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Synthesis and Spectral Characteristics of Unsymmetrical Porphirazines with Triphrnylmethyl Groups

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Abstract—Condensation of 4-(*p*-triphenylmethylphenoxy)-1,2-dicyanobenzene with 1,2-di(methylthio)maledinitrile or 2,3-dicyano-5,6-diphenylpyrazine afforded symmetric and unsymmetrical porphirazines. The effect of their structural modification on the spectral characteristics was investigated.

Porphirazines and their close structural analogs attract great attention nowadays. Versatile information on synthesis and properties of various porphirazines are summarized in books [1, 2] and reviews [3, 4].

Intense research is directed now to as synthesis and investigation of properties of unsymmetrical phthalocyanines and porphirazines applied as materials for liquid crystals [5], for nonlinear optics [3], and thin-film microelectronics [6].

These compounds can be divided in three groups: A_3B, ABAB, and AABB where A and B are different circumferential fragments of the porphirazine molecule. Although publications treating these compounds are numerous, the studies where symmetric and unsymmetrical compounds of all possible types (A_4, A_3B, ABAB, AABB, AB_3, B_4) have been isolated and characterized are rare. Two among them consider compounds with a changing overall number of π-electrons [7, 8], and one report describes a series of compounds with circumferential fragments of isoelectronic structure [9].

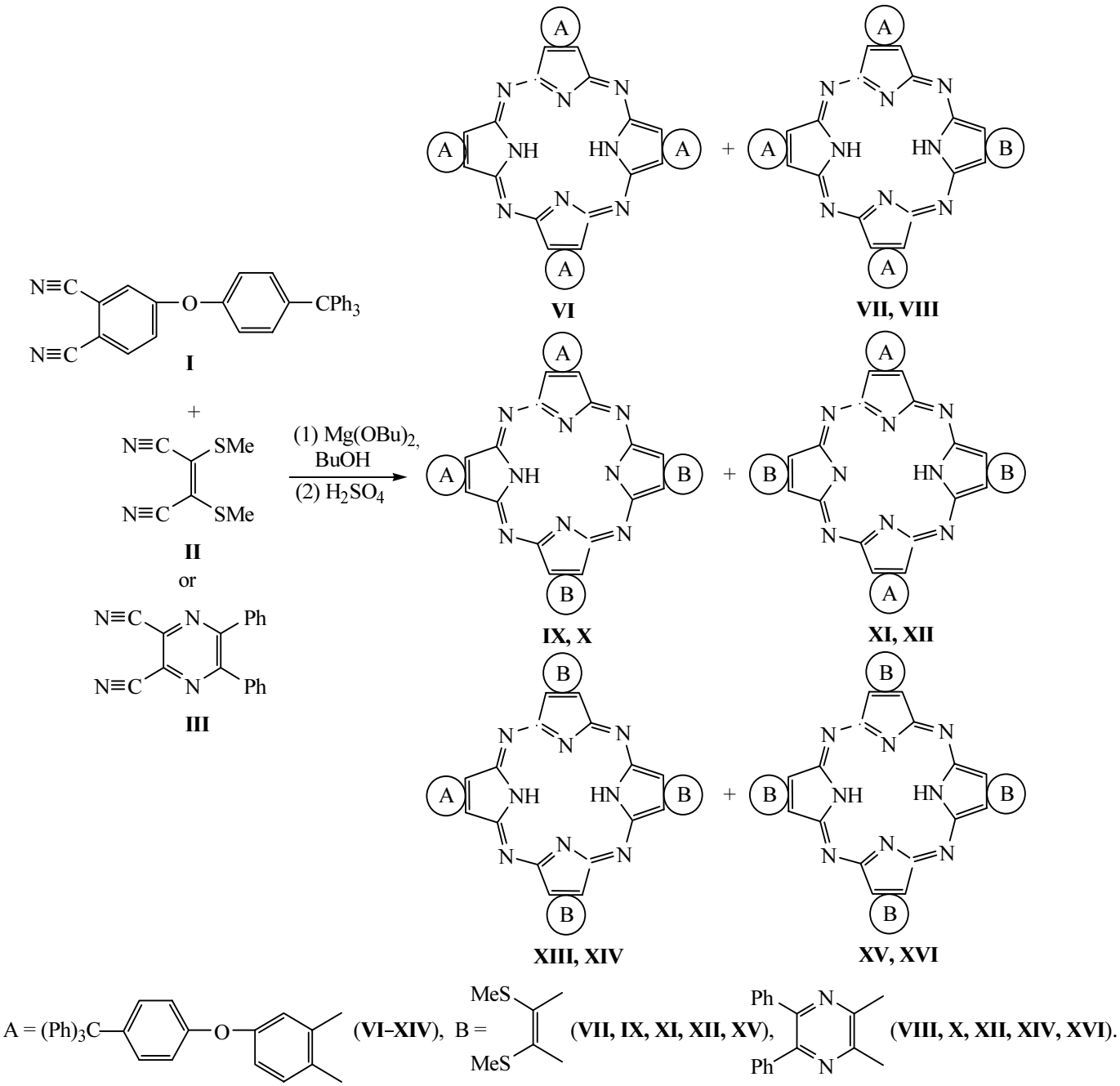
The optimal procedure for the synthesis of these porphirazines is a condensation of two phthalocyanogens (*ortho*-dinitriles or 1,3-diiminoisoindolines) where one among reagents possesses bulky substituents imparting solubility in organic media. The commonly used substituents are *tert*-butyl [10], alkyl or alkoxy groups [11, 12]. In this way the products are more easily separated by chromatography, and it is possible to isolate all compounds in the individual state. The second component for condensation is usually a phthalocyanogen without bulky substituents. Therefore the six components of the porphirazines mixture possess different solubility and thus are differently retained in the chromatographic column facilitating their separation. However successful separation was sometimes achieved only using the most efficient chromapographic methods (e.g., preparative HPLC).

It should be noted that the spectral characteristics of these compounds are poorly studied. Their theoretical analysis is virtually lacking, the effect on the electronic spectra produced by the nature of A and B fragments, molecular symmetry, and alteration of the p-electrons number in the macroring is insufficiently understood. The best studied in this respect are compounds of A_3B and ABAB types since for these compounds convenient and highly selective synthetic procedures were developed, like ring expansion in boron subphthalocyanines (A_3B) [13] and cross-condensation of 1,3-diiminoisoindoline derivatives with 1,1,3-trichloro-isoindolenines [14]. It was established that spectral characteristics of these compounds significantly depended on the electronic structure of A and B fragments [15].

We report here on the synthesis and some properties of porphirazines of A_4, A_3B, ABAB, and AABB types prepared by condensation of 4-(*p*-triphenylmethyl-phenoxy)-1,2-dicyanobenzene (**I**) (obtained by nucleophilic substitution [16] of a nitro group in 4-nitrophthalodinitrile under the action of 4-triphenylmethylphenol) with 1,2-di-(methylthio)maledinitrile (**II**) or 2,3-dicyano-5,6-diphenylpyrazine (**III**). The synthesis of 4-nitrophthalodinitrile (**IV**) and 4-trimethylphenol (**V**) are described in EXPERIMENTAL.

In both cases the condensation by Linstead method [17] gave rise to six-component mixtures according to a scheme:

Scheme.



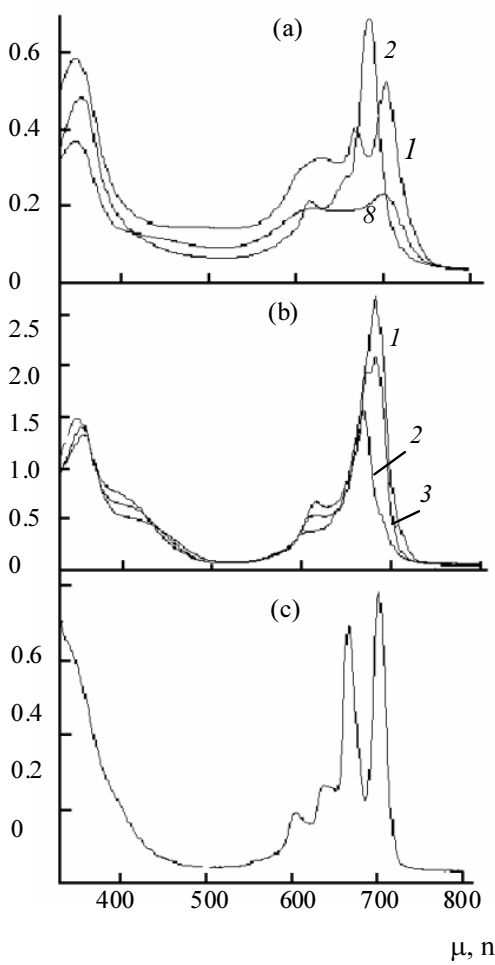
Compounds A_4 (**VI**), A_3B (**VII, VIII**), AABB (**IX, X**), and ABAB (**XI, XII**) were isolated from mixture obtained by column chromatography.

The use of nitrile **II** as second component resulted in porphirazines with nonisoelectronic structure, and porphirazines prepared involving nitrile **III** possessed isoelectronic structure.

Homogeneity of porphirazines obtained was proved by TLC, their composition and structure were confirmed by elemental analysis, electronic and ^{1}H NMR spectroscopy.

The electron absorption spectra of porphirazines of unsymmetrical structure **VII–XII** are presented on the figure. For comparison the electronic spectrum of phthalocyanine **VI** is also shown.

The electron absorption spectra of porphirazines **VII, IX**, and **XI** (see figure) contain strong absorption bands originating from π,π*-transitions in visible (*Q*-bands) and



Electron absorption spectra in chloroform of porphirazines: (a) *1,* **VII**; *2,* **IX**; *3,* **XI**; (b) *1,* **VIII**; *2,* **X**; *3,* **XII**; (c) phthalocyanine **VI**.

UV region (*B*-bands). The replacement of substituted benzene rings by two methylthio groups resulted in a smaller red shift of the *Q*-bands maxima in the porphirazines A_4, A_3B, ABAB, AABB, and B_4 [18], the maxima of the *B*-bands located in the region 350 nm remaining practically intact. Apparently these alterations are caused by decrease in the overall number of the π-electrons in the macroring. The character of the spectra resembles that of the spectra of unsymmetrically substituted porphirazines of the similar structure prepared from 1,2-diphenylmaledinitrile and phthalodinitrile [8]. This change in the spectral characteristics may be rationalized applying the widely used four-orbital model of Gouterman [19]. According to the model the longwave bands in the electronic spectra of pophirazines are ascribed to the electron transitions from the A_{1u} orbital to two orthogonallt directed orbitals e_g* that are degenerate in porphirazines of D_{4h} symmetry (e.g., for metal complexes of phthalocyanines). The degeneration is removed in compounds of lower symmetry, and the *Q*-band splits in two components of similar intensity. The splitting is very sensitive to the character of the macrocycle, and in keeping with theoretical predictions concerning unsymmetrical porphirazines it should be maximal for compounds of ABAB type and minimal for AABB type. Just this pattern is observed in our study. Therewith the absorption maxima for compound **XI** of ABAB type appear in the region close to the absorption region of compounds A_4 and B_4.

On substitution of dimethylthio groups by diphenylpyrazine moieties the electronic spectra of un-symmetrically substituted porphirazines **VIII, X**, and **XII** (see figure) suffer significant changes. First of all in the spectra appear new broad bands in the region 400–420 nm that we believe to originate from a charge transfer from the donor to acceptor part of the molecule, the diphenylpyrazine moiety playing part of the latter. In both cases the absorption spectra of AABB type compounds are very similar, and only a blue shift of the *Q*-band by 14 nm is observed in going from compound **IX** to compound **X.** The shift is due to decrease in the HOMO a_{1u} energy caused by electron-withdrawing substituents. For compounds **XII** of ABAB type a splitting of the *Q*-band in two components (Δλ 9 nm) is also observed; however it is considerably less than in the electronic spectrum of compound **XI** (Δλ 83 nm). In the spectrum of compound **VIII** of A_3B type the observed splitting of the *Q*-band is also less than in the spectrum of compound **VII**.

In the ^{1}H NMR spectra of porphirazines **VIII, X**, and **XII** containing diphenylpyrazine moieties resonances from three groups of aromatic protons are observed. The proton signals from phenyl substituents of the pyrazine rings appear in the region 8.25–7.90 ppm, those from isoindole fragments at 7.60–7.30 ppm, the resonance of protons from tetraphenylmethane groups is present in the region 7.30–7.15 ppm. As to the ^{1}H NMR spectra of sulfur-containing porphirazines **VII, IX**, and **XI**, they contain in the region 3.37–2.49 ppm the signals of aliphatic protons from methyl groups, and the resonances from aromatic protons of isoindole fragments and tetraphenylmethane substituents appear in the same regions as in the spectra of porphirazines **VIII, X**, and **XII**.

The identification of A_3B type porphirazines was performed by analysis of the integral intensities of signals corresponding either to the phenyl protons of substituents in diphenylpiperazine fragments of compound **VIII** seen as a most downfield doublet signal at 8.21–8.09 ppm, or to the methyl groups of the SMe moieties in porphirazine

VII appearing as a multiplet at 3.34–3.23 ppm Isomeric porphirazines of AABB and ABAB are indistinguishable by composition but easily identified with the use of ^{1}H NMR spectra. For instance, in the spectrum of porphirazine **XI** the signals of the four SMe groups are registered as a broadened singlet at 2.49 ppm whereas for compound **IX** of AABB this resonance is split in two components at 3.37 and 2.96 ppm

In the IR spectra of porphirazines synthesized common absorption bands are present. For instance, the bands in 2975–2880 cm^{-1} region correspond to C–H bonds vibrations, strong bands at 1388–1380 cm^{-1} belong to vibrations of C–C bonds in tetraphenylmethane groups, less strong bands at 1050–1040 cm^{-1} originate from vibrations of C–O bonds.

Our results permit a conclusion that the main factor governing the spectral characteristics of the unsym-metrically substituted porphirazines is the overall number of π-electrons in the molecule alongside the symmetry of the macroring. Also the compounds are more sensitive to structural alterations where the number of of π-electrons in the molecule is subject to changes.

EXPERIMENTAL

Electron absorption spectra of compounds obtained were measured on spectrophotometer Hitachi UV-2000 from solutions in $CHCl_3$, IR spectra were recorded on spectrophotometer Avatar 360 FT-IR in the region 400–4000 cm^{-1} from KBr pellets. ^{1}H NMR spectra (200 MHz) were registered on spectrometer Bruker AM-200 in $CDCl_3$, internal reference TMS. FAB mass spectrum was measured in a matrix of *m*-nitrobenzyl alcohol on Bruker Reflex III instrument.

4-Nitro phthalonitrile (**IV**) [20], 4-triphenylmethylphenol (**V**) [21], 1,2-di(methylthio)malenitrile (**II**) [22], and 2,3-dicyano-5,6-diphenylpyrazine (**III**) [23] were prepared along known procedures.

4-(*p*-Triphenylmethylphenoxy)-1,2-dicyanobenzene (I). A mixture of 2.6 g (0.015 mol) of 4-nitrophthalonitrile **(IV)**, 6.9 g (0.015 mol) of 4-triphenylmethylphenol (**V**), 2.7 g of K_2CO_3, and 50 ml of DMF was stirred for 10 h at 110°C. On cooling the reaction mixture was poured into 300 ml of water. The precipitate was filtered off, washed with water, dried in air at 80°C, and subjected to chromatography on aluminum oxide of II grade activity (eluent benzene). The solvent was removed to afford 4.8 g (69%) of compound **I** as light yellow powder, mp 216–218°C, R_f 0.59 (chloroform, Silufol). IR spectrum, ν, cm^{-1}: 3468, 2928, 2223 (C≡N), 1593, 1489, 1386 (C–C), 1281, 953, 748. FAB mass spectrum, *m/z*: 463.1 $[M+H]^+$, 386.1 $[M+H-C_6H_5]^+$. Found, %: C 86.22; H 5.05; N 5.88. $C_{33}H_{22}N_2O$. Calculated, %: C 85.68; H 4.80; N 6.06.

Condensation of 4-(*p*-triphenylmethylphenoxy)-1,2-dicyanobenzene (I) with 1,2-di(methylthio)-malenitrile (II). Into a suspension of magnesium 1-butanol-ate prepared by boiling for 2 h 0.2 g of magnesium in 50 ml of anhydrous 1-butanol was charged a mixture of 2.3 g (0.005 mol) of compound **I**, 0.35 g (0.002 mol) of compound **II**, and the reaction mixture was heated at reflux for 3 h. Then the butanol was distilled off to dryness, the residue was dissolved in 100 ml of concn. sulfuric acid, and after keeping for 5 min the solution was poured into 300 ml of water. The separated precipitate was filtered off, washed with water till pH 7, then with 50 ml of acetone, and dried. Then the product was dissolved in benzene and subjected to chromatography on aluminum oxide of II grade activity (eluent benzene–acetone, 10:1 by volume). The product separated in the column into 4 zones containing respectively porphirazines of types A_4, A_3B, ABAB, and AABB that were isolated by removing solvent from the corresponding fractions.

Tetra[4-(*p*-triphenylmethylphenoxy)]phthalocyanine (VI) (A_4). Blue powder, well soluble in benzene, chloroform, insoluble in acetone, DMF, water. Yield 0.25 g (11%). Electron absorption spectrum, λ_{max}, nm (D/D_{max}): 703 (1.00), 666 (0.88), 637 (0.35), 605 (0.24), 343 (0.77). Found, %: C 85.80; H 5.10; N 5.70. $C_{132}H_{90}N_8O_4$. Calculated, %: C 85.60; H 4.90; N 6.05.

Tri[4-(*p*-triphenylmethylphenoxybenzo)]-1,2-di(methylthio)porphirazine (VII) (A_3B). Dark-green powder, well soluble in benzene, chloroform, insoluble in acetone, DMF, water. Yield 0.09 g (8%). Electron absorption spectrum, λ_{max}, nm (D/D_{max}): 703 (0.90), 667 (0.69), 632 (0.56), 348 (1.00). IR spectrum, ν, cm^{-1}: 2979 (C–H), 2923, 1650, 1470, 1384 (C–C), 1230, 1164, 1048 (C–O), 886, 749, 701. ^{1}H NMR spectrum, δ, ppm: 7.60–7.35 m (9H), 7.32–7.18 m (57H), 3.33–3.23 m (6H), 0.33 s (2H). Found, %: C 81.50; H 4.75; N 7.00. $C_{103}H_{74}N_8O_3S_2$. Calculated, %: C 80.55; H 4.86; N 7.30.

***cis*-Di[4-(*p*-triphenylmethylphenoxybenzo)]di-[1,2-di(methylthio)]porphirazine (IX) (AABB)**. Blue powder, well soluble in benzene, chloroform, insoluble in acetone, DMF, water. Yield 0.04 g (9%). Electron absorption spectrum, λ_{max}, nm (D/D_{max}): 683 (1.00), 616 (0.31), 353 (0.70). IR spectrum, ν, cm^{-1}: 2985 (C–H), 2921, 1655, 1479, 1388 (C–C), 1239, 1168, 1049 (C–O), 888, 750, 688. ^{1}H NMR spectrum, δ, ppm: 7.40–7.38 m (6H), 7.31–7.22 m (38H), 3.37 s (6H), 2.96 s (6H), 2.49 m

(12H), 0.42 s (2H). Found, %: C 72.02; H 5.05; N 8.85. $C_{74}H_{58}N_8O_2S_4$. Calculated, %: C 72.88; H 4.79; N 9.19.

***trans*-Di[4-(*p*-triphenylmethylphenoxybenzo)]-di[1,2-di(methylthio)]porphirazine (ABAB) (XI)**. Violet powder, well soluble in benzene, chloroform, insoluble in acetone, DMF, water. Yield 0.03 g (14%). Electron absorption spectrum, λ_{max}, nm (D/D_{max}): 700 (0.63), 622 (0.53), 347 (1.00). IR spectrum, ν, cm^{-1}: 2978 (C–H), 2924, 1648, 1471, 1380 (C–C), 1235, 1161, 1047 (C–O), 881, 755, 679. ^{1}H NMR spectrum, δ, ppm: 7.45–7.40 m (6H), 7.35–7.25 m (38H), 2.49 m (12H), 0.31 s (2H). Found, %: C 73.90; H 5.15; N 8.70. $C_{74}H_{58}N_8O_2S_4$. Calculated, %: C 72.88; H 4.79; N 9.19.

Condensation of 4-(*p*-triphenylmethylphenoxy)-1,2-dicyanobenzene (I) with 2,3-dicyano-5,6-diphenylpyrazine (III). Into a suspension of magnesium 1-butanolate prepared by boiling for 2 h 0.2 g of magnesium in 50 ml of anhydrous 1-butanol was charged a mixture of 2.3 g (0.005 mol) of compound **I**, 0.7 g (0.002 mol) of compound **III**, and the reaction mixture was heated at reflux for 4 h. Then the butanol was distilled off to dryness, the residue was dissolved in 100 ml of concn. sulfuric acid, and after keeping for 5 min the solution was poured into 300 ml of water. The separated precipitate was filtered off, washed with water till pH 7, then with 50 ml of acetone, and dried. Then the product was dissolved in benzene and subjected to chromatography on aluminum oxide of II grade activity (eluent benzene–acetone, 10:1 by volume). The product separated in the column into 4 zones containing respectively porphirazines of types A_4, A_3B, ABAB, and AABB that were isolated by removing solvent from the corresponding fractions.

Tetra[4-(*p*-triphenylmethylphenoxy)]-phthalocyanine (A_4) (VI). Yield 0.30 g (13%).

Tri[4-(*p*-triphenylmethylphenoxybenzo)](4,5-diphenylpyrazino)porphirazine (VIII) (A_3B). Dark-green powder, well soluble in benzene, chloroform, insoluble in acetone, DMF, water. Yield 0.08 g (6%). Electron absorption spectrum, λ_{max}, nm (D/D_{max}): 683 (1.00), 616 (0.25), 402 sh, 350 (0.55). IR spectrum, ν, cm^{-1}: 2973 (C–H), 2880, 1454, 1384 (C–C), 1225, 1091, 1049 (C–O), 881, 706, 620. ^{1}H NMR spectrum, δ, ppm: 8.25–7.90 m (10H), 7.60–7.35 m (9H), 7.30–7.15 m (57H), 0.32 s (2H). Found, %: C 84.90; H 5.07; N 8.29. $C_{117}H_{78}N_{10}O_3$. Calculated, %: C 84.05; H 4.70; N 8.38.

***cis*-Di[4-(*p*-triphenylmethylphenoxybenzo)]di-(4,5-diphenylpyrazino)porphirazine (X) (AABB)**. Blue-green powder, well soluble in benzene, chloroform, insoluble in acetone, DMF, water. Yield 0.14 g (8%). Electron absorption spectrum, λ_{max}, nm (D/D_{max}): 670 (1.00), 607 (0.24), 423 sh, 356 (0.85). IR spectrum, ν, cm^{-1}: 2975 (C–H), 2886, 1458, 1385 (C–C), 1221, 1096, 1048 (C–O), 882, 701, 614. ^{1}H NMR spectrum, δ, ppm: 8.30–7.90 m (20H), 7.65–7.41 m (6H), 7.40–7.25 m (38H), 0.41 s (2H). Found, %: C 83.45; H 5.12; N 10.35. $C_{102}H_{66}N_{12}O_2$. Calculated, %: C 82.13; H 4.59; N 11.27.

***trans*-Di[4-(*p*-triphenylmethylphenoxybenzo)]-di(4,5-diphenylpyrazino)porphirazine (XII) (ABAB)**. Blue powder, well soluble in benzene, chloroform, insoluble in acetone, DMF, water. Yield 0.09 g (5%). Electron absorption spectrum, λ_{max}, nm (D/D_{max}): 683 (1.00), 672 (0.92), 616 (0.25), 412 sh, 354 (0.67). IR spectrum, ν, cm^{-1}: 2978 (C–H), 2889, 1457, 1381 (C–C), 1229, 1091, 1041 (C–O), 888, 711, 605. ^{1}H NMR spectrum, δ, ppm: 8.35–7.80 m (20H), 7.75–7.65 m (6H), 7.55–7.30 m (38H), 0.29 s (2H). Found, %: C 83.15; H 4.08; N 10.86. $C_{102}H_{68}N_{12}O_2$. Calculated, %: C 82.13; H 4.59; N 11.27.

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