibit a wealth of spontaneously occurring topological defects¹, and therefore they constitute a prime choice for experimental investigations on creating and manipulating (new) topological structures. Achieving control over the topological defects that are formed spontaneously in liquid crystals is generally achieved by appropriate selection of the liquid crystal and its anchoring conditions at interfaces. A few years ago, complex 3D networks of defect lines have been unveiled experimentally in thin films of cholesteric liquid crystals mixed with solid microspheres^{2,3} (see also Ref. 4 for very recent developments), including knotted and linked lines. Mixing complex micro-objects with liquid crystals has been explored theoretically and experimentally also, including non-orientable ribbon-like colloids in chiral nematics⁵ as well as knotted rope-like colloids in nonchiral nematics⁶.

Recently, research on topology has reached beyond the state of the art, by using cholesteric liquid crystals confined in two dimensions (films) or three dimensions (droplets), without the need to use colloidal particles in order to create complex topologies. Both two-dimensional and three-dimensional confinement of a cholesteric under perpendicular surface anchoring conditions can forbid the establishment of a continuous helical director field, a phenomenon often called frustration, thereby fostering the appearance of metastable topological defects. In particular, metastable particle-like topological structures have been predicted and observed in frustrated cholesteric films a few years ago.⁷ Since then, the topological diversity of such systems has been explored and a variety of individual⁸ as well as linked and self-assembled⁹ structures have now been identified. On the other hand, in the case of frustrated cholesteric droplets, the existence of a rich variety of free-standing metastable topological structures has been numerically unveiled¹⁰, among which knots and links, which remain elusive so far.

Creating and manipulating knots and links contributes to the multidisciplinary challenge of taming free-standing three-dimensional topological structures. In parallel to experimental investigations performed by the liquid crystal community, the engineering and observation of vortex knots has been achieved in other fields, such as optics¹¹ and hydrodynamics¹². Metastable knots in condensed matter come with an essential added value: the long-term preservation of the information, so that it can be read again by using appropriate control strategies. An important example is provided by point-like topological excitations in magnetic materials

(so-called skyrmions) that can be turned on and off¹³ and show promise for the elaboration of future ultra-high density magnetic devices. Liquid crystal-based materials are consequently promising because they combine remote-controlled features to topological diversity.

Non-chiral nematic liquid crystals confined in nontrivial volumes with handles have been described recently, under perpendicular surface anchoring conditions¹⁴. In contrast, and quite surprisingly, only a few experimental studies report on how cholesteric liquid crystals adapt to confinement in a simple spherical volume, under perpendicular surface anchoring conditions. In 1973, Candau *et al.* have described the 3D radial distribution of the director when $p > R$, where R represents the droplet radius and p the cholesteric pitch¹⁵. When $p < R$, the authors report a radial distribution that is similar to what is observed with a parallel surface anchoring^{16,18}. Candau *et al.* foresaw the possibility to form other topological defects in order to satisfy perpendicular boundary conditions, however without experimental support. In 1982, Kurik and Lavrentovich reported on the observation of an equatorial disclination and point surface singularity¹⁹. For a pitch that is sufficiently small ($p < R = 10$), these authors concluded that both perpendicular and parallel surface anchoring cases behave similarly whereas for larger pitch values ($p > R = 5$) a novel defect appears. In 1993, Kitzerow and Crooker reported on the observation of fingerprint patterns that consist of concentric, elliptical or parallel lines and they suggested that these correspond to the same 3D director field, observed under different angles.²⁰

Here, we report on the observation and the manipulation of complex free-standing metastable topological architectures in frustrated cholesteric droplets. From the structural point of view, we experimentally unveil a rich structural topological diversity that support the static predictions made in Ref. 10 and we bring evidence of novel topological structures for large values of the ratio R/p , that were not reported so far.¹⁰ Additionally, we experimentally demonstrate contactless real-time reconfiguration of complex three-dimensional director fields by using optical external fields. As a result we envision the development of new types of photonic elements based on structured soft media, for instance high-dimensional rewritable topological memories or innovative 3D optical phase masks.

4.2 Topological diversity

In the first part of this work we have evidenced topological diversity on cholesteric droplets, using spherical droplets with perpendicular anchoring conditions immersed in a high-viscosity surrounding fluid. In practice, the droplets were quenched thermally, then the samples were heated above the nematic-isotropic transition temperature and left to relax at room temperature.²¹ Such a procedure corresponds to the experimental counterpart of the simulated temperature quench reported in Ref. 10, as strategy that has been proposed to reach high energy orientational configurations.¹⁰ The dimensionless parameter $N=2d/p$, which represents the number of π turns of the director along the droplet diameter d facilitates the comparison with previous numerical predictions where N has been chosen as a control parameter to explore the zoology of metastable states.

Fig 4.1: Examples of complex metastable topological structures in cholesteric droplets with perpendicular surface anchoring. Experimental conditions: pitch $p=55\ \mu\text{m}$, droplet diameter $d=105\ \mu\text{m}$ (a,c) and $d=125\ \mu\text{m}$ (b,d), which correspond to $N = 3.8$ and $N=4.5$. (a,b) XPOL imaging, with crossed polarizer and analyzer (c,d) FT imaging, with full transmission. Scale bars: $50\ \mu\text{m}$. Bottom row: numerically predicted nontrivial topological states when $N=5$, which consist of one (e), two (f), three (g) and four (h) disclination loops that are knotted or linked, as indicated in the insets. Sketches adapted from Ref. 10.

Recent numerical investigations have predicted a climax of topological complexity for intermediate values of N , especially with the emergence of knotted

and linked director fields in the range $4 < N < 5$. However, an experimental proof for this prediction has remained elusive so far. In this collaborative work, we found a few complex metastable states that confirm these predictions partially. Two examples that corresponds to $N=3.8$ and $N=4.5$ are shown in Fig 4.1. The visual inspection of Fig 4.1 allow drawing conclusions : (i) the absence of a dark cross in the internal part of the droplet in XPOL images (crossed polarizer and analyzer) indicates highly inhomogeneous director fields and (ii) FT (full transmission) images show an entanglement of disclination lines. Even in the absence of any reconstruction of the three-dimensional director field via fluorescence confocal polarizing microscopy or nonlinear microscopy, these results indicate that the structures we observe correspond to nontrivial topological states.

Fig. 4.2: High-chirality regime. Typical XPOL (upper row) and FT (bottom row) images of short-pitch cholesteric droplets with perpendicular (a,b,c,d) and parallel (e,f) surface anchoring. Perpendicular case : pitch $p = 12,3 \mu\text{m}$, droplet diameter $d = 139 \mu\text{m}$, $N \approx 23$. The two sets of pictures correspond to different imaging planes that allow to visualize the surface (a,b) and the equatorial plane (c,d) of the droplet. Parallel case: pitch $p = 12,3 \mu\text{m}$, droplet diameter $d = 121 \mu\text{m}$, $N = 20$. Scale bars: $50 \mu\text{m}$.²¹

Following the work reported in Ref.10, another intriguing behavior was predicted in the high-chirality regime. For $N \gg 1$, disclination lines should lie nearby the surface of the droplet and organize into two-dimensional layered patterns that dictate the nature of the bulk director field. In particular, a uniformly

spiraling disclination should promote a uniformly twisted director field.¹⁰ This prediction is consistent with the fact that the present case is the inverted analog of solid colloids with perpendicular surface anchoring immersed in uniformly twisted cholesteric films, a system that was analyzed theoretically in Ref.22 and observed experimentally in Ref.3.

Fig. 4.2 shows a typical situation encountered for short-pitch cholesterics, where panels (a,b) and (c,d) correspond to two different imaging planes at $N \approx 23$. The surface of the droplet is brought into focus in Fig. 4.2a,b, which clearly demonstrates the presence of a layer-like disclination pattern. In Fig. 4.2 c,d, the focus was done on the equatorial plane of the droplet, i.e. the spiral is out of focus in that case. These results demonstrate experimentally the surface character of the spiraling defect lines, whose "spiral pitch" λ satisfies $\lambda \approx p$ as expected theoretically. However, the bulk ordering of the droplet differs from the predicted cholesteric ground state.¹⁰ Instead we observe an onion-like structure with a radial defect (Fig. 4.2c,d), similar to the one observed for short-pitch cholesteric droplets with parallel surface anchoring. This is emphasized in Fig. 4.2e,f presenting XPOL and FT images of a cholesteric droplet with parallel boundary conditions at $N \approx 20$. These results bring a direct proof that a screening mechanism is actually at work in the high-chirality regime, where the perpendicular surface anchoring conditions are replaced by parallel ones.

4.3 Opto-molecular control over topological transitions

The level of frustration of a cholesteric droplet with perpendicular boundary conditions can be described accurately by the diameter-to-pitch ratio d/p . Consequently, molecular chirality can be considered as a control parameter to prepare tailored-made metastable states. Arguably, light-responsive cholesteric liquid crystals constitute an ideal system to investigate molecular control over topological transitions, as the photo-induced modifications of chirality have been shown to be controllable gradually, precisely and reversibly.²³ Photo-responsive cholesterics are usually prepared by doping a nematic liquid crystal with a few percent of chiral molecular photo-switches (Fig. 4.3).^{23,24} In this chapter, we choose light-driven molecular motors as dopants, because under irradiation with UV light, the handedness of these molecules is switched, but their overall shape is maintained.²⁵⁻²⁹ For small concentrations of dopant, the pitch of the resulting

cholesteric liquid crystal is completely determined by the structure of the dopant and by its concentration. Consequently, by adjusting the concentration of the chiral motor in the nematic liquid crystal, the chiral character of the system can be defined precisely. For low levels of doping, the modification in elastic constants is usually negligible.^{25,30}

Fig. 4.3: Photo-switches based on overcrowded alkenes.

In particular for the system we investigate here, it has been shown that assuming the same elastic constants for pure E7, and for E7 doped with molecular motors, theoretical models are in good agreement with experimental results.²⁵ Importantly, and in contrast to what happens when azobenzene-based molecules are used as photo-switchable dopants,^{31,32} our system does not suffer from expulsion of the photo-isomer towards the droplet boundaries under irradiation, because all isomers of these molecular motors show a high solubility in E7.^{25,28,33,34}

The concentration of molecular motor was tuned to reach the high-chirality regime ($N \gg I$) in the initial state. Under irradiation with UV light, the chirality of the system is modified at the level of the molecular motor, and transmitted to the mesoscopic level of the cholesteric liquid crystal. Specifically, the motor has an overall helical shape that is right-handed in the stable state, and left-handed for its photo-isomer. The ratio between these two forms determines the effective molecular chirality that is amplified by the cholesteric helix. Initially, the structural changes associated with the appearance of the photo-isomerization of **m₁** express at the supramolecular level first as an increase of the cholesteric pitch. After a few minutes of irradiation the compensation point is reached, which corresponds to a pseudo-nematic liquid crystal mixture ($N = 0$) and UV irradiation is then stopped. Importantly, we have shown previously that upon irradiation, the reorganization of the liquid crystal follows the kinetics of photo-isomerization of the motor,²⁵ which means that in principle any value of the cholesteric pitch, hence N , can be reached by tuning the characteristics of irradiation. The photo-chemical reaction being fully reversible, thermal relaxation brings the system back to the initial state.

Fig. 4.4: Optical chiral control. Light-induced structural changes followed by thermal relaxation of cholesteric droplets with photo-tunable pitch in the case of parallel (upper row) and perpendicular (bottom row) surface anchoring, using motor m1. All pictures correspond to XPOL imaging. Parallel case: droplet diameter $d = 30 \mu\text{m}$, $N \approx 33$ before illumination is turned on. Illumination time is 0 s (a), 13 s (b), 23 s (c), 30 s (d) and 35 s (e) whereas relaxation time after UV radiation is turned off is 52 s (f), 74 s (g), 85 s (h) and 1057 s (i). Perpendicular case: droplet diameter $d = 34 \mu\text{m}$, $N \approx 20$ before illumination is turned on. Illumination time is 0~s (j), 20 s (k), 35.5 s (l), 47.6 s (m) and 163.7 s (n) whereas relaxation time after UV radiation is turned off is 15.5 s (o), 25.4 s (p), 40.9 s (q) and 171.3 s (r). Scale bars: $20 \mu\text{m}$ (a-i) and $10 \mu\text{m}$ (j-r).

We first investigate the case of droplets with parallel surface anchoring in order to benchmark the opto-molecular control of the director field structuring in spherical confinement. Indeed, the expected structural scenario as d/p is varied, is well-known in that case¹⁷ and correspond to an onion-like structure with a radial (or diametral) defect at large N as shown in Fig. 4.2e,f whereas the director field tends to a bipolar structure as N reaches zero. Our proposition to vary the chirality parameter in a continuous manner thus offers an original opportunity to explore the structural bifurcation scenario for the three-dimensional director field. The results are shown in the upper part of Fig. 4.4, with $N \approx 33$ initially. As the UV irradiation is turned on, the pitch of the spiraling structure monotonously increases (Fig. 4.4b) to eventually disappear (Fig. 4.4c) and exhibit a bipolar configuration (Fig. 4.4d). When chirality almost vanishes the UV illumination is turned off (Fig. 4.4e) and the system is left to relax at room temperature. A reverse scenario is then observed (Fig. 4.4f-i). These results bring a vivid demonstration of three-dimensional photo-induced transformations, which extend previous results limited to tuning in the high-chirality regime.³⁵

The case of photo-responsive droplets with perpendicular surface anchoring is shown in the bottom panel of Fig. 4.4, where the initial condition (Fig. 4.4j) corresponds to $N \approx 20$ and exhibits a structure similar to the one presented in (Fig. 4.2a-d). Drastic changes of the three-dimensional director field are observed as the pitch increases under UV illumination until the pseudo-nematic state is eventually reached (Fig. 4.4n). The observed structural scenario points out a distinct exploration of the free energy landscape. Indeed abrupt spatio-temporal changes of the order parameter occurring during a thermal quench possibly lead to any orientational state whereas continuous variation of the pitch during the opto-molecular process is related to smooth configuration changes.

Fig. 4.5: Photo-induced topological transitions. XPOL imaging observation of light-induced structural change for a photo-active cholesteric droplet with perpendicular surface anchoring, using motor m_2 . Droplet diameter is $d \approx 90 \mu m$ and $N \approx 40$ before UV illumination is turned on, see panel (a). Transition from complex (b) to much simpler (i) topological state takes place as irradiation time t increases: $t = 339.2$ s (b), $t = 473$ s (c), $t = 486.2$ s (d), $t = 496.2$ s (e), $t = 595.6$ s (f), $t = 639.8$ s (g), $t = 646.5$ s (h) and $t = 647.6$ s (i). Presence of blue color on images (b) to (i) is due to high UV light intensity. Scale bar: $20 \mu m$

Full exploration of the free energy landscape will consequently require the development of advanced control strategies. However, the stability of the target structure and the kinetics of the configurational changes can be controlled by

tuning the power of irradiation and/or the kinetics of relaxation of the dopant through molecular design. Indeed, it is known that the efficiency of the photo-step depends on the electronic structure of the overcrowded double bond and that the efficiency of molecular motors can be controlled optically by using pulsed light.³⁶ Independently, the kinetics of the thermal relaxation of molecular motors are determined by the transition state energies. By expanding the upper half of the motor, contracting the overcrowded double bond or by decreasing the steric hindrance of the substituents in the upper half, the relaxation is slowed down significantly and the photo-isomer is stabilized.³⁷ Moreover, as the reorganization of the nematic host is much faster than the isomerization of the motor, the kinetics of texture changes in the droplets are fully determined by the kinetics of the molecular motor.^{25,28} Consequently, molecular design gives the freedom to adjust the kinetics of the system, depending on the target application.

We also explore topological transformations under chiroptical molecular control by using another molecular motor $\mathbf{m}_2$ (see Methods), in order to demonstrate the generic character of the approach we propose. The motor $\mathbf{m}_2$ is characterized by a longer half-life time (about three times longer than that of $\mathbf{m}_1$) that leads to a long-term stability of the topological pattern obtained in the photo-stationary state (Fig. 4.i). Moreover, different irradiation conditions allow to observe a larger number of intermediate patterns during photo-induced transformation of cholesteric droplets doped with $\mathbf{m}_2$. In particular, as shown in Fig. 4.5, we observe well defined transformations between different topological states.

4.4 Discussion

Experimental demonstration of both metastable and multistable complex topological states in chiral nematic spherical droplets with perpendicular boundary conditions is reported. Among the unveiled three-dimensional defect structures, highly complex ones are likely to qualify as free-standing knotted and/or linked director fields. Although direct three-dimensional determination of the disclination lines entanglement remains a necessary experimental step to take, present results support recent predictions stressing that the interplay between confinement and chirality in spherical geometry may lead to high level of topological diversity.¹⁰ Present work and the one reported in Ref. 14 that deals with the interplay between confinement and nontrivial geometries in the absence of chirality thus complement

one another. Moreover, the extreme sensitivity of liquid crystal systems under external fields (e.g. thermal, electrical, magnetic or optical ones) allows envisioning new applications, such as high-dimensional rewritable topological memories for example.

Another issue raised by the present work concerns bulk structuring in the high-chirality regime. Indeed, although predicted subsurface disclination lines presenting a smectic-like order¹⁰ are experimentally confirmed, the expected uniformly twisted cholesteric bulk ordering is not found. Instead, an onion-like structure having a radial defect is observed. The similarity of the latter director field with that of cholesteric droplets with parallel surface anchoring stresses the screening effect of the subsurface defect structure unveiled in Ref.10, which provide a droplet with perpendicular surface anchoring with an effective parallel one. Our experiment of photo-induced topological transformations under varying pitch thus appears as the chiral analog of the topological dynamics of defects reported in Ref. 39 in the case of achiral nematic droplets with boundary conditions varying from perpendicular to parallel and vice versa.

Finally, these results are relevant in terms of shaping light fields also, and could thus set the basis for optical reading of topological memories. Moreover, our results could promote the development of enhanced spin-orbit topological shaping of light by using liquid crystal defects, an approach that has been limited so far to optical vortex generation by using either hedgehog⁴⁰, umbilical⁴¹ or Schlieren⁴² defects in nematics, toron defect structures in cholesterics⁴³ and focal conic domains in smectics⁴⁴.

4.5 Methods

4.5.1 Preparation of photo-active cholesteric droplets

A photo-responsive cholesteric liquid crystal is prepared by dissolving 1 wt % of light-driven molecular motor **m**₁ (2((2S)-(P)-4-fluoren-9-ylidene-3-methyl-1,2,3,4-tetrahydro-phenanthrene)) in dichloromethane and then added to the nematic liquid crystal mixture E7. Molecular motor **m**₁ is characterized by a half-life time of $\tau_1 = 190$ s in hexane. Similarly, another photo-responsive liquid crystal is prepared by dissolving 0.34 wt% of light-driven molecular motor **m**₂ ((R)-9-(2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene) and 0.03 wt % of shape-persistent chiral dopant ((R)-2,2-1.3-Propylenedioxy0-1.1-

binaphthalene) in dichloromethane and then added to E7. The characteristic half-time of $\mathbf{m}_2$ is $\tau_2 = 580$ s in hexane. These photo-responsive cholesterics are ready for use after the solvent is evaporated at $T = 40^\circ$ under a stream of nitrogen. For microspheres doped with $\mathbf{m}_1$, perpendicular surface anchoring is ensured by using a 5 mM solution of SDS in MiliQ water whereas a 3wt % polyvinyl alcohol (PVA) solution in 1:1 mixture of MiliQ water and glycerol is used in the parallel case. For microspheres doped with $\mathbf{m}_2$, perpendicular surface was ensured by using polydimethylsiloxane.

For homeotropic droplets, the use of both SDS and PDMS lead to observing a black cross between crossed-polarizers for small enough N values, which indicates strong perpendicular boundary conditions. For the droplets in PVA/glycerol solution, the well-known radial texture was observed for large enough N values, which constitutes a clear signature for planar anchoring.

4.5.2 Optical control of photo-active cholesteric droplets

Irradiation with UV light was performed by using a Hönle bluepoint LED lamp ($\lambda = 365$ nm). Droplets doped with $\mathbf{m}_1$ and with parallel surface anchoring were irradiated at intensity ≈ 40 mW/cm² (for 90s) and at intensity ≈ 180 mW/cm² for perpendicular surface anchoring. Droplets doped with $\mathbf{m}_2$ were irradiated with an intensity of ≈ 340 mW/cm². They were observed using Olympus BX51 polarized optical microscope and images recorded with a DP73 Olympus camera. The value of N was evaluated from crossed-polarized images before the UV light was turned on from the relationship $N = d/\Delta$ where Δ is the spatial period of the bulk onion-like structure at $t = 0$ s, see Fig. 4.4a for the parallel case and Fig. 4.4j for the perpendicular case.

4.6 Acknowledgements

We acknowledge the collaboration with the research team SINGULAR of Dr. Etienne Brasselet (CNRS UMR 5798 and University of Bordeaux, France). The textures shown in Fig. 4.1 and Fig. 4.2 were prepared by Dr. Tetiana Orlova in Bordeaux.

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Chapter 5

Superstructures of cholesteric droplets as all-optical switchable distributors of light

Light technology is based on generating, detecting and controlling the wavelength, polarization and direction of light. Emerging applications range from electronics and telecommunication to health, defence and security. In particular, data transmission and communication technologies are currently asking for increasingly complex and fast devices, and therefore there is a growing interest in materials that can be used to transmit light and also to control the distribution of light in space and time. In this chapter, we present chiral nematic microspheres whose shape enables them to reflect light of different wavelengths and handedness in all directions. Self-assembled in organized hexagonal superstructures, these microspheres of well-defined sizes communicate optically with high selectivity for the colour and chirality of light. Importantly, when the microspheres are doped with photo-responsive molecular switches, their chiroptical communication can be tuned, both gradually in wavelength and reversibly in polarization. Since the kinetics of the “on” and “off” switching can be adjusted by molecular engineering of the dopants and because the photonic cross-communication is selective with respect to the chirality of the incoming light, these photo-responsive microspheres show potential for chiroptical all-optical distributors and switches, in which wavelength, chirality and direction of the reflected light can be controlled independently and reversibly.

Part of this chapter has been published: S.J. Abhoff, S. Sukas, T. Yamaguchi, C. A. Hommersom, S. Le Gac, and N. Katsonis “Superstructures of chiral nematic microspheres as all-optical switchable distributors of light”, *Scientific Reports* **2015**, 14183.

5.1 Introduction

Spherical microspheres of liquid crystals have been investigated experimentally since the discovery of liquid crystals in the late 19th century. Otto Lehmann reported as early as 1904 on the study of para-azoxyanisole microspheres, with the aim to decipher the nature of the liquid crystalline order.¹ More recently, the emergence of soft photonics has triggered a renewed interest into microspheres of liquid crystals, as combining the birefringence of the liquid crystal with a spherical topology gives rise to unprecedented optical properties²⁻⁴. These special optical properties provide new opportunities in terms of optical vortex generation⁵, omnidirectional lasing⁶, chiral sorting⁷, and photonic cross-communication^{8,9}.

A major obstacle towards the development of new technologies based on liquid crystal microspheres lies in controlling their size and size distribution, which is also essential to control and harness their internal structure, as size and structure are intimately correlated for confined liquid crystals.¹⁰ Recent progresses in microfluidics with, specifically, the emergence of droplet microfluidics have addressed this challenge by providing platforms enabling the large-scale production of micrometer-size objects with well-defined sizes, shapes, and narrow size distributions^{4,11,12}. In this context, producing microspheres of cholesteric liquid crystals shows particular potential as cholesteric liquid crystals reflect light selectively: only a narrow range of wavelengths is reflected, with a specific polarisation. Selective reflection confers cholesteric microspheres with potential applicability as optical couplers for microfluidic systems, autonomous sensors, and building blocks for high-security identification tags because highly complex optical patterns can emerge when the droplets are assembled as monolayers⁸ or bilayers¹³.

Close packed monolayers of cholesteric droplets can be formed by simple self-assembly, provided the droplets display a sufficiently narrow size distribution. The colour that is reflected selectively by a droplet embedded in this superstructure, is centred around the wavelength $\lambda(\theta) = n \cdot p \cdot \cos(\theta)$, where p is the pitch of the cholesteric helix, n is the optical index and θ is the angle between the incident light and the axis of the cholesteric helix. In cholesteric droplets with planar surface anchoring, the helix propagates radially in all directions¹³⁻¹⁶. As a consequence, a droplet illuminated from the top can reflect light of different colours, however each colour is only reflected in a specific direction. The colour of the central reflection

spot is centered around $\lambda(0) = n \cdot p$ whilst the cones of light reflected in the periphery are characterised by shorter wavelengths. For example, for the part of the droplet where the helical axis is tilted at an angle of $\theta = 45^\circ$ with respect to the incoming light beam, the reflected light will be directed towards the plane of the self-assembled droplets, with equal intensity along all directions. This property provides superstructures of cholesteric droplets with potential applicability as distributors of light, routing specific wavelengths uniformly towards a certain direction of the sample. Conventional hybrid distributors and switches are slow and require more energy because of the conversion from light to electricity (and conversely). This is why all-optical distributors are becoming very appealing systems to develop data transmission further. However, their potential applicability remains limited by their lack of versatility: most all-optical distributors remain beam splitters, with restricted capabilities since they typically split the light into two sub-beams only, or guide the light in a single pre-defined direction¹⁷.

In this chapter, we present a superstructure of self-assembled cholesteric droplets that can distribute incoming light in any direction and display selectivity with respect to polarity of the incoming light. In this structure, we also include light-responsive droplets that operate as switches within the superstructures. These switching units allow controlling the colour and polarisation of light, which is reflected selectively for a desired direction of reflection. In so doing, we demonstrate that the wavelength and polarization of light, on one hand, and the angle of reflection, on the other hand, can be decoupled within these photonic superstructures. Using light as an external trigger to switch the distribution of light beams offers remote, temporal and local controllability and consequently constitutes an attractive alternative to conventional hybrid distributors of light.

5.2 Results and Discussion

5.2.1 Preparation of liquid crystal droplets in a microfluidic setup

The photo-controllable cholesteric liquid crystal was prepared following the usual procedure, by doping a conventional nematic liquid crystal (E7) with a light-responsive molecular motor **1**-(M), at a concentration of 4.9 wt%. In the dark, the resulting cholesteric liquid crystal is characterised by a pitch $p = 350$ nm and a reflection band centered around $\lambda = 530$ nm at normal incidence.

Fig. 5.1: Generation of cholesteric droplets and their assembly into superstructures. (a) Light-responsive molecular dopant **1-(M)**, its photo-isomer **1-(P)** and shape-persistent chiral dopants **2-(S)** and **2-(R)**. The values of helical twisting powers (HTP) are given for the nematic host E7. (b) Schematic representation of a photo-responsive cholesteric liquid crystal. The pitch p corresponds to a full helix turn. (c) The microfluidic set-up. The droplets are dispersed in an aqueous carrier solution containing a surface agent that promotes planar surface anchoring of the liquid crystal molecules. (d-f) Microscopy images of droplet superstructures under crossed polarizers (d) Close-packed superstructure of droplets doped with **2-(S)**. (e) Close-packed superstructure of droplets doped with **2-(R)**. (f) Close-packed superstructure of droplets doped with **1-(M)**.

We prepared passive cholesteric droplets by doping E7 with 3.8 wt% of shape persistent chiral dopants **2-(R)** and its enantiomer **2-(S)**, which are both efficient dopants for a range of nematic liquid crystals²⁰⁻²². The resulting cholesterics are respectively left-handed (LH) and right-handed (RH), and are both reflecting in the red at normal incidence, with reflection bands centered around $\lambda_{\text{LH}}=715\text{ nm}$ and $\lambda_{\text{RH}}=700\text{ nm}$, respectively.

The droplets were produced at room temperature using a dedicated microfluidic set-up consisting of a glass/silicon microchip and a MFCS Fluigent

system for fine control of the flow rates in the device (Fig. 5.1c). Specifically, the liquid crystal was introduced in a flow-focusing configuration with a (1:1) glycerol/water carrier solution supplemented with 3wt% polyvinylalcohol (PVA) (Fig. 5.1b). PVA ensures a planar orientation of the liquid crystal molecules at the interface with the carrier. Upon deposition from the carrier solution onto glass slides, and following partial evaporation of the carrier, self-assembly of the droplets into hexagonal, two-dimensional, closely packed superstructures was observed. Optical microscopy confirmed that the droplets are monodisperse (Fig. 5.1d-f). Their diameters were fine-tuned by adjusting the two flow rates, and they typically ranged from 150 μm to 180 μm .

5.2.2 Chiroptical communication in a hexagonal array of droplets

A homogeneous superstructure of photo-responsive droplets doped with **1**-(M) was prepared, and its collective optical response to illumination with white light was investigated. Fig. 5.2a represents a side view of these droplets, once assembled at the air/carrier interface. The droplets present a green central reflection accompanied by blue reflection spots pointing towards their six neighbours (Fig. 5.2b). These peripheral reflections arise from chiroptical communication between the droplets⁸. At normal incidence, a certain wavelength $\lambda(0) = n p$ is reflected upwards and appears as a central reflection spot (Fig. 5.2a, red arrow). Depending on the geometry of the droplet at the incidence point of light, the angle θ between the incoming light beam and the axis of the cholesteric helix varies between 0° and 90° . For $\theta = 45^\circ$ the incoming light is reflected towards the nearest neighbour of the droplet, giving rise to a cross-communication signal (blue arrow). For $\theta < 45^\circ$ the incoming light is reflected towards the air/carrier interface, where it is totally internally reflected in an angle $\alpha = -\theta$ and hits the nearest neighbour or one of the next nearest neighbours which will then reflect the light back up (green arrows). For $\theta > 45^\circ$ the light is reflected towards the nearest neighbour but from there it cannot be reflected back up. These different pathways for light give rise to the observed complex cross-communication pattern.

Fig 5.2: All-optical tuning of the cross-communication pattern in a hexagonal superstructure of droplets. a) The mechanism of cross-communication. The pathways leading to the central reflection is represented with red arrows, while the blue and green arrows show the reflections due to direct and indirect communication, respectively. The scheme above the central droplet shows its appearance when observed under the microscope with crossed polarizers. b-g) The snapshots taken with crossed polarizers represent one photo-responsive droplet doped with 1-(M), embedded in a close-packed hexagonal array of similar droplets. Upon activation with UV light for 2 min the dopant is converted into 1-(P), which induces the tuning of the central reflection color and the pattern of photonic interaction. Images were taken at 20 s intervals.

The droplets doped with 1-(M) respond to the ultraviolet component of the incoming light. Upon isomerisation of 1-(M), the cholesteric helix unwinds (Fig. 5.1c), which induces a red shift of the central reflection spot. Moreover, this colour shift is accompanied by a complete rearrangement of the cross-communication pattern (Fig. 5.2b-e). Interestingly, this intricate photo-induced pattern shows a higher level of complexity than in other previously reported arrays of liquid crystal droplets. This difference is likely due to the fact that previous investigations involved the self-assembly of droplets trapped in between two glass slides, a design that is restricting the cross-talk to direct communication⁹. In contrast, in the

superstructure presented here, the droplets self-assemble at the air/carrier interface, thereby enabling indirect communication mediated by total internal reflection also.

Increased complexity in the photo-induced optical pattern demonstrates clear potential in terms of applications to high-security identification tags. Using these light-responsive superstructures, dynamic patterns could be created with a fine control over the number and location of cross-communication spots simply by extending the illuminated area. In addition, the wavelength could be controlled dynamically and independently within the complete spectrum of light (including the invisible range of UV- and infrared light) and the chirality of the reflected light could be controlled as well. Mixed superstructures composed by photo-active, photo-passive or even non-cholesteric droplets, would lead to patterns being as unique as easy to generate.

5.2.3 Cholesteric droplets as chiroptical distributors and switches

Combining right-handed (RH) and left-handed (LH) droplets allows the preparation of a heterogeneous superstructure where chiroptical cross-communication between droplets of opposite chirality can be investigated, provided they have comparable sizes. Such a mixed superstructure is shown Figure 3. Under crossed linear polarizers, both series of droplets display a full cross-communication pattern, comparable to the one observed for homogeneous arrays (Fig. 5.3a,b). In contrast, under irradiation with right handed circularly polarized white light, both the central reflection and the peripheral colours of the LH droplets embedded in a network of RH droplets switch off (Fig. 5.3c,d). The disappearance of the central reflection spot ($\theta = 0^\circ$) is attributed to the selective reflection of cholesteric liquid crystals, and is thus in agreement with the fact that cross-communication is based on selective reflection. More surprisingly, we observe that the reflection is only highly selective in polarization for $\theta = 0^\circ$. When $\theta \neq 0^\circ$, the reflection involves more complex polarization modes^{23, 24}, that subsist even under irradiation with right handed light (Fig. 5.3c), although they are much less intense. Nevertheless these results indicate that the cross-communication between droplets of opposite chirality is switched off under illumination with circularly polarised light and prove that the photonic cross-communication is selective with respect to the chirality of the incoming light - a result that opens up exciting perspectives in terms of chiroptical switching in all-optical distributors.

Fig. 5.3: Mixed superstructure of cholesteric droplets doped with 1-(S) and 1-(R), performing as a chiroptical distributor of light. a,b) Under crossed polarizers, both types of droplets are visible clearly. c,d) Selective visualization of RH droplets by illumination with RH circular polarized light. The LH droplets become almost invisible (they are circled in orange as a guide to the eyes).

Based on the chiroptical selectivity of the cross-communication pattern, we designed a switching unit for the cross-communication between droplets. To demonstrate the switchable functionality, a mixed network was designed out of RH droplets doped with 2-(S) and photo-responsive droplets doped with 1-(M). Under right-handed circularly polarised light, no communication is established between the two series of droplets because the photo-responsive droplets are left-handed in their stable state (Fig. 5.4). Alternatively, under irradiation with UV light, the handedness of the photo-responsive droplets is inverted, and both series of droplets start to communicate, as evidenced by their reflection pattern (Fig. 5.4a). After the UV light is stopped, the cholesteric helix relaxes back to equilibrium, which is shown by a continuous change in reflection pattern, and eventually its disappearance under illumination with right-handed light (Fig. 5.4b). Noticeably, the photo-step is completed after about 30 s, *i.e.*, it is much faster than their relaxation in the dark, that takes over 50 min to complete. The relaxation kinetics can be adjusted by modifying the intensity of irradiation or by molecular engineering of the photo-responsive dopant²⁵. Overall, these results demonstrate that photo-responsive cholesteric droplets constitute controllable and reversible switching units that are selective for both the wavelength and polarisation of light.

Fig. 5.4: Photo-responsive cholesteric droplets as chiroptical switches for distributors of light. a) A photo-responsive droplet doped with 1-(M) is inserted in a superstructure of LH droplets and the resulting array is observed under crossed polarizers. The central photoactive droplet is not visible initially. After 30 s of irradiation with UV light, the central reflection appears, accompanied with photonic cross-communication. b) After irradiation with UV light stops, the droplet relaxes and the reflection signals disappear. The last two images are taken after about 50 min of relaxation using circular polarized light and linear polarized light respectively. For linear polarized light the reflection signals of all droplets are visible.

5.2.4 In-situ formation of cholesteric microbeads

The cholesteric droplets exhibit excellent stability over several months as long as they are kept in the carrier solution. The assemblies of droplets, however, show limited stability of up to several hours due to evaporation of the carrier solution, which increases the surface tension and leads to their deformation over time. One option to alleviate evaporation consists in parking the droplets between two glass slides,⁹ although that alternative restricts the cross-talk to direct

communication only, and consequently reduced the complexity of the pattern drastically. Another and more attractive alternative consists in stabilising the droplets partially by using *in-situ* polymerization. With this in mind, we generated droplets of a cholesteric doped with **2**-(R) supplemented with 5 wt% of a cross-linking monomer and traces of photoinitiator that absorbs in the visible range. The droplets were produced in the same microfluidic approach under exclusion of light and collected together with the carrier solution in a small vial. A fraction of the emulsion was subsequently deposited on a glass slide, and after self-assembly into a hexagonal superstructure, the droplets were polymerized under UV light.

Fig. 5.5: Polymer-stabilized cholesteric microbeads. The cholesteric order, provided by doping with **2**-(S), is mostly preserved after polymerization and the droplets do not deform after the carrier solution has evaporated. a) Reflected light under crossed polarizers. b) Reflected right-handed circular polarized light. c) Transmitted light under crossed polarizers. d) Transmitted light under parallel polarizers.

One day after polymerisation, optical microscopy revealed that the spherical shape of the droplets was preserved by *in-situ* polymerization and, more importantly, that the cross-communication pattern between the microbeads exhibited only minor changes (Fig. 5.5a,b). Specifically, the red central reflection is less intense, which could be an indication of a red-shifting of the cholesteric pitch following polymerization – a phenomenon that has been observed upon polymerisation of thin films of cholesteric liquid crystals earlier²⁶. Next to the increased stability of these chiral objects, we observe that the liquid crystalline order is disrupted upon *in-situ* polymerization, and consequently the special optical properties of the microbeads is not preserved perfectly (Fig. 5.5 c,d). We attribute this introduction of disorder to the fact that polymerization is initiated in

topological defect areas preferentially. As the presence of topological defects in liquid crystal droplets is unavoidable, we conclude *in-situ* polymerization is not likely to provide perfectly organized cholesteric beads. Other strategies to freeze the cholesteric order have been proposed and could be considered as alternatives.

5.3 Conclusion

Monodisperse droplets of cholesteric liquid crystals were prepared using a continuous flow approach, with fine control over the size distribution. These chiral objects were submitted to in-situ polymerisation, while their shape was preserved successfully. Beyond all-optical distributors and switches, these stabilised microbeads could reveal instrumental for applications ranging from chiral sorting⁷ to biomimetic materials²⁷.

We found that two-dimensional, closely packed, hexagonal superstructures that are formed by self-assembly of cholesteric droplets exhibit complex cross-communication that is revealed simply by observation under crossed polarisers. Moreover, we show that photonic cross-communication between objects of opposite chirality can be switched on and off, by irradiation with circularly polarised white light, which highlights that cross-communication is selective with respect to the chirality of the incoming light. Next we demonstrate that cross-communication between the droplets can be switched on and off reversibly, by using photo-responsive liquid crystals. These results confirm that cholesteric droplets are promising building blocks for the design of all-optical switchable distributors of light. Importantly for their applicability to data communication, the selective reflection of these building blocks can be adjusted to virtually cover the whole spectrum of light - including the near infrared. Our results consequently demonstrate the potential of photo-responsive droplets of liquid crystals as chiroptical switching and distributing micro-units in future all-optical data transmission technologies.

5.4 Methods

5.4.1 Synthesis of the dopants

Light-responsive molecular dopant **1** was synthesized following a procedure adapted from the literature^{28, 29}. Subsequently, the two enantiomers were separated by chiral HPLC on a CHIRALPAK AD-H column using a methanol/ethanol (1:1)

mobile phase, affording >99% ee of **1**-(M). The synthesis of the shape-persistent chiral dopants **2**-(S) and **2**-(R) was carried out as described earlier²².

5.4.2 Preparation of the cholesteric liquid crystals

E7 is a commercially available nematic liquid crystal (Merck) that is liquid crystalline at room temperature. It was dissolved in dichloromethane and mixed with 3.8 wt% **2**-(S), 3.8 wt% **2**-(R) or 4.3 wt% **1** to provide right-handed (RH), left-handed (LH) and a photo-responsive, initially left-handed cholesteric liquid crystal, respectively. Dichloromethane was evaporated at 43 °C under a stream of argon for 2 h, the vials were left at 43 °C for further evaporation overnight. The mixtures were then heated to 80 °C, stirred for 1 h and finally left to cool down to room temperature.

Carrier solution: Polyvinylalcohol (PVA, $M \approx 35.000$, Sigma-Aldrich) was dissolved in MilliQ water under vigorous stirring at 80 °C (reflux). After cooling down to room temperature, glycerol was added to this solution and the mixture was stirred for at least 30 min to obtain 3 wt% PVA in a 1:1 solution of MilliQ water and glycerol.

5.4.3 Preparation of the liquid crystal droplets

The droplets were generated using a microfluidic system designed for focusing flow technique³⁰. The cholesteric mixture (main stream) and the carrier solution (focusing stream) were pumped into a microfluidic device through its inlets using a Fluigent MFCS-Flex pressure control panel. The droplet emulsion was collected via the outlet into a container. Droplet formation for the required diameter was realized by adjusting the pressure ratios between the main stream and the focusing stream. The process was monitored using a Labsmith SVM340 inverted microscope.

5.4.4 Preparation of the liquid crystal microbeads

For the polymer-stabilised microbeads, 4.7 wt% of the reactive mesogen 4-(3-acryloyloxypropyloxy)-benzoic acid 2-methyl-1,4-phenylester and 0.2 wt% of the photoinitiator Irgacure 379 (Ciba) were dissolved in dried dichloromethane and mixed with E7. Afterwards this solution was added to 3.9 wt% of the chiral dopant **1**-(R), mixed thoroughly, the dichloromethane was evaporated at 43 °C under a stream of argon for 2h and the vial was left at 43°C for further evaporation

overnight. The mixture was then heated to 80°C, stirred for 1h and finally left to cool down. The preparation and storage of the polymerisable mixture was done in the dark.

For polymerization, about 20 μL of polymerisable droplets were deposited on a microscope glass slide. After formation of a superstructure of droplets, the sample was irradiated with a Spectroline long wave pencil lamp ($2 \text{ mW}/\text{cm}^2$) for 20 min.

5.4.5 Optical characterization

The arrays of droplets were observed under a polarized optical BX51 microscope from Olympus, equipped with an Olympus DP73 digital camera using a UV cut-off filter ($\lambda > 400 \text{ nm}$). For the images under circular polarized light, a U-TP137 quarter wave plate was used in the path of the light coming from the microscope. For photo-activation of the homogeneous superstructure of photo-responsive droplets the UV produced by the microscope halogen light source was sufficient, and no other external UV source was used. For photo-activation of the switchable droplets in the mixed superstructures, the samples were irradiated with a Hoenle bluepoint LED lamp ($\lambda = 365 \text{ nm}$, $350 \text{ mW}/\text{cm}^2$).

5.5 Acknowledgements

The synthesis of motor **1** was performed by Tadatsugu Yamaguchi. The synthesis of the shape-persistent dopant was performed by Rianne Hommersom. We acknowledge the collaboration with Dr. S. Le Gac and Dr. S. Sukas (BIOS, Lab on a Chip Group, University of Twente, Enschede, The Netherlands) who designed and fabricated the microfluidic set-up.

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Chapter 6

An artificial seed pod from enantiomerically paired networks

Mechanical movements in plants have been studied for hundreds of years. Botanical strategies for achieving motion often rely on generating helical systems such as in coiling plant tendrils, spasmoneme springs and the opening of seedpods. While a number of artificial systems can mimic these biological devices, the development of chemical systems capable of driving such deformations by the action of molecular-level phenomena is still in its infancy. Here, we describe a functional polymer network that converts nanoscale information into macroscopic work to mimic the ultimate mechanical function used by seedpods to propagate life. The bio-inspired springs operate by photochemically initiated trans to cis molecular isomerization that drives the dynamic reorganization of a micro patterned liquid crystal polymer film. The changes in molecular orientation induce helical deformities and mechanical stress at the macroscopic level and open the artificial seed pod.

Part of this chapter is included in a submitted publication: S.J. Asshoff, F. Lancia, S. Iamsaard, B. Matt, S.P. Fletcher and N. Katsonis: “Mimicking chiral seed pod mechanics with enantiomerically paired photo-responsive networks”.

6.1 Introduction

Engineering stimuli-responsive materials has become a major challenge and the variety, efficiency and kinetics of movements seen in the plant and animal kingdoms have given inspiration for artificial actuation systems of all kinds¹⁻³. However, the precise reproduction of natural systems is not required, or even necessarily desirable, as the materials and assembly methods most suited to manipulation by humans are likely very different than those used by nature. Arguably, more practically useful materials can be developed by taking lessons from biological construction principles and learning how to exploit these in our technological applications.

Fig. 6.1: The Bauhinia variegata seedpod and the engineering of artificial pod mimics based on a bar-patterned material. a) Photography of a flat, closed seedpod and the two enantiomeric helical valves after the pod has opened. Reproduced with permission from [13] (Copyright 2011 AAAS). b) Close up of the inner wall of a valve, showing with a broken line the direction of the cells, which is at an angle to the edge of the pod. The inset shows that, in each valve of a seedpod, the fibres are oriented perpendicularly. Reproduced with permission from [14] (Copyright 2014 AAAS). c) Schematic representation of the artificial valve designed in this work, and a microscopy image for the bar-type patterned material. The chirality of these valves is controlled entirely by the fabrication process.

Our understanding of the highly complex processes involved in biological mechanics has improved recently through a multidisciplinary approach, and a reoccurring theme is that nature often creates helices in order to achieve motion. Examples of biological systems built on helical motion include powerful engines such as spasmoneme springs, phototropism or stem twining, and plant tendrils that coil and wind. One fascinating class of movement is seen in the chiral seed pods of *Bauhinia variegata*. These pods feature a flat hull comprised of two narrow sides, each of which has two fibrous layers oriented at angles of $+45^\circ$ and -45° respective to the pods longitudinal axis. The opening of the seed pod is initiated by drying. When the pod dries, each fibrous layer shrinks perpendicularly to its orientation, inducing spontaneous saddle-like curvature. This curls the originally flat sides into two oppositely handed helices and leads to seed dispersal (Fig. 6.1)⁵.

We recently reported that light driven molecular motion could be converted into macroscopic helical motion and used to perform work. In that system, azobenzene switches embedded in spring-like liquid-crystalline based soft-polymers underwent *trans*- to *cis*-isomerization, which was converted and amplified into winding and unwinding motions such as those plant tendrils use to help the plant access sunlight. This molecular shape change is amplified from the switch to the macroscale by a change in molecular ordering, that results in mechanical stress. The uniform molecular organizations of these materials was capable of translating the mechanical stress into macroscopic bending, curling or twisting of the polymer film, but we realized that achieving the complex 3D shapes and shape transformations is essentially related to the chirality of the system, that involved molecular chirality and a microscopic twisted configuration in the organization of the thin film of liquid crystal. The influence of chirality on material properties and the role of its amplification or frustration on different length scales remain to be understood and is not easily controllable. However, as micro-patterning of liquid crystal polymers has been reported,⁶ we reasoned that such an approach could be used to introduce asymmetry into the material in a controlled way and alter its mechanical response to stress. Here, we show that this approach allows mimicking a complex biological function.

Mechanistically, seed pods in *B. variegata* act as an energy storage system which brutally releases this energy when the pod opens up. Artificial systems capable of releasing energy to disperse cargo are interesting for soft robotics,⁷ micro transport and delivery systems.⁸ Light is attractive to use as an external

stimuli, when compared to temperature or humidity, as it can be easily controlled effect a specific location for precise time.

The bio-inspired actuation system described below mimics the mechanics of opening of a seed pod, but differs from the natural system in key ways, such as being driven by UV light instead of humidity. In place of the two-layer fibrous system seen in biology, we use a single-layer of a polymerized liquid crystal film. The rod-shaped liquid crystal mesogens self-assemble into organized superstructures that can be manipulated by several stimuli. Stabilized by a polymer network these materials can be designed to function as single unit and do not need any further assembly, which classifies them as smart materials.⁹ Our thin polymer film has a lateral periodic bar-type pattern including two types of bars: i) bars that have a lower liquid-crystalline order (LLCO) and show little photo-induced anisotropic deformation, and ii) bars that present a higher liquid crystalline order (HLCO) and show strong photo-induced anisotropic deformation. Importantly, the bars feature density gradients, through the thickness of the film, in opposite directions. Ribbons cut from this film deform into different macroscopic shapes, and due to the gradients of density, some of these are chiral.

Fig. 6.2: a) Molecular components of the photo-actuating material. Trans-azobenzene (in orange) and cis-azobenzene (in red). The green rods represent the nematic liquid crystals. b) Schematic representation of the photo-induced shape changes.

Fig. 6.3: Preparation of micropatterned ribbons: a) A glass cell filled with the LC mixture was placed on a hot plate at 60 °C and covered by a metal mask that has bar-shaped gaps. After irradiation with UV light for 20 min the mask was removed and the cell was flipped over. The black and grey arrows next to the top corner of the cell represent the rubbing directions of the cell's top and bottom glass slide. b) The flipped cell was irradiated with visible light for 90 min and then post-cured overnight at 60 °C. c) The cell was opened and d) ribbons were cut from the polymerized film. e) The detached ribbons formed different shapes (i.e. flat or curled/twisted) depending on the angle of cutting and the bars of different molecular order and polymer densities. f) Under UV irradiation the ribbons show actuation due to the photo-isomerization of the azobenzene switch.

6.2 Results

6.2.1 Composition of the photo-responsive liquid crystal

The polymer film is made of a nematic liquid crystal containing reactive mesogens **2 a-c**, commercially available E7 (Merck) **3**, a polymerizable photo-switch **1** and a photoinitiator that responds to both UV and visible light (Fig. 6.2). Compound **1** isomerizes under irradiation with UV light, from the mesogenic *trans*-isomer to the bent *cis*-isomer and relaxes in the dark ($t_{1/2} \sim 15$ min in solution under ambient light). When a nematic liquid crystal is doped with **1**, mesogenic *trans*-**1** aligns with the other mesogens to have a common direction of longitudinal axes (director). Under UV-light, isomerization of **1** to the bent *cis*-isomer decreases the order of the nematic liquid crystal, inducing anisotropic deformation – that is the film expands in one direction along the director and contracts in the other two

directions. This actuation of homogeneous azobenzene-doped liquid crystal polymer films has been studied well and used for various applications^{10, 11}.

6.2.2 Preparation of the patterned polymer film

The un-polymerized liquid crystal mixture was introduced into a glass cell coated with a polyimide layer that induces planar alignment. The polymerization was performed at 60 °C in a two stage process. First, irradiation with UV-light through a metal mask for 20 min (Fig. 6.3a) was used to introduce ‘bars’ in the material. Then, the cell was flipped and after removal of the photomask the opposite side of the mixture was irradiated with visible light ($\lambda > 400$ nm) for 90 min (Fig. 6.3b).

During the first polymerization step, the switches within the bars photo-isomerize to the *cis*-state and this disrupts the liquid crystalline order. The lower liquid crystalline order (LLCO) will be fixed by the first polymerization step. There is also a gradient in the polymer density along the thickness of the film from the side close to the UV-light (higher density) to the side further from the UV-light (lower density). During the second stage, the bars that were previously covered by the metal mask polymerize in a highly organized state (HLCO bars). Since the cell was flipped between the two irradiation steps the gradient of polymer density in these HLCO bars will run oppositely to the gradient in the LLCO bars. Due to the differences in the molecular organization of the two bars, the bars are clearly visible under the microscope and even by simple visual inspection.

6.2.3 The geometry of the polymer shapes depends on cutting direction and their actuation by UV light

Cutting strips out of this film at different angles leads to different 3D shapes. The shape is dictated by the strain induced during the polymerization process. Apart from some shrinking due to the cross-linking of the molecules, the anisotropic deformation of the LLCO bars induced mechanical strain, which strongly influences the macroscopic deformation of the strips compared to strips cut from homogeneously polymerized films (Fig. 6.4). The initial shapes of the strips match those found for the biological systems in the dried state (Fig. 6.5).^{12, 13}

Fig. 6.4: Photo-actuation of a strip cut in 135 ° angle out of the reference samples. The references were polymerized homogeneously with visible light and UV light respectively. No reference shows any significant photo-response.

The deformations created during polymerization can be greatly enhanced by shining UV light on the strips. Of the two sets of bars, one barely changes when irradiated, while the other exhibits mechanical motion. We regard the LLCO bars that barely change under UV light as synthetic equivalents of the rigid fibers in the biological seed pod material. The HLCO bars where the azobenzenes isomerize under UV light show strong anisotropic deformation. This behavior is equivalent of the anisotropic shrinkage of the soft seed pod tissue. Notably, we only observe further coiling and twisting of the strips. Park and co-workers have shown that the direction of curvature, that is a sense of negative or positive curvature, depends on the direction of polymer density gradient along the thickness of the film¹⁴. Since the order of the polymer network is different in the two kinds of bars, and their density gradients run in opposite directions – isomerization of the azobenzenes affects each of the bars differently. Here, it appears that the initial shapes formed are due to internal stress within the strips originating from the LLCO bars. During UV irradiation of the polymerized strips the HLCO bars bend in the same direction intensifying the initial curvature leading to further bending, curling or twisting of the ribbons.

Fig. 6.5 shows the shapes obtained by cutting in different directions. At 0°, the cutting direction is aligned with the direction of the bars and perpendicular to the director of the mesogens. During polymerization the LLCO bars elongate along the cutting direction and shrink perpendicular to it. Therefore ribbons cut at 0° curl

into an open ring, and under UV light these strips curl even more. This increase in curing is because the polymer network density is highest at the outside of the open ring, which was close to the light source during polymerization. This side of the strip is stiffer and deforms less during isomerization of the azo-switch. The *inside* of the strips has a lower density polymer network, and the ribbons deform more strongly on that side, further contributing to the curling of the open ring.

Fig. 6.5: Initial states of ribbons cut in different angles. 0° is parallel to the direction of the bars. All ribbons cut in angles between 5° and 85° were twisted in a left-handed way. All ribbons cut in angles between 95° and 175° were twisted in a right-handed way. The angles parallel to the cell edges and close to them (around 0°, 90°, 180°) formed achiral shapes like flat ribbons or open rings. Under UV light all spiral ribbons twist more, the flat ribbons bend and the open ring curls stronger.

Strips cut at 90° to the bars do not curl or twist initially. However, they bend slightly along their short axis because on the side that was polymerized with visible light the LLCO bars extend along the short axis of the strip. During UV irradiation the HLCO bars also deform and apart from extending parallel to the short axis the ribbons also shrink along the long axis. Because of the higher density of polymer

in the HLCO bars at the outside of the ribbons, this side shrinks less and the opposite side shrinks more which leads to bending along the long axis.

All other directions of cutting lead to initial twisting of the strips into spirals. The spirals cut at an angle smaller than 90° are right-handed and the spirals cut at angles wider than 90° are left-handed with the strongest twist shown by the strips cut at 45° and 135° . Looking at the 45° -strip from the side that was irradiated by UV light during polymerization which ends up inside the spirals, the LLCO bars run from the left side diagonal upwards. As these bars shrink along their short axis the ribbon curls into a left-handed spiral. The opposite is true for the 135° -ribbon. During UV-irradiation the spirals twist further because also the HLCO bars shrink in the same direction. Table S1 gives an overview of initial shapes and modes of the photo-actuation.

6.2.4 Photo-responsive actuator inspired by a seed pod

A V-like, that is two valves in 45° and 135° direction that are connected at one end, was cut in the film after opening the liquid crystal cell. The width of the valves was $770\text{ }\mu\text{m}$ and the length was about 1.2 cm. After cutting, one valve was detached from the glass slide and stuck on top of the other one to form the seed pod mimic (Fig. 5a and b).

This seed pod mimic was irradiated with UV light for 30s. During the first 18 s the valves first bent along their long axis, then they bent along their short axes and the re-straightened seed pod mimic looks as if it was filled with air (Fig. 6.6c and d). After 12 more seconds, during which the pod barely changed, the valves suddenly detached from each other and twisted into spirals, so the pod brutally opened up (Fig. 6.6. 6.6e). This rapid opening and twisting motion has also been observed in nature, where the strain that is released at that moment is used to distribute the seeds.

Even after the slow relaxation of the switches the valves of the seed pod will untwist only very partially. The absence of full reversibility shows that there is already some initial strain in the closed seed pod, which keeps it closed and flat shape, since the two valves are fold on top of each other and press in opposite directions trying to twist with opposite handedness.

Fig. 6.6: Preparation and opening of the photo-responsive seed pod mimic. a) cutting of a “V” shape and folding into the seed pod mimic. b) closed flat seed pod mimic. c)-e) Activation with UV light leads to deformation and sudden opening of the seed pod when the valves twist into spiral ribbons of opposite handedness.

6.3 Discussion

This actuator demonstrates the formation of chiral macroscopic shapes without containing any chiral molecules. Instead of an assembly of hard fibers and elastic material that responds to humidity changes as it is found in natural seed pods, the photo-active seed pod consists of a material that contains bar-type areas that show a low degree of actuation between areas that show a strong mechanical responds. For processing, this gives the advantage that the whole pod is made from the same liquid crystalline mixture. No additional steps are needed, to include and organize fibers or layers. By using light as a stimulus instead of humidity the actuation can be directed to specific locations and the kinetics of the process can be controlled, too. These properties make the artificial seed pod interesting for technical and mechanical applications. We envision that this artificial system could open new perspectives for soft robotics or micro transport and delivery systems. Contact-free and precisely controllable in terms of space and time, they might even be able to outperform a strict mimic of Nature’s model.

6.4 Methods

6.4.1 Preparation of the polymer film

The non-photo-responsive reactive mesogens **2a-c** (Synthon chemicals) were mixed in a ratio of: **2a:2b:2c** = 2:3:1 and mixed with 11 wt% of E7 (Merck Germany). To this mix 5.4 wt% of the azo switch **1** was added. **1** was synthesized in our labs. To initiate the polymerization 1 wt% of the photoinitiator Irgacure 189 (Ciba) was used. All compounds were added and mixed using Dichloromethane. After evaporation of the solvent the nematic mixture was introduced into a glass cell with alignment coating inducing antiparallel, planar alignment of the mesogens. The cell thickness was 25 μm .

The liquid crystal film in the cell was polymerized at 60 °C using a UV pencil lamp (Spectroline 36-380, $\lambda = 365 \text{ nm}$, $1.000 \mu\text{W}/\text{cm}^2$) and a halogen lamp (Edmund Fiber-Lite MI-150 Illuminator, $2.5 \text{ mW}/\text{cm}^2$) and a UV cut-off filter ($\lambda > 400 \text{ nm}$). First the cell was irradiated with UV-light through a metal mask (width and distance of the bars was about 950 μm) for 20 minutes. Subsequently the mask was removed, the cell was flipped and irradiated for 1.5h with visible light ($\lambda > 400 \text{ nm}$). Afterwards the cell was left in the dark at 60 °C overnight for post-polymerization.

6.4.2 Preparing the strips and the seed pod mimic

After polymerization, the cell was frozen using liquid nitrogen and opened with a surgery knife. The strips and V-shapes were cut using a razor blade and in case of the seed pod mimic folded and clamped using tweezers.

6.4.3 Photo-actuation experiments

The samples were activated using a Hoenle bluepoint LED lamp (365nm, $340 \text{ mW}/\text{cm}^2$) and recorded using a Dinolite USB camera.

6.5 Acknowledgements

The synthesis of the chiral dopants were performed by Dr. Benjamin Matt and Supitchaya Iamsaard. Control experiments were performed by Federico Lancia. Prof. Stephen Fletcher (University of Oxford, UK) is acknowledged for a fruitful collaboration.

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Chapter 7

Self-organizing nanoparticles in twisted liquid crystals

Organizing magnetic nanoparticles into long range and dynamic assemblies would not only provide new insights into physical phenomena but also open opportunities for a wide spectrum of applications. Our approach towards this achievement consists in promoting the self-organization of magnetic nanoparticles in liquid crystals. Here, we show that twisted liquid crystals can be used as efficient anisotropic templates for super-paramagnetic nanoparticles, and demonstrate the formation of hybrid soft magnets at room temperature. As liquid crystals are known to reorganize under a variety of external stimuli, this approach allows envisioning the development of dynamic templates for the self-organization of nano-objects.

Part of this chapter has been published as: B. Matt, K.M. Pondman, S.J. Asshoff, B. ten Haken, B. Fleury, and N. Katsonis “Soft Magnets from the Self-Organization of Magnetic Nanoparticles in Twisted Liquid Crystals” *Angew. Chem. Int. Ed.* **2014**, 53, 12446–12450.

7.1 Introduction

Magnetic nanoparticles (NPs) are highly attractive objects for a wide spectrum of applications ranging from contrast enhancement in magnetic resonance imaging, drug delivery and hyperthermia treatment of tumors, to ultra-high density data storage.^{1,2} Developing these applications requires organizing these magnetic NPs into long range assemblies, for which the remnant magnetization and coercive field would be adjustable in-situ and at room temperature: the remnant magnetization characterizes the ability to store information and the coercive field, i.e. the field that is necessary to demagnetize a material, reveals the ease to erase this information. Recent investigations have shown that superstructures of magnetic nanoparticles can be formed by means of crystallization³ or by harnessing the properties of dual-responsive NPs.⁴ Alternatively, the approach described in the chapter involves using liquid crystals as platforms for promoting the self-organization of nano-objects.⁵⁻¹⁰

Scheme 7.1: Liquid crystals template the anisotropic organization of superparamagnetic nanoparticles. As a result, magnetic properties emerge at the macroscopic level.

Early investigations have demonstrated that the coercivity of ferromagnetic nanoparticles can be tuned by adjusting the structure of the crystalline superlattices they form.³ Alternatively, using liquid crystals as templates allows envisioning dynamic self-assemblies of nanoparticles, because liquid crystals are known to reorganize under a variety of external stimuli, including irradiation with light.¹¹⁻¹³ While recent investigations have focused on tuning the optical properties of metallic nanoparticles embedded in liquid crystals,¹⁴⁻¹⁶ these achievements have only hinted at the potential of liquid crystals in moderating the properties of magnetic NPs, likely due to the unspecific aggregation of these nanoparticles in usual liquid crystal hosts.¹⁷ In some cases, unspecific aggregation was avoided in part by using very diluted solutions of ferromagnetic nanoparticles in nematic liquid crystals.¹⁸ Recently, experimental proof was given that colloidal suspensions of ferromagnetic nanoplatelets in nematic liquid crystals could form macroscopic ferromagnetic phases at room temperature.¹⁹ However, tuning the magnetic properties of NPs by controlling their organization in liquid crystals was not reported to date. In this chapter, we reach beyond the superparamagnetic properties of nanoparticles by promoting their organization in a twisted liquid crystal. The liquid crystal acts as an anisotropic template that promotes anisotropy of the network of nanoparticles, and this translates into the emergence of new magnetic properties at the macroscale (Scheme 7.1).

Fig. 7.1: a) Synthesis of FePd nanoparticles by thermal decomposition of metallo-complexes Fe(acac)₃ and Pd(acac)₂ in a 5:1 ratio. b) TEM image of FePd nanoparticles (scale bar is 50 nm). c) Magnetization versus field recorded at 300 K (blue) and 10 K (green) for the free FePd nanoparticles. The curves do not reveal any significant hysteresis

at 300 K. A hysteretic behaviour appears and increases at lower temperatures and the coercive field reaches 220 Oe at 10 K.

7.2 Results and discussion

The nanoparticles were prepared using thermal decomposition of metalloc complexes $\text{Fe}(\text{acac})_3$ and $\text{Pd}(\text{acac})_2$ in a 5:1 ratio, in the presence of oleic acid and oleylamine (Fig. 7.1a). The average size of the FePd nanoparticles obtained through this procedure is ~ 18 nm, as determined by transmission electron microscopy (TEM, Fig. 7.1b). A superconducting quantum interference device (SQUID) was used in order to characterize the magnetic properties of these NPs. At room temperature, the dependence of the sample magnetization (M) on the external magnetic field (H) is typical for superparamagnetic nanoparticles: temperature-dependence of the sample magnetization, as manifested in the zero-field-cooled (ZFC) and field-cooled (FC) curves, indicates a blocking temperature of $T_B \sim 310$ K (Fig. 7.2b). No hysteresis is observed in the M-H curves and the magnetization of the NPs follows the variations of the magnetic field H (Fig. 7.1c). It appears that the dynamic reversal of the NP's magnetization, i.e. their superparamagnetism, is efficient enough not to provoke magnetic clumping and that the organic coating efficiently prevents agglomeration (Fig. 7.2a). In fact, the FePd nanoparticles obtained through this procedure were highly dispersible in non-polar organic solvents such as hexane or dichloromethane, on a time-scale of a week and at room temperature, which is a requirement to limit unspecific aggregation in the liquid crystal matrix.

Fig. 7.2: (a) Picture of a colloidal solution of FePd particles in hexane (2% wt). The solution shows no signs of agglomeration for about a week. (b) Field-cooled (FC) and zero

field-cooled (ZFC) magnetization of the MNPs as a powder under a 100 Oe applied magnetic field.

The hybrid film was prepared following a method in the previous chapters, in particular in Chapter 6.²⁰ Because of the chemical composition of the surfactants covering the nanoparticles, we anticipated that the anchoring of the liquid crystal on the nanoparticles is homeotropic, as reported for similar surfactants before.²¹ The cholesteric matrix was composed by a mixture of polymerizable and non-polymerizable mesogens that display liquid crystallinity at room temperature (Fig. 7.3). 1 wt% of photoinitiator was added to the mixture also. Magnetic NPs were eventually incorporated as 1 wt% in the liquid crystal blend. The resulting material was then introduced into a 50 μm -thick cell promoting a twist geometry, in which the orientation of the liquid crystal director changes smoothly by 90° from the bottom surface to the top surface (Fig. 7.4a,b). Traces of chiral dopant were added to the blend also. The handedness of the twist is imposed by the handedness of the chiral dopant.

Fig. 7.3: Molecular composition of the cholesteric liquid crystal film. a) Monomers constituting the polymerizable host matrix. b) Non polymerizable liquid crystal (E7) c) Chiral dopant S-811 which induces a left-handed twist in the liquid crystal. d) Traces of photoinitiator was added to ensure polymerization upon irradiation with visible light.

Although the self-organization of magnetic NPs can be achieved and studied in native liquid crystals, we sought to transform the hybrid NP-LC material into a solid film that could be easily handled at room temperature. Thus, irradiation of the cell with visible light ensured the formation of a hybrid polymer network that could be extracted simply by opening the cell. Before polymerization at $T = 45^\circ\text{C}$, the filled cell was pre-heated for two minutes at 80°C above the cholesteric to isotropic transition temperature ($T_{\text{iso}} \approx 68^\circ\text{C}$) of the mixture. After the cell was

brought back to room temperature the structure of the polymerized film was investigated further.

Fig. 7.4: Molecular orientation in a twist-cell through the thickness of the film a) top view, b) side view. c) Schematic representation of a disclination line (full black dot) that runs parallel to the walls of the cell. d) Schematic representation of the film and the cross-sections that were used for optical microscopy and for TEM. e) Polarized optical microscopy image of a cross-section confirming that the nanoparticles are confined in two dimensions. f) TEM of a cross-section of the film.

Under crossed polarizers, optical microscopy reveals a network of solid, uninterrupted lines that correspond to chains of NPs (Fig. 7.5a). Noticeably, these lines have the same width. Additional structural information was gained by observing the film between parallel polarizers. In a twist cell, liquid crystals rotate the polarization direction of linearly polarized light by 90° , causing the film to be bright between crossed polarizers, and dark between parallel polarizers. Consequently, the texture of the twisted nematic, when viewed between parallel polarizers, is a representation of the defects in the texture (Fig. 7.5b and c). Comparison of the textures observed under crossed and parallel polarizers leads to the conclusion that the magnetic NPs are localized in defect zones and that the network of NPs corresponds to a network of topological defects within the thin film. This observation is in agreement with previous investigations on nanoparticles dispersed in thermotropic liquid crystals, where nanoparticles are being trapped in various topological defects.^{22, 23} In the present material, small aggregates of nanoparticles were also visible outside the network of chains. Typically, this nonspecific aggregation could be limited by adjusting the concentration of NPs. Optimal networks were obtained when NPs were added in ratios ranging from 0.5 wt% to 3 wt% (Fig. 7.6). Confocal microscopy revealed that the NPs are all located in the same focal plane, i.e. the network of

nanoparticles is two dimensional (Fig. 7.7). Breaking the thin film along its edge and analyzing cross-sections allows gaining information about the localization of the networks in the thickness of the film (Fig. 7.4d). Polarized optical microscopy (POM) and transmission electron microscopy (TEM) images of cross-sections of the film confirmed that the nanoparticles are confined in two dimensions within the film (Fig. 7.4e,f).

Fig. 7.5: a) Optical microscopy image of the network formed in a thin film containing 0.5 wt% of FePd NPs (crossed polarizers). b,c) Optical microscopy under parallel polarizers, evidencing the preferential localization of magnetic nanoparticles along disclination lines. The arrows show the directions of polarization. In a twist cell, liquid crystals rotate the polarization direction of linearly polarized light by 90°, causing the film to be bright between crossed polarizers, and dark between parallel polarizers. d) Magnetization versus field curves recorded at 300 K (blue) and 10 K (green) for FePd nanoparticles organized in the film. An increase of the magnetic anisotropy is revealed in the film, for which the coercitive field is 300 Oe at 10 K.

Fig. 7.6: Comparison of networks obtained in presence of FePd NPs added in 0.1 wt% (a), 0.5 wt% (b), and 3 wt% (c). Scale bar is 100 μm.

Fig. 7.7: Confocal images obtained by selecting the focal plane which corresponds to the top (a), middle (b) and bottom (c) of a film doped with 1 wt% FePd nanoparticles. A focused image is obtained only in the middle of the film.

Based on these results we looked for an explanation as to why the magnetic networks that are formed are confined within a specific plane, in the thickness of the film. When the liquid crystal undergoes a transition from the isotropic state to the liquid crystalline state (and before any polymerization occurs) disclination lines appear throughout the sample, but in the absence of any NPs these defect lines disappear in less than one minute (Fig. 7.8). These disclination lines (twist walls) have been observed previously in twisted nematic liquid crystals, as a result of the isotropic-to-nematic phase transition.²⁴ When planar anchoring is strong on both sides of the cell, the twist walls are expected to run in the middle of the sample (Fig. 7.4c), and importantly, these defect zones are confined in two dimensions. In agreement with previous reports on NP organization in liquid crystals, we anticipated that the NPs would be trapped in these topological defects because these regions display a higher degree of disorder. Indeed, when located in the cores of the twist walls, that remain isotropic even below T_{iso} , the NPs allow for a decrease in the energy of the system and in so doing, also allow the stabilization and visualization of these defect lines that are confined in two dimensions. Earlier experimental results are consequently in agreement with our conclusions according to which the network of nanoparticles that is formed is two dimensional.²⁴

Fig. 7.8: Evolution of defect network in the cholesteric liquid crystal matrix as a function of time during cooling process from isotropic state to room temperature without nanoparticles (a) and with 1 wt% FePd nanoparticles (b). Optical microscopy was performed under cross polarizers; scale bar is 100 μm .

Fig. 7.9: Comparison of films obtained after polymerization in presence of FePd NPs added in 1 wt% without addition of chiral dopant in a twist cell (a) and in a planar cell(b). Scale bar is 50 μm .

Significantly, the networks were never observed when polymerization was performed without heating above T_{iso} , or in 25 μm -thick cells. Networks of nanoparticles were also observed in twist cells in the absence of traces of chiral dopant (Fig. 7.9a), but with specificities in geometry and with different dynamics of formation.²⁵ Overall, these experiments highlight that the 2D network of nanoparticles is formed because of the twist geometry (Fig. 7.4), in other words

because of the macroscopic chirality that is imposed by anchoring conditions to the twist cell. To confirm this conclusion further, we have carried out the very same experiments in planar cells, where the formation of networks was never observed (Fig. 7.9b).

The magnetic properties of the NPs arranged in structured networks were evaluated and compared to those of the free NPs. At room temperature, the network of nanoparticles displays superparamagnetic behavior, which means that the self-organization does not affect the magnetic properties of the particles (Fig. 7.5d). The saturation magnetization of the particles in the liquid crystal matrix is slightly lower than the magnetization of the free particles. We attribute this effect to a decrease of inter-particles magnetic interactions once they are diluted in the liquid crystal matrix. In contrast, at lower temperatures, the behavior of the NPs involved in the 2D network deviates from the behavior as a powder of nanoparticles (Fig. 7.1c, Fig. 7.5d and Fig. 7.10). At 10 K, the hysteresis cycle of the networks reveals a coercive field of 300 Oe, whereas the coercive field measure for free nanoparticles is 200 Oe. This change demonstrates that confinement, together with the alignment of the nanoparticles, enables the emergence of shape and thus magnetic anisotropy in the hybrid material.

Fig. 7.10: Full scale magnetization vs field curve for FePd nanoparticles forming a network in a thin film containing 0.5 wt% of FePd NPs at a) 150K and b) 50K.

A magnetic field was applied to the 2D network prior to polymerization, in order to further promote the emergence of shape anisotropy within the film and to reveal it at room temperature. For this experiment, the ratio of NPs in the matrix was increased to 3 wt% in order to obtain a denser network. Polarized optical microscopy of the resulting material reveals that the chains of nanoparticles orient into parallel lines, as a response to the applied magnetic field (Fig. 7.11). In turn, we do not exclude that the network of defects follows the reorganization of the nanoparticles. At 300 K, the magnetic anisotropy of the film is revealed by the slopes of the first magnetization curves recorded at two different orientations with respect to the applied field (Fig. 7.11c). When the NP chains are aligned with the direction of the field, the magnetization reaches saturation much faster than when the particles lines are perpendicular to the magnetic field. This result reveals the existence of an easy axis of magnetization in the materials that is parallel to the lines of NPs. The emergence of macroscopic anisotropy at room temperature is also demonstrated by the appearance of hysteresis loops on M vs H curves. Whereas no hysteresis can be detected at 300 K on the film prepared without applying any magnetic field, the 2D linear network shows remnant magnetization (Fig. 7.12). Thus we have demonstrated that organizing superparamagnetic nanoparticles in a twisted liquid crystal allows for the tuning of their magnetic properties. The hysteretic behavior exhibited by the system is characteristic for a soft magnet.

The normalized remnant magnetization increases when recorded from perpendicular to parallel alignment of the NPs lines. To detect a stronger and thus more reliable effect, measurements were performed at 10K also. At low temperature, the normalized remnant magnetization M/M_{sat} increases from 0.3 to 0.4 from perpendicular to parallel alignments respectively (Fig. 7.11d). As the typical measurement error with SQUID is less than 2%, this 25% variation of the magnetization between the parallel and perpendicular cases is significant. At this temperature, the coercive field reaches 300 Oe. The width of the hysteresis loops shows that the remnant magnetization is increased significantly by the shape anisotropy created in the film.

Fig. 7.11: a) Polarized optical microscopy image of the structure of the network obtained when a magnetic field is applied during polymerization of the film containing 3 wt% of FePd NPs. The orientation of the lines is dictated by the orientation of the magnet, while the disclination lines create ramifications of the structure. b) Comparison of the network using parallel polarization (arrows indicate the directions of polarization). c) First magnetization vs field curves recorded at 300K when NP lines are oriented parallel (blue) and perpendicular (red) with respect to the applied magnetic field. The corresponding hysteresis loops are shown Figure S8. d) Normalized magnetization vs field curves recorded at 10K for parallel (blue) and perpendicular (red) orientations revealing a remnant magnetization of $M/M_{\text{sat}} = 0.4$ and $M/M_{\text{sat}} = 0.3$ for respectively parallel and perpendicular orientations. The black segments at $H=0\text{Oe}$ are intended to highlight the variation of remnant magnetization between the two possible orientations of the lines. This M/M_{sat} variation corresponds to a decrease of 25%.

Fig. 7.12: Normalized magnetization vs field recorded at 300K for the FePd nanoparticles linearly organized in the film and oriented parallel (a) and perpendicularly (b) with respect to the applied magnetic field. Strong variations of the magnetization at fields greater than 500 Oe are attributed to the tendency of the film to move in order to align the easy axis of magnetization to the applied magnetic field. The noise in the signal recorded in the perpendicular orientation likely originates in the tendency of the film to align along the applied magnetic field, which makes the sample move during measurements.

Fig. 7.13: Picture of the experimental setup for the alignment of nanoparticles in the liquid crystal matrix during polymerization on a heating plate at 45°C. The size of the magnet is 35 mm x 7 mm.

In conclusion, creating networks of magnetic nanoparticles in twisted liquid crystals provides a means of tuning their magnetic response. The remnant magnetization that emerges from the organization of the nanoparticles transforms the hybrid material into a soft magnet. The effects we observe remain modest, as they originate in the anisotropic templating effect of the twisted liquid crystal. However, we anticipate that the anisotropic magnetization would be strengthened by the use of magnetic nanorods, because nanorods have an intrinsic shape anisotropy that would add to the anisotropy of the matrix. Ultimately, the use of photo-responsive chiral dopants allows envisioning the use of light as an external trigger, in order to switch the magnetic properties of the film, on and off, reversibly. Our results demonstrate the potential of complex fluids for tuning the magnetic properties of nanoparticles as they emerge at the macroscopic level.

7.3 Methods

Nanoparticle synthesis

FePd particles were prepared by high temperature decomposition, a method adapted from.²⁶ Benzylether (99%), 1,4-tetradecanediol (97%), oleic acid (90%), oleylamine (70%), Iron(III)acetylacetonate ($\text{Fe}(\text{acac})_3$), Pd(II)acetylacetonate ($\text{Pd}(\text{acac})_2$) (99%), were purchased from Sigma Aldrich and used as received. $\text{Fe}(\text{acac})_3$ (1.7 mmol) and $\text{Pd}(\text{acac})_2$ (0.3 mmol), 1,2-tetradecanediol (10 mmol), oleic acid (6 mmol), oleylamine (6 mmol) and butylether (20mL) were mixed and magnetically stirred under nitrogen. The mixture was heated to 200°C for 2 hours and then under a blanket of nitrogen heated to reflux (300°C) for 2 hrs. It was subsequently cooled down to room temperature, dissolved in ethanol (40 mL) and the material was eventually separated via centrifugation (8000g, 30 min). The material was dispersed in hexane in the presence of 0.05 mL oleic acid. The centrifugation was repeated three times to remove excess material. The resulting product was dried under vacuum and stored under nitrogen. Samples for TEM analysis were obtained by deposition of 5 μL of a 0.5 wt% solution of the particles in hexane onto 100-mesh carbon-coated copper grids. After 1 min, the excess liquid was blotted away with filter paper. After drying, images were obtained using a Philips CM300ST-FEG electron microscope.

Sample preparation

The monomers C₆M, C₆BP and C₆BPN were purchased from Synthon Chemicals and mixed in a 2:3:1 ratio by weight. The nematic liquid crystal E7₇ (Merck) was added to the monomer mixture to prevent crystallization in a 2:3 ratio by weight in favour of the monomer mixture. A chiral dopant (S811) was added as traces to the mixture (0.04 wt%). The handedness of the twist is imposed by the handedness of the chiral dopant.

All compounds were dissolved and mixed in dichloromethane purchased from Sigma-Aldrich. The solvent then was evaporated at 48°C under nitrogen stream. Irgacure 819 was eventually added as a photoinitiator (1 wt%). The nanoparticles were first dispersed in hexane and sonicated for 10 minutes before they were mixed with the liquid crystal. The solvent was evaporated at 48°C under nitrogen stream.

Film preparation

The cholesteric mixture containing the nanoparticles was heated at 80°C (isotropic state) and directly introduced into a 50 µm gap twist cell (EHC, Japan). After cooling down to the liquid crystalline mesophase at 45°C, the cell was irradiated from the top with visible light ($\lambda > 420$ nm) by using an Edmund MI-150 High-intensity Illuminator to initiate the polymerization that was completed within 90 min. A picture of the experimental set-up used for polymerization under a magnetic field, is shown Fig. 7.13. Eventually, the twist cells were frozen with liquid nitrogen and then opened using a scalpel to reveal the polymer film.

Magnetic measurements

The magnetic measurements were performed with a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 K and 300 K for DC applied fields ranging from -7 T to 7 T. The film was directly wrapped around the sample holder for measurements in the parallel alignment and restrained in a plastic film for other measurements.

Film characterization

Textures were investigated in transmission and reflection modes by using a polarizing microscope (BX51 from Olympus). The images were obtained by using an Olympus DP73 digital camera. TEM measurements have been carried out at the Wageningen Electron Microscopy Center (WEMC). The film was first embedded in a resin using an epoxy embedding medium kit from Sigma Aldrich. Thin sections (70 nm to 90 nm) were prepared with a Reichert Ultracut S ultramicrotome using a Diatome diamond knife (ultra 45°). The sections were deposited on copper slot grids (G205-Cu) and the electron microscope was operated at 80 kV.

7.4 Acknowledgements

Dr. Kirsten M. Pondman, and Prof. B. ten Haken (Neuroimaging Group, University of Twente, The Netherlands) are acknowledged for the synthesis of the superparamagnetic nanoparticles. Dr. B. Fleury (Sorbonne Université, UPMC University Paris 06, CNRS, France) is acknowledged for the SQUID measurements. Dr. Benjamin Matt is acknowledged for initiating the project.

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Summary

The aim of this thesis was to develop smart materials based on nematic (achiral) and cholesteric (chiral) liquid crystals, with a special focus on the amplification of chirality in these materials. Liquid crystals organize spontaneously into phases that display orientational order, their specific geometry being determined by the anisotropy in shape of the molecules, their intermolecular interactions and their conditions of confinement.

The organization of liquid crystals provides them with unique properties such as selective reflection of light, anisotropic deformation and sensitivity for temperature and electric, magnetic or electro-magnetic fields. The responsiveness of liquid crystals makes them ideal candidates for the design and development of smart materials, with potential applications to soft robotics or to sensing. Future challenges for smart materials based on liquid crystals involve the design of increasingly complex switchable properties, wider tuning ranges, higher energy efficiencies and contact-free control and driving systems. Using light as an external trigger appears as a very relevant approach to address this challenge, as light is a versatile, precise and clean source of energy, that is usually well compatible with soft matter. A complementary strategy to address this challenge consists in drawing inspiration from the versatility and efficiency of biological systems and use biological approaches in the design of novel liquid crystal materials.

The use of photo-responsive liquid crystals supposes that a dynamic behavior is introduced into passive materials. Here, the responsiveness to light is encoded by doping the liquid crystals with molecular motors or switches. The photo-isomerization of these dopants occurs at the nano-scale but can be amplified up to the macroscale by modifying the optical and mechanical properties of the whole molecular material.

Chapter 1 provides a general introduction to nematic and cholesteric liquid crystals, with a special focus on those of their mechanical and optical properties that will be discussed in the experimental chapters. **Chapter 2** provides a more specific overview over the recent literature closely related to cholesteric liquid crystals doped with light-responsive motors and switches, and their applications.

Chapter 3 describes the kinetics of photo-responsive cholesteric liquid crystals that are doped specifically with light-driven molecular motors. We demonstrate that the reorganization of the cholesteric helix is determined by the kinetics of the thermal relaxation of the molecular motors. Therefore, kinetics for photo-tuning of the pitch and handedness of a cholesteric doped with molecular motors and thus the wavelength and polarity of such a cholesteric liquid crystal can be controlled by judicious choice of the dopant.

In **Chapter 4**, photo-responsive cholesteric liquid crystals were confined into spherical droplets. In these droplets, a wealth of complex topological structures was observed, as predicted by recent theoretical investigations. These topological structures have been observed under the polarized optical microscope and remotely controlled with irradiation with UV light. Notably, the droplets investigated in this chapter were polydisperse.

In **Chapter 5**, the optical properties of the cholesteric droplets presented in Chapter 4 were investigated. Monodisperse cholesteric microspheres were prepared by using a microfluidic set-up. The microspheres self-assemble in hexagonal superstructures, in which they can communicate optically. This wavelength-sensitive and polarity-sensitive photonic cross-communication has been switched and tuned gradually by using irradiation with UV light.

Chapter 6 describes the preparation of an achiral liquid crystalline polymer thin film. The film is cut in strips that spontaneously formed various chiral and achiral shapes. Moreover, these strips twist/curl under UV light. Inspired by plant movements, the ribbons were assembled like a seed pod that opened abruptly into two helical valves, upon irradiation with UV light.

Chapter 7 widens the scope of this thesis by dealing with magnetic properties and nanoparticles. In this chapter I report on twisted liquid crystals that are used as efficient anisotropic templates for superparamagnetic nanoparticles and demonstrate the formation of hybrid soft magnets at room temperature. This work can be seen as the basis for composite materials in which nano-objects are organized in the liquid crystal texture. By using photo-responsive liquid crystals, the texture and thus the mesoscale organization of the particles could be tuned. At the same time using liquid crystal textures as templates for other types of nano-objects *e.g.* gold nanorods would allow tuning different properties such as the optical properties related to plasmon resonance.

Overall, the experimental effort presented in this thesis involves the **control and amplification of chirality** at different length scales. In Chapters 3 to 5 chirality is added on the molecular level and then amplified up to the micron scale. In contrast, the nematic polymer films described in Chapter 6 are achiral but the strips cut from those films twist into chiral shapes. Here the asymmetry is induced by a gradient of polymer density, *i.e.* chirality originates at the microscopic level and is only expressed visibly at the macroscopic scale. Finally, in Chapter 7, the cholesteric liquid crystal is doped with chiral molecules and would usually form a microscopic helix structure; however, due to the confinement the cholesteric liquid crystal is not able to form this helix structure properly but forms a twisted configuration instead. Since similar twisted configurations can also be formed by nematic liquid crystals (given the right confinement conditions) and since the liquid crystals in chapter 7 do not show the typical properties of cholesteric liquid crystals (like the selective reflection), it appears as if the molecular chirality is not expressed in the micro- and macroscale. Chirality plays a crucial role for all molecular materials and the questions of how to induce amplify or suppress chirality and what effect this has on the material properties remain an intriguing topic for this research field.

Samenvatting

Het doel van dit proefschrift was het ontwikkelen van de zogenoemde slimme (smart) materialen gebaseerd op nematische (achirale) en cholesterische (chirale) vloeibare kristallen, met de focus op de amplificatie van chiraliteit in deze materialen. Deze vloeibare kristallen kunnen zich spontaan op een bepaalde wijze oriënteren ten opzichte van elkaar, waarbij hun specifieke geometrie wordt bepaald door de anisotropie van de moleculen, de intermoleculaire interacties en de condities van insluiting.

De manier waarop vloeibare kristallen zijn georganiseerd, geeft ze unieke eigenschappen zoals selectieve reflectie van licht, anisotropische vervorming en gevoeligheid voor temperatuursveranderingen en elektrische, magnetische of elektromagnetische velden. Het reactievermogen van vloeibare kristallen maakt hen ideale kandidaten voor het ontwerpen en ontwikkelen van slimme materialen met mogelijke toepassingen in zachte robotica en waarneming. Toekomstige uitdagingen voor deze slimme materialen gebaseerd op vloeibare kristallen, zijn o.a. het ontwerpen van nog complexere schakel eigenschappen, een breder afstemmingsbereik, hogere energie efficiëntie en contact-vrije controle van de drijvende krachten. Het gebruik van licht als een externe prikkel lijkt een hele relevante benadering voor deze uitdaging, omdat licht een diverse, precieze en schone energiebron is die meestal geschikt is voor zacht materiaal. Een complementaire strategie om deze uitdaging aan te gaan, is inspiratie putten uit de diversiteit en efficiëntie van biologische systemen en een biologische benadering te gebruiken voor het ontwerpen van nieuwe vloeibaar kristallijne materialen.

Door het gebruik van licht-gevoelige vloeibare kristallen veronderstelt men dat er een dynamisch gedrag geïntroduceerd wordt in passieve materialen. In dit geval wordt de sensibiliteit voor licht gecodeerd door de vloeibare kristallen te doteren (verrijken) met doteerstoffen die fungeren als moleculaire motors of schakelaars. De fotoisomerisatie van deze

doteerstoffen gebeurt op nanoschaal maar kan geamplificeerd worden naar macroschaal door de optische en mechanische eigenschappen van het gehele moleculaire materiaal te modificeren.

Hoofdstuk 1 is een algemene introductie over nematisch en cholesterisch vloeibaar kristallijn materiaal, met de focus op de mechanische en optische eigenschappen van vloeibare kristallen welke beschreven staan in de experimentele hoofdstukken. **Hoofdstuk 2** geeft een specifiek overzicht van de recente literatuur met betrekking tot cholesterische vloeibare kristallen verrijkt met licht-gevoelige doteerstoffen en hun toepassingen.

Hoofdstuk 3 beschrijft de kinetiek van licht-gevoelige cholesterische vloeibare kristallen, die specifiek zijn gedoteerd met licht-gevoelige moleculaire motors. Wij laten zien dat de reorganisatie van de cholesterische helix wordt bepaald door de kinetiek van de thermische relaxatie van deze specifieke doteerstoffen. Zodoende kunnen de spoed en de draairichting van de helix van een cholesterisch vloeibaar kristal, gedoteerd met moleculaire motors, d.m.v. van licht afgesteld worden en kunnen dus ook de golflengte en polariteit van zulke cholesterische vloeibare kristallen worden gecontroleerd door een verstandige keuze van de doteerstof.

In **hoofdstuk 4** zijn de licht-gevoelige cholesterische vloeibare kristallen ingesloten in bolvormige druppels. Zoals voorspeld in recent theoretisch onderzoek, werd er een wereld aan complexe topologische structuren geobserveerd in deze druppeltjes. Deze topologische structuren werden geobserveerd onder een optische polarisatiemicroscopie en van afstand bestuurd d.m.v. bestraling met UV-licht. De bestudeerde druppels waren polydispers.

In **hoofdstuk 5** werden de optische eigenschappen van de cholesterische druppeltjes, beschreven in hoofdstuk 4, verder onderzocht. Gelijkvormige

cholesterische microdeeltjes werden bereid middels een microfluidische opstelling. Deze microdeeltjes vormen uit zichzelf hexagonale superstructuren, waarbinnen zij optisch kunnen communiceren. Deze golfleengte- en polariteit-gevoelige fotonische kruis-communicatie wordt aan- en uitgeschakeld via een gedoseerde bestraling met UV-licht.

Hoofdstuk 6 beschrijft de preparatie van een dunne, achirale vloeibaar kristallijne polymeer laag. Deze laag werd in dunne stroken gesneden die vervolgens spontaan verschillende chirale en achirale vormen aannamen. Bovendien krulden deze stroken onder invloed van UV-licht. Geïnspireerd op bewegingen van planten werden de stroken samen gebracht als een zaadhuls, welke abrupt openbarstte in twee spiraalvormige helften na bestraling met UV-licht.

Hoofdstuk 7 verbreedt het blikveld van dit proefschrift door gebruik te maken van magnetische eigenschappen van nanodeeltjes. In dit hoofdstuk rapporteer ik hoe gekrulde vloeibare kristallen gebruikt worden als efficiënte anisotrope mallen voor super-paramagnetische nanodeeltjes en demonstreer ik de vorming van hybride zachte magneten bij kamertemperatuur. Dit werk kan gezien worden als de basis voor samengestelde materialen waarin nano-objecten georganiseerd zijn binnen in het vloeibaar kristallijne materiaal. Door gebruik te maken van lichtgevoelige vloeibare kristallen, kan de samenstelling en dus de organisatie van de deeltjes op mesoschaal worden gereguleerd. Door gebruik te maken van vloeibaar kristallijne structuren als basis voor andere nanovoorwerpen zoals gouden nanostaafjes, kunnen tegelijkertijd verschillende eigenschappen afgesteld worden, zoals optische eigenschappen gerelateerd aan plasma resonantie.

Samenvattend hebben de experimenten beschreven in dit proefschrift betrekking op de controle en amplificatie van chiraliteit op verschillende ordes van grootte. In de hoofdstukken 3 tot en met 5 is chiraliteit op een moleculair niveau toegevoegd en versterkt op micro-schaal. De nematische

polymeer lagen beschreven in hoofdstuk 6, zijn daarentegen achiraal. Maar eenmaal gesneden in dunne stroken worden het chirale structuren. Hier wordt de asymmetrie veroorzaakt door een gradiënt van polymeer dichtheid, d.i. de chiraliteit ontstaat op microscopische schaal en is alleen zichtbaar op macroscopische schaal. Uiteindelijk worden de cholesterische vloeibare kristallen in hoofdstuk 7 gedoteerd met chirale moleculen om een microscopische helix structuur te vormen. Echter, door de insluiting zijn de vloeibare kristallen slechts in staat tot een gedeeltelijke vorming van de helix structuur (twist). Dit betekent dat moleculaire chiraliteit wordt onderdrukt op micro- en macroschaal. Chiraliteit speelt een cruciale rol in alle moleculaire materialen en de vraag is hoe we de chiraliteit kunnen induceren, versterken of onderdrukken en welk effect dit heeft op materiaal eigenschappen. Dit blijft een intrigerend onderwerp in dit onderzoeksveld.

Acknowledgements

I am grateful to many, many people that have helped me in different ways during my time as a PhD student.

First of all I am thankful to Prof. Nathalie Katsonis, who gave me the opportunity to be part of a starting research team, to work on a fascinating topic and develop in the lab and on several international conferences and meetings. I learned a lot from you about working and living as a researcher.

I acknowledge Prof. Jeroen Cornelissen as the head of our research group for the discussions we had throughout the years, in which he always found some commendations and motivating words.

I acknowledge all my collaboration partners: Dr. Alessandro Bosco from Trieste, Prof. Feringa from Groningen, Tetiana and the SINGULAR team from Bordeaux, Dr. Severine Le Gac and Sertan from the BIOS group, Prof. Stephen Fletcher from Oxford, Kirsten and Prof. B. ten Haken from the Neuroimaging Group and Dr. Benoit Fleury from Paris. Parts of the common works are described in this thesis and have been published in scientific journals, which shows that these collaborations were fruitful and in many ways enjoyable, too. I am especially thankful to Prof. Ben Feringa for the chance to experience some engaging days in his labs in Groningen. Also, I would like to thank Prof. Stephen Fletcher for the time with his nice and motivated research team in Oxford. Moreover, I thank Prof. Alberta Ferrarini for helpful and inspiring discussions.

Of course, I also enjoyed the access to techniques in labs of other groups within MESA+: I thank the MTP group and especially Clemens for all the help with and access to microscopes, DSC, TGA, contact angle and rheology measurements. I also thank Mark Smithers for the TEM and SEM measurements.

Within our labs, I am grateful to Nicole and Izabel for being always helpful no matter how many inconveniences I caused, to Marcel for all the technical help and his ever-lasting good mood, to Regine for my Samenvatting, to Richard for help and maintenance of all kind of equipment, Melissa for insights into the world of viruses and the related biochemistry and for our

early morning conversations. I am also thankful to Tibor for scientific discussions on “how things work”. And I thank Jurriaan, Wim, Pascal, Dodo and Bianca who I unfortunately have not worked that much with but still appreciate for all kind of nice contacts from conversations about babies to scientific advice.

And now to my post-doc colleagues and PhD fellows:

I would like to thank all members and former members of the MnF-BNT cluster. Within these 4,5 years so many people have been part of my everyday lab life, so please forgive me if I do not mention all names here and be assured that I am still thankful to every single one who made my time here exciting and happy (or sometimes at least less difficult :P).

I would like to mention only the few colleagues that had the biggest impact on my work: First of all from the liquid crystal clan, dear Supitch, cutest of all lab mates, thank you so much for sharing the lab space, for all the molecules you synthesized, for the great trips we made and the many scientific discussions and happy/funny/”nasty” chats we had. A huge thanks goes to my beloved Ben for help inside and outside the lab, our special breaks, coffees and “champagne”. I am also thankful to Wilfried for sharing ups and downs of our lab and life experiments and many “wise” postdoc advices. And a special thank you goes to Federico for help during my pregnancy and mom-of-a-new born-baby time – in short: IOU!!

Further, I thank Melanie and Pieter for the help during my start in Twente; Rajesh, the incarnation of kindness, for the USB microscope; Shirish, my comic fan fellow, for tips and tricks concerning “my best friend” – the computer; Alejandro for help whenever I messed up something in their lab again; Tom for balancing the lab climate, Rianne for help with all the bio lab tools and Carmen for help with all “hard core chemistry” issues, for scientific discussions and motivational chats about chemistry and life.

Of course, there are/were people at this university like the highly talented and kind Jenny, the jolly power girl Wies, the pure and beautiful Veronica, the wise and funny Francesco, the smart and tough Nana, the sporty and helpful Diana, sharing and caring Raluca, the pretty and honest Carlo, the down-to-earth and gracious Emanuela, the stylish and understanding Jordi

and the crazy and entertaining Kim, who all had extremely positive but rather indirect impacts on my work.

Just like my dear friends from outside of this university and like my dear family, these friends and colleagues were so very important to my success. However they were important in a way that cannot even be appropriately described and honored in these acknowledgements, so I prefer to do that in another way.

At last, a great thank you to my paranymphs, the amazing Roberto and the unforgettable Raquel. The three of us started together in 2011 and since then you accompanied me in the lab and in my life. We shared hobbies, celebrated with food, fun and music several happy occasions. You listened to countless complains and sad stories of mine, we were happy, sorry and excited for each other. I thank you so much for supporting me during all those years up to the moment in front of the committee!

THANK YOU ALL and I wish you all the best for research and for life!

About the author

Sarah Jane Aßhoff was born in Bremen, Germany, on 19th February 1985. She studied Chemistry at the University of Bremen, where she received her degree (Chemie Diplom) in 2010. During her undergraduate training period she has investigated the synthesis and characterization of novel chiral gold nanoparticles, at the Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM Bremen, under the direction of PD Dr. A. Hartwig.

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Sarah is currently author or co-author of six peer-reviewed publications. She was the recipient of the first poster award at the Dutch chemistry conference Chains (2011) and was selected to participate to the 63^d Lindau Nobel Laureate meeting on Chemistry (2013). She was also discussion group leader at the Gordon Research Seminars on Polymers (2013).

List of publications

- S.J. Aßhoff, S. Iamsaard, F. Lancia, B. Matt, S.P. Fletcher and N. Katsonis “Mimicking seedpod mechanics with enantiomerically paired photo-responsive soft materials”, *submitted*.
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