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Förster energy transfer in cholesteric mixtures: a new type of phototunable fluorescent material

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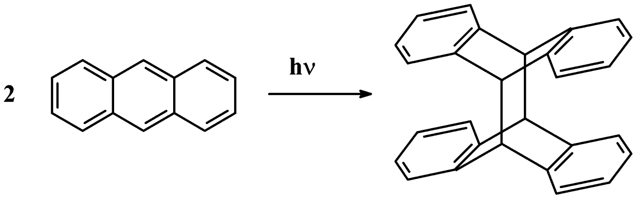
A new approach to the creation of cholesteric glass-forming materials with photovariable fluorescent properties is suggested. This approach is based on Förster type energy transfer from a photochemically active donor to a highly fluorescent acceptor. For this purpose, a cholesteric mixture containing two fluorescent dopants based on anthracene (**Dianthr**) and stilbene (**DCM**) was prepared and studied. The absorbance peak of **DCM** molecules overlaps the emission peak of **Dianthr**. The possibility of using energy transfer in cholesteric mixtures containing a photoactive energy donor capable of photobleaching is demonstrated. It is shown that UV irradiation of planarly oriented films of the mixture leads to photodimerization of the **Dianthr** dopant. This photoreaction results in a significant decrease in the emission intensity of the **DCM** dopant. In all cases the emitted light is strongly circularly polarized, and the degree of polarization does not change during photoreaction. Such types of photopatternable glass-forming cholesteric materials combining fluorescent properties, the possibility of energy transfer between two fluorescent dyes and a photoactivity of one fluorescent component, provide new opportunities for optical data recording and storage.

1. Introduction

In recent years, the attention of many research groups has been focused on the development of new polymeric materials possessing luminescent and electroluminescent properties [1–5]. This interest is explained by the fast growing area of applications such as display and information technologies, telecommunications, data storage, etc. Fluorescent dyes dissolved in polymers can be considered as promising active elements for one- or two-photon information recording and storage systems [2–4]. Moreover, cholesteric liquid crystalline materials with fluorescent additives have been shown to be very interesting from the applications point of view due to the combination of the unique optical properties provided by a helical supramolecular structure with light emission [6–21].

In recent work we combined the emission properties of fluorescent dyes and the unique optical properties of cholesteric liquid crystals, with the possibility for photoregulation of helix pitch [20] or photobleaching phenomena [21]. For this purpose we prepared mixtures containing cholesteric cyclosiloxanes as matrices, fluorescent dopants as emissive additives, and a chiral-photochromic dopant which can change its helix twisting power under UV light irradiation. This allowed us to prepare a cholesteric material capable of photoregulating the helix pitch and selective light reflection band position. The variation in the selective light reflection wavelength leads to modulation of the fluorescence intensity and the dissymmetry factor.

More recently we used a fluorescent dopant based on anthracene molecules which are capable of photodimerization under UV irradiation [7]:



This process leads to switching from the anthracene group, highly fluorescent in the blue and near-UV spectral regions, to dimers which emit no visible light.

An interesting aspect of the photophysics of fluorescent molecules involves the possibility of singlet–singlet energy transfer (Förster-type) between two molecules with overlapped absorbance and fluorescence spectra [22]. This type of energy transfer was successfully studied and discussed in recent papers concerning lasing phenomena in cholesteric materials [18, 19].

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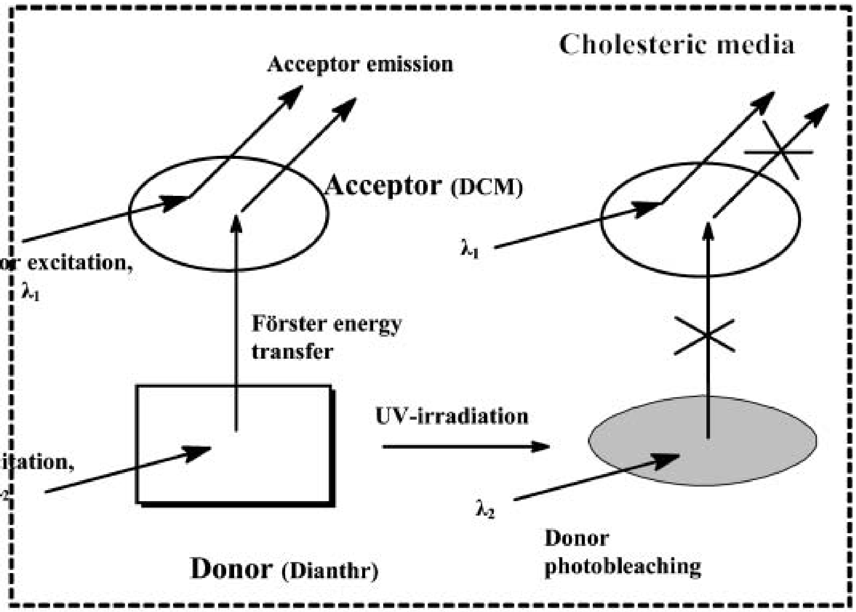


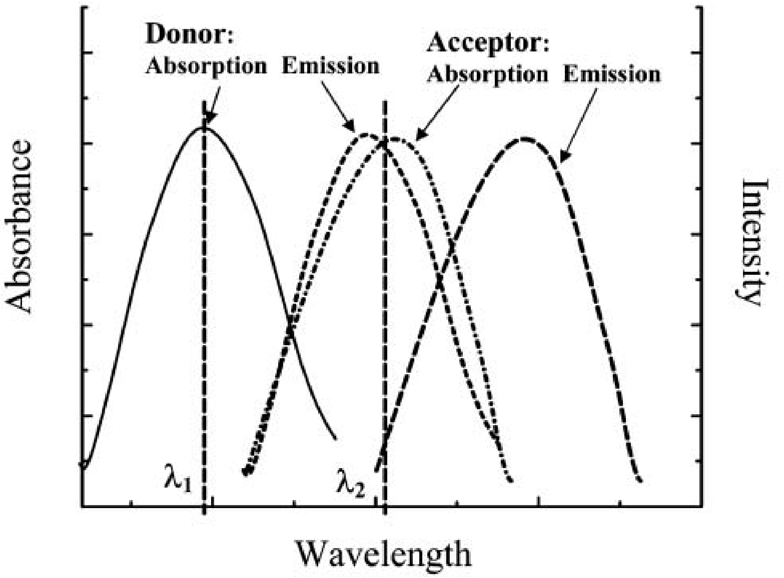
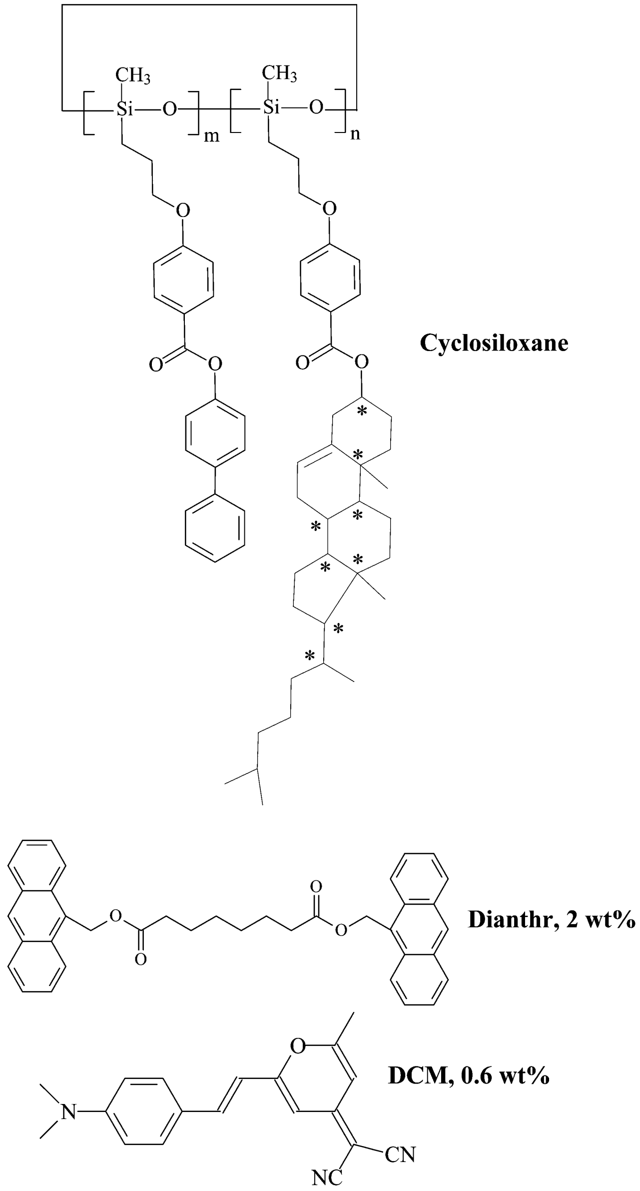


Figure 1. Schematic representation of the main concept used for creation of a new photoactive cholesteric material based on Förster energy transfer.

In this paper, we suggest a new approach for the creation of cholesteric glass-forming materials with photovariable fluorescent properties. This approach is based on Förster-type energy transfer from a photochemically active donor to a highly fluorescent acceptor. Figure 1 represents the main principle of this approach. Before UV irradiation and photobleaching of the donor an emission in the visible range is observed under excitation with light of wavelengths coinciding with the absorbance peaks of both donor and acceptor molecules (λ_1 and λ_2, respectively). After donor photobleaching excitation in the spectral region of its absorbance (λ_1) becomes almost impossible. At the same time the emission intensity does not change under excitation by the longer wavelength light (λ_2).

In order to realize this concept we prepared a mixture containing cholesteric cyclosiloxane as a glass-forming oligomer matrix and two fluorescent dopants: the anthracene derivative **Dianthr** as a donor, and **DCM** as an acceptor (scheme 1). The mixture forms only a



Scheme 1. Structure of cholesteric cyclosiloxane and two photoactive fluorescent dopants.

cholesteric mesophase with clearing temperature of about 170°C and glass transition at 50°C.

2. Experimental

2.1. *Synthesis*

The fluorescent dopant **Dianthr** was synthesized according to standard esterification techniques using DCC [23]. T_m=110–112°C; IR (cm^{-1}): 2930, 2864 (CH_2), 11728 (C=O in RCOOR′), 1623, 1590 (C–C in Ar). Cholesteric cyclosiloxane (Wacker) and 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyrane (**DCM**) were used as received. Cholesteric cyclosiloxane has a clearing temperature of 189–192°C and a glass transition at ~50°C. A mixture containing 2 wt% of **Dianthr** and 0.6 wt% of **DCM** was prepared by dissolving the components in dichloromethane followed by solvent evaporation at 60°C. The mixture was dried in vacuum at 130–140°C for two hours.

2.2. *Investigation of phase behaviour*

The phase transition temperatures of the mixtures were studied by polarizing optical microscopy, using a Leitz Laborlux 12 Pol S polarization microscope with a Mettler FP-80 hot stage.

2.3. *Photo-optical and fluorescence investigations*

Photochemical properties were studied using a special set-up [21] equipped with a Xe lamp (1000 W, Müller Elektronik Optik), two monochromators (SpectraPro 300 I, Acton Research, Polytec), controlled by an NCL single-channel spectroscopy detection system (Roper Scientific GmbH, Germany). For UV irradiation, a 200 W ultra high pressure mercury lamp (Oriel Company) was used. Using filters, light with a maximum wavelength of 365 nm was selected. A water filter prevented heating of the samples due to IR irradiation by the lamp. Quartz lenses were used to obtain plane-parallel light beams. During irradiation, a constant temperature of test samples was maintained using a Mettler FP-80 heating unit. The intensity of UV radiation amounted to 3.4 mW cm^{-2}.

The photochemical properties of the mixture were studied by illuminating 20 µm thick films sandwiched between two flat glass plates. A planar texture was obtained by shear deformation of the samples, which were heated to temperatures well above the glass transition temperature (140°C) followed by slow cooling to room temperature at 1° min^{-1}). Fluorescence spectra were recorded with the detection normal to the plane of the film, while the excitation beam was positioned at 30° to the normal and at the same side of the film as the emission detector. Circularly polarized absorbance and fluorescence spectra were obtained using a combination of a linear polarizer with a broad band quarter-wave plate.

3. Results and discussion

Figure 2 shows the absorbance and fluorescence spectra of both fluorescent substances dissolved separately in the same cyclosiloxane matrix. It can be seen that **Dianthr** dopant absorbs light in the UV spectral region whereas **DCM** has an absorbance peak in the visible

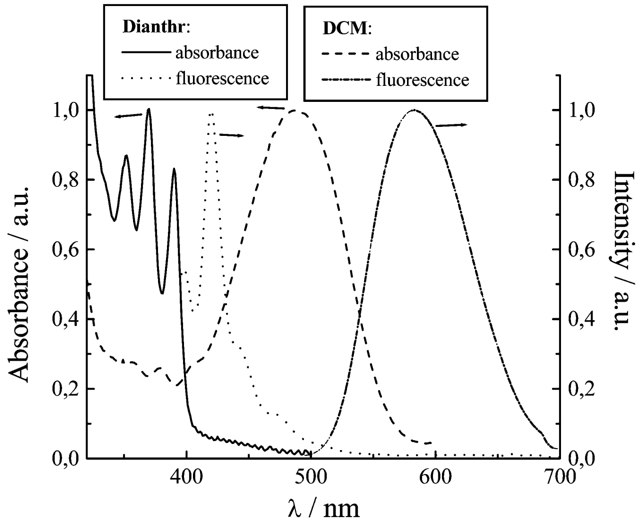


Figure 2. Normalized absorbance and fluorescence spectra of model cholesteric mixtures containing **Dianthr** and **DCM** dopants; excitation wavelengths are: 390 nm (**Dianthr**) and 490 nm (**DCM**). Absorbance corresponding to selective light reflection is not shown in this figure.

part of the spectrum. The most important spectral feature is related to the noticeable overlapping of the fluorescence peak of **Dianthr** with the absorbance of **DCM**. This suggests the possibility of singlet–singlet energy transfer (Förster-type) from the anthracene moiety to **DCM** molecules. The degree of this spectral overlapping is not great; nevertheless it is sufficient for efficient energy transfer.

UV irradiation of planarly oriented films of the mixture leads to a strong decrease in the absorbance of **Dianthr** dopant (figure 3). The peak corresponding to **DCM** absorption and the selective light reflection band remain almost unchanged. This suggests the occurrence of a photocycloaddition process involving anthracene fragments and the absence of any side photoprocesses. Thus the **DCM** dopant exhibits very good photochemical stability under these conditions.

The fluorescence spectra of the mixture are characterized by the almost complete absence of **Dianthr** dopant emission at any excitation wavelength (figure 4); only a very small peak at $\lambda=420$ nm can be detected. The strong quenching of anthracene fluorescence is associated with two possible phenomena: (i) Förster energy transfer from the anthracene fragments to **DCM** molecules, or (ii) strong light absorbance in this spectral region due to the presence of **DCM** dopant.

Photobleaching of **Dianthr** dopant under UV leads to a marked drop (*c*. 30%) of fluorescence intensity in the case of the short wavelength excitation light (390 nm),

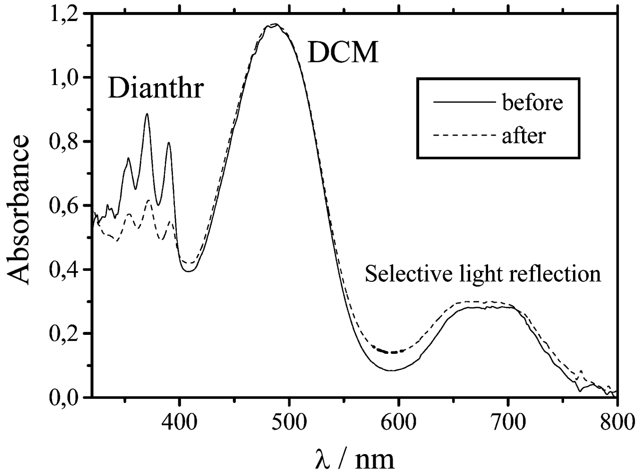


Figure 3. Absorbance spectra of a planarly oriented mixture film before and after 100 min of UV irradiation (365 nm).

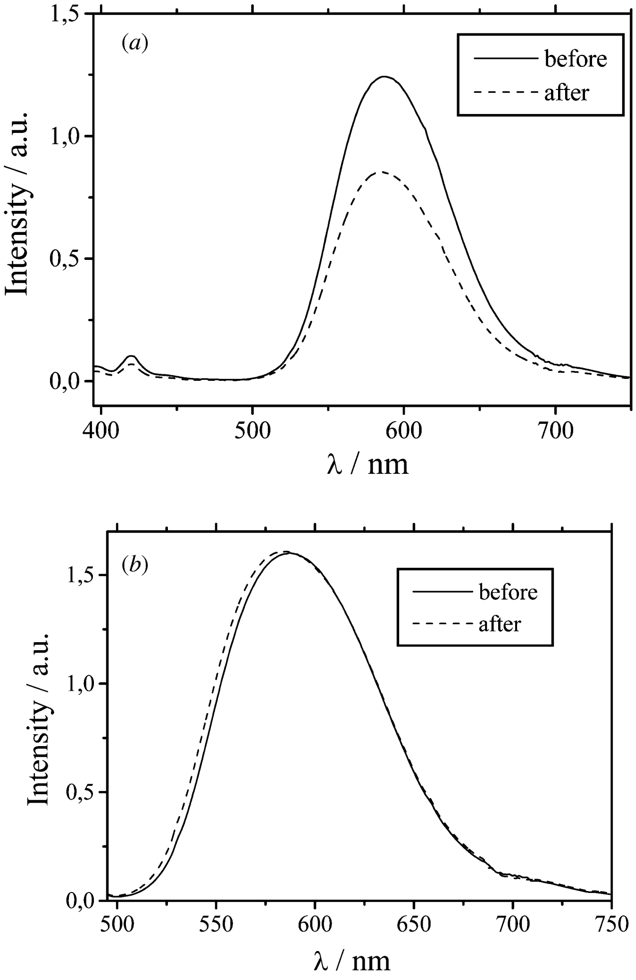


Figure 4. Non-polarized fluorescence spectra of a mixture before and after irradiation, obtained with different wavelengths of excitation light: (*a*) 390 nm, (*b*) 490 nm.

figure 4(*a*). The emission intensity excited by visible light coinciding with **DCM** absorbance has the same value as before UV irradiation, figure 4(*b*). This fact also demonstrates the occurrence of energy transfer between different chromophores because emission intensity decreases due to reducing **Dianthr** dopant concentration during UV irradiation.

The most important parameter characterizing the polarization state of emitted light from chiral media is the dissymmetry factor g_e defined as

$$g_e = 2(I_L - I_R)/(I_L + I_R)$$

where I_L and I_R are the intensities of the left- and right-handed circularly polarized light, respectively. We have calculated the dissymmetry factor of fluorescence for the mixture before and after irradiation. Figure 5 shows the wavelength dependence of the dissymmetry factor together with the absorbance spectra before and after UV irradiation. The dissymmetry factor is negative in the spectral range almost coinciding with the selective light reflection peak (minimum value of the dissymmetry factor was observed at 664 nm, whereas the absorbance maximum corresponding to selective light reflection was at 676 nm, see figure 5). At the long wavelength edge of the selective light reflection band the dissymmetry factor changes sign and becomes large and positive. This is in accordance with the photonic band gap theory for cholesteric liquid crystals. The dissymmetry factor is large in the centre of the stop band and the right-circularly polarized light is allowed to propagate leading to a negative g_e. The edges of the stop band are characterized by an enhanced density of states for the left circularly polarized light according to the photonic crystal theory, leading to the propagation of the left-circularly polarized fluorescence.

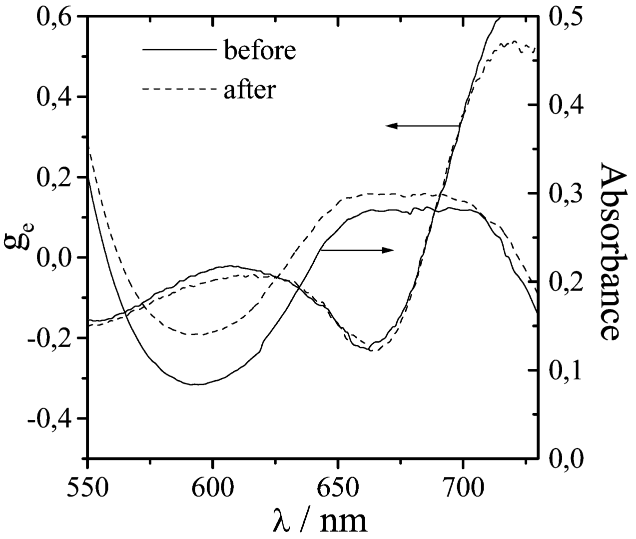


Figure 5. Absorbance and dissymmetry factor spectra of fluorescence before and after UV irradiation.

UV irradiation leads to almost negligible changes of the dissymmetry factor (figure 5). The degree of circular polarization is also independent of the wavelength of the excitation light. These two facts allow one to conclude that only **DCM** emits light independently of the manner of the excitation, and the degree of polarization is mostly determined by the orientation of the dye molecules.

In conclusion, for the first time we have demonstrated the possibility of using energy transfer in cholesteric mixtures containing a photoactive energy donor capable of photobleaching. Such types of photopatternable glass-forming cholesteric materials combining fluorescent properties, the possibilty of energy transfer between two fluorescent dyes, and a photoactivity of one fluorescent component pitch, provide new opportunities for optical data recording and storage.

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