Synthesis and spectral properties of new planar binuclear phthalocyanines sharing the benzene ring

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New planar binuclear phthalocyanines sharing the benzene ring were synthesized and their spectral properties were studied. Intense absorption in the near-IR region (~850 nm) was observed for the first time.

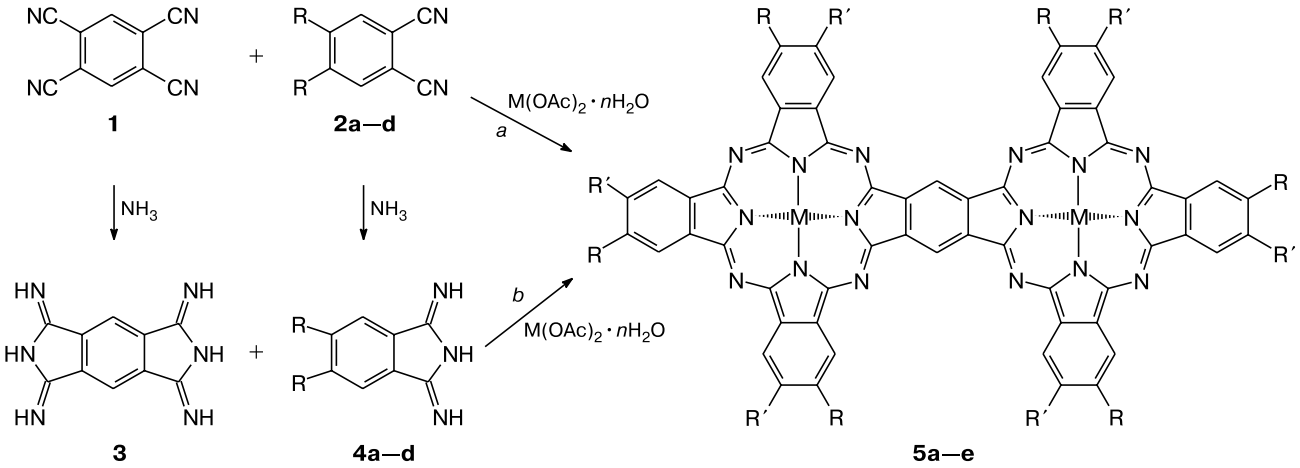
Key words: phthalocyanines, zinc complexes, magnesium complexes, electronic absorption spectra.

Planar binuclear phthalocyanines sharing the benzene or naphthalene ring are characterized by an extended π system responsible for intraelectronic conjugation between two macrocycles. These compounds can exhibit unique spectral properties due to which they can be used in different fields.[1—3] Unfortunately, there is contradictory information not only about the choice of the optimal procedure for the synthesis of these compounds but also about their spectral properties.

In the present study, we developed a one-pot procedure for the synthesis of metal-containing planar binuclear phthalocyanines (Scheme 1).

An attempt to prepare complexes **5a—e** by fusion of the starting phthalogens **1** and **2a—d** in the presence of zinc or magnesium acetate in a ratio of 1 : 20 : 10 (Scheme 1, pathway *a*) led to the formation of the target products in trace amounts. It appeared that the reaction proceeded primarily as oligomerization of tetranitrile **1** giving rise to

Scheme 1



M = Zn (**5a—d**), Mg (**5e**)

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

Reagents and conditions: *a*. fusion, 230 °C; *b*. *N*,*N*-dimethylaminoethanol, refluxing, 3.5 h.

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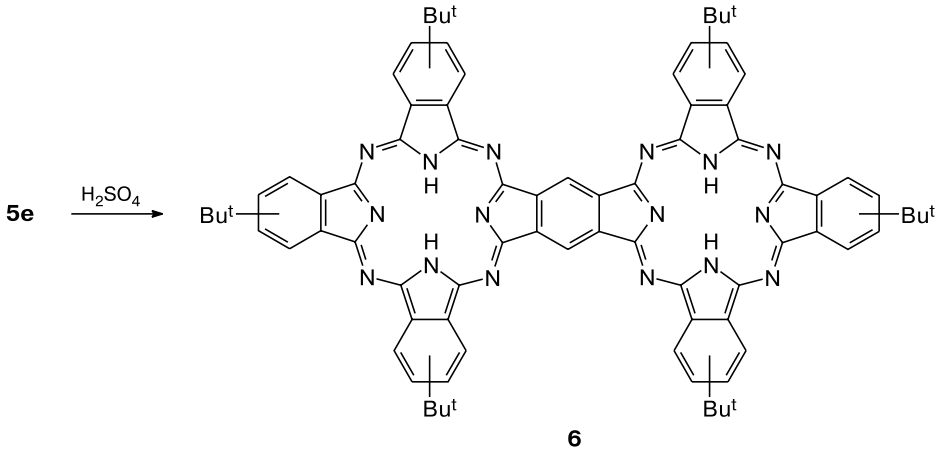
Scheme 2



the corresponding phthalocyanines, as evidenced by the results of electronic absorption spectroscopy and mass spectrometry of soluble components. The reactions with the use of 1,3-diiminoisoindolines **3a** and **4a—d** as the starting compounds in the presence of zinc or magnesium acetates afforded target compounds **5a—e** in 8—10% yields (Scheme 1, pathway *b*). The mixtures of phthalocyanine products were separated by gel-permeation chromatography on BioBeads SX-1 with the use of THF as the eluent. The first fraction consisted primarily of oligomeric products with weights from 5000 to 35000 (mass-spectrometric data); the second fraction, of target binuclear phthalocyanines **5a—e**; the third fraction, of monophthalocyanines produced by self-cyclization of **4a—d**.

Treatment of magnesium complex **5e** with concentrated H_2SO_4 afforded ligand **6** in virtually quantitative yield (Scheme 2). Under these conditions, zinc complexes **5a—d**, unlike complex **5e**, do not undergo demetallation.

It is known that NMR spectroscopy not always provides clear information about the structures of phthalocyanines primarily because of aggregation of phthalocyanine molecules. As a result, signals in the spectra are strongly broadened or nonresolved.[4] In the ^1H NMR spectra of compounds **5a—e** and **6** in $CDCl_3$, signals for aromatic protons were absent. After the addition of a few drops of C_5D_5N to solutions of the complexes under study in $CDCl_3$, the spectra became interpretable. For example, the signals for the aliphatic protons are observed at δ 1.20—4.10 depending on the nature of substituents. The signals for the protons of six benzene rings are observed at δ 8.10—8.30 and 9.34—9.50; the signals for the protons of the shared benzene ring, at δ 11.10—11.50 (2 H). The compositions of compounds **5a—e** and **6** were confirmed by the presence of molecular ions in the MALDI-TOF mass spectra with a characteristic isotope cluster. The mass spectra of binuclear complex **5e** and the corresponding ligand **6** are exemplified in Fig. 1.

In addition, binuclear phthalocyanines **5a—e** and **6** were characterized by electronic absorption spectra. We observed for the first time intense absorption of com-

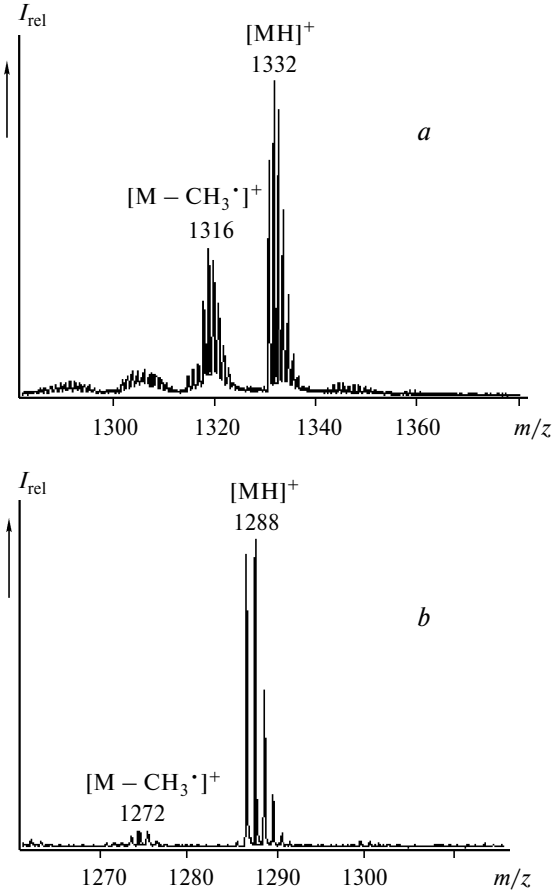


Fig. 1. Mass spectra (MALDI-TOF) of the Mg complex **5e** (*a*) and phthalocyanine **6** (*b*).

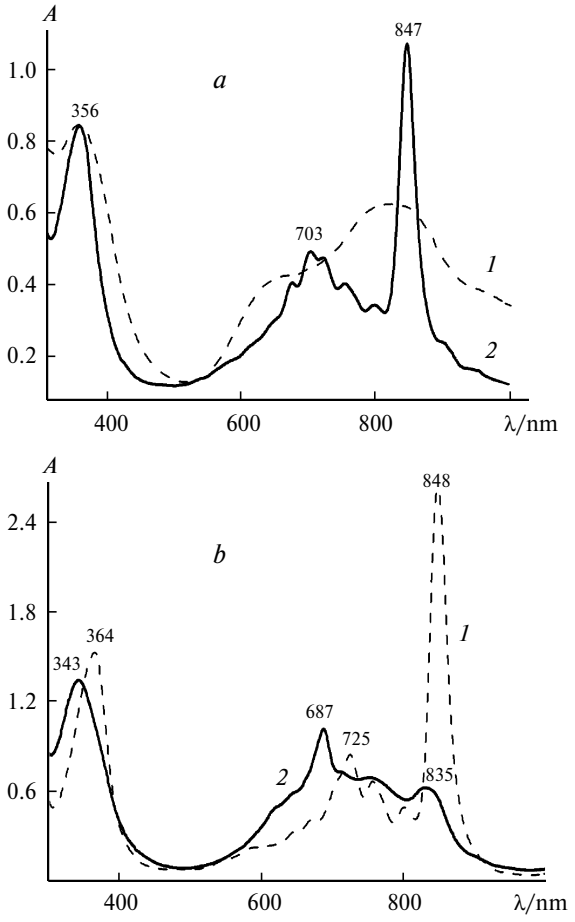


Fig. 2. Electronic absorption spectra of phthalocyanines **5a** in chloroform (*a*, curve *1*) and THF (*a*, curve *2*), **5e** (*b*, curve *1*), and **6** (*b*, curve *2*) in THF.

plexes **5a—e** in the near-IR region, which is very important from the practical point of view.[5,6] The character of the electronic spectra of compounds **5a—e** substantially depends on the nature of the solvent (Fig. 2, *a*). For example, diffuse absorption is primarily observed in the 600—900 nm region in noncoordinating solvents, such as C_6H_6, $CHCl_3$, or Et_2O. Absorption becomes more pronounced with increasing polarity of the solvent (dioxane or THF), and the intensity of the band at 850 nm gradually increases. In coordinating solvents (DMF or pyridine), this band is shifted to 858—861 nm, the character of the electronic absorption spectra remaining unchanged.

The electronic absorption spectrum of magnesium binuclear complex **5e** differs from that of the corresponding ligand **6** (Fig. 2, *b*).

There is contradictory information about the electronic absorption spectra of structurally similar planar binuclear phthalocyanines.[7,8] As a rule, spectral studies were limited to the 300—800 nm region and the electronic spectra in nonpolar solvents were reported (or described). We demonstrated that clear information about the pronounced main absorption band is absent in the spectra recorded in such solvents. Due to an extension of the range of electronic absorption spectra to 1000 nm and the use of polar solvents, we observed for the first time intense absorption of planar binuclear phthalocyanines sharing the benzene ring in the near-IR region.

To conclude, we synthesized new planar binuclear phthalocyanines **5a—e** and **6**. An approach to the synthesis of free binuclear ligands was developed using demetallation of magnesium complex **5e** as an example. The structures of the reaction products were confirmed by NMR spectroscopy and mass spectrometry. The influence of the nature of the solvents on the character of the electronic absorption spectra of these complexes was studied. Intense absorption of metal complexes **5a—e** in the near-IR region was found for the first time.

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 ThermoSpectronic Helios-α spectrophotometer in 0.5 cm quartz cells in C_6H_6, $CHCl_3$, Et_2O, dioxane, THF, and pyridine. The mass spectra were obtained on an Autoflex II instrument (MALDI-TOF, 2,5-dihydroxybenzoic acid as the matrix). Column chromatography was carried out on BioBeads SX-1 (BioRad). All solvents were purified according to standard procedures immediately before use. The salts $Zn(OAc)_2 \cdot 2H_2O$ and $Mg(OAc)_2 \cdot 4H_2O$ were kept in a vacuum drying oven at 100 °C for 4 h prior to the synthesis. Compound **1** (Aldrich) was used without pre-purification. Compounds **2a**,[9] **2b**,[10] **2c**,[11] **2d**,[12,13] **3**,[7] **4a—c**,[14] and **4d**[15] were prepared according to procedures published earlier.

Bis{7^2,8^2,12^2,13^2,17^2,18^2-hexaethyltribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphirino(zinc)}[*b*,*e*]benzene (5a). The salt $Zn(OAc)_2 \cdot 2H_2O$ (155 mg, 0.71 mmol) was added to a solution of compounds **3** (30 mg, 0.14 mmol) and **4a** (568 mg, 2.83 mmol) in *N*,*N*-dimethylaminoethanol (50 mL). The reaction mixture was stirred at room temperature for 15 min, refluxed for 4 h, and treated with water. The phthalocyanine products were separated and washed with CH_3OH (3×50 mL). Compound **5a** was purified on BioBeads SX-1 using THF as the eluent and obtained in a yield of 16 mg (8%). MS (MALDI-TOF), *m*/*z* (I_{rel} (%)): 1414 $[M]^+$ (96). ^{1}H NMR (THF-d_8+Py-d_5), δ: 1.68—1.70 (m, 36 H, $CH_2C\underline{H}_3$); 3.10—3.30 (m, 24 H, $C\underline{H}_2CH_3$); 8.30 (s, 4 H, Ar); 9.40 (s, 8 H, Ar); 11.10 (s, 2 H, Ar). UV-Vis (THF), λ_{max}/nm (logε): 356 (4.79), 703 (4.59), 847 (4.93).

Bis{7^2,8^2,12^2,13^2,17^2,18^2-hexabutyltribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphirino(zinc)}[*b*,*e*]benzene (5b). The synthesis and purification were carried out analogously to **5a**. Compound **5b** was prepared from compounds **3** (32 mg, 0.15 mmol), **4b** (771 mg, 3.00 mmol), and $Zn(OAc)_2 \cdot 2H_2O$ (164 mg, 0.75 mmol) in a yield of 24 mg (9%). MS (MALDI-TOF), *m*/*z* (I_{rel} (%)): 1751 $[M]^+$ (100), 1694 $[M - C_4H_9^{\bullet}]^+$ (15). ^{1}H NMR (THF-d_8+Py-d_5), δ: 1.20 (m, 36 H, $CH_2CH_2CH_2C\underline{H}_3$); 1.64—1.76 (m, 24 H, $CH_2CH_2C\underline{H}_2CH_3$); 1.81—2.00 (m, 24 H, $CH_2C\underline{H}_2CH_2CH_3$); 3.20—4.09 (m, 24 H, $C\underline{H}_2CH_2CH_2CH_3$); 8.25 (s, 4 H, Ar); 9.34 (s, 8 H, Ar); 11.50 (s,

2 H, Ar). UV-Vis (THF), λ_{max}/nm (logε): 359 (4.85), 704 (4.62), 847 (4.92).

Bis{7^2,8^2,12^2,13^2,17^2,18^2-hexapropyloxytribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphirino(zinc)}[*b*,*e*]benzene (5c). The synthesis and purification were carried out analogously to **5a**. Compound **5c** was prepared from compounds **3** (21 mg, 0.10 mmol), **4c** (522 mg, 2.00 mmol), and $Zn(OAc)_2 \cdot 2H_2O$ (110 mg, 0.50 mmol) in a yield of 14 mg (8%). MS (MALDI-TOF), *m*/*z* (I_{rel} (%)): 1774 $[M]^+$ (100), 1716 $[M - OC_3H_7^{\bullet}]^+$ (55). ^{1}H NMR (THF-d_8+Py-d_5), δ: 1.32 (m, 36 H, $OCH_2CH_2C\underline{H}_3$); 1.98—2.20 (m, 24 H, $OCH_2C\underline{H}_2CH_3$); 3.90—4.10 (m, 24 H, $OC\underline{H}_2CH_2CH_3$); 8.10 (s, 4 H, Ar); 9.50 (s, 8 H, Ar); 11.40 (s, 2 H, Ar). UV-Vis (THF), λ_{max}/nm (logε): 360 (4.73), 716 (4.62), 842 (4.90).

Bis{7(8)^2,12(13)^2,17(18)^2-tri-*tert*-butyltribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphirino(zinc)}[*b*,*e*]benzene (5d). The synthesis and purification were carried out analogously to **5a**. Compound **5d** was prepared from compounds **3** (42 mg, 0.20 mmol), **4d** (804 mg, 4.00 mmol), and $Zn(OAc)_2 \cdot 2H_2O$ (219 mg, 1.00 mmol) in a yield of 28 mg (10%). MS (MALDI-TOF), *m*/*z* (I_{rel} (%)): 1414 $[M]^+$ (100), 1399 $[M - CH_3^{\bullet}]^+$ (15). ^{1}H NMR (THF-d_8+Py-d_5), δ: 1.79 (s, 54 H, $C\underline{H}_3$); 8.22—9.40 (m, 18 H, Ar); 11.20 (s, 2 H, Ar). UV-Vis (THF), λ_{max}/nm (logε): 358 (4.64), 717 (4.45), 835 (5.01).

Bis{7(8)^2,12(13)^2,17(18)^2-tri-*tert*-butyltribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphirino(magnesium)}[*b*,*e*]benzene (5e). The synthesis and purification were carried out analogously to **5a**. Compound **5e** was prepared from compounds **3** (40 mg, 0.19 mmol), **4e** (764 mg, 3.80 mmol), and $Mg(OAc)_2 \cdot \cdot 4H_2O$ (203 mg, 0.95 mmol) in a yield of 35 mg (14%). MS (MALDI-TOF), *m*/*z* (I_{rel} (%)): 1332 $[MH]^+$ (100), 1316 $[M - CH_3^{\bullet}]^+$ (49). ^{1}H NMR (THF-d_8+Py-d_5), δ: 1.71 (s, 54 H, $C\underline{H}_3$); 8.15—9.34 (m, 18 H, Ar); 11.35 (s, 2 H, Ar). UV-Vis (THF), λ_{max}/nm (logε): 364 (4.76), 725 (4.51), 848 (4.99).

Bis{7(8)^2,12(13)^2,17(18)^2-tri-*tert*-butyltribenzo[*g*,*l*,*q*]-5,10,15,20-tetraazaporphirino}[*b*,*e*]benzene (6). Complex **5e** (15 mg, 0.01 mmol) was dissolved in concentrated H_2SO_4, kept for 15 min, and poured onto ice. The phthalocyanine product that precipitated was filtered off and repeatedly washed with water to neutral pH. Compound **6** was obtained in a yield of 14 mg (98%). MS (MALDI-TOF), *m*/*z* (I_{rel} (%)): 1288 $[MH]^+$ (100), 1272 $[M - CH_3^{\bullet}]^+$ (11). ^{1}H NMR (THF-d_8+Py-d_5), δ: –2.6 (br.s, 4 H, N$\underline{H}$); 1.74 (s, 54 H, $C\underline{H}_3$); 8.12—9.29 (m, 18 H, Ar); 11.25 (s, 2 H, Ar). UV-Vis (THF), λ_{max}/nm (logε): 343 (5.11), 687 (4.98), 835 (4.79).

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