Structural modification of unsymmetrically substituted monophthalocyanines by nucleophilic reactions

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New 2-nitro-substituted phthalocyanine zinc complexes were synthesized. The nucleophilic substitution of the NO_2 group was used for the first time for the structural modification of unsymmetrically substituted monophthalocyanines. The electronic absorption spectra of phthalocyanines were studied.

Key words: unsymmetrically substituted monophthalocyanines, synthesis, nucleophilic substitution.

Unsymmetrically substituted monophthalocyanines have attracted attention because of the unique optical, spectroscopic, and catalytic properties[1] and the ability to form ordered Langmuir—Blodgett monolayers.[2] Unsymmetrical complexes are used in nonlinear optics[3] and photodynamic cancer therapy.[4]

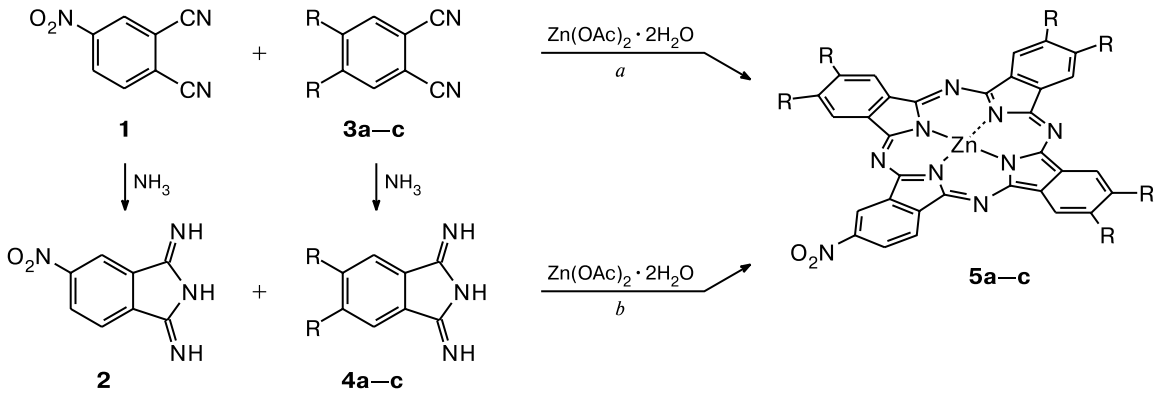
In recent years, the use of different types of unsymmetrically substituted monophthalocyanines in the synthesis of heteronuclear[5] and polynuclear complexes[6] has attracted considerable interest.

The aim of the present study was to develop approaches to the synthesis of unsymmetrical phthalocyanine complexes of the A_3B type containing three identical isoindole fragments by the structural modification of mononitrophthalocyanines.

Mononitrophthalocyanines are synthesized primarily by mixed cyclization starting from phthalonitriles or the corresponding 1,3-diiminoisoindolines.[7—9] Synthesis of these compounds by expansion of alkyl-substituted subphthalocyanine boron complexes with 5-nitro-1,3-diiminoisoindoline was documented.[10,11] However, both reactions afford the target products of A_3B type in rather low yields.

The previously unknown phthalocyanines **5a—c** were synthesized by fusion of phthalonitriles **1** and **3a—c** in the presence of zinc acetate in a ratio of 1 : 3 : 4 (Scheme 1, *a*).

Scheme 1



R = Et (**a**), Bu^n (**b**), OPr^n (**c**)

Reagents and conditions: *a*. fusion, 160 °C, 3 h; *b*. DMAE, refluxing, 2.5 h.

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The reaction afforded a statistical mixture of mixed cyclization products, the yields of the target compounds **5a—c** being only 1.5—2%. It has been noted[4] that it is necessary to increase the amount of phthalonitrile A by at least a factor of 10 compared to the amount of phthalonitrile B with the aim of preparing predominantly one product of the A_3B type. Actually, we succeeded in increasing the yields of complexes **5a—c** to 5—6% by increasing the amount of phthalonitriles **3a—c** to 10 equivalents. Further increase in the amount of **3a—c** has virtually no effect on the yields of **5a—c** but is accompanied by an increase in the amount of by-products due to their self-cyclization.

1,3-Diiminoisoindolines are often used as the starting compounds to increase the yields of the target mixed cyclization products.[7,9] Actually, we prepared **5a—c** in 14—16% yields by refluxing 1,3-diiminoisoindolines **2** and **4a—c** in *N*,*N*-dimethylaminoethanol (DMAE) in the presence of zinc acetate. We failed to prepare the target products by mixed cyclization of 1,3-diiminoisoindolines with phthalonitriles in the presence of zinc acetate. In this case, both components underwent independent self-cyclization.

The IR spectra of the previously unknown phthalocyanines **5a—c** have absorption bands in the regions of 1336—1340 and 1520—1524 cm^{-1} belonging to symmetric and antisymmetric vibrations of the NO_2 group. The MALDI-TOF mass spectra of compounds **5a—c** contain peaks of molecular ($[MH]^+$) and fragment ($[MH - NO_2]^+$) ions. In addition to the molecular ion peaks, the molecular ions ionized by chlorine, $[M + {}^{35}Cl]^-$, were detected with the use of the ESI method ($CHCl_3$ + MeCN) in the negative ionization mode. All peaks observed in the mass spectra are characterized by isotope splitting corresponding to the natural isotopic abundance.

The electronic absorption spectra of mononitrophthalocyanines **5a—c** are characterized by splitting of their Q bands. Earlier, using related compounds as an example, this splitting has been demonstrated to be associated[7,9] with lowering of the symmetry due to the electronic interaction between the electron-withdrawing and electron-donating substituents in unsymmetrical molecules. The electronic absorption spectrum of phthalocyanine **5b** is shown as an example in Fig. 1. Structurally related copper and vanadyl complexes are characterized by analogous electronic spectra.[7,9]

As a rule, mononitrophthalocyanines are the final target compounds, and the nucleophilic substitution of the nitro group in such complexes has not been hitherto investigated. We demonstrated for the first time that it is possible, in principle, to perform nucleophilic substitution of the NO_2 group in phthalocyanines **5a—c** with the aim of modifying their structures to prepare new unsymmetrically substituted monophthalocyanines (Scheme 2).

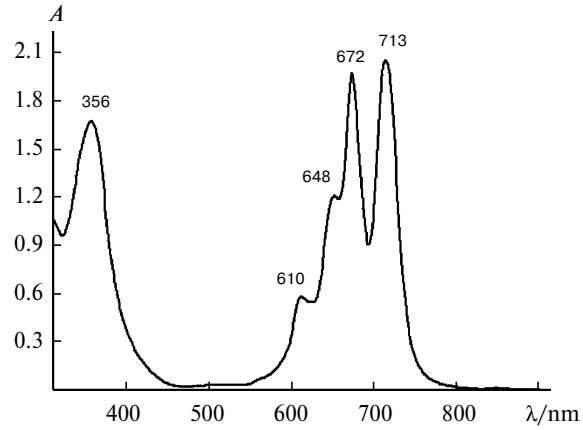
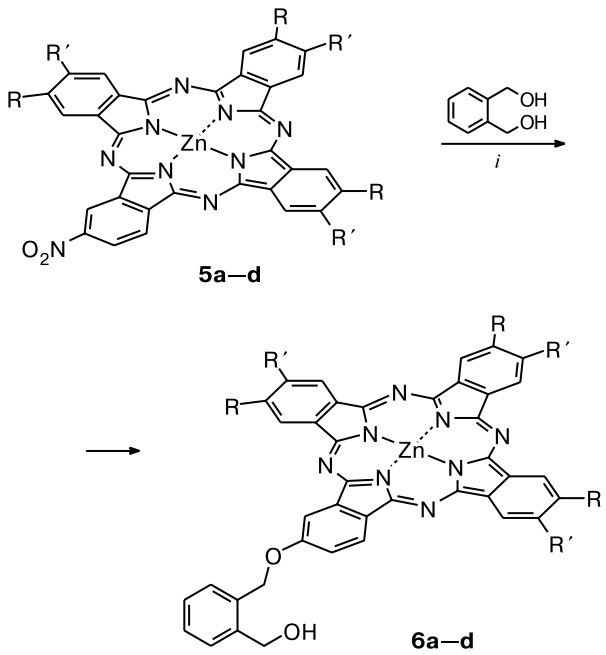


Fig. 1. Electronic absorption spectrum of phthalocyanine **5b** ($CHCl_3$).

Scheme 2



R = R′ = Et (**a**), Bu^n (**b**), OPr^n (**c**); R = Bu^t, R′ = H (**d**)

Reagents and conditions: *i*. DMSO, K_2CO_3, 40—80 °C, 50 h or DMSO, NaH, 20—25 °C, 30—45 min.

The reactions of phthalocyanines **5a—c** and the known[1] *tert*-butyl derivative **5d** with benzene-1,2-dimethanol for 50 h in the presence of K_2CO_3 as a base afforded **6a—d** products, respectively, in trace amounts. The use of a stronger base, *viz.*, sodium hydride, led to an increase in the yield of target products **6a—d** and a substantial decrease in the reaction time. It was convenient to monitor the course of the reaction by electronic spectroscopy. The Q bands of the starting nitrophthalocyanines **5a—d** are split. The electronic spectral patterns of the

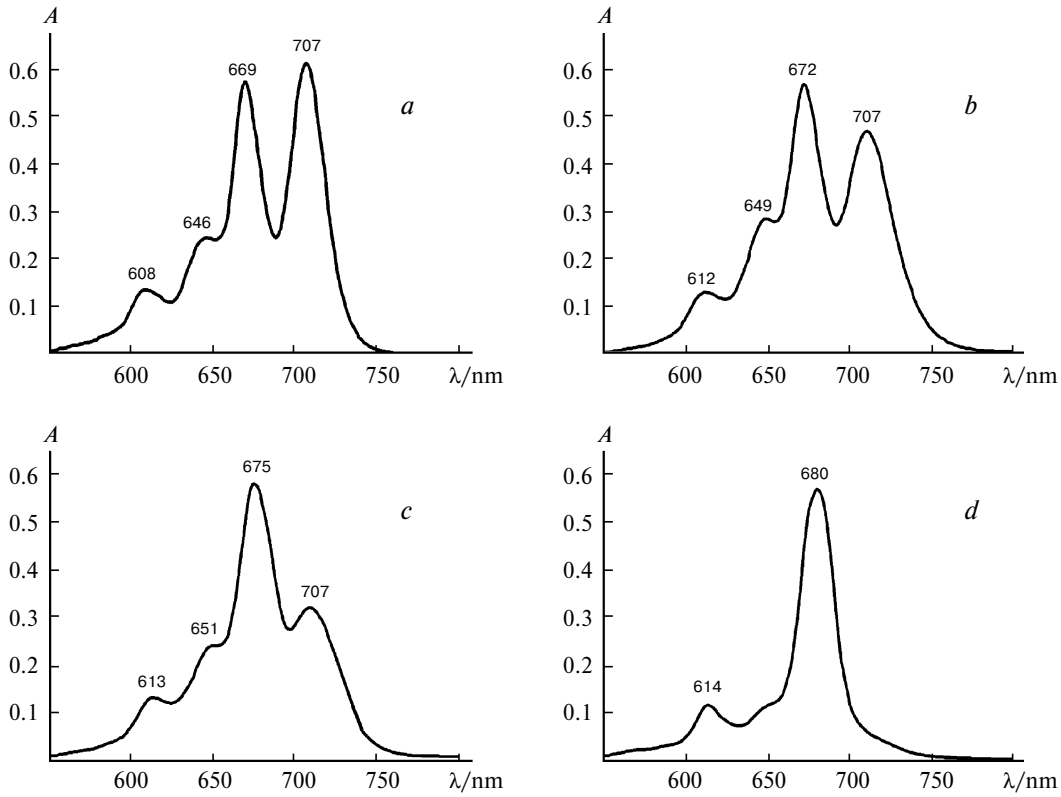


Fig. 2. Changes in the electronic absorption spectrum of **5d** under the action of NaH (DMSO) at 25 °C after 5 (*a*), 15 (*b*), 30 (*c*), and 45 min (*d*).

final products **6a—d**, which have no simultaneously electron-donating and electron-withdrawing substituents, should be typical of mononuclear metal complexes, which is actually observed. The changes in the electronic absorption spectrum of the reaction mixture in the course of the synthesis of compound **6d** is shown as an example in Fig. 2.

During the nucleophilic substitution, splitting of the Q band gradually disappeared.

A prolonged contact of phthalocyanines with a strong base is undesirable and leads to their gradual decomposition, which was confirmed by control experiments.

The IR spectra of new complexes **6a—d** contain characteristic broad absorption bands of the OH group in the 3100—3400 cm^{-1} region. The mass spectra obtained by the MALDI-TOF and ESI ($CHCl_3$) methods have the molecular ion peaks $[MH^+]$ and $[M + Cl]^-$ (for ESI) and the characteristic fragment ions $[M - C_8H_9O^{\bullet}]^+$. The peaks of all ions observed in the mass spectra are characterized by isotope splitting corresponding to the natural isotopic abundance.

Compounds **6a—d** were characterized also by electronic absorption spectra. The spectrum of phthalocyanine **6c** is shown as an example in Fig. 3.

The introduction of the OH group allowed us to perform further modification giving rise to phthalocyanines

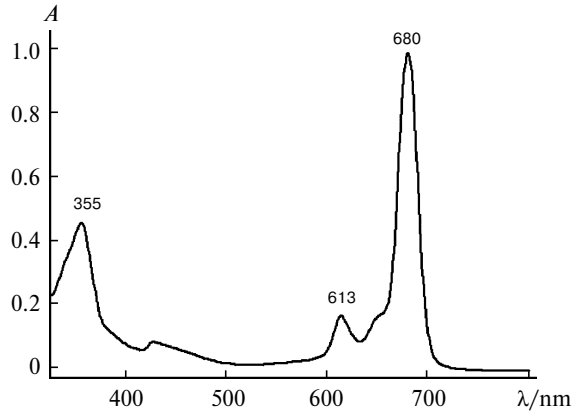
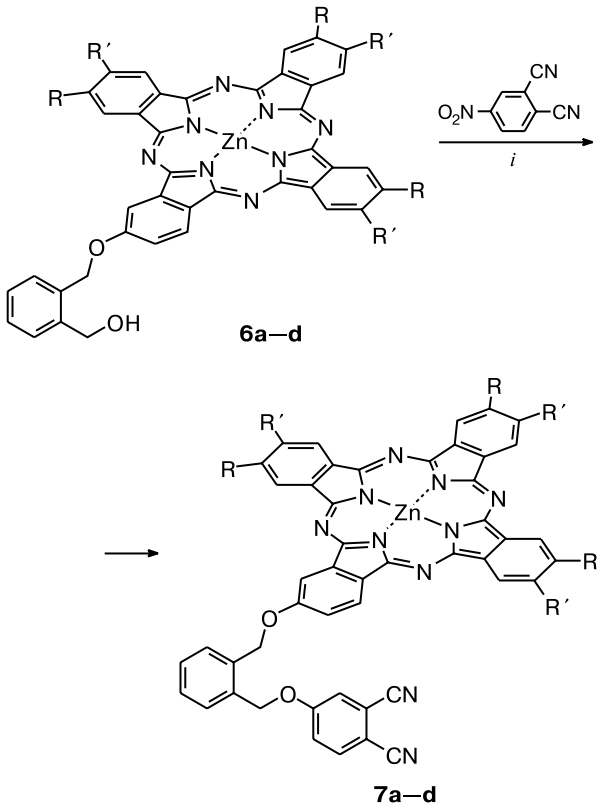


Fig. 3. Electronic absorption spectrum of phthalocyanine **6c** ($CHCl_3$).

containing the phthalonitrile fragment. The reactions of complexes **6a—d** with 4-nitrophthalonitrile in DMSO in the presence of NaH afforded phthalocyanines **7a—d** in virtually quantitative yields (Scheme 3).

The above-described approach to the synthesis of unsymmetrically substituted phthalocyanines containing active CN groups is an alternative to mixed cyclization of phthalonitriles with different structures, which we have developed earlier.[12] We used these compounds in the

Scheme 3



R = R′ = Et (**a**), Bu^n (**b**), OPr^n (**c**); R = Bu^t, R′ = H (**d**)

Reagents and conditions: *i*. DMSO, NaH, 35—40 °C, 5—10 min.

synthesis of heterometallic and heteroligand dinuclear phthalocyanines.[12]

Experimental

The ^{1}H NMR spectra were recorded on a Bruker AM-300 instrument operating at 300.13 MHz. The electronic absorption spectra were measured on a Helios-α spectrophotometer in 0.5 cm quartz cells in $CHCl_3$ and DMSO. The mass spectra were obtained on Autoflex II (MALDI-TOF, 2,5-dihydroxybenzoic acid as the matrix) and Finnigan LCQ (electrospray ionization (ESI)) instruments. The IR spectra were recorded on a Nicolet Nexus IR-Fourier spectrometer in KBr pellets or as Nujol mulls. Column chromatography was performed on silica gel 60 (40—63 μm; Merck) and BioBeads SX-1 and SX-8 (BioRad). All solvents were purified according to standard procedures immediately before use. Prior to syntheses, $Zn(OAc)_2 \cdot 2H_2O$ was kept *in vacuo* at 100 °C for 4 h. Phthalonitriles **1**,[13] **3a**,[14] **3b**,[15] and **3c** [16] were prepared according to known procedures. 5-Nitro-1,3-diiminoisoindoline (**2**) and 2-nitro-9,16,23-tri-*tert*-butylphthalocyanine zinc complex (**5d**) were synthesized according to a procedure described earlier.[1]

5,6-Dialkyl-1,3-diiminoisoindolines 4a—c (general procedure). A solution of 4,5-diethylphthalonitrile (**3a**) (0.90 g, 4.89 mmol) in MeOH was saturated with gaseous NH_3 for 30 min and kept in a closed vessel for 80 h. Then the reaction mixture was concentrated and the product was reprecipitated with hexane from a solution in MeOH. Compound **4a** was obtained in a yield of 0.98 g (97%). IR (Nujol mulls), ν/cm^{-1}: 3290 (N—H), 1577 (C=NH). ^{1}H NMR (CD_3OD), δ: 1.03 (t, 6 H, C$\underline{H}_3$CH$_2$, J = 6.2 Hz); 1.82 (q, 4 H, CH$_3$C$\underline{H}_2$, J = 7.5 Hz); 3.28 (s, 1 H, NH); 4.89 (s, 2 H, NH); 7.40 (s, 2 H, Ar). **5,6-Dibutyl-1,3-diiminoisoindoline (4b)** was synthesized analogously in 95% yield. IR (Nujol mulls), ν/cm^{-1}: 3210 (N—H), 1550 (C=NH). ^{1}H NMR (CD_3OD), δ: 1.06 (t, 6 H, C$\underline{H}_3$CH$_2$CH$_2$CH$_2$, J = 6.5 Hz); 1.86—1.98 (m, 4 H, CH$_3$C$\underline{H}_2$CH$_2$CH$_2$); 2.02—2.16 (m, 4 H, CH$_3$CH$_2$C$\underline{H}_2$CH$_2$); 3.09 (t, 4 H, CH$_3$CH$_2$CH$_2$C$\underline{H}_2$, J = 8.0 Hz); 3.34 (s, 1 H, NH); 4.82 (s, 2 H, NH); 7.54 (s, 2 H, Ar). **5,6-Dipropyloxy-1,3-diiminoisoindoline (4c)** was synthesized analogously in 96% yield. IR (Nujol mulls), ν/cm^{-1}: 3240 (N—H), 1561 (C=NH). ^{1}H NMR (CD_3OD), δ: 1.09 (t, 6 H, C$\underline{H}_3$CH$_2$CH$_2$O, J = 6.3 Hz); 1.82—1.97 (m, 4 H, CH$_3$C$\underline{H}_2$CH$_2$O); 3.12 (t, 4 H, CH$_3$CH$_2$C$\underline{H}_2$O, J = 7.8 Hz); 3.41 (s, 1 H, NH); 4.78 (s, 2 H, NH); 7.48 (s, 2 H, Ar).

9,10,16,17,23,24-Hexaethyl-2-nitrophthalocyanine zinc complex (5a). A mixture of compounds **2** (50 mg, 0.26 mmol) and **4a** (158 mg, 0.78 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (113 mg, 0.52 mmol) in DMAE was refluxed for 2.5 h. After cooling, the reaction mixture was treated with water. The products that precipitated were filtered off, successively washed with water and hot MeOH, and chromatographed on SiO_2 ($CHCl_3$—Py, 100 : 1, as the eluent). Phthalocyanine **5a** was obtained in a yield of 29 mg (14%). IR (KBr), ν/cm^{-1}: 1338 ($\nu_s(NO_2)$), 1520 ($\nu_{as}(NO_2)$). MS (ESI), m/z (I_{rel} (%)): 790 [M + H]$^+$ (100), 744 [M + H − NO$_2$]$^+$ (16). ^{1}H NMR ($CDCl_3$ + Py-d$_5$), δ: 1.18 (t, 18 H, C$\underline{H}_3$CH$_2$, J = 8.0 Hz); 1.56—1.69 (m, 12 H, CH$_3$C$\underline{H}_2$); 8.74 and 9.08 (both d, 1 H each, Ar, J = 9.0 Hz); 8.79, 8.89, 8.98, 9.00, 9.14, 9.17, and 9.92 (all s, 1 H each, Ar). Absorption spectrum ($CHCl_3$), λ_{max}/nm (logε): 360 (4.31), 610 (3.83), 650 (4.15), 670 (4.43), 713 (4.49).

9,10,16,17,23,24-Hexabutyl-2-nitrophthalocyanine zinc complex (5b) was prepared analogously. Phthalocyanine **5b** was isolated by chromatography on SiO_2 ($CHCl_3$—Py, 1000 : 1, as the eluent) in a yield of 40 mg (16%). IR (KBr), ν/cm^{-1}: 1340 ($\nu_s(NO_2)$), 1522 ($\nu_{as}(NO_2)$). MS (ESI), m/z (I_{rel} (%)): 959 [M + H]$^+$ (100), 913 [M + H − NO$_2$]$^+$ (6). ^{1}H NMR ($CDCl_3$ + Py-d$_5$), δ: 1.18 (t, 18 H, C$\underline{H}_3$CH$_2$CH$_2$CH$_2$, J = 8.0 Hz); 1.60—1.70 (m, 12 H, CH$_3$C$\underline{H}_2$CH$_2$CH$_2$); 1.75—2.05 (m, 12 H, CH$_3$CH$_2$C$\underline{H}_2$CH$_2$); 3.47 (t, 12 H, CH$_3$CH$_2$CH$_2$C$\underline{H}_2$, J = 8.0 Hz); 8.75 and 9.08 (both d, 1 H each, Ar, J = 9.0 Hz); 8.70, 8.88, 8.94, 8.96, 9.14, 9.16, and 9.95 (all s, 1 H each, Ar). Absorption spectrum ($CHCl_3$), λ_{max}/nm (logε): 356 (4.32), 610 (3.90), 648 (4.19), 672 (4.47), 713 (4.51).

2-Nitro-9,10,16,17,23,24-hexapropyloxyphthalocyanine zinc complex (5c) was prepared analogously. Phthalocyanine **5c** was isolated in a yield of 35 mg (14%) by chromatography successively on BioBeads SX-1 and SX-8 (THF as the eluent). IR (KBr), ν/cm^{-1}: 1339 ($\nu_s(NO_2)$), 1524 ($\nu_{as}(NO_2)$). MS (ESI), m/z (I_{rel} (%)): 971 [M + H]$^+$ (100), 925 [M + H − NO$_2$]$^+$ (11). ^{1}H NMR ($CDCl_3$ + Py-d$_5$), δ: 1.16 (t, 18 H, C$\underline{H}_3$CH$_2$CH$_2$O, J = 7.0); 1.55—1.68 (m, 12 H, CH$_3$C$\underline{H}_2$CH$_2$O); 3.66 (t, 12 H, CH$_3$CH$_2$C$\underline{H}_2$O, J = 8.0 Hz); 8.76 and 9.10 (both d, 1 H each, Ar, J = 8.0 Hz); 8.72, 8.84, 8.95, 8.97, 9.13, 9.15, and 9.96 (all s, 1 H each, Ar). Absorption spectrum ($CHCl_3$), λ_{max}/nm (logε): 361 (4.32), 610 (3.86), 651 (4.14), 669 (4.45), 708 (4.50).

2-(2-Hydroxymethylbenzyloxy)-9,10,16,17,23,24-hexaethylphthalocyanine zinc complex (6a). A mixture of NaH (3 mg, 0.130 mmol), benzene-1,2-dimethanol (8 mg, 0.065 mmol), and **5a** (10 mg, 0.013 mmol) in DMSO (2 mL) was kept at 20—25 °C for 30 min. After completion of the reaction, the mixture was treated with water. The phthalocyanine products that precipitated were filtered off, successively washed with water and hot MeOH, and chromatographed on SiO_2 ($CHCl_3$—THF, 50 : 1, as the eluent). Phthalocyanine **6a** was obtained in a yield of 8 mg (75%). IR (KBr), ν/cm^{-1}: 3100—3600 (OH). MS (MALDI-TOF), m/z (I_{rel} (%)): 882 $[M + H]^+$ (100), 761 $[M - C_8H_9O^{\bullet}]^+$ (22). ^1H NMR (THF-d_8 + Py-d_5), δ: 1.75 (t, 18 H, $C\underline{H}_3CH_2$, J = 8.0 Hz); 3.09—3.33 (m, 12 H, $CH_3C\underline{H}_2$); 5.00 and 5.54 (both s, 2 H each, CH_2); 7.33—7.90 (m, 4 H, Ar); 8.76—9.18 (m, 9 H, Ar). Absorption spectrum ($CHCl_3$), λ_{max}/nm (logε): 352 (4.55), 617 (4.15), 686 (4.90).

2-(2-Hydroxymethylbenzyloxy)-9,10,16,17,23,24-hexabutylphthalocyanine zinc complex (6b) was prepared analogously. Phthalocyanine **6b** was isolated by chromatography on SiO_2 ($CHCl_3$—THF, 100 : 1, as the eluent) in a yield of 7 mg (79%). IR (KBr), ν/cm^{-1}: 3150—3550 (OH). MS (MALDI-TOF), m/z (I_{rel} (%)): 1050 $[M + H]^+$ (100), 929 $[M - C_8H_9O^{\bullet}]^+$ (26). ^1H NMR (THF-d_8 + Py-d_5), δ: 1.16 (t, 18 H, $C\underline{H}_3CH_2CH_2CH_2$, J = 8.0 Hz); 1.60—1.75 (m, 12 H, $CH_3C\underline{H}_2CH_2CH_2$); 1.80—2.05 (m, 12 H, $CH_3CH_2C\underline{H}_2CH_2$); 3.22 (t, 12 H, $CH_3CH_2CH_2C\underline{H}_2$, J = 7.0 Hz); 4.95 and 5.70 (both s, 2 H each, CH_2); 7.30—7.89 (m, 4 H, Ar); 8.82—9.24 (m, 9 H, Ar). Absorption spectrum ($CHCl_3$), λ_{max}/nm (logε): 352 (4.61), 617 (4.21), 686 (4.94).

2-(2-Hydroxymethylbenzyloxy)-9,10,16,17,23,24-hexapropyloxyphthalocyanin zinc complex (6c) was prepared analogously. Phthalocyanine **6c** was isolated by chromatography on SiO_2 ($CHCl_3$—THF, 25 : 1, as the eluent) in a yield of 7 mg (72%). IR (KBr), ν/cm^{-1}: 3100—3590 (OH). MS (MALDI-TOF), m/z (I_{rel} (%)): 1060 $[M + H]^+$ (100), 939 $[M - C_8H_9O^{\bullet}]^+$ (12). ^1H NMR (THF-d_8 + Py-d_5), δ: 1.33 (t, 18 H, $C\underline{H}_3CH_2CH_2O$, J = 7.0 Hz); 2.10—2.18 (m, 12 H, $CH_3C\underline{H}_2CH_2O$); 4.49 (t, 12 H, $CH_3CH_2C\underline{H}_2O$, J = 8.0 Hz); 4.98 and 5.66 (both s, 2 H each, CH_2); 7.38—7.86 (m, 4 H, Ar); 8.50—8.89 (m, 9 H, Ar). Absorption spectrum ($CHCl_3$), λ_{max}/nm (logε): 355 (4.32), 613 (3.94), 680 (4.65).

2-(2-Hydroxymethylbenzyloxy)-9,16,23-tri-*tert*-butylphthalocyanine zinc complex (6d) was prepared analogously. Phthalocyanine **6d** was isolated by chromatography on SiO_2 ($CHCl_3$—THF, 50 : 1, as the eluent) in a yield of 13 mg (80%). IR (KBr), ν/cm^{-1}: 3100—3610 (OH). MS (MALDI-TOF), m/z (I_{rel} (%)): 882 $[MH]^+$ (100), 761 $[M - C_8H_9O^{\bullet}]^+$ (13). ^1H NMR (THF-d_8 + Py-d_5), δ: 1.79 (s, 27 H, Me); 4.92 and 5.73 (both s, 2 H each, CH_2); 7.36—8.34 (m, 4 H, Ar); 9.18—9.63 (m, 12 H, Ar). Absorption spectrum ($CHCl_3$), λ_{max}/nm (logε): 350 (4.56), 613 (4.18), 680 (4.96).

2-[2-(3,4-Dicyanophenoxymethyl)benzyloxy]-9,10,16,17,23,24-hexaethylphthalocyanine zinc complex (7a). A mixture of NaH (1.4 mg, 0.057 mmol), 4-nitrophthalonitrile (**1**) (5 mg, 0.028 mmol), and **6a** (5 mg, 0.006 mmol) in DMSO (2 mL) was kept at 35—40 °C for 6 min. Then the reaction mixture was treated with water. The flaky precipitate that formed was filtered off and successively washed with water and hot MeOH to obtain complex **7a** in a yield of 5.5 mg (97%).

2-[2-(3,4-Dicyanophenoxymethyl)benzyloxy]-9,10,16,17,23,24-hexabutylphthalocyanine zinc complex (7b) (98% yield), **2-[2-(3,4-dicyanophenoxymethyl)benzyloxy]-9,10,16,17,23,24-propyloxyphthalocyanine zinc complex (7c)** (98% yield), and **2-[2-(3,4-dicyanophenoxymethyl)benzyloxy]-9,16,23-tri-*tert*-butylphthalocyanine zinc complex (7d)** (97% yield) were prepared analogously.

Proof of the structures of compounds **7a—d** and their electronic absorption spectra have been published earlier.[12]

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