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PAPER

Reversible photochemical control of cholesteric liquid crystals with a diamine-based diarylethene chiroptical switch†

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Upon addition of a chiral dopant to a nematic liquid crystal, amplification of molecular chirality can occur and consequently a cholesteric liquid crystal is formed. A major challenge in materials science consists in designing efficient chiral dopants that allow for control over chiral amplification by use of an external trigger, for example by irradiation with light, and thereby achieving the control of the dynamic and responsive structure of cholesteric liquid crystals. Here, a chiral photochromic switch bearing two chiral imine units connected *via* phenyl spacers was synthesized and characterized in solution, where it can be photo-chemically converted from a colourless ring-opened form **1o** to a coloured ring-closed form **1c**, reversibly. We show that a small amount of **1o** used as a dopant induces the formation of a stable cholesteric liquid crystal. The retention of the photochromic properties of **1**, when used as a chiral dopant, allows for reversible photocontrol over the period of the cholesteric helix, and shows the highest values of helical twisting power achieved so far with diarylethene-based photoswitchable dopants.

Introduction

Phototunable chiral liquid crystals (LCs) are dynamic materials that have demonstrated extensive applicability in several fields of materials science including optical rewritable information storage[1] and dynamic colour control.[2] A very promising approach consists of using these tunable materials to design smart and broadband reflective devices.[3] Phototunbale cholesteric liquid crystals can be formed by using switchable molecules as chiral dopants for nematic liquid crystals. A major challenge to create these materials is to design and synthesize switchable chiral dopants that are not only excellent helicity inducers but also photoswitches with a high thermal stability. A wide range of chiral photoswitchable dopants providing control over the period of cholesteric liquid crystals has been developed in recent years.[4] While azobenzene-based chiral dopants have received most attention,[5,6] the properties of other classes of photo-responsive molecules as dopants have been investigated also,[7] including fulgides,[8] olefins,[9] chiroptical overcrowded alkenes[10] (as well as structurally analogous molecular motors),[11,12] and diarylethenes.[13–15]

Diarylethenes are a class of compounds that can be switched from a colourless open form to a coloured closed form upon irradiation with UV light and returned to the open form by irradiation with visible light.[16] The thermal stability of both the open and the closed form is an important property of diarylethenes, which contrasts with, for example, the thermal reversibility observed for azobenzenes and spiropyrans. This thermal stability allows for the state of diarylethenes to be controlled selectively by UV and visible irradiation. The synthesis of diarylethene-based mesogens has been reported.[17] Although attractive, this approach is hindered both by the synthetic cost of the mesogens and by their high transition temperatures. Alternatively, the use of chiral photoswitches as dopants allows envisioning of precise and reversible photocontrol over the helicity and the pitch of cholesteric liquid crystals (the pitch of a cholesteric helix is defined as the unit length for a complete rotation). The propensity of a chiral dopant to induce cholesteric order in a nematic environment is characterised by its helical twisting power (HTP). So far, diarylethene derivatives have shown moderate HTPs, up to 28.6 μm^{-1} as reported by Irie and coworkers.[15d]

This value remains significantly lower than HTPs reported for some azobenzenes, which can reach 158 μm^{-1}.[18] However, despite their high efficiency in inducing chiral order, the use of azobenzenes as chiral photoswitchable dopants is hampered by their lack of thermal stability—one way switching from the *trans* to the *cis* form can be controlled by irradiation with UV light but the kinetics of the reverse reaction are entirely determined by the structure of the azobenzene-based molecule and thus the reverse reaction is often not controllable by an external trigger. While

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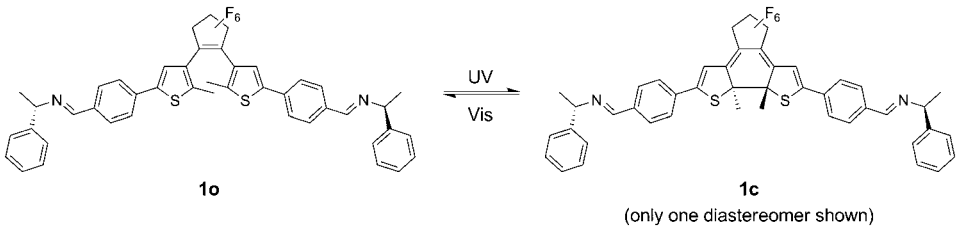


Fig. 1 Diarylethene-based liquid crystal dopant **1** in its open (**1o**) and closed (**1c**) form.

diarylethenes provide a prospectful alternative to azobenzenes because of the thermal stability of both open and closed forms, their HTPs have to be improved in view of future applications where visible light is employed because high dopant ratios have to be used when chiral dopants have a low HTP, which gives rise to several related problems, *e.g.* phase separation.

In this contribution, we report on the synthesis of diarylethene **1** and its photochromic properties both in solution and as a chiral dopant (Fig. 1). To the best of our knowledge, the HTP of **1** used as a chiral switch is the highest reported for a diarylethene-based dopant. Importantly, the HTP value of diarylethene **1** is sufficiently high to induce the formation of a cholesteric mesophase in both its open (**1o**) and its closed form (**1c**), in contrast to the majority of previous designs where only the open form showed a non-negligible HTP.[13,14,15b] Finally, we demonstrate that the photochromic properties of **1** in solution are retained in the liquid crystalline matrix and that photocontrol of the whole mesophase can be achieved reversibly by irradiation with UV and visible light. With optimization of their HTPs, diarylethene-based dopants are prospectful alternatives to azobenzene-based dopants for reversible photocontrol of the structure of cholesteric liquid crystals.

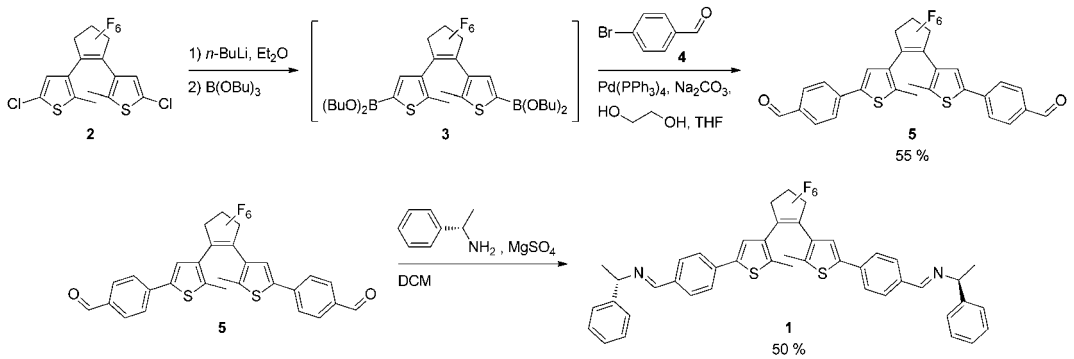
Results and discussion

The design of diarylethene **1** is based on two chiral imine units connected to a diarylethene photochromic unit through phenyl spacers. The chiral units are introduced using phenyl-aldehyde moieties, which react readily with chiral amines (Scheme 1). Incorporation of phenyl groups directly attached to the diarylethene unit allows for extension of the conjugated core of the molecule, which induces a red shift in the absorption of the closed form, compared to 1-phenylethylimine-based diarylethene designs earlier reported by our group.[13] This red shift in the absorption spectrum of the closed form results in an increase in the photostationary state. The choice of the central moiety was motivated by the fact that perfluorinated cyclopentene-based systems provide better photochemical stability for diarylethenes, compared to perhydrogenated moieties.[19] The design of **1** also took into account that enhancing the mesogenic character of the molecule enhances its solubility in nematic hosts, thereby allowing higher doping ratios to be used without the problem of phase separation.

Diimine diarylethene **1o** was prepared using a two-step synthesis from the dichloro-substituted diarylethene **2** *via* derivative **5**.[20] Conversion of **5o** to **1o** was achieved by condensation with a chiral amine (Scheme 1). This approach can potentially allow for facile variation through the use of other chiral secondary amines.

The photoswitching behaviour of **1o** in solution was studied using ^{1}H NMR, UV/Vis, and CD spectroscopy. The ^{1}H NMR spectrum of **1o** shows the absorption of two methyl groups attached to the thiophene moieties at 1.99 ppm and the aromatic protons between 7.20 and 8.40 ppm. Irradiation of the sample at 365 nm results in a decrease in the absorption at 1.99 ppm and the appearance of a new band at 2.20 ppm in addition to the shifting of one of the aromatic absorptions to 6.73 ppm, which is indicative of the formation of the closed-ring isomer **1c**.[21] Based on the integration of the absorption bands assigned to the methyl groups, the ratio **1o**:**1c** at the photostationary state (PSS_{365nm}) was determined to be 2 : 98. This excellent value is an important feature of diarylethene **1** in view of future applications.

The UV/Vis spectrum of a sample of **1o** in hexane (2.0×10^{-5} M) shows an absorption maximum at 322 nm (Fig. 2a). Irradiation at 365 nm results in the appearance of a broad absorption with a maximum at 595 nm, indicative of the



Scheme 1

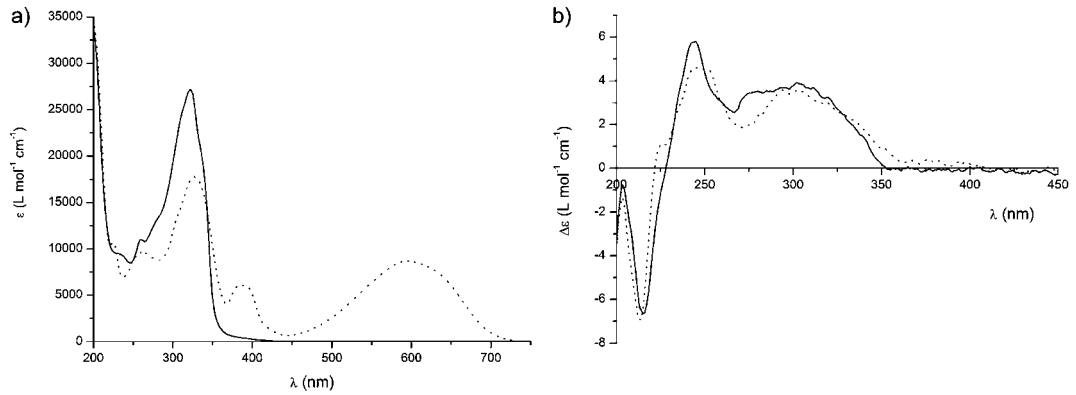


Fig. 2 UV-vis absorption (a) and CD spectra (b) of 1o (solid lines) and at $PSS_{365\ nm}$ in hexane (2.0×10^{-5} M) at 20 °C (dashed lines).

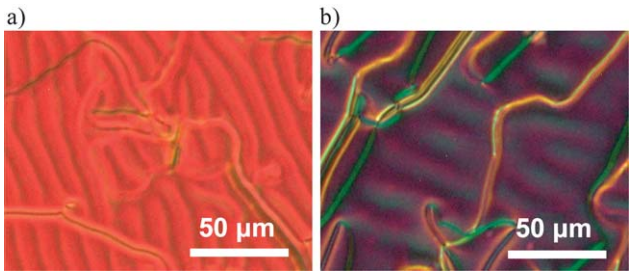


Fig. 3 Textures observed with 5CB doped with **1o** (2,9 wt%) using polarized optical microscopy under homeotropic anchoring conditions (on a glass slide functionalised with octadecyltrichlorosilane). Size of both images: 156 µm × 121 µm a) before irradiation at 365 nm and b) after 10 min irradiation at 365 nm.

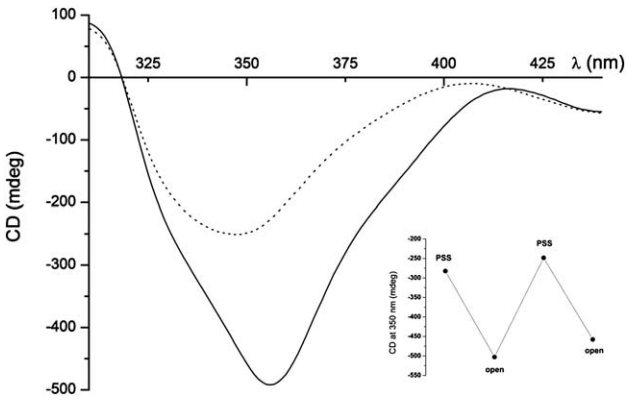


Fig. 4 CD spectra of **1** in 5CB: spectrum of 5CB doped with **1o** (solid line) and spectrum of the cholesteric mixture at PSS_{365nm} (dashed line). The spectra were recorded at normal incidence and the cell was rotated through several angles around the direction of the beam to ensure the absence of artefacts arising from linear dichroism. The inset shows the result of monitoring of two cycles of irradiation with UV and visible light, by using CD spectroscopy. This monitoring demonstrates reversible switching of **1** in a liquid crystalline environment.

formation of **1c**.[22] An isosbestic point was maintained at 343 nm. In contrast, the CD spectrum of **1o** in hexane did not change significantly upon irradiation at 365 nm, indicating that switching of the diarylethene unit does not induce a CD effect in addition to the CD signal attributed to the chirality of the imine groups (Fig. 2b).

Doping of nematic liquid crystals 4′-pentyl-4-biphenylcarbonitrile (5CB) or E7 with 2.9 and 2.1 wt% of **1o** respectively resulted in the observation of a fingerprint-like texture[23] that is characteristic of the formation a stable cholesteric mesophase (Fig. 3a). When the cholesteric mixture of **1o** in 5CB was irradiated at 365 nm, the characteristic fingerprint texture was retained (Fig. 3b); however, the periodicity of the fingerprint texture increased, indicating that the pitch of the cholesteric helix had lengthened, and consequently that **1c** has a lower HTP than **1o**. That the mesophase remained cholesteric indicates that the HTP of **1c** is sufficient to induce the formation of a stable cholesteric liquid crystal. This observation contrasts with the behaviour of previously described diamine-based diarylethene dopants[13] and other diarylethene-based dopants,[14,15b] for which the HTP of the closed form is too low to induce the formation of a cholesteric mesophase. Subsequent irradiation of the sample with visible light (λ > 420 nm) resulted in the formation of a cholesteric texture with the same periodicity as observed prior to irradiation at 365 nm.

Circular dichroism (CD) was employed to study the photochemically induced modification in the helical structure of the cholesteric liquid crystals. Nematic liquid crystals based on non-chiral compounds, *e.g.* 5CB and E7, do not give rise to CD signals. However, the presence of a chiral molecular dopant can induce CD signals through the formation of chiral molecular architectures, such as the helical ordering of mesogens in cholesteric liquid crystals. Planar orientation of the sample was ensured by using an adapted cell (see experimental section) and checked by observing the characteristic oily streak texture by optical microscopy, under cross polarizers. The CD spectrum of both **1o** and **1c** shows an intense negative band at 340 nm, which corresponds to the absorption region for 5CB (Fig. 4). With the values of cholesteric pitch we are using (see Table 1), the

Table 1 Pitch values, HTP and handedness of the cholesteric liquid crystals formed by doping nematic hosts 5CB and E7 with diarylethene **1**

Nematic host	wt-% of **1**	Pitch (µm^{-1})	HTP of **1o** (µm^{-1})	HTP at **PSS** (µm^{-1})
5CB	2.9	2.5	−44	−30
E7	2.1	2.7	−50	−35

reflection band of the cholesteric LC is to the red of the absorption band. Moreover, the dielectric anisotropy and the linear dichroism of 5CB are both positive, therefore it is possible to determine the handedness of the cholesteric helix induced by **1o** and **1c** based on induced CD spectra.[24] The negative bands in the absorption region of 5CB indicate that a left-handed cholesteric helix is formed, and therefore that the HTP of **1o** and **1c** are negative. The sign of HTPs determined by CD spectroscopy is in agreement with earlier reports using a related dopant in the same nematic host.[13] Moreover, the relative intensities of the CD spectra indicate that the HTP of **1** at the $PSS_{365\ nm}$ is lower (in magnitude), than the HTP of **1o**.

The switching of **1** in a cholesteric liquid crystalline environment was reproduced over a few cycles without any significant alteration of the CD spectra shown in Fig. 4.

The absolute values of HTP of **1o** and $\mathbf{1}_{PSS}$ in 5CB and E7 were determined with the Grandjean–Cano method (Table 1).[25] The HTPs measured did not differ significantly between 5CB and E7, which can be rationalised on the basis of the similarity of the molecular composition of the two nematic hosts.

Conclusions

In conclusion, we have synthesized a chiral diarylethene dopant with higher helical twisting power than other diarylethene-based dopants reported so far. Its light-switchable properties were demonstrated, both in solution and in a liquid crystalline matrix. Diarylethene **1** was used as a chiral dopant in nematic hosts 5CB and in E7. To the best of our knowledge, in comparison to previously reported chiral diarylethene-based dopants,[13–15] diarylethene **1** shows the best doping performances reported for a chiral diarylethene so far. Because the aromatic core of **1** was extended in comparison to previous designs of chiral diarylethene dopants,[13] this molecule, used as a dopant in nematic liquid crystals, was shown to induce the formation of a cholesteric mesophase in both its open and closed forms. Importantly and in contrast with azobenzene-based chiral dopants, both **1c** and **1o** are thermally stable and thus they both induce the formation of thermally stable cholesteric liquid crystals.

We found that the open form **1o**, which has a flexible chemical structure, has a higher HTP than the closed form **1c**, whose structure is more rigid. This result is in agreement with recent investigations by Akagi *et al.* who reported powerful helicity inducers with a flexible structure.[26]

Finally, through irradiation with UV and visible light, reversible photocontrol of the period of the cholesteric helix was achieved. These results provide new opportunities for the development of light-driven chiral molecular switches as building blocks or components for smart functional materials.

Experimental

Materials

All reagents are of commercial grade and used as received unless stated otherwise. Solvents for spectroscopic measurements were UVASOL (Merck) grade. The liquid crystalline materials E7 and 4′-pentyl-4-biphenylcarbonitrile (5CB) were purchased from Merck Japan and from Aldrich, respectively. NMR spectra of samples dissolved in $CDCl_3$ were recorded using a Varian Unity AS400. Melting points (uncorrected) were determined using a Büchi B-545 melting point device. Mass spectra (HRMS) were obtained using a Thermo Scientific LTQ XL and LTQ Orbitrap XL spectrometer.

Spectroscopy

UV-vis spectra were recorded at room temperature using a JASCO V-630 spectrophotometer in 1 cm pathlength quartz cuvettes (conc. of **1o** 2.0×10^{-5} M). CD spectra were recorded on JASCO J-815 spectropolarimeter using a custom built sample holder for liquid crystal cells, at normal incidence. The cells purchased from EHC (Japan) had the following specifications: thickness 8 μm, planar alignment, antiparallel, with capillary fill. UV irradiation experiments were performed with a Spectroline ENB-280C/FE UV lamp (range: 320–380 nm with a maximum at 365 nm). Irradiation experiments with visible light were performed with a Thorlabs OSL1-EC fiber illuminator together with a long pass filter (range: 450–750 nm).

Microscopy

Liquid crystalline textures were observed by polarized optical microscopy. Pitches were determined by the Grandjean-Cano technique using a plan-convex converging lens (radius = 25.119 mm).

Synthesis

3,3′-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-(5-aldehyde)-phenylchloro-2-methylthiophene) (5). 3,3′-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-chloro-2-methylthiophene) (**2**, 3.30 g, 7.55 mmol) was dissolved in a flame dried flask in anhydrous Et_2O (150 mL). *n*-BuLi (11.7 mL, 1.6 M in hexane, 18.7 mmol) was added slowly by syringe at rt and the mixture was stirred for 30 min. Tributylborate (5.22 mL, 19.3 mmol) was added dropwise and the mixture was stirred for 40 min at rt. In a second flask, a mixture of *p*-bromobenzaldehyde (**4**, 2.82 g, 15.2 mmol), tetrakis-(triphenylphosphine)palladium(0) (0.33 g, 0.29 mmol), THF (60 mL), 2 M aqueous Na_2CO_3 (40 mL), and ethylene glycol (3 mL) was heated to 50 °C. The reaction mixture containing the crude boronic ester **3** was added slowly by syringe after which the resulting mixture was heated at reflux for 16 h. The mixture was diluted with Et_2O (150 mL) and washed with brine (100 mL). The brine solution was extracted with diethyl ether (100 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (silica gel, pentane–ethyl acetate 5 : 1, R_f 0.3) yielded dialdehyde **5** as a brown solid (2.4 g, 55%). mp 199–200 °C; ^{1}H NMR (400.1 MHz, $CDCl_3$) δ 10.01 (s, 2H), 7.90 (d, $J = 8.2$ Hz, 4H), 7.70 (d, $J = 8.3$ Hz, 4H), 7.44 (s, 2H), 2.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4 (d), 143.5 (s), 140.9 (s), 138.9 (s), 135.6 (s), 130.7 (d), 126.4 (s), 125.9 (d), 124.4 (d), 14.9 (q); HRMS (APCI): calcd for $C_{29}H_{17}F_6O_2S_2$ ($[M - H]^-$): 575.0569, found: 575.0537.

***N*,*N*′-(((4,4′-(Perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))bis(4,1-phenylene))bis(methanylylidene))bis-(1-phenylethanamine) (1).** L(-)-α-Methylbenzylamine (0.12 g, 1.0 mmol) was added to a mixture of 4,4′-(4,4′-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))dibenzaldehyde

(0.20 g, 0.35 mmol), $MgSO_4$ (0.42 g 3.5 mmol), and anhydrous CH_2Cl_2 (100 mL) in a flame dried flask. The resulting mixture was stirred for 16 h at rt. The $MgSO_4$ was removed by filtration and the filtrate was concentrated *in vacuo*, yielding a dark brown oil which was crystallized from EtOH affording diimine **1** as a brown solid (140 mg, 50%). Analytical data: mp 68.4–70.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 2H), 7.79 (d, J = 8.3 Hz, 4H), 7.57 (d, J = 8.3 Hz, 4H), 7.44 (d, J = 7.1 Hz, 4H), 7.39–7.31 (m, 6H), 7.25 (t, J = 7.3 Hz, 2H), 4.56 (q, J = 6.6 Hz, 2H), 1.99 (s, 6H), 1.61 (d, J = 6.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (d), 145.2 (s), 142.1 (s), 141.8 (s), 136.0 (s), 135.3 (s), 129.1 (d), 128.6 (d), 127.0 (d), 126.8 (d), 126.1 (s), 125.7 (d), 123.1 (d), 80.0 (d), 25.0 (q), 14.8 (q); ^{19}F NMR (376 MHz, $CDCl_3$) δ −110.0 (t, J = 5.1 Hz, 4F), 131.8–131.9 (m, 2F); HRMS (ESI): calcd for $C_{45}H_{37}F_6N_2S_2$ ([M + H]$^+$): 783.2297, found: 783.2287.

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