Photoinduced changes of absorption and circular dichroism in a chiral nematic phase containing a photochromic fulgide

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Abstract

Mesophases composed of a nematic mixture (ZLI1132) alone or with a chiral inductor (twisted nematic phase) were doped with a photochromic furylfulgide (FFU) and irradiated with visible and UV light. FFU shows great fatigue resistance and high repeatability of photochromic cycles in these media. Quantum yields for the photoconversions are very similar to values previously reported in solution. Besides the photochromic changes in absorption spectra, a great and reversible circular dichroism change in the chiral nematic phase was observed in the visible absorption band of the cyclic isomeric form of FFU upon UV irradiation. This change is due to the mesophase-induced chiral absorption. The potential of this signal for information storage is discussed.

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1. Introduction

A photochromic compound exists as two stable or metastable isomers, that differ in absorption spectrum and that can be interconverted by light absorption or thermally [1,2]. Photochromic families of compounds include azobenzenes [3], spiropyrans [4], spirooxazines [5], chromenes [6], diarylethenes [7], and fulgides and fulgimides [8], among others [9].

Several fulgides photoisomerize between two thermally stable isomers by a reversible pericyclic reaction. In these systems, there is a remarkably large shift in the absorption between the two isomers (ca. 150–200 nm). An open ring structure absorbs only in the UV and a close ring structure with extended conjugation has a moderate intensity absorption in the green region (absorption coefficient at the maximum between 5 × 10³ and 5 × 10⁴ M⁻¹ cm⁻¹). Additional favorable features include a high interconversion efficiency that can be tuned by substituents and high fatigue resistance [8]. In furyl fulgides and other heteroaryl fulgides, the thermal decoloration is greatly suppressed because the lower aromatic stabilization of these moieties in comparison to phenyl results in a lower excess energy of the close form with respect to the open one. Finally, adequate methylation of the furyl ring eliminates undesirable side reactions that compete with the photochromic cycle, such as E-Z isomerization and H migration [10–12].

Photoinduced changes of macroscopic properties have been extensively studied because of their applicability in memories and switches [13]. The use of light to produce the changes has many interesting features, such as possibility of remote control, ease of dosification, and target tunability through wavelength selection. Photochromic systems offer in principle the possibility to store and read information due to
their bistable nature with different absorption spectra. Their main drawback, when the signal is detected by absorption spectroscopy, is that the monitoring light is the same as the photolyzing light, therefore limiting the lifetime of the stored information. One way to overcome this difficulty is to use the photochromic transformation to induce a bulk change of properties in a host phase in which the photochromic system can be embedded, dispersed, covalently linked or even can be a constituent of an attached phase or command layer [14]. In such systems, the change of bulk properties can be detected independently of the phototransformation even if it is performed optically.

Mesophases present interesting properties that make them suitable as host phases and therefore have been frequently used with this purpose. High order, susceptibility, and reversibility due to fluidity are amongst these properties. The change in the microscopic order that can be controlled by the photochromic transformation acts as a very suitable switch that can be monitored by means of the change in several other physical properties independently of the change in absorption itself, therefore minimizing the perturbation of the system, both thermal and photochemical [14–20].

In this work, we study the photochromic transformation of a furylfulgide (whose structure is given in Fig. 1) in a nematic phase and in a chiral nematic phase produced by addition of a chiral inductor to the first. The furylfulgide selected has high efficiencies for the photochemical conversions, is highly reversible and fatigue resistant upon irradiation, and has no photochemical side reactions (i.e. $E$–$Z$ isomerization). Besides the expected reversible spectral modifications, changes in circular dichroism were photoinduced in the visible with a high signal to noise ratio.

2. Experimental

2.1. General methods

UV–vis spectra were recorded in a HP8452A diode array spectrophotometer, and linear dichroism measurements were performed in the same instrument with a film polarizer placed before the sample. Circular dichroism measurements were performed in a Spectro-Polarimeter Jasco J-20. Birefringence set-up was described previously [19]. A Lumatec Superlite SUV-DC-P irradiator with a 200 W short arc mercury lamp was used for irradiation cycles, with suitable filters for the isolation of UV (UG11, Schott) and visible (GG420, Schott) light. Total power of the irradiating light for the calculation of quantum yields was measured with a piroelectric power/energy meter (Melles Griot). Polarized microscopy

![Fig. 1. Structure of the furylfulgide (FFU) used in this work and its photochromic transformation, of the liquid crystal mixture ZLI1132, and of the chiral inductor S811.](image-url)
was performed on a transmission microscope (Leitz DMR) equipped with film polarizers (Melles Griot).

2.2. Materials

Cells of parallel polyimide rubbed layers, spaced 4 and 10 μm, ITO coated, were purchased from E.H.C. Co. Ltd. (Japan). Commercial liquid crystal mixture ZLI1132 (Licristal/Merck), and chiral inductor S811 (Licristal/Merck) were used as supplied. The value of helical twisting power (HTP) for this system is 13.9 μm−1 M−1 [21]. Synthesis of the furylfulgide photochromic compound (FFU) was performed following a modification [22] of Heller’s method [23] for similar heterocyclic fulgides, comprising two successive Stobbe condensations and a final dehydration, as it is described in Scheme 1.

2.3. Sample preparation

Mixtures of ZLI1132, S811, and the photochromic dye were prepared by weighting each component and then stirring for at least 6 h in the dark. The concentration of the chiral inductor was between 10 and 20% (w/w), and the amount of the photochromic compound was less than 2.5% (w/w) in all experiments. Cells were filled at room temperature by capillary effect, and orientation was verified by polarized microscopy.

3. Results and discussion

The furylfulgide under study (FFU) experiences a photochromic transformation between an open form, $E$, and a closed form, $C$, as illustrated in Fig. 1. The system shows excellent photochromic behavior both in nematic and in cholesteric phases. No thermal reactions were detected in hours at room temperature, and no sign of fatigue was observed even after more than one hundred irradiation cycles (UV and visible irradiation).

UV–vis spectra of $E$ and $C$ forms in cholesteric phase are shown in Fig. 2. The samples present the reflection band, characteristic of a cholesteric mesophase in a planar alignment, in the visible–NIR region. The concentration of the chiral inductor was kept lower than 20% (w/w) to prevent overlap of the cholesteric reflection band with the absorption band of the $C$ isomer of the fulgide. In the case of the spectra in Fig. 2, the reflection band can be observed with maximum at 755 nm. The addition of FFU up to 2.5% (w/w) did not modify the position of this band. Thus, the pitch of the mesophase was not appreciably modified by the presence of the dopant.

The absence of a coexistence of phases (TN-I) upon photo-transformation was verified by polarized microscopy, in all the mixtures prepared.

The pitch of the chiral nematic phase did not show any change after irradiation of the samples with UV light (see Fig. 2), even for the more concentrated samples prepared.
This can be better appreciated in the differential spectrum of Fig. 2. It confirms that the pitch of the mesophase is mainly controlled by the chiral dopant (S811), which is in a higher amount than the photochromic dopant (a racemic mixture of atropoisomers). Fulgides, with their small geometric change between E and C isomers do not perturb greatly the order of the mesophase [24].

Photocycling processes under UV and visible light irradiation were followed at each absorption maximum, as depicted in Fig. 3. Quantum yields of both cycling and opening processes were calculated from irradiation curves [25] in cholesteric phase. The quantum yield for the coloration process ($\Phi_{E \rightarrow C}$) can be calculated from Eq. (1), taking into account that the total absorbance at the irradiation wavelength is kept low ($A < 0.05$) [25]:

$$\frac{d[E]}{dt} = \Phi_{E \rightarrow C} I_0 E = \Phi_{E \rightarrow C} \frac{I_a(E)}{l} \varepsilon_E[E] \ln 10$$ (1)

In Eq. (1), $E$ is the concentration of the E form of the fulgide (Fig. 1), $I_0$ the incident photon flux, $I_a(E)$ the photon flux absorbed by $E$, $l$ the optical path length, and $\varepsilon_E$ is the weighted absorption coefficient of $E$ that takes into account the absorption spectrum and the filter transmission profile. A similar equation holds for the irradiation in the visible, from which the quantum yield for the ring opening reaction can be obtained, $\Phi_{C \rightarrow E}$. Considering that C absorbs in the UV, its reversion to $E$ by UV light should be considered in Eq. (1) by a subtractive term $\Phi_{C \rightarrow E} I_a(C)$ [25]. Nevertheless this contribution is negligible because $\Phi_{C \rightarrow E}$ is 10% of $\Phi_{E \rightarrow C}$ (see Table 1) and the absorption coefficient of C is smaller than that of E in the UV (see Fig. 2). Under irradiation conditions in the visible for the $C \rightarrow E$ conversion only C absorbs light. Photocconversion curves at two monitoring wavelengths are shown in Fig. 3 for UV and visible irradiation [26]. Quantum yields are given in Table 1. Results were similar to those informed in isotropic solutions of common solvents, as shown in Table 1 [11,27,28].

Order properties of liquid crystalline phases were studied by linear dichroism and birefringence measurements for nematic phase and by circular dichroism (CD) for cholesteric phase. In the nematic phase, no difference was observed between polarized UV–vis absorption spectra with parallel and perpendicular light (referred relative to the direction of alignment of the mesophase), neither before nor after conversion to the closed form. Thus, there is not an appreciable preferential orientation of the dopant dye in the mesophase, for any of the two isomeric forms. Furthermore, no change in the birefringence signal was observed after photoconversion of the fulgide to the photostationary state in this phase.

On the other hand, samples of twisted nematic phase containing FFU posses a strong CD in the UV region [29], and a large photoinduced change in the CD was observed in this phase in the visible after UV irradiation. Fig. 4 shows differential CD spectra (with respect to the initial state) of

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Table 1

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<tbody>
<tr>
<td>$E$-FFU</td>
<td>$\lambda_{MAX}$ (nm)</td>
<td>350*</td>
<td>347</td>
</tr>
<tr>
<td>$C$-FFU</td>
<td>$\lambda_{MAX}$ (nm)</td>
<td>496</td>
<td>510</td>
</tr>
<tr>
<td>$\Phi_{E \rightarrow C}$ (366 nm)</td>
<td>0.54*</td>
<td>0.62</td>
<td>0.58</td>
</tr>
<tr>
<td>$\Phi_{C \rightarrow E}$ (492 nm)</td>
<td>0.06*</td>
<td>0.04</td>
<td>0.042</td>
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</table>

* From differential spectrum.
* Measured with polychromatic light as described in Section 2.
* ±15%.
FFU in the photostationary state after UV and visible irradiation, respectively. The sample was tested up to a total of 20 irradiation cycles (conversion was controlled by absorption spectroscopy), and CD spectra were recorded after the first cycle, after 10 cycles, and after 20 cycles (UV and visible half-cycles). CD signals were exactly the same in all cases within experimental error. After the 20 cycles, the same sample was irradiated with UV light and recovered in solution of dichloromethane (5 mL). CD spectrum of this sample was recorded. The solution was further irradiated with visible and UV light up to the respective photostationary states (in each case), and CD spectra were recorded in solution after each irradiation hemicycle, but no signal was detected. This indicates that the photoinduced CD signal in chiral nematic phase was purely due to the characteristic order of the mesophase, and not to an enantiomeric enrichment of the C form due to a facilitation of one of the possible conrotatory pericyclic reaction pathways by the chiral phase [30,31].

The induced CD signal can be used to estimate the preferential orientation of the FFU in the nematic layers of the chiral phase. The linear dichroism (LD) is related to the circular dichroism according to the following equation [32]:

$$\Delta \chi_{CD}(\lambda) = \frac{\nu\Delta \chi_{LD}(\lambda)}{2}$$

where $\Delta \chi_{CD}$ and $\Delta \chi_{LD}$ are the differences of absorption coefficients between clockwise and counterclockwise circularly polarized light (CD), and between parallel and perpendicular linearly polarized light (LD), respectively. $P$ is the pitch of the cholesteric phase (negative for the left-handed system used in the experiments), $\nu$ is the refractive index of the nematic layer, and $\nu$ is the wavenumber of the light. The difference between both components of the linearly polarized absorption estimated from Fig. 4 using Eq. (2) is $\Delta \chi_{LD} = 10^{-3}$, at 492 nm.

The sign indicates a very mild preferential orientation of the absorption transition moment parallel to the nematic director. Considering that the visible absorption transition of the C isomer forms a small angle with the long molecular axis of the molecule, we conclude that C slightly aligns its longer molecular axis parallel to the director of the mesophase. The small absolute value is consistent with the absence of linear dichroism in the nematic phase, assuming that the order within each layer of the chiral phase is similar to that in the nematic phase, since the mesogenic mixture (ZLI1132) is the same in both phases. The small value of the dichroism justifies the use of isotropic absorption coefficients to estimate the quantum yields.

In conclusion, FFU shows excellent photochromic properties in nematic and chiral nematic mesophases, without any appreciable change of its photochromic properties, as compared to its behavior in solution.

In the case of the cholesteric phase, a strong signal due to the C isomer of the guest was observed in the 400–550 nm region. This signal can be photomodulated (with visible and UV light) and is perfectly reproducible after several cycles. Thus, after doping with a relatively small amount of a photochromic compound, a physical property (circular dichroism) of the cholesteric mesophase can be easily controlled by photolysis. At least 20 cycles were performed with no signal of fatigue. Though monitoring light in CD experiments is absorbed by the sample and is thus potentially destructive upon monitoring, the system can be probed by optical rotatory dispersion at wavelengths where no absorption takes place.

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Appendix A. Experimental details and spectroscopic data for compounds presented in Scheme 1

A.1. 1-(2,5-Dimethyl-furan-3-yl)-2-methyl-propan-1-one (3)

To a mixture of 2,5-dimethylfuran (480 mg, 5.0 mmol) and isobutyric anhydride (1.00 g, 6.0 mmol) was added dropwise SnCl4 (0.2 mL, 2.0 mmol) at room temperature. The reaction mixture was heated at 110–120°C for 4 h. The reaction was quenched by addition of 5% hydrochloric acid (30 mL) and extracted with methylene chloride (3 × 25 mL). The combined organic layers were washed with an aqueous saturated solution of sodium chloride (2 × 25 mL), dried (Na2SO4), and the solvent evaporated. The residue was purified by column chromatography (silica gel) eluting with hexane to afford 420 mg (50% yield) of pure compound I as a colorless oil. 1H RMN (200 MHz, CDCl3) δ 1.15 (d, J = 7.0 Hz, 6H, (CH3)2CH–), 2.26 (s, 3H, Me at Ar), 2.54 (s, 3H, Me at Ar), 3.05 (sept, J = 7.0 Hz, 1H, (CH3)2CH–), 6.20 (s, 3H, H–3).

A.2. 2-Isopropyl-4-isopropylidene-2′,5′-dimethyl-5-oxo-2,3,4,5-tetrahydro-[2,2′]-bifuranyl-3-carboxylic acid ethyl ester (4)

To a solution of diisopropylamine (0.6 mL, 5.0 mmol) in anhydrous tetrahydrofuran (60 mL) was added a 1.3 M solution of n-butyllithium in hexane (3.3 mL, 4.3 mmol) at –78°C under argon atmosphere. The mixture was stirred at this temperature for 5 min. Then, a solution of isopropylidene diethyl
succinate was added (compound 2 [22]; 830 mg, 4.0 mmol) in tetrahydrofuran (10 mL). The mixture was allowed to warm smoothly to 0 °C and was kept at this temperature for 5 min. The reaction mixture was again cooled at −78 °C and ketone 3 (640 mg, 3.9 mmol) was added. The mixture was stirred at room temperature for 48 h. The reaction mixture was worked up by addition of an aqueous saturated solution of ammonium chloride (50 mL), and was extracted with methylene chloride (3 × 25 mL). The combined organic layers were washed with an aqueous saturated solution of sodium chloride (3 × 20 mL), dried (Na2SO4), and solvent was evaporated. The product was purified by column chromatography (silica gel) employing a mixture of hexane–ethyl acetate (99:1) as eluent to give 400 mg of compound 4 (14% yield) as a mixture of diastereomers: 1H RMN (500 MHz, CDCl3) δ 0.89 (d, J = 6.8 Hz, 3H, (CH3)2bCH), 0.90 (d, J = 6.8 Hz, 3H, (CH3)2aCH), 0.97 (t, J = 7.1 Hz, 3H, CH3CH2COO−), 1.37 (s, 3H, (CH3)2aCH), 2.04 (sept, J = 6.6 Hz, 1H, (CH3)2bCH), 1.72 (s, 3H, (CH3)bC), 2.21 (s, 3H, Me at Ar), 3.77 (dq, J = 10.8, 7.1 Hz, 1H, CH3CH2bCOO−), 3.88 (dq, J = 10.8, 7.1 Hz, 1H, CH3CH2aCOO−), 3.96 (s, 1H, H-2′), 5.73 (s, 1H, H-3′).

A.3. Furfurylguile (Z)-3-[1-(2,5-dimethylfuran-2-yl)-2-methylpropylidene]-4-isopropylidene-dihydrofuran-2,5-dione (6)

A solution of lactone 4 (14 mg, 0.042 mmol) in anhydrous ethanol (24 mL) was treated with an aqueous saturated solution of potassium hydroxide (6 mL), and the reaction mixture was stirred at 78 °C for 4 h. The reaction mixture was allowed to cool to room temperature, and was partitioned between water (40 mL) and methylene chloride (30 mL). The aqueous phase was extracted with methylene chloride (2 × 30 mL). The combined organic layers were acidified until pH 1, and were extracted with chloroform (3 × 30 mL). The organic phase was washed with an aqueous saturated solution of sodium chloride (2 × 30 mL), dried (Na2SO4), and the solvent was evaporated to afford 10 mg (79% yield) of diacid 5 as a EZ mixture that was used as such in the next step.

A suspension of 5 in toluene (10 mL) was treated with acetic anhydride (0.1 mL) and the mixture was stirred at room temperature for 24 h. The solvent was evaporated and the residue was purified by column chromatography (silica gel) employing a mixture of hexane–ethyl acetate (97:3) as eluent to afford 2 mg of fulgide E-6 and 3 mg of Z-fulgide Z-6 (overall yield 52%). Purity was checked by TLC on silica (RE isomer) δ 0.639; Rf(Z isomer) = 0.506; elution solvent: 20% ethyl acetate, 80% hexane).

E isomer: Rf = 0.56 (hexane–ethyl acetate, 4:1); 1H RMN (500 MHz, CDCl3) δ 0.88 (broad s, 3H, (CH3)2bCH), 1.26 (broad s, 3H, (CH3)2aCH), 1.37 (t, J = 7.3 Hz, 3H, CH3), 1.89 (s, 3H, CH3), 2.26 (s, 3H, CH3), 2.28 (s, 3H, CH3), 4.29 (sept, J = 6.4 Hz, 1H, (CH3)2aCH), 5.93 (s, 1H, H′-3′).

Z isomer: Rf = 0.51 (hexane–ethyl acetate, 4:1); 1H RMN (500 MHz, CDCl3) δ 1.04 (d, J = 6.6 Hz, 3H, (CH3)2bCH), 1.19 (d, J = 6.6 Hz, 3H, (CH3)2aCH), 2.06 (s, 3H, CH3), 2.15 (s, 3H, CH3), 2.28 (s, 3H, CH3), 2.40 (s, 3H, CH3), 2.83 (sept, J = 6.8 Hz, 1H, (CH3)2bCH), 5.87 (s, 1H, H′-3′).

NMR spectroscopic data of both isomers match those depicted in the literature [27].

A.4. 4-Isopropyl-2,8,8,8a-tetramethyl-8a-dihydro-1,6-dioxo-s-indacene-5,7-dione (7)

A solution of E-fulgide (E-6) in chloroform was irradiated with a Xe arc lamp (60 W) and a filter array to isolate the 300–360 nm light region. New signals appear corresponding to the closed colored form corresponding to compound 7: 1H RMN (200 MHz, CDCl3) δ 0.98 (s, 3H, Me at C-8), 1.17 (d, J = 7.2 Hz, (CH3)2bCH), 1.18 (d, J = 7.0 Hz, (CH3)2aCH), 1.29 (s, Me at Cs), 1.54 (s, Me at Csa), 2.12 (s, Me at C2), 3.31 (sept, J = 7.0 Hz, 1H, (CH3)2bCH), 5.73 (s, 1H, H′-3′).

References


[21] Value informed by the provider. A chiral nematic phase can be seen as a layered structure with molecules oriented along an axis that helically twists across these layers. The pitch \( q \) of the twisted nematic phase is the distance between layers that have director aligned in the same direction. The pitch determines the position of the reflection band characteristic of the twisted nematic phases, which arises on a Bragg-type diffraction. The concentration of the chiral inducer, \( C \), determines the pitch through its helical twisting power \( \beta \); \( q = (C \beta)^{-1} \). S. Pieraccini, M.I. Donnoli, A. Ferrarini, G. Gottarelli, G. Licini, C. Rovini, S. Superchi, G.P. Spada, J. Org. Chem., 68 (2003) 519–526.


[26] The differences in the initial and final values for the absorbance at 366 nm in Fig. 3 probably arise from the error introduced by mounting and dismounting the cell-holder for irradiation. In the UV the ITO-covered glass, the liquid crystal (ZLI) and the chiral inducer (S811) absorb. Also a background interference pattern due to the thin layer of the sample (see Figs 2 and 4), with amplitude in the range of the difference apparent in Fig. 3 and dependent on slight angle variations of the sample positioning, may contribute to the small single wavelength absorbance differences noticed. The absorbance at 492 nm was used for calculations of quantum yields and the concentration of the \( E \) isomer was inferred assuming that all the photochromic compound is either in one or the other isomer \( (\lvert E \rvert + \lvert C \rvert = c_0) \). Full reversibility was always assessed by complete spectra, as those of Figs 2 and 4.


[29] A strong circular dichroism in the UV region is expected due to the presence of the chiral dopant at relatively high concentration. In fact, the signal saturates below 320 nm. The reflection band was also set in the NIR, far from the observed region, by adjusting the concentration of the chiral inducer (7% (w/w) in these samples).

