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Nucleophilic Substitution in 4-Bromo-5-nitrophthalodinitrile: XV.[1] Synthesis of Bis-4,5-(phenylsulfanyl)phthalonitrile, Octakis-4,5-(phenylsulfanyl)phthalocyanines, and Their Sulfo and Alkylsulfamoyl Derivatives

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Abstract—Novel water- and organic-soluble derivatives of octakis-4,5-(sulfanylphenyl)phthalocyanine and its magnesium and aluminum complexes were synthesized starting from 4,5-bis(phenylsulfanyl)phthalonitrile obtained by nucleophilic substitution of the bromine and nitro group in 4-bromo-5-nitrophthalonitrile. Spectral and luminescence characteristics of the newly synthesized compounds were studied.

Keywords: phthalocyanines, electronic absorption spectra, fluorescence spectra, association

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The porphyrin chromophore, which is the key structural unit of both natural and synthetic tetrapyrrole compounds, can be modified by the replacement of the methine by aza bridges, as well as β annealtion of carbo- and heterocyclic fragments and introduction of various substituents [2–4]. Phthalocyanine (Pc) and its derivatives and metal complexes are closely related to porphyrin. Due to their intense blue green color, high coloring properties, and photo- and chemical stability; these compounds are used as dyes and pigments [2], highly efficient catalysts [2, 5], components of lubricant compositions [6], and electrochromic materials [4, 7]. Phthalocyanines are also used in information recording and storage systems [4], as well as in photodiagnostics and photodynamic therapy [8–10].

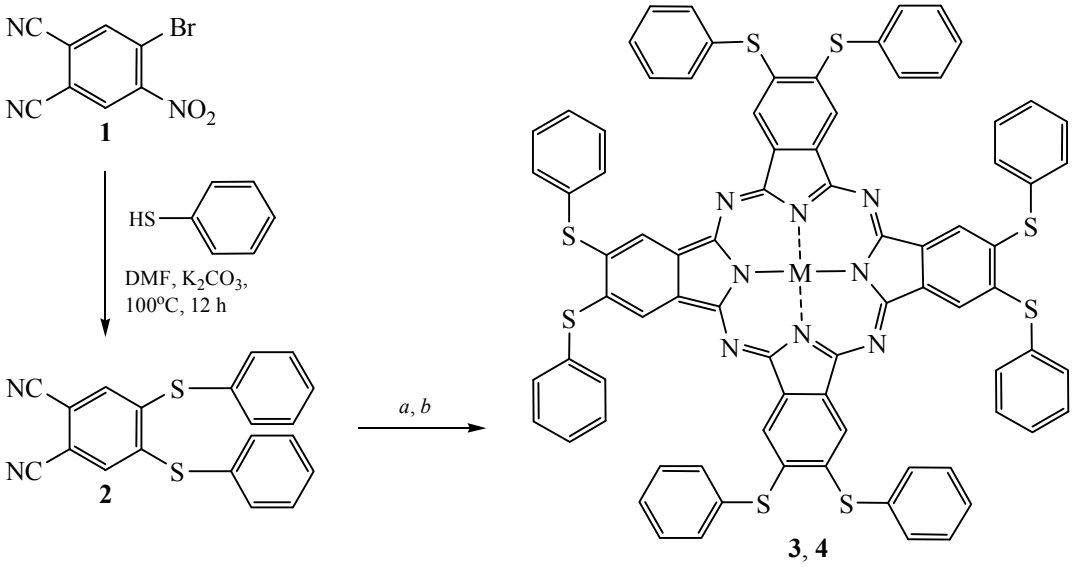
Research into the photodynamic therapy applications of these compounds seems to be the most urgent issue at present [8–10]. Sensitizers for photodynamic therapy should meet a number of requirements [10]. In particular, the molecule should have both a hydrophobic and a hydrophilic units, peak absorbance in the therapeutic window range (630–730 nm), and intense fluorescence and/or high singlet oxygen quantum yield.

In this connection, Pcs containing peripheral phenylsulfanyl substituents appear to hold great promise, because such substituents are known to cause a bathochromic shift of the longwave (*Q*) band in the electronic absorption (UV-Vis) spectra [10–12]. The presence of an aluminum atom in the macrocyclic core, too, is known to shift the *Q* band to longer waves and, in addition, imparts well-defined luminescence properties to such Pc derivatives [2, 10–12]. For example, Maevskii et al. [13] have recently reported the development of a second-generation photosensitizer Photosense on the basis of a sulfonated aluminium Pc derivative with combines near-optimal photophysical characteristics and other necessary properties second-generation photosensitizer Photosence [13]. Furthermore, Pc derivatives were proposed as promising candidates for the development of efficient photosensitizing agents against bacterial and fungal infections [14, 15].

The disadvantage of phenylsulfanyl-substituted Pcs is that they are insoluble in water. The water solubility of Pc derivatives is generally enhanced via peripheral sulfo substitution [2].

[1] For communication XIV, see [1].

Scheme 1.



a, $Mg(OAc)_2 \cdot 4H_2O$ 180–185°C, 2 h; *b*, $AlCl_3$ 200°C, 2 h; M = Mg(II) (**3**), Al(III) (**4**).

The goal of the present work was to synthesize novel water- and organic-soluble derivatives of a highly symmetrical octakis(phenylsulfanyl)-substituted phthalocyanine and its aluminum complex.

The first stage of the work involved the synthesis of 4,5-bis(phenylsulfanyl)phthalonitrile **2** via the nucleophilic substitution of bromine and nitro group in 4-bromo-5-nitrophthalonitrile **1** [16] by phenylsulfanyl fragments (Scheme 1). The reaction was performed in aqueous DMF at 80–85°C for 9 h in the presence of potassium carbonate as a deprotonating agent [17]. The yield of compound **2** was 85%.

Compound **2** was previously synthesized starting from 4,5-dichlorophthalonitrile [18, 19]. Tau and Nyokong [18] performed this synthesis in dry DMSO at 90°C for 14.5 h, whereas Koptyaev et al. [19] used dry *n*-hexanol as a solvent and accomplished the process at 110°C for 8 h. The yield of the target product **2** was 82–83% [18, 19]. Comparing the published and our own results, we can see that the use of 4-bromo-5-nitrophthalonitrile instead of commercial 4,5-dichlorophthalonitrile allows 4,5-bis(phenylsulfanyl)phthalonitrile to be prepared with a slightly higher yield and in slightly milder conditions and a shorter time.

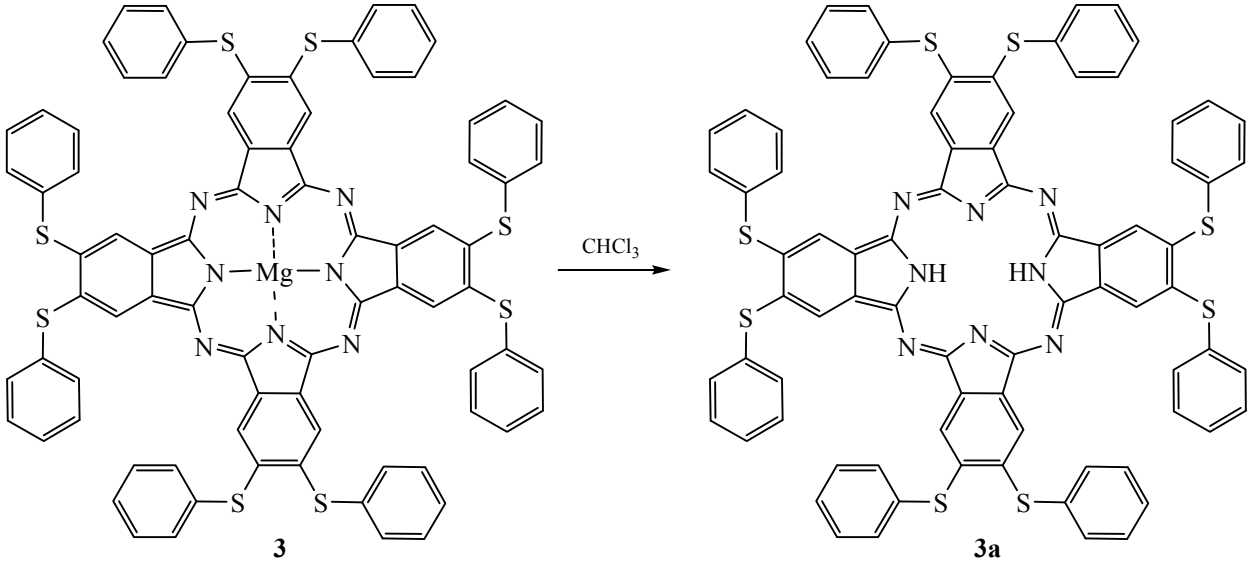
B MALDI−TOF mass spectrum of phthalonitrile **2** contained a molecular ion peak at *m*/*z* 345.72. The elemental analysis and IR spectrum were in a good agreement with those reported in [18, 19].

Further on we reacted compound **2** with magnesium acetate tetrahydrate or anhydrous aluminum chloride at 180–200°C for 2 h to obtain highly symmetrical octakis-substituted metal phthalocyanines **3** and **4** (Scheme 1).

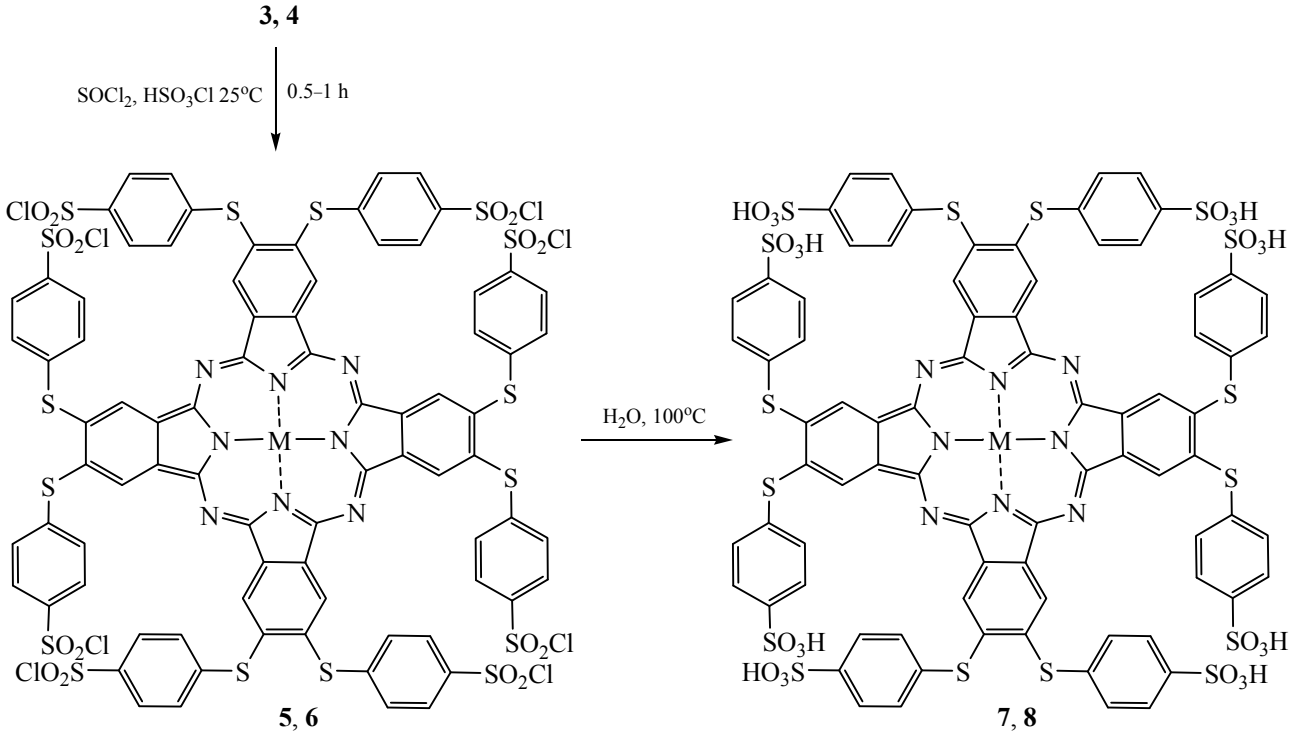
It was found that complex **3** in chloroform underwent dissociation even upon short standing because of the presence of traces of HCl in the solvent. As a result, the UV-Vis spectrum of this phthalocyanine, which initially showed a single *Q*-band in the longwave region (703 nm), later got more complicated and already showed two of almost equal intensity at 675 and 710 nm. This transformation implied that the symmetry of Pc chromophore had changed from D_{4h}, which is characteristic of metal Pcs, to D_{2h}, which is characteristic Pc ligands [20] and was indicative of the formation of a metal-free phthalocyanine **3a** (Scheme 2).

Products **3** and **4** were identified by elemental analysis, MALDI-TOF mass spectrometry, and UV-Vis and IR spectroscopy. According to the mass spectral data, compound **4** contains a chlorine extra ligand on aluminum. The IR spectra of metal phthalocyanines **3** and **4** no longer show the stretching vibration band of the cyano groups of the starting phthalonitrile **2** but at the same time preserve the C–S–C stretching vibration band at 695 cm^{-1}. The IR spectrum of the metal-free phthalocyanine **3a** contains the N–H stretching vibration bands of the endocyclic imino groups at 3055 and 1008 cm^{-1}.

Scheme 2.



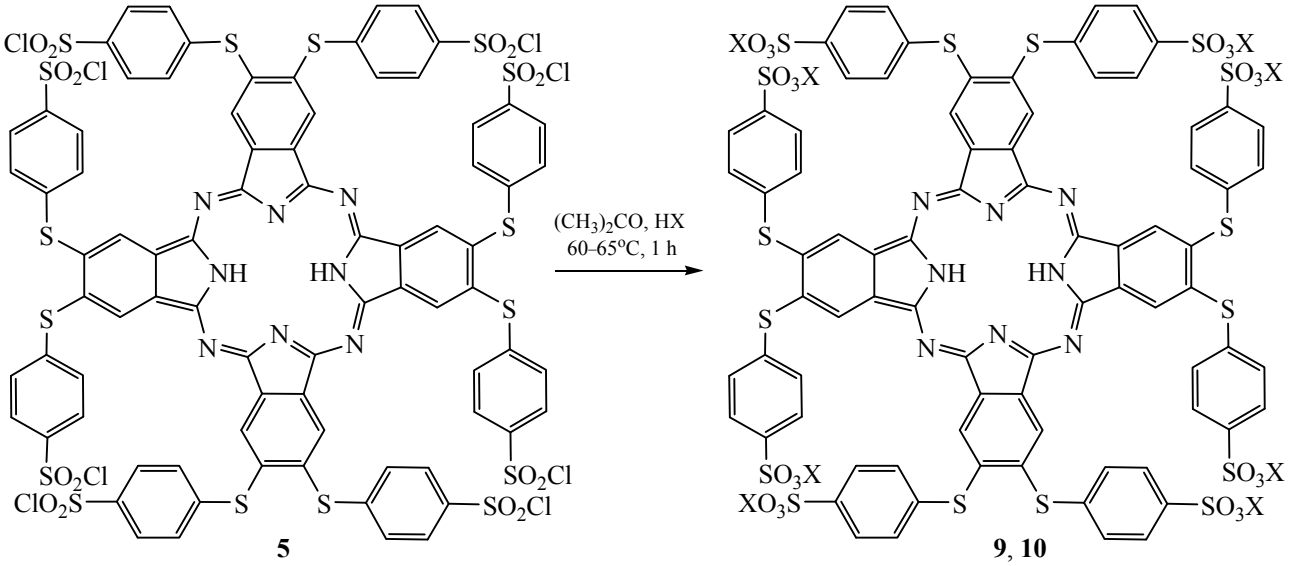
Scheme 3.



M = Mg (**3**), HH (**5**, **7**), AlCl (**4**, **6**, **8**).

Compounds **3** and **4** were used as precursors for their subsequent chemical modification to octakis-4,5-(phenylsulfanyl)phthalocyanine sulfonyl chlorides **5** and **6**. To this end, Pc derivatives **3** and **4** were reacted with a mixture of chlorosulfonic acid and thionyl chloride (Scheme 3). The reaction time of aluminum complex **4** was 1 h. Compound **3** underwent dissociation to form the corresponding metal-free derivative, and, therefore, it was allowed to react no longer than 0.5 h, because upon longer reaction time the reaction product destroyed and the yield was much lower.

Scheme 4.



5 **9**, **10**

X = $N(C_2H_5)_2$ (**9**), $NHC_{18}H_{37}$ (**10**).

The synthesized compounds were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of compound **5** displays a downfield singlet signal (δ 7.71 ppm) from 16 phthalocyanine benzene ring protons. The signal at 7.54 ppm belongs to the phenyl protons located ortho to the S bridge, and the signal at 7.63 ppm is assignable to the benzene ring protons ortho to the sulfo groups.

In the UV-Vis spectrum of compound **5** in chloroform, two longwave bands are observed at 675 and 710 nm, which suggests dissociation of phthalocyanine **3** during synthesis and isolation of the resulting sulfonyl chloride.

Due to their high reactivity, compounds **5** and **6** could be immediately used to synthesize sulfonic acids and alkylsulfamoyl derivatives. Sulfonic acids **7** and **8** were obtained by hydrolysis of the corresponding sulfonyl chlorides (Scheme 3). The products were characterized by elemental analysis, UV-Vis and ^{1}H NMR spectroscopy, and MALDI-TOF spectrometry. The mass spectra contain peaks at *m*/*z* 2029.79 and 2161.65, assigned to the $[M + Li + 2H]^+$ and $[M + 2Na]^+$ ions.

The ^{1}H NMR spectra of sulfonic acids **7** and **8** display show downfield signals of the protons in position 3, located ortho to the sulfo groups, at 7.96 (**7**) and 8.57 ppm (**8**), respectively. The signal at 7.63 ppm, which was observed in the spectrum of the starting sulfonyl chloride, disappears, and the SO_3H proton appears as a singlet at 11.20 (**7**) or 11.36 (**8**) ppm.

In view of the fact that metal-free alkyl-substitute Pc derivatives can exhibit liquid-crystalline properties [21, 22], we synthesized alkylsulfamoyl derivatives **9** and **10,** starting from metal-free phthalocyanine sulfonyl chloride **5** (Scheme 4). The synthesis involved treatment of solution compound **5** in acetone with a double molar excess of diethyl- or octadecylamine under reflux for 1 h. The yields of compounds **9** and **10** were 84 and 67%, respectively.

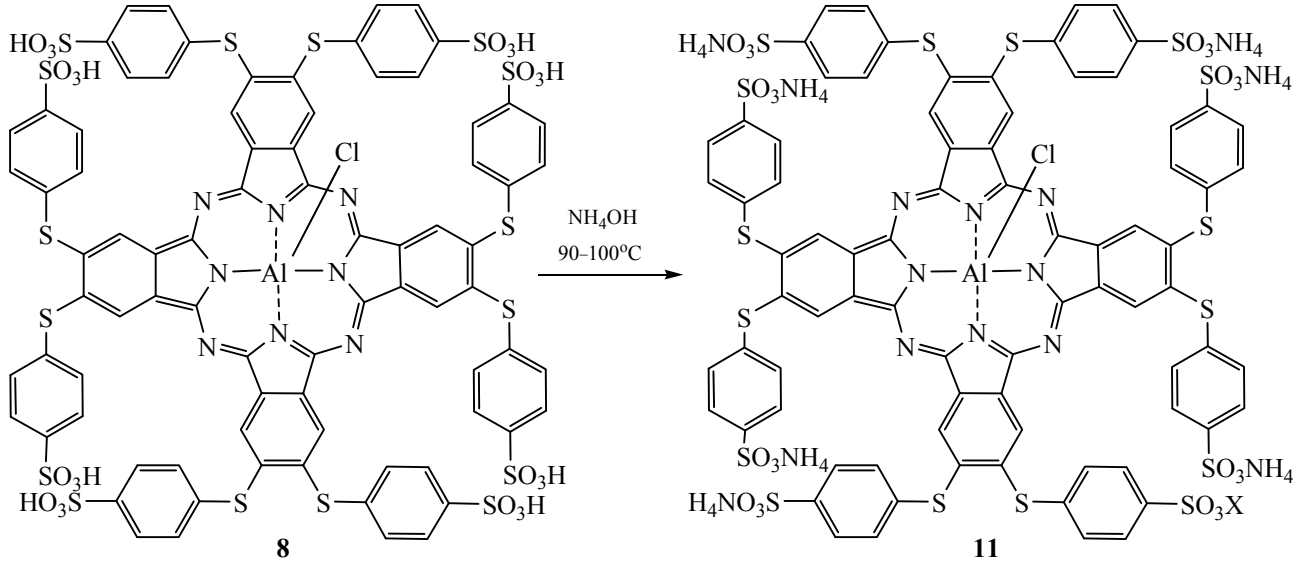
The synthesized compounds were insoluble in water, scarcely soluble in DMF, and readily soluble in chloroform. Solutions of compounds **9** and **10** in concentrated sulphuric acid rapidly decolorized, implying decomposition of the solutes.

Alkylsulfamoyl derivatives **9** and **10** were characterized by elemental analysis, UV-Vis and ^{1}H NMR spectroscopy, and MALDI-TOF mass spectrometry. The mass spectrum of compound **9** contains a signal at *m*/*z* 2594.57, corresponding to the molecular ion $[M + Na + K]^+$.

To decrease the hygroscopicity of sulfo derivative **8**, it was converted into ammonium salt **11** (Scheme 5).

One of the important requirements to photosensitizers for photodynamic therapy consists in the lack of tendency for association in solutions of biocompatible surfactants and other model systems, because it is the nonassociated form that is responsible for the efficiency of singlet oxygen generation [23, 24]. As known [25, 26], molecular association is accompanied

Scheme 5.



by fluorescence quenching because of the increased probability of intermolecular radiationless transitions in the associates. As a result, the relaxation of the excitation state of the sensitizer is complicated by the vibrational process of internal conversion, thereby decreasing the fluorescence quantum yield. Therefore, an aggregated sensitizer exhibits a lower photodynamic activity than a non-aggregated one [27, 28].

We have analyzed the UV-Vis and fluorescence spectra of octakis-4,5-(phenylsulfanyl)phthalocyaninea **3a** and its aluminum complex **4**, as well as sulfo derivatives **7** and **8** (see table). The UV-Vis spectrum of aluminum phthalocyanine **4** in chloroform displays a visible absorption band. The extinction coefficient of this band (ε 98700) and the fact that it follows the Lambert–Bouguer–Beer law point to the absence of association in this solvent. It should be noted that, like all the fluorescence spectra obtained in the present work, the fluorescence spectrum of compound **4** is a mirror image of its UV-Vis spectrum (Fig. 1). The Stokes shift is 9 nm (see table).

The UV-Vis spectrum of aluminum octakis-4,5-(4-sulfophenylsulfanyl)phthalocyanine **8** in water and aqueous alkaline solutions provides evidence to show that, due to the presence of eight strong hydrophilic centers (sulfo groups), this compound is present in an associated form, namely, the spectrum displays a broadened absorption band with its maximum (678 nm) in the transparency window (Fig. 2), as well as a shoulder at 710–715 nm. The UV-Vis spectrum of ammonium salt **11** and the starting sulfonic acid **8** are identical to each other.

Compound **8** is readily soluble in 96% ethanol, where it is also associated, and it is only at the concentration of 0.5×10^{-6} M that the molecule is present in a completely free form. Therewith, the absorbance at 678 nm decreases and at 715 nm increases. Dilution to the concentration of 0.5×10^{-7} M leads to an appearance of bands at 645 and 725 nm, and the first of these bands is 4 times weaker than the second (Fig. 3).

Figure 4 shows the electronic absorption and emission spectra octakis-4,5-(phenylsulfanyl)phthalocyanine

Absorption and fluorescence spectroscopy data for compounds **3a**, **4**, **7**, and **8**

Comp. no.	Solvent	λ_{max}, nm	λ_{fl}, nm	Stokes shift, nm	Φ_{fl}, %
3a	$CHCl_3$	(675), 710	722	11	7.14
4	$CHCl_3$	725	734	9	32.97
7	C_2H_5OH (aq.)	(648), 715	724	9	18.46
8	C_2H_5OH (aq.)	716	727	11	22.13

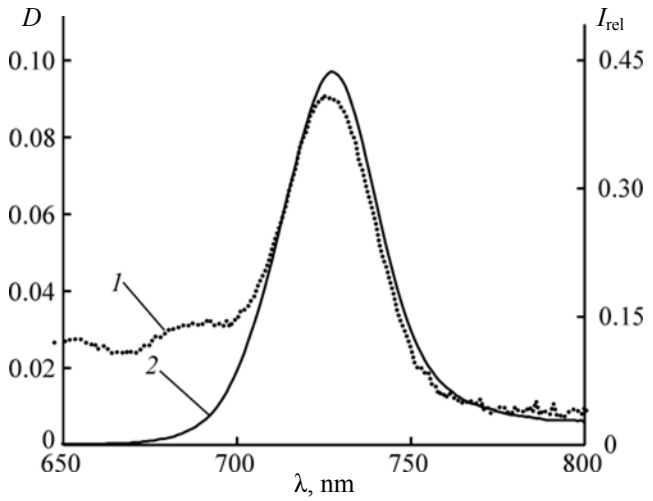


Fig. 1. (*1*) Absorption and (*2*) emission spectra of compound **4** in chloroform (0.50×10^{-7} M).

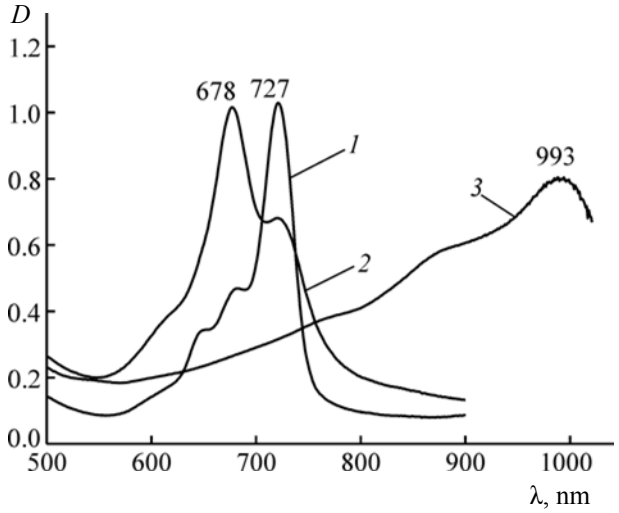


Fig. 2. Electronic absorption spectra (0.5×10^{-5} M) of compound **8** in (*1*) DMF, (*2*) water, and (*3*) H_2SO_4.

3a in chloroform, as well as the spectra of the corresponding sulfo derivative **7** in 96% ethanol. Unlike the absorption spectrum of compound **3a**, which displays two strong longwave bands corresponding to the electronic transitions in the main conjugation contour of the phthalocyanine chromophore, the emission spectrum contains a single band at 722 nm (Fig. 3, see table).

The fluorescence quantum yields of complexes **4** and **8** are higher than those of the corresponding ligands **3a** and **7** (see table). This fact can be explained by that the introduction of a metal containing an extra ligand into compounds **3a** and **7** decreases the tendency of the resulting metal phthalocyanines for aggregation.

The value of the Stokes shift of bands in the UV-Vis and fluorescence spectra of porphyrins and phthalocyanines relates to the degree of noncoplanarity of the macrocycles [29]. Thus, the Stokes shift increases from 6 to 11 nm in going from a tetra-*tert*-butyl-substituted phthalocyanine [29] to phthalocyanine **3a** containing eight bulky phenylsulfanyl fragments.

Alkylsulfamoyl-substituted phthalocyanines **9** and **10**, which contain branched or long-chain alkyl fragments, are associated even in chloroform (Fig. 5), as evidenced by the broadening of longwave absorption bands and the presence in the range 615–630 nm of bands half as intense as the *Q* band. Therewith, this intensity ratio does not change via an increase in the intensity of the *Q* band even when the solutions are diluted to a concentration of 10^{-7} M.

Thus, in the present work we synthesized water-soluble (sulfonic acids and their salts) and organic-soluble [diethyl and octakisdecylsulfamoyl-substituted] derivatives octakis-4,5-(sulfanylphenyl)phthalocyanine and its aluminum complex obtained starting from 4,5-bis(sulfanylphenyl)phthalonitrile. It was found that the starting octakis-4,5-(sulfanylphenyl)phthalocyanine and its aluminum complex, as well as aluminum oktakis-4,5-(4-sulfophenylsulfanyl)phthalocyanine exhibit luminescent properties. The fluorescence quantum yield aluminum oktakis-4,5-(4-sulfophenylsulfanyl)-phthalocyanine and its sulfo derivative is higher than

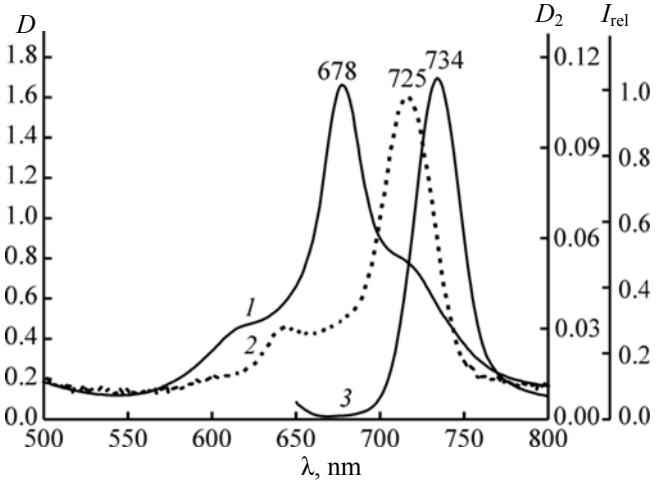


Fig. 3. (*1*, *2*) Absorption and (*3*) emission spectra of compound **8** in ethanol. *c*, M: (*1*) 1.2×10^{-5} and (*2*, *3*) 0.5×10^{-7} M.

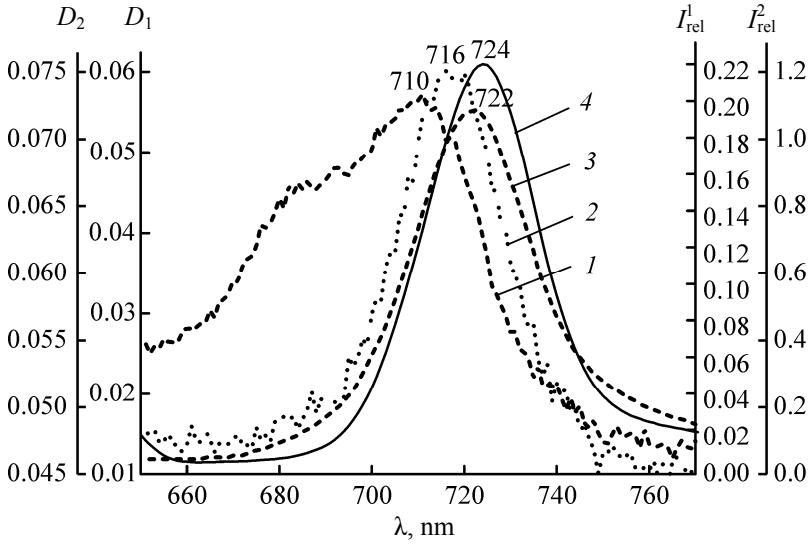


Fig. 4. (*1*, *2*) Absorption and (*3*, *4*) emission spectra of compounds (*1*, *3*) **3a** in chloroform and (*2*, *4*) **7** in ethanol (0.5×10^{-7} M).

those of the corresponding ligands, which is explained by the fact that the metal atom and the extra ligand on it decrease the tendency of the complexes for aggregation.

EXPERIMENTAL

The UV-Vis spectra were recorded in organic solvents (DMF and chloroform), aqueous alkaline media, and concentrated sulfonic acid on a HITACHI U-2001 spectrophotometer at room temperature in the range 325–900 nm. The IR spectra were run on an Avatar 360 FTIR ESP instrument in the range 400–4000 cm^{-1} for thin films (chloroform, **2–6**, **9**, **10**) and KBr pellets (**7**, **8**, **11**). The ^1H NMR spectra of solutions in $CDCl_3$ (**5**) or DMSO-d_6 (**7**, **8**) were obtained on a Bruker DRX-500 spectrometer. Elemental analysis was per-formed on a Thermo FlashEA 1112 CHNSO analyzer. Before analysis the samples were heated at 110°C for 2 h. The MALDI-TOF mass spectra were measured on a Shimadzu Biotech Axima Confidence in the positive ion mode, using 2,5-dihydroxybenzoic acid as a matrix. The samples were prepared mixing equal volumes of chloroform or aqueous ethanol solutions of the analytes (10^{-4}–10^{-5} M) with a THF solution of the matrix (30 mg/mL). The fluorescence spectra were measured on a Cary Eclipse Varian spectrofluorimeter in quartz cells (10×10 mm) for ethanol or chloroform solutions with the optical density of no higher than 0.1 (at maximum absorption).

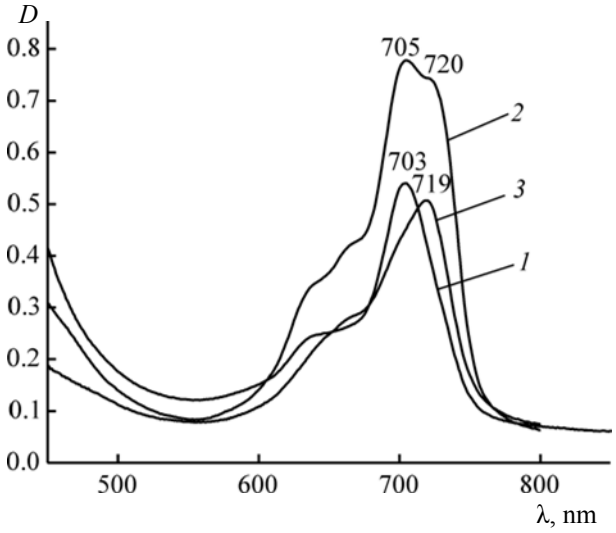


Fig. 5. Electronic absorption spectra in chloroform (c = 0.65×10^{-5} M) of compounds (*1*) **5**, (*2*) **9**, and (*3*) **10**.

The fluorescence quantum yields were determined by the comparison method by Eq. (1) using as reference a solution of PcZn in propan-1-ol (Φ_{fl} = 0.45, λ_{ex} = 600 nm).

$$\Phi_F^R = \frac{G^R \cdot n^2_{1\text{-prop}} \cdot A^S(\lambda_{ex})}{G^S \cdot n^2_{THF} \cdot A^R(\lambda_{ex})} \Phi_F^{SH}. \quad (1)$$

Here G is the integrated emission area; n, refractive index of the solvent; A, optical density ($\leq$ 0.02) at the excitation wavelength; and $\Phi_{fl}\Phi$, fluorescence quantum yield.

4-Bromo-5-nitrophthalonitrile (1) was synthesized as described in [16]. mp 140–142°C. Found, %: C 38.10; H 0.76; N 16.50. $C_8H_2BrN_3O_2$. Calculated, %: C 38.16; H 0.80; N 16.67.

Bis-4,5-(phenylsulfanyl)phthalonitrile (2). A solution of 2.76 g (0.02 mol) of potassium carbonate in 7 mL of water was added to a solution of 2.52 g (0.01 mol) of compound **1** and 2.2 g (2.36 mL, 0.02 mol) of benzenethiol in 50 mL of DMF. The reaction mixture was stirred at 80–85°C for 9 h until it became turbid due to abundant precipitate formation. The target product was then filtered off, washed first with propan-2-ol until the odor of benzenethiol disappeared completely and then with water, and dried at 80–90°C. Yield 85% (3.00 g). IR spectrum, ν, cm^{-1}: 2231 (CN), 1609 (C–$C_{skeleton}$), 1282 (C_{Ar}–H), 691 (C–S–C). Mass spectrum, *m*/*z*: 345.72 $[M + H]^+$. Found, %: C 69.55; H 3.60; N 8.02; S 18.25. $C_{20}H_{12}N_2S_2$. Calculated, %: C 69.74; H 3.51; N 8.13; S 18.62.

Magnesium octakis-4,5-(phenylsulfanyl)phthalocyanine (3). A mixture of 0.345 g (1 mmol) of 4,5-bis-(sulfanylphenyl)phthalonitrile and 0.107 g (0.05 mmol) of magnesium acetate tetrahydrate was heated for 2 h at 180–185°C. The reaction mixture was then cooled down, dissolved in chloroform, filtered, and subject to column chromatography on M60 silica using toluene as an eluent. Yield 0.29 g (84%). IR spectrum, ν, cm^{-1}: 1577 (C–$C_{skeleton}$), 1507 (–N=), 1257 (C_{Ar}–H), 690 (C–S–C), 645 (C–H_{def}). Mass spectrum, *m*/*z*: 1402.86 $[M]^+$. Found, %: C 68.25; H 3.81; N 7.61; S 18.05. $C_{80}H_{48}MgN_8S_8$. Calculated, %: C 68.53; H 3.45; N 7.99; S 18.29.

Octakis-4,5-(phenylsulfanyl)phthalocyanine (3a). Compound **3 (**0.1 g, 0.7 mmol) was dissolved in 2 mL of chloroform, and the solvent was then removed by distillation. The residue was purified by column chromatography on M60 silica, using chloroform as an eluent. Yield 0.082 g (82%). Mass spectrum, *m*/*z*: 1380.92 $[M]^+$. Found, %: C 69.51; H 3.80; N 8.00; S 18.25. $C_{80}H_{50}N_8S_8$. Calculated, %: C 69.64; H 3.65; N 8.12; S 18.59.

Aluminum octakis-4,5-(phenylsulfanyl)phthalocyanine (4). A mixture of 0.345 g (1 mmol) of 4,5-bis-(sulfanylphenyl)phthalonitrile and 0.066 g (0.5 mmol) of anhydrous aluminum chloride was heated for 2 h at 190–200°C. The reaction mixture was then cooled down, dissolved in chloroform, filtered, and subjected to column chromatography on M60 silica, using chloroform as an eluent. Yield 0.24 g (67%). IR spectrum, ν, cm^{-1}: 1579 (C–$C_{skeleton}$), 1506 (–N=), 1257 (C_{Ar}–H), 690 (C–S–C), 679 (C–H_{def}). Mass spectrum, *m*/*z*: 1441.91 $[M + H]^+$. Found, %: C 66.15; H 3.76, N 7.42; S 17.55. $C_{80}H_{48}AlClN_8S_8$. Calculated, %: C 66.72; H 3.36; N 7.78; S 17.81.

Synthesis of octakis-4,5-(phenylsulfanyl)phthalocyanine (5) and its aluminum complex (6). Compound **3** (0.28 g, 0.2 mol) or **4** (0.29 g, 0.2 mol) was added to a vigorously stirred mixture of 2 mL (18 mmol) of chlorosulfonic acid and 2 mL (18 mmol) of thionyl chloride. The resulting mixture was stirred at 20°C for 0.5–1 h and then poured into ice treated with NaCl. The precipitate was filtered off and dried in a dessicator over H_2SO_4 for 3 days. The target compounds were extracted with acetone, and the solvent was removed by distillation to obtain dark green solids readily soluble in acetone and DMF and moderately soluble in chloroform.

Octakis-4,5-(phenylsulfanyl)phthalocyanine (5). Yield 0.39 g (85%). IR spectrum, ν, cm^{-1}: 3530 (OH), 3152 (NH), 1612 (C–$C_{skeleton}$), 1521 (–N=), 1323 (S=O), 1289 (C_{Ar}–H), 1012 ($NH_{endocycl}$), 721 (C–H_{def}), 695 (C–S–C). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 7.71 s (16H, H^1), 7.63 d (16H, H^3, J_{HH} = 8.2 Hz), 7.54 d (16H, H^2, J_{HH} = 8.2 Hz).

Complex 6. Yield 0.37 g (78%). IR spectrum, ν, cm^{-1}: 3541 (OH), 1616 (C–$C_{skeleton}$), 1532 (–N=), 1320 (S=O), 1289 (C_{Ar}–H), 711 (C–H_{def}), 692 (C–S–C).

Synthesis of octakis-4,5-(4-sulfophenylsulfanyl)-phthalocyanine (7) and its aluminum complex 8. Compound **5** or **6 (**0.2 g, 0.1 mmol) was heated until dissolution with 10 mL of water in a porcelain dish and water was then removed. The resulting sulfonic acid was purified by column chromatography on M60 silica using water as an eluent.

Octakis-4,5-(4-sulfophenylsulfanyl)phthalocyanine (7). Yield 0.17 g (84%). IR spectrum, ν, cm^{-1}: 3536 (OH), 3150 (NH), 1612 (C–$C_{skeleton}$), 1523 (–N=), 1162 (S=O), 1281 (C_{Ar}–H), 1011 ($NH_{endocycl}$), 722 (C–H_{def}), 692 (C–S–C). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.20 s (8H, SO_3H), 7.96 s (16H, H^1), 8.73 d (16H, H^3, J_{HH} = 8.2 Hz), 8.52 d (16H, H^2, J_{HH} = 8.2 Hz). Mass spectrum, *m*/*z*: 2029.79 $[M + Li + 2H]^+$. Found, %: C 46.75; H 3.26; N 5.42; S 24.89. $C_{80}H_{50}N_8O_{24}S_{16}$. Calculated, %: C 47.56; H 2.49; N 5.55; S 25.39.

Complex 8. Yield 0.17 g (82%). IR spectrum, ν, cm^{-1}: 3550 (OH), 1614 (C–$C_{skeleton}$), 1532 (–N=), 1164 (S=O), 1290 (C_{Ar}–H), 712 (C–H_{def}), 692 (C–S–C), ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 11.37 s (8H, SO_3H), 8.57 s (16H, H^1), 8.73 d (16H, H^3, J_{HH} = 8.2 Hz), 8.52 d (16H, H^2, J_{HH} = 8.2 Hz). Mass

spectrum, *m*/*z*: 2161.65 $[M + 2Na]^+$. Found, %: C 45.95; H 3.06; N 5.24; S 24.34. $C_{80}H_{48}AlClN_8O_{24}S_{16}$. Calculated, %: C 46.18; H 2.33; N 5.39; S 24.65.

Synthesis of alkylsulfamoyl derivatives of octakis-4,5-(phenylsulfanyl)phthalocyanine (9, 10). Diethylamine (0.07 g, 1 mmol, 0.5 mL, ρ 0.7056 g/cm^3) or octadecylamine (0.27 g) was added to a solution of 0.22 g (0.1 mmol) of compound **5** in 30 mL of acetone. The resulting mixture was heated under reflux (60–65°C) for 1–1.5 h, after which acetone was removed by distillation, the target product was extracted with chloroform, and purified by column chromatography in chloroform.

Compound 9. Yield 0.21 g (84%). IR spectrum, ν, cm^{-1}: 3070 (NH), 1612 (C–$C_{skeleton}$), 1520 (–N=), 1160 (S=O), 1279 (C_{Ar}–H), 1011 ($NH_{endocycl}$), 723 (C–H_{def}), 692 (C–S–C). Mass spectrum, *m*/*z*: 2594.57 $[M + Na + K - 2H]^+$. Found, %: C 54.67; H 5.25; N 8.40; S 20.80. $C_{112}H_{123}N_{16}O_{16}S_{16}$. Calculated, %: C 54.95; H 5.06; N 8.58; S 20.95.

Compound 10. Yield 0.27 g (67%). IR spectrum, ν, cm^{-1}: 3072 (NH), 2919, 2850 (CH_2, CH_3), 1637 (C–$C_{skeleton}$), 1577 (NH), 1510 (–N=), 1388 (NH_{def}), 1174 (S=O), 1006 ($NH_{endocycl}$), 754 (C–H_{def}), 696 (C–S–C). Found, %: C 65.75; H 9.06; N 5.49; S 12.49. $C_{224}H_{346}N_{16}O_{16}S_{16}$. Calculated, %: C 66.72; H 8.65; N 5.56; S 12.72.

Synthesis of ammonium salt of aluminum octakis-4,5-(4-sulfophenylsulfanyl)phthalocyanine (11). A mixture of 0.10 g (0.05 mmol) of compound **8** and 5 mL of 24% aqueous ammonia was heated in a porcelain dish until the solvent evaporated completely, and the resulting compound was extracted by DMF and purified by column chromatography on M60 silica, using DMF as an eluent. Yield 0.082 g (80%). IR spectrum, ν, cm^{-1}: 1615 (C–$C_{skeleton}$), 1527 (–N=), 1160 (S=O), 1280 (C_{Ar}–H), 723 (C–H_{def}), 693 (C–S–C). Found, %: C 42.85; H 3.45; N 9.94; S 22.88. $C_{80}H_{72}AlClN_{16}O_{24}S_{16}$. Calculated, %: C 43.34; H 3.27; N 10.11; S 23.14.

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