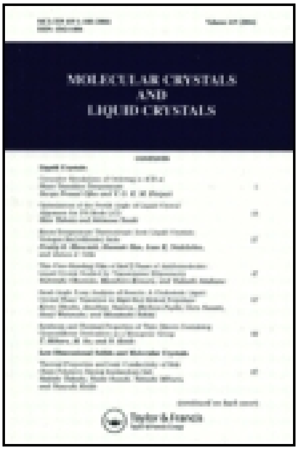

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Novel UV Sensor Based on a Liquid Crystalline Mixture Containing a Photoluminescent Dye

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The Erythemal Response Spectrum is a scientific expression that describes the skin sensitivity to the ultraviolet radiation. A long exposure to UV radiation causes skin erythema once a threshold dose has been exceeded.

We present a sensor based on a liquid crystalline mixture, containing dye, that absorbs photons at UV wavelength and emits them in the visible range of the electromagnetic spectrum. In particular the absorption spectrum of the mixture can be modulated to be similar to the Erythemal Response Spectrum. This system presents several innovative features: the absorption range of the mixture can be varied to be sensitive to different wavelengths, the luminescence intensity can be tuned, the system can be implemented on flexible devices, providing the possibility to create a dosimeter for ultraviolet radiation.

Keywords: liquid crystals; photoluminescence; UV sensors

INTRODUCTION

The stratospheric depletion has one of its consequence in the increase of UV radiation reaching the earth surface. The effect of UV radiation on living organism has been studied in many research areas, from environmental science to agriculture, microbiology and human health.

Exposure to ultraviolet radiation can be dangerous for human health. High energy photons of the UV radiation can induce photochemical

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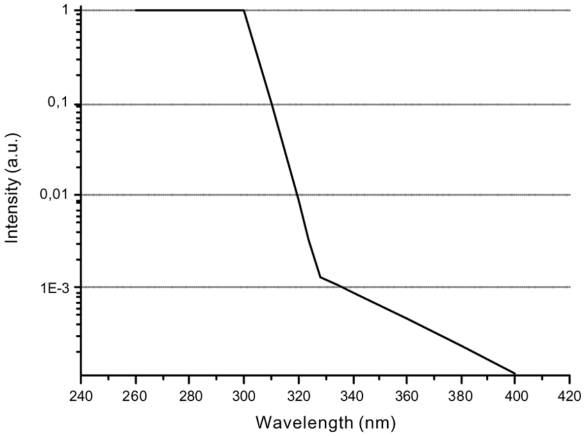

FIGURE 1 Erythemal Response Spectrum (ERS).

alteration that may cause biological effects. The organs that are most critically affected by a long exposure to the UV are eyes and skin. The biological effects are directly related to the wavelength of the incident photons. UV radiation is divided into three ranges: UVA (320–400 nm), UVB (280–320 nm) and UVC (100–280 nm).

In 80's Mckinley and Diffey proposed an erythemal response spectrum (ERS) related to human skin (Fig. 1), i.e., a spectrum of the relative sensitivity of the skin as a function of the wavelength of the incident radiation. This spectrum has become a widely accepted standard [1].

Multiplying the solar spectrum at the earth surface by the ERS standard, the effective solar spectrum is obtained, that shows how important is the role of UVB radiation in the skin reaction. UV are absorbed into the human skin, producing erythema, burn and eventually skin cancer, due to the DNA damage.

In the past years several devices were developed in order to monitor the erythemal effect of UV radiation, the most popular among them are based on the Robertson-Berger Spectrophotometer developed in 70's. The principle of operation of this device is the following: the sunlight passes through a quartz window and then through a UV transparent filter (Schott UGS) that absorbs almost all the visible light except a small part of red light (700–850 nm). The radiation transmitted by the filter hits a UV sensitive phosphorescent material, (MgWO.sub.4) that absorbs radiation and emits it as visible green light. The fluorescence light goes through a second filter (Corning 4010) that stops the red light. The intensity of the fluorescence light is measured by a solid state photodiode GaAsP, not sensitive to red light and with a maximum of sensitivity at the green wavelength. This device is a solar blind detector system that responds to UVB [2–5]. In the following years, other devices were developed with the ability to sufficiently mimic the human skin.

The use of AlxGa1-xN alloys was reported for applications as solar UV monitoring, due to their intrinsic visible-blindness and the possibility of tailoring the absorption edge from 365 nm to 200 nm by modifying the Aluminium content [6]. Subsequently photo-detectors based on AlxGa1-xN/GaN wide band gap semiconductors were developed to obtain a system that was chemically, mechanically and thermally more stable. Finally, using a AlxGa1-xN/GaN p-i-n junction based on a graded AlGaN layer with a proper layer structure design an improved spectrum response and a lower dark current were obtained [7].

Recently the use of liquid crystalline materials as active elements in UV sensors has been proposed. In particular two cholesteric liquid crystal mixtures, that change their colour when exposed to UV radiation, have been proposed. The first mixture is based on a cholesteric system (nematic + optically active dopant) doped with ergosterol (provitamin D2) or with 7-dehydrocholesterol (provitamin D3) [8,9]. In the second cholesteric mixture a nematic component, sensitive to UVB and based on a derivative of cinnamate (CH=CH−COO) [10], has been used. In both cases the change of selective reflection wavelengths (helical pitch), following UV exposure, is the basic effect. The main drawback is that in these systems a simple change in the color of the mixture cannot give quantitative information on the effective absorbed UV dose. In order to have a physical quantity, directly related to the absorbed amount of UV radiation and easily detectable, without adding suitable and expensive optical and electronic components, increasing the device complexity, a new type of liquid crystals based UV detectors has been developed. The system is based on the optical effect of a liquid crystalline photo-luminescent mixture prepared using cyanobiphenyl materials, together with nematic liquid crystals and chiral dopants [11]. The fluorescent behavior of 4-alkyl-4′-cyanobiphenyl (nCB) materials has been extensively studied in homogeneous solutions as well as for the pure material. In low concentrations the excited singlet state $1(\mathrm{nCB})^*$ has a strong emission at 330 nm with a short lifetime (~1 ns) but at higher concentrations there is an excimers formation $2(\mathrm{nCB})^*$ that efficiently emit at 400 nm with a longer lifetime (~10 ns). The emitted light can be monitored by a photodiode. The disadvantage is related to the fact that the light emitted by the mixture is still very close to the UV part of the electromagnetic spectrum.

In this study another photosensitive liquid crystalline mixture is presented to improve the performance of the previous one based on cyanobiphenyl materials, by including a photoluminescent dye, within the liquid crystal mixture of nematic and chiral compounds, with a high emission in the visible range.

EXPERIMENTS AND DISCUSSION

The cholesteric liquid crystal mixture is prepared using a nematic compound and a chiral dopant. The nematic liquid crystal is used to control the transition temperature from nematic to isotropic, in order to give a better stability to the mixture even at high temperatures. The chiral component is used to enhance the absorption hence the emission efficiency of the whole mixture. Finally the mixture is doped by a photoluminescent dye: N,N-dimethyl-4(4-nitrostyryl)aniline, its chemical formula is shown in Figure 2.

The homologue (diethyl-) of this dye was used in [12] to estimate the order parameter of a nematic liquid crystal by its polarized luminescence. The dye absorbs in 220–350 nm range and emits at 573 nm, due to a π-π^* transition. The cholesteric MLC-6248 as a chiral dopant and the nematic MLC-6816 as a host material are used. MLC-6816 belongs to cyclohexylcyclohexanes and has only the nematic phase ($30^\circ \rightarrow N \rightarrow 76.5^\circ \rightarrow I$), MLC-6248 is a non-mesogenic compound with the following temperature diagram: $K \rightarrow 48^\circ \rightarrow I$. The chiral compound was used to improve the absorption and emission efficiency of the whole mixture, while the nematic compound was used to stabilize it in temperature. The choice to use a common solvent, in which simply dissolve the dye, is not a viable one for a device that has to be exposed to direct sunlight.

All liquid crystals are supplied by Merck (Germany). For our experiment the following liquid crystal mixture is prepared:

$$99.7\% \{80\% \text{MLC-6816} + 20\% \text{MLC-6248}\} + 0.3\% \text{dye}$$

The concentration of the dye is fixed at 0.3 wt. % due to the solubility of this material in the liquid crystal compound. The liquid crystal mixture is placed in a sandwich cell between two fused silica plates with a thickness in the range between 1 and several tenths of

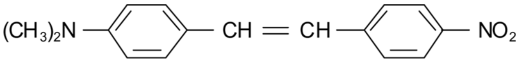

FIGURE 2 Chemical formula of the photoluminescent dye.

microns. It is known that some dyes are very soluble in LC. If a small amount of dichroic dye ("guest") is dissolved in nematic LC ("host"), the dye molecules align along the preferable orientation of the LC molecules (director). The obtained mixture possesses dichroic absorption. The same effect is observed for a cholesteric liquid-crystals (CLC) host: if a small amount of dye, possessing linear dichroic absorption, is dissolved in the CLC, the elongated dye molecules follow the helical director orientation and the helical arrangement transforms linear dichroism into a circular dichroism. By LC-molecule reorientation, the absorption properties can be affected. This helical structure optimizes the absorption of light from the mixture.

A fiber optic spectrophotometer and an Halogen-Deuterium lamp (AVS-S2000 and DH-2000, Avantes, The Netherlands) are used for absorption measurements together with an heating stage for optical bench (Serie F, Calctec, Italy) to investigate the stability of the mixture at increasing temperatures. For the photoluminescence measurements a mercury lamp is used as UV light source (HG 100 AS, Jelosil, Italy).

The typical experimental setup's for absorption (left) and emission (right) measurements are drawn in Figure 3. The spectrophotometer sensor is aligned at 90° with respect to the light source in the emission measurements setup in order to avoid detection of the direct exciting radiation.

In solution, the photoluminescent dye absorbs UV radiation and emits light in the visible range. In Figure 4 the absorption and emission spectra of the liquid crystal-dye mixture for different thicknesses, 10, 40 and 60 μm, of the cell are shown. Figure 5 shows how

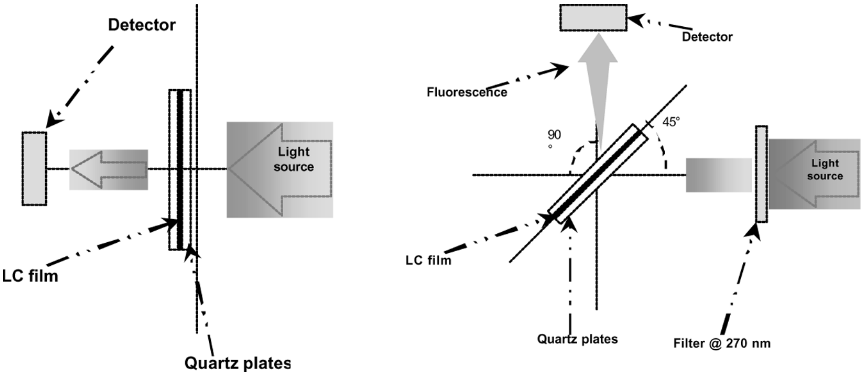

FIGURE 3 Typical experimental setup for absorption (left) and emission measurements (right).

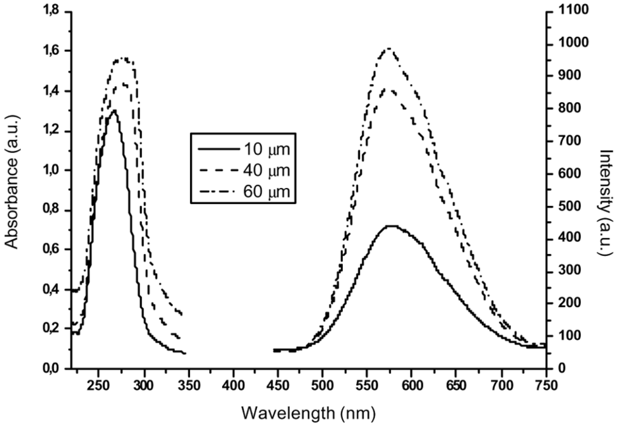

FIGURE 4 Absorption (left) and emission (right) spectra of the liquid crystal-dye mixture for different thicknesses, 10, 40 and 60 μm.

our mixture behaviour, for different cell thicknesses, is close to the effective solar spectrum. A modulation of the absorption spectrum and the right condition that better mimic the human skin behaviour is obtained varying the thickness of the cell.

Data in Figure 4 suggest that a cell with 60 μm thickness is the best choice. Figure 6 shows how the absorption spectrum is constant in temperature from 0°C to 80°C.

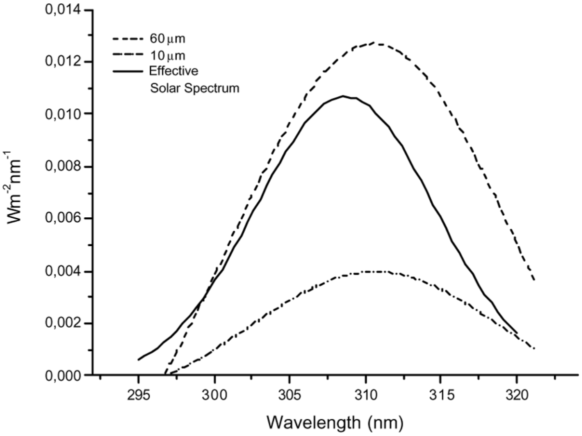

FIGURE 5 Spectral irradiance of the mixture compared to the effective solar spectrum.

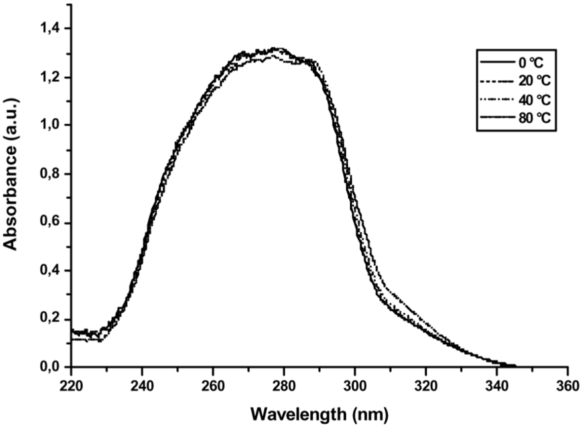

FIGURE 6 Absorption spectrum of the mixture as a function of temperature.

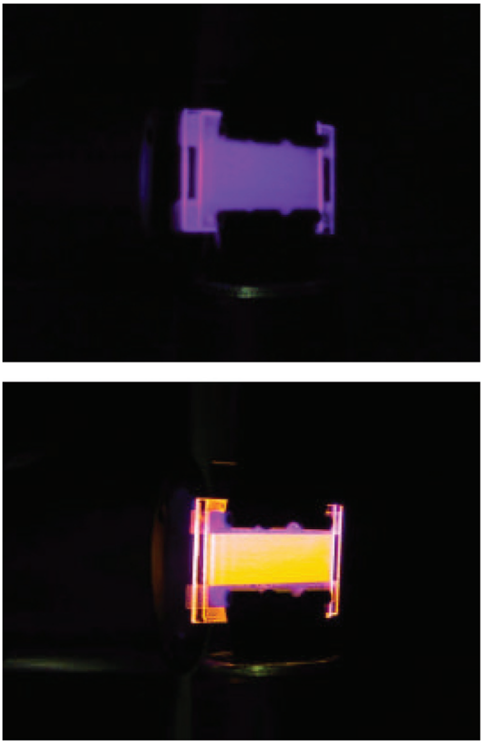

FIGURE 7 Light emitted by a cell containing a cyanobiphenyl mixture (top) and by a cell containing a cholesteric-dye mixture (bottom) when illuminated with a Mercury lamp filtered at 270 nm.

Figure 7 shows a comparison between the emitted fluorescent light from a mixture with cyanobiphenyl materials and the mixture with the photoluminescent dye when illuminated with a mercury lamp filtered at 270 nm. It is clearly seen that the emission intensity coming out from the liquid crystal and dye mixture is more intense than the other cell. Moreover the emission wavelengths in the yellow-orange range are easier to detect in a device that uses commercial photodiodes to provide quantitative information.

Finally the possibility to mix the dye with a polymer, for istance, PMMA (Polymethyl-methacrylate), transparent to UV, has been examined. The mixture results more stable mechanically and in temperature but its absorption properties are affected by the solvatochromic effect that makes it not suitable for a UV dosimeter.

Stability and good emission properties are important but also other characteristics of the sensor such as the low costs of production together with its capability to be encapsulated in a flexible substrate are of fundamental importance in the development of a device. In a possible prototype, a filter could be placed in front of our sensor in order to prevent the visible light to hit our mixture, then the photoluminescence could pass through a second filter in order to select the maximum wavelength of emission. A photodiode could be placed just after the second filter in order to quantitatively measure the emitted light.

CONCLUSIONS

We have characterized a liquid crystals and photoluminescent dye mixture suitable as active material for new kind of UV sensors. This material is stable in a wide temperature range, and its absorption can be modulated. Moreover the properties of the system do not strongly depend on the angle of the incident light. Temperature stability of the system is a property of fundamental importance when designing a particular device that will undergo a continuous exposure to the direct sunlight.

The sensor is based on the photoluminescent effect of the dye, providing a way to develop a device that indicates for instance the daily dose of UV exposure for applications in medicine, pharmacology or cosmetics.

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