

Synthesis and Spectral Characteristics of Phthalocyanines of Unsymmetrical Structure Containing Fragments of 3,6-Didecyloxyphthalonitrile and 2-Methyl-5,6-dicyanobenzimidazole

N. E. Galanin, E. V. Kudrik, and G. P. Shaposhnikov

Ivanovo State University of Chemical Engineering, Ivanovo, 153000 Russia
e-mail: ttoc@isuct.ru

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Abstract—By alkylation of 3,6-dihydroxyphthalonitrile with 1-bromodecane and by reaction of 4,5-diaminophthalodinitrile with acetic acid were synthesized respectively 3,6-didecyloxyphthalonitrile (*A*) and 2-methyl-5,6-dicyanobenzimidazole (*B*). The random condensation of the dinitriles obtained provided unsymmetrical phthalocyanines of A_3B , $AABB$, and AB_3 type. Their spectral characteristics were investigated.

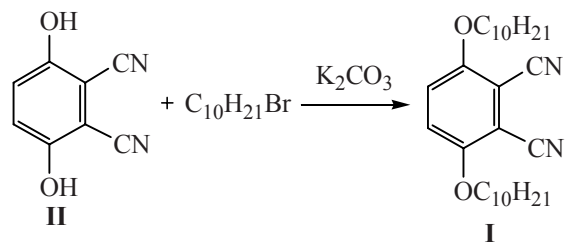
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Phthalocyanines belong to aromatic macrorings possessing a number of unique characteristics governing the range of their application. These compounds are used as valuable dyes [1], catalysts of various redox processes [2] etc. A special place in the series of this class compounds belongs to phthalocyanines of unsymmetrical structure where alternation occurs of nonuniformly substituted isoindole fragments bound by bridging nitrogen atoms. These compounds proved to be very promising as materials for nonlinear optics [3], liquid crystals substances [4, 5], and as compounds capable of providing highly regular monomolecular layers. Therefore the synthesis of these compounds is an essential problem.

According to the generally applied classification the unsymmetrical phthalocyanines are subdivided in three types: A_3B , $ABAB$, and $AABB$, where *A* and *B* are various peripheral fragments of the phthalocyanine molecule. Note that unlike the symmetrical analogs the phthalocyanines of unsymmetrical structure are relatively poorly documented. It is due to the difficulties met in their preparation, isolation, and purification.

Several methods exist for the synthesis of unsymmetrical phthalocyanines. However the most convenient procedure of preparation of these compounds is the random condensation of two different dinitriles or 1,3-diiminoisoindolines where one of the components contains bulky substituents providing for solubility of

the target substances in organic solvents. It was previously established [6] that 3,6-didecyloxyphthalonitrile (**I**) at heating with lithium 1-pentanolat in 1-pentanol was not capable to form a symmetrical octaalkoxyphthalocyanine due to sterical hindrances. In order to increase the selectivity of the random condensation nitrile **I** (component *A*) was also used in this study. It was prepared by alkylating 3,6-dihydroxyphthalonitrile (**II**) with 1-bromodecane in the presence of potassium carbonate.

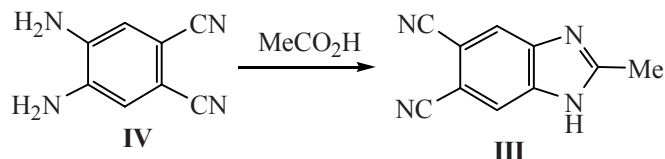


Our procedure is distinguished from that of [7] by the use of DMF instead of acetone as solvent. Therefore we were able to carry out the alkylation at 100°C and thus to reduce the process time from 56 to 20 h and to increase the yield of dinitrile **I** from 65 to 95%. Its composition and structure were confirmed by elemental analysis and IR spectrum. IR spectrum of compound **I** contained absorption bands in the region 3032–2936 cm^{−1} corresponding to the stretching vibrations of the C–H bonds in the alkyl groups, and also a band at 2304 cm^{−1} from the stretching vibrations of cyano groups. The bands

at 1116 and 1080 cm^{-1} originate from the stretching vibrations of the $\text{C}_{\text{Ar}}\text{--O}$ and $\text{C}_{\text{Alk}}\text{--O}$ bonds of the alkoxy substituents.

We employed as component *B* 2-methyl-5,6-dicyanobenzimidazole (**III**). The compounds containing benzimidazole structure attract interest for the benzimidazole heterocycle sometimes imparts to these compounds fluorescence property [8]. Besides the presence in the imidazole ring of pyrrole and pyridine type nitrogen atoms capable of entering into hydrogen bonds should favor formation of supermolecular aggregates arising in the course of crystallization or association. In their turn the supermolecular aggregates underlie the formation of columnar mesophases [9], and therefore the alkoxy-substituted phthalocyanine containing imidazole fragment can be promising for preparation of liquid crystal materials.

The synthesis of nitrile **III** was performed by the reaction of 4,5-diaminophthalonitrile (**IV**) prepared as described in [10] with excess acetic acid.



Compound **III** is a light-yellow powder soluble in hot water, DMF, acetone, dilute water solutions of mineral acids and alkali. Its composition and structure were confirmed by elemental analysis, IR and mass spectrum (ionization by electron impact). In the IR spectrum of dinitrile **III** the band at 3416 cm^{-1} corresponds to the vibrations of the N–H bond of the imidazole ring, in the region 2936 cm^{-1} appeared the bands of the stretching vibrations of the C–H bonds in the methyl group, the band at 2232 cm^{-1} belongs to the vibrations of cyano groups.

The mass spectrum of compound **III** contains the peak of the molecular ion of m/z 182 $[M]^+$, and also of its fragmentation products of m/z 167 $[M - \text{CH}_3]^+$ and 154 $[M - \text{HCN}]^+$.

The random condensation of nitriles **I** and **III** by heating with lithium butanolate in butanol followed by demetallation of the obtained dilithium phthalocyanines with acetic acid led to the formation of a mixture of unsymmetrically substituted phthalocyanines **V–VIII** in keeping with Scheme 1.

Phthalocyanines A_3B (**V**), $AABB$ (**VI**), and AB_3 (**VII**) due to their high solubility in organic solvents were

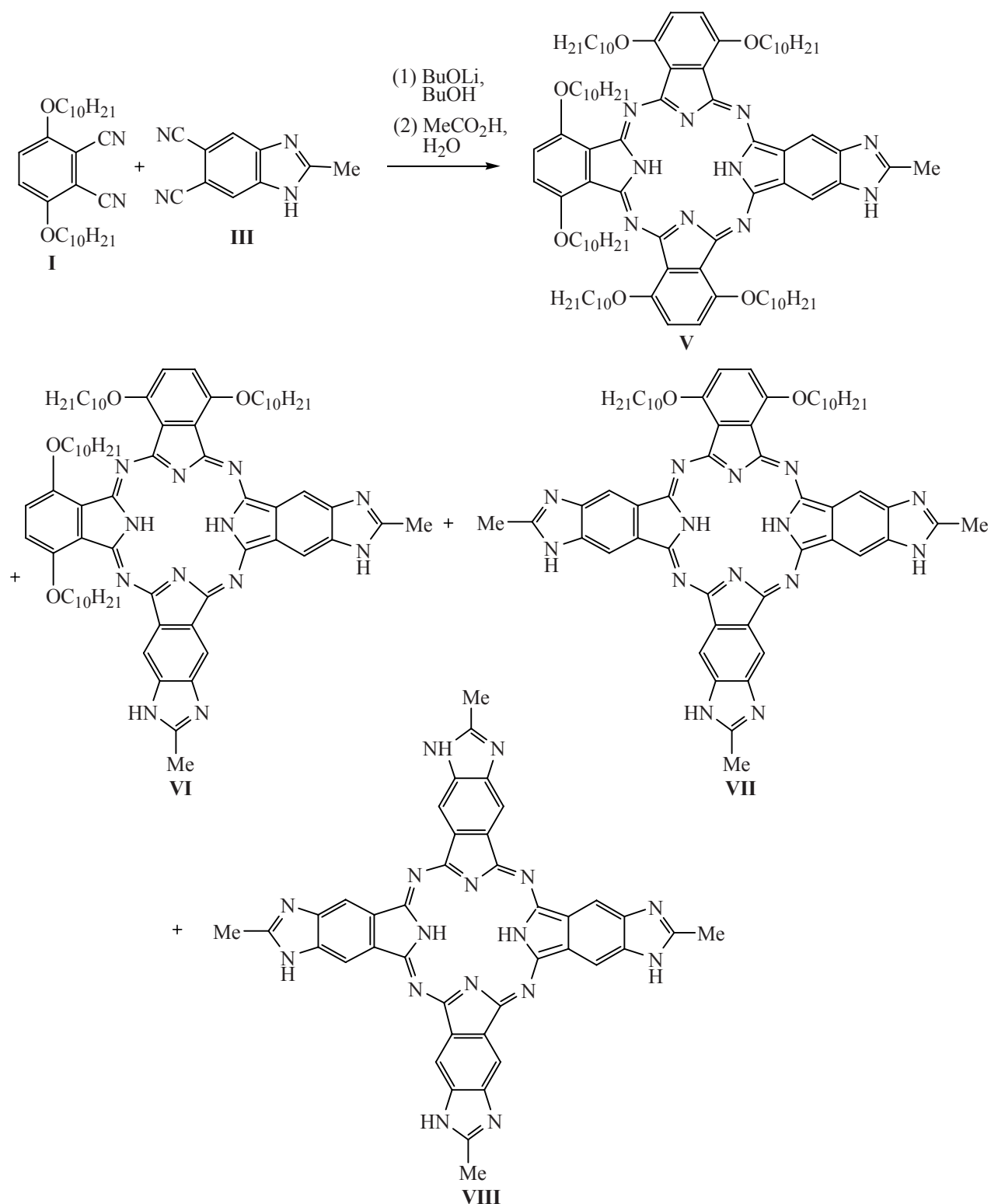
isolated from the mixture obtained by column chromatography. It turned out unexpectedly that phthalocyanine of the $ABAB$ structure did not form in significant amount in the course of the synthesis. It is evidently due to the more planar structure of the *cis*-isomer **VI** and therefore to its higher thermodynamic stability.

The homogeneity and structure of obtained phthalocyanines was proved by TLC, elemental analysis, vibration, ^1H NMR, and electronic spectroscopy.

In the IR spectra of obtained phthalocyanines **V–VII** a number of common bands is present. For instance, absorption bands in the region 3300–3286 cm^{-1} characterize the vibrations of N–H bonds in the imidazole rings, the bands at 3081–3076 cm^{-1} belong to the vibrations of N–H bonds of the endocyclic imino groups, the strong bands at 2954–2853 cm^{-1} correspond to the vibrations of C–H bonds of alkyl moieties. The strong bands at 1767, 1728, 1726, 1504, 1270 cm^{-1} characterize the vibrations of C = C and C = N bonds in the macroring and the benzimidazole structures. The bands at 1120 and 1179 cm^{-1} correspond to the vibrations of $\text{C}_{\text{Ar}}\text{--O}$ bonds, those at 1060 and 1058 cm^{-1} , to $\text{C}_{\text{Alk}}\text{--O}$ bonds.

In the ^1H NMR spectra of phthalocyanines **V–VII** five groups of signals are observed characterizing the proton resonances of endocyclic N–H groups, of oxydecyl substituents, of methyl groups from imidazole fragments, of aromatic protons of benzene rings, and of proton signals of N–H groups in the imidazole rings. Therewith in going from compound **V** to compound **VII** the positions of the signals change insignificantly, only their intensity varies. For instance, in phthalocyanine **V** the proton peak of the N–H group in the imidazole ring appears as a singlet at 8.97 ppm, two protons of the benzene ring from the benzimidazole structure are observed as a singlet at 8.51 ppm, the six protons from the decyloxy-substituted benzene rings give a multiplet in the region 6.90–7.10 ppm. In a stronger field at 4.01–3.95 ppm appears a triplet corresponding to 12 protons of the α -methylene groups of the oxydecyl substituents. The multiplet in the region 2.60–2.45 belongs to three protons of the methyl group at the imidazole fragment, the broadened singlet in the region 2.05–1.55 ppm characterizes the resonance of 96 protons of the 48 methylene groups of the oxydecyl, and the singlet at 0.88 ppm corresponds to 18 protons of the six terminal methyl groups of the same substituents. The most upfield singlet at -0.67 ppm belongs to two protons of the endocyclic imino groups. In the ^1H NMR spectra of compounds **VI** and **VII** the relative intensity of signals corresponding to the protons of CH_3 and N–H groups of the imidazole

Scheme 1.



fragments increased, and insignificant upfield shift of the proton peaks of the endocyclic imino groups was observed. This fact suggests that the molecules of compounds **VI** and **VII** have more planar structure.

The electron absorption spectra of phthalocyanines **V**–**VII** contain strong absorptions corresponding to π – π^* transitions in the visible (Q-bands) and UV region (B-bands).

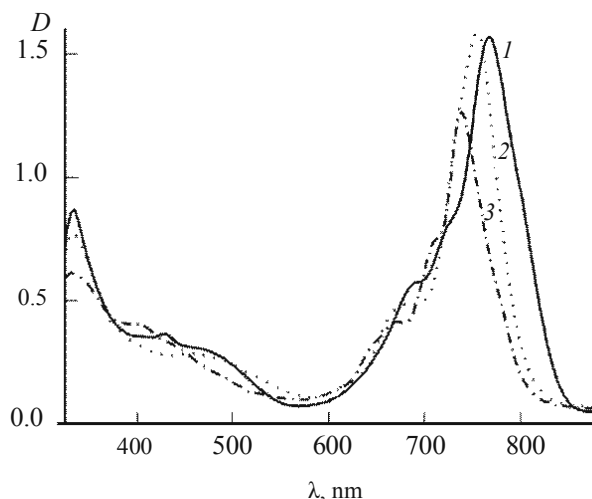


Fig. 1. Electron absorption spectra in CHCl_3 . (1) compound **V**; (2) compound **VI**; (3) compound **VII**.

In the electron absorption spectrum of phthalocyanine **V** (Fig. 1, 1) the Q-band is split in three components with the maxima at 767, 724, and 689 nm. Three-band spectrum in the longwave region is one of the characteristic features of metal-free phthalocyanines of the A_3B type, and the most longwave component corresponds to the charge transfer from the donor part of the molecule to the acceptor one [11], whose role play here the fragments of 2-methylbenzimidazole. A similar spectral pattern was previously observed for a phthalocyanine of the A_3B type containing three fragments of 3,6-dipentoxyphtalonitrile and one of unsubstituted phtalonitrile [12].

In the electron absorption spectrum of compound **VI** (Fig. 1, 2) the Q-band is split in two components with the maxima at 755 and 675 nm. The decrease in the number of bands in the spectrum of phthalocyanines of

the $AABB$ type compared with the compounds of the A_3B type can be understood involving a four-orbital model of Gouterman [13]. In keeping with this model the longwave bands in the electron absorption spectra of symmetrical phthalocyanines are regarded as electron transition from the a_{1u} orbital to two normal to each other degenerate orbitals e_g^* . In event of unsymmetrically substituted phthalocyanines the degeneration is removed, and the Q-band splits in two components of close intensity. The splitting in accordance with the theoretical prediction should be the least for compound of the $AABB$ type. In our case we observe just this pattern.

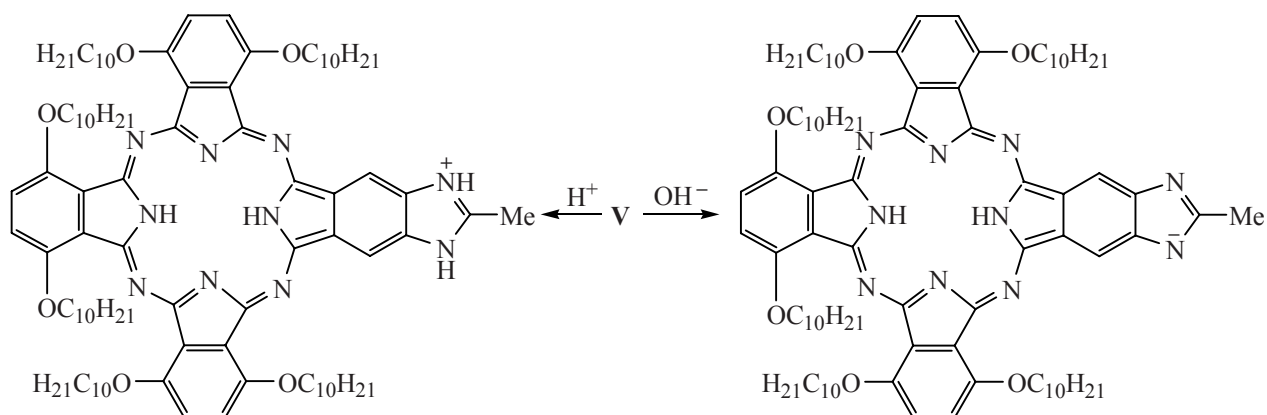
As to the electronic spectrum of compound **VII** (Fig. 1, 3), its character as expected is similar to that of the spectrum of phthalocyanine **V**. The Q-band is also split in three components with the maxima at 738, 708, and 669 nm, thus compared with the spectrum of compound **V** the maxima of bands suffer blue shift by 29, 16, and 20 nm respectively. This fact may be attributed to the decrease in the energy of HOMO a_{1u} under the effect of three moieties of 2-methylbenzimidazole acting as electron-acceptor substituents.

The spectra of compounds **V–VII** contain broadened bands in the region 401–463 nm that we believe to be the bands of charge-transfer from the donor to the acceptor part of the molecule.

The imidazole fragments included in the molecules of phthalocyanine **V–VII** are of amphoteric character and are capable of reacting with acids and bases. For instance, these reactions of compound **V** can be represented by Scheme 2.

These properties of the imidazole fragments suggest that the electronic spectra of the synthesized phthalocyanines should suffer significant changes depending on

Scheme 2.



the pH of the environment. Actually, the electron absorption spectrum of compound **V** registered in chloroform with added diethylamine (Fig. 2, 1) contains a Q-band with the maxima at 751 and 671 nm, therefore a blue shift of the maxima by 16–18 nm occurs compared with their position in the pH-neutral solvent. Besides the spectrum becomes two-band, and this may be ascribed to increased symmetry of the molecule. Evidently here considerably decreased the electron-acceptor capacity of the *B* fragment leading to diminished polarization of the whole molecule.

Another pattern was observed on registering the electron absorption spectrum of compound **V** in chloroform acidified with HCl (Fig. 2, 2). In this case a red shift of the Q-band maxima was observed to 865 and 751 nm, namely, by 98 and 62 nm. This may be due to the increase in the acceptor properties of fragment *B* and consequently the higher degree of the molecule polarization. This assumption is supported by the considerably increased relative intensity of the absorption band at 545 nm that is a charge-transfer band.

The electron absorption spectrum of phthalocyanine **VII** in the acidified chloroform contains a broadened Q-band with the maxima at 859 and 770 nm corresponding to the red shift of the band by 105 nm. The diffuse character of the band suggests a strong association of compound **VII** in solution. The band at 558 nm is also a charge-transfer band. As to the Soret band, it also undergoes the red shift by 40 nm.

Unlike compound **V**, the electronic spectrum of compound **VI** does not suffer considerable changes on adding to the chloroform solution of diethylamine. Evidently the formation of phthalocyanine **VI** dianion does not affect significantly the dipole moment of the molecule that governs the spectral characteristics of compound **VI**.

EXPERIMENTAL

Electron absorption spectra of compounds obtained were measured on a spectrophotometer Hitachi UV-2001, ^1H NMR spectra in CDCl_3 , on a spectrometer Bruker AMD-200 (200 MHz, internal reference TMS), IR spectra, on spectrophotometer Avatar 360 FT-IR in the range 400–4000 cm^{-1} from thin films, mass spectra were registered on a GC-MS instrument Varian Saturn 2000R. Elemental analysis was carried out on a FlashEA 1112 CHNS-O Analyzer.

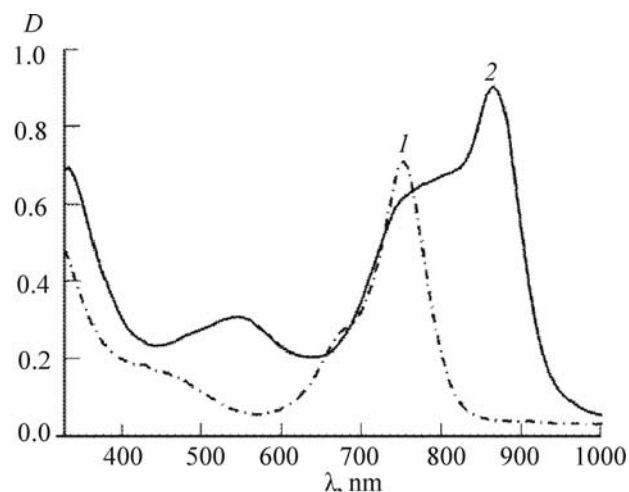


Fig. 2. Electron absorption spectra of compound **V**. (1) in $\text{CHCl}_3 + \text{NHEt}_2$, (2) in $\text{CHCl}_3 + \text{HCl}$.

3,6-Didecyloxyphthalonitrile (I). A mixture of 10.0 g (0.0625 mol) of 3,6-dihydroxyphthalonitrile (**II**), 55.2 g (0.25 mol) of 1-bromodecane, 34.5 g (0.25 mol) of K_2CO_3 , and 50 ml of DMF was stirred at 100°C for 20 h. On completion of the reaction the reaction mixture was cooled, diluted with water, and the separated precipitate was filtered off. The reaction product obtained was recrystallized from petroleum ether and DMF, washed with 50 ml of acetone, and dried at room temperature. Yield 26 g (95%), white powder, mp 148°C , well soluble in benzene, chloroform, insoluble in water, sparingly soluble in DMF and acetone. IR spectrum, ν , cm^{-1} : 3096, 3032, 2936, 2304, 1528, 1416, 1336, 1220, 1116, 1080, 832. Found, %: C 76.91; H 10.26; N 6.14. $\text{C}_{28}\text{H}_{44}\text{O}_2\text{N}_2$. Calculated, %: C 76.32; H 10.06; N 6.36.

2-Methyl-5,6-dicyanobenzimidazole (III). A mixture of 1.0 g (6.3 mmol) of 4,5-diaminophthalonitrile (**IV**) and 10 ml of acetic acid was heated to boiling and maintained at this temperature for 2 h, then the reaction mixture was cooled and poured into 50 ml of ice-water mixture. The separated precipitate was filtered off, washed with water, recrystallized from water, and dried. Yield 0.86 g (75%), light-yellow powder, mp 245°C , soluble in hot water, acetone, DMF, in dilute water solutions of mineral acids and alkali. IR spectrum, ν , cm^{-1} : 3416, 2936, 2232, 1664, 1600, 720. Mass spectrum (electron impact), m/z (I_{rel} , %): 182 [M] $^+$ (10), 167 [$M - \text{CH}_3$] $^+$ (100), 154 [$M - \text{HCN}$] $^+$ (25). Found, %: C 65.11; H 3.50; N 30.59. $\text{C}_{10}\text{H}_6\text{N}_4$. Calculated, %: C 65.93; H 3.32; N 30.75.

Condensation of 3,6-didecyloxyphthalonitrile (I) with 2-methyl-5,6-dicyanobenzimidazole (III). Into

a solution of lithium 1-butanolate in 1-butanol prepared from 0.2 g of lithium and 30 ml of anhydrous 1-butanol was charged 1.0 g (2.3 mmol) of compound **I**, and the mixture was kept at reflux for 1 h, then 0.7 g (4.0 mmol) of compound **III** was added, and the mixture was heated at reflux for 3 h more. The reaction mixture was cooled, and 10 ml of acetic acid and 20 ml of water was added, the separated precipitate was filtered off, washed on the filter with 30 ml of acetone, and dried. The residue was dissolved in benzene and subjected to chromatography on a column packed with silica gel 60 (eluent toluene–acetone, 10:1 v/v). Therewith the mixture separated into three zones containing phthalocyanines **V**, **VI**, and **VII** respectively.

1,4,8,11,15,18-Hexadecyloxy-2,3-(2-methylimidazolo)phthalocyanine (V) (A₃B). Yield 0.09 g (8%), green powder, well soluble in benzene, chloroform, insoluble in acetone and water. Electron absorption spectrum, $\lambda_{\max}$, nm ($D/D_{\max}$), (CHCl₃): 767 (1.00), 724 (0.51), 689 (0.36), 426 (0.23), 334 (0.55); (CHCl₃ + NHET₂): 751 (1.00), 674 (0.41), 463 (0.22), 330 (0.68); (CHCl₃ + HCl): 864 (1.00), 751 (0.68), 547 (0.34), 335 (0.77). IR spectrum, ν , cm⁻¹: 3286, 3081, 2954, 2923, 2853, 1728, 1599, 1504, 1377, 1270, 1182, 1121, 1060, 966, 889, 807, 760, 722, 597. ¹H NMR spectrum, δ , ppm: –67 s (2H), 0.88 s (18H), 1.55–2.05 s (96H), 2.45–2.60 m (3H), 3.95–4.01 t (12H), 6.90–7.10 m (6H), 8.51 s (2H), 8.97 s (1H). Found, %: C 75.01; H 9.15; N 8.64. C₉₄H₁₄₀N₁₀O₆. Calculated, %: C 74.96; H 9.37; N 9.30.

cis-1,4,8,11-Tetradecyloxydi[2,3-(2-methylimidazolo)]phthalocyanine (VI) (AABB). Yield 0.08 g (6%), violet powder, well soluble in benzene, chloroform, insoluble in acetone and water. Electron absorption spectrum, $\lambda_{\max}$, nm ($D/D_{\max}$), (CHCl₃): 754 (1.00), 674 (0.31), 463 (0.18), 331 (0.49); (CHCl₃ + HCl): 859 (1.00), 770 (0.91), 558 (0.52), 370 (1.55). IR spectrum, ν , cm⁻¹: 3300, 3081, 2954, 2924, 2853, 1767, 1726, 1614, 1499, 1467, 1367, 1278, 1216, 1179, 1058, 945, 823, 748, 640, 581. ¹H NMR spectrum, δ , ppm: –0.75 s (2H), 0.85 s (12H), 1.65–2.08 s (64H), 2.45–2.68 m (6H), 3.93–4.00 t (8H), 6.90–7.10 m (4H), 8.58 C (4H), 8.95 s (2H). Found, %: C 81.50; H 4.75; N 7.00. C₇₆H₁₀₂N₁₂O₄. Calculated, %: C 73.16; H 8.24; N 13.47.

1,4-Didecyloxytri[2,3-(2-methylimidazolo)]-phthalocyanine (VII) (AB₃). Yield 0.12 g (5%), violet powder, well soluble in benzene, chloroform, sparingly soluble in acetone, insoluble in water. Electron absorption spectrum, $\lambda_{\max}$, nm ($D/D_{\max}$), (CHCl₃): 738 (1.00), 708 (0.58), 669 (0.33), 401 (0.32), 331 (0.48). IR spectrum, λ , cm⁻¹: 3301, 3086, 2952, 2928, 2859, 1766, 1477, 1455, 1271, 1222, 1168, 1052, 755, 576. ¹H NMR spectrum, δ , ppm: –0.92 s (2H), 0.83 s (6H), 1.65–2.05 s (32H), 2.50–2.55 m (9H), 4.15–4.25 t (4H), 6.95–7.00 m (2H), 8.54 s (6H), 8.95 s (3H). Found, %: C 71.01; H 6.05; N 18.55. C₅₈H₆₄N₁₄O₂. Calculated, %: C 70.42; H 6.52; N 19.82.

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