Vibronic and Electric Properties of Semiconductor Structures Based on Butyl-Substituted Mono- and Triphthalocyanine Containing Erbium Ions

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The Raman spectra have been obtained and the temperature dependence of the conductivity of organic semiconductor structures based on butyl-substituted erbium monophthalocyanine and erbium triphthalocyanine has been studied. It has been found experimentally that the activation energy decreases dramatically and the Raman spectra exhibits four new peaks in the region of large Raman shifts as the molecular structure of the samples becomes more complicated.

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INTRODUCTION

Organic semiconductors currently belong to the most interesting and promising materials for modern microelectronics [1–3]. Semiconductor structures that consist of polymers, oligomers, and hybrid organic compounds are relatively inexpensive to manufacture; they can be high-purity substances containing up to $10^{14}-10^{16}$ impurity atoms in 1 cm³ [4]. These substances, which can be supported on flexible substrates, also exhibit a number of other advantages [2]. Some organic semiconductors, such as anthracene, polyacrylonitrile, and indigo, are very promising for optoelectronics. For example, they can be used for the development of light-emitting structures, thermistors, piezo-electric cells, IR radiation detectors, lasers, and other devices [2].

Phthalocyanines (synthetic green pigments) belong to a class of organic semiconductor structures. They are characterized by the presence of a conjugation system in their molecules. Current carriers are formed in phthalocyanines by the excitation of π electrons delocalized over the system of conjugated bonds. The energy required for the formation of nonequilibrium charge carriers decreases as the number of conjugations in the molecule increases [5]. The lanthanide compounds of phthalocyanines and their derivatives can form a class of complex molecular compounds. The simplest of them is a monophthalocyanine molecule, which consists of an organic ligand and a lanthanide ion, whereas a triphthalocyanine molecule, which consists of three parallel planar ligands and two lanthanide ions arranged between them, exhibits the most complex structure [6, 7]. Triphthalocyanines have been synthesized recently; therefore, the vibronic and electrophysical properties of the above compounds are practically not understood.

The aim of this work was to study changes in the vibronic and electrophysical properties of organic semiconductors based on butyl-substituted phthalocyanine complexes containing erbium ions on going from a simple monophthalocyanine structure to complex molecules such as triphthalocyanine.

Test samples and experimental procedure. The test semiconductor complexes of erbium phthalocyanines were synthesized from organic ligands in the course of a chemical reaction on boiling in *o*-dichlorobenzene with erbium acetate [6]. The erbium triphthalocyanine complexes were synthesized from free ligands in boiling alcohol [6]. The resulting organic structures were supported on quartz substrates using the liquid-drop adsorption method.

The Raman spectra were measured using a Jobin Yvon HR800 Raman spectrometer. A 632.82-nm He–Ne laser was used as the excitation source.

The electric conductivity of the organic structures was measured by the two-probe method. Contacts were made with silver paste. The control resistance measurements performed at various contact geometries demonstrated that the resistance of the contacts was much lower than the resistance of the samples and it had no effect on the measured values. The specific conductivity σ was 2×10^{-5} or $3 \times 10^{-10} \Omega^{-1}$ cm⁻¹ for structures such as erbium triphthalocyanine or erbium monophthalocyanine, respectively, at room temperature. The temperature dependence of the electric conductivity of



Fig. 1. Dependence of the electric conductivity of the samples of semiconductor structures based on butyl-substituted phthalocyanine containing erbium ions on the reciprocal of the temperature: (1) erbium triphthalocyanine and (2) erbium monophthalocyanine.

samples was measured over the temperature range from 22 to 200°C. The current intensities were measured with a Keithley 6487 picoammeter. The current–voltage characteristics of the test structures remained linear over the entire test temperature range. All of the measurements were performed in a vacuum at the pressure $P = 10^{-4}$ Torr.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the conductivity of structures based on butyl-substituted erbium monophthalocyanine (curve 2) and erbium triphthalocyanine (curve 1). The resulting curves exhibit an activation character, and they can be described by the following expression:

$$\sigma = \sigma_0 e^{-Ea/kT},\tag{1}$$

where σ_0 is a parameter that depends on the semiconductor structure and type, E_a is the activation energy, k is the Boltzmann constant, and T is temperature. The activation energies were found equal to 0.65 and 0.12 eV for erbium mono- and triphthalocyanine structures containing peripheral butyl substituents, respectively.

The parameters found are inconsistent with the characteristic activation energy of charge carriers in phthalocyanine semiconductor complexes, which can vary from 1 to 2 eV [4]. Rousseau et al. [8] found that, in complex structures such as bis(phthalocyanine), an energy value of 1 eV corresponds to the electron transition from the highest occupied molecular orbital to the lowest unoccupied orbital. According to Rousseau et al. [8], the energy difference corresponding to the electron transition between the molecular orbitals e_1 and e_3 , which is referred to as a charge-transfer band, was esti-



Fig. 2. Raman spectra of butyl-substituted erbium phthalocyanine structures over the range $100-4000 \text{ cm}^{-1}$: (1) erbium monophthalocyanine and (2) erbium triphthalocyanine.

mated at 2 eV. The published and experimental data indicate that the experimental activation energies are inconsistent with the energies of the main electron transitions. The low activation energies in the test samples suggest the occurrence of additional energy states that predominantly contribute to the electric conductivity of phthalocyanine complexes. Kazanskii et al. [9] hypothesized that such energy values are due to electrostatic potential fluctuations as a result of the presence of charged ions. The appearance of new states can be due to the insertion of a complex-forming metal into the molecular structure of a ligand, or these new energy states are formed by the interaction of a few organic ligands with each other.

The former reason for this low activation energy is difficult to confirm because the effect of a complexforming agent was ignored in the theoretical calculations of electron transitions in complex organic molecules. The appearance of interactions between organic ligands results in phthalocyanine ring deformations; in turn, this can be detected by changes in the positions of Raman lines.

The Raman spectra (Fig. 2) of the test structures consist of large numbers of peaks due to the stretching and deformation vibrations of molecular groups that constitute a phthalocyanine ring.

Aromatic benzene rings manifest their vibronic properties as narrow peaks at 1676, 1609, 1551, and 945 cm⁻¹ [10, 11]. On going to smaller wavenumbers, lines characteristic of pyrrole-ring -C=C- vibrations were detected at 1461 and 1350 cm⁻¹ [11]. Narrow Raman lines at 1302, 1222, and 1112 cm⁻¹ correspond to the deformation vibrations of carbon–hydrogen bonds. Bridging vibrations, which are characteristic of the -C=N atomic combination, manifest themselves as three Raman peaks at 788, 775, and 718 cm⁻¹ [10, 11].

JETP LETTERS Vol. 85 No. 12 2007



Fig. 3. Raman spectra of erbium phthalocyanine structures over the range $100-2000 \text{ cm}^{-1}$: (1) erbium monophthalocyanine and (2) erbium triphthalocyanine.

Lines at 816, 683, 643, 561, and 570 cm⁻¹ correspond to the out-of-plane vibrations of a phthalocyanine ring [11].

The Raman spectra shown in Fig. 3 indicate that molecular structure transformation also resulted in the appearance of four new peaks in the region of high frequency (Raman) shifts. Peaks at 366, 279, 208, and 122 cm^{-1} equidistantly follow each other at a distance of about 79 cm⁻¹ between them.

Bao et al. [12] found that a pair of lines arranged at a distance of 70 cm⁻¹ from one another can appear in the Raman spectra of sandwich structures such as rare earth bis(phthalocyanines). Such lines are characteristic of the weak out-of-plane vibrations of phthalocyanine rings. Note that the above sequence of peaks was not observed in the Raman spectra of planar structures such as erbium monophthalocyanine (see Fig. 3, curve 1).

CONCLUSIONS

In this work, the vibronic and electrophysical properties of organic semiconductor structures based on butyl-substituted erbium mono- and triphthalocyanine have been studied. The results obtained for the temperature dependence of the electric conductivity allow us to determine the activation energy of the charge carriers. The activation energy decreases significantly as the number of organic ligands in the molecular structure increases. The activation energies found for the butylsubstituted erbium mono- and triphthalocyanine suggest that energy states resulting from the interaction of a few organic ligands make the predominant contribution to the electric conductivity of the samples. Raman light scattering reveals four new lines at 122, 208, 279, and 366 cm⁻¹ appearing in the region of large Raman shifts on going from the planar structure of butyl-substituted erbium monophthalocyanine to sandwich structures such as erbium triphthalocyanine. Analyzing published data, we conclude that the four lines observed correspond to the weak out-of-plane vibrations of phthalocyanine rings. The above lines were not observed in the Raman spectra of the semiconductor structures based on butyl-substituted erbium monophthalocvanine. Thus, peripheral substituents have no effect on the positions of the observed Raman peaks.

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REFERENCES

- 1. Yu. A. Chaplygin, *Nanotechnology in Electronics* (Tekhnosfera, Moscow, 2005) [in Russian].
- 2. A. Yashchenko, Illyuminator **4** (6), 5 (2003).
- 3. A. Borzenko, PC Week/RE 46, 31 (2001).
- M. Pope and C. E. Swenberg, *Electronic Processes in* Organic Crystals (Clarendon, Oxford, 1982; Mir, Moscow, 1985).
- L. I. Boguslavskiĭ and A. V. Vannikov, Organic Semiconductors and Biopolymers (Nauka, Moscow, 1968) [in Russian].
- V. E. Pushkarev, M. O. Breusova, E. V. Shulishov, and Yu. V. Tomilov, Russ. Chem. Bull. 54, 2087 (2005).
- N. Ishikawa, T. Lino, and Y. Kaizu, J. Phys. Chem. A 106, 9543 (2002).
- R. Rousseau, R. Aroca, and M. L. Rodriguez-Mendez, J. Mol. Struct. 356, 49 (1995).
- A. G. Kazanskii, E. I. Terukov, A. V. Ziminov, et al., Pis'ma Zh. Tekh. Fiz. **31** (18), 37 (2005) [Tech. Phys. Lett. **31**, 782 (2005)].
- 10. F. Lu, J. Cui, and X. Yan, Spectrochim. Acta A **63**, 550 (2006).
- 11. M. Bao, R. Wang, L. Rintoul, et al., Vibr. Spectrosc. 40, 47 (2006).
- 12. M. Bao, Y. Bian, L. Rintoulet, et al., Vibr. Spectrosc. **34**, 283 (2004).

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