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Time-programmed helix inversion in phototunable liquid crystals†‡

Cite this: *Chem. Commun.*, 2013, **49**, 4256

Received 1st October 2012,
Accepted 27th November 2012

DOI: 10.1039/c2cc37161h

www.rsc.org/chemcomm

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Doping cholesteric liquid crystals with photo-responsive molecules enables controlling the colour and polarisation of the light they reflect. However, accelerating the rate of relaxation of these photo-controllable liquid crystals remains challenging. Here we show that the relaxation rate of the cholesteric helix is fully determined by helix inversion of the molecular dopants.

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 colour that is reflected to be modified.[5,6] The most efficient approach towards designing phototunable cholesteric mesophases involves chiral and photo-responsive dopants such as azobenzenes,[7] overcrowded alkenes[8] 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 polarised 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 material's stability 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 phototunable 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 colour-stable materials.[11] However, their relaxation is still too fast to be neglected.[7,12] Alternatively, other applications require colour-tunable systems that restore their initial colour 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 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.

Achieving control over the rate of winding and unwinding of the cholesteric helix requires an improved understanding of the interplay between isomerisation of the photo-responsive dopants (at the molecular level) and the reorganisation which occurs at the macroscopic level. Previously we have demonstrated that the kinetics of photo-induced texture rotation are determined by the dopants (molecular rotary motors), provided that the rate of photo-isomerisation of these dopants is significantly slower than the characteristic time of reorganisation of the liquid crystal host.[13,14] In this communication we demonstrate for the first time that the relaxation of phototunable cholesteric liquid crystals can be time-programmed by judicious choice of the exact structure of the dopant. Moreover, we investigate the kinetics of relaxation of cholesteric liquid crystals doped with three different overcrowded alkenes and compare their dynamic behaviour to (i) the isomerisation rate of

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† This article is part of the *ChemComm* 'Emerging Investigators 2013' themed issue.
‡ Electronic supplementary information (ESI) available: Experimental details, CD-spectra, results of fits and a movie showing photoisomerisation followed by UV/Vis spectroscopy. See DOI: 10.1039/c2cc37161h

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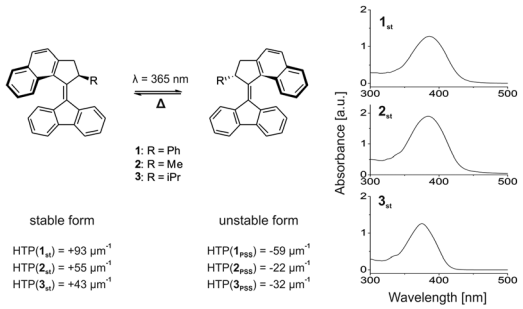

Fig. 1 Overcrowded alkenes used as dopants. HTP values reported here are measured for the nematic host E7 and expressed as a mole fraction (left panel). The UV/Vis absorption spectra of the stable forms are measured in *n*-hexane (right panel).

the dopants in solution and (ii) the typical reorganisation times for the nematic liquid crystal used as a host.

Phototunable cholesteric liquid crystals were prepared by doping a nematic liquid crystal (E7, Merck) with a series of overcrowded alkenes (5 wt% to 15 wt%) synthesised according to literature procedures[15] and purified by Chiral Technologies Europe (Fig. 1).

In solution, overcrowded alkenes undergo a *cis–trans* isomerization around their central double bond upon irradiation with UV light (Fig. 1, right panel) 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 (HTPs). Considering that at the 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 overcrowded alkene **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: $\lambda_0 = np$, where p is the pitch of the cholesteric helix and n is the refractive index of E7.[18] For low concentrations of the dopant, a linear relation is observed between the dopant concentration and the inverse of the pitch: $\mathrm{HTP} = 1/(c \times \mathrm{ee} \times p)$, 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 behaviour over the whole visible range.

Upon irradiation of the cells with UV light, the proportion of stable form of the dopants decreases in favour 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. 2). The UV/Vis spectra recorded *in situ* show a red-shift of the reflection band, which corresponds to an increase in cholesteric pitch, and consequently to unwinding of the cholesteric helix (Fig. 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 μm^{-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 from the decrease in the overall transmittance of the samples (Fig. 2b).

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. 2c, see ESI‡ for experimental conditions). 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 favour 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 polarised IR spectroscopy.[5] Here, we demonstrate helix inversion for cholesteric liquid crystals doped with molecules **1**, **2** and **3**. Experimental evidence is provided by UV/Vis spectroscopy, where disruption of the cholesteric order was observed (Fig. 2b and c), and by circular dichroism (Fig. S1, ESI‡).

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 for the cholesteric helix doped with **1**). In contrast to the photoswitching step, thermal relaxation is not dependent on the

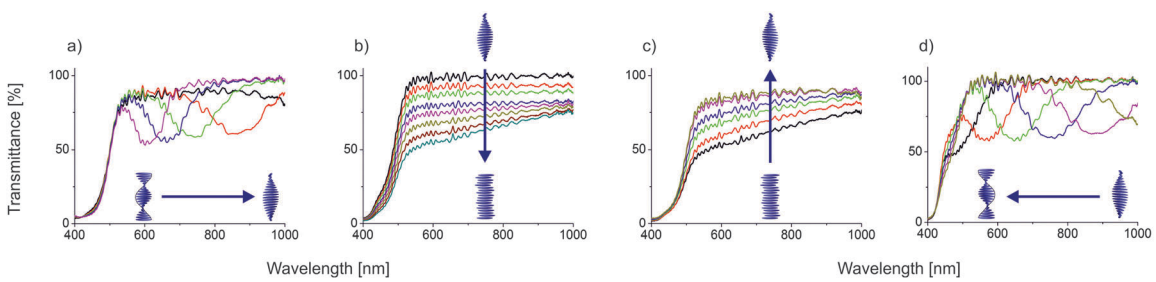

Fig. 2 Photo-isomerization of a cholesteric liquid crystal formed by E7 doped with molecule **1** (6 wt%), as followed by UV/Vis spectroscopy (only representative spectra are shown). First, irradiation triggers the unwinding of the cholesteric helix and the reflection colour undergoes a red-shift (a). Once the helix is unwound, disruption of the cholesteric order results in diffusion and a corresponding decrease in 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).

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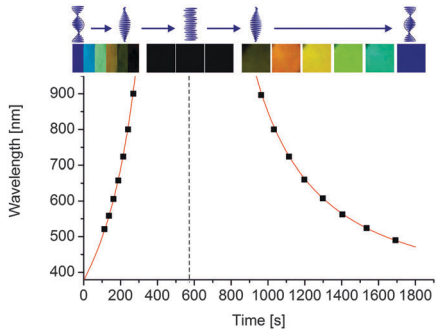

Fig. 3 Thermal (helix-inverting) relaxation of a cholesteric liquid crystal doped with molecule **1**, as followed by UV/Vis spectroscopy. The data points correspond to the right edge of the selective reflection band and were fitted according to eqn (1). The top panel shows the reflection colours and pictograms of the cholesteric helix.

conditions of irradiation. In fact, once the photostationary state has been reached, the relaxation of the system depends only on the thermal isomerisation 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 were fit using the following equation:

$$\lambda = \frac{n \times 10^3/c}{|\mathrm{HTP_{st}} - \Delta\mathrm{HTP} \times \chi_{\mathrm{unst,PSS}} \exp(-k_{\mathrm{rel}} t)|} \qquad (1)$$

where λ is the position of the reflection band (expressed in nm), n is the refractive index, c is the concentration of the dopant, $\mathrm{HTP_{st}}$ is the HTP (expressed in μm^{-1}) of the stable form, ΔHTP is the difference of HTPs between the stable and the unstable isomer, $\chi_{\mathrm{unst,PSS}}$ is the molar fraction of unstable form at the 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 ESI‡ 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** is 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 $\lambda_0 = f(t)$.

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 $\tau_{\mathrm{nem}} = D^2\gamma/k_2$ where D is the thickness of the cell, γ is the twist viscosity coefficient and k_2 is the twist elastic constant of the nematic host. For a thickness in the micron range, τ_{nem} is of the order of seconds. The reorganization time is less than the characteristic relaxation times of most overcrowded alkenes ($\tau_{\mathrm{photo}} \approx 200$ 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 1 Comparison between rate constant of the relaxation process (k_{rel}) for the dopant in solution and for the cholesteric helix

Dopant	k_{rel} for dopant in solution[a] [s^{-1}]	k_{rel} for cholesteric helix[b] [s^{-1}]	$\chi_{\mathrm{unst,PSS}}$[b]	$\mathrm{HTP_{st}}$[b] [μm^{-1}]
1	1.18×10^{-3}	1.27×10^{-3}	0.995	100.5
2	3.64×10^{-3}	3.89×10^{-3}	0.993	34.5
3	7.32×10^{-3}	1.16×10^{-2}	0.880	48

[a] Measured. [b] Values extracted from fits assuming $\mathrm{HTP_{st}} = -\mathrm{HTP_{unst}}$.

In conclusion, 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 optimised successfully in solution through variations in molecular structure, our results evidence that helix inversion in phototunable liquid crystals can be also dramatically accelerated, and consequently holds great potential towards using new cholesterics for smart materials with sophisticated functions.

The authors thank Prof. A. Ferrarini for discussions and helpful suggestions. The work was supported by NWO (Vidi Grant).

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