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Temperature-driven luminescence switching of europium(III) in a glass dispersed liquid crystal film

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Glass dispersed liquid crystal films doped with the tris(β-diketonato)europium(III) complex [Eu(dbm)$_3$(gly)] (Hdbm = dibenzoylmethane, gly = 1,2-dimethoxyethane) were prepared. The liquid crystal host was 4-pentyl-4′-cyanobiphenyl (5CB); a mixed silica–titania glass with a refractive index close to that of 5 CB was chosen as the glass matrix. The photoluminescence intensity was measured as a function of temperature. A strong intensity change was observed at the nematic-to-isotropic transition.

1. Introduction

Several types of liquid crystal displays (LCDs) are known: for example, dynamic scattering mode display, twisted nematic display, and dispersed liquid crystal display [1]. Dispersed liquid crystal displays are a more recent type of LCD and involve micrometer-sized droplets of a nematic liquid crystal in a solid, isotropic matrix [2]. These displays do not require polarizers. Polymer dispersed liquid crystals (PDLCs), where the matrix is an optically transparent polymer film, have been well studied [3]. PDLCs are already used in some applications due to their good optical contrast, low power consumption and easy fabrication. PDLCs are made by microencapsulation and phase separation methods. In the microencapsulation method, the GDLC layer is prepared from an emulsion of a water-insoluble liquid crystal in an aqueous solution of a water-soluble polymer. In the second method, phase separation is induced in a homogeneous solution of the polymer and liquid crystal. Levy *et al.* demonstrated that the sol–gel process can be used for preparing films of glass dispersed liquid crystals (GDLCs) [4, 5]. The glass films have dispersed liquid crystalline droplets with a diameter varying between 1 and 180 μm. Surface Si–CH$_2$–CH$_3$ or Si–CH$_3$ groups form the orienting layer on the pore cage. More recent studies proposed different sol–gel precursors to lower the threshold voltage and to decrease the differences between the refractive indices of the matrix and the liquid crystal [6–13]. A patented method uses a mixture of organoalkoxysilanes with other metal alkoxides. The oxide formed by hydrolysis of the added metal alkoxide must have a refractive index larger than 1.52 to match the refractive index of the nematic liquid crystal mixture [11]. Amine side groups provide the orienting surface in the droplets.

Colour displays based on GDLCs were investigated by Levy *et al.* [14]. These GDLCs were doped with dyes; rhodamine 6G, fluorescein or oxazine-1 were used as matrix dopant. The liquid crystal microdroplets were doped with the B3 dye (Hoffman la Roche), specifially designed for liquid crystal doping [14]. On the other hand, europium(III) compounds are well known red-emitting phosphors, and can be doped into sol–gel glasses [15, 16]. An advantage of europium(III) compounds is the small band widths of their luminescence transitions, which results in luminescent light of a high spectral purity.

In this paper, we report the use of a simple type of GDLC to test the application of lanthanide-doped luminescent GDLC films. The incorporation of a liquid crystal in a sol–gel film and the solubility a europium(III) β-diketonate complex in this matrix was tested. The variation of the luminescence intensity of a europium(III) complex as a function of temperature was recorded; a strong change in the luminescence intensity was observed at the nematic-to-isotropic transition.

2. Experimental

The [Eu(dbm)$_3$(gly)] complex was synthesized according to a (slightly changed) procedure described by Evans *et al.* [17]. Monoglyme (gly, 1,2-dimethoxyethane, 6.24 mmol) was added to a suspension of Eu$_2$O$_3$ (99.9%, 2.74 mmol) in 30 ml of toluene. Dibenzoylmethane (Hdbm, 14.96 mmol) was slowly added to the vigorously

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stirred suspension, and the mixture was heated at reflux for 1 week. Toluene was removed under vacuum and the solids were dried for 3 days in a vacuum oven. The purity was verified by CHN analysis ($C_{exp.} = 64.6$, $H_{exp.} = 4.8$; $C_{calc.} = 64.54$, $H_{calc.} = 4.75\%$).

The fluorescent GDLC films were prepared by mixing 1 ml of *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane with 0.2 ml of tetraethyl orthotitanate (TEOT) in a glove box (nitrogen atmosphere). The mixture was stirred for several minutes and 0.2 ml of the liquid crystal 5CB was added. Up to 25 mg of the [Eu(dbm)$_3$(gly)] could be dissolved giving a clear yellowish solution. The lanthanide-doped mixture was removed from the glove box for further processing. Films were made by dipping one side of a glass substrate in the solution or by pipetting a small volume onto a flat surface. The coated glass substrates were put in small glass vials which were then placed in a large beaker containing a small volume of distilled water. The beaker was covered with a glass plate, and the metal alkoxides hydrolysed and polymerized in the humid atmosphere. Opaque gels were formed after 2 days at room temperature, and the beakers were then placed in an oven at 60°C. After 2 days of drying, europium(III)-doped GDLCs with a good film integrity were obtained.

A [Eu(dbm)$_3$(gly)] reference sample was prepared by making a film with the same procedure as above but with no liquid crystal added. The reference samples were transparent and crack-free.

The luminescence spectra of europium(III) were recorded on an Edinburgh Instruments FS-900 spectrofluorimeter. This UV/Vis instrument is equipped with a xenon arc lamp and a red-sensitive photomultiplier (300–850 nm). 5CB was purchased from Merck; europium(III) oxide was kindly provided by Rhodia. *N*-(2-Aminoethyl)-3-aminopropyltrimethoxysilane and tetraethylorthotitanate were purchased from Gelest. The other chemicals were purchased from ACROS or Sigma–Aldrich.

3. Results and discussion

The mechanism of switching of a GDLC film doped with luminescent dyes is different from that of a GDLC based on the transmission of (coloured) light. In the transmission type of GDLC display, the light cannot pass through the GDLC layer in the OFF state (dark) because it is scattered due to the difference in refractive index between the glass matrix and the unaligned LC droplets. If the layer is in the ON state, all the liquid crystals are aligned by an external electric field. Light can pass through the GDLC layer without significant light scattering because the refractive index of the LC droplets in the viewing direction is now similar to the refractive index of the matrix. This mechanism is explained in detail elsewhere [9]. For displays prepared by a combination of a GDLC film and a luminescent back plane the procedure is the same. UV light used to excite the phosphors passes in the ON state (luminescence) and is scattered in the OFF state (zero or only weak luminescence).

If the film itself is doped with a phosphor, another mechanism must be taken into account. Labes and coworkers studied luminescent europium(III) compounds in nematic liquid crystal electro-optic cells that mainly consisted of a nematic liquid crystal between two transparent electrodes [18–21]. UV light was used to excite the luminescent compound. Due to the large internal scattering of the UV light in the OFF state the absorption by the luminescent dopand is enhanced, thus giving the layer a visible colour. Because the emitted luminescence is in a random direction, the viewing angle can be improved. In the ON position the UV light passes through the layer with less absorption, and thus less luminescence is produced. The mechanism is expected to be similar in GDLCs doped with luminescent dyes and is shown in figure 1.

A well-known nematic liquid crystal is 4-pentyl-4′-cyanobiphenyl (5CB); it is a crystalline solid at room temperature and becomes liquid crystalline at 22.5°C (nematic phase) and an isotropic liquid at 35.0°C. Once melted, 5CB remains liquid crystalline at room temperature due to supercooling. This liquid crystal in the

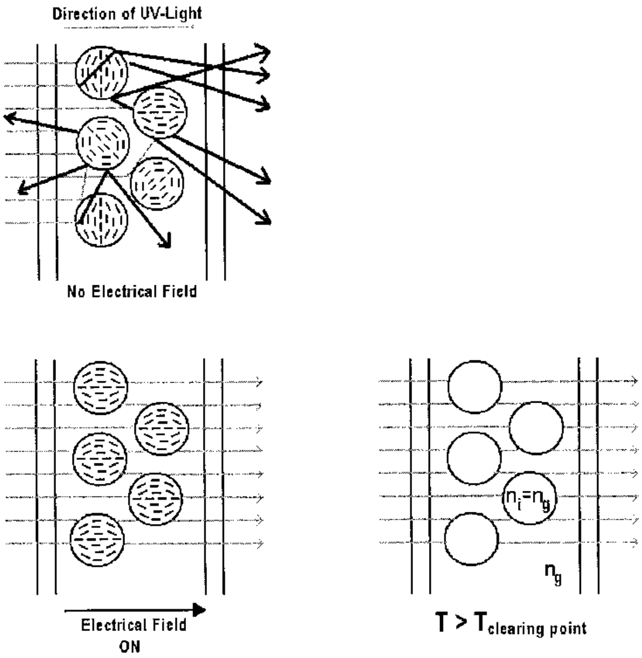

Figure 1. The mechanism of a luminescent GDLC film during (*a*) OFF and (*b*) ON states. (*c*) When the film is heated above the clearing point, the refractive index of the isotropic liquid (n_i) becomes similar to the refractive index of the glass (n_g).

nematic phase scatters incident light very strongly. In a GDLC film the LC droplets cause the whole sample to be turbid. If the liquid crystal molecules are aligned by an external electric field, the fluid is 'isotropic' in the direction or perpendicular to the direction of the applied field (along the direction of the optic axis). This is also the case in a GDLC, if the refractive index of the matrix matches the refractive index of the liquid crystal.

Another way to make 5CB isotropic is to heat the sample above the nematic-to-isotropic transition (clearing point). When the film is heated above the clearing point, the refractive index of the isotropic liquid becomes similar to that of the glass (figure 1). As observed by polarizing optical microscopy, the nematic-to-isotropic transition in the europium(III)-doped luminescent GDLC film appeared around 34°C. This temperature is lower than the clearing point of pure 5CB. Changes in the clearing point of 5CB can be due to partial dissolution of other components such as methanol (which is a reaction product in the sol–gel synthesis process) or a change in the interactions at the matrix and liquid crystal interface [22].

Like all trivalent lanthanide ions, the absorption cross-section of europium(III) is small. This problem can be overcome by the antenna effect; UV light is absorbed by the ligand and transferred to the europium ion [23]. Here, dibenzoylmethane (Hdbm) is used as the light-absorbing ligand; monoglyme (gly, 1,2-dimethoxyethane) is used to exclude water molecules. Exclusion of water molecules from the first coordination sphere of the europium(III) atom is necessary, because they can effectively quench excited states of the lanthanide ions. The most intense luminescence band in the [Eu(dbm)$_3$(gly)] complex is centred in the red spectral region around 612 nm.

The change of luminescence intensity in [Eu(dbm)$_3$(gly)]-doped GDLCs was tested by heating a GDLC film from room temperature to 50°C while monitoring the luminescence intensity. 5CB, dispersed in the SiO$_2$–TiO$_2$ matrix, becomes isotropic above the liquid crystal–liquid transition (clearing point) at 34.0°C. The experimental set-up of the spectrofluorimeter is given in figure 2.

The luminescence intensity of the europium(III)-doped luminescent GDLC film was measured as a function of temperature. Only the intensity of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition was monitored; this transition accounts for more than 70% of the total intensity of the emitted light. A short scan was used to reduce the measurement time because excitation over a longer period can affect the temperature of the sample. The intensity of the europium(III) complex itself decreases as a function of temperature because quenching by non-radiative decay is more important at higher temperature. A reference sample containing [Eu(dbm)$_3$(gly)], but without the liquid crystal 5CB was prepared. The temperature dependence is shown in figure 3. All spectra were corrected for this decrease in intensity.

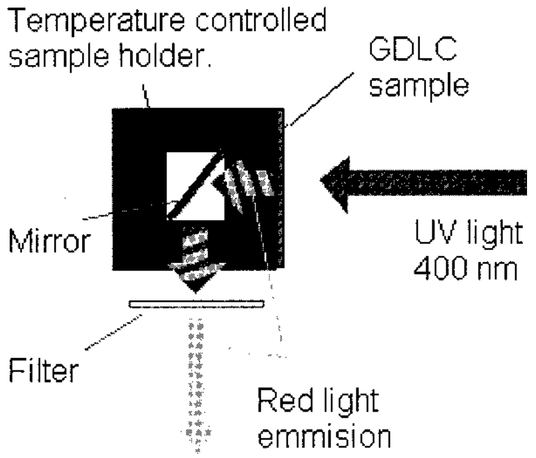

Figure 2. Experimental set-up for measuring the luminescence intensity of an europium(III)-doped GDLC film.

The temperature dependence of the luminescence in a glass dispersed liquid crystal film doped with [Eu(dbm)$_3$(gly)] is shown in figures 4 and 5. The contrast ratio, between the luminescence of the sample heated at 50°C (dispersed 5CB in the isotropic phase) and the luminescence of the sample at room temperature (dispersed 5CB in the nematic phase), is about 1:4.

The signal at room temperature is intense and has a high spectral purity. The intensity decrease around the clearing point at 34°C is sharp. The decrease in intensity before the clearing point can be explained by the temperature dependence of the refractive index and the anisotropy of the liquid crystalline phase. The anisotropy and the birefringence decrease with increasing temperature [24];

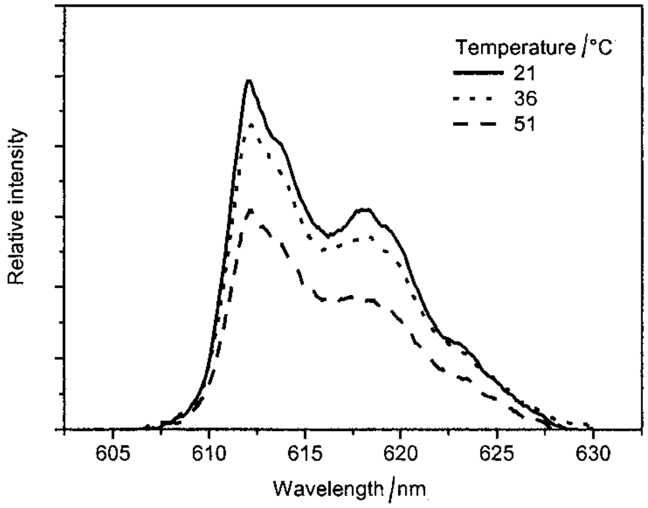

Figure 3. Temperature dependence of luminescence in the reference sample doped with [Eu(dbm)$_3$(gly)].

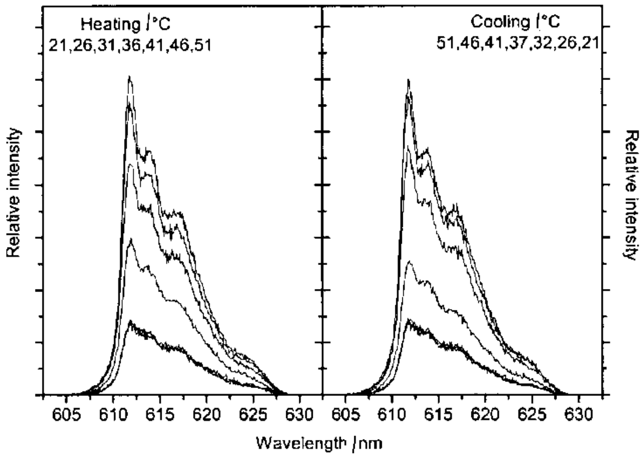

Figure 4. The decrease and increase of the $^5D_0 \rightarrow {}^7F_2$ transition intensity of a glass dispersed liquid crystal film doped with [Eu(dbm)$_3$(gly)] during heating and cooling.

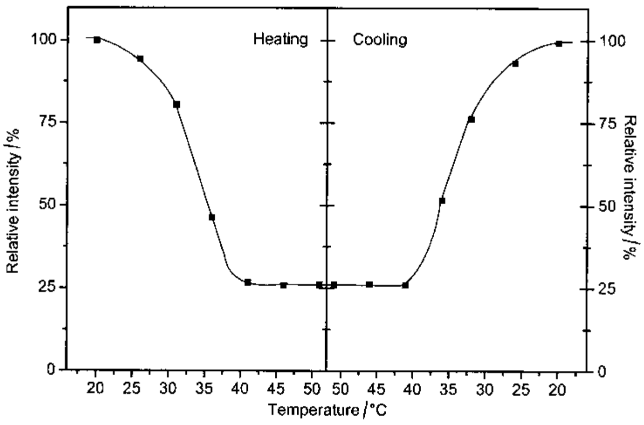

Figure 5. The relative intensity change of the $^5D_0 \rightarrow {}^7F_2$ transition during heating and cooling a glass dispersed liquid crystal film doped with [Eu(dbm)$_3$(gly)].

the temperature dependence is very pronounced at the clearing point [25]. The luminescence intensity corrected for temperature change remains constant after the clearing point. Very recently, Bünzli and co-workers used changes in the luminescence intensity of a liquid crystalline europium(III) compound to detect phase transitions [26]. In their case, the luminescence of a pure complex was investigated, while our system is a host–guest system.

Linearly polarized luminescence can be expected for lanthanide complexes with oriented chromophores [27], the intensity of the luminescence depending on the orientation of the incident light and the orientation of the aligned complex. In our study, there is no structural evidence that the ligand is aligned. Because no electrical alignment is used, the orientation of the lanthanide complexes in the liquid crystalline phase with respect to the incident light beam is always random. It is difficult to answer at present the question as to whether the europium(III) compound is dissolved in the glass matrix or in the liquid crystalline host. We think that the europium(III) complex is distributed over the two phases, because it is known that this type of europium(III) complex is soluble in both sol–gel glass and 5CB [16, 28].

4. Conclusions

In summary, luminescent GDLC films doped with a tris(β-diketonato)europium(III) complex were prepared successfully. Intense metal-centred luminescence could be measured. The temperature-driven switching capacity of the samples was tested. The intensity decrease between the ON and OFF state was measured by recording the luminescence intensity while heating the samples from room temperature to above the clearing point. The luminescent films have a contrast ratio of 1:4 when heated and show a sharp decrease in intensity near the clearing point. The red luminescence at room temperature is intense and has a high spectral purity.

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