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STUDY OF LIQUID CRYSTAL CELL DOPED WITH BODIPY FOR LASING APPLICATION

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The organic semiconductors BODIPY derivative was studied for lasing application. The nematic liquid crystal doped with BODIPY derivative was researched as gain medium for distributed feedback laser. Reflection spectrum for nematic liquid crystal and emission spectra of nematic liquid crystals doped with BODIPY derivative at the laser pumping with wavelength of 532 and 515 nm were determined. Obtained spectra correspond to the regime which is close to the threshold.

Key words: *organic semiconductors; feedback distributed laser; emission spectrum.*
UDC: 621.382.592

1. Introduction

Recent reports on the possibility of optical gain in organic semiconductor crystals and in amorphous semiconductor thin films have prompted the search for new inexpensive promising materials for the manufacture of organic DFB microlasers generating light in the visible region of the spectrum [1–3]. Ultimately, the properties of these materials can create preconditions for the practical application of organic films in lasers with both optical and electric pumping [4, 5]. The most practical advantage associated with organic-based structures is the almost unlimited design and creation of various molecular architectures. It is also easily realized in the photonic devices [6, 7]. The advantages of organic semiconductors over inorganic analogs are due to the following factors where the first is that the synthetic procedure is simpler and faster, if possible, without the use of cost catalysts [8–10]. It is a variety of basic platforms, which have properties that determine their possible implementation in organic semiconductor structure (ambipolar foresight, stability, variety of colors, etc.). There is easy tuning with a simple chemical modification. They are more stable in comparison to traditional Ir (III) and Pt (II) complexes [11]. Therefore, organic compounds are less susceptible to schedules after application to the substrate, whereas inorganic complexes require precise and delicate temperature control during application.

It should be noted that organic emitters are cheap (both for production and for recycling), environmentally friendly, easy to manufacture on any substrate [12]. Moreover, devices based on them have shown excellent biocompatibility [13]. Expanding of the chemical space of organic compounds by developing reproducible and scalable protocols for both their synthesis and controlled crystallization followed by experimental validation have a significant impact on understanding of their physical properties [14–16]. Organic semiconductors have shown great potential as laser gain materials due to a combination of high available optical gain, solution processability and broad emission spectra [17]. The main elements of organic lasers, like all others, are an active medium, an optical feedback structure, and a pump source. The gain available in a material increases with increasing density of excited state luminophores. This density, in turn, depends on the level of the pumping force. As a result, this leads to the characteristic threshold behavior of lasers. Namely, when lasing only begins once the pumping becomes enough to provide a sufficiently high density of the luminophores in the excited state for the gain to compensate loss.

One of the challenges is to minimize the gain required to achieve a lasing to minimize the required pump energy. It is clear, that this minimization requires the simultaneous optimization of both the optical feedback structure and the absorption of organic material at the generation wavelength. Despite a sharp decrease in the lasing thresholds, efforts to optimize the geometric parameters of DFB lasers and materials continue. Materials for organic laser gain media can be obtained from molecules with a wide spectrum of molecular weights. One of promising materials for laser applications are BODIPY and their derivatives. They are of interest due to their high photoluminescence quantum yield, often approaching 100 %. BODIPYs offer a variety of sites for functionalization and the position has an impact on the fluorescence and the stimulated emission characteristics [17, 18]. In ref. [19] was shown that BODIPYs are better in terms of threshold and dye loading in comparison to the standard laser dye such as DCM.

Therefore, study of new active hybrid systems (organic compounds) allows optimization of the lasing properties and helps to combine them with already known devices for the development of various elements such as biochemical labels, fluorescent switches, and sensors. However, despite on the rapid progress, there are certain limitations and problems in the manufacture of functional elements of DFB microlasers based on organic semiconductors and nanoparticles on a commercial scale. Therefore, such materials and structures require further detailed research.

In this work the organic semiconductors BODIPY derivative will be studied for lasing application. Emission spectra of BODIPYs dissolved in cholesteric liquid crystalline media will be obtained.

2. Results and Discussions

It is known that distributed feedback lasers do not require external mirrors. The role of a resonator is played by a grating. In such a cavity the mirrors are not localized but distributed along the propagation of the radiation generated by the active medium. The grating period determines the possible lasing wavelength, and it must fall within the luminescence spectral region of the gain medium. The grating is formed in the volume of the gain medium at the stage of laser fabrication.

In our research, the nematic liquid crystals doped with BODIPY derivative were selected as gain medium of the distributed feedback lasers. These organic compounds were adjusted between two glass plates. The distance between which was 25 μm and was fixed with special spacers. This structure is a vertical cavity laser. Such choice is explained by fact that liquid crystals can slow down and even trap light with wavelengths near the photonic bandgap. Thus, such materials are interesting in designing new laser light sources. It should be noted that nematic liquid crystals are the most popular in industrial applications due to the relatively low viscosity and existence in an extensive range of temperatures. Therefore, the cholesteric-nematic mixture was used to create a periodic structure of the distributed feedback lasers.

In the first step of our research the emission spectra of the solution (10^{-5} M in CH_2Cl_2) and of the vacuum-deposited film of bThBODIPY were recorded (Fig. 1). The blue shift of the film spectrum in comparison to the solid sample was obtained. This slight blue-shift is due to the general larger population of the less energetic vibrational states as a result a smaller reorganization energy in the solid state. However, there was red shift of the film at the edge of the lowest energy absorption band compared to the solution. The sharp profile of the less energetic band is characteristic of the BODIPY unit of the molecule, whereas the other bands have charge transfer character between the donor and the acceptor components, as observed for similar BODIPY derivatives [20].

It is well known that the emission wavelength of the cholesteric liquid crystal lasers can be tuning by using different angle pitch gradients. It can be provided by changing the composition. In our case the E7 nematic liquid crystal was mixed with the chiral CB15 impurity in such proportion that the high reflectivity area of the nematic liquid crystals grating is consistent with the photoluminescence spectra of bThBODIPY.

Reflection spectrum of the obtained liquid crystal cell is shown in Fig. 2. It can be seen from Fig. 2 that maximum reflectance is about 100 % on the wavelength range from 600 to 700 nm. The full width at half maximum is about 120 nm that is typically for such crystals.

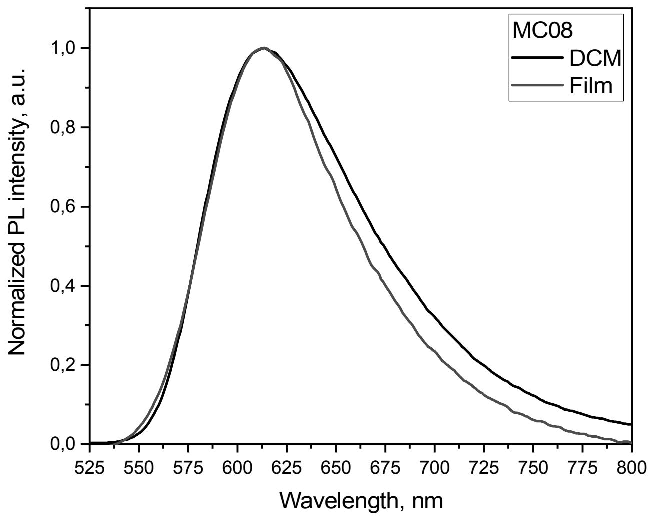

Fig. 1. Photoluminescence spectra in solution (10−5 M in CH2Cl2, black) and for the vacuum deposited film of bThBODIPY

The nematic liquid crystal was doped with BODIPY derivative with a certain concentration of weight. The lasing properties of BODIPY derivative were studied by pumping manufactured active elements of DFB lasers with radiation of different wavelengths. Two types of lasers were used for it. The first one was a second harmonic Nd:YAG laser with the wavelength of 532 nm in a pulsed mode. The second one was a "Light Conversion" PHAROS femtosecond laser with the wavelength of 515 nm in the pulsed mode. The circuits for excitation of active elements of DFB lasers with different lasers are practically similar.

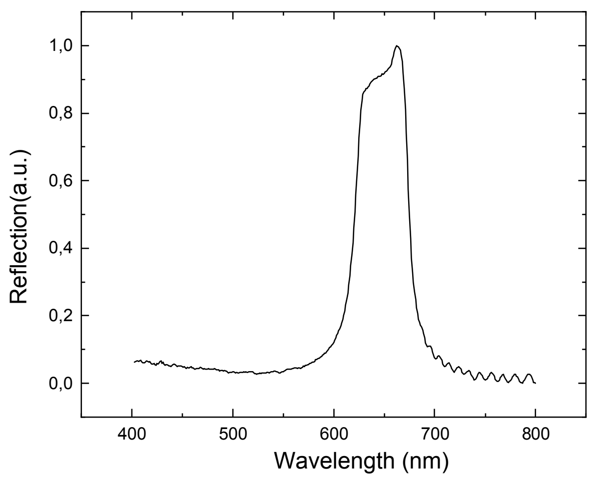

Fig. 2. Reflection spectra of cholesteric liquid crystal cell

Fig. 3 shows the pumping scheme using the "Light Conversion" PHAROS femtosecond laser. It can operate in the modes of generating pulse radiation at wavelengths of 1030 nm, 515 nm, and 343 nm with a pulse duration from 190 fs to 10 ps. The study of the nematic liquid crystals doped with BODIPY derivative lasing properties was carried out under pumping by radiation with the wavelength of 515 nm and an energy of up to 30 mJ. In addition, a second harmonic Nd:YAG laser with the wavelength of 532 nm in a pulsed mode was used for pumping.

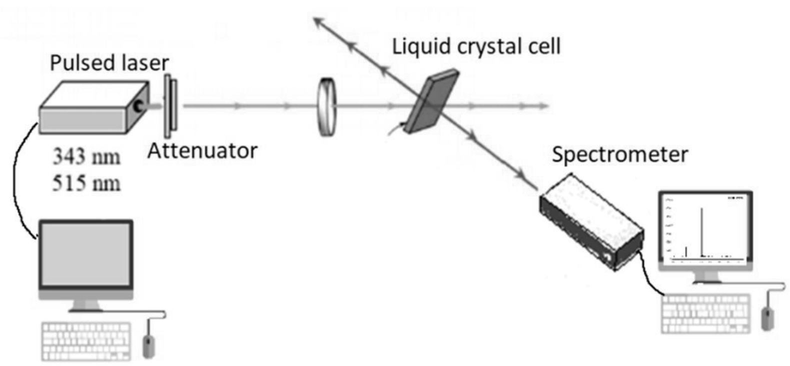

Fig. 3. Scheme of pumping DFB lasers based on nematic liquid crystals doped with BODIPY derivative

The nematic liquid crystals cell doped with BODIPY derivative was attached to the goniometer. The optimal angle of incidence of the pump beam was selected experimentally. The beam was focused by a lens onto the cell with a diameter of about 0.5–1 mm. The laser control system provided a smooth change in a wide range of pump parameters: frequency, pulse duration, and pump energy. An additional attenuator in the circuit made it possible to reduce the energy to the minimum value. The emission spectra were recorded with a spectrometer. Several experimental samples were made, and a series of emission spectra were obtained to study the lasing properties of the DFB lasers based on nematic liquid crystals doped with BODIPY derivative. Fig. 4 shows a photo of a liquid crystal cell excited by radiation with the wavelength of 515 nm.

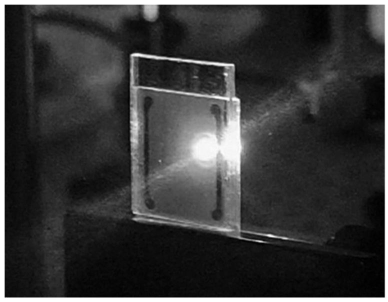

Fig. 4. Liquid crystal cell doped with BODIPY derivative at the excitation of radiation with wavelength of 515 nm

The first set of studies was carried out with the pumping of active elements by a Nd:YAG laser with the wavelength of 532 nm in a pulsed mode. The pulse duration was 10 μs. The most typical results are shown in Fig. 5, 6 and 7.

As can be seen from Fig. 5, the emission spectrum of the cell practically repeats the photoluminescence spectrum of ThBODIPY. It is obvious that in this case the pump energy is below the threshold value. The photoluminescence spectrum begins to narrow slightly in the region of the wavelengths of the highest gain with the increase in the excitation energy. It indicates that the lasing threshold is approaching (Fig. 6). The peak on the photoluminescence curve becomes more pronounced and narrows at the wavelength of the highest gain at the further increase in the pump energy (Fig. 7). This mode corresponds to an insignificant excess of the lasing threshold.

Studies have shown that the lasing peak for the structure under study is formed at the wavelength of 625 nm at the pumping by radiation with the wavelength of 532 nm. However, further changes in the pump parameters did not result in the higher gain and, accordingly, the narrower radiation peak.

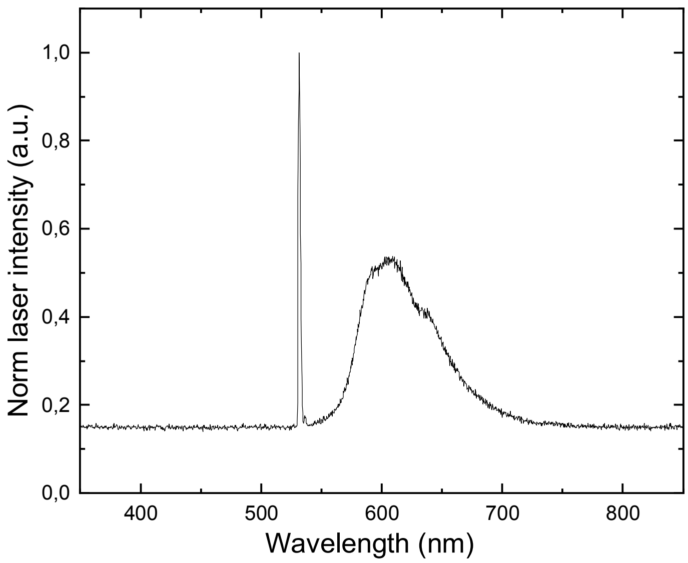

Fig 5. Emission spectrum of nematic liquid crystal doped with BODIPY derivative at the laser pumping with wavelength of 532 nm at the pulse duration of 10μs and the energy about 1 μJ

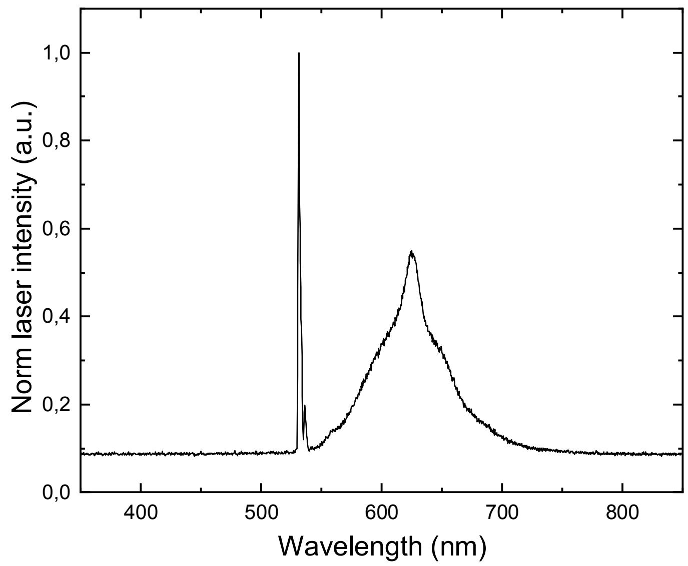

Fig. 6. Emission spectrum of nematic liquid crystal doped with BODIPY derivative at the laser pumping with wavelength of 532 nm at the pulse duration of 10μs and the energy about 5 μJ

Subsequent research was carried out using the “Light Conversion” PHAROS femtosecond laser at the wavelength of 515 μm. The study of the lasing properties of BODIPY derivative was carried out at various parameters of pump radiation: energy, frequency, pulse duration. The most typical results are shown in Figs. 8 and 9.

Studies have shown that two lasing peaks are formed at wavelengths of 608 nm and 669 nm at the pumping of radiation with the wavelength of 515 nm for the structure under study. The ratio of the peaks heights changes and different gains are observed at different wavelengths at the insignificant changes in the tilt angle of the cell (Fig. 9).

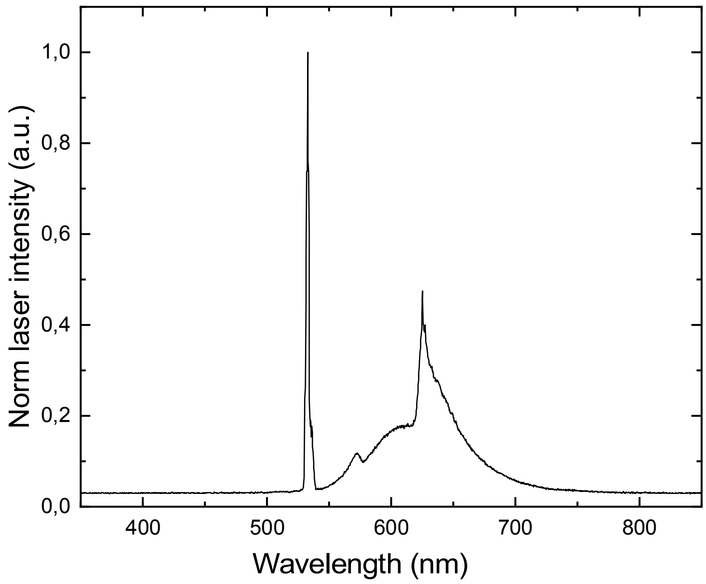

Fig. 7. Emission spectrum of nematic liquid crystal doped with BODIPY derivative at the laser pumping with wavelength of 532 nm at the pulse duration of 10μs and the energy of about 12 μJ

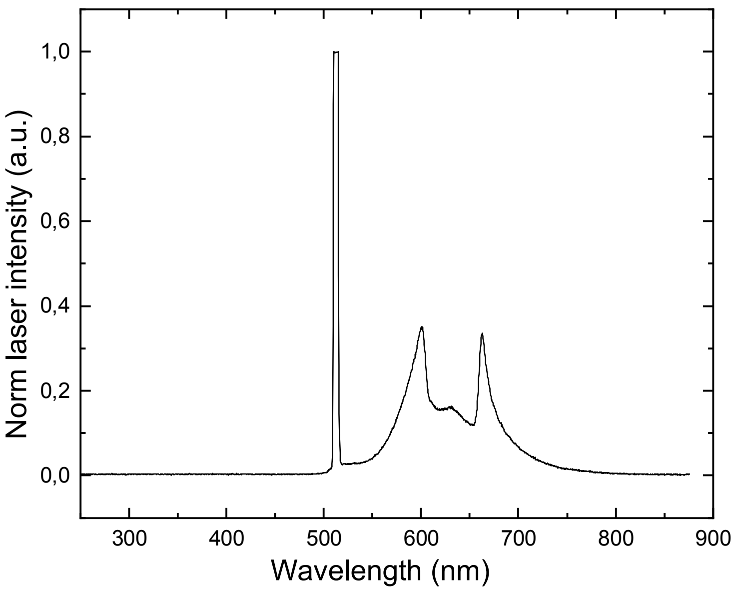

Fig. 8. Emission spectrum of nematic liquid crystals doped with BODIPY derivative at the laser pumping with wavelength of 515 nm at the pulse duration of 10 ps and the energy about 17 μJ

The study of the manufactured active elements was carried out at various pump parameters; however, it was not possible to achieve significant gain at one of the possible lasing wavelengths of 608 nm or 669 nm even at the highest pump energies. Thus, the emission spectra narrowing was obtained with the formation of characteristic peaks at the wavelength of 625 nm at the pumping of radiation with the wavelength of 532 nm, and at the wavelengths of 608 nm and 669 nm at the pumping of radiation with the wavelength of 532 nm. This indicates that a slight excess of the lasing threshold was achieved in the manufactured active elements. However, the gain is insufficient to further narrow the lasing peaks.

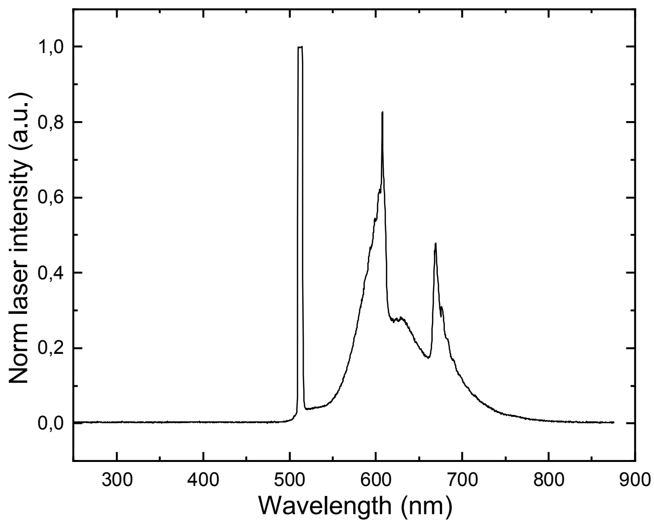

Fig. 9. Emission spectrum of nematic liquid crystals doped with BODIPY derivative at the laser pumping with wavelength of 515 nm at the pulse duration of 10 ps and the energy about 32 μJ

Conclusion

The nematic liquid crystals doped with BODIPY derivative was studied as gain medium for distributed feedback laser applications. However, it was not possible to achieve high gain and obtain narrow lasing peaks with this structure. It can be explained by the low quantum yield of the BODIPY derivative. Thus, it must be improved to use this material as a gain medium for DFB lasers, However, it should be noted that it can be successfully used in various OLED structures.

Acknowledgment

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ДОСЛІДЖЕННЯ РІДКОКРИСТАЛІЧНОГО ЕЛЕМЕНТА, ЛЕГОВАНОГО BODIPY, ДЛЯ ЛАЗЕРНОГО ЗАСТОСУВАННЯ

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Досліджено застосування похідної органічних напівпровідників BODIPY для лазерної генерації. Нематичний рідкий кристал, легований похідною BODIPY, досліджено як середовище підсилення для лазера із розподіленим зворотним зв'язком. Визначено спектр відбивання нематичного рідкого кристала та спектри випромінювання нематичних рідких кристалів, легованих похідною BODIPY, у випадку лазерного накачування з довжинами хвиль 532 та 515 нм. Отримані спектри відповідають режиму, близькому до порогового.

Ключові слова: *органічні напівпровідники; лазер із розподіленим зворотним зв'язком; спектр випромінювання.*