Time-Programmed Helix Inversion in Phototunable Liquid Crystals

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Electronic Supplementary Information (ESI)

1. Experimental details:

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 λ=365 nm by using a Hönle LED lamp (600mW/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.

2. CD-spectra:

A Jasco J715 was used for CD-measurements. A UV pencil lamp (4.4 mW/cm^2 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.

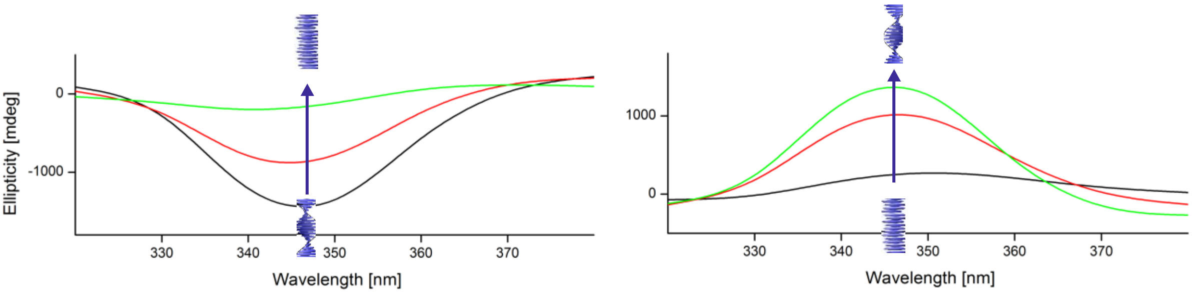


Fig. 1: CD spectra following the relaxation of the same cholesteric liquid crystal; both helix unwinding (left) and helix rewinding (right) are observed.

3. Relaxation kinetics

The color 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 (main text). The data have been fitted using a least square minimization procedure with Eq. 1 (main text) 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 unsable 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 $krel$ 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 colesteric helix can be expressed in terms of the HTPs of the two isomers of the motor HTP_{st} and HTP_{unst}, namely

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

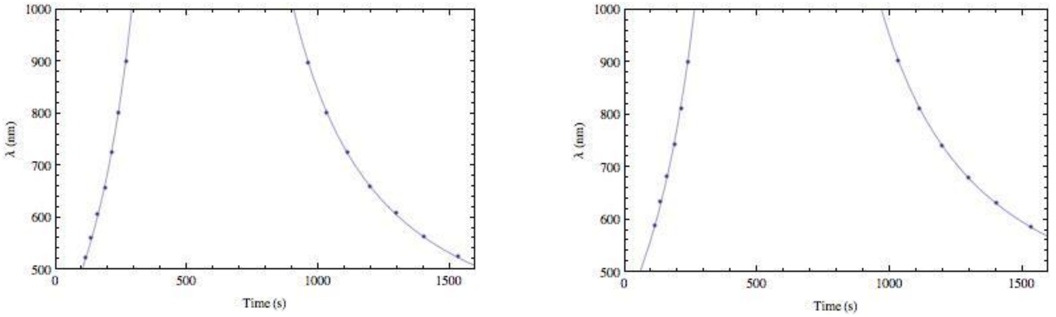
Finally, Eq. 1 can be easily derived by substitution of the previous formula.

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.

Data used for the fits:

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

Dopant 1



Left edge

Right edge

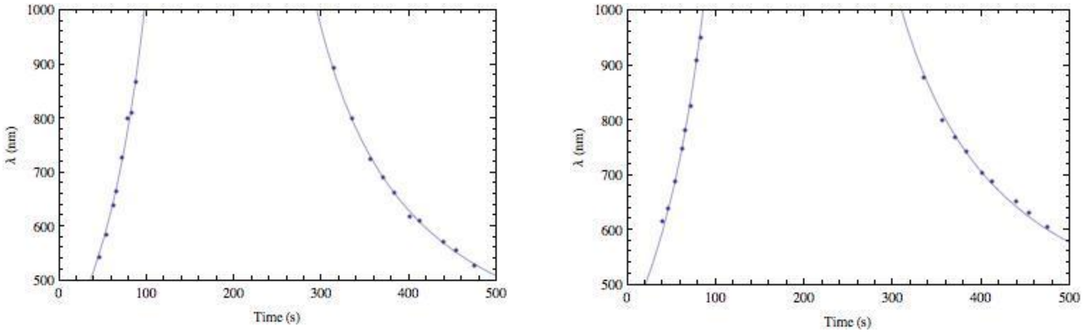
Table Ia: Fitting parameters for **1**.

	Left edge	**Right edge**	**Average**
k_{rel} [s^{-1}]	1.28·10^{-3}	1.26·10^{-3}	1.27·10^{-3}
HTP_{st} [μm^{-1}]	106	95	100.5
$\Delta HTP\ x_{unst,PSS}$ [μm^{-1}]	212	188	200

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

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

Dopant 2



Left edge

Right edge

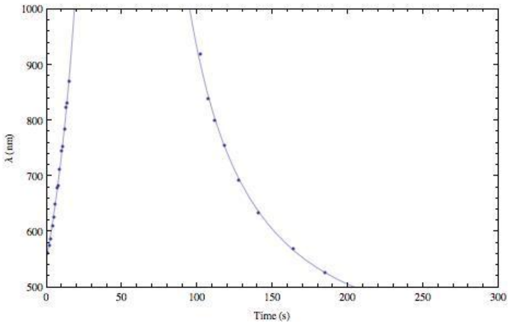
Table IIa: Fitting parameters for **2**.

	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} [μm^{-1}]	37	32	34.5
$\Delta HTP\ x_{unst,PSS}$ [μm^{-1}]	73.0	63.9	68.5

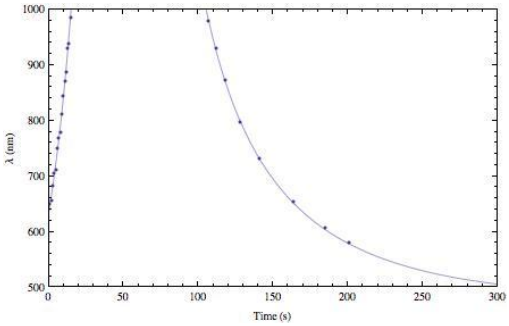
Table IIb: Results obtained from the fitting parameters reported in Table IIa, assuming $HTP_{st} = -HTP_{unst}$.

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

Dopant 3



Left edge



Right edge

Table IIIa: 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} [μm^{-1}]	51	45	48
$\Delta HTP\ x_{unst,PSS}$ [μm^{-1}]	90	79	84.5

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

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

4. Movie:

The photo-isomerisation of the cholesteric liquid crystal doped with molecule **3** has been followed with UV/Vis-spectroscopy. One spectrum was taken every 500ms. This spectra collection has been used to prepare a real-time movie (see ESI Movie 1). You can see the reflection band shifting over time, importantly, the shift of the reflection band does not occur as a continuous process: between two well-defined reflection bands, other reflection patterns with less defined character are observed (see movie in ESI). Indeed photo-induced unwinding of the cholesteric helix can be compared to unwinding processes of cholesteric liquid crystals under electric fields, where unwinding involves twist wall growing steps which remove one complete or half a twist unit, in turn.[i] Here, we observed that the difference between the number of pitches of two neighboring reflection bands with defined shapes corresponds to about one pitch also.

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[i] R. B. Meyer, *Appl. Phys. Lett.*, 1968, **12**, 281.