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FULLERENE- AND NANOTUBE-DOPED LIQUID CRYSTAL SYSTEMS OPTICAL LIMITERS IN THE NEAR INFRARED

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Optical limiting (OL) properties of the liquid crystal systems based on structure formed by fullerenes, nanotubes and cyanobiphenyl derivatives have been studied under conditions of the laser beam influence at wavelength of 1080 and 805 nm. It has been shown that the systems studied could be applied as OL elements in the near infrared spectral ranges. The comparative data with other nonlinear structures used as OL systems have been discussed.

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1. Introduction

Organic nanophotonics tasks and new nanotechnology developments have provoked research in designing new materials for effective optical limiting (OL) in order to protect both human eyes and technical devices, as well as and information processing network from high laser irradiation. Wide interest has been expressed in nonlinear optical properties of organic conjugated systems doped with fullerenes [1-9] and nanotubes [10]. The optical properties, which are conditioned by excitation of π-electrons, demonstrate that a new charge transfer complex is formed between an organic molecules and nanoobjects, for example, between a donor fragment of an organic molecule and fullerenes [11-15]. This complex is of a higher excited state absorption cross section than the ground state one. That is why; fullerene-doped systems are reverse saturable absorption (RSA) materials and may be used for a sensor and eye protection as nonlinear optical absorbers. Moreover, a large value of the light-induced change in refractive index in these compounds contributes significantly to the OL effect due to energy losses by diffraction. It also predicts large nonlinear refraction n_2 and third order susceptibility $\chi^{(3)}$, which allows the materials to be used for modulation and conversion of a laser beam over broad spectral range [16].

In the present paper the optical limiting properties of the composites including PVK-CN, fullerenes and cyanobiphenyl derivatives have been studied under conditions of the laser beam influence at wavelength of 1080 and 805 nm. It has been shown that the systems studied can be applied as OL elements in the near infrared spectral ranges. The comparative data with other nonlinear structures used as OL systems have been discussed.

2. Experimental

The liquid crystal (LC) material from cyanobiphenyl group has been chosen as an electrooptical matrix. The two chromophore molecule are presented in **Fig. 1, *a*** and ***b***

Mol 1.

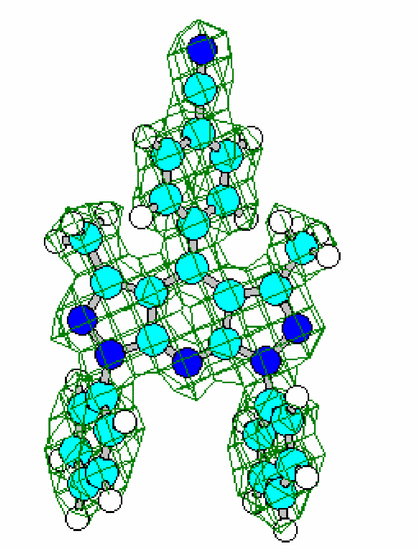

Fig. 1 a. CN-chromophore electrostatic charge density distribution. The calculated state dipole moemnt is equal to 1.41 D.

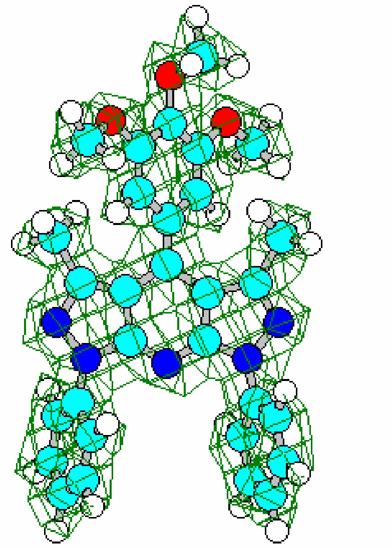

Fig. 1 b. Methoxy- modified chromophor. State dipole moment is equal to 2.07 D.

have been used as photosensitive components. These chromophores have been synthesized by a method described in the papers [17,18]. C_{60} fullerenes have been used as sensitizers. Composite structures were made in the ratio of 1 photosensitive component to 2 electro-optical LC one. The relation between photosensitive chromophore and the fullerene was equal to 5:1. Using the fullerene sensitization, the homogeneous systems were obtained with good matching between the refractive indices of photosensitive organic molecule and LC for ordinary wave. It should be emphasized that the fullerene sensitization allows shifting the absorption spectrum of pure LC towards a wavelength of the laser irradiation. The traditional classical *S*-type LC cells possessing initial planar orientation were prepared. The thickness of the cells was equal to about 10 μm. The alignment films based on non-photosensitive polyimides 81A and 81B were used here.

The pulsed Nd-YAG laser was applied as a fundamental laser source at the wavelength of 1080 nm. Passive modulation was performed by a LiF crystal. Its pulse duration was equal to about 10 ns , frequency repetition was equal to about 10 Hz and a laser spot on the sample surface was 1-1.5 mm in diameter. The femtosecond pulsed irradiation of a quasi-CW Ti-sapphire laser with pulsewidth of 30 fs, the repetition frequency of 82 MHz, the power of 150 mW was used to study OL at wavelength of 805 nm. The spot diameter at the film surface was 0.2 mm. Beam energies incident on and transmitted through the sample were measured. A set of neutral light filters was used to vary the incident beam energy. The OL scheme was analogous to that presented in paper [19].

3. Results and discussion

Main results of the OL investigation of the compounds mentioned above are shown in Fig. 2 and Fig. 3.. One can see substantial non-linear intensity dependences of the OL. These figures clearly show presence of the nonlinear optical processes described by fourth rank polar tensors. The accent has been given namely on the near IR spectral range. Different mechanisms have been proposed to explain the OL results in the near IR [20-30]. Our own results and the data of other scientific groups [20-30] show presence of different mechanisms like as multiphoton absorption, light-induced charge-transfer complex (CTC) formation, plasmon resonance, laser-induced heating, laser-induced scattering, carriers free absorption, and others. These factors may be considered as the main factors determining the OL in the near-IR spectral ranges.

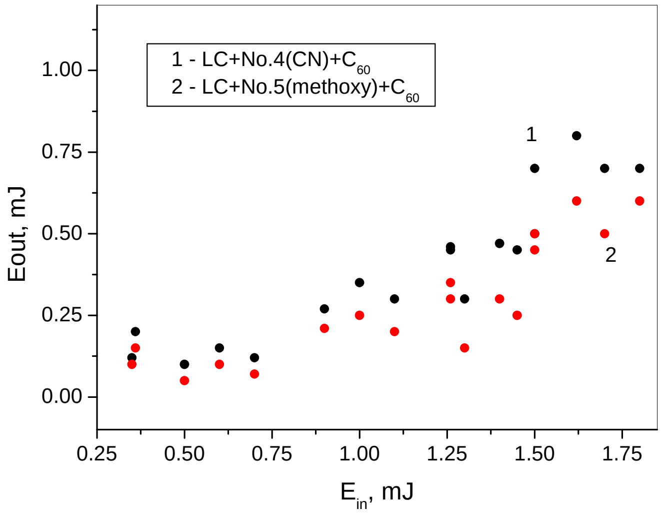

Fig.2. Dependence of the output energy on the input one for the LC systems doped with chromophore mentioned above and fullerene C_{60}. Wavelength of irradiation was 1080 nm.

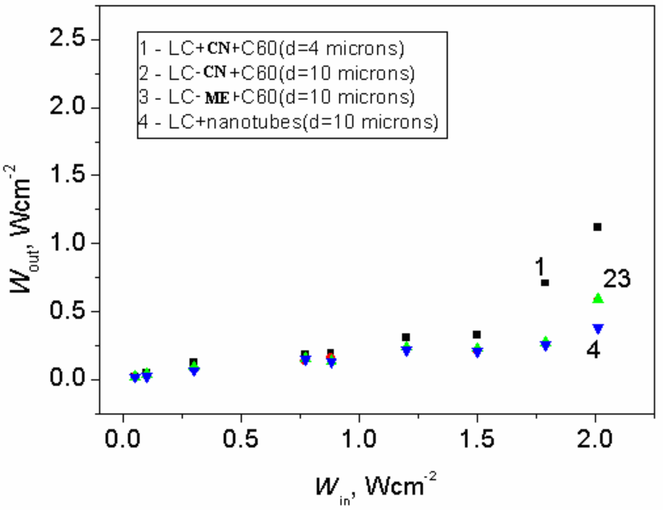

Fig.3. Dependence of the output power on the input one for the LC systems doped with chromophore mentioned above and fullerene C_{60}. Wavelength of irradiation was 805 nm.

Let us to discuss the results presented in Fig.3 when the samples have been treated at wavelength of 1080 nm under nanosecond pulse regime. One can see that the effective OL could be observed for both chromophores. Really, larger than 10 fold attenuation has been observed for the chromophore methoxy and a little bit less value has been found for chromophores cyan. The systems limit the laser energy up to 0.156 J·cm^{-2} that corresponded to the laser sport of 1 mm and input energy close to 1.25 mJ. When the input energy density exceeds the value of 0.15 – 1.7 J·cm^{-2} the heating of the LC predicts increase in the transmission. Two mechanisms should be considered to explain the OL results for the current structures. They are: charge transfer complex formation and two photon absorption processes. The first quantum chemical simulation to support the complex formation for the systems mentioned above has been shown in paper [31].Principal difference of the investigated chromophoe consists in the different values of the dipole moments. Generally the enhanced state dipole moments cause additional enhancement of the nonlinear optical susceptibility. However in such complex systems this fact is not so obvious. Moreover, the fullerene C_{60} has the exited transition from the ground state to the first exited state at 2.33 eV, which close to the laser wavelength of 532 nm. Thus, the two photon process should be discussed in the current experiment that influences the nonlinear attenuation too. The increase in the TPA coefficients for the systems studied is shown in Fig.4.

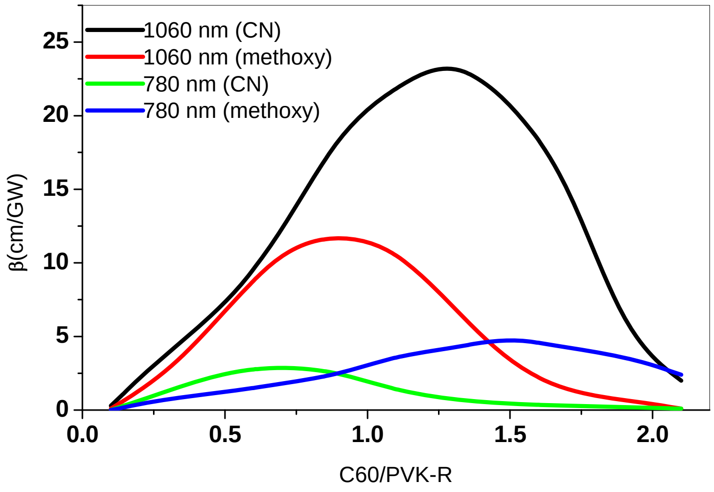

Fig. 4. Theoretically simulated dependences of the TPA coefficient β versus the different ratio between the fullerene and PVK-R.

The calculated dependences of the TPA coefficient β versus the ratio between fullerene and PVK are presented in Fig. 4. The calculations were performed by the B3LYP DFT method. Before the mixture of the investigated chromophore and of the surrounding PVK polymer was optimized assuming the frozen polymer surrounding background. After step-by-step procedure was applied to achieve the conference of the minimum of total energy. The values of the TPA were calculated following the method described for the guest-host chromophore in papers [32-33].

One can see that for the two principal wavelengths – 780 nm and 1060 nm there is a large difference in the values of the TPA. It may be explained by the resonance dependences, however it also indicates on a drastic enhancement of the trapping intra-energy gap levels. It should be added that during the calculations we have added additional contributions of the electron-phonon interactions on the borders chromophore-polymer to achieve a good convergence of the calculated results. One of an interesting discovery obtained from these calculations is a fact that for the 780 m wavelength the maximum of the TPA is shifted towards the higher fullerene/PVK ratio. Moreover, the maximal values of the TPA are larger for the methoxy groups compared to the cyan ones despite the state dipole memns are higher for the cyan group. The situation is principally different during undergoing to the IR spectal range where the number of trapping electron-vibration states is increased drastically, which give additional resonant contribution to the b. One can see principal difference consists in fact that in this case the CN group have larger effect. Moreover, its value is shifted to larger ratio. This fact may contribute a competition between the dipole-dipole interactions and the positions of the resonant levels on the borders chromophore-surrounding polymer. The shift of the maxima reflects such competition.

The results of the quantum chemical simulation shown above can support the difference in the OL results obtained at wavelength of 1080 nm and 805 nm. Returning to the Fig.4, one can conclude that less OL at wavelength of 805 nm could been explained by the difference in TPA process at these wavelength. By the way, the fact is: the forbidden transition at 1.6 eV for pure fullerene C_{60} can be activated in our case when the LC systems have been doped with fullerene-containing chromophores of cyan and methoxy. 3 fold attenuation has been observed for the LC cell with the thickness of 4 micrometers and with the chromophores cyan. More than 5 fold attenuation has been found for the 10 micrometers LC structures with the chromophores cyan and methoxy. More than 10 times attenuation has been revealed for the LC with nanotubes. It should be mentioned that the level of attenuation can be increased when nanotubes has been added in the LC. In this case the increase in the nonlinear absorption can be predicted by the odd electron from nanotubes core.

4. Conclusion

The near infrared optical limiting properties of the structures based on PVK-derivatives-C_{60} in the liquid crystal electrooptical media have been studied to apply these materials as effective nonlinear absorber in order to protect the human eyes and technical devices from high laser irradiation. The OL threshold and the level of destruction of different nanomaterials have been shown in the comparative data. It was shown that CN substitution of the pyrazoloquinoline gives substantially better results with respect to the methoxy derivatives. The basic mechanism responsible for the infrared optical limiting has been discussed. The quantum-chemical simulation has been made to support the OL in the near IR.

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