

COANP-fullerenes system for optical modulation

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Abstract. The advanced investigations of π -conjugated organic molecule COANP sensitized with fullerenes have been revealed to consider this system as an affective medium for optical limiting and phase modulation. The special accent has been given to influence of the nanostructured relief at the interface on the spectral and photoconductive features.

1. Introduction

Materials with π -conjugated organic molecules [1-4] are ones of the perspective media used for optical modulators, in particular for optical limiter. These materials can be polarized at a distance more than molecules dimension that leads to the appearance of nonlinear properties of the medium.

In our previous works [5, 6] we have considered the optical limiting properties of 2-cyclooctylamino-5-nitropyridine (COANP) solution doped with fullerenes C₇₀. Experiments demonstrated the limiting of the laser radiation with energy density from 0.1 J/cm² up to 0.6 J/cm². We have obtained the maximum attenuation of the laser radiation with energy density of 0.35 J/cm² for the solution COANP-C₇₀ with fullerene content of 20 wt.%. The energy value passed through solution has been decreased up to 18 times.

Reverse saturable absorption (RSA) and the complex formation process have been considered as the main mechanisms responsible for the optical limiting (OL) of COANP-C₇₀ system. The RSA mechanism, as the first one, is based on a difference in cross section for excited state of the fullerene molecule and unexcited ones. The cross section of singlet-triplet excited states in the fullerene is larger than the one of the unexcited molecule. The population of excitation levels increases with laser energy increase, so absorption increases as well.

The complex formation process, as the second OL mechanism, is corresponded to the following reason. Intermolecular charge transfer complex with large absorption cross section can be formed in π -conjugated organic system doped with C₇₀ due to the large electron affinity energy of fullerene. The electron affinity of acceptor fragment NO₂ in COANP is close to 0.45 eV. This parameter for fullerene is 2.65 eV that leads fullerene attracts weakly bound electrons from COANP donor part. Moreover, the distance for the electron pathway is larger for the *intermolecular* charge transfer than the one for the *intramolecular* transfer process. These two facts provoke the formation of the large dipole moment correlated with the increased absorption cross section under the laser irradiations. The model of the



intermolecular charge transfer process which can dominate on the intramolecular one is shown in figure 1.

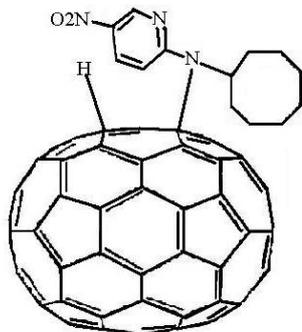


Figure 1. Possible interpretation of the *intermolecular* electron transfer in the COANP-fullerene system

The formation of the intermolecular charge transfer complex C_{70} -NO₂ has been supported by the results of DSC analysis (figure 2). The results of DSC demonstrate shifting of the transition temperature values (such as a melting point, a point of crystallization and a glass transition temperature) in the case of adding some amount of fullerene C_{70} in COANP.

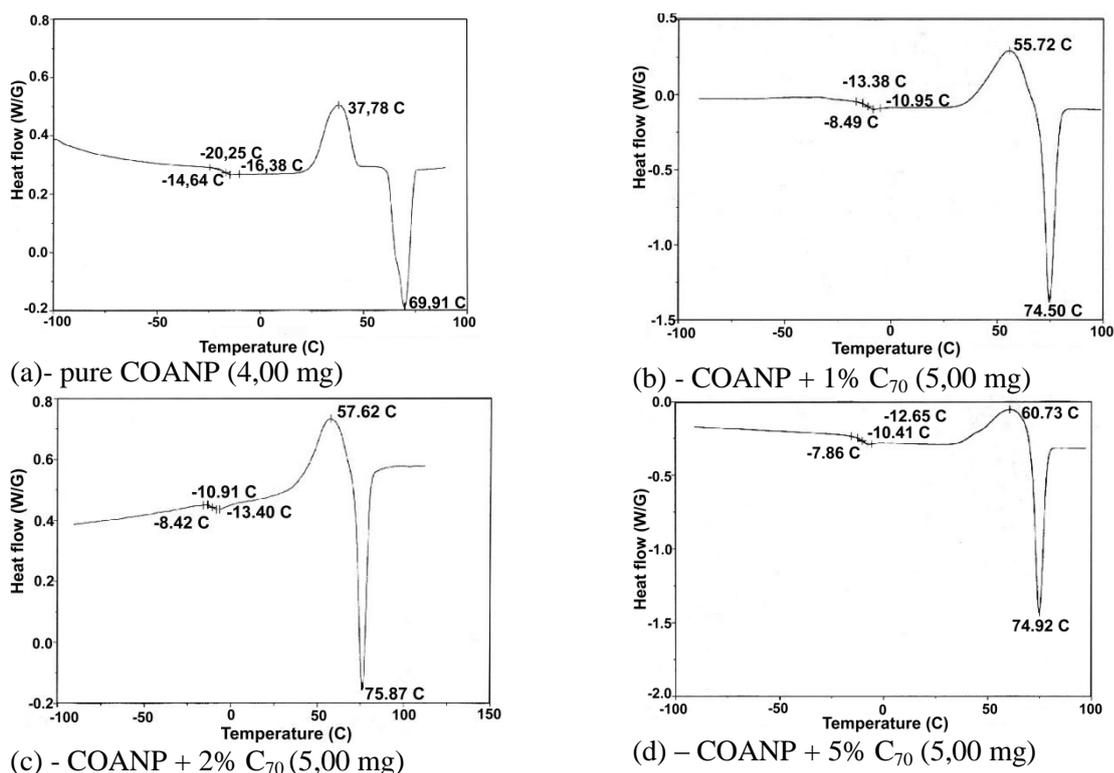


Figure 2. Results of DSC method for: (a) - pure COANP (4,00 mg), (b) - COANP with fullerene C_{70} of 1.0 wt. % (5,00 mg), (c) - COANP with fullerene C_{70} of 2.0 wt. % (5,00 mg), (d) - COANP with fullerene C_{70} of 5.0 wt. % (5,00 mg).

To support the concept of the *intermolecular* complex formation we have studied the transmittance spectra of 1% COANP solution in toluene doped with malachite green and fullerenes C_{70} (figure 3) as

well. The bathochromic shift for COANP solution doped with fullerenes C_{70} has been obtained. There has been no additive effect of malachite green dye as a sensitizer for COANP solution.

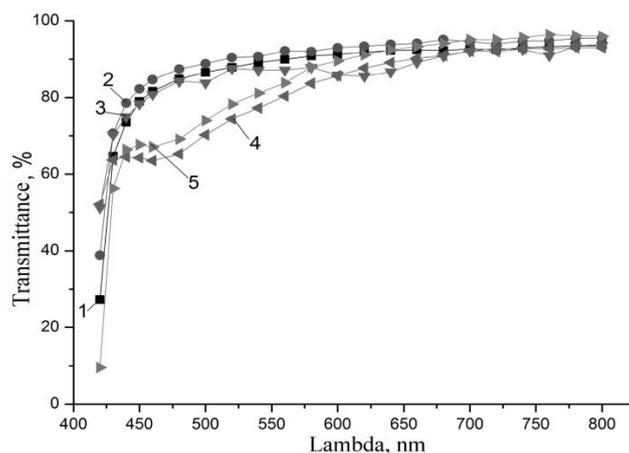


Figure 3. The transmittance spectra of 1% COANP solution in toluene: 1 – pure mol. COANP, 2 – COANP + malachite green of 0.1 wt. %, 3 – COANP + malachite green of 1.0 wt. %, 4 – COANP + C_{70} of 0.1 wt. %, 5 – COANP + C_{70} of 0.5 wt. %

The complex based on the COANP- C_{70} has been included into the liquid crystal (LC) cells and it has been considered for the increase of the materials applicable in optoelectronics devices. For example, the calculated nonlinear coefficients for the LC system doped with the COANP- C_{70} have been found as: $n_2 = 0,77 \times 10^{-10} \text{ cm}^2/\text{W}$ and $\chi^{(3)} = 2.4 \times 10^{-9} \text{ cm}^3/\text{erg}$ [7], which coincided with the comparatively observed for the LC doped with the PANI- C_{60} with $n_2 = 0,12 \times 10^{-11} \text{ cm}^2/\text{W}$ and $\chi^{(3)} = 3.42 \times 10^{-10} \text{ cm}^3/\text{erg}$. Nonlinear properties of the LC-fullerene system via increase of the system dipole polarizability has been obtained analogous the procedure shown in work [8]. The influence of the refractivity change due to the modification of the substrate relief has been discussed too [9,10].

2. Experimental

In the current study we have explored the mutual effect the sensitization of the nematic LC with COANP – fullerenes complex and formation of the carbon nanostructured substrate relief on the doped LC properties. The LC cell has been consisted from two glass substrates with indium tin oxide (ITO) coating. The carbon nanotubes structure relief is created on the ITO under the electric field of 100 and 200 V/cm. The mixture LC-COANP- C_{70} has been used as a filling for cell.

3. Results and discussion

Transmittance spectra measurements of empty LC cell with carbon nanotubes relief and filling with LC-COANP- C_{70} complex are shown at the figure 4. One can see that the transparency of the doped LC structure can be increased drastically via ITO coating modified with the oriented in the electric field carbon nanotubes (CNTs) use. It can be explained via decrease of the Fresnel losses due to the reason that the refractive index of the CNTs is close to 1.1. Moreover, we can conclude for the filled LC cell that the self-arrangement of LC molecules with the transition from the nematic phase to quasi-smectic one can be provoked. The LC phase order parameter change leads to the transmittance increases as well. Furthermore, under these conditions the decrease of the level of the bias voltage has been obtained.

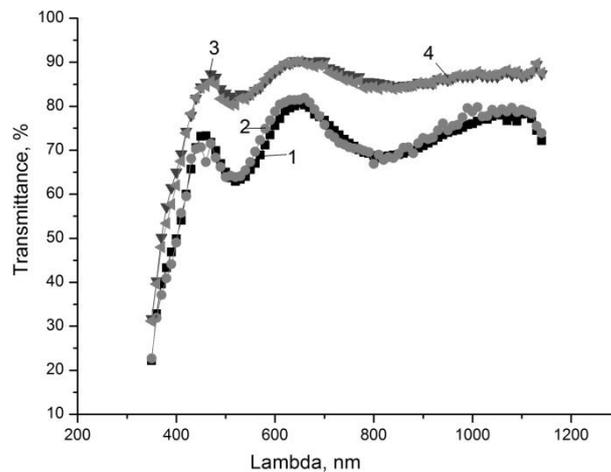


Figure 4. The transmittance spectra of the full and empty LC cell: 1 – LC cell empty, relief ITO+CNTs (100 V/cm) + SEW, 2 - LC cell empty, relief ITO+CNTs (200 V/cm) + SEW, 3 – LC+COANP+C₇₀, relief ITO+CNTs (100 V/cm) + SEW, 4 – LC+COANP+C₇₀, relief ITO+CNTs (200 V/cm) + SEW

Quantum chemical calculations with LAMMPS program have been done, which demonstrate the conjunction of carbon nanotubes with ITO substrate (figure 5).

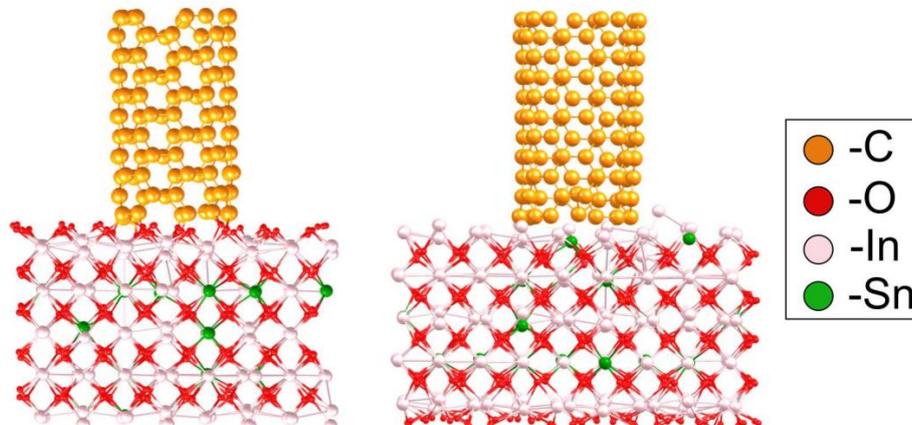


Figure 5. The model of the conjunction of carbon nanotubes with ITO substrate

One can see that the formation of a chemical bond between carbon nanotubes and ITO layer exists. The connection between two conductivity materials, such as ITO and carbon nanotubes leads to the conductivity increase and consequently to change the temporal characteristics (switch-on and switch-off time) of LC cell.

4. Conclusion

To summarize the results, it can be concluded that both the LC mesophase doping procedure as well as the interface relief nanostructuring process provoke the following features:

- 1). Observed transmittance increase permits to use the optoelectronic devices, for example the spatial light modulators and optical limiters, with good advantage.
- 2). Decreased level of the bias voltage which activates the LC cell and prognoses to improve the LC speed permit to consider the COANP-fullerene structures as the systems applied for the display and biomedicine technique.

3). Knowledge and experience used to study the intermolecular charge transfer process testify that the LC-COANP-fullerene materials can be proposed to be used not only in the visible spectral range but in the near IR-spectral range too.

Acknowledgments

The obtained results have been supported by RFBR grant #13-03-00044 (2013-2015), project “Nanocoating-GOI” (2012-2015) and international FP7 Program, Marie Curie Action, Project “BIOMOLEC” (2011-2015). Authors wish to thank their colleagues Dmitry Kvashnin (Emanuel Institute of biochemical physics RAS, Institute of Science and Technology “MISiS”) and Pavel Sorokin (Technological Institute for Superhard and Novel Carbon Materials, Institute of Science and Technology “MISiS”) for quantum chemical calculations. The authors appreciate their colleagues from the department for “Photophysics of media with nanoobject”, Vavilov State Optical Institute and abroad too for the helpful discussion.

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