

Synthesis and Spectral Properties of Unsymmetrical Benzoporphyrins Containing Phenoxy Groups or Quinoxaline Fragments

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Abstract—Condensation of phthalimide and 4-*tert*-butylphthalimide with zinc(II) acetate gave 3-(3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidenemethyl)-1*H*-isoindol-1-one and 5-*tert*-butyl-3-(5-*tert*-butyl-3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidenemethyl)-1*H*-isoindol-1-one, respectively. Their reactions with 4-phenoxyphthalimide and quinoxaline-2,3-dicarboximide in the presence of Zn(OAc)₂ led to the formation of zinc complexes of *cis*-4,4'-diphenoxytetrabenzoporphyrin and *cis*-di(4-*tert*-butylbenzo)diquinoxalinoporphyrin. The complexes were converted into the free bases by treatment with sulfuric acid. Spectral properties of the obtained porphyrin derivatives were studied.

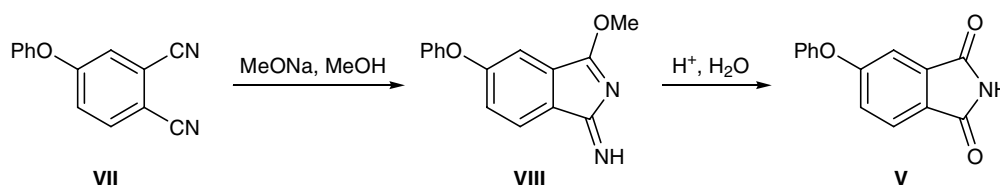
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Porphyrins and their analogs belong to a large class of macrocyclic tetrapyrrole systems. Scientific and practical interests in these compounds originate from the fact that some their derivatives (hemoglobin, myoglobin, cytochromes, chlorophyll, etc.) are very important in the nature. Studies on the structure and properties of natural porphyrins and their synthetic analogs make it possible to solve some problems related to photosynthesis, binding and activation of molecular oxygen, and synthesis of effective models of enzymatic systems which can find application in technics, technology, and medicine.

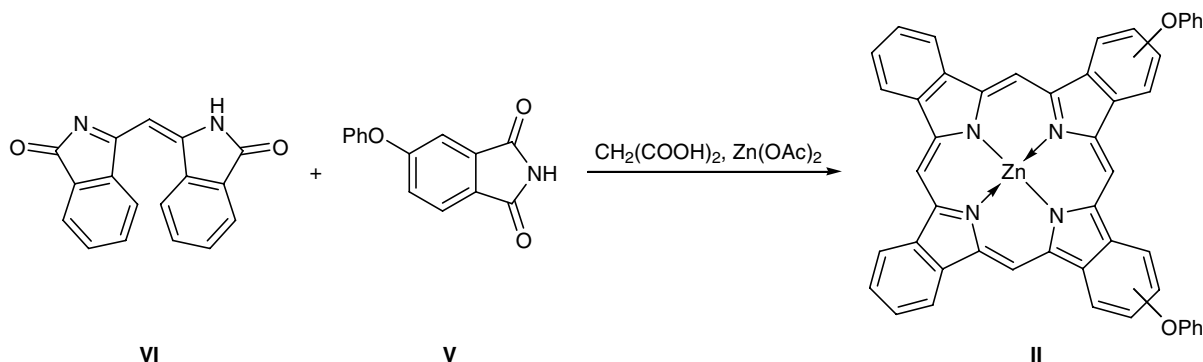
Benzo-fused derivatives constitute a large group of synthetic porphyrin analogs. Among these, tetrabenzoporphyrin (**I**) and its metal complexes [1–5], as well as various *meso*-aryl-substituted tetrabenzoporphyrins [6–11], were studied most thoroughly. The available information on unsymmetrical tetrabenzoporphyrins is concerned mainly with *meso*-aryl-substituted derivatives [12–14], while those having no substituents in the

meso positions have been studied to a considerably lesser extent. Monobenzoporphyrin and its metal complexes (which were detected for the first time in oil [15] and were then prepared by synthetic methods [16, 17]) may be regarded as first representatives of that group of compounds. The procedure proposed in [17] is based on the Diels–Alder reaction of protoporphyrin IX dimethyl ester with dimethyl acetylenedicarboxylate, followed by elimination of the angular methyl group from the adduct. However, this procedure has a limited applicability; therefore, Sapunov et al. [18] later proposed to obtain unsymmetrical benzoporphyrins by joint condensation of imides derived from two different *ortho*-dicarboxylic acids [18]. A drawback of this method is that the reaction gives a mixture of porphyrins which are often difficult to separate on a preparative scale. The most reasonable procedure for the synthesis of unsymmetrical benzoporphyrins is likely to be stepwise condensation [12–14, 19] which was applied by us to obtain (*cis*-

Scheme 1.



Scheme 2.



4,4'-diphenoxytetrabenzoporphyrinato)zinc(II) (**II**) and [*cis*-di(4-*tert*-butylbenzo)diquinoxalinoporphyrimato]-zinc(II) (**III**). Complexes **II** and **III** are characterized by a large dipole moment, and they attract interest from both theoretical and practical viewpoints. It is known that structurally related unsymmetrical porphyrazines containing both electron-donor and electron-withdrawing substituents and possessing a high dipole moment are very promising for use in various fields of science and technics [20–22].

The starting compounds for the synthesis of porphyrin **II** were phthalimide (**IV**) and 4-phenoxyphthalimide (**V**). By condensation of phthalimide (**IV**) with zinc(II) acetate according to the procedure reported in [14] we obtained 3-(3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidenemethyl)-1*H*-isoindol-1-one (**VI**). The second component, 4-phenoxyphthalimide (**V**), was prepared by the transformation of 4-phenoxyphthalonitrile (**VII**) into 1-alkoxy-3-imino derivative **VIII** and hydrolysis of the latter to imide **V** by treatment with dilute HNO₃ (Scheme 1).

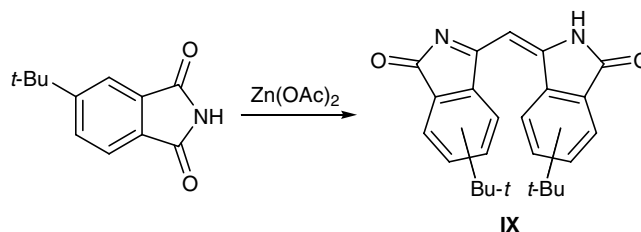
The structure of compound **V** was confirmed by the analytical and spectral data. The ¹H NMR spectrum of **V** contained a singlet at δ 10.46 ppm from the NH proton, a multiplet at δ 7.94–7.68 ppm from three aromatic protons in the isoindole fragment, and a multiplet at δ 7.35–7.15 ppm from five protons of the phenoxy group.

By heating compound **VI** with excess imide **V** and malonic acid in the presence of zinc acetate we obtained *cis*-4,4'-diphenoxytetrabenzoporphyrin complex **II** (Scheme 2). Apart from complex **II**, the reaction also gave zinc complexes of compound **I** and tetra-(4-phenoxybenzo)porphyrin. Complex **II** was isolated from the reaction mixture by column chromatography.

In the synthesis of zinc complex **III**, the first component was 5-*tert*-butyl-3-(5-*tert*-butyl-3-oxo-2,3-di-

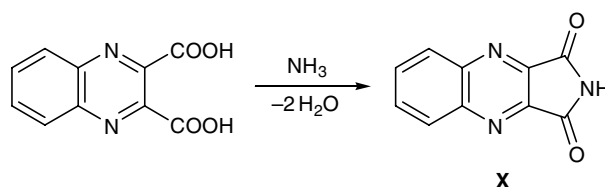
hydro-1*H*-isoindol-1-ylidenemethyl)-1*H*-isoindol-1-one (**IX**) which was prepared by analogy with compound **VI**, i.e., by condensation of 4-*tert*-butylphthalimide with zinc(II) acetate (Scheme 3).

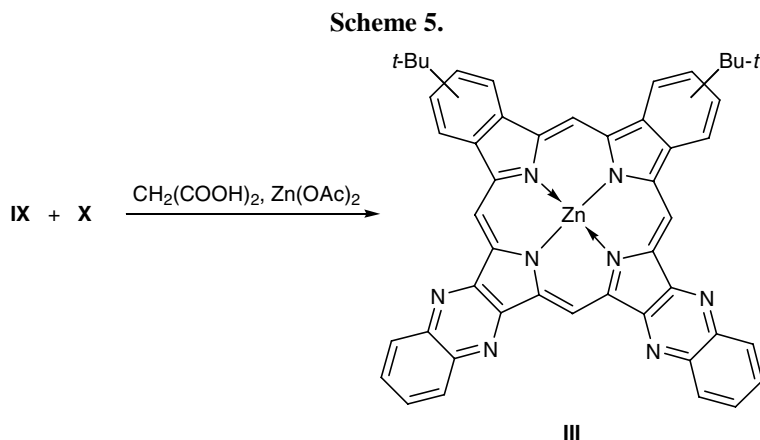
Scheme 3.



Here, 4-*tert*-butylphthalimide was selected taking into account that the presence of *tert*-butyl groups in porphyrin molecules endows them with a high solubility in organic solvents. Furthermore, *tert*-butyl groups do not affect the electronic absorption spectra of porphyrins to a considerable extent [23]. The structure of compound **IX** was confirmed by elemental analysis and electronic, IR, and ¹H NMR spectroscopy. The electronic absorption spectrum of **IX** resembles that of compound **VI** [14]. Bis-isoindole **IX** showed in the ¹H NMR spectrum a singlet at δ 10.72 ppm from the NH proton, signals from six protons of the isoindole fragments appeared in the region δ 7.44–7.21 ppm, a singlet at δ 6.48 ppm was assigned to resonance of the CH proton, and protons in the *tert*-butyl groups gave an upfield singlet at δ 1.98 ppm.

Scheme 4.





The second component was quinoxaline-2,3-dicarboximide (**X**). It was prepared by passing dry NH_3 through molten quinoxaline-2,3-dicarboxylic acid at 250°C over a period of 10 min (Scheme 4). [*cis*-Di(4-*tert*-butylbenzo)diquinoxalinoporphyrinato]zinc(II)

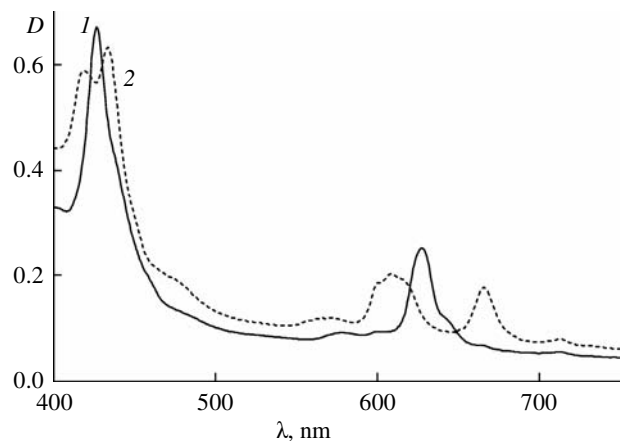


Fig. 1. Electronic absorption spectra of (1) zinc complex **II** and (2) free ligand **XI** in chloroform.

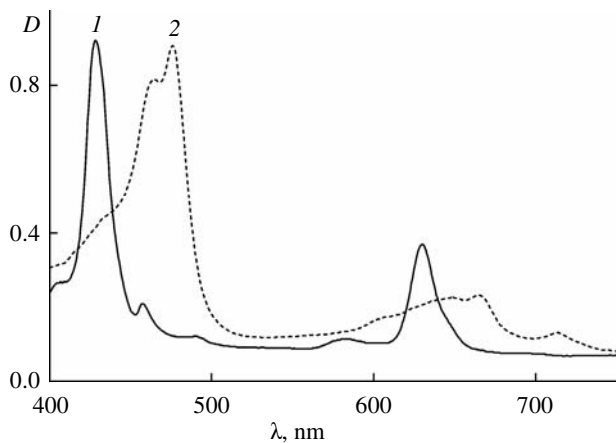


Fig. 2. Electronic absorption spectra of (1) zinc complex **III** and (2) free ligand **XII** in chloroform.

(**III**) was synthesized by reaction of dimer **IX** with excess imide **X** and malonic acid in the presence of zinc(II) acetate (Scheme 5). As in the synthesis of complex **II**, a mixture of zinc complexes of tetra(4-*tert*-butylbenzo)porphyrin and tetraquinoxalinoporphyrin and complex **III** was formed. The latter was isolated from the product mixture by column chromatography.

Insofar as (tetrabenzoporphyrinato)zinc(II) and (tetraquinoxalinoporphyrinato)zinc(II) are poorly soluble in most organic solvents, in both cases only a mixture of two porphyrin complexes was separated by chromatography. Molecules **II** and **III** are more polar than zinc complexes of tetra(4-*tert*-butylbenzo)porphyrin and tetra(4-phenoxybenzo)porphyrin, and they contain two rather than four solubilizing substituents; therefore, their chromatographic mobility is considerably lower than that of the corresponding tetra-substituted compounds, and their isolation involves no difficulties. Reprecipitation of complexes **II** and **III** from concentrated sulfuric acid gave metal-free *cis*-4,4'-diphenoxytetrabenzoporphyrin (**XI**) and *cis*-diquinoxalinodi(4-*tert*-butylbenzo)porphyrin (**XII**) which were purified by column chromatography. Complexes **II** and **III** and ligands **XI** and **XII** are dark green crystalline substances that are readily soluble in a number of organic solvents. Their structure was proved by the analytical data and electronic and ^1H NMR spectra.

The electronic absorption spectra of complexes **II** and **III** are shown in Figs. 1 and 2; the spectral patterns are typical of tetrabenzoporphyrin metal complexes: a strong Soret band and less intense *Q* band are present. However, unsymmetrical structure of the porphyrin macroring strongly affects the character and position of the main absorption bands. In addition, the spectral properties largely depend on the nature of

molecular fragments. The Soret band in the spectrum of complex **II** (Fig. 1) is insignificantly displaced (by 2 nm) to the blue region relative to the corresponding band in the spectrum of (tetrabenzoporphyrinato)-zinc(II) [5]. On the other hand, the Soret band was strongly broadened, which may be due to superposition of intramolecular charge-transfer band and the presence of isomers with different positions of the phenoxy groups, whose spectral parameters may be different. The *Q* band is slightly displaced red ($\Delta\lambda = 3$ nm) due to substituent effects and polarization of the molecule. The spectrum of complex **II** also contained a weak absorption band at λ 646 nm which was not observed in the spectrum of (tetrabenzoporphyrinato)zinc(II). We believe that this band also originates from intramolecular charge transfer.

The electronic absorption spectrum of complex **III** (Fig. 2) is more similar to the spectrum of (tetrabenzoporphyrinato)zinc(II) [5]. A small red shift of the *Q* band ($\Delta\lambda = 5$ nm) should be noted, while the position of the Soret band is the same as in the spectrum of (tetrabenzoporphyrinato)zinc(II). A weak charge-transfer band at λ 492 nm was also present in the spectrum of complex **III**.

More considerable differences were observed in the spectra of metal-free compounds **XI** and **XII** (Figs. 1, 2). As in the spectrum of tetrabenzoporphyrin, the Soret band of **XI** and **XII** is split into two components, but the splitting is less pronounced, presumably due to reduced molecular orbital symmetry. The bands are broadened and displaced toward longer wavelengths. The shift is insignificant for porphyrin **XI** (Fig. 1): it amounts to 4–5 nm relative to tetrabenzoporphyrin [24]; while in the spectrum of compound **XII** (Fig. 2) the difference in the position of the Soret band reaches 45–47 nm. These findings may be rationalized in terms of a larger dipole moment of molecule **XII** compared to **XI** and the effect of additional ring fusion. In the spectrum of **XI** we observed a shoulder at λ 476 nm, which is likely to correspond to charge transfer.

As concerns absorption in the *Q*-region, porphyrin **XI** displayed a charge-transfer band with its maximum at λ 713 nm in addition to two absorption bands typical of all tetrabenzoporphyrins. Analogous bands are also observed in the spectra of unsymmetrical porphyrines characterized by a high dipole moment [25]. A charge-transfer band (λ_{max} 714 nm) was also distinguished in the electronic absorption spectrum of compound **XII**. The *Q* band in the spectrum of **XII**

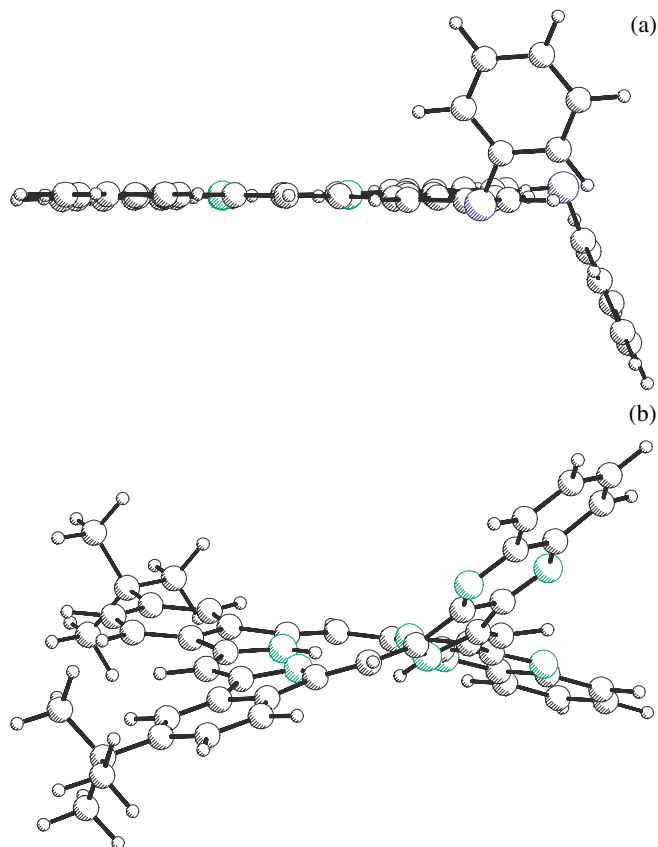


Fig. 3. Structures of molecules (a) **XI** and (b) **XII** according to AM1 calculations.

was strongly broadened, and its short-wave component was displaced to longer wavelengths. In the spectrum of tetra(4-*tert*-butylbenzo)porphyrin [23], the maximum of the short-wave component of the *Q* band is located at λ 607 nm, whereas the corresponding maximum in the spectrum of **XII** appears at λ 649 nm. Presumably, this is the result of strong polarization of molecule **XII** and extension of the conjugation system due to fusion of pyrazine rings.

The ^1H NMR spectrum of complex **II** contains three groups of signals. Four *meso*-protons resonate as three singlets in the most downfield region, at δ 10.22, 9.81, and 9.64 ppm; these protons are magnetically nonequivalent due to unsymmetrical structure of molecule **II**. A multiplet in the region δ 7.85–7.65 ppm corresponds to resonance of 14 protons in the isoindole fragments, and 10 protons in the phenoxy groups give a multiplet at δ 7.43–7.18 ppm. The spectral pattern becomes more complicated in going to complex **III**. The *meso*-protons give a multiplet at δ 11.33–11.11 ppm. Signals from eight protons in the benzene rings appear as a multiplet in the δ region 10.05–

9.76 ppm, and protons in the isoindole fragments resonated as a six-proton multiplet at δ 8.48–8.35 ppm. In the upfield region, a singlet at δ 1.84 ppm is observed due to 18 protons in the *tert*-butyl groups.

Metal-free porphyrins **XI** and **XII** showed in the ^1H NMR spectra upfield signals from the intracyclic NH protons. In the spectrum of **XI**, the NH signal is a broadened singlet at δ –2.94 ppm, and compound **XII** gives two singlets at δ –1.9 and –2.2 ppm owing to unsymmetrical structure of molecule **XII** and probably distortion of planar structure due to high dipole moment. We performed AM1 semiempirical quantum-chemical calculations of the structure of molecules **XI** and **XII** (Fig. 3). It is seen that the macroring in molecule **XI** is planar and that molecule **XII** strongly deviates from planar structure; obviously, this factor largely determines the spectral properties of the latter.

Thus we have synthesized unsymmetrical benzo-porphyrins containing electron-donor or electron-withdrawing substituents and examined their spectral properties.

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi UV-2000 spectrophotometer. The IR spectra (400–4000 cm^{-1}) were recorded in KBr on an Avatar 360 FT-IR spectrometer. The ^1H NMR spectra were obtained on a Bruker WM-400 instrument (400 MHz) using HMDS as internal reference.

4-Phenoxyphthalonitrile (**VII**) was synthesized according to the procedure reported in [26], and 4-*tert*-butylphthalimide was prepared as described in [27].

4-Phenoxyphthalimide (V). 4-Phenoxyphthalonitrile (**VII**), 3 g, was added to a solution of sodium methoxide prepared from 0.2 g of metallic sodium and 50 ml of methanol, and the mixture was stirred for 2 h at 20°C. The resulting solution of 3-methoxy-1*H*-isoindol-1-imine (**VIII**) was added to 200 ml of 5% nitric acid. After 30 min, the precipitate was filtered off, washed with water, and dried. Yield 3.4 g (93%), white powder, mp 112–113°C. The product is readily soluble in DMF, DMSO, and acetone and sparingly soluble in hot water. IR spectrum, ν , cm^{-1} : 3200 (N–H), 2936 (C–H), 1762 (C=O), 1043 (C–O). ^1H NMR spectrum (CDCl_3), δ , ppm: 10.46 s (1H), 7.94–7.68 m (3H), 7.35–7.15 m (5H). Found, %: N 5.7. $\text{C}_{14}\text{H}_9\text{NO}_3$. Calculated, %: N 5.8.

5-*tert*-Butyl-3-(5-*tert*-butyl-3-oxo-2,3-dihydro-1*H*-isoindol-1-ylidenemethyl)-1*H*-isoindol-1-one

(**IX**). A mixture of 3 g of 4-*tert*-butylphthalimide and 6 g of zinc(II) acetate dihydrate was heated to 250°C and was kept for 20 min at that temperature. The mixture was cooled, ground, washed in succession with a 10% solution of sodium hydroxide, water, 10% hydrochloric acid, and water again (to pH 7), and dried. The product (a red powder) was dissolved in chloroform, and the solution was subjected to column chromatography on aluminum oxide (activity grade II) using chloroform as eluent. Yield 0.8 g (29%), dark red powder, mp 246–247°C. Compound **IX** is readily soluble in acetone, pyridine, DMF, acetic acid, and chloroform and insoluble in water. Electronic absorption spectrum (CHCl_3), λ_{max} , nm: 358, 516, 552. IR spectrum, ν , cm^{-1} : 3274 (N–H), 2970 (C–H), 1720 (C=O). ^1H NMR spectrum (CDCl_3), δ , ppm: 10.72 s (1H), 7.44–7.21 m (6H), 6.48 s (1H), 1.98 s (18H). Found, %: C 78.20; H 7.95; N 6.20. $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_2$. Calculated, %: C 77.68; H 6.78; N 6.51.

Quinoxaline-2,3-dicarboximide (X). Dry gaseous ammonia was passed over a period of 10 min through 5 g of quinoxaline-2,3-dicarboxylic acid heated to 250°C. The melt was cooled, ground, and dissolved in 100 ml of a 10% solution of sodium carbonate, and the solution was extracted with diethyl ether (3×50 ml). The extracts were combined and evaporated. Yield 3.6 g (79%), white powder. The product is readily soluble in water, dilute acids and alkalis, DMF, and acetone. Found, %: N 20.80. $\text{C}_{10}\text{H}_5\text{N}_3\text{O}_2$. Calculated, %: N 21.10.

($2^{2(3)}, 7^{2(3)}$ -Diphenoxytetrabenzoporphyrinato)-zinc(II) (II). A mixture of 0.3 g of compound **VI**, 0.6 g of imide **V**, 1 g of malonic acid, and 0.5 g of zinc(II) acetate dihydrate was heated for 30 min at 250°C and for 30 min at 320°C. The melt was cooled, ground, and dissolved in chloroform, and the solution was subjected to column chromatography on aluminum oxide of activity grade II using chloroform as eluent. The second green fraction was collected, and the solvent was removed. Yield 0.11 g (13%), dark green powder. The complex is readily soluble in benzene, chloroform, DMSO, and DMF, and insoluble in water. Electronic absorption spectrum (CHCl_3), λ_{max} , nm (D/D_{max}): 646 sh, 628 (0.37), 578 (0.14), 427 (1.00). ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 10.22 s (1H), 9.81 s (2H), 9.64 s (1H), 7.85–7.65 m (14H), 7.43–7.18 m (10H). Found, %: C 77.20; H 3.85; N 7.15. $\text{C}_{48}\text{H}_{28}\text{N}_4\text{O}_2\text{Zn}$. Calculated, %: C 76.04; H 3.72; N 7.39.

2²⁽³⁾,7²⁽³⁾-Diphenoxytetrabenzoporphyrin (XI).

A 0.05-g portion of complex **II** was dissolved in 10 ml of concentrated sulfuric acid, and the solution was kept for 30 min at 20°C and poured into 50 ml of water. The precipitate was filtered off, washed in succession with water, 10% aqueous ammonia, and water again (to pH 7), dried, and dissolved in chloroform, and the solution was subjected to column chromatography on aluminum oxide of activity grade II using chloroform as eluent. A green fraction was collected and evaporated. Yield 0.03 g (70%), dark green powder. The product is readily soluble in benzene, chloroform, DMSO, and DMF and insoluble in water. Electronic absorption spectrum (CHCl₃), λ_{max}, nm (*D/D*_{max}): 713 (0.12), 666 (0.30), 609 (0.32), 434 (1.00), 419 (0.93). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 10.31 s (1H), 9.78 s (3H), 7.78–7.55 m (14H), 7.46–7.21 m (10H), –2.94 s (2H). Found, %: C 82.70; H 5.06; N 7.90. C₄₈H₃₀N₄O₂. Calculated, %: C 82.98; H 4.35; N 8.06.

2²⁽³⁾,7²⁽³⁾-Di-*tert*-butyldibenzo[*a,g*]diquinoxalino[2,3-*l*:2',3'-*q*]porphyrinato)zinc(II) (III). A mixture of 0.3 g of compound **IX**, 0.5 g of imide **X**, 1 g of malonic acid, and 0.5 g of zinc(II) acetate dihydrate was heated for 1 h at 260°C and for 30 min at 330°C. The melt was cooled, ground, and dissolved in benzene, and the solution was applied to a column charged with aluminum oxide of activity grade II. The column was eluted with benzene to collect the second green fraction. Removal of the solvent gave 0.09 g (15%) of complex **III** as a dark green powder readily soluble in benzene, chloroform, DMSO, and DMF and insoluble in water. Electronic absorption spectrum (CHCl₃), λ_{max}, nm (*D/D*_{max}): 631 (0.40), 584 (0.12), 492 (0.13), 457 (0.23), 429 (1.00). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 11.33–11.11 m (4H), 10.05–9.76 m (8H), 8.48–8.35 m (6H), 1.84 s (18H). Found, %: C 73.30; H 5.35; N 13.95. C₄₈H₂₆N₈Zn. Calculated, %: C 72.96; H 4.59; N 14.18.

2²⁽³⁾,7²⁽³⁾-Di-*tert*-butyldibenzo[*a,g*]diquinoxalino[2,3-*l*:2',3'-*q*]porphyrin (XII). A 0.04-g portion of complex **III** was dissolved in 10 ml of concentrated sulfuric acid. The solution was kept for 40 min at 20°C and poured into 50 ml of water. The precipitate was filtered off, washed in succession with water, 10% aqueous ammonia, and water again (to pH 7), dried, and dissolved in chloroform. The solution was subjected to column chromatography on aluminum oxide of activity grade II using chloroform as eluent. A green fraction was collected, and removal of the solvent gave 0.025 g (76%) of compound **XII** as a dark green

powder readily soluble in benzene, chloroform, DMSO, and DMF and insoluble in water. Electronic absorption spectrum (CHCl₃), λ_{max}, nm (*D/D*_{max}): 714 (0.15), 666 (0.26), 649 (0.25), 476 (1.00), 465 (0.90), 435 sh. ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 11.41–11.28 m (4H), 9.98–9.75 m (8H), 8.31–8.18 m (6H), 1.86 s (18H), –1.9 s (1H), –2.2 s (1H). Found, %: C 81.25; H 4.46; N 14.88. C₄₈H₂₈N₈. Calculated, %: C 80.43; H 3.94; N 15.63.

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