Glass-forming photoactive cholesteric oligomers doped with quantum dots: novel materials with phototunable circularly polarised emission

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Glass-forming photoactive cholesteric oligomers doped with quantum dots: novel materials with phototunable circularly polarised emission

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Novel glass-forming photoactive cholesteric mixtures doped with CdSe quantum dots were prepared and studied. The photooptical and fluorescent properties of these materials were studied. The possibility of phototuning of circularly polarised emission using ultraviolet irradiation was demonstrated.

\textbf{Keywords:} cholesteric oligomers; quantum dots; circularly polarised fluorescence; phototuning

1. Introduction

Cholesteric materials doped with small amounts of fluorescent compounds have attracted great attention from researchers. Such interest has arisen because these materials have unique emission properties [1–9]. The cholesteric helical structure can be considered as being a one-dimensional photonic crystal having a band gap with spectral position ($\lambda_{\text{max}}$) determined by the value of the helix pitch ($P$) and proportional to the average refractive index ($n$):

$$\lambda_{\text{max}} = nP.$$  \hspace{1cm} (1)

The pitch of the helix can be controlled by the chemical structure of the substances used in the preparation of the materials and by the application of different external fields [1–9]. One of the most promising tools for the control of helix pitch is light action. In a number of papers, approaches for the creation of cholesteric low-molar-mass materials with photocontrollable helix pitch and band gap position have been demonstrated [10–15]. Most of these approaches are based on the introduction of chiral-photochromic fragments into the cholesteric materials which are capable of photoisomerising under light irradiation to give a drastic change in their helical twisting power. As a result of irradiation, helix untwisting or twisting and a shift of the photonic band gap position take place.

In our previous paper [16] exploring this principle, we, for the first time, prepared cholesteric materials using as base the cyclic siloxanes and sorbide chiral dopant with phototunable circularly polarised emission. Ultraviolet (UV) irradiation and the resultant shift in the selective light reflection peak position result in a change in the fluorescent dye emission intensity and the degree of circular polarisation, characterised by the dissymmetry factor $g_e$:

$$g_e = 2(I_L - I_R)/(I_L + I_R),$$  \hspace{1cm} (2)

where $I_L$ and $I_R$ are the intensities of the left- and right-handed circularly polarised light, respectively.

A similar approach has been used for the creation of cholesteric materials possessing phototunable lasing properties [17, 18].

In all papers devoted to cholesteric fluorescent systems as fluorescent dopants organic dyes have been used. One of the strong disadvantages of these dyes is their instability caused by photobleaching or photodegradation. In order to avoid this disadvantage, in the present paper we for the first time use as fluorescent dopants quantum dots (QDs) or inorganic semiconductor particles having extremely high photostability, broad absorbance band, high quantum yields of emission and other promising characteristics [19, 20].

Despite the relatively large number of publications describing liquid crystal (LC) composites doped with different nanoparticles [21–27], to the best of our knowledge there is only one recent paper [28] devoted to the study of circularly polarised light emission of QDs dispersed in cholesteric material. Taking into account this fact, this preliminary communication is devoted to the demonstration of phototunable circularly polarised fluorescent properties.
in cholesteric materials containing QDs as a fluorescent dopant.

As cholesteric matrix material we have chosen a glass-forming cholesteric cyclosiloxane manufactured by the Wacker Company (Germany). It displays a selective light reflection of left-handed circularly polarised light in the blue region of the spectrum ($\lambda_{\text{max}} \sim 450$ nm). The clearing temperature of cyclosiloxane is 180–182°C; the glass transition temperature is $\sim 50$°C. As chiral-photochromic dopant responsible for the helix phototuning properties we have used 3.2 wt% of a derivative of isosorbide and cinnamic acid, $\text{Sorb}$ [16, 29, 30]; see Scheme 1.

This substance possesses a high helical twisting power and induces the formation of a right-handed cholesteric helical structure. UV irradiation induces thermally irreversible E–Z isomerisation of $\text{Sorb}$ in respect of C=C bonds that is accompanied by a decrease of molecular anisometry (Figure 1(a)) and a lowering of the helical twisting power. Introduction of this dopant into the cyclosiloxane matrix leads to a partial helix untwisting and to a shift of the selective light reflection to the red spectral region (Figure 1(b)).

A small number of CdSe ZnS-coated quantum dots (0.5%) were added to the mixture. These types of inorganic nanoparticles have good fluorescent properties and are widely used as a component in nanocomposite preparation [21–27].

The main goal of this paper is to describe the first results of the study of the optical and fluorescent properties QD-containing cholesteric materials and to demonstrate the possibility of photovariation of circularly polarised fluorescent properties in such materials.

2. Results and discussion

Figure 1(b) demonstrates the logarithmic transmittance spectra of the planar-oriented samples of the initial mixture that have been UV irradiated for different time periods. After each irradiation cycle the films were annealed at 130°C in order to achieve an equilibrium value of the helix pitch (ca. 5 min) and the selective light reflection wavelength; they were then slowly cooled down to room temperature (1 K/min) to exclude any mechanical deformation of the helical structure. As can be clearly seen in Figure 1(b), irradiation results in a shift of the selective light reflection peak to shorter wavelengths, which is related to the decrease in the helical twisting power of $\text{Sorb}$.

QD absorbance appears as a typical broad shoulder at wavelengths below ca. 500 nm, which is clearly
seen for films of the mixture before UV irradiation (Figure 1(b)) and coincides with the selective reflection band after helix twisting.

Let us consider how the shift of selective light reflection influences the fluorescent properties of planar-oriented mixture films. Figures 2(a)–(d) show the spectra of the left-handed circularly polarised component of the emission of the non-irradiated and irradiated films together with the corresponding logarithmic transmittance spectra. The position of the emission maximum is completely different for the non-irradiated samples (518 nm) and the film irradiated for 3 min (551 nm) (Figures 3(a) and (d)). In other words, UV irradiation allows one to manipulate the fluorescence peak shape and emission colour. It can be clearly seen, especially from Figures 2(b) and (c), that the selective light reflection peak coincides completely with the intensity gap observed in the emission spectra. It is worth noting that the right-handed circularly polarised component
of the fluorescence is not influenced by the spectral position of the selective light reflection band. Both the position of the maximum as well as the shape of the spectra in the films are different from the QD solution in chlorophorm (the dashed line in Figure 1).

The appearance of two circularly polarised fluorescence peaks in Figures 2(b) and (c) is related to the strong coincidence of the photonic band with the maximum of the non-polarised fluorescence peak. That is why in this spectral region the intensity of the left-handed circularly polarised light emission decreases almost to zero, whereas two emission peaks are observed at the ‘shoulders’ of the photonic band gap.

Using the right- and left-handed circularly polarised fluorescence spectra and Equation (2), the dissymmetry factor $g_e$ was calculated for films before and after UV irradiation (Figure 3). First, it is worth noting that the values of the dissymmetry factor are negative in the spectral regions corresponding to the photonic band and completely coincide with the peaks of the selective light reflection, gradually shifting to the short-wavelength spectral region under UV irradiation. The values of $g_e$ are very high and achieve results equal to the theoretical values (−2) (see Equation (2)), which demonstrates the extremely high degree of circular polarisation of the emitted light within the selective light reflection peaks. Similar high values of the dissymmetry factor have been observed in only a few papers [8, 9] and this indicates a good planar alignment of the cholesteric materials in cells.

Second, at both shoulders of the photonic bands there is a change in the sign of the dissymmetry factor. This effect is the result of a slight amplification in the left-handed emission components in these spectral ranges. It is interesting to note that for most organic fluorescent dyes such a phenomenon is observed at the long-wavelength shoulder of the photonic bands. It is explained by orientation of the dye molecules and their transition electronic moments along the director of the LC matrix [31]. Thus, we may assume that in our case the electronic transition

Figure 2. Logarithm transmission and left-handed circularly polarised fluorescence spectra before (a) and after 1 (b), 2 (c) and 3 min (d) of UV irradiation followed by annealing at 130°C (150°C for 3 min). The excitation light wavelength is 400 nm. The dashed line shows the normalised fluorescence spectra of QDs in chlorophorm solution (colour version online).
moments of the QDs are oriented randomly, which promotes emission amplification at both shoulders.

In summary, for the first time we have obtained cholesteric oligomeric materials for which it is possible to a photochemically tune of the intensity and degree of circular polarisation emission of QDs embedded in a glass-forming matrix. Our future efforts will be focused on the study of relations between the size and shape of nanoparticles and the photooptical properties of such systems, and also on the investigation of lasing phenomena.

3. Experimental section

3.1 Synthesis of CdSe quantum dots

QDs of the core/shell structure (CdSe core and ZnS shell) were synthesised according to the standard method [32]. Briefly, an appropriate amount of trioctylphosphine oxide (Aldrich Chemical, Milwaukee, WI) was heated to 180°C under argon atmosphere, dried and degassed at this temperature under vacuum. Then, trioctylphosphine oxide was heated to 340°C under argon flow, with intensive stirring. Solutions of dimethylcadmium (Strem, Bischheim, France) and selenium (elemental powder; Aldrich) precursors in trioctylphosphine (Fluka, Buchs, Switzerland) were injected through a syringe in less than 1 second. The reaction mixture was cooled to 300°C and a 1 M solution of dimethylzinc (Aldrich) in heptane and a solution of hexamethyldisilthiane (Fluka) were added dropwise under vigorous stirring. The reaction mixture was cooled to 50°C, and QDs were precipitated out from the solution by adding anhydrous methanol followed by centrifugation at 14,000 rpm. The precipitate was washed with methanol, and QDs were dissolved in chloroform (Sigma Chemical, St. Louis, MO). The procedure that we describe permits the synthesis of homogeneous QDs emitting fluorescence from nearly 500 nm to 620 nm depending on their diameters. For this research we used perfectly homogeneous QDs possessing a CdSe core of approximately 3.6 nm in diameter with an epitaxially grown ZnS shell of several monolayers in thickness.

The fluorescence spectrum of the QDs used in this work is shown in Figure 1(a) ($\lambda_{\text{max}}=525$ nm).

The phase transition temperatures of the mixture were determined by polarising optical microscope investigations performed using a LOMOP-112 polarising microscope (USSR) equipped with a Mettler TA-400 (Switzerland) heating stage. The clearing temperature of the obtained mixture was 171–175°C, which is about 10 degrees lower than that for the pure cyclosiloxane used as a matrix; the glass transition temperature was the same as for cyclosiloxane (~50°C). Aggregation and phase separation did not take place during the mixture preparation and the mixture was quite homogeneous. The absence of nanoparticle aggregation was confirmed by the results of fluorescent microscopy. It is worth noting that doping of cyclosiloxane with chiral-photochromic dopant and QDs does not lead to any noticeable change in the optical quality of planar-oriented films, which remain rather transparent.

For the optical and photooptical studies, 25-µm-thick films sandwiched between two flat glass plates were prepared. The thickness of the test samples was controlled by glass beads. For the preparation of a good planar texture we used a LC photoalignment technique. Glass plates were spin-coated with a solution of poly[4-(3-carboxy-4-hydroxy-phenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt (Aldrich), 2 mg/mL. After drying at room temperature, the glass plates coated by this polymer were irradiated by the polarised polychromatic light of a mercury lamp (~15 mW/cm², 30 min). A Glan-Taylor prism was used as a polariser. A planar texture was obtained by shear deformation of the samples, which were heated up to temperatures well above the glass transition temperature (130°C). After irradiation prior to performing absorbance and fluorescence measurements, the samples were annealed for about 20 min followed by cooling to room temperature at a rate of 1 degree/min.

The transmittance spectra of planar-oriented films were recorded on a Unicam UV-500 UV-Vis spectrophotometer (England).
Photochemical investigations were performed using an optical set-up equipped with a DRSh-250 ultra-high-pressure mercury lamp. To prevent the heating of the samples due to the infrared irradiation of the mercury lamp, a water filter was introduced in the optical scheme. To assure a plane-parallel light beam, a quartz lens was applied. Using the filter, the intensity of the light was measured using a LaserMate-Q (Coherent) intensity meter (∼2 mW/cm²).

The fluorescence spectra were recorded using a Shimadzu RF-5301PC spectrofluorophotometer (Japan) with the detection normal to the plane of the film, whereas the excitation beam was positioned at a certain angle from the back side of the film, whereas the excitation beam was positioned at a certain angle from the back side of the film. Circularly polarised absorbance and fluorescence spectra were obtained by using a combination of a linear polariser with a broad-band quarter-wave plate.

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References