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Comparative analysis of absorption spectra in zinc phthalocyanine films on different substrates

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Films of butyl-substituted zinc phthalocyanine were fabricated on various substrates using vacuum deposition. Optical studies of the resulting films were conducted, during which their electronic absorption spectra were measured. Analysis of the characteristics of the electronic absorption spectra revealed a dependence of the properties of the butyl-substituted zinc phthalocyanine films on the nature of the substrates. It was established that the crystalline form of butyl-substituted zinc phthalocyanine films on the surfaces of organic and inorganic materials exhibits a metastable α -phase and a stable β -phase, respectively. Further research revealed a significant influence of the interaction between butyl-substituted zinc phthalocyanine molecules and substrate molecules on the film properties. For the potential use of butyl-substituted zinc phthalocyanine films as an active element in gas sensors, it is necessary to consider the nature of the interaction between butyl-substituted zinc phthalocyanine molecules and substrate molecules.

Keyword: zinc phthalocyanine, films, glass, polyvinyl chloride, absorption spectrum, molecular orbitals.

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Introduction

The optical and electrophysical properties of inorganic semiconductors (silicon, germanium, gallium arsenide, etc.) have been studied quite thoroughly. The majority of microelectronic devices are based precisely on the inorganic semiconductors listed above. To analyze the properties of inorganic semiconductors, band theory was developed, which describes the electron spectrum in a periodic crystal potential reasonably well [1]. Alongside inorganic semiconductors, organic semiconductors are widely used in areas such as solar cells, gas sensors, displays, biosensors, etc. Molecular orbital theory was developed to analyze the optical and electrophysical properties of organic semiconductors, and describes with varying degrees of approximation the energy states (spatial distribution and electron energy), types of molecular orbitals, the shape of organic molecules, etc.

Organic semiconductors include, in particular, metal phthalocyanines with conjugated carbon-carbon and nitrogen-carbon bonds. Metal phthalocyanines, both in solutions and in the form of films, are currently finding limited application in solar cells [2, 3, 4] and gas sensors [5, 6, 7]. In metal phthalocyanine molecules, fluorine atoms, chlorine atoms, butyl groups, and other substituents can be used instead of hydrogen atoms in the benzene rings. For example, the characteristics of zinc phthalocyanines with various substituents for hydrogen atoms in the benzene rings have been studied [8, 9]. The optical properties of metal phthalocyanine films also strongly depend on the nature of the substrates on which they are deposited [10]. In particular, zinc phthalocyanine films are capable of exhibiting semiconductor properties [11].

In this paper, samples of the organic semiconductor butyl-substituted zinc phthalocyanine were fabricated and investigated. All samples were obtained by vacuum deposition

onto different substrates. An inorganic material (silicate glass) and an organic substance (heat-treated polyvinyl chloride) were used as substrates. The aim of this paper was to study the influence of organic and inorganic substrates on the characteristics of the absorption spectra in butyl-substituted zinc phthalocyanine films and their polymorphic properties.

Experimental section

The butyl-substituted zinc phthalocyanine films were obtained by thermal vacuum deposition. Powder in the form of needle-shaped crystallites of butyl-substituted zinc phthalocyanine was the starting material, and silicate glass and heat-treated polyvinyl chloride (polyvinyl chloride-polyacetylene copolymer) were used as targets (substrates). The chemical formula of butyl-substituted zinc phthalocyanine with 8 butyl groups instead of hydrogen atoms in the benzene rings can be written as ZnPcBu_8 , where the symbol Pc denotes the complex $\text{C}_{32}\text{H}_8\text{N}_8$, and Bu denotes butyl, C_4H_9 . The films of butyl-substituted zinc phthalocyanine on glass and on the polyvinyl chloride-polyacetylene (PVC-PAC) film were designated as ZnPcBu_8 – SG and ZnPcBu_8 – PVC-PAC, respectively. The films of butyl-substituted zinc phthalocyanine on the PVC-PAC film and on silicate glass were obtained by sublimation of the ZnPcBu_8 powder at a heating temperature of 380 °C for 10 min. The crystalline structures of ZnPcBu_8 films exist mainly in two forms: a metastable α -form and a stable β -form. The crystalline structure of metallophthalocyanine films is influenced by several deposition parameters, including the substrate material. This study investigated the influence of the substrate material on the crystalline structure of ZnPcBu_8 films.

The deposition of butyl-substituted zinc phthalocyanine films onto the substrates was carried out in a VUP-5 vacuum system. The light absorption spectra in the butyl-substituted zinc phthalocyanine films were obtained using an Option Optics 2000 spectrometer with a dynamic range of 300–1100 nm. A 10 mW tungsten lamp was used as the radiation source.

Results and Their Discussion

For the butyl-substituted zinc phthalocyanine films on silicate glass and on the PVC-PAC surface, the radiation absorption spectra were measured at a measurement temperature of $T = 22$ °C (figure).

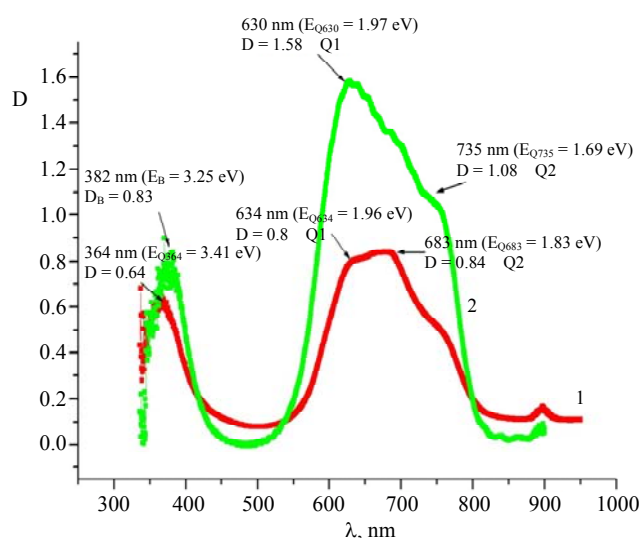


Fig. Absorption spectra of butyl-substituted zinc phthalocyanine films: 1 – ZnPcBu_8 film on glass, 2 – ZnPcBu_8 film on PVC-PAC

The absorption spectrum of the ZnPcBu_8 – SG film has two characteristic bands in the visible radiation range: the Q-band in the range of 550–800 nm and the B-band in the range of 350–500 nm. In the absorption spectrum, the B-band has one absorption peak, and the Q-band has two absorption peaks. The first peak of the Q-band corresponds to a wavelength of $\lambda_{Q1} = 634$ nm ($E_{Q1} = 1.96$ eV), the second peak of the Q-band corresponds to a wavelength of $\lambda_{Q2} = 683$ nm ($E_{Q2} = 1.83$ eV). The half-width of the Q-band is approximately $\Delta\lambda_{Q1/2} = 170$ nm. The peak of the B-band corresponds to a wavelength of $\lambda_B = 364$ nm ($E_B = 3.41$ eV). The full width at half maximum of the B-band is approximately $\Delta\lambda_{B1/2} = 64$ nm.

The absorption spectrum of the ZnPcBu_8 – PVC-PAC film has two characteristic absorption bands: the Q-band in the range of 500–850 nm and the B-band in the range of 350–500 nm. In the absorption spectrum, the B-band has one absorption peak, and the Q-band has two extreme absorption peaks (see figure). The first peak of the Q-band corresponds to a wavelength of

$\lambda_{Q1} = 630$ nm ($E_{Q1} = 1.97$ eV), the second peak of the Q-band corresponds to a wavelength of $\lambda_{Q2} = 735$ nm ($E_{Q2} = 1.69$ eV). The half-width of the Q-band is approximately $\Delta\lambda_{Q1/2} = 188$ nm. The peak of the B-band corresponds to a wavelength of $\lambda_B = 382$ nm ($E_B = 3.25$ eV). The full width at half maximum of the B-band is approximately $\Delta\lambda_{B1/2} = 57$ nm or in energy units $E_{B1/2} = 0.51$ eV.

Molecules of butyl-substituted zinc phthalocyanine in the ZnPcBu₈ – SG and ZnPcBu₈ – PVC-PAC films form molecular crystallites due to van der Waals interactions and short-range repulsive forces. Coulomb forces act over a longer range between the Zn²⁺ ions of different ZnPcBu₈ molecules. The interaction of butyl-substituted zinc phthalocyanine molecules in the ZnPcBu₈ – SG and ZnPcBu₈ – PVC-PAC films occur due to van der Waals forces at a close range of about 0.35 nm and Coulomb forces at a long range of about 0.38 nm for the α -phase and, accordingly, at a close range of 0.32 nm and a long range of 0.49 nm for the β -modification of ZnPcBu₈.

The butyl-substituted zinc phthalocyanine molecule has 38 delocalized π -electrons. In the macrocycle of ZnPcBu₈, there are 18 delocalized π -electrons, and 20 delocalized π -electrons are located in the 4 isoindole groups. Upon light absorption, the delocalized π -electrons of the ZnPcBu₈ molecule transition from the ground state to excited electronic states. For the absorption spectra in the ZnPcBu₈ – SG and ZnPcBu₈ – PVC-PAC films, the Q-band corresponds to the singlet-singlet electronic transition $S_0 \rightarrow S_1$, and the B-band corresponds to the singlet-singlet electronic transition $S_0 \rightarrow S_2$. The butyl-substituted zinc phthalocyanine molecule is characterized by the D_{4h} point group symmetry, which corresponds to a planar square spatial structure. The molecular orbitals of the butyl-substituted zinc phthalocyanine molecule with the D_{4h} point group symmetry are characterized by the symmetry of the molecular orbitals a_{1u} , a_{2u} , b_{1u} , b_{2u} , and e_g . Light absorption in the Q-band in the ZnPcBu₈ – SG and ZnPcBu₈ – PVC-PAC films occurs at the conjugated double carbon-carbon bonds of the benzene rings ($n = 13$) and the conjugated double nitrogen-carbon bonds ($m = 6$) in the macrocycle. Here, n is designated as the number of conjugated double

carbon-carbon bonds C=C and m as the number of conjugated double carbon-nitrogen bonds C=N. According to Davydov's theory, in the crystalline structures of metal phthalocyanines (MPc), the splitting of the Q-band into two peaks is caused by the interaction of MPc molecules with each other (dipole-dipole interaction of neighboring molecules). The degree of splitting of the Q-band into two peaks characterizes the interaction energy between MPc molecules that are in positions with different symmetry groups [12]. In the ZnPcBu₈ – SG film, the Q-band in the absorption spectrum splits into two peaks: an absorption peak Q1 $\lambda_m = 634$ nm ($E = 1.96$ eV) and an absorption peak Q2 $\lambda_m = 683$ nm ($E = 1.82$ eV) (see figure). Here, the doubly degenerate molecular orbital LUMO $1e_g(\pi^*)$ splits into two molecular orbitals, LUMO+1 and LUMO-1. The absorption peak Q1 ($E = 1.96$ eV) corresponds to the electronic transition from HOMO $1a_{1u}(\pi)$ to LUMO+1, and the absorption peak Q2 ($E = 1.82$ eV) corresponds to the electronic transition from HOMO $1a_{1u}(\pi)$ to LUMO-1. The figure shows that the optical density D of the high-energy peak Q1 ($E = 1.96$ eV) is lower than that of the low-energy absorption peak Q2 ($E = 1.82$ eV). This ratio of optical densities in the absorption spectrum indicates that the arrangement of zinc phthalocyanine molecules in the ZnPcBu₈ – SG film is in the stable β -phase [13, 14, 15]. It should be noted that the peaks Q1 ($\lambda_m = 634$ nm) and Q2 ($\lambda_m = 683$ nm) of the absorption spectra of the ZnPcBu₈ film practically coincide with the peaks at 632 and 689 nm of the ZnPc film in reference [15]. This may indicate that in the β -phase ZnPcBu₈ film, replacing the hydrogen atoms in the benzene rings with a butyl group does not significantly change the energy of the electronic transitions in the Q-band. The absorption peak of the B-band with a wavelength of $\lambda_m = 364$ nm ($E_B = 3.41$ eV) is caused by the electronic transition from the HOMO-1 $1a_{2u}(\pi)$ molecular orbital to the LUMO $1e_g(\pi^*)$ molecular orbital. It is worth noting that the absorption peak of the B-band at $\lambda_m = 364$ nm ($E_B = 3.41$ eV) of the ZnPcBu₈ film differs from the absorption peak of the B-band at $\lambda_m = 340$ nm ($E_B = 3.65$ eV) of the ZnPc film in reference [15] by 24 nm (or 0.24 eV). This indicates that replacing the hydrogen atoms in the benzene rings with butyl groups increases

the energy of the electronic transitions in the B-band by 0.24 eV. It can be assumed that the electronic transition $\text{HOMO-1 } 1a_{2u}(\pi) \rightarrow \text{LUMO } 1e_g(\pi^*)$ in the ZnPcBu_8 film, compared to the ZnPc film, occurs to a lower vibrational level of the $1e_g(\pi^*)$ molecular orbital.

In the ZnPcBu_8 – PVC-PAC film, the Q-band in the absorption spectrum splits into two extreme peaks: an absorption peak Q1 $\lambda_m = 630$ nm ($E = 1.97$ eV) and an absorption peak Q2 $\lambda_m = 738$ nm ($E = 1.68$ eV) (see figure). Consequently, the doubly degenerate molecular orbital $\text{LUMO } 1e_g(\pi^*)$ splits into two molecular orbitals, $\text{LUMO}+1$ and $\text{LUMO}-1$, upon interaction between ZnPcBu_8 molecules. The absorption peak Q1 ($E = 1.97$ eV) corresponds to the electronic transition from $\text{HOMO } 1a_{1u}(\pi)$ to $\text{LUMO}+1$, and the absorption peak Q2 ($E = 1.82$ eV) corresponds to the electronic transition from $\text{HOMO } 1a_{1u}(\pi)$ to $\text{LUMO}-1$. The figure shows that the optical density D of the high-energy peak Q1 ($E = 1.97$ eV) is greater than that of the low-energy absorption peak Q2 ($E = 1.69$ eV). This ratio of optical densities indicates that the zinc phthalocyanine molecules in the ZnPcBu_8 – PVC-PAC film are in the metastable α -phase [13, 14, 15].

Thus, the crystalline form of butyl-substituted zinc phthalocyanine on the surfaces of PVC-PAC and silicate glass has the metastable α -phase and the stable β -phase, respectively. The different polymorphism of the crystalline ZnPcBu_8 films has a noticeable effect on the characteristics of the film absorption spectra. It should be noted that for the development of gas sensors based on butyl-substituted zinc phthalocyanine deposited onto inorganic and organic substrates, it is necessary to consider the nature of the interaction between the butyl-substituted zinc phthalocyanine molecules and the substrate molecules.

Conclusion

A study was conducted on the influence of organic (polyvinyl chloride-polyacetylene) and inorganic (silicate glass) substrates on the polymorphism of butyl-substituted zinc phthalocyanine films. The influence of the polymorphism of butyl-substituted zinc

phthalocyanine on the characteristics of the light absorption spectra was revealed. The influence of polymorphism on the electronic transitions in butyl-substituted zinc phthalocyanine films was established.

As a result of the performed analysis of the absorption spectra of butyl-substituted zinc phthalocyanine films on organic and inorganic substrates, the following conclusions were drawn:

1. In crystalline films of ZnPcBu_8 – PVC-PAC in the α -phase and ZnPcBu_8 – SG in the β -phase, the Q-band in the absorption spectra splits into two main peaks. The high-energy peak Q1 is caused by the electronic transition from the $\text{HOMO } 1a_{1u}(\pi)$ molecular orbital to the $\text{LUMO}+1$ molecular orbital with an energy $E_{Q1} = 1.97$ eV. The low-energy peak Q2 is caused by the electronic transition from the $\text{HOMO } 1a_{1u}(\pi)$ molecular orbital to the $\text{LUMO}-1$ molecular orbital with an energy $E_{Q2} = 1.69$ eV.

2. In the crystalline film ZnPcBu_8 – SG in the β -phase, the Q-band in the absorption spectrum splits into two main peaks. The high-energy peak Q1 is caused by the electronic transition from the $\text{HOMO } 1a_{1u}(\pi)$ molecular orbital to the $\text{LUMO}+1$ molecular orbital with an energy $E_{Q1} = 1.96$ eV. The low-energy peak Q2 is caused by the electronic transition from the $\text{HOMO } 1a_{1u}(\pi)$ molecular orbital to the $\text{LUMO}-1$ molecular orbital with an energy $E_{Q2} = 1.83$ eV.

3. For the ZnPcBu_8 – SG film in the β -phase, the energy $E_{Q2-\beta}$ of the $\text{HOMO } 1a_{1u}(\pi) \rightarrow \text{LUMO}-1$ electronic transition is 0.14 eV higher than the energy $E_{Q2-\alpha}$ in the ZnPcBu_8 – PVC-PAC film in the α -phase. Most likely, the electronic transition in the α -phase ZnPcBu_8 film occurs to a lower energy vibrational level compared to the ZnPcBu_8 – SG film in the β -phase. It can also be assumed that the energy level of $\text{LUMO}-1$ depends on the crystalline form of the films and, consequently, on the nature of the substrate.

4. The energy of the electronic transitions for the absorption peaks of the B-band of butyl-substituted zinc phthalocyanine molecules differs for different substrates. For the ZnPcBu_8 – PVC-PAC film in the α -phase, the energy of the $1a_{2u}(\pi) \rightarrow 1e_g(\pi^*)$ electronic transition of the B-band is $E_{B-\alpha} = 3.25$ eV. For the ZnPcBu_8 – SG film in the β -phase, the energy of the $1a_{2u}(\pi) \rightarrow 1e_g(\pi^*)$ electronic transition of the

B-band is $E_{B-\beta} = 3.41$ eV. For the ZnPcBu_8 – SG film in the β -phase, the energy of the electronic transition $E_{B-\beta} = 3.41$ eV exceeds the energy $E_{B-\alpha}$ for the ZnPcBu_8 – PVC-PAC film in the α -phase by 0.07 eV.

Thus, we summarize the overall results of the studies of optical films of butyl-substituted zinc phthalocyanine on different substrates.

1. For ZnPcBu_8 – PVC-PAC films in the α -phase and ZnPcBu_8 – SG films in the β -phase, the energies of the HOMO $1a_{1u}(\pi) \rightarrow \text{LUMO}+1$ electronic transitions, characteristic of the high-energy peak of the Q-band absorption spectra, are

practically independent of the crystalline form of the films and, consequently, indirectly through the film polymorphism, independent of the nature of the substrate.

2. For ZnPcBu_8 – PVC-PAC films in the α -phase and ZnPcBu_8 – SG films in the β -phase, the energies of the HOMO $1a_{1u}(\pi) \rightarrow \text{LUMO}-1$ electronic transitions, characteristic of the low-energy peak of the Q-band absorption spectra, depend on the crystalline form of the films and, consequently, indirectly through the crystalline form of the films, depend on the nature of the substrate.

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