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СИНТЕЗ И СПЕКТРАЛЬНЫЕ СВОЙСТВА ФТАЛОЦИАНИНОВ С 2,3,5-ТРИМЕТИЛФЕНОКСИ- И НИТРОГРУППАМИ

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На основе 4-бром-5-нитрофталонитрила синтезирован фталонитрил, содержащий на периферии фрагмент 2,3,5-триметилфенола и нитрогруппу. На его основе «нитрильным» методом осуществляли синтез тетра-4-(2,3,5-триметилфенокси)тетра-5-нитрофталоцианинов цинка и магния. Последний использован для получения соответствующего фталоцианина – лиганда. Все синтезированные соединения охарактеризованы данными дифференциальной сканирующей калориметрии, элементного анализа, ^{1}H ЯМР, инфракрасной спектроскопии и MALDI-TOF спектрометрии. Для фталоцианинов изучены спектрально-люминесцентные свойства, а также кислотно-основные свойства фталоцианина – лиганда. Обнаружено, что рассматриваемые соединения являются термически устойчивыми до 300 °С. При исследовании электронных спектров поглощения обнаружено, что природа металла-комплексообразователя практически не влияет на положение Q полос синтезированных соединений в ДМФА и хлороформе. Переход к пиридину сопровождается сильным гипсохромным сдвигом Q полос синтезированных металлофталоцианинов, а спектры растворов в концентрированной серной кислоте характеризуются батохромным сдвигом Q полос всех рассмотренных соединений более чем на 100 нм. Все рассмотренные в данной работе фталоцианины обладают люминесцентными свойствами. Отмечено, что введение нитрогрупп в молекулу смешаннозамещенного фталоцианина цинка с триметилфенокси- и нитрогруппами резко увеличивает Стоксов сдвиг с сохранением квантового выхода, т.е. без потери эффективности люминесценции. Величина квантового выхода зависит от природы металла-комплексообразователя и снижается в ряду: ZnPc > MgPc > H_2Pc. Электронные спектры поглощения тетра-4-(2,3,5-триметилфенокси)тетра-5-нитрофталоцианина в среде растворителей основной природы (пиридин, ДМФА, ДМСО) содержат единичную нерасщепленную Q-полосу. Кроме того, указанное соединение проявляет свойства двухосновной NH-кислоты и образует устойчивый комплекс с переносом протонов, теряющий свою кинетическую устойчивость при добавлении н-бутиламина.

Ключевые слова: 2,3,5-триметилфенол, фталоцианины, синтез, термогравиметрия, люминесценция, кислотно-основные свойства

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SYNTHESIS AND SPECTRAL PROPERTIES OF PHTHALOCYANINES WITH 2,3,5-TRIMETHYLPHENOXY AND NITRO GROUPS

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Phthalonitrile containing a 2,3,5-trimethylphenol fragment and a nitro group at the periphery was synthesized on the basis of 4-bromo-5-nitrophthalonitrile. Tetrakis-2,9,16,24-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,25-nitrophthalocyanine and its metallocomplexes with zinc and magnesium were synthesized on its basis by the "nitrile" method. The latter was used to obtain the corresponding phthalocyanine - ligand. All synthesized compounds were characterized by differential scanning calorimetry, elemental analysis, ^{1}H NMR, infrared spectroscopy and MALDI-TOF spectrometry. Spectral-luminescent properties, as well as acid-base properties of the phthalocyanine - ligand, were studied for phthalocyanines. It was found that the compounds under consideration are thermally stable up to 300 °C. When studying the electronic absorption spectra, it was found that the nature of the complexing metal has virtually no effect on the position of the Q bands of the synthesized compounds in DMF and chloroform. The transition to pyridine is accompanied by a strong hypsochromic shift of the Q bands of the synthesized metal phthalocyanines, and the spectra of solutions in concentrated sulfuric acid are characterized by a bathochromic shift of the Q bands of all the compounds considered by more than 100 nm. All the phthalocyanines considered in this work have luminescent properties. It is noted that the introduction of nitro groups into the molecule of mixed-substituted zinc phthalocyanine with trimethylphenoxy and nitro groups sharply increases the Stokes shift while maintaining the quantum yield, i.e. without losing the luminescence efficiency. The quantum yield depends on the nature of the complexing metal and decreases in the series: ZnPc > MgPc > H_2Pc. Electronic absorption spectra of Tetrakis-2,9,16,23-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,24-nitrophthalocyanine in basic solvents (pyridine, DMF, DMSO) contain a single unsplit Q-band. In addition, this compound exhibits the properties of a dibasic NH-acid and forms a stable proton-transfer complex that loses its kinetic stability upon addition of n-butylamine.

Keywords: 2,3,5-trimethylphenol, phthalocyanines, synthesis, thermogravimetry, luminescence, acid-base properties

The demand for phthalocyanines is explained, on the one hand, by the relative ease of their production, and on the other hand, by a unique combination of physical and chemical properties: intense absorption in the visible and near IR spectral range, high thermal, chemical and photostability [1-7].

It is known that the presence of phenoxy groups in the phthalocyanine molecule leads to the solubility of such compounds in various organic solvents [3], promotes effective disaggregation of phthalocyanine molecules [8], imparts electrocatalytic properties and allows for the effective identification of an important biological analyte - nicotinamideadeninedinucleotide (NADH) [9, 10], liquid crystal [3, 11], nonlinear optical [12, 13], antioxidant [14], antiviral and antimicrobial [15], fluorescent properties and the ability to generate singlet oxygen [16]. Phenoxy-substituted phthalocyanines can be recommended as green filters for liquid crystal displays [17], potential switches in optical signal processing systems [18]. The introduction of alkyl fragments into phenoxy groups allows obtaining compounds with liquid crystal [19], nonlinear optical [13] and fluorescent properties [13, 20].

At the same time, there is a complete lack of data on the properties of mixed-substituted phthalocyanines containing, in addition to phenoxy groups, electron acceptor nitro groups, which are capable of strongly polarizing the chromophore system of phthalocyanine. This will shift the emission bands to the region of longer wavelengths, which makes such dyes interesting for use in the creation of LEDs [21].

Therefore, the aim of this work was to synthesize 4-(2,3,5-trimethylphenoxy)-5-nitrophthalonitrile, which is not presented in the literature, to synthesize the corresponding octasubstituted phthalocyanines on its basis, and to study the physicochemical properties of the obtained compounds.

EXPERIMENTAL-METHODICAL PART

Elemental analysis was performed on a FlashEA 1112 CHNS–O Analyzer. MALDI-TOF mass spectra were obtained on a Shimadzu Biotech Axima Confidence mass spectrometer in positive ion mode. 2,5-Dihydroxybenzoic acid was used as a matrix. Samples were prepared by dissolving the compounds in chloroform or aqueous ethyl alcohol ($C = 10^{-4} - 10^{-5}$ mol/L), then mixed in a 1:1 (v/v) ratio with a matrix solution (30 mg/mL) in tetrahydrofuran. IR spectrum (**1**) was recorded on an Avatar 360 FT-IR ESP in the region of 400-4000 cm^{-1} in thin films. ^1H NMR spectra of solutions of the synthesized compounds in DMSO d6 (**1**) and CDCl3 (**2a,b, 3**) were recorded on a Bruker DRX-500 device with an internal standard TMS. Studies of the thermal-oxidative destruction of the synthesized compounds were carried out on a synchronous thermal analysis device STA 449 F3 Jupiter from Netzsch (Germany) in an oxygen-argon atmosphere, the heating rate was 5 °C/min, and the crucible material was aluminum oxide. Electronic absorption spectra were recorded in chloroform on a HITACHI U-2001 spectrophotometer at room temperature in the wavelength range of 325-900 nm. The luminescent properties of the synthesized phthalocyanines were studied on an Agilent Cary Eclipse fluorescence spectrophotometer.

Synthesis of 4-(2,3,5-trimethylphenoxy)-5-nitrophthalonitrile (1).

In a two-necked flask were placed 50 ml of N,N-dimethylformamide (DMF), 0.5 g (0.2 mmol) of 4-bromo-5-nitrophthalonitrile, 0.28 g (0.2 mmol) of 2,3,5-trimethylphenol. Then a solution of 0.28 g (0.2 mmol) of potassium carbonate in 2 ml of water was added and the mixture was kept at 35 °C for 2 h with constant stirring. After stirring, the reaction mixture was poured into water, the resulting precipitate was filtered, washed with isopropanol, then with water until the smell of isopropanol disappeared, and dried at 70-80 °C.

Yield: 0.45 g (74%). Found, %: C 66,23; N 13,45; H 4,64. $C_{17}H_{13}N_3O_3$. Calc., %: C 66,44; N 13,67; H 4,26. MALDI-TOF, m/z, (%): 307 (100). ^1H NMR (500 MHz, DMSO-d6), δ, ppm: 8.32 s (H3, 1H, PhCN), 7.11 s (H6, 1H, PhCN), 7.05 s (H4, 1H, OPh), 6.71 s (H6, 1H, OPh).

Synthesis of Tetrakis-2,9,16,23-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,24-nitrophthalocyanines (general method):

In a quartz test tube equipped with a thermometer, 0.124 g (0.4 mmol) of ground phthalonitrile 1, 0.2 mmol of acetate of the corresponding metal and 0.096 g (1.6 mmol) of urea were introduced, after which the mixture was heated at 200-240 °C and maintained at this temperature until the reaction mixture solidified. After heating, the reaction mixture was cooled, the obtained phthalocyanines were extracted with dichloromethane and subjected to column chromatography on silica gel M60. Then the solvent was distilled off, the substance was dried at 80 °C.

Tetrakis-2,9,16,23-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,24-nitrophthalocyaninato Zn(II) (2a): synthesized according to the general method from compound 1 and 0.04 g of zinc acetate dihydrate at 200 °C.

Yield: 0,094 g (72%). MALDI-TOF, m/z (%): 1295 $[M+H]^+$ (100). Found, %: C 62.98; H 4.40; N 12.68. $C_{68}H_{52}N_{12}O_{12}Zn$. Calc., %: C 63.09; H 4.05; N 12.98. NMR ^1H (500 MHz, $CDCl_3$), δ, ppm.: 8.31 s (H3, 4H, Pc), 7.10 s (H6, 4H, Pc), 7.05 s (H4, 4H, OPh), 6.70 s (H6, 4H, OPh).

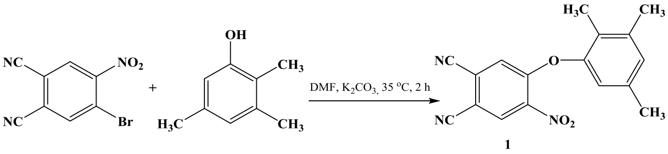
Tetrakis-2,9,16,23-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,24-nitrophthalocyaninato Mg(II) (2b): synthesized according to the general method from compound 1 and 0.04 g of zinc acetate tetrahydrate at 240 °C.

Yield: 0,086 g (67%). MALDI-TOF, m/z (%): 1253 $[M]^+$ (100). Found, %: C 65.00; H 4.28; N 13.43. $C_{68}H_{52}N_{12}O_{12}Mg$. Calc., %: C 65.16; H 4.18; N 13.41. NMR ^1H (500 MHz, $CDCl_3$), δ, ppm.: 8.32 s (H3, 4H, Pc), 7.10 s (H6, 4H, Pc), 7.05 s (H4, 4H, OPh), 6.71 s (H6, 4H, OPh).

Tetrakis-2,9,16,23-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,24-nitrophthalocyanine (3): was synthesized from 0.05 g of compound **2b**. The said substance was dissolved in a mixture of hydrochloric acid (5 wt. %) and chloroform. The solvent was then distilled off, the compound was washed with water until a neutral environment was obtained, dissolved in dichloromethane, and final purification was carried out using column chromatography on silica gel M60, eluting with dichloromethane.

Yield: 0,042 g (92%). MALDI-TOF, m/z (%): 1231 $[M]^+$ (100). Found, %: C 66.28; H 4.65; N 13.45. $C_{68}H_{54}N_{12}O_{12}$. Calc., %: C 66.33; H 4.42; N 13.65. ^{1}H NMR (500 MHz, $CDCl_3$), δ, ppm.: 8.31 s (H3, 4H, Pc), 7.10 s (H6, 4H, Pc), 7.02 s (H4, 4H, OPh), 6.73 s (H6, 4H, OPh).

RESULTS AND DISCUSSION



Scheme 1
Схема 1

In the first stage, the initial 4-(2,3,5-trimethylphenoxy)-5-nitrophthalonitrile was synthesized using a known method [22] on the basis of 4-bromo-5-nitrophthalonitrile (Scheme 1). The duration of the synthesis was increased in comparison with that proposed in the literature from 0.5 to 2 h, since with a synthesis duration of 30 min the yield of the target compound is 36% and, according to mass spectrometry data, the presence of unreacted initial 4-bromo-5-nitrophthalonitrile is observed.

The obtained phthalonitrile was studied by ^{1}H NMR, IR spectroscopy and MALDI-TOF mass spectrometry.

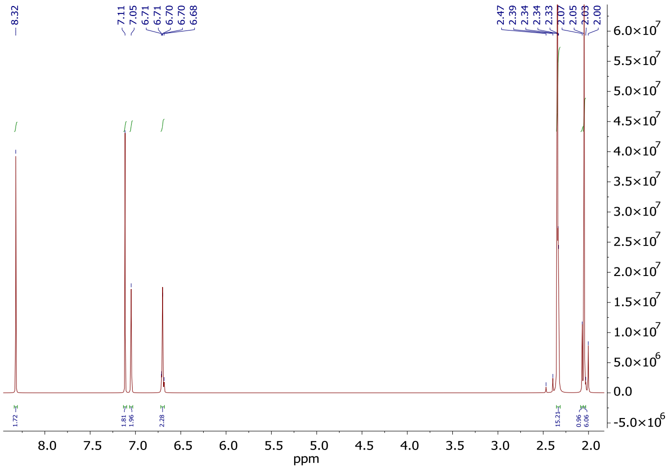


Fig. 1. ^{1}H NMR spectrum of 4-(2,3,5-trimethylpenoxy)-5-nitrophthalonitrile 1

Рис. 1. ^{1}H ЯМР спектр 4-(2,3,5триметилфенокси)-5-нитрофталонитрила 1

The ^{1}H NMR spectrum of compound **1** (Fig. 1) contains 4 signals with an integrated intensity of 2, located in the weak field region. In the weakest field, at 8.32 and 7.11 ppm, singlets of protons in positions 6 and 3 of the benzene ring of the phthalonitrile molecule are recorded. The signals at 7.05 and 6.77 ppm are due to protons 5 and 4 of the trimethylphenoxy groups.

In the IR spectrum of 4-(2,3,5-trimethylphenoxy)-5-nitrophthalonitrile **1**, there are bands of valence vibrations of the introduced 2,3,6-trimethylphenoxy substitutes at 2964, 2854 (CH_3) and 1218 cm^{-1} (Ar-O-Ar), bands of valence vibrations of cyano groups at 2235 cm^{-1}, as well as bands at 1539 and 1368 cm^{-1} corresponding to the valence and deformation vibrations of the nitro group.

A single peak of the molecular ion of compound **1** was detected in the mass spectrum at 307 Da, corresponding to the molecular mass of the compound under study. The experimentally obtained isotopic distribution (Fig. 2A) corresponds to the theoretically calculated one (Fig. 2B).

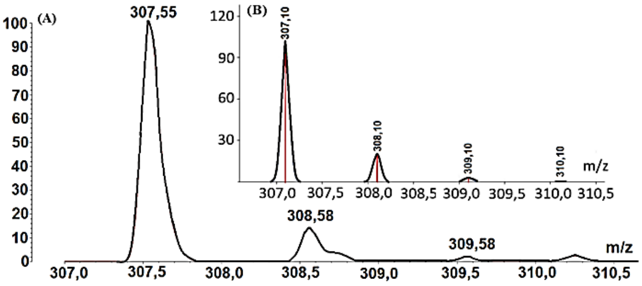


Fig. 2. MALDI-TOF mass-spectrum of phthalonitrile 1. Experimentally obtained (a) and theoretical (б) isotopic distribution

Рис. 2. Масс-спектр MALDI-TOF фталонитрила 1. Экспериментально полученное (а) и теоретическое (б) изотопное распределение

Since phthalonitrile **1** was further intended to be used in high-temperature synthesis of metal phthalocyanines, it was of interest to study the processes occurring with the synthesized substance at elevated temperatures. For this purpose, compound **1** was studied by differential scanning calorimetry. It was noted that phthalonitrile 1, combining fragments of 2,3,5-trimethylphenol and nitro groups at the periphery, melts at 197-199 °C, which is accompanied by the appearance of an endo-peak on the DSC curve. No mass loss was recorded at this temperature (Fig. 3, curve 1).

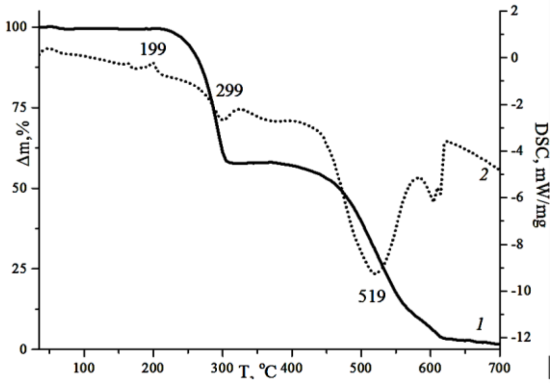
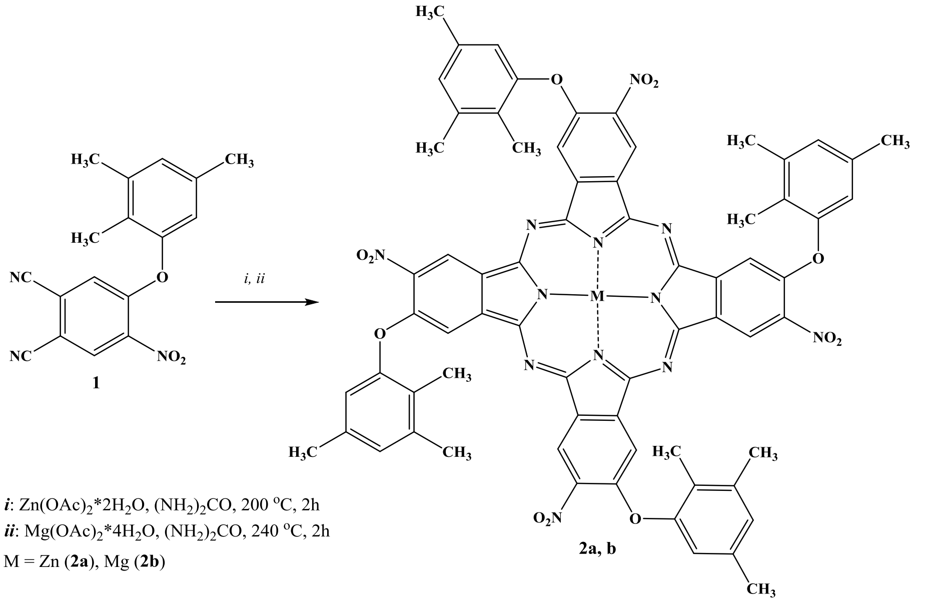


Fig. 3. Thermogram of compound **1**: 1 – TG, 2 – DSC

Рис. 3. Термограмма соединения **1**: 1 – ТГ, 2 – ДСК

At 299 °C, an exo-peak was detected, corresponding to the onset of thermal destruction, occurring in two stages, the first of which is accompanied by a 41% mass loss, indicating the splitting off of the 2,3,5-trimethylphenol fragment, and the second by the final decomposition of the compound and the appearance of an endo-peak on the DSC curve at 519 °C (Fig. 4). Then, phthalonitrile **1** was used in the synthesis of new mixed-substituted metal phthalocyanines (Scheme 2).

Magnesium(II)phthalocyanine **2b** was dissolved in a mixture of hydrochloric acid (5 wt. %) and chloroform (Scheme 3). The solvent was distilled off, and the resulting phthalocyanine ligand **3** was washed with water until a neutral medium, dissolved in dichloromethane, and chromatographically purified.

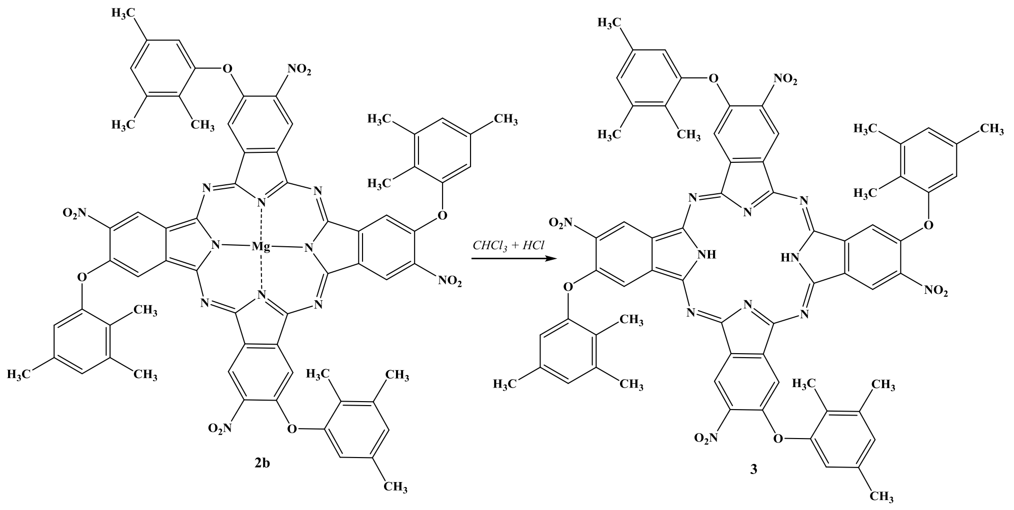


1

i: Zn(OAc)$_2$*2H$_2$O, (NH$_2$)$_2$CO, 200 °C, 2h
ii: Mg(OAc)$_2$*4H$_2$O, (NH$_2$)$_2$CO, 240 °C, 2h
M = Zn (**2a**), Mg (**2b**)

2a, b

Scheme 2
Схема 2



2b

3

Scheme 3
Схема 3

Phthalocyanines **2a,b** and **3** were identified and then their resistance to thermal-oxidative destruction, spectral-luminescent and acid-base properties were studied.

^{1}H NMR spectra of phthalocyanines **2a,b** and **3** are practically identical to the spectrum of compound 1, and contain 4 signals with an integrated intensity of 1, located in the weak field region, the positions of which practically do not change in comparison with the spectrum of the initial phthalonitrile.

In addition to the peak of the main molecular ion, MALDI-TOF mass spectra also contained signals of its fragments, the appearance of which is apparently associated with partial dealkylation of trimethylphenoxy groups. Based on the analysis of thermograms of zinc phthalocyanine **2a**, it was found that this compound retains thermal stability up to 316 °C. At this temperature, an exo-peak is observed on the DSC curve (Fig. 4) and a 9% loss in sample mass. The main loss in sample mass (by 73%) is observed in the temperature range of 500-620 °C and is accompanied by the appearance of two exo-peaks on the DSC curve at 529 and 611 °C.

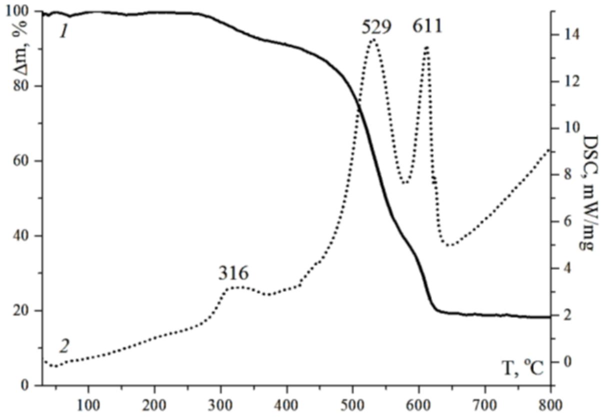


Fig. 4. Thermogram of compound **2a**: 1 – TG, 2 – DSC
Рис. 4. Термограмма соединения **2a**: 1 – ТГ, 2 – ДСК

The electronic absorption spectra of the synthesized phthalocyanines were studied. The results are summarized in the table. It was found that the nature of the complexing metal has virtually no effect on the position of the Q-bands of the synthesized compounds in DMF (Table).

In solutions in concentrated sulfuric acid, a significant bathochromic shift of the long-wave absorption bands of the synthesized phthalocyanines by more than 100 nm is observed compared to the spectra in organic solvents, associated with protonation at the meso-nitrogen atoms of the phthalocyanine macroring [1, 2] (Table).

It was found that the nature of the complexing metal has virtually no effect on the position of the Q-bands of the synthesized compounds in DMF (table). When moving to solutions in concentrated sulfuric acid, a significant bathochromic shift of the long-wave absorption band by more than 100 nm is observed, associated with protonation at the meso-nitrogen atoms of the phthalocyanine macroring [1, 2] (Table).

The Q-bands of the synthesized compounds in pyridine solutions undergo a strong hypsochromic shift compared to solutions in chloroform in the case of zinc(II) phthalocyanines **2a** and magnesium(II) phthalocyanines **2b** (Table, Fig. 5). The luminescent properties of the synthesized compounds were studied in this solvent.

Table

Spectral and luminescent properties of synthesized compounds

***Таблица.* Спектрально-люминесцентные свойства синтезированных соединений**

№	M	Absorption maxima, λ, нм				Fluorescence in Py		
		DMF	$CHCl_3$	H_2SO_4	Py	I_{lum}	Stokes shift, nm	φ, %
2a	Zn	703	706	824	684	723	49	15
2b	Mg	704	711	828	674	730	28	5
3	HH	702	682, 703	796, 835	702	725	52	1

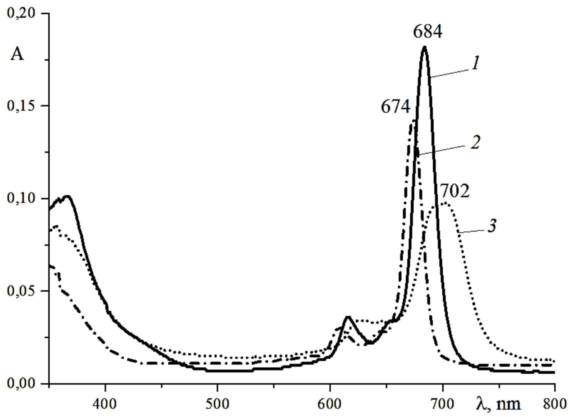


Fig. 5. UV-Vis spectra in Py: 1 - **2a**, 2 - **2b**, 3 – **3**
Рис. 5. Электронные спектры поглощения в Py: 1 - **2a**, 2 - **2b**, 3 - **3**

It was found that there is a decrease in the quantum yield of luminescence of the synthesized phthalocyanines in the series: ZnPc(**2a**) > MgPc(**2b**) > H_2Pc (**3**) (Table, Fig. 6).

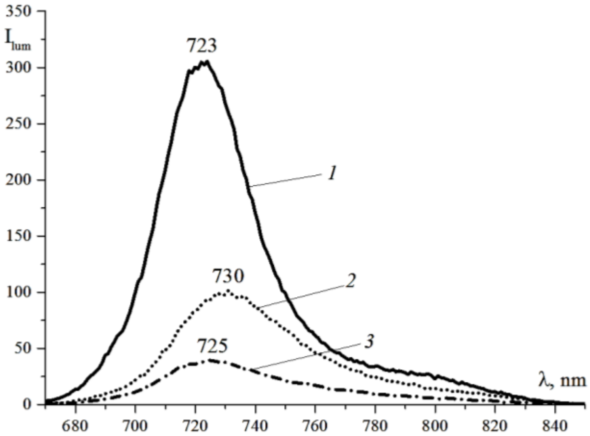


Fig. 6. Fluorescent spectra in Py: 1 - **2a**, 2 - **2b**, 3 – **3**
Рис. 6. Спектры флуоресценции в Py :1 - **2a**, 2 - **2b**, 3 - **3**

The Stokes shift values for zinc phthalocyanine **2a** and the corresponding phthalocyanine ligand are close, but for magnesium phthalocyanine **2b** the Stokes shift decreases sharply (table), which is associated with the depolarization of the chromophore system of phthalocyanine in the case of the introduction of a magnesium atom, which has the strongest metallic properties [22].

Data on the spectral-luminescent properties of tetrakis-2,9,16,24-(3,4,5-trimethoxyphenoxy)phthalocyaninato zinc(II) have been found in the literature [13]. The quantum yield for this compound in dichloromethane is 15%, and the Stokes shift is 12 nm.

From a comparison of the above phthalocyanine and the mixed-substituted zinc phthalocyanine **2a** synthesized in this work, which contains nitro groups at the periphery in addition to trimethylphenoxy groups, the Stokes shift of which is 49 nm (table), it is evident how strongly the nitro groups polarize the chromophore system of phthalocyanine [21]. It should be noted that the quantum yields of tetrakis-2,9,16,24-(3,4,5-trimethoxyphenoxy)phthalocyaninato zinc(II) [13] and tetrakis-2,9,16,24-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,25-nitrophthalocyaninato zinc(II) are the same, i.e. no loss of luminescence efficiency is observed.

The electronic absorption spectra of tetrakis-2,9,16,23-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,24-nitrophthalocyanine **3** in basic solvents (pyridine, DMF, DMSO) contain a single unsplit Q-band corresponding to the symmetry group of the D_4h molecule (Figs. 6, 7).

Q-band in UV-Vis spectra of tetrakis-2,9,16,23-(2,3,5-trimethylphenoxy)tetrakis-3,10,17,24-nitrophthalocyanine **3** в DMSO at T = 298 K A is observed at 702 nm, i.e. this compound exhibits the properties of a dibasic NH acid and forms a complex with proton transfer that is stable over time.

In this complex, the protons of the NH groups, bound to the oxygen atom of the dimethylsulfoxide molecules, are located on opposite sides of the macrocycle, which ensures a favorable spatial arrangement of the base molecules [23, 24].

When *n*-butylamine additives are introduced into DMSO, the proton transfer complex loses its kinetic stability. Thus, when the *n*-butylamine content (pKa^{298} = 10.60 [25]) in DMSO is more than 4.27 mol/l (T = 333K), a simultaneous decrease in the intensity of the unsplit Q-band and its bathochromic shift by 34 nm are observed in the electronic absorption spectrum of phthalocyanine **3** (Fig. 7), and the color of the solution changes from green to violet.

Thus, in the course of this work, a new 4-(2,3,5-trimethylphenoxy)-5-nitrophthalonitrile was synthesized, on the basis of which the corresponding mixed-substituted phthalocyanine and its metal complexes with zinc and magnesium were obtained. It was found that the specified compounds are thermally stable up to 300 °C. All phthalocyanines considered in this work have luminescent properties. It is noted that the introduction of nitro groups into the phthalocyanine molecule with trisubstituted phenoxy groups sharply increases the Stokes shift with the preservation of the quantum yield, i.e. without loss of luminescence efficiency. Phthalocyanine – ligand exhibits the properties of a dibasic NH-acid and forms a stable complex with proton transfer, which loses its kinetic stability upon the addition of *n*-butylamine.

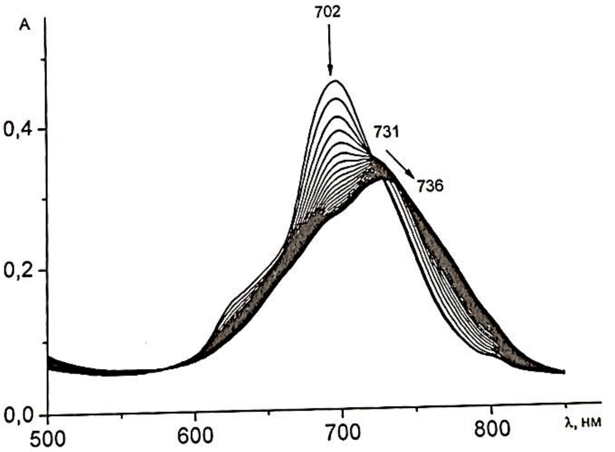


Fig. 7. The change in the UV-Vis spectra of $H_2Pc(3)$ under the influence of *n*-butylamine in DMSO at T= 333 K for 37 min
Рис. 7. Изменение ЭСП $H_2Pc(3)$ под влиянием *н*-бутиламина в ДМСО при T=333 K в течение 37 мин

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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