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Synthesis of (2,3-Diphenyl)pyrazinotribenzoporphyrazine

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Abstract—By the method of template cyclotetramerization magnesium(II) (2,3-diphenyl)pyrazinotribenzoporphyrazinate was synthesized, and it was converted into (2,3-diphenyl)pyrazinotribenzoporphyrazine. (2,3-Diphenyl)-pyrazinotribenzoporphyrazine and (2-phenyl)imidazolotribenzoporphyrazine were synthesized from 5,7-diphenyl-1,4-diazepinotribenzoporphyrazine by vacuum sublimation.

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Porphyrazines with fused heterocycles (imidazolo-, pyridino-, pyrazino-, pyridazino-, diazepinoporphyrazine) are azaanalogs of well-understood phthalocyanine. The existing publications make it possible to search among compounds of this series for substances with valuable applied properties [1–5]. Recently the unsymmetrical porphyrazines attract much attention due to their optical characteristics.

The target of this study was the synthesis of (2,3-diphenyl)pyrazinotribenzoporphyrazine $Bz_3Ph_2PyzPzN_2$. We first obtained a magnesium complex with (2,3-diphenyl)pyrazinotribenzoporphyrazine by template cyclotetramerization of phthalonitrile with 5,6-diphenyl-2,3-dicyanopyrazine in the ratio 3 : 1 applying the magnesium butylate. The magnesium complexes with pyrazinoporphyrazine are known to be more soluble in organic solvents than the ligands [6], therefore we prepared by template cyclotetramerization the magnesium complex of (2,3-diphenyl)pyrazinotribenzoporphyrazine, which was isolated by column chromatography from the mixture of magnesium complexes of di-, tri-, and tetrapyrazinoporphyrazines (Scheme 1).

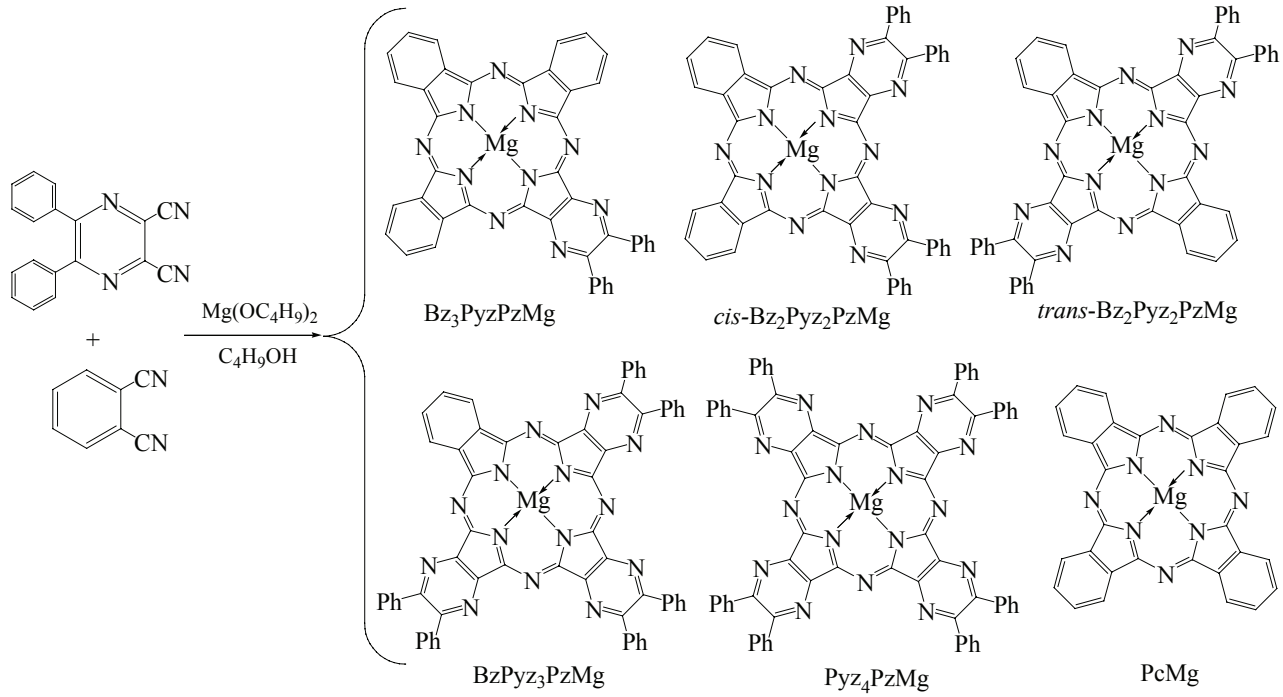
Due to the low yield of $Bz_3Ph_2PyzPzMg$ (5%) we decided to prepare it through a phthalocyanine intermediate (Scheme 2) along the procedure developed for obtaining phthalocyanines of low symmetry [7].

$Bz_3Ph_2PyzPzMg$ was isolated by column chromatography on silica gel. The elution was carried out with $CHCl_3$ containing from 30 to 40% methanol. The isolation of porphyrazine $Bz_3Ph_2PyzPzMg$ in the pure state requires repeated chromatographic purifications. The elemental analysis indicated that composition of the complex contained two water molecules. Similar aqua complexes magnesium forms with the other porphyrazines [8–10]. IR spectrum of the complex $Bz_3Ph_2PyzPzMg$ contains a set of bands corresponding to the stretching and bending vibrations of functional groups present in its structure: bands of the stretching vibrations of the C=N bonds in the porphyrazine ring and the pyrazine fragments (1475 and 1441 cm^{-1} respectively), C–N bonds (3050 cm^{-1}), and C=C bonds in the phenyl fragments (1441 cm^{-1}). The band corresponding to the stretching vibrations of C_{Ph}–C_{Pz} appears at lower wavenumber (1136 cm^{-1}). The character of the electron absorption spectrum (EAS) of the complex shows that the compound is present in an associated state. At the addition of a little pyridine the associates are decomposed (Fig. 1). $Bz_3Ph_2PyzPzMg$ is prone to strong aggregation. Due to its association and aggregation we failed to register its ^1H NMR spectrum.

The EAS of the complex in neat trifluoroacetic and sulfuric acids are shown on Fig. 2, 3. In the 100% trifluoroacetic acid $Bz_3Ph_2PyzPzMg$ is present in a protonated form as indicated by the red shift of the spectrum characteristic of the porphyrazine complexes [11]. On the dissolution of $Bz_3Ph_2PyzPzMg$ in 100% sulfuric aci the color of the solution changed from blue-green to light red, and new absorption bands at 489 and 531 nm appear in EAS. It is presumable that in sulfuric acid radical forms of the complex are present.

The ligand $Bz_3Ph_2PyzPzH_2$ was obtained by the

Scheme 1.



demetalation of the complex $Bz_3Ph_2PyzPzMg$ by treating it with trifluoroacetic acid at room temperature. The ligand $Bz_3Ph_2PyzPzH_2$ like its magnesium complex is prone to association in solutions.

Recently [12] 5,7-diphenyl-1,4-diazepinotribenzoporphyrazine and its magnesium complex were synthesized for the first time. The fragmentation of the molecular ion of $Bz_3Ph_2DzPzMg$ at the electron impact at 43 eV led to phenylacetylene elimination and to the contraction of the diazepine ring giving magnesium (2-phenyl)imidazolotribenzoporphyirazinate $Bz_3PhImHPzMg$. Thus the possibility to modify the diazepine ring was demonstrated leading to obtaining new porphyrazines without the template cyclotetramerization.

Therefore we carried out a vacuum sublimation of 5,7-diphenyl-1,4-diazepinotribenzoporphyrazine[1]

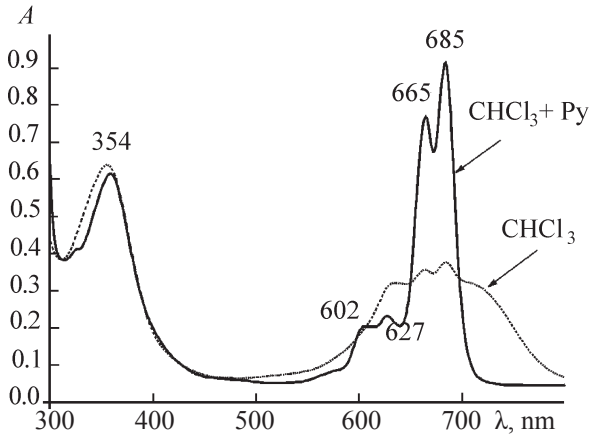


Fig. 1. EAS of $Bz_3Ph_2PyzPzMg$ in chloroform and in chloroform with added pyridine.

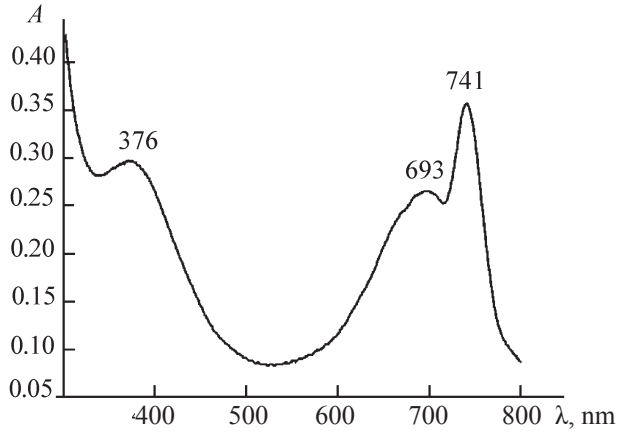
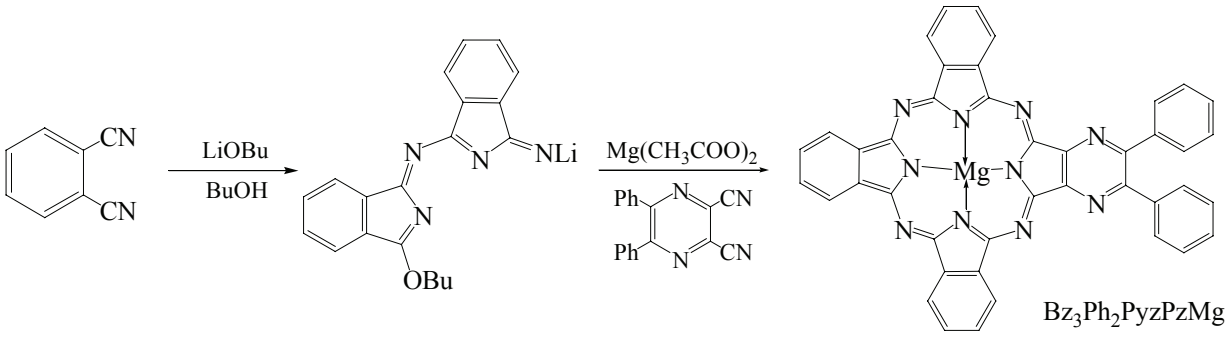


Fig. 2. EAS of $[Bz_3(Ph)_2PyzPzMg]$ in 100% trifluoroacetic acid.

[1] The sublimation of Bz_3DzPzH_2 was performed in the Institute of Solution Chemistry of the Russian Academy of Sciences under the supervision of Leading Researcher, Candidate of Chemical Science V.B. Sheinin.

Scheme 2.



and found that in the course of the sublimation $(Bz_3Ph_2DzPzN_2)\cdot 4H_2O$ afforded a mixture of two compounds: (2,3-diphenyl)pyrazinotribenzoporphyrazine and (2-phenyl)imidazolotribenzoporphyrazine (Scheme 3). It was confirmed by the data of mass spectrometry. EAS of the mixture in chloroform solution is shown on Fig. 4.

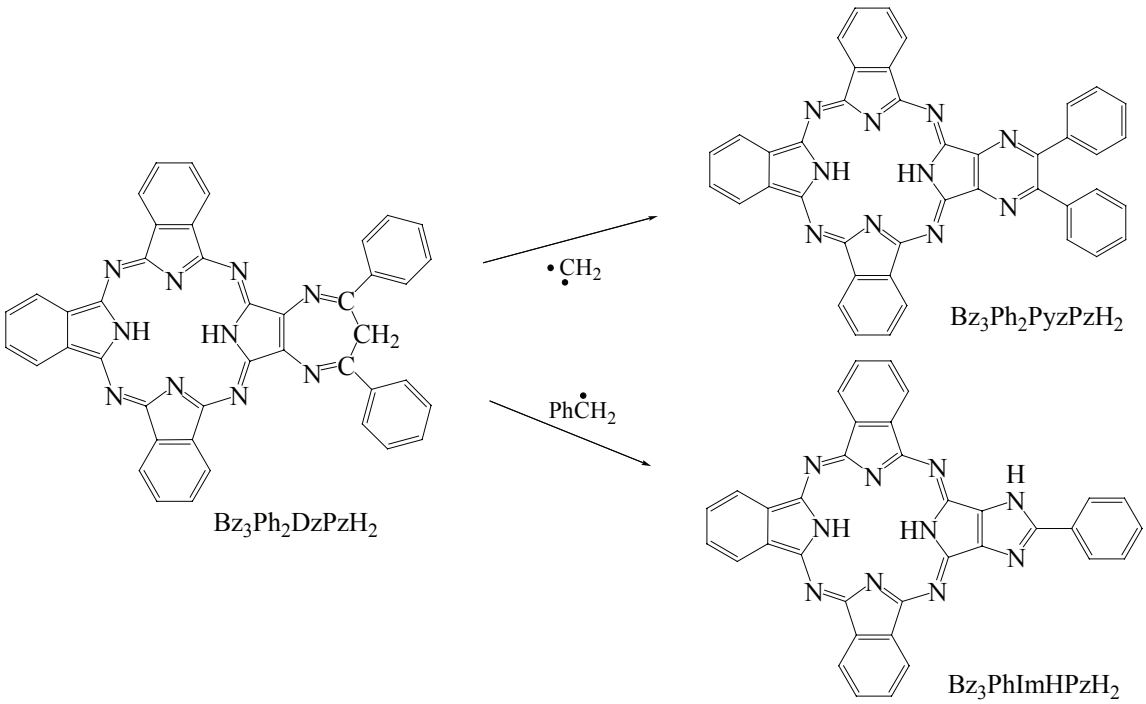
The mixture of two porphyrazines was separated by column chromatography on silica gel with elution by chloroform with variable content of methanol. The identity of (2,3-diphenyl)pyrazinotribenzoporphyrazine prepared by sublimation and by template cyclotetramerization was proved by mass spectrometry and electron absorption spectroscopy (Figs. 5, 6).

Thus the vacuum sublimation can be used in the synthesis of new porphyrazines. It is especially interesting in the case of $Bz_3PhImHPzH_2$, which cannot be obtained directly by the template cyclotetramerization since 4,5-dicyanoimidazole is inert under the conditions of this synthesis [13]. Using for initial products various diazepine derivatives of porphyrazine it is possible to synthesize imidazole derivatives of porphyrazine with various substituents in the position *2* of the imidazole ring.

EXPERIMENTAL

Electron absorption spectra (EAS) were registered

Scheme 3.



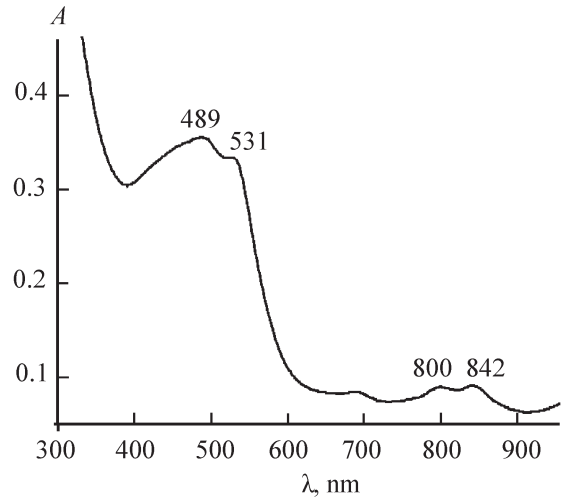


Fig. 3. EAS of $Bz_3Ph_2PyzPzMg$ in 100% H_2SO_4.

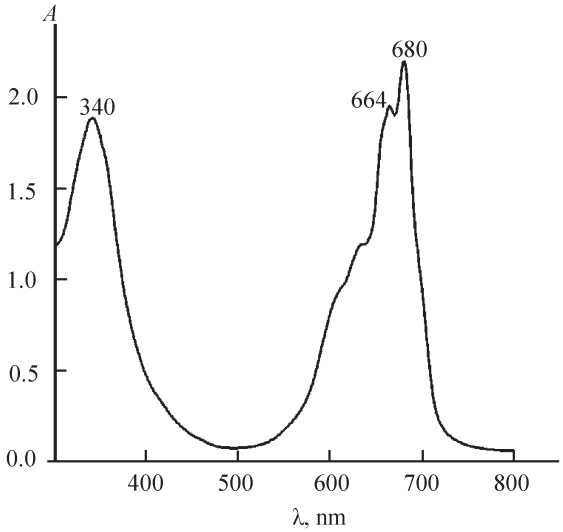


Fig. 5. EAS $Bz_3Ph_2PyzPzH_2$ in mixed solvent $CHCl_3$–CH_3OH.

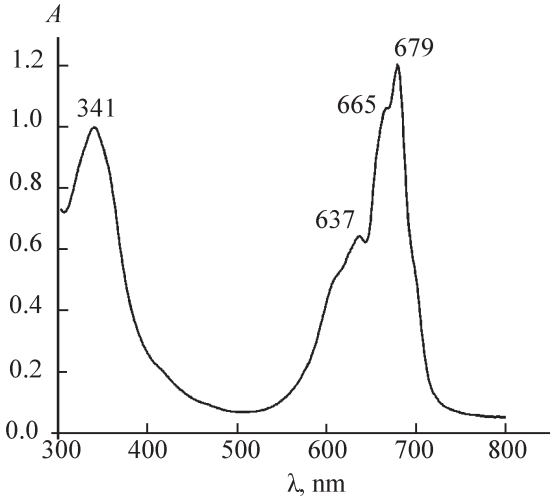


Fig. 4. EAS of the porphyrazines mixture in chloroform solution.

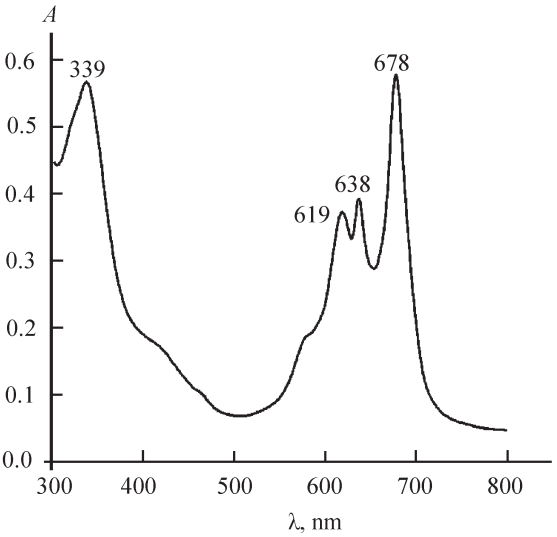


Fig.6. EAS of $Bz_3PhImHPzH_2$ in mixed solvent $CHCl_3$–CH_3OH.

on spectrophotometers Hitachi U-2000, Agilent 8453, Shimadzu UV-1800 from 10^{-6}–10^{-5} M solutions of porphyrazines and their complexes in the wave range of 300–800 nm using quartz cells. IR spectra were recorded on Fourier spectrophotometers NIC 5DX, Avatar 360 FT-IR ESP (400–4000 cm^{-1}), and Bruker Vertex 70 equipped with ATR-device Bruker Platinum from samples pelletized with KBr. MALDI-TOF mass spectra were measured on a spectrometer Ultraflex (Bruker Daltonics) using as matrix 3,5-dihydroxybenzoic acid, and without it. Elemental analysis was carried out on instruments EA Euro 3000 (Kehatech) and Elementar Vario EL.

Diaminomaleodinitrile, dibenzoylmethane, phthalonitrile, ethanol, methanol from Aldrich, Acros Organics, 4,5-dichloro-1,2-dicyanobenzene, 4-*tert*-butylphthalonitrile from TCI Europe were used without additional purification. Butanol was distilled on CaO (bp 118°C).

Chloroform was refluxed on CaO and distilled at the atmospheric pressure (bp 80–81°C).

2,3-Dicyano-5,6-diphenylpyrazine was prepared as described in [14].

(2,3-Diphenyl)pyrazinotribenzoporphyrazinato-magnesium(II). To 50 ml of freshly distilled anhydrous butanol was added 0.024 g (3.5 mg-atom) of lithium metal, the obtained slurry of lithium butylate was cooled,

0.89 g (7 mmol) of phthalonitrile was added thereto, the reaction mixture was heated till it became light green, and again it was cooled, 1.97 g (7 mmol) of 5,6-diphenyl-2,3-dicyanopyrazine and 0.39 g (2.8 mmol) of magnesium acetate was added. The mixture was heated for 6 h at the boiling point of butanol. In the course of the reaction the mixture turned from light green to dark green. On the completion of the reaction butanol was distilled off, the residue was dried at room temperature for 48 h. The dry residue (yield 80% with respect to porphyrazines) was extracted with chloroform in the Soxhlet extractor to separate from insoluble magnesium phthalocyanine. The obtained mixture of magnesium pyrazinoporphyrazinates was separated by column chromatography on silica gel, eluent 40% methanol solution in chloroform. On removal of the solvent the reaction product was dried in a vacuum at 60°C (yield 38% from the mixture Mg-pyrazinoporphyrazinates). EAS (in pyridine), λ, nm (log ε): 362 (4.94), 607 (4.48), 628 (4.52), 666 (5.07), 681(5.11). IR spectrum (KBr), ν, cm^{-1}: 3050 w (–CH), 1660 w, 1606 w, 1537 w, 1475 m, 1441 w, 1346 m, 1331 m, 1288 w, 1248 w, 1188 w, 1155 m, 1136 m, 1113 m, 1078 m, 1059 m, 958 w, 947 w, 889 m, 843 w, 771 m, 754 m, 729 s, 698 s, 667 w, 638 m. Found, %: C 68.74; H 3.64; N 18.70. $C_{42}H_{22}N_{10}Mg·2H_2O$. Calculated, %: C 69.39; H 3.60; N 19.27.

(2,3-Diphenyl)pyrazinotribenzoporphyrazine. The magnesium complex was dissolved in a little trifluoroacetic acid in the dark. The solution obtained was poured in cold distilled water. The separated precipitate was filtered off, washed with water till neutral washings, and with methanol. Yield 70%. EAS (in pyridine), λ, nm (log ε): 348 (4.21), 613 (3.86), 670 (4.31), 683 (4.37). Found, %: C 74.79; H 3.60; N 20.21. $C_{42}H_{22}N_{10}$. Calculated, %: C 75.44; H 3.62; N 20.95.

2,3-Dicyano-5,7-diphenyl-6*N*-1,4-diazepine [15]**.** A mixture of 5 g (0.028 mol) of diaminomaleodinitrile, 12.5 g (0.056 mol) of dibenzoylmethane, and 2 g of P_2O_5 in 160 ml of ethanol was stirred fo 1 h at room temperature. To the mixture more 3 g of P_2O_5 was added, and it was refluxed at the boiling point of ethanol while continuous stirring for 2 h. The reaction mixture obtained was concentrated and cooled. The separated yellow-brown crystals were filtered off, dried, and recrystallized from acetonitrile. Yield 8 g (96%), yellow crystals, mp 249–251°C [15]. IR spectrum, ν, cm^{-1}: 3080, 2250, 1607, 1540, 1460, 1330, 1262, 1200. Found, %: C 76.89; H 3.87; N 18.75. $C_{19}H_{12}N_4$. Calculated, %: C 77.01; H 4.08; N 18.91.

Magnesium(II) 5,7-Diphenyl-1,4-diazepinotribenzoporphyrazinate. In 60 ml of boiling freshly distilled butanol was dissolved 1 g (41 mg-atom) of magnesium metal. To the formed slurry of magnesium butylate was added 2.21 g (7.5 mmol) of 2,3-dicyano-5,7-diphenyl-6*N*-1,4-diazepine and 9.55 g (75 mmol) of phthalonitrile, the mixture was stirred at the boiling point of butanol for 4h. In the course of the reaction the mixture turned from light green to dark green. It was washed with methanol to remove unreacted nitriles. The dry residue (10.3 g, yield 69% with respect to porphyrazines) was extracted with dichloromethane, 7.2 g of insoluble magnesium phthalocyanine was separated. The obtained mixture of of magnesium pyrazinoporphyrazinates (2.6 g) was separated by column chromatography on Al_2O_3 (II grade of activity), eluent 5% methanol solution in dichloromethane. On removal of the solvent the reaction product was dried in a vacuum at 40°C. Yield of $[Bz_3Ph_2DzPzMg]·H_2O$ 630 mg (34% with respect to 2,3-dicyano-5,7-diphenyl-6*N*-1,4-diazepine). EAS (in pyridine), λ, nm (log ε): 357 (4.78), 657 (4.76), 696 (4.82). IR spectrum, ν, cm^{-1}: 690 w, 729 s, 754 s, 889 w, 1055 s, 1084 s, 1117 s, 1184 w, 1280 s, 1332 s, 1444 m, 1485 s, 1525 m, 1610 m, 1631 m, 1059 m. ^1H NMR spectrum (DMSO-d_6, 363 K), δ, ppm: 4.42 br (2H, CH_2), 7.60–7.70 (6H, m,*p*-Ph), 8.20–8.30 (6H, β-Bz), 8.54 d (4H, *o*-Ph, *J* 7 Hz), 9.30–9.40 (2H, α-Bz), 9.40–9.50 (4H). Mass spectrum (MS FD), *m*/*z* (ESI) ($I_{otn.}$, %): 705 (100) $[M + H]^+$, 722 (45) $[M + H_2O]^+$, 740 (10) $[M + 2H_2O]^+$. Calculated, %: C 69.69; H 3.81; N 18.90. $C_{43}H_{24}MgN_{10}·H_2O$. Found, %: C 69.71; H 4.08; N 18.19.

5,7-Diphenyl-1,4-diazepinotribenzoporphyrazine. **[**$Bz_3Ph_2DzPzN_2]·4H_2O$ was obtained and identified along procedure [12]. The magnesium complex was dissolved in a little trifluoroacetic acid in the dark. The solution obtained was poured in cold distilled water. The separated precipitate was filtered off, washed with water till neutral washings, and subjected to column chromatography on Al_2O_3 (II grade of activity), eluent 5% methanol solution in dichloromethane. On removal of the solvent the reaction product was dried in a vacuum at 40°C. Yield 60%. EAS (pyridine), λ, nm (log ε): 349 (4.56), 629 (4.33), 678 (4.33), 711 (4.41); ($CHCl_3$): 346 (4.52), 625 (4.23), 676 (4.31), 716 (4.31). IR spectrum, ν, cm^{-1}: 617 m, 655 w, 690 m, 734 s, 873 s, 1001 s, 1093 w, 1118 s, 1182 m, 1317 m, 1444 s, 1494 m, 1537 m, 1610 w, 1064 m, 3298 w (NH). ^1N NMR spectrum (THF-d_8, 330 K), δ, ppm: –1.33 br (2H, NH-Pz), 4.61 br (2H, CH_2), 7.50–7.60 (6H, m,*p*-Ph); 8.03 (4H, β-Bz), 8.23 (2H), 8.79 d (4H, *o*-Ph, *J* 6.7 Hz); 9.11 (2H, α-Bz), 9.16 (2H), 9.32 (2H).

Mass spectrum (MS FD), *m*/*z* (MALDI-TOF) (I_{rel}, %): 683 (100) $[M + H]^+$, 705 (27) $[M + Na]^+$. Found, %: C 68.53; H 4.30; N 18.67. $C_{43}H_{24}N_{10}\cdot 4H_2O$. Calculated, %: C 68.43; H 4.54; N 18.55.

Sublimation of 5,7-diphenyl-1,4-diazepinotribenzoporphyrazine. The ligand was dissolved in chloroform, and the solution was placed in a trap containing glass rings. Chloroform was evaporated. The test tube with the trap was placed in the oven equipped with temperature control, and the device was connected to a vacuum line. The sublimation was performed twice. At 180°C over 2 h the synthesis proceeded with the formation of (2,3-diphenyl)pyrazinotribenzoporphyrazine, (2-phenyl) imidazolotribenzoporphyrazne and side tarry products. To remove the latter the sublimation was repeated for the second time at 350°C over 6 h. The mixture separated into zones. The MALDI-spectrum of the sample after sublimation demonstrated the presence of two compounds: (2,3-diphenyl)-pyrazinotribenzoporphyrazine and (2-phenyl)imidazolotri-benzoporphyrazine.

$Bz_3Ph_2PyzPzH_2$. EAS (pyridine), λ, nm (log ε): 348 (4.21), 613 (3.86), 670 (4.31), 683 (4.37). Mass spectrum (MS FD), *m*/*z* (MALDI-TOF) (I_{rel}, %) 668 (100) $[M - H]^-$. Found, %: C 74.83; H 3.71; N 20.56. $C_{42}H_{22}N_{10}$. Calculated, %: C 75.44; H 3.62; N 20.95.

$Bz_3PhImHPzH_2$. Mass spectrum (MS FD), *m*/*z* (MALDI-TOF) (I_{rel}, %): 580 (100) $[M - H]^-$. Found, %: C 71.78; H 3.40; N 23.96. $C_{35}H_{20}N_{10}$. Calculated, %: C 72.40; H 3.47; N 24.12.

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