

## Synthesis and Photophysical Properties of Phthalocyanines with 4-(1-Methyl-1-phenylethyl)phenoxy Groups

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*This work is devoted to the study of synthesis and investigation of spectroscopic-luminescent and photochemical properties of metal complexes of octa-substituted phthalocyanines containing from four to eight fragments of cumylphenol and 1-benzotriazolyl- or nitro-groups. The objects of study were synthesized by “nitrile” method by heating the corresponding 4,5-substituted phthalonitriles with zinc and magnesium acetate, aluminum chloride.*

**Keywords:** Synthesis, phthalodinitrile, phthalocyanine, phenoxy groups, fluorescence, singlet oxygen.

## Синтез и фотофизические свойства фталоцианинов с 4-(1-метил-1-фенилэтил)феноксигруппами

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*Работа посвящена изучению синтетических подходов и исследованию спектрально-люминесцентных и фотохимических свойств металлокомплексов октазамещенных фталоцианинов, содержащих от 4 до 8 4-(1-метил-1-фенилэтил)феноксигрупп, а также 1-бензотриазолил- или нитрогруппы. Объекты исследования синтезировали «нитрильным» методом нагревания соответствующих 4,5-замещенных фталонитрилов с хлоридом алюминия, ацетатом цинка и магния.*

**Ключевые слова:** Синтез, фталонитрил, фталоцианин, феноксигруппы, флуоресценция, синглетный кислород.

## Introduction

Phthalocyanines containing on the periphery oxyaryl fragments exhibit wide range of properties useful in an applied sense. Thus, the presence of four 4-(1-methyl-1-phenylethyl)phenoxy- groups on the periphery of phthalocyanine molecule gives to such compounds photoactivity,<sup>[1]</sup> liquid-crystal,<sup>[2]</sup> luminescent<sup>[3]</sup> and sensor<sup>[4]</sup> properties. Copper tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanines were studied as a component of complex heterogeneous solar fuel.<sup>[1]</sup> Corresponding lead metal complex was investigated by way of optical limiting device both as fixed on solid organic substrate<sup>[5]</sup> and as nematic liquid crystal composites.<sup>[6]</sup> Thereby, the introduction of 4-(1-methyl-1-phenylethyl)phenoxy-groups on the periphery of phthalocyanine macrocycle gives the number of useful properties to the compounds described.

The study of usage of porphyrins and their synthetic analogues called phthalocyanines is also of interest. Macroheterocyclic compounds using as sensitizers have to satisfy the number of requirements such as presence in the molecule structure of both hydrophobic and hydrophilic fragments, absorption maximum at 630–730 nm, intensive fluorescence and so on.<sup>[7]</sup> By means of this, the development and the investigation of novel phthalocyanine synthetic methods seems to be important work.

Present paper is devoted to synthesis and study of spectroscopic-luminescence and photochemical properties of octasubstituted phthalocyanine metal complexes containing from four to eight 4-(2-phenylisopropyl)phenol fragments, as well as 1-benzenetriazolyl- or nitro groups.

## Experimental

Electronic absorption spectra (UV-Vis) were registered on Shimadzu UV-1800 spectrophotometer for solutions of tetraazaporphyrins and their complexes in the concentration range equal to  $10^{-6}$ – $10^{-5}$  mol/L at wavelengths interval from 300 to 900 nm using quartz cells. <sup>1</sup>H NMR spectra were recorded on Bruker (200 and 600 MHz) spectrometer in deuterated chloroform (CDCl<sub>3</sub>) and deuterated dimethylsulfoxide (DMSO-*d*<sub>6</sub>). FT-IR spectra were obtained for the samples pressed with KBr on Avatar 360 FTIR spectrometer. MALDI-TOF mass-spectra were recorded on Shimadzu Biotech Axima confidence spectrometer using 3,5-dihydroxybenzoic acid as matrix and in the absence of it. Fluorescent spectra were registered on RF-6000 SHIMADZU spectrofluorometer using quartz cells (10·10 mm) in methanol and chloroform. Fluorescence quantum yields (Φ<sub>F</sub>) determination was carried out by comparison method using solution of unsubstituted zinc phthalocyanine (ZnPc) in 1-propanol as fluorescent standard (Φ<sub>F</sub>(ZnPc) = 0.45 at λ<sub>ex</sub> = 600 nm<sup>[8]</sup>) and calculated by equation:<sup>[9]</sup>

$$\Phi_F^R = \frac{G^R \cdot n_{1-propanol}^2 \cdot A^S(\lambda_{ex})}{G^S \cdot n_{CHCl_3}^2 \cdot A^R(\lambda_{ex})} \cdot \Phi_F^{SH}$$

where *G* – integral radiation region, *n* – solvent refractive index, *A* – absorption (≤0.02) at the excitation wavelength, Φ<sub>F</sub> – fluorescence quantum yield.

The quantum yields of singlet oxygen generation were determined by comparison method<sup>[10]</sup> using equation:

$$\Phi_{\Delta} = \frac{k_{(i)} \cdot S_{(ZnPc)} \cdot \Phi_{\Delta(ZnPc)}}{k_{(ZnPc)} \cdot S_{(i)}}$$

where *k*<sub>(i)</sub>, *k*<sub>(ZnPc)</sub> – rate constants of 1,3-diphenylisobenzofuran decomposition reaction in the presence of the investigated Pc and standard (ZnPc, Φ<sub>Δ</sub>(ZnPc)=67 % in DMSO<sup>[11]</sup>); *S* is a total amount of light absorbed by the compound. Chemical reaction rate constants (*k*<sub>(i)</sub>, *k*<sub>(ZnPc)</sub>) were found from the kinetic equation of the first order, reduced to a linear form: lnC = lnC<sub>0</sub> – *k*·*t*, where value of *k* was calculated as the tangent of the slope of the linear function to the time axis –*t*gα = *k*. The concentration of decolorizing diphenylisobenzofuran was found from the Bouguer – Lambert – Beer law: *A*(λ)=ε(λ)·*l*·*C*, where *A*(λ) – the optical density; ε(λ) – the molar absorption coefficient; *l* – the layer thickness of the test solution, *C* – the concentration of the dissolved compound.

The solutions were irradiated with the ALKHT-ELOMED laser apparatus at a wavelength of 670 nm, with continuous operation and an optical radiation power of 1.2 W. The experiment was carried out under standard conditions with bubbling air into the photosensitizer solution.

**4-[4-(1-Methyl-1-phenylethyl)phenoxy]-5-nitrophthalonitrile (4).** A mixture of 0.25 g (1 mmol) of 4-bromo-5-nitrophthalonitrile (1) and 0.21 g (1 mmol) of 4-(2-phenylisopropyl)phenol was dissolved in 30 mL of DMF, and a solution of 0.14 g (1 mmol) of potash in 2 mL of water was added. The resulting mixture was stirred at 25 °C for 0.5 hours, then poured into water. The precipitate formed was collected on a filter and washed with 2-propanol, then with water and dried in air at 80–90 °C. Yield: 0.32 g (91 %). Found, %: C 71.95, H 5.00, N 10.74. C<sub>23</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>. Calculated: C 72.05, H 4.47, N 10.96. *m/z* (*I*<sub>rel</sub>, %): 383.11 (100) [M]<sup>+</sup>. IR (KBr) ν<sub>max</sub> cm<sup>-1</sup>: 2922, 2850 (CH<sub>3</sub>), 2226 (CN), 1556 (asym. NO<sub>2</sub>), 1334 (sym. NO<sub>2</sub>), 1210 (Ar-O-Ar). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ<sub>H</sub> ppm: 8.33 s (H<sub>1</sub>, 1H), 7.87 d (H<sub>2</sub>, 1H), 7.05 m (H<sub>3</sub>, 4, 4H), 7.12 m (H<sub>5-7</sub>, 5H), 1.76 s (CH<sub>3</sub>, 6).

**4-(1-Benzotriazolyl)-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitrile (5).** *Method 1:* A mixture of 0.21 g (1 mmol) of 4-(2-phenylisopropyl)phenol and 0.290 g (1 mol) of 4-(1-benzotriazolyl)-5-nitrophthalonitrile (3) was dissolved in 50 mL of DMF, then 0.138 g of potash, dissolved in 2 mL of water, was added to the solution. The reaction mixture was kept at room temperature for 1 hour. The precipitate was filtered off, washed with 2-propanol, then with water and dried at 80–90 °C. Yield: 0.39 g (87 %), m.p. 209–212 °C. Found, %: C 76.49, H 4.64, N 15.14. Calculated, %: C 76.42, H 4.65, N 15.37. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ<sub>H</sub> ppm: 8.70 s (1H, H<sub>1</sub>), 8.16 d (1H, H<sub>3</sub>, *J* = 8 Hz), 7.85 s (1H, H<sub>2</sub>), 7.8 d (1H, H<sub>4</sub>, *J* = 7.9 Hz), 7.65 t (1H, H<sub>5</sub>), 7.5 t (1H, H<sub>6</sub>), 7.27 t (2H, H<sub>13-14</sub>), 7.20 m (4H, H<sub>8-10,15</sub>), 7.05 d (2H, *J* = 8.1 Hz, H<sub>11,12</sub>), 1.60 s (6H, CH<sub>3</sub>). *Method 2:* A mixture of 0.12 g (0.1 mmol) of 1-benzotriazole and 0.38 g (0.1 mmol) of phthalonitrile (4) was dissolved in 50 mL of DMF, and then 0.14 g (0.1 mmol) of potash dissolved in 5 mL of water was added to the solution. The reaction mixture was kept at room temperature for 1 hour. The precipitate was filtered off, washed with 2-propanol, water and dried at 80–90 °C. Yield: 0.37 g (81 %). Found, %: C 76.55, H 4.50, N 15.12. C<sub>27</sub>H<sub>17</sub>N<sub>5</sub>O. Calculated, %: C 76.42, H 4.65, N 15.37. IR (KBr) ν<sub>max</sub> cm<sup>-1</sup>: 2914, 2863 (CH<sub>3</sub>), 2230 (C≡N), 1218 (Ar-O-Ar), 1045 (N=N), 745 (C-N).

**Di-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitrile (6).** *Method 1:* Compound 6 was synthesized using 4.24 g (0.02 mol) of 4-(1-methyl-1-phenylethyl)phenol. The reaction mass was stirred at 85–90°C for 8 hours. After heating, the reaction mass was poured into water. The resulting viscous red-brown liquid, which contained the desired product, was separated on a separatory funnel and placed in a 100 mL conical flask, then 10 mL of a mixture of isopropyl alcohol and water (1 : 1 v/v) were added, covered with a glass funnel and left for 3 days. Initially, the unpainted water-alcohol layer became a saturated red-brown color, and the target phthalonitrile precipitated in the form of light beige lumps to the bottom of the flask. The resulting precipitate was filtered off, washed with 2-propanol to colorless filtrates, then with water until the pronounced odor of 2-propanol disappeared and dried in air at 80°C. Yield: 2.40 g (44%). m.p. 123–125°C. IR spectrum (KBr) ν cm<sup>-1</sup>: 2967, 2929, 2869 (CH<sub>3</sub>), 2233 (CN),

1589 (C-C, skeletal), 1318, 1162 (C<sub>Ar</sub>-H, def.), 1217 (Ar-O-Ar). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 7.33 s (H<sub>1</sub>, 2H), m 7.01–7.03 (H<sub>2</sub>, 4H), 6.96–6.98 m (H<sub>3</sub>, 4H), 7.09–7.17 m (H<sub>4,6</sub>, 10H) 2.19 s (CH<sub>3</sub>, 12H). *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 549.19(34.95) [M+H]<sup>+</sup>, 588.13(83.23) [M+K]<sup>+</sup>. Found, %: C 82.95, H 6.02, N 5.11; C<sub>38</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>; Calculated: C 83.19, H 5.88, N 4.96. *Method 2*: 0.38 g (1 mmol) of compound **4** and 0.21 g (1 mmol) of 4-(1-methyl-1-phenylethyl)phenol were dissolved in 10 mL of DMF, then a solution of 0.14 g (0.1 mmol) of potassium carbonate in 1 mL of water was added. The reaction mass was stirred at 80–90°C for 8–9 hours. Then it was poured into water. It was not possible to obtain compound **6** by this method. *Method 3*: 0.25 g (1 mmol) of 4-bromo-5-nitrophthalonitrile and 0.21 g (2 mmol) of 4-(1-methyl-1-phenylethyl)phenol in 15 mL of DMF were dissolved in a two-necked flask equipped with a stirrer and reflux condenser. Then 0.28 g (2 mmol) of potassium carbonate was added. The reaction mass was stirred at 80–90°C for 8 hours. During the synthesis, the reaction mass acquired a dark green color. Then the reaction mass was poured into water, the precipitate formed was collected on a Schott filter and washed with 2-propanol and water, after which it was dried at 80–90°C. Yield: 0.45 g (82%). m.p. 126–129°C. IR ν cm<sup>-1</sup>: 2964, 2930, 2864 (CH<sub>3</sub>), 2232 (CN), 1590 (C-C, skeletal), 1312, 1161 (C<sub>Ar-H</sub>, def.), 1218 (Ar-O-Ar). *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 629.59(98.88) [M+2K]<sup>+</sup>.

*Tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]tetra-5-nitrophthalocyaninates of magnesium, zinc and aluminum (7a-c)*. *General technique*. A thoroughly ground mixture of 0.38 g (1 mmol) of 4-[4-(1-methyl-1-phenylethyl)phenoxy]-5-nitrophthalonitrile (**4**), 0.05 g (0.8 mmol) of urea and 0.05 mmol of the corresponding metal salt was heated at 185–230 °C for 2 hours. At the end of the process, the reaction mass was washed with diluted hydrochloric acid to remove urea decomposition products, then with water until the reaction to chloride anions with silver nitrate disappeared, then it was dried in air at 70–80 °C, dissolved in chloroform and subjected to column chromatography on alumina eluting with chloroform.

*Tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]tetra-5-nitrophthalocyaninatomagnesium (7a)*. Obtained according to the general procedure using 0.11 g (0.5 mol) of magnesium acetate tetrahydrate at a temperature of 185–190 °C for 2 hours. Yield: 0.30 g (77 %). Found, %: C 70.82, H 4.54, N 10.52. C<sub>92</sub>H<sub>68</sub>MgN<sub>12</sub>O<sub>12</sub>. Calculated: C 70.93, H 4.40, N 10.79. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 1557.9 (100) [M]<sup>+</sup>.

*Tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]tetra-5-nitrophthalocyaninatozinc (7b)*. Obtained according to the general method using 0.11 g of zinc acetate dihydrate at a reaction temperature of 185–190 °C for 2 hours. Yield: 0.30 g (76 %). Found, %: C 68.92, H 4.44, N 10.31. C<sub>92</sub>H<sub>68</sub>ZnN<sub>12</sub>O<sub>12</sub>. Calculated: C 69.11, H 4.29, N 10.51. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 1598.89 (100) [M]<sup>+</sup>.

*Tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]tetra-5-nitrophthalocyaninatoaluminum (7c)*. Obtained according to the general method, using 0.07 g of anhydrous aluminum chloride at a reaction temperature of 215–220 °C for 2 hours. Yield: 0.26 g (66 %). Found, %: C 68.77, H 4.40, N 10.33. C<sub>92</sub>H<sub>68</sub>AlClN<sub>12</sub>O<sub>12</sub>. Calculated: C 69.23, H 4.29, N 10.53. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 1598.12 (83.22) [M+2H].

*Tetra-4-(1-benzotriazolyl)-tetra-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninates of magnesium, zinc and aluminum (8a-c)*. *General technique*: A thoroughly ground mixture of 0.045 g (0.1 mmol) of 4-(1-benzotriazolyl)-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitrile (**5**), 0.05 g (0.8 mmol) of urea and 0.05 mmol of the salts. The metals were heated at 195–230 °C for 2 hours. At the end of the process, the reaction mass was washed with diluted hydrochloric acid to remove urea decomposition products, then with water until the reaction to chloride anions with silver nitrate disappeared, then it was dried in air at 70–80 °C, then it was dissolved in chloroform and subjected to column chromatography on alumina eluting with chloroform. A dark green solid is obtained, insoluble in water, highly soluble in chloroform and DMF.

*Tetra-4-(1-benzotriazolyl)-tetra-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninatomagnesium (8a)*. Obtained according to the general method using 0.011 g of magnesium acetate tetrahydrate at a reaction temperature of 195–200 °C for 2 hours. Yield: 0.018 g (39 %). Found, %: C 75.38, H 4.36, N 14.92. C<sub>116</sub>H<sub>84</sub>N<sub>20</sub>O<sub>4</sub>Mg. Calculated, %: C 75.46, H 4.59, N 15.17. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 1846.44 (100) [M+H]<sup>+</sup>.

*Tetra-4-(1-benzotriazolyl)-tetra-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine zinc (8b)*. Obtained according to the general method using 0.011 g of zinc acetate dihydrate at a reaction temperature of 195–200 °C for 2 hours. Yield: 39.6 mg (84 %). Found, %: C 71.98, H 4.56, N 14.40. C<sub>116</sub>H<sub>84</sub>N<sub>20</sub>O<sub>4</sub>Zn. Calculated, %: C 72.46, H 4.40, N 14.57. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 1888.49 (89) [M+H]<sup>+</sup>.

*Tetra-4-(1-benzotriazolyl)-tetra-5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine aluminum (8c)*. Obtained according to the general method using 0.007 g of anhydrous aluminum chloride at a reaction temperature of 220–230 °C for 2 hours. Yield: 32.5 mg (69 %). Found, %: C 73.12, H 4.70, N 14.48. C<sub>116</sub>H<sub>84</sub>N<sub>20</sub>O<sub>4</sub>AlCl. Calculated, %: C 73.93, H 4.49, N 14.87. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 1885.45 (92.3) [M+H]<sup>+</sup>.

*Octa-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninates of magnesium, zinc and aluminum (9a-c)*. *General technique*: A thoroughly ground mixture of 55 mg (0.1 mmol) of compound **6**, 50 mg (0.8 mmol) of urea and 0.1 mmol of acetate or chloride of the corresponding metal was heated at 155–170 °C for 1.5 hours. At the end of the process, the reaction mass was dissolved in chloroform and subjected to column chromatography on alumina, eluting with chloroform. Dark green solids obtained, insoluble in water, readily soluble in chloroform, acetone and DMF.

*Octa-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninatomagnesium (9a)*. Obtained according to the general procedure using 21.4 mg of magnesium acetate tetrahydrate. Yield: 37 mg (67 %). Found, %: C 81.82, H 6.10, N 5.00. C<sub>152</sub>H<sub>128</sub>N<sub>8</sub>O<sub>8</sub>Mg. Calculated: C 82.27, H 5.81, N 5.05. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 2219.04 (100) [M]<sup>+</sup>.

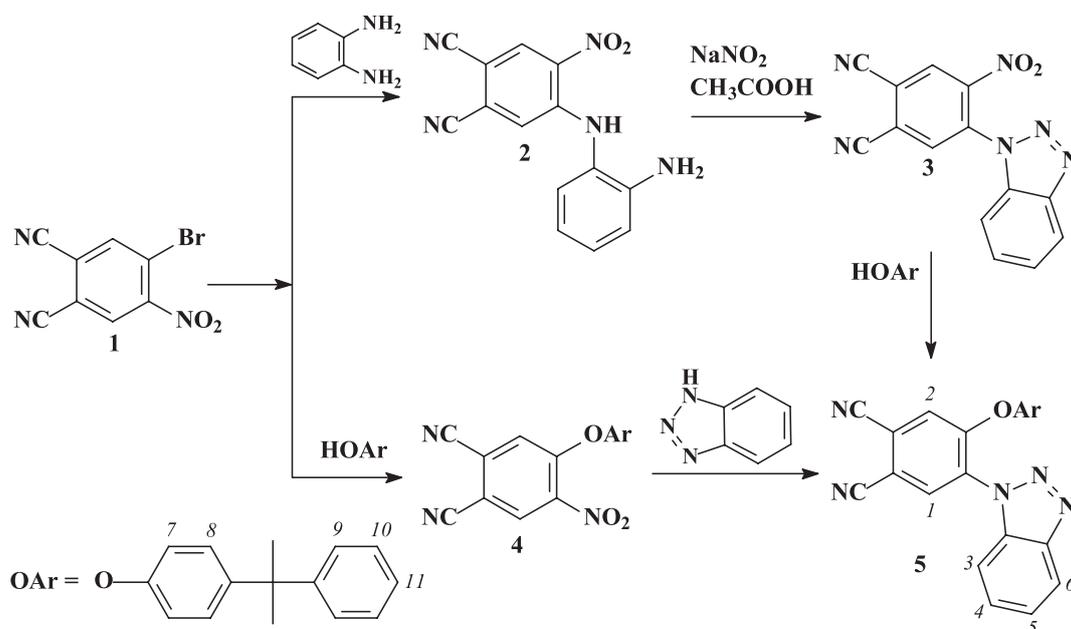
*Octa-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyaninatozinc (9b)*. Obtained according to the general procedure using 21.7 mg of zinc acetate dihydrate. Yield: 28.8 mg (53 %). Found, %: C 80.48, H 6.05, N 4.87. C<sub>152</sub>H<sub>128</sub>N<sub>8</sub>O<sub>8</sub>Zn. Calculated: C 80.78, H 5.71, N 4.96. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 2260.00 (92.75 %) [M]<sup>+</sup>. IR (KBr) ν<sub>max</sub> cm<sup>-1</sup>: 2965, 2933, 2869 (CH<sub>3</sub>), 1604 (C-C, stretch), 1270, 1131 (C<sub>Ar-H</sub>, bend), 1213 (Ar-O-Ar).

*Octa-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine aluminum (9c)*. Obtained according to the general procedure using 13.3 mg of anhydrous aluminum chloride. Yield: 40.0 mg (71 %). Found, %: C 80.36, H 6.39, N 4.88. C<sub>152</sub>H<sub>128</sub>ClN<sub>8</sub>O<sub>8</sub>Al. Calculated: C 80.88, H 5.72, N 4.96. *m/z* (*I*<sub>rel</sub><sup>+</sup>, %): 2258.58 (93.78) [M+H]<sup>+</sup>. IR (KBr) ν<sub>max</sub> cm<sup>-1</sup>: 2936, 2944, 2853 (CH<sub>3</sub>), 1567 (C-C, stretch), 1322, 1160 (C<sub>Ar-H</sub>, bend), 1214 (Ar-O-Ar).

## Results and Discussion

An integral part of this work is the preparation of synthetic precursors of the target octasubstituted phthalocyanines – the corresponding 4-(1-methyl-1-phenylethyl)phenoxy substituted phthalonitriles. The target products were obtained on the basis of 4-bromo-5-nitrophthalonitrile (**1**), since this compound is a highly active substrate for the production of both uniformly substituted and bifunctionally substituted phthalonitriles.<sup>[12–14]</sup> Compound **4** was synthesized by the interaction of **1** with 4-(2-phenylisopropyl)phenol in aqueous DMF containing 10 % water, according to the procedure.<sup>[14]</sup>

Since we have previously shown<sup>[15]</sup> that 4-(aryloxy)-5-nitrophthalonitriles may act as the starting materials for the synthesis of the corresponding benzotriazolyl substituted



Scheme 1.

compounds with aryloxy groups, an attempt was made to obtain benzotriazolyl substituted phthalonitrile **5** based on **4** (Scheme 1). It was found the usage of both above and the previously proposed methodologies<sup>[12]</sup> allowed to obtain phthalonitrile **5** with 73 % yield.

We attempted to synthesize di-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalonitrile (**6**) based on nitro-substituted phthalonitrile **4**, but the target compound was not obtained. This can be explained by the significant deactivation of the nitro group of compound **4** in nucleophilic substitution reactions during interaction with a 4-(2-phenylisopropyl)phenol bulk molecule.

Compound **6** was synthesized with 44 % yield in aqueous DMF in the presence of potash as a deprotonating agent<sup>[16]</sup> at 85–90 °C. An attempt to increase the yield of the target product varying the temperature of the synthesis was also unsuccessful. Thus, the temperature was increased to 120 °C, the reaction mixture was completely ground, and a decrease to 60 °C led to the formation of only nitro-substituted phthalonitrile **4**. An increase in the duration of synthesis to 12 and up to 24 hours caused the formation of a mixture of products **4** and **6**, which could not be separated.

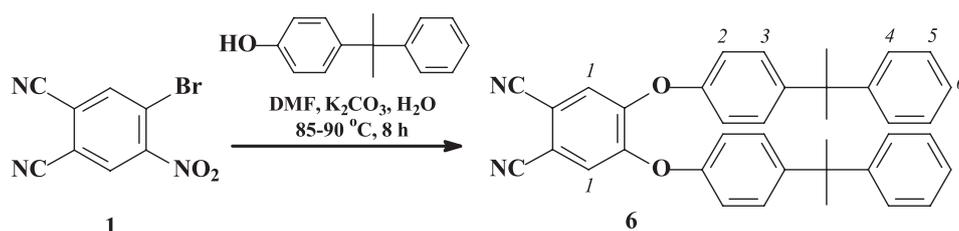
Finally, an attempt was made to synthesize compound **6** from **1**, modifying Scheme 2 by excluding water from the components of the reaction mixture. During the synthesis, the reaction mixture turned to green. Upon completion

of heating, when pouring into water, a precipitate of light green color was formed; it can be dissolved in chloroform. In the UV-Vis spectra in the long wavelength region, two intense absorption bands are observed (Figure 1), which is typical for metal-free phthalocyanines.<sup>[17]</sup> Thus, at 85–90 °C in the absence of water, using potassium carbonate, the metal complex of the corresponding phthalocyanine with potassium is formed and the target phthalonitrile is contaminated with it. This fact can be explained by the low melting point of nitrile **6** (122–125 °C).

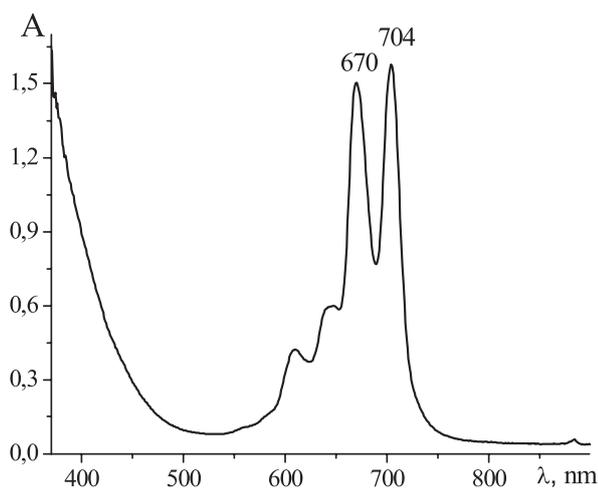
All the compounds obtained were identified using elemental analysis data, MALDI-TOF mass spectrometry, <sup>1</sup>H NMR, IR spectroscopy. It was found, that the physicochemical properties of phthalonitrile samples synthesized by various methods are completely identical, which confirms the purity of the obtained compounds and the suitability of all the above approaches.

In the IR spectra of phthalonitriles (**4–6**) the stretching vibration of C≡N at 2230–2240 cm<sup>-1</sup>, the vibrations of methyl and methylene groups of 4-(1-methyl-1-phenylethyl)phenoxy groups at 2950–2830 cm<sup>-1</sup>, as well as symmetric (1340–1385 cm<sup>-1</sup>) and asymmetric (1525–1565 cm<sup>-1</sup>) vibrations of the NO<sub>2</sub> group<sup>[18,19]</sup> of compound **4** are observed.

While studying the compound **4** by IR spectroscopy upon heating, it was found to be decomposed at 365 °C.



Scheme 2.



**Figure 1.** Electronic absorption spectrum of phthalocyanine 6 in chloroform.

Fixation in the IR spectra of gaseous degradation products of **4** revealed the presence of carbon monoxide. The next decomposition stage, proceeding at 475 °C, is accompanied by the release of methyl isocyanate, as well as phenol. That is, at this stage the participation in the process of thermal destruction of peripheral substituents: nitro- and 4-(1-methyl-1-phenylethyl)phenoxy groups is observed. The final decomposition of compound **4** is fixed at 630 °C. Carbon monoxide and cyanoacetic acid were recorded as the main gaseous products at this stage,

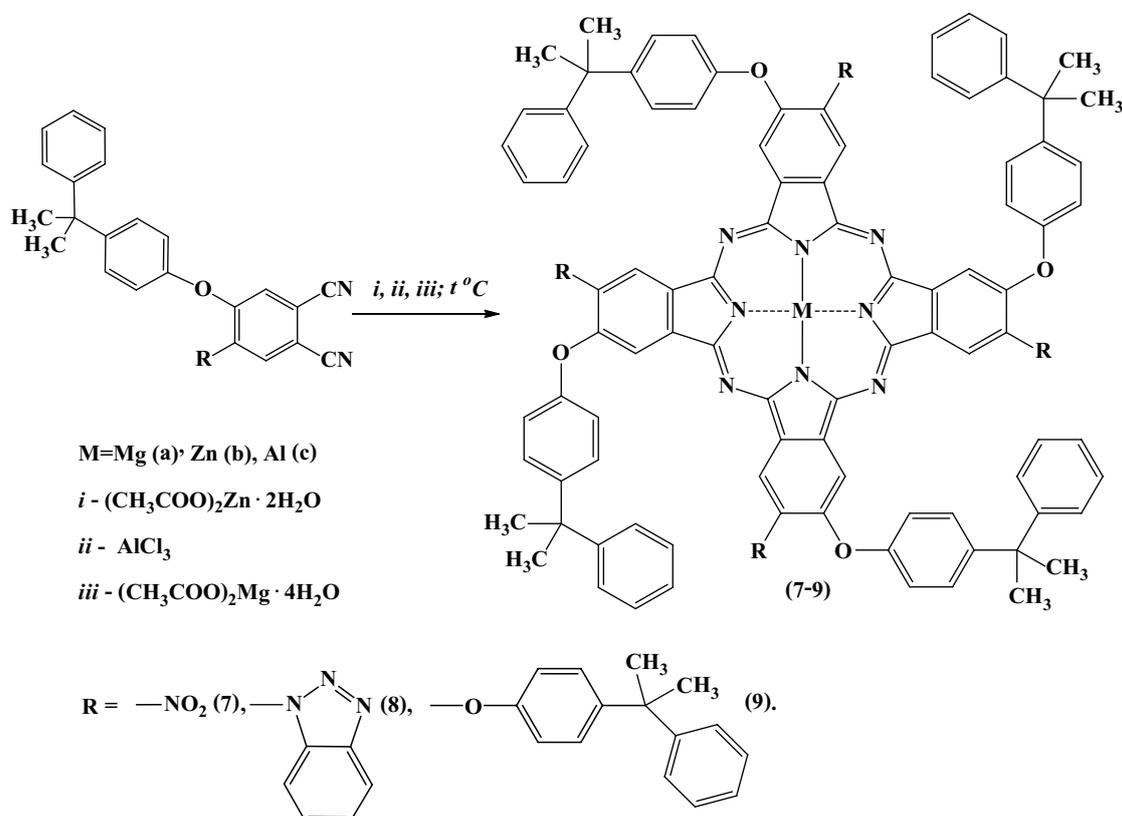
which indicates the complete decomposition of the phthalonitrile molecule **4**.

The metal complexes of 4-(1-methyl-1-phenylethyl)phenoxy substituted phthalocyanines of zinc, aluminum and magnesium (Scheme 3) were obtained by template co-condensation of the corresponding nitriles.

The process of thermooxidative degradation of the compounds synthesized in the presence of atmospheric oxygen is studied. It was found, that the temperature parameters of the decomposition of phthalonitriles **5** and **6**, containing two bulky fragments, are very close (Table 1), while the introduction of the nitro group into **4** leads to a decrease in the temperature at which mass loss begins.

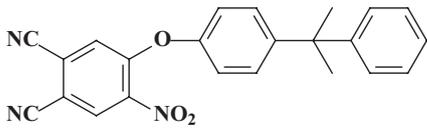
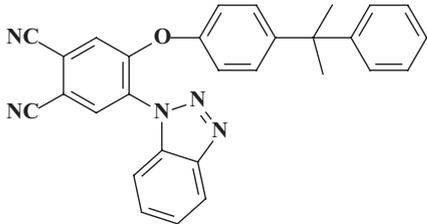
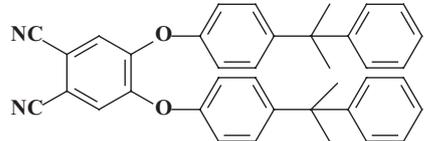
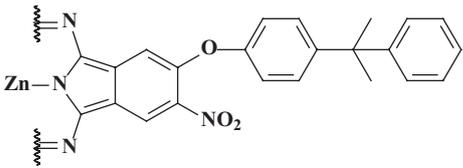
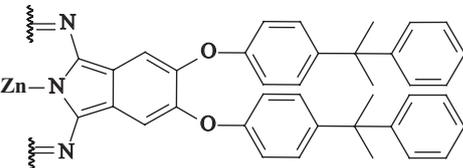
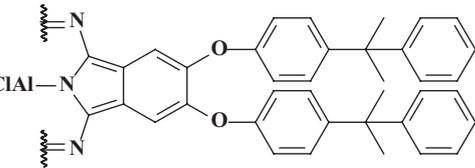
A lot of phthalocyanines exhibit fluorescence in the red spectral region, as well as the ability to generate singlet oxygen. Moreover, the position of the emission band maximum and the quantum yield of fluorescence and generation of singlet oxygen depend on many factors, such as the nature of phthalocyanine (the nature and position of substituents, the nature of the metal complexing agent), and the nature of the solvent.<sup>[20–27]</sup> As an example, Figures 2 and 3 show the UV-Vis and fluorescence spectra of the Mg(II), Zn(II), and Al(III) metal complexes of tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]tetra-5-nitrophthalocyanine in chloroform. Table 2 presents the maxima of the emission of the main fluorescence band, Stokes shifts, quantum yields of fluorescence ( $\Phi_F$ ) and generation of singlet oxygen ( $\Phi_\Delta$ ). Measurements were carried out using dichloromethane solutions to avoid possible protonation.

According to Table 2, the structure of metal complexes of octasubstituted phthalocyanines containing



**Scheme 3.**

**Table 1.** Parameters of the thermooxidative degradation of the compounds synthesized.

No.	Compound	$T_{\text{melt}}$ , °C	$T_{\text{exo}}$ , °C		$\Delta T$ , °C
			I stage	II stage	
4		124	280	544	475–600
5		128	291, 333	576	490–625
6		148	320	568	500–650
7b		–	311	479, 500	390–540
8b		–	492	549	520–580
8c		–	485	547	560–600

The temperature of the onset of mass loss of phthalonitriles **4–6** is naturally lower in comparison with the corresponding phthalocyanines **7, 8**. It was noted, that the transition from octa-4,5-[4-(1-methyl-1-phenyl-ethyl)phenoxy]phthalocyaninate of zinc to its 4-nitro substituted analogue is accompanied by a significant decrease in the temperature of the onset of weight loss (Table 1). Replacing a zinc atom with an aluminum atom does not significantly affect the resistance of phthalocyanines to thermal oxidative degradation.

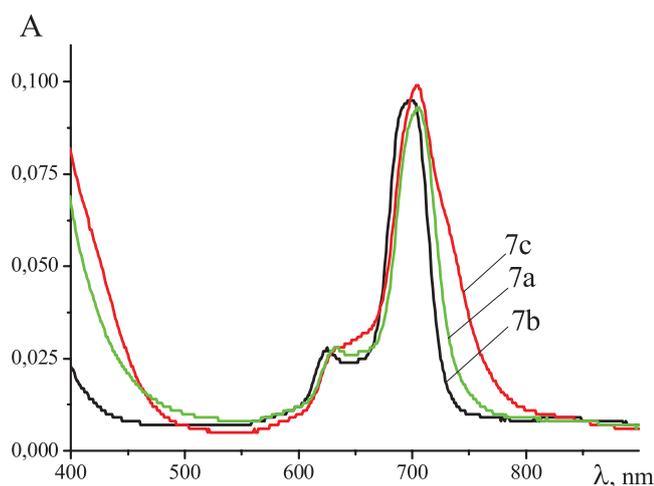
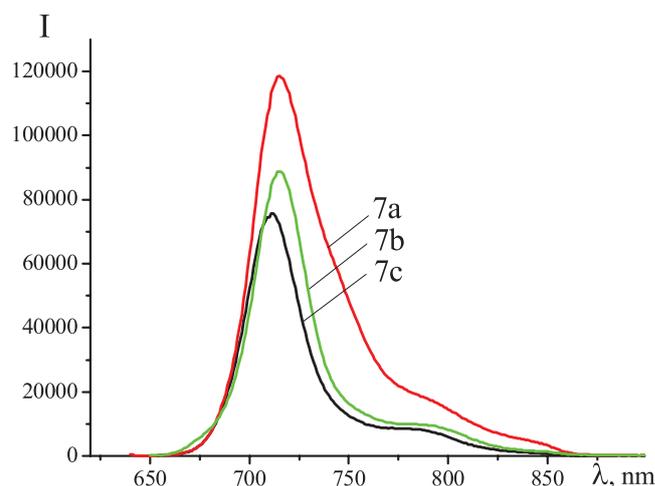
4-(1-methyl-1-phenylethyl)phenoxy groups at the periphery has a noticeable effect on their spectroscopic-luminescent and photochemical properties. Thus, the dependence of the quantum yield of fluorescence and the generation of singlet oxygen on the nature of metals was found; in the series  $\text{Mg} > \text{Al-Cl} > \text{Zn}$ , the  $\Phi_{\text{F}}$  values decrease,<sup>[20–22]</sup> while the  $\Phi_{\Delta}$  values increase on the contrary.<sup>[28]</sup> An analysis of the results showed the presence of a pronounced effect of the heavy atom on the photophysical properties of the studied phthalocyanines. Thus, the highest  $\Phi_{\text{F}}$  values are observed

for Mg(II) phthalocyanines and the highest  $\Phi_{\Delta}$  values – for Zn(II) phthalocyanines (Figure 4), which indicates an increase in the fraction of nonradiative transition to the triplet state preceding the generation of singlet oxygen.<sup>[29]</sup>

In addition, the quantum yields of fluorescence and singlet oxygen generation depend on the nature and bulk of peripheral substituents. According to the data in Table 2, the highest values of  $\Phi_{\text{F}}$  and  $\Phi_{\Delta}$  are shown in the metal complexes of octa-4,5-[4-(1-methyl-1-phenylethyl)phenoxy]phthalocyanine. The presence on the periphery,

**Table 2.** Data of phthalocyanines fluorescent spectra in dichloromethane solution.

M	Q, nm	Fluorescence, nm		Stokes shift, nm	$\Phi_F$	$\Phi_A$
		$S_1 \rightarrow S_0$				
Pc 7						
Mg (7a)	704	715		11	0.4	0.07
Zn (7b)	698	711		13	0.24	0.24
Al-Cl (7c)	705	715		10	0.33	0.22
Pc 8						
Mg (8a)	690	694		4	0.49	0.12
Zn (8b)	680	695		15	0.29	0.42
Al-Cl (8c)	698	702		4	0.43	0.18
Pc 9						
Mg (9a)	684	689		5	0.6	0.2
Zn (9b)	681	687		6	0.39	0.61
Al-Cl (9c)	696	699		3	0.49	0.46

**Figure 2.** Electronic absorption spectra of Mg, Zn, Al tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]-tetra-5-nitrophthalocyanines in chloroform.**Figure 3.** Fluorescence spectra of Mg, Zn, Al tetra-4-[4-(1-methyl-1-phenylethyl)phenoxy]-tetra-5-nitrophthalocyanines in chloroform.

along with the residues of 4-(1-methyl-1-phenylethyl)phenoxy fragments, of less bulky benzotriazole groups having significantly smaller sizes and volumes reduces the quantum yields of fluorescence and generation of singlet oxygen.

The lowest quantum yield values are demonstrated by phthalocyanines with nitro groups (Figure 4), which is due to the occurrence of strongly pronounced association processes, which noticeably affect the UV-Vis spectra of these compounds.

## Conclusion

Thus, derivatives of 4-(1-methyl-1-phenylethyl)phenoxy substituted phthalonitrile containing nitro group,

benzotriazolyl-fragment, and also an additional residue of 4-(2-phenylisopropyl)phenol (bifunctionally substituted phthalonitrile) were synthesized in this work. Using the template cyclotetramerization method by fusing the obtained phthalonitriles with Mg(II), Zn(II) acetates and Al(III) chloride, the corresponding metal phthalocyanines were synthesized. All the compounds obtained were identified using elemental analysis data, MALDI-TOF mass spectrometry,  $^1\text{H}$  NMR, IR spectroscopy.

The resistance of the synthesized phthalonitriles and phthalocyanines to thermal oxidative degradation was determined. It was established, that the compounds with nitro groups have lower mass loss temperatures; the replacement of the zinc atom in the coordination cavity of phthalocyanine by an aluminum atom does not significantly affect the thermal stability.

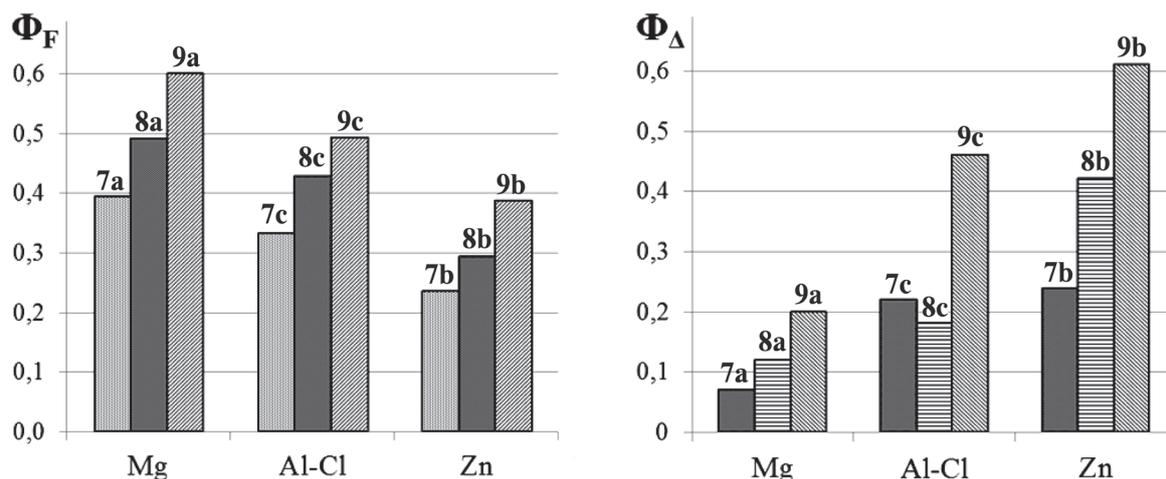


Figure 4. Diagram of fluorescence quantum yield dependence on the nature of metal and substituents.

For all synthesized phthalocyanines, the photophysical properties were studied. The quantum yields of fluorescence and singlet oxygen generation were calculated, and the dependence of these indicators on the nature of metals and substituents was revealed.

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