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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. Beside from 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.

Keywords: Liquid crystals; Photochromism; Fulgides; Circular dichroism; Memories and data storage

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], diaryethenes [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 5×10^3 and 5×10^4 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

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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

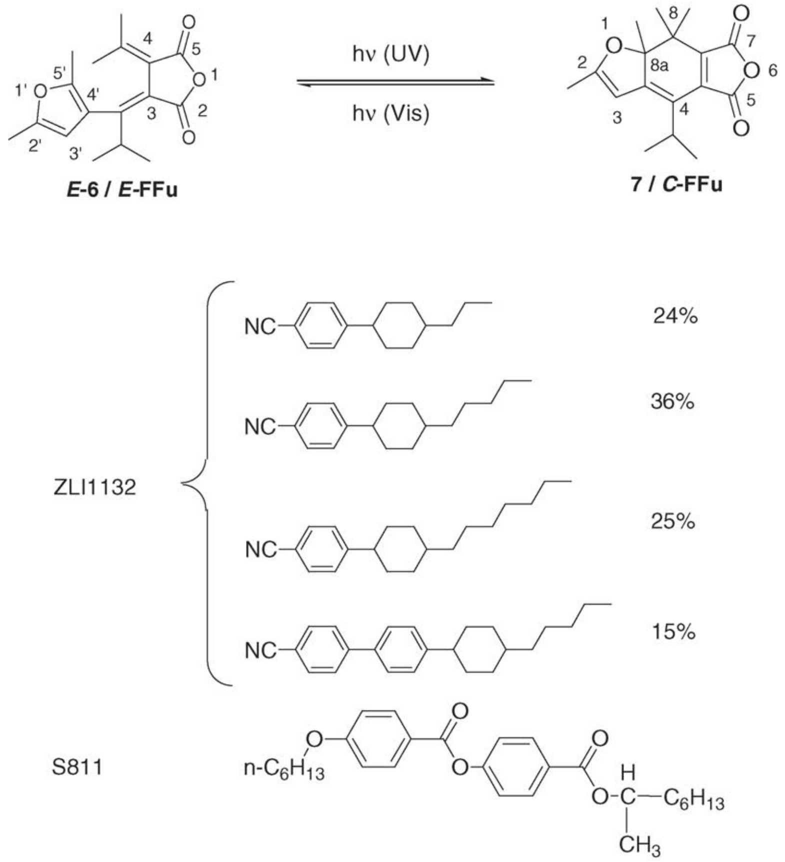

Fig. 1. Structure of the furylfulgide (FFU) used in this work and its photochromic transformation, of the liquid crystal mixture ZLI1132, and of the chiral inductor S811.