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Synthesis and Spectral Properties of Unsymmetrical Phthalocyanines from 3,6-Dioctyloxyphthalonitrile and 3,4,5,6-Tetrachlorophthalonitrile

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Abstract—The random condensation of 3,6-dioctyloxyphthalonitrile (component A) with 3,4,5,6-tetrachlorophthalonitrile (component B) results in unsymmetrical phthalocyanines of A_3B, ABAB, and AABB types. Their spectral properties were studied.

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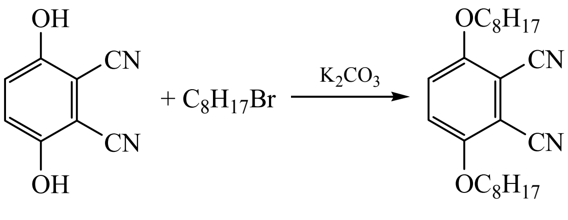
The unsymmetrically substituted phthalocyanines and porphyrazines are very interesting compounds. When the molecule contains both electron-releasing and electron-withdrawing substituents, they have a polarized electronic structure [1] and are promising for the use in optics [2, 3]. Moreover, the phthalocyanines containing bulky alkyl or alkoxy substituents often exhibit the liquid crystal properties [4–6]. The features of the molecular and electronic structures of the unsymmetrically substituted phthalocyanines provide a possibility of their use in the nanotechnology. [7]

This work reports the data on the synthesis of unsymmetrical phthalocyanines containing both strong electron-releasing and electron-withdrawing substituents, and on their spectral properties.

The random condensation of two differently substituted phthalonitriles A and B [8, 9] is the most frequent method of the synthesis of similar compounds. In this work, 3,6-dioctyloxyphthalonitrile **I** and 3,4,5,6-tetrachlorophthalonitrile **II** were used as components A and B, respectively.

We have chosen compound **I** due to the presence of two bulky alkoxy substituents in its molecule resulting in significant steric hindrances for the symmetrical octaoctyloxyphthalocyanine formation that increases the reaction selectivity. Nitrile **I** was obtained by the alkylation of 3,6-dihydroxyphthalonitrile **III** with 1-bromooctane in DMF in the presence of K_2CO_3 (Scheme 1).

Scheme 1.

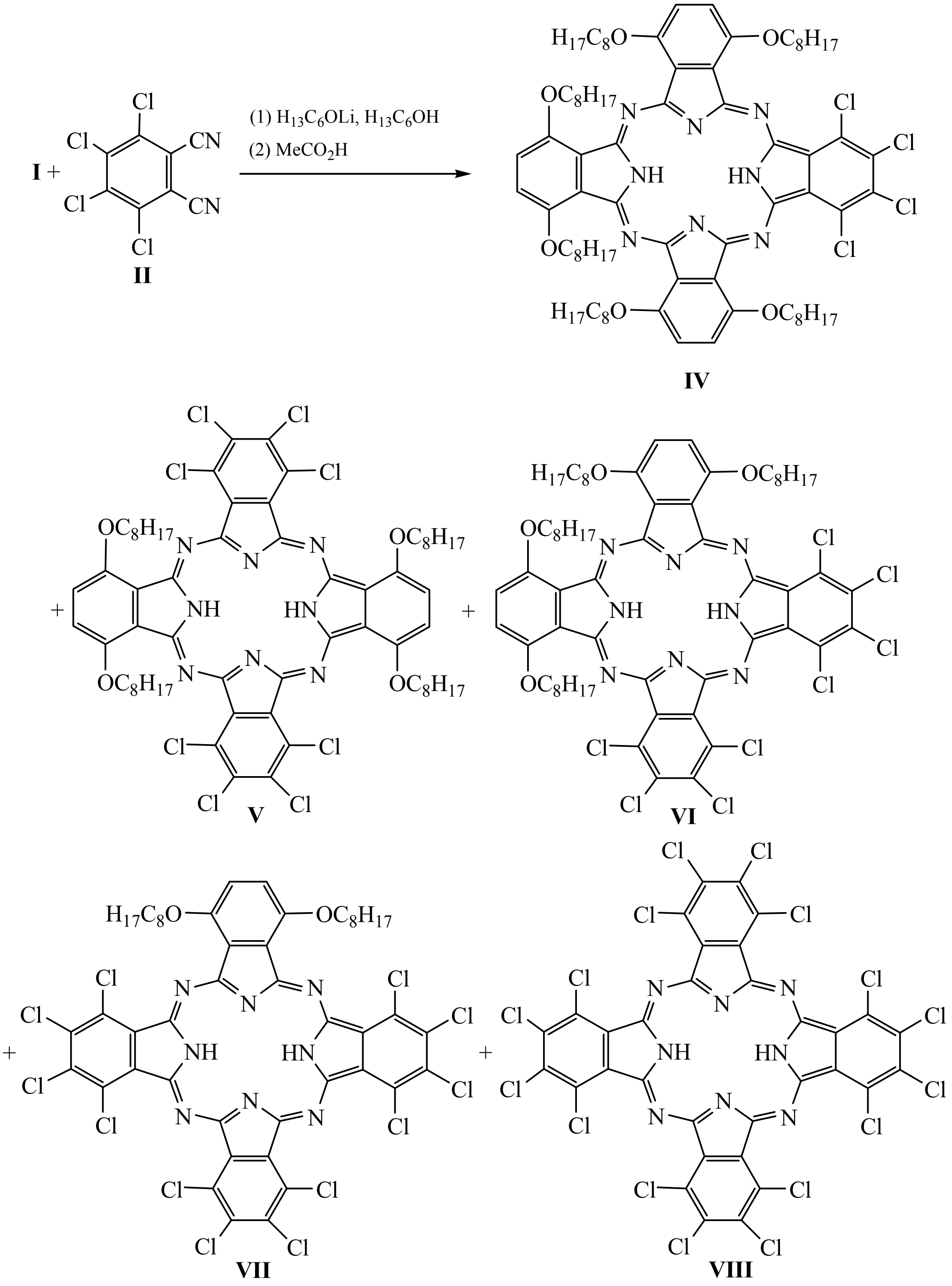


III **I**

Compound **I** is a light-gray powder soluble in benzene and chloroform and sparingly soluble in DMF and acetone. Its composition and structure were confirmed by the elemental analysis data, IR and ^{1}H NMR spectroscopy, and mass spectrometry.

In the IR spectrum of **I** there are absorption bands at 3087 and 2919 cm^{-1} originating from the C–H bonds vibrations in the aryl and alkyl substituents, respectively. The absorption band at 2224 cm^{-1} belongs to the cyano groups vibrations. The absorption bands at 1198 and 1078 cm^{-1} indicate the presence of the C–O–C fragment. The ^{1}H NMR spectrum of nitrile **I** contains a singlet at 7.17 ppm corresponding to the resonance of two aromatic protons. A triplet at 4.08–4.04 ppm belongs to four α-protons of the alkyl groups; four β-protons, and four γ-protons resonate as two triplets at 1.86–1.82 and 1.50–1.46 ppm, respectively. A multiplet at 1.32–1.25 ppm corresponds to the proton resonance of sixteen terminal methylene groups. Six methyl protons resonate as a triplet at 0.90–0.87 ppm. The EI mass spectrum of nitrile **I** contains the following signals, *m*/*z*: 384 $[M]^+$, 357 $[M - HCN]^+$, 255 $[M - OC_8H_{17}]^+$, 126 $[M - 2OC_8H_{17}]^+$.

Scheme 2.



The heating of a mixture of nitriles **I** and **II** in a molar ratio of 3:1 in the boiling 1-hexanol in the presence of lithium 1-hexanolate followed by the treatment with acetic acid results in a mixture of phthalocyanines **IV–VIII**. 1,4,8,11,15,18-Hexaoctyloxy-22,23,24,25-tetrachlorpphthalocyanine **IV** (A_3B), 1,4,15,18-tetraoctyloxy-8,9,10,11,22,23,24,25-octachlorophthalocyanine **V** (ABAB) and 1,4,8,11-tetraoctyloxy-15,16,17,18,22,23,24,25-octachlorophthalocyanine **VI** (AABB) were isolated by the column chromatography (Scheme 2).

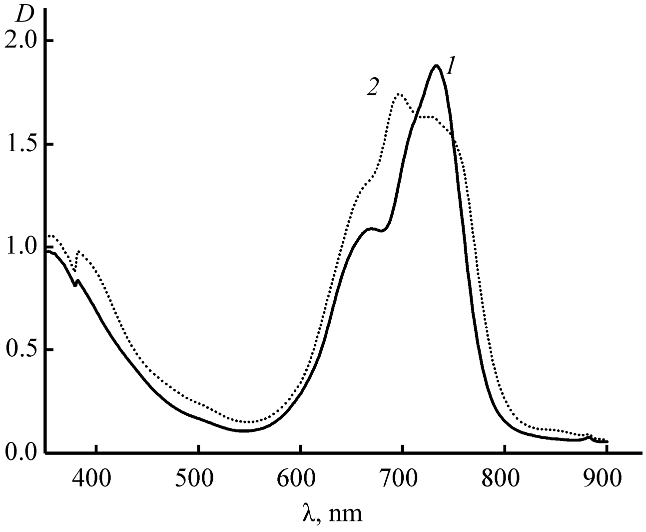


Fig. 1. Electronic spectra of compound **IV** in (*1*) $CHCl_3$ and (*2*) [$CHCl_3$ + 10% $NHEt_2$].

As expected, octyloxyphthalocyanine (A_4) did not form under these experimental conditions. The phthalocyanines **VII** and **VIII** cannot be chromatographically isolated owing to a poor solubility in organic solvents.

The composition and structure of compounds **IV**–**VI** were confirmed by the elemental analysis data, IR, ^{1} H NMR, and electronic spectroscopy.

Their IR spectra contain some common absorption bands. Thus, the bands at 3280–3269 cm^{-1} are assigned to the N–H bond vibrations of the intracyclic imino group; a strong absorption band at 2955–2855 cm^{-1} corresponds to the vibrations of the C–H bonds of alkyl moieties; the absorption bands at 1498–1465 and 1274–1272 cm^{-1} belong to the vibrations of the C=C and C=N bonds in the macrocycle. In the IR spectra there are also the absorption bands at 1135–1130 (C_{Ar}–O), 1060–1056 (C_{Alk}–O), and 757–753 cm^{-1} (C–Cl).

The ^{1}H NMR spectra of phthalocyanines **IV**–**VI** contain three groups of signals corresponding to the resonance of the protons of the benzene rings, alkoxy substituents and the intracyclic N–H groups. When going from compound **IV** to **VI** the position of the signals varies slightly. Thus, in the case of the phthalocyanine **IV** a multiplet at 7.19–7.16 ppm belongs to six aromatic protons of the isoindole fragment. A multiplet at 4.17–4.11 ppm corresponds to the resonance of 12 methylene α-protons of six alkoxy substituents; 12 β-protons resonate as a multiplet at 1.88–1.84 ppm. The remaining 60 methylene protons give rise to a multiplet at 1.30–1.27 ppm. A triplet at 0.89–0.87 ppm belongs to 18 methyl protons. Two protons of the intracyclic imino groups are registered as a broad singlet at 1.06 ppm.

In the ^{1}H NMR spectra of compounds **V** and **VI** the signal of the intramolecular imino groups is shifted upfield to 0.10 and 0.41 ppm, respectively. This fact indicates a somewhat more planar molecular structure of compounds **V** and **VI**. The *cis*-isomer **VI** is slightly more distorted than the *trans*-isomer **V**.

In the ^{1}H NMR spectra of compounds **V** and **VI** the signals are broadened at the sample solutions concentrations of 1×10^{-3} M. When the solutions were diluted 10 times, the signals become more pronounced. These spectral changes are known [10] to appear in the case of compounds, which tend to associate in a solution. We believe that compounds **V** and **VI** have the significantly greater dipole moments than **IV**. Therefore, the main reason of their association in organic solvents is the dipole-dipole interaction.

The electron absorption spectra of phthalocyanines **IV**–**VI** are characterized by an intense absorption corresponding to the π–π*-transitions in the visible (*Q*-band) and UV range (*B*-band).

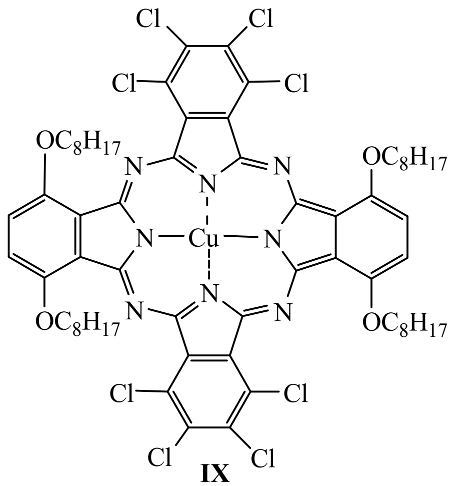
In the electron absorption spectrum of phthalocyanine **IV** (A_3B) (Fig. 1, curve *1*) the long-wave band is split in two components with the maxima at 733 and 669 nm. The short-wave part of this band contains an inflection at 706 nm. This character of the spectrum in the long-wave region is one of the characteristic features of the A_3B type phthalocyanines free of metal. The most long-wave component of the *Q*-band is the band of a charge-transfer from the donor to the acceptor part of the molecule [11]. In this case the tetrachlorobenzene fragment plays the acceptor role. The *B*-band has a maximum at 353 nm.

The presence of the electron-withdrawing substituents in the phthalocyanine molecules leads to an increase in their acidity [12]. So, the addition of a base to a solution of compounds **IV**–**VI** should result in changing their electron absorption spectra due to the dianions formation. Indeed, the addition of 10% of diethylamine to a solution of **IV** in chloroform causes the dianion formation, which is confirmed by the blue shift of the long-wavelength and short-wavelength components of a *Q*-band by 2 and 7 nm and by an increase in the relative intensity of the band at 697 nm (Fig. 1, curve *2*). The reason for this should be regarded as an increase in the molecular orbitals symmetry. The position of a *B*-band is not changed at the formation of dianion.

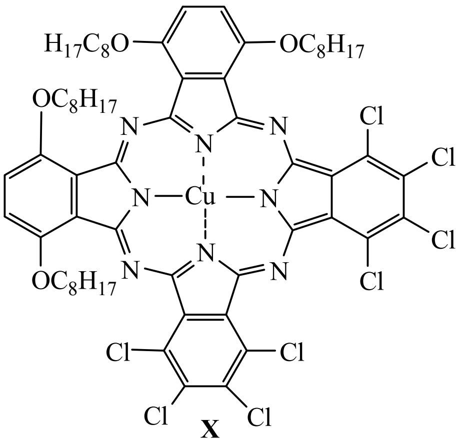
In the electronic spectrum of compound **V** (ABAB) (Fig. 2, curve *1*) the *Q*-band is split into three components with maxima at 847, 734, and 667 nm. An increase in the splitting degree of the *Q*-band is characteristic of the *trans*-isomers of the unsymmetrical phthalocyanines. According to the four-orbital Gouterman model [13] this is caused by the removal of the degeneracy of two lowest π*-molecular orbitals. In the spectrum of the dianion of **V** (Fig. 2, curve *2*) the *Q*-band suffers a red shift. Its short-wave component is shifted to 692 nm. The band at 734 nm is shifted to 758 nm with a simultaneous decrease in its relative intensity. The long-wave component is shifted to 853 nm. As in the case of phthalocyanine **IV**, the formation of the dianion of **V** does not significantly change the position of the *B*-band.

As would be expected, the electronic spectrum of phthalocyanine **VI** (AABB) (Fig. 3, curve *1*) contains only two components of the *Q*-band with maxima at 737 and 667 nm. These bands are in the same areas as in the spectrum of compound **V**. However, if the spectrum of the latter contains the strongest band at 667 nm, in the spectrum of phthalocyanine **VI** the band with a maximum at 737 nm is the strongest. In the spectrum of the dianion of compound **VI** (Fig. 3, curve *2*) the long-wavelength component of the *Q*-band undergoes a blue shifting to 691 nm, i.e., by 45 nm. Its long-wave part contains an inflection at 759 nm.

To study the effect of the complexation on the spectral properties of phthalocyanines **V** and **VI**, we synthesized their complexes **IX** and **X**, respectively, by the reaction with copper acetate in a DMF solution.



IX



X

The electron absorption spectrum of the metal complex **IX** (Fig. 4, curve *1*) contains two components of the *Q*-band with the maxima at 740 and 662 nm. In the case of compound **X** (Fig. 4, curve *2*), there is no splitting of the *Q*-band with a maximum at 658 nm. This change in the spectrum is due to an increase in the symmetry of the occupied molecular orbitals as a result of replacing two intracycle hydrogen atoms with the copper cations.

In the electron absorption spectra of phthalocyanines **V** and **VI** and their complexes **IX** and **X** there is a noticeable bands broadening, which confirms the assumption made earlier on the association of the synthesized phthalocyanines in a solution owing to the dipole–dipole interaction.

EXPERIMENTAL

The electron absorption spectra were measured on a Hitachi UV-2001 spectrophotometer. The IR spectra

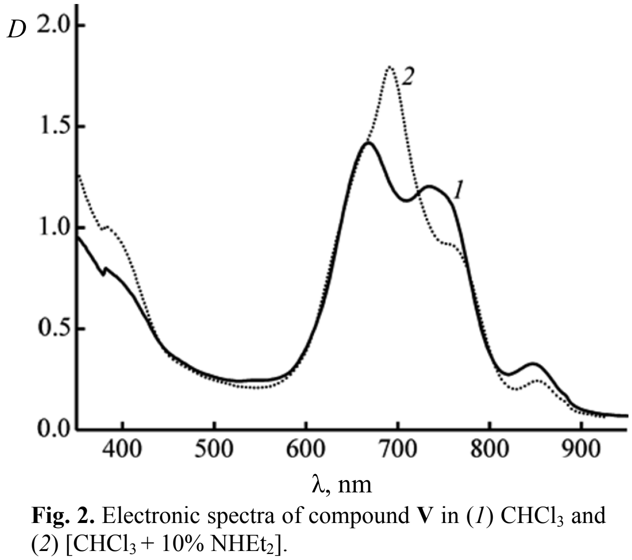


Fig. 2. Electronic spectra of compound **V** in (*1*) $CHCl_3$ and (*2*) [$CHCl_3$ + 10% $NHEt_2$].

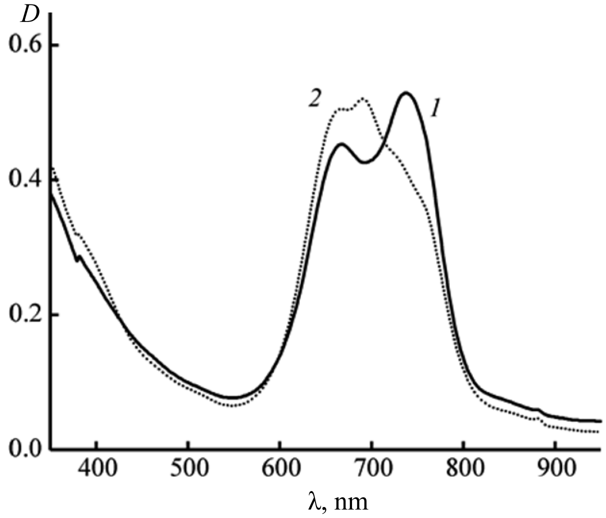


Fig. 3. Electronic spectra of compound **VI** in (*1*) $CHCl_3$ and (*2*) [$CHCl_3$ + 10% $NHEt_2$].

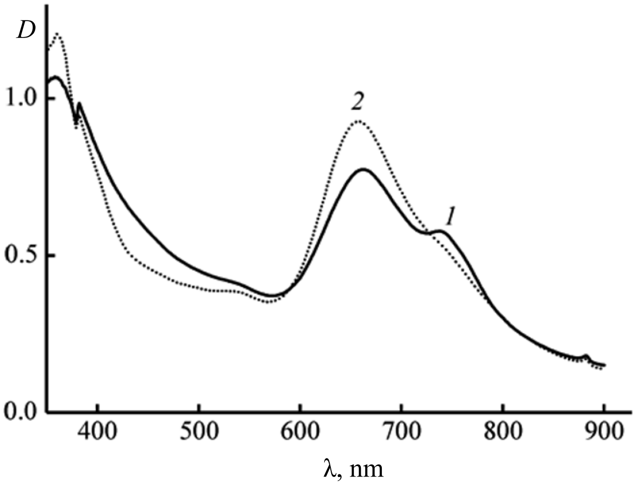


Fig. 4. Electronic spectra of compounds (*1*) **IX** and (*2*) **X** in $CHCl_3$.

were recorded on an Avatar 360 FT-IR spectrophotometer in the range of 400–4000 cm^{-1} from thin films on a TlI glass. The ^{1}H NMR spectra were registered on a Bruker Avance- 500 instrument using $CDCl_3$ as a solvent. The mass spectra were taken on a Varian Saturn 2000R GC-mass spectrometer. The elemental analysis was performed on a Flash EA 1112 CHNS-O analyzer.

3,4,5,6-Tetrachlorphthalonitrile **II** (98%) and 3,6-dihydroxyphthalonitrile **III** (98%) were purchased from Aldrich and used without further purification.

3,6-Dioctyloxyphthtalonitrile (I). A mixture of 2.0 g (12.5 mmol) of 3,6-dihydroxyphthtalodinitrile **III**, 5.3 g (27.5 mmol) of 1-bromooctane, 6.9 g (50 mmol) of K_2CO_3, and 30 ml of DMF was stirred at 130°C for 10 h, then cooled, and diluted with 100 ml of water. The precipitate was filtered off, washed with 20 ml of 10% HCl solution, 50 ml of water, 20 ml of acetone, and dried. Yield 4.5 g (94%), pale gray powder, soluble in benzene, chloroform, slightly soluble in acetone. IR spectrum, ν, cm^{-1}: 3087, 2919, 2851, 2224, 1496, 1463, 1287, 1199, 1078, 832, 469. ^{1}H NMR spectrum, δ, ppm: 7.17 s (2H), 4.08–4.04 t (4H), 1.86–1.82 t (4H), 1.50–1.46 t (4H), 1.29 m (16H), 0.90–0.87 t (6H). Mass spectrum, *m*/*z* (I_{rel}, %): 384 (55) $[M]^+$, 357 (69) $[M - HCN]^+$, 255 (100) $[M - OC_8H_{17}]^+$, 126 (72) $[M - 2OC_8H_{17}]^+$. Found, %: C 74.71; H 9.47; N 7.12. $C_{24}H_{36}N_2O_2$. Calculated, %: C 74.96; H 9.44; N 7.28.

Condensation of 3,6-dioctyloxyphthalonitrile (I) with 3,4,5,6-tetrachlorophthalonitrile (II). To a boiling solution of lithium 1-hexanolate in 1-hexanol, prepared by dissolving 0.1 g of lithium in 20 ml of anhydrous 1-hexanol, were added 0.8 g (2.1 mmol) of compound **I** and 0.18 g (0.7 mmol) of compound **II**. After 4 h, the reaction mixture was cooled and mixed with 50 ml of acetone and 5 ml of acetic acid. The precipitate was filtered off, washed with 50 ml of acetone, and dried. The residue was dissolved in chloroform and chromatographed on a column filled with aluminum oxide of **II** grade activity eluting with a chloroform–acetone mixture (100:1). The phthalocyanines **IV**–**V** were isolated.

1,4,8,11,15,18-Hexaoctyloxy-22,23,24,25-tetrachlorophthalocyanine (IV) (A_3B). Yield 0.12 g (12%), green waxy substance, well soluble in benzene and chloroform, poorly soluble in acetone. Electron absorption spectrum, λ_{max}, nm (D/D_{max}): in $CHCl_3$, 733 (1.00), 706 pl, 669 (0.58), 353 (0.52); in [$CHCl_3$ + 10% $NHEt_2$], 731 (0.93), 697 (1.00), 662 (0.74), 355 (0.61). IR spectrum, ν, cm^{-1}: 3275, 2954, 2922, 2860, 1470, 1273, 1134, 1059, 795, 757. ^{1}H spectrum, δ, ppm: 7.19–7.16 m (6H), 4.17–4.11 m (12H), 1.88–1.84 m (12H), 1.30–1.27 m (60H), 1.06 s (2H), 0.89–0.87 t (18H). Found, %: C 67.81; H 7.99; N 9.27. $C_{80}H_{110}Cl_4N_8O_6$. Calculated, %: C 67.59; H 7.80; N 9.98.

1,4,15,18-Tetraoctyloxy-8-,9,10,11,22,23,24,25-octachlorophthalocyanine (V) (ABAB). Yield 0.13 g (29%), green waxy substance, well soluble in benzene and chloroform, poorly soluble in acetone. Electron absorption spectrum, λ_{max}, nm (D/D_{max}): in $CHCl_3$, 847 (0.23) 734 (0.85) 667 (1.00) 351 (0.67); in [$CHCl_3$ +

10% $NHEt_2$], 853 (0.14), 758 (0.51), 692 (1.00) 350 (0.71). IR spectrum, ν, cm^{-1}: 3269, 2955, 2925, 2855, 1616, 1498, 1466, 1274, 1130, 1058, 753. ^1H spectrum, δ, ppm: 6.95–6.89 m (4H), 4.15–4.08 m (8H), 1.85–1.82 m (8H), 1.35–1.32 m (40H), 0.87 m (12H), 0.10 s (2H). Found, %: C 59.34; H 5.84; N 8.39. $C_{64}H_{74}Cl_8N_8O_4$. Calculated, %: C 59.00; H 5.72; N 8.60.

1,4,8,11-Tetraoctylooxy-15,16,17,18,22,23,24,25-octachlorophthalocyanine (VI) (AABB). Yield 0.11 g (25%), green waxy substance, well soluble in benzene and chloroform, poorly soluble in acetone. Electron absorption spectrum, λ_{max}, nm (D/D_{max}): in $CHCl_3$, 737 (1.00) 667 (0.86) 352 (0.71); in [$CHCl_3$ + 10% $NHEt_2$] 759 pl, 691 (1.00) 664 (0.97), 354 (0.79). IR spectrum, ν, cm^{-1}: 3280, 2956, 2926, 2855, 1465, 1378, 1273, 1131, 1056, 752. ^1H spectrum, δ, ppm: 7.17 s (2H), 7.10 s (2H), 4.11–4.01 m (8H), 1.87–1.85 m (8H), 1.38–1.34 m (40H), 0.90 m (12H), 0.41 s (2H). Found, %: C 59.42; H 5.25; N 8.11. $C_{64}H_{74}Cl_8N_8O_4$. Calculated, %: C 59.00; H 5.72; N 8.60.

General procedure for the synthesis of phthalocyanines (IX, X). A mixture of 10 mg (0.008 mmol) of compound **V** or **VI**, 25 mg (0.10 mmol) of copper(II) acetate tetrahydrate, and 20 ml of DMF was heated for 1 h. After cooling, to the reaction mixture was added 100 ml of water and 20 ml of chloroform. The organic layer was separated, washed with 20 ml of water, and dried. The residue was dissolved in benzene and chromatographed on a column filled with aluminum oxide II grade activity eluting with a benzene–acetone mixture (10:1) and collecting the main violet zone.

Copper 1,4,15,18-Tetraoctyloxy-8,9,10,11,22,23,-24,25-octachlorophthalocyaninate (IX). Yield 8 mg (75%), dark violet waxy substance, well soluble in benzene and chloroform, poorly soluble in acetone. The electronic spectrum ($CHCl_3$), λ_{max}, nm (D/D_{max}): 740 (0.54) 662 (0.72) 352 (1.00). Found, %: C 56.03, H 5.48; N 8.19. $C_{64}H_{72}Cl_8CuN_8O_4$. Calculated, %: C 56.34, H 5.32; N 8.21.

1,4,8,11-Tetraoctyloxy-15,16,17,18,22,23,24,25-octachlorophthalocyaninate (X). Yield 7 mg (66%), dark violet waxy substance, well soluble in benzene and chloroform, poorly soluble in acetone. Electron absorption spectrum, λ_{max}, nm (D/D_{max}): 658 (0.77) 360 (1.00). Found, %: C 56.87, H 5.71; N 8.03. $C_{64}H_{72}Cl_8CuN_8O_4$. Calculated, %: C 56.34, H 5.32; N 8.21.

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