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Changes in the optical properties of butyl-substituted zinc phthalocyanine in interaction with ammonia

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Solutions of butyl-substituted zinc phthalocyanine in tetrahydrofuran and mixed solutions of butyl-substituted zinc phthalocyanine in tetrahydrofuran with an aqueous solution of ammonia were prepared. The light absorption spectra of the initial and mixed solutions of butyl-substituted zinc phthalocyanine were measured. The light absorption spectra of the initial and mixed solutions of butyl-substituted zinc phthalocyanine were analyzed. As a result of the research, the effect of ammonia molecules on butyl-substituted zinc phthalocyanine molecules in mixed solutions was found, which manifested itself in a change in the parameters of the light absorption spectra. It is shown that ammonia molecules slightly increase the absorption of light in the Q-band, practically do not change the half-width of the absorption spectra and slightly reduce the energy of electronic transitions characteristic of the Q and B-bands. A possible explanation of the effect of ammonia on the parameters of the light absorption spectra in butyl-substituted zinc phthalocyanine molecules is given.

Keywords: zinc phthalocyanine, absorption spectra, tetrahydrofuran, ammonia, molecular orbitals.

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Introduction

The optical, electrical, and electrophysical properties of metal phthalocyanines (MPc) have been widely studied for a long time for determining their possible applications in microelectronics, optoelectronics, optics, and medicine. MPc, capable of dissolving in water, are trying to be used in photodynamic therapy [1–3]. MPc can be used in solar cells as effective chromophores [4,5]. MPc and metal diphthalocyanine films, especially with complexing agents with a positive charge of more than two, can be used in gas sensors [6–8]. MPc are organic semiconductors, since they exhibit semiconductor properties in air, usually of the *p* type of conductivity. MPc as semiconductors are still significantly inferior to inorganic semiconductors in practical application. The properties of MPc are studied both in MPc films and in MPc solutions in various solvents. MPc films can be used as an active layer for gas sensors when interacting with gases [9]. The interaction of gases with MPc films leads to a change of the optical density of peaks of the Q and B bands of the absorption spectrum, photoluminescence intensity, and surface resistivity. MPc solutions can be used as an active light absorber in Gretzel cells [4.10]. The B-band of the light absorption spectrum is mainly used in Gretzel cells with an optical MPc absorber. The MPc properties strongly depend on the nature of the metal as a complexing agent, as well as on the substituents at the ends of benzene rings. Chlorine, fluorine, butyl groups, and other substituents can be present at the ends of the benzene rings of the MPc instead of hydrogen atoms. MPCs are much better soluble in various organic solvents due to the substituents on the benzene rings. The properties of MPCs of transition metals (nickel, cobalt, copper, zinc, etc.) are the most well studied presently. Part of the study is devoted to zinc phthalocyanines, including those with various substituents at the ends of benzene rings [11,12]. The optical properties of zinc phthalocyanine are determined by its π-electronic system, which is created by double conjugated carbon-nitrogen bonds and double conjugated carbon-carbon bonds.

A starting solution of butyl-substituted zinc phthalocyanine in tetrahydrofuran (THF) (C_4H_8O) and a mixed solution in a mixture of THF + aqueous solution of ammonia ($NH_3, + H_2O$) were prepared in this study. Linear optical properties were studied in the obtained solutions. The chemical formula of butyl-substituted zinc phthalocyanine with 8 butyl groups can be written in general form $[Zn(C_{32}H_8N_8)(C_4H_9)_8]$ or in short $ZnPcBu_8$, here the symbol Pc stands for complex $C_{32}H_8N_8$, i.e., a truncated phthalocyanine molecule without a complexing agent and without 8 hydrogen atoms. The zinc ion Zn^{2+} will act as a complexing agent in the butyl-substituted zinc phthalocyanine complex, and $PcBu_8$ will act as a ligand. In reality, the zinc ion is positively charged (Zn^{2+}) in the $ZnPcBu_8$ molecule, and the ligand is negatively charged ($(PcBu_8)^{2-}$), i.e. the molecule has an induced dipole moment, therefore, the zinc ion has acceptor properties in the $ZnPcBu_8$ molecule, and the ligand ($PcBu_8$) exhibits donor properties. The zinc ion Zn^{2+} is bound to nitrogen atoms of the tetraporphyrin macro ring of the ligand by two covalent bonds and two coordination bonds in the molecule (Fig. 1). The distance $Zn^{2+}-N$ between the zinc ion Zn^{2+}

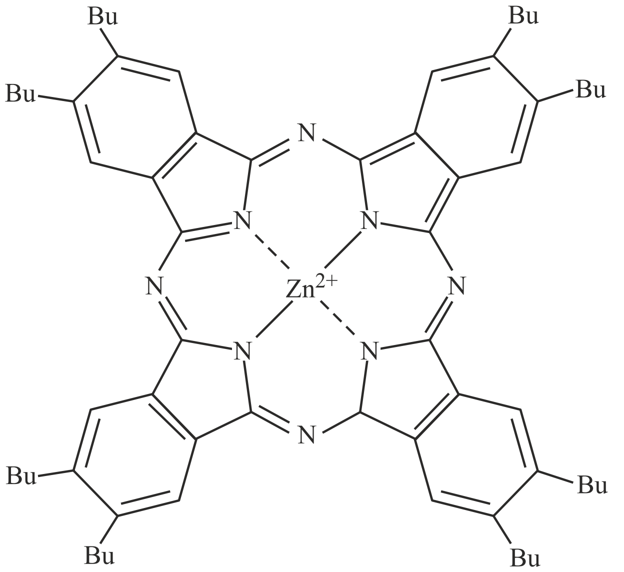

Figure 1. The structure of the butyl-substituted zinc phthalocyanine molecule.

and the four closest nitrogen atoms N is 0.1 nm, the distance between C and N in the macro ring is the same and is 0.13 nm, the distance between C and C in benzene rings is 0.13 nm [13,14].

In total, the molecule of butyl-substituted zinc phthalocyanine $ZnPcBu_8$ contains 13 conjugated carbon-carbon double bonds and 6 conjugated carbon-nitrogen double bonds. 9 of 13 conjugated carbon-carbon double bonds belong to benzene rings and 4 are on isoindole. The tetraporphyrinized macro-ring of $ZnPcBu_8$ molecule includes 6 conjugated double carbon-nitrogen bonds. In total, there are 38 delocalized π-electrons in the butyl-substituted zinc phthalocyanine molecule: 26 on benzene rings and 12 on the macro ring. These delocalized π-electrons are excited from the electronic ground state to the excited electronic states, when exposed to light, and therefore create Q- and B-bands in the absorption spectra. The delocalized π-electrons, cause the photoluminescence process during transition from the excited electronic state to the ground state.

The purpose of this work is to study the effect of ammonia molecules in an aqueous solution on the light absorption spectra of butyl-substituted zinc phthalocyanine in a polar solvent THF.

1. Experimental part

A solution of butyl-substituted zinc phthalocyanine in a polar solvent THF was prepared. Zinc phthalocyanine was purchased from Sigma-Aldrich with the following complex characteristics: Dye content — 97%, Q-band — 650–750 nm, B-band — 340–360 nm. A blue powder with weight of 1 mg ($ZnPcBu_8$) was dissolved in 100 ml of THF to obtain a solution of butyl-substituted zinc phthalocyanine with a molar mass of M = 1025 g/mol. A homogeneous blue solution of butyl-substituted zinc phthalocyanine in THF [$ZnPcBu_8$ + THF] was obtained as a result with a molar concentration of $c = 10^{-5}$ mol/l. The light absorption spectra of this solution [$ZnPcBu_8$ + THF] in the visible range were measured in a cuvette with a volume of 200 l. Then an aqueous solution of 10% ammonia with a volume of 50 μl was added to the solution [$ZnPcBu_8$ + THF]. A solution of [$ZnPcBu_8 + THF + NH_3 + H_2O$] was obtained as a result. Light absorption spectra were measured to determine the effect of ammonia molecules on the linear optical properties of weakly interacting zinc butyl-substituted phthalocyanine molecules.

The molecules of butyl-substituted zinc phthalocyanine dissolved in THF at low concentrations of the order of 10^{-5}–10^{-6} mol/l, are far from each other (very weak interaction of ZnPcBu molecules$_8$ among themselves). The THF solvent is a polar coordinating solvent, therefore THF molecules (C_4H_8O) can form coordinating bonds to a greater extent with zinc ions (Zn^{2+}) and to a lesser extent with eight butyl groups (C_4H_9) at the ends of the benzene rings. Each $ZnPcBu_8$ molecule is surrounded by a multitude of THF molecules with a dipole moment $\mu = 1.7$ D. $ZnPcBu_8$ and C_4H_8O molecules interact due to Van der Waals dipole forces according to the law $F_{d-d} = (C/R^7)$, here F_{d-d} is the force of dipole-dipole attraction between $ZnPcBu_8$ and C_4H_8O, C is a coefficient depending on the electron polarizability and ionization potentials of the interacting molecules, R is the distance between the interacting molecules of $ZnPcBu_8$ and C_4H_8O.

Light absorption spectra in solutions of [$ZnPcBu_8$ + THF] and [$ZnPcBu_8 + THF + NH_3 + H_2O$] were obtained using OceanOptics 2000+ spectrometer with a spectral range of 300–1100 nm. 10 mW tungsten lamp was used as a radiation source to acquire the light absorption spectra.

2. Results and discussion

The effect of ammonia molecules in an aqueous solution on the linear optical properties of butyl-substituted zinc phthalocyanine in a polar solvent THF was studied in this paper. Small molecules of ammonia NH_3 interact with large molecules of $ZnPcBu_8$ when an aqueous ammonia solution with a dipole moment $\mu = 1.5$ D is added to [$ZnPcBu_8$ + THF] solution. $ZnPcBu_8$ and NH_3 molecules interact due to the Van der Waals dipole forces according to the law $F_{d-d} = (C/R^7)$, here F_{d-d} is the force of dipole-dipole attraction between molecules $ZnPcBu_8$ and NH_3, C is a coefficient depending on the electron polarizability and ionization potentials of interacting molecules, R is the distance between interacting molecules of $ZnPcBu_8$ and NH_3. NH_3 molecules have donor properties due to an unshared pair of electrons, and zinc ions Zn^{2+} in $ZnPcBu_8$ molecules have acceptor properties due to transfer of electrons to the acceptor ligand $PcBu_8$. An unshared electron pair NH_3 is transferred to the zinc ion Zn^{2+} via a donor-

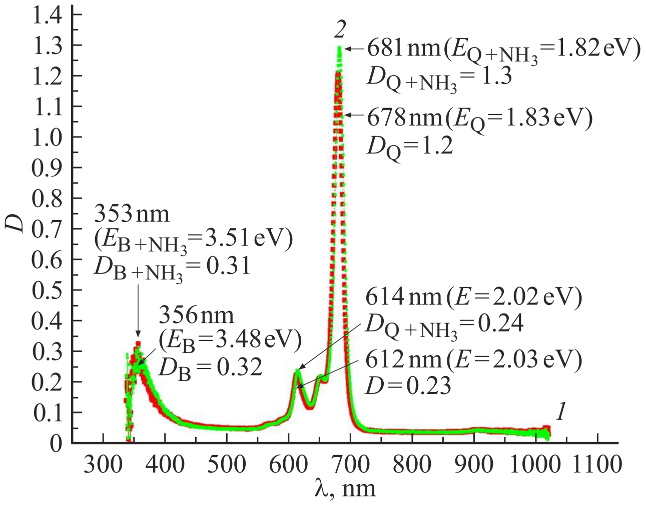

Figure 2. Light absorption spectra for $ZnPcBu_8$ solutions in the optical range of 350–1000 nm; *1* — red absorption spectrum (solution $[ZnPcBu_8 + THF]$ without exposure to ammonia), *2* — green absorption spectrum (solution $[ZnPcBu_8 + THF + NH_3 + H_2O]$ in case of ammonia exposure).

acceptor mechanism in case of interaction between NH_3 molecules and zinc ions Zn^{2+} in $ZnPcBu_8$ molecules. This interaction leads to the creation of a coordination bond between zinc ions Zn^{2+} and NH_3 molecules. The formation of the coordination bond $Zn^{2+}{-}NH_3$ can change the light absorption and photoluminescence spectra [6]. Thus, at least 4 coordination bonds can be formed in the molecules of butyl-substituted zinc phthalocyanine in case of interaction with THF and ammonia molecules: 2 coordination bonds $Zn^{2+}{-}N$ inside the macro ring of $ZnPcBu_8$ molecule, 1 coordination bond $Zn^{2+}{-}O$ with the oxygen atom of THF C_4H_8O molecule and 1 coordination bond $Zn^{2+}{-}N$ bond with nitrogen atoms of the ammonia molecule NH_3. It should be noted that zinc ions Zn^{2+} can create up to a maximum of 6 coordination bonds, for example, an additional 1 coordination bond above the plane and another 1 coordination bond below the plane of $ZnPcBu_8$, with nitrogen or oxygen atoms.

The presence of delocalized πelectrons in the molecules of butyl-substituted zinc phthalocyanine leads to noticeable absorption of light in the visible range of 350–1000 nm. The light absorption spectra of the solution of $[ZnPcBu_8 + THF]$ were measured without exposure to molecules of ammonia NH_3, and the light absorption spectra of the solution of $[ZnPcBu_8 + THF + NH_3 + H_2O]$ were measured during exposure to NH_3 (Fig. 2). The light absorption spectra of the solutions of $[ZnPcBu_8 + THF]$ and $[ZnPcBu_8 + THF + NH_3 + H_2O]$ were measured at a temperature of $t = 25°C$.

Analyzing the data of the light absorption spectra in Fig. 2, we observe that the solutions have two main absorption peaks and associated Q- and B-absorption bands, as well as one absorption peak VS associated with an oscillatory satellite. The peak of the light absorption Q-band of the solution $[ZnPcBu_8 + THF]$ without exposure to NH_3 gas corresponds to the wavelength of $\lambda_m = 678$ nm ($E_Q = 1.83$ eV), the peak of the absorption B-band corresponds to the wavelength $\lambda_m = 353$ nm ($E_B = 3.51$ eV) and VS peak corresponds to the wavelength $\lambda_m = 612$ nm ($E_B = 2.03$ eV). The peak of the light absorption Q-band of the solution $[ZnPcBu_8 + THF + NH_3 + H_2O]$ exposed to NH_3 gas corresponds to the wavelength $\lambda_m = 681$ nm ($E_Q = 1.82$ eV), the peak of the absorption B-band corresponds to the wavelength $\lambda_m = 356$ nm ($E_B = 3.47$ eV) and the VS peak corresponds to the wavelength $\lambda_m = 614$ nm ($E_B = 2.02$ eV). Optical density (D) of the peak of the Q-band of solutions of $[ZnPcBu_8 + THF]$ and $[ZnPcBu_8 + THF + NH_3 + H_2O]$ is equal to $D_Q = 1.2$ and $D_{Q+NH_3} = 1.3$, respectively. Optical density (D) of the peak of the B-band peak of solutions of $[ZnPcBu_8 + THF]$ and $[ZnPcBu_8 + THF + NH_3 + H_2O]$ is equal to $D_Q = 0.31$ and $D_{Q+NH_3} = 0.32$, respectively. Peak half-widths of the Q-band of solutions of $[ZnPcBu_8 + THF]$ and $[ZnPcBu_8 + THF + NH_3 + H_2O]$ are almost identical and amount to $\Delta\lambda = 16$ nm. Peak half-widths of the B-bands of solutions of $[ZnPcBu_8 + THF]$ and $[ZnPcBu_8 + THF + NH_3 + H_2O]$ are almost identical and equal to $\Delta\lambda = 33$ nm. The optical density of the peak of the Q-band peak of solution of $[ZnPcBu_8 + THF]$ of the absorption spectrum increased by 1.1 times after exposure to NH_3 gas. The optical density (D) of the peak of the B band of the absorption spectrum of the solution of $[ZnPcBu_8 + THF]$ practically did not change after the exposure to NH_3 gas. Half-widths of the absorption spectrum Q-bands of solutions of $[ZnPcBu_8 + THF]$ and $[ZnPcBu_8 + THF + NH_3 + H_2O]$ are the same and equal to $\Delta\lambda = 16$ nm. Half-widths of the absorption spectrum Q-bands of solutions of $[ZnPcBu_8 + THF]$ and $[ZnPcBu_8 + THF + NH_3 + H_2O]$ are almost identical and amount to $\Delta\lambda = 33$ nm. The difference of the half-widths of the absorption spectra of B- and Q-bands is 17 nm, i.e. the B-band is almost two times wider than the Q-band. Analyzing the effect of ammonia on the solution of $[ZnPcBu_8 + THF]$, it is possible to come to the following experimental facts:

1) Q- and B-bands shifted to the long-wavelength region by 3 nm;

2) the peak optical density of the Q-band of the light absorption spectrum (LAS) increased by 1.1 times, the peak value of the B-band of the LAS practically did not change;

3) The half-widths of the Q- and B-bands of the LAS have not changed much.

Light absorption in the Q-band with peaks $\lambda_m = 678$ and 681 nm occurs on conjugated carbon-carbon double bonds of benzene rings ($n = 13$) and conjugated nitrogen-carbon double bonds ($n = 6$) in the macrocycle of $PcBu_8$ ligand. Here n is the number of conjugated double bonds C=C and C=N. A graph of the absorption spectrum in the optical range of 550–750 nm has been added for a more detailed analysis of the Q-band of butyl-substituted zinc phthalocyanine (Fig. 3).

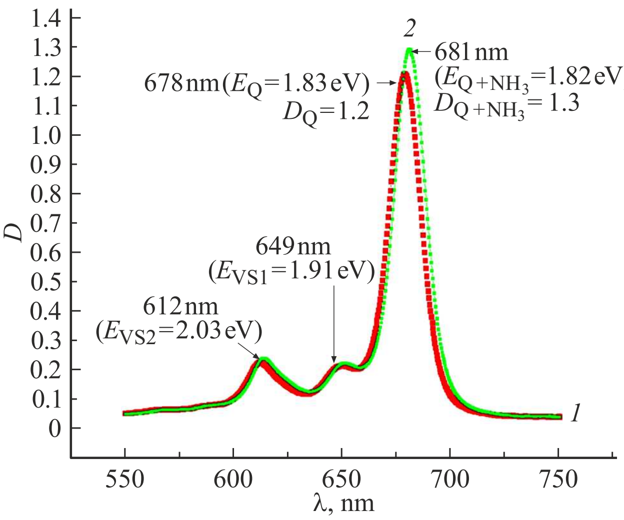

Figure 3. Light absorption spectra of the solutions of $ZnPcBu_8$ in the optical range of 550−750 nm; *1* — red absorption spectrum (solution of [$ZnPcBu_8$ + THF] without exposure to ammonia), *2* — green absorption spectrum (solution of [$ZnPcBu_8$ + THF + NH_3 + H_2O] exposed to ammonia).

Absorption peaks with wavelengths of $\lambda_m = 678$ and 681 nm (Q-band) in solutions of [$ZnPcBu_8$ + THF] and [$ZnPcBu_8$ + THF + NH_3 + H_2O] correspond to the electronic transition from HOMO $1a_{1u}(\pi)$ to LUMO $1e_g(\pi^*)$, here HOMO is the highest occupied molecular orbital, LUMO lowest unoccupied molecular orbital, π — electrons in the ground state, π^* — electrons in the excited state). The energy interval of the solution of [$ZnPcBu_8$ + THF] between the ground state of HOMO and the excited state of LUMO is $E_{\text{HOMO-LUMO}} = 1.83$ eV (or E_Q). The energy interval of the solution of [$ZnPcBu_8$ + THF + NH_3 + H_2O] between the ground state of HOMO and the excited state of LUMO is $E_{\text{HOMO-LUMO}} = 1.82$ eV (or E_{Q+NH_3}). The difference of energy intervals of the solutions of [$ZnPcBu_8$ + THF] and [$ZnPcBu_8$ + THF + NH_3 + H_2O] is $E_Q - E_{Q+NH_3} = 0.01$ eV, which corresponds to the energy of stretch vibrational levels C=N. This electronic transition occurs from the singlet electronic ground state S_0 to the stretch vibrational levels C=N of the singlet first excited state S_1. Therefore, light absorption occurs at a lower vibrational level C=N of the singlet first excited state S_1 during the exposure of $ZnPcBu_8$ molecules to ammonia molecules.

Light absorption in the B-band with peaks of $\lambda_m = 353$ and 356 nm occurs on conjugated carbon-carbon double bonds of pyrolytic rings ($n = 6$), i.e. radiation excites 12 π-electrons in $ZnPcBu_8$ molecule. Absorption peaks with wavelengths of $\lambda_m = 353$ and 356 nm (B-band) in solutions of [$ZnPcBu_8$ + THF] and [$ZnPcBu_8$ + THF + NH_3 + H_2O] correspond to the electronic transition from HOMO-1 $1a_{2u}(\pi)$ to LUMO $1e_g(\pi^*)$. The difference of energy intervals of solutions of [$ZnPcBu_8$ + THF] and [$ZnPcBu_8$ + THF + NH_3 + H_2O] is $E_B - E_{B+NH_3} = 0.04$ eV, which corresponds to a decrease of the energy of stretch vibrational levels C=C [13,15]. The vibrational level C=C corresponds to an energy of 0.18 eV without exposure to ammonia, and it can be assumed that the vibrational level corresponds to 0.14 eV when exposed to ammonia. This electronic transition takes place from the singlet electronic ground level S_0 to the stretch vibrational levels C=C of the second singlet excited level S_2. Therefore, it can be assumed that when $ZnPcBu_8$ molecules are exposed to ammonia molecules, light absorption occurs at a lower vibrational level C=C of the singlet second excited level S_2. The main parameters of light absorption spectrum of solutions of [$ZnPcBu_8$ + THF] and [$ZnPcBu_8$ + THF + NH_3 + H_2O] without and under the impact of gas molecules are listed in the table.

Thus, we came to the following experimental results as a result of the analysis of the light absorption spectrum of the initial and mixed solutions of [$ZnPcBu_8$ + THF] and [$ZnPcBu_8$ + THF + NH_3 + H_2O]:

1) the optical density (D) of the peak of the Q-band increases by 1.1 times in mixed solution of [$ZnPcBu_8$+THF+NH_3+H_2O] in case of exposure of butyl-substituted zinc phthalocyanine molecules to ammonia molecules, D of the peak of the B-band practically does not change. It can be assumed that the increase of the optical density of the Q-band peak in case of exposure of ammonia molecules is caused by an increase of the probability of the electron transition HOMO $1a_{1u}(\pi)$ LUMO $1e_g(\pi^*)$ or an increase of photon absorption by a lower vibrational level C=N of the first excited state S_1;

2) the light absorption spectrum half-width of Q- and B-bands in the initial solution of [$ZnPcBu_8$ + THF] and mixed solution of [$ZnPcBu_8$ + THF + NH_3 + H_2O] is the same. Consequently, the interaction of molecules of ammonia NH_3 with molecules of butyl-substituted zinc phthalocyanine $ZnPcBu_8$ does not lead to any additional expansion of light absorption spectrum. Therefore, it can be assumed that the light absorption spectrum half-width is determined mainly by the interaction of molecules of THF C_4H_8O with molecules of butyl-substituted zinc phthalocyanine $ZnPcBu_8$, while butyl-substituted zinc phthalocyanine forms coordination bonds with ammonia molecules that do not lead to any noticeable change of the light absorption spectrum half-width;

3) when butyl-substituted zinc phthalocyanine molecules are exposed to ammonia molecules, a slight downward energy shift takes place in the light absorption spectra by approximately 0.01 eV for the Q band and 0.04 eV for the B band. Such a small decrease of the energy is typical for vibrational transitions of excited singlet levels S_1 and S_2. It can be assumed that π-electrons of the butyl-substituted zinc phthalocyanine molecule nonradiatively move from a higher to a lower vibrational level in case of light absorption during the exposure to ammonia molecules, which is caused by stretch vibrations conjugated by double bonds C=N and C=C.

Parameters of the light absorption spectra of solutions of [ZnPcBu$_8$+THF] and [ZnPcBu$_8$+THF+NH$_3$+H$_2$O] without- (index „1“) and with (index „2“) exposure to NH$_3$ molecules

Parameters	Wavelength of peak, nm	Peak half-width, nm	Peak shift, nm	Energy of electron-transition, eV	Shift of energy level, eV	Optical density D	Relation D_2/D_1
Solution 1 [ZnPcBu$_8$+THF] without NH$_3$							
B band	353	33		3.51	0.04	0.31	
Q band	678	16		1.83	0.01	1.2	
VS1-oscillations of satellite	649			1.91		0.22	
VS2-oscillations of satellite	612	20		2.03	0.01	0.23	
Solution 2 [ZnPcBu$_8$+THF+NH$_3$ +H$_2$O] with NH$_3$							
B-band	356	33	3	3.47		0.32	
Q-band	681	16	3	1.82		1.3	1.1
VS1-oscillations of satellite	649			1.91		0.22	
VS2-oscillations of satellite	614	20	2	2.02		0.24	

Conclusion

The solutions of [ZnPcBu$_8$ + THF] and [ZnPcBu$_8$ + +THF + NH$_3$ + H$_2$O] were created and their linear optical properties in case of exposure of butyl-substituted zinc phthalocyanine molecules to ammonia molecules were studied in the work. The change of light absorption spectrum of butyl-substituted zinc phthalocyanine in case of exposure to ammonia molecules was analyzed.

The following conclusions can be drawn as a result of the studies of the solutions of [ZnPcBu$_8$ + THF] and [ZnPcBu$_8$ + THF + NH$_3$ + H$_2$O] without and under the exposure to ammonia molecules:

1. The energy $E_{\mathrm{HOMO\text{-}LUMO}}$ of the energy gap of the Q-band of butyl-substituted zinc phthalocyanine is equal to $E_{\mathrm{Q}} = 1.83\,\mathrm{eV}$ and decreases to $E_{\mathrm{Q+NH_3}} = 1.82\,\mathrm{eV}$ in case of exposure to molecules of NH$_3$. The decrease of energy can be explained by the electronic transition from the singlet ground state S$_0$ to a lower vibrational level C=N of the singlet first excited state S$_1$. The optical density D of the peak of the light absorption spectrum Q-band increases by 1.1 times in case of exposure to NH$_3$ molecules compared to D without exposure to NH$_3$.

2. The energy E_{B} of the electron transition, characteristic of the B-band of butyl-substituted zinc phthalocyanine, is 3.51 eV and decreases to $E_{\mathrm{B+NH_3}} = 3.48\,\mathrm{eV}$ in case of exposure to NH$_3$ molecules. The decrease of energy can be explained by the electronic transition from the singlet ground state S$_0$ to a lower vibrational level C=C of the singlet second excited state S$_2$. The optical density (D) of the peak of the B-band of the light absorption spectrum in case of exposure to NH$_3$ gas practically does not change compared to D without exposure to NH$_3$.

3. The half-width of peaks of Q-, B-, and VS-bands of light absorption spectrum in zinc butyl-substituted phthalocyanine molecules does not change in case of exposure to NH$_3$ molecules and amounts to $\lambda_m = 16\,\mathrm{nm}$ for the Q band, $\lambda_m = 33\,\mathrm{nm}$ for the B-band and $\lambda_m = 20\,\mathrm{nm}$ for the VS2-band. This can be explained by the fact that the half-width of the Q- and B-bands of the light absorption spectra of butyl-substituted zinc phthalocyanine is determined mainly by the interaction with THF molecules.

Conflict of interest

The authors declare that they have no conflict of interest.

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