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Synthesis and Study of Properties of the Sulfonaphthylazophenoxyphthalonitrile and Related Phthalocyanine

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Abstract—The 4-[4'-(5-sulfonaphthylazo)phenoxy]phthalonitrile potassium salt was synthesized by the reaction of 4-chlorophthalonitrile with 5-(4'-hydroxyphenylazo)-1-naphthalenesulfonic acid, and on its basis was obtained tetra-4-[4'-(5-sulfonaphthylazo)phenoxy]phthalocyanine. The products were characterized by elemental analysis, IR and electron spectroscopy. The effect of the introduced substituent on the spectral and other properties of the synthesized compounds was demonstrated.

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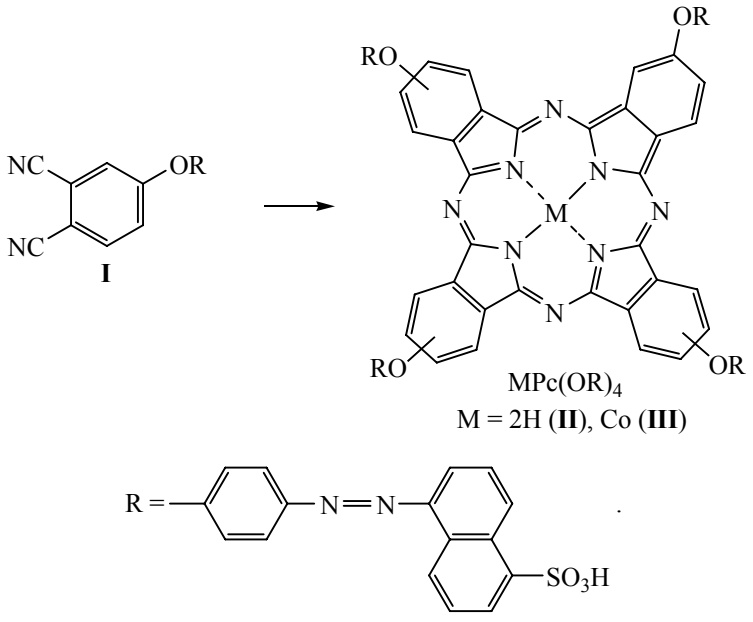
Substituted phthalocyanines (Pc) containing sulfo-, aryloxy-, and other groups [1–3] are well represented in the literature. However, data on the binding of azo and phthalocyanine chromophores are limited [4], although such compounds are of particular interest to scientists and practitioners, in particular as dyes.

This communication is devoted to the synthesis and study of physico-chemical properties of nitrile **I** and phthalocyanines **II** and **III** based on it, containing in their structure a fragment of the azo dye (Scheme 1).

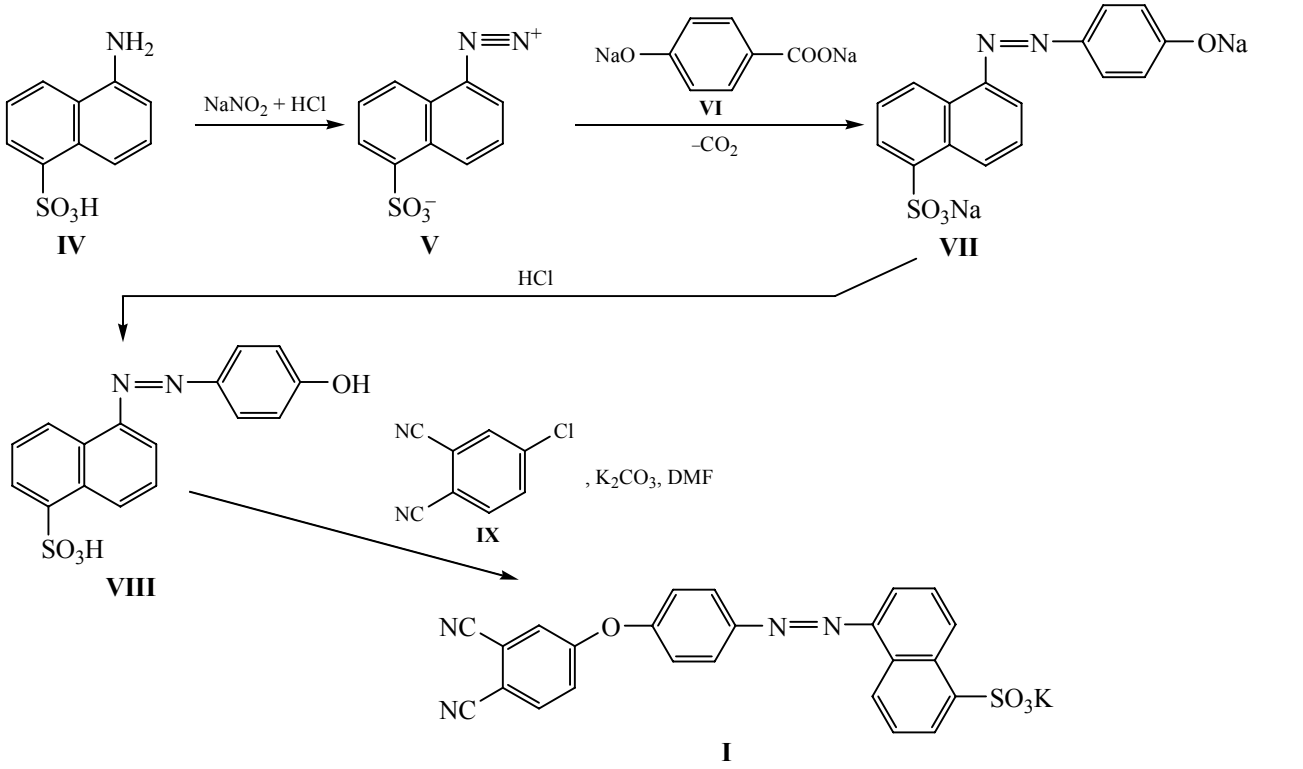
The nitrile **I** was synthesized in correspndence with the Scheme 2.

Diazotization of 5-amino-1-naphthalenesulfonic acid (**IV**) afforded the diazo compound **V**, which was introduced to the azo coupling reaction with the *p*-

Scheme 1.



Scheme 2.



hydroxybenzoic acid sodium salt **VI**. This reaction belongs to a particular case when the azo coupling takes place with the displacement of substituents (carboxyl group) [5]. The resulting dye **VIII** was isolated as 5-(4'-hydroxyphenylazo)-1-naphthalenesulfonic acid by adding concentrated hydrochloric acid to the solution of compound **VII**.

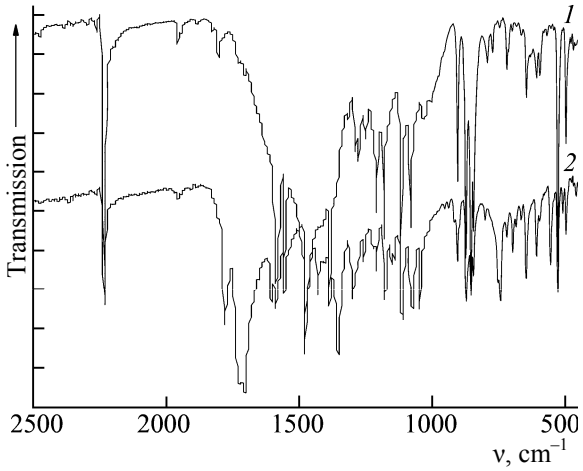


Fig. 1. IR spectrum: (*1*) 4-chlorophthalonitrile **IX** and (*2*) compound **I**.

Then we used 4-chlorophthalonitrile **IX**, obtained by the known procedure [6], and by nucleophilic substitution of chlorine atom in **IX** by the residue R of the azo dye **VII** in the medium of DMF, in the presence of K_2CO_3, we obtained 4-[4'-(5-sulfonaphthylazo)phenoxy]phthalonitrile potassium salt **I**. Choice of 4-chlorophthalonitrile **IX** as a substrate for the reaction of nucleophilic substitution is due to existing in its benzene ring of electron-withdrawing substituents (C≡N group), which induce an effective positive charge on the chlorine-containing carbon atom and thus contribute to the replacement of the halogen atom. The use of DMF as a solvent due to the fact that in polar solvents the reaction rate of nucleophilic substitution increases by 3–5 orders of magnitude compared with non-polar solvents [7]. From the data in the literature [8] we know that the role of K_2CO_3 consists in the transformation of ArOH into the ArO^- anion, which is more reactive in nucleophilic substitution than ArOH.

Compound **I** is a red-orange substance, soluble in water, DMF, acetone, and ethanol. Its identification was performed using the data of elemental analysis and infrared spectroscopy. Comparing the IR spectra of the source target nitriles, **IX** and **I** (Fig. 1), note the

preservation of the bands at 2230–2240 cm^{-1} corresponding to stretching vibrations of nitrile groups. In the spectrum of the nitrile **I** appears an absorption band in the range of 1250–1260 cm^{-1} characteristic of the Ar–O–Ar vibrations, bands in the ranges 1430–1350 and 1210–1150 cm^{-1} related to the symmetrical and asymmetrical S=O vibrations in the in sulfo group. The band at 1630–1575 cm^{-1} due to the stretching vibrations of the azo group (N=N) [9].

By heating the nitrile **I** at a temperature of 205–210°C with K_2CO_3, which serves as an alkaline agent [10], and subsequent reprecipitation of the product by adding concentrated sulfuric acid, we isolated phthalocyanine **II**. Synthesis of compound **III** was carried out by annealing the nitrile **I** with anhydrous cobalt chloride at 195–200°C.

The resulting complex **III** and compound **II** were reprecipitated from concentrated sulfuric acid, and final purification of **II** and **III** was performed by column chromatography on a M60 silica gel using DMF as eluent.

Tetra-4-[4'-(5-sulfonaphthylazo)phenoxy]phthalocyanine **II** is a substance of dark green color, and its cobalt complex **III** is a blue-green powder. The phthalocyanines **II** and **III** are readily soluble in DMSO, DMF and aqueous alkaline solutions.

To identify the compounds **II** and **III** we used the data of elemental analysis, IR and electron spectroscopy.

When comparing the infrared spectra of the synthesized phthalocyanines **II, III** with the spectra of H_2Pc and CoPc [11] was noted the coincidence of a large number of bands, However, the resolution of the spectrum (the number and clarity of bands) in the synthesized compounds are smaller, which is characteristic of phthalocyanine sulfonic acids [12] (Fig. 2). In addition, in the spectra of phthalocyanines **II** and **III** there are absorption bands noted for the nitrile **I** and the corresponding to Ar–O–Ar, S=O, and N=N vibrations in the substituent R. Analysis of electron absorption spectra (EAS) of the phthalocyanine **I** in organic solvents (DMF, DMSO) revealed the presence of a doublet in the long wavelength region (see the table and Fig. 3), which is characteristic of the metal-free compounds and is explained by the D_{2h} symmetry [13]. In going from the phthalocyanine **II** to its complex with cobalt **III** is observed an increase in symmetry from D_{2h} to D_{4h} resulting in the merging two components of the *Q* band in the EAS into one [13]. This band is shifted bathochromically in comparison with the CoPc *Q*-band (see the table and Fig. 3).

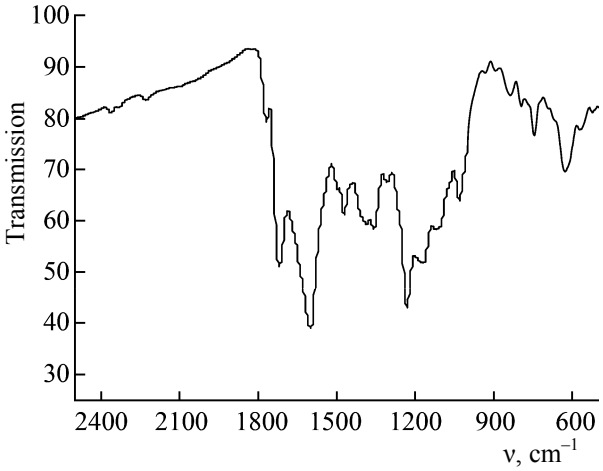


Fig. 2. IR spectrum of phthalocyanine **II**.

The position of bands in electron absorption spectra

Comp. no.	λ_{max}, nm (D/D_{max})			
	DMSO	DMF	0.5% NaOH	$H_2SO_{4\ vonc}$
II	325 (1.00), 634 (0.98), 675 (0.90)	672 (1.00), 698 (0.98), 325 (0.97), 645 sh (0.63)	622	524 (1.00), 825 (0.69)
III	326 (1.00), 668 (0.94), 605 sh (0.45)	666 (1.00), 325 (0.98), 600 sh (0.27)	628 (1.00), 675 (0.88)	811 (1.00), 524 (0.52)
VIII	–	385	–	524
X	–	660 (1.00), 330 (0.43), 385 (0.36), 597 sh (0.21)	–	784 (1.00), 524 (0.40), 693 (0.24)

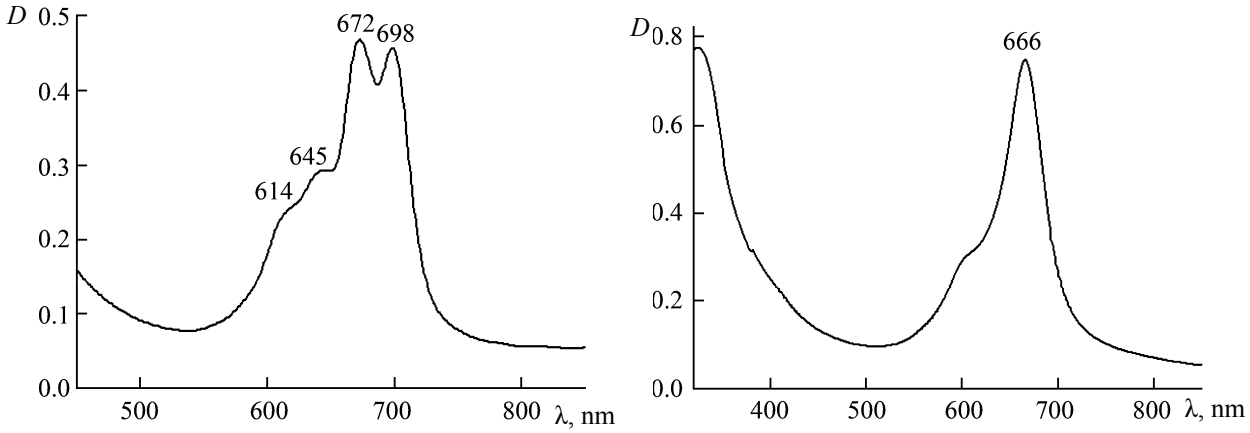


Fig. 3. The electron absorption spectra in DMF.

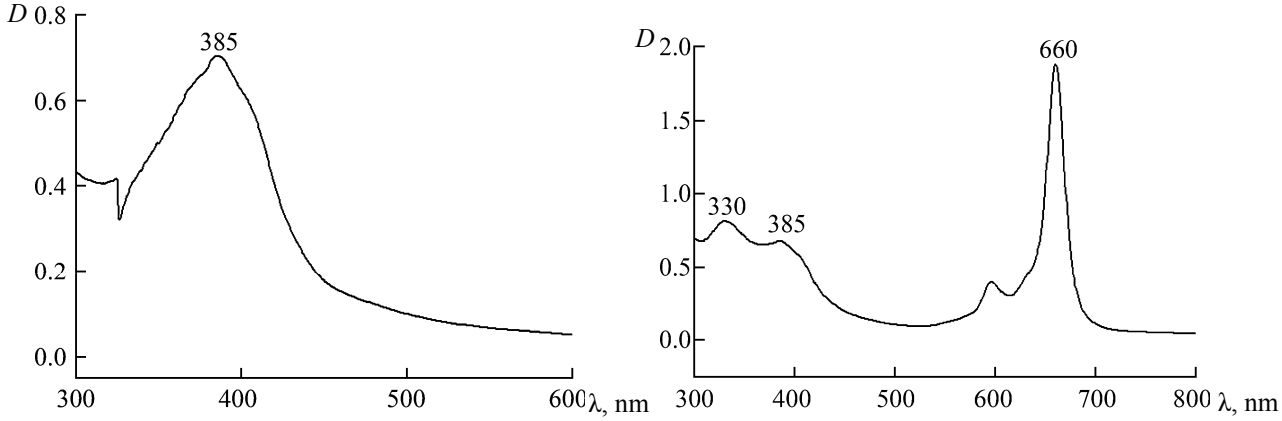


Fig. 4. The electron absorption spectra in DMF.

A distinctive feature of the spectra of phthalocyanines **II** and **III** solutions in organic solvents is the presence of absorption bands at 325–326 nm due to electron transitions in the chromophore system of the azo dye attached to the benzene rings of phthalocyanine macroring (see the table).

Due to the absence in the EAS of a pronounced absorption in the region characteristic for the azochromophore R, in order to confirm further the structure of the obtained phthalocyanine was prepared a mechanical mixture **X** containing CoPc + dye **VIII** in the ratio 1: 4 and, a the EAS of this mixture was compared with the EAS of compounds **III** and **VIII** (see the table). We noted the following. The EAS of the dimethylformamide solution of azo dye **VIII** contains a strong absorption band with a maximum at 385 nm (Fig. 4). In the spectrum of the mixture **X** there are 3 absorption bands, two of them are in the UV area: the CoPcs Soret band at 330 nm and absorption at 385 nm, noted earlier in the spectrum of the dye **VIII** (Fig. 4). The EAS of complex **III** contains two absorption bands, therewith the *Q*-band is broadened and shifted bathochromically by 6 nm compared with the *Q*-band of the mixture **X** (Fig. 3). Moreover, when the azo-chromophore is chemically bound to the phthalocyanine macroring the nature of the absorption in the UV area is changed: this band becomes wider and significantly increases in intensity, and is observed a 5 nm hypsochromic shift of this band in comparison with the CoPc Soret band of the mixture **X**. Absorption of the fragment of azo dye in the EAS of CoPc(4-OR)$_4$ **III** in organic solvents is veiled, probably due to the overlap of that this band by the Soret band. The intensity of the band due to the azochromofor absorption is much less than of the *Q*-band, although the molar the ratio of the azo dye to the Pc is 4: 1. This fact was previously reported in the literature [14] and

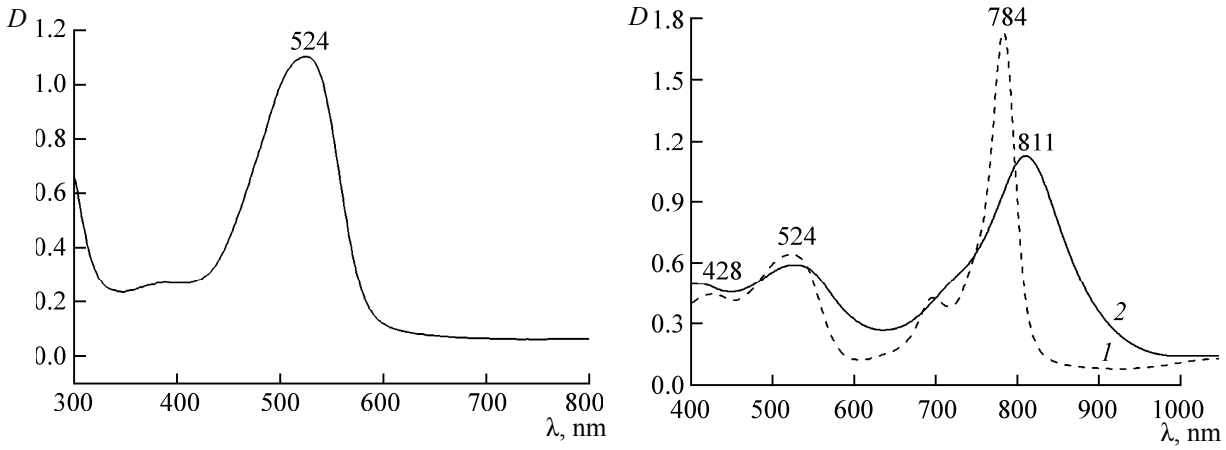


Fig. 5. The electron absorption spectra in concentrated H_2SO_4.

explained by the low value of its extinction coefficient compared with that of the phthalocyanine *Q*-band.

Due to the difficulty to distinguish the azo chromophore absorption in organic solutions of the synthesized complex **III**, we compared the EAS of the above compounds in concentrated sulfuric acid. In this case, unlike the spectrum of compound **III** in DMF, we revealed the bands at 524 nm due to absorption of the azo dye fragment and the weak Soret band. Similar bands are revealed in the spectrum of the mixture **X** (Fig. 5). In the long-wavelength region of the spectrum the *Q*-band of complex **III** is broadened and shifted bathochromically by 27 nm compared with the corresponding band of the mixture **X**.

As can be seen from the table and Fig. 5, in the EAS of both dye **VIII**, and phthalocyanines **II** and **III** occurs bathochromic shift of the absorption bands when going from organic solvents to sulfuric acid, obviously due to the processes of protonation [15].

Four sulfonic groups in the molecules of the synthesized phthalocyanine **II** and **III** provide them with good solubility in aqueous alkaline media. In the EAS in going from organic solvents to 0.5% solution of NaOH is observed hypsochromic shift of the long-wavelength band, which is associated with increased propensity of the molecules to the association in solution (Fig. 6).

Thus, the features of the spectral manifestations of the compounds **II** and **III** confirm the fact of chemical bonding of the azo and phthalocyanine chromophores.

Traditional for the compounds of the phthalocyanine series is their application as light-resistant dyes and pigments [5]. In this regard, we studied the color properties of the synthesized phthalocyanines **II** and **III**. We found that they show a substantivity toward protein and cellulose fibers and colorize them in bright green or blue green color.

EXPERIMENTAL

The electron absorption spectra of the synthesized metal complexes were recorded in the region of 300–900 nm on a HITACHI U-2001 spectrophotometer at room temperature. The solvents used are DMF, DMSO, 0.5% solution of NaOH, and sulfuric acid. The IR spectra were obtained on an AVATAR 360 FT-IR ESP spectrophotometer. The samples were prepared by standard KBr-tabletting technique. Elemental analysis was performed on a CHNS-O Flash EA 1112 series analyzer.

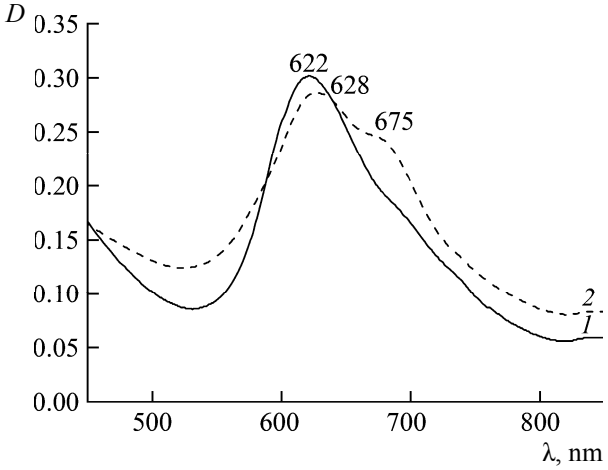


Fig. 6. The electron absorption spectra in 0.5% solution of NaOH: (*1*) compound **II** and (*2*) complex **III.**

1-Diazo-5-naphthalenesulfonic acid (V). To a porcelain cup equipped with a stirrer and a thermometer placed in a water bath was poured 150 ml of water heated to 35°C and at continuous stirring added 22.3 g (0.1 mol) of 1-amino-5-naphthalenesulfonic acid. The solution was then acidified with 30 ml (0.27 mol) of concentrated hydrochloric acid, and at stirring for 30 min at 30°C to it was slowly added dropwise 24 ml (0.13 mol) of 30% solution of sodium nitrite from a dropping funnel. In the course of the reaction was maintained acidic reaction of medium.

5-(4'-Hydroxyphenylazo)-1-naphthalenesulfonic acid (VIII). In a porcelain cup, equipped with a stirrer and thermometer was added 32 ml of 25% solution of sodium carbonate and 13.8 g (0.1 mol) of *p*-hydroxybenzoic acid. The solution was cooled by adding ice to 8–10°C and 15 g of sodium chloride was added. Then, at vigorous stirring from the dropping funnel was added dropwise a solution of 1-diazo-5-naphthalenesulfonic acid. The azo coupling was carried out at a temperature of 14–15°C. After the introduction of the whole amount of 1-diazo-5-naphthalenesulfonic acid the stirring was continued for another 30 min. Then to the solution was added concentrated hydrochloric acid, the dye precipitated was filtered off on a Buchner funnel and dried in a drier at 50°C. Yield 29.8 g (95%). Found, %: C 58.21, H 3.86, N 8.56, S 9.51. $C_{16}H_{12}N_2O_4S$. Calculated, %: C 58.53, H 3.68, N 8.53, S 9.76. IR spectrum (KBr), ν cm^{-1}: 1563 (N=N), 1030 (S=O). EAS, λ max, nm: 385 (DMF), 524 (H_2SO_4 conc.).

4-[4'-(5-Sulfonaphthylazo)phenyloxy]phthalonitrile potassium salt (I). A flask equipped with stirrer, reflux condenser and thermometer was charged with 30 ml of DMF, 1.63 g (0.01 mol) of 4-chlorophthalonitrile, 7.2 g (0.015 mol) of potassium carbonate and 4.92 g (0.015 mol) of 5-(4'-hydroxyphenylazo)-1-naphthalenesulfonic acid. The resulting mixture was heated with stirring to 140–150°C and held at that temperature for 3 h. End of reaction was determined from the completness of dissolution of a sample of the reaction mixture in water. DMF was evaporated under vacuum. The 4-[4'-(5-sulfonaphthylazo)phenoxy]-phthalonitrile potassium salt was extracted with acetone in a Soxhlet apparatus. Acetone was distilled off, dry residue was mixed with ethanol, the solution in the alcohol solution was filtered and ethanol was distilled off. The resulting product was dried under vacuum. Yield 3.65 g (74.1%), mp 120–125°C. Found, %: C 58.43, H 2.80, N 11.28, S 6.38. $C_{24}H_{13}KN_4O_4S$. Calculated, %: C 58.52, H 2.66, N 11.37, S 6.51. IR spectrum (KBr): 2231 (C≡N), 1182 (Ar–O–Ar), 1586 (N=N), 1118 (CS), 1208, 1386 (S=O).

Tetra-4-[4'-(5-sulfonaphthylazo)phenyloxy]-phthalocyanine (II). To a porcelain cup was placed a pounded mixture of 0.49 g (0.001 mol) of 4-[4'-(5-sulfonaphthylazo)phenyloxy]phthalonitrile potassium salt and 0.21 g (0.0015 mol) of potassium carbonate. The mixture was heated to 210–215°C and kept for 1 h. After cooling, the reaction mixture was crushed and dissolved in concentrated sulfuric acid. The resulting solution was poured on ice, the precipitate formed was filtered off on a Schott filter, washed with water till neutral reaction. Final purification was performed by column chromatography on silica gel M 60 using DMF as eluent. Yield 0.63 g (33.7%). Found, %: C 62.12, H 3.62, N 12.05, S 6.45. $C_{96}H_{58}N_{16}O_{16}S_4$. Calculated, %: C 63.36, H 3.21; N 12.31, S 7.05. EAS, λ_{max}, nm: 325, 645, 672, 698 (DMF); 325, 634, 676 (DMSO), 622 (0.5% aqueous solution of NaOH); 524, 825 (H_2SO_4 conc.).

Tetra-4-[4'-(5-sulfonaphthylazo)phenyloxy]-phthalocyanine cobalt (III). A well pounded mixture of 0.48 g (1 mmol) of 4-[4'-(5-sulfonaphthylazo)-phenyloxy]phthalonitrile potassium salt and 0.04 g (0.3 mmol) of anhydrous cobalt chloride was heated to a temperature of 195–200°C and kept for 30 min. After cooling, the reaction mixture was crushed and dissolved in concentrated sulfuric acid. The resulting solution was poured on ice. The precipitate was filtered off on a Schott filter, washed with water till neutral reaction. Final purification was performed by column chromatography on silica gel M 60, using DMF as eluent. Yield 0.23 g (50%). Found, %: C 53.4, H 2.5, N 10.1, S 4.9. $C_{96}H_{56}CoN_{16}O_{16}S_4$. Calculated, %: C 61.4, H 3.01, N 11.9, S 6.8. EAS, λ_{max}, nm: 325, 666; 600 sh. (DMF); 326; 668, 605 sh. (DMSO), 628, 675 (0.5% aqueous NaOH); 524, 811 (H_2SO_4 conc.).

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