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Enhancing the luminophore emission of chiral polymer-dispersed liquid crystals

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ABSTRACT

Chiral polymer-dispersed liquid crystals can enhance the emission of organic luminophores introduced into the composition. Such optical materials are useful for creating panoramic optical film for pressure and temperature sensors. The optical properties of chiral polymer-dispersed crystals, doped with platinum porphyrin complex, were experimentally investigated. The dependence of the luminophore emission on the pressure and temperature was measured.

1. Introduction

Materials which undergo changes in their properties under the influence of various external factors (temperature, pressure, and strain) attract the attention of researchers for the development of panoramic optical sensors. For example, organic luminophores are widely used to indicate the surface pressure distribution in various fields of science and technology.

The use of organic luminophores is based on the process of luminescence quenching by oxygen. Fluorescent molecules that are sensitive to oxygen, and a small amount of polymer binder, are dissolved in a solvent and used to cover the test surface by spraying. After evaporation of the solvent, a coating containing the luminescent molecules has been formed. The luminophore molecules are excited by light with a certain wavelength, and they emit light with a different wavelength. The luminescence intensity depends on the properties of the luminophore and the polymer, the luminophore concentration, and the oxygen concentration in the environment, which depends on pressure. This method of measuring pressure or oxygen concentration is called Pressure-Sensitive Paint (PSP). Full details of such sensors and their application can be found in the reviews [1–5].

One of the problems of this method is that it is difficult to obtain a uniform distribution of the luminophore molecules on the test surface, and a uniform thickness of the luminophore coating when spraying the solution. Therefore, it is important to develop film sensors based on these substances, which can overcome these challenges. Clearly, the encapsulation of the luminophore in a polymer matrix will change the kinetics of its luminescence quenching and pressure sensitivity. Optimization of the functional properties of these materials requires a comprehensive approach to both the choice of the polymer and luminophore. In particular, the film sensors require luminophores with a high quantum yield of the luminescence. Further improvement of fluorescent sensors is associated with the synthesis of new stable compounds having high quantum yield. This is a long and expensive chemical process. An alternative is to look for physical effects that can change the sensitivity and response time of the sensor, within a predetermined range of oxygen concentrations, for compounds which are already known.

One possible approach is to use photonic crystals (PC). A PC is a structurally ordered medium with dielectric properties that vary periodically in one, two, or three, dimensions [6]. PCs therefore have photonic bandgaps (PBG), where electromagnetic waves cannot propagate because of the reflections from the material structure. However, at the edges of the PBG, the luminescence intensity of a luminophore contained within the PC increases by an order of magnitude. The modification of the spectrum of a pure PC can be achieved by controlling its anisotropy. One such material is a liquid crystal (LC) which has a strong anisotropy of the dielectric constant. Creation of PC-structures with LCs is promising for the control of optical properties.

The control of the properties of PC-structures with a LC, is the subject of numerous studies and reviews. The main reason for this is the discovery of lasing in chiral liquid crystals (CLC) doped with dyes

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[7–16]. Chiral liquid crystals, with helical structure, are one-dimensional PCs with a photonic band gap (the area of selective scattering of light) for light with a particular circular polarization: a polarization which coincides with the sign of the cholesteric helix when propagating along the optical axis of the CLC. Light waves with the opposite direction of circular polarization pass through the CLC almost unchanged. The presence of the band gap affects the luminescence spectrum of the guest molecules. The density of photonic states is sharply increased by PBG edges. The intensity of the luminescence is almost zero inside the band gap, and increases at its edges with strong fluctuations.

Another possibility to change the luminophore emission is to use chiral polymer-dispersed liquid crystals (PDLC). PDLCs are droplets of cholesteric liquid crystals (ChLC) which are uniformly dispersed in the polymer matrix [17,18]. In recent years researchers have been intensively studying laser dyes embedded into a chiral PDLC, where stable random lasing was found [19–22].

Therefore, the use of chiral PDLCs to modify the properties of the luminophores conventionally used in optical sensors for pressure, shows huge promise. The purpose of this paper is to investigate the influence of chiral PDLCs on the amplitude and dynamic characteristics of the porphyrin platinum complex, and to study their dependence on pressure.

2. Experimental technique and materials

To measure the dependence of the luminescence (intensity and quenching time) on the pressure, a test sample was placed in a pressure chamber, where the pressure was decreased by the backing pump and was monitored by a vacuum gauge. The measurements of the characteristics were performed at pressures of 10^5 Pa and 10^2 Pa. This pressure range is realised in many industrial plants, and in particular, in a wind tunnel. A schematic of the measurement setup is shown in Fig. 1.

Plane polarized light from a KLM532 SLN-100 laser (1) is interrupted by the disk of the modulator (2), and falls on the beam splitter (3). A plane light wave is shown by the double-sided arrows. Part of the beam is reflected and sent to photodetector 1 (4) for control of the laser intensity. The other part of the beam passes through a standard quarter-wave plate (5) and becomes, depending on its orientation, left or right circularly polarized. When the shutter (6) is open, light reflects off the mirror (7), passes through a quartz window (10) and falls onto the sample (8) which is contained in the chamber (9). Reflected light from the sample passes through lens (11) and is sent to photodetector 2 (13). Depending on the wavelength range, we used either filter 1 (λ = 641 nm) for the red or filter 2 (λ = 532 nm) for the green (12). Signals from the photomultipliers (PMT) 1 and 2 were recorded with a Tektronix TDS 1012 oscilloscope in standby mode. The experiment starts the moment the shutter is opened (6). Measured signals were averaged over 16 pulses to ensure reliability.

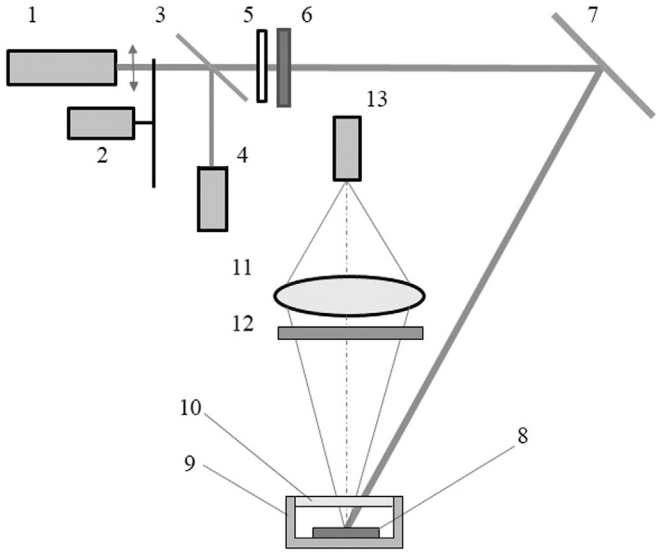

Fig. 1. Schematic of measurement apparatus 1 - laser, 2 - modulator, 3 - beam splitter, 4 - photodetector 1, 5 - ¼ λ plate, 6 – mechanical shutter, 7- mirror, 8 - test sample, 9 - pressure chamber, 10 - quartz window, 11- lens, 12 - light filter 1 or 2, and 13 - photodetector 2.

The spectral characteristics were measured when the modulator was disconnected, and light could pass through the lens onto the entrance slit of the spectrophotometer (Colibry) via an optical waveguide. Luminescence decay parameters (attenuation time and intensity) of the samples were determined using a pulsed nitrogen laser, operating at λ = 330 nm with a 20 ns pulse duration.

Test samples (40 μm film thickness) were composed of a luminophore, liquid crystals, a binder, and a solvent. The polyvinyl acetate (PVA) was used as the binder (polymer matrix), and octaetyl platinum porphyrin (PtOEP) was used as the luminophore, because the cholesteric liquid crystals we used were cholesterol esters (pelargonate, valerate, and chloride). Selection of the polymer was determined from the fact that the LCs are in the polymer matrix in droplet form. They make a so-called bipolar texture, and have optical properties similar to those of the planar texture LCs [17] with photonic bandgaps.

Thin and durable films were formed on a support by the pouring method, using 12% PVA solution when the solvent (a mixture of acetone and toluene) has dried. The PtOEP luminophore is not dissolved in this solution. The texture of the film containing only the luminophore is shown in Fig. 2a) (polarizing microscope). When LCs are introduced into the solution and are stirred using ultrasound (30 min), the film with the texture shown in Fig. 2b) is formed. Visually, the film acquires a pink hue, indicating a partial dissolution of the polymer in the mixture of the luminophore and the LCs. Determination of the distribution of the luminophore between the matrix and LC drops requires additional investigation.

3. Experimental results and discussion

The first objective was to study the effect of the polymer matrix properties on the initial components: the luminophore and the LCs.

The polymer matrix affects the optical properties of both the luminophore and the LCs. Fig. 3 shows the transmission spectra (1) and luminescence (2) of PtOEP. It can be seen that this luminophore has one of its absorption bands coinciding with the green laser wavelength, λ = 529 nm. This allows us to effectively excite at this wavelength and have maximum signal-to-noise ratio.

3.1. Effect of the luminophore concentration

The intensity of luminophore luminescence when doped into the polymer matrix decreases in the comparison with the intensity of pure luminophore luminescence. At pressure P = 10^5 Pa, it depends on its concentration (Fig. 4). Investigation of the dependence of the luminescence intensity on the luminophore concentration in the polymer

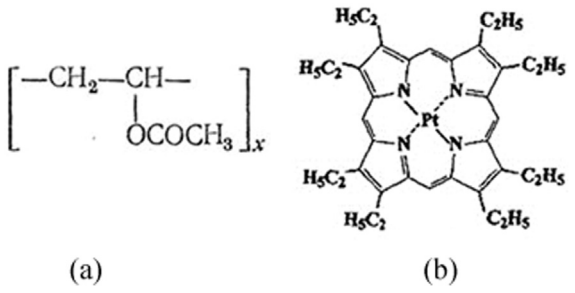

Fig. 2. The chemical structure of the polymer (a) and platinum porphyrin complex (b).