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# Octaarylsubstituted Si(IV) Porphyrazine and Corrolazine: Synthesis by Complexation Method and Formation of μ-Oxo Dimers

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Dedicated to Corresponding Member of the Russian Academy of Sciences G.N. Vorozhtsov on the occasion of his 90th Anniversary

*The reaction of octaphenylporphyrazine with trichlorosilane in pyridine produces dihydroxysilicon octaphenylporphyrazine $(HO)_2SiPzPh_8$ in 75% yield. This method has been shown to be more efficient than the previously used tetramerization of the corresponding diiminoimide in the presence of $SiCl_4$. When refluxing in dry pyridine in the presence of tributylchlorosilane ($Bu_3SiCl$) and tributylamine as a base the axial substitution with formation of $(Bu_3SiO)_2SiPzPh_8$ is observed. Under action of Mg–$Bu_3SiCl$ system the porphyrazine macrocycle undergoes reductive contraction with formation of corrolazine $(Bu_3SiO)SiCzPh_8$. Treatment of corrolazine complexes $(Alk_3SiO)SiCzPh_8$ and $(Alk_3SiO)SiCz(^tBuPh)_8$ (Alk=Pr or Bu) by hydrofluoric acid results in formation of corresponding fluoride derivatives. When attempting to separate them by column chromatography on aluminum oxide ($CH_2Cl_2$:$CH_3OH$ = 98:2), formation of μ-oxo dimers $O[SiAr_8]_2$ most likely occurs.*

**Keywords:** Silicon porphyrazine (tetraazaporphyrin), silicon corrolazine (triazacorrole), synthesis, axial fluoride ligands, μ-oxo dimers.

# Октаарилзамещенные Si(IV) порфиразин и корролазин: синтез методом комплексообразования и образование μ-оксо-димеров

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*Реакция октафенилпорфиразина с трихлорсиланом в пиридине приводит к образованию дигидроксикремний-октафенилпорфиразина $(HO)_2SiPzPh_8$ с выходом 75%. Показано, что этот метод эффективнее ранее применявшейся тетрамеризации соответствующего дииминоимида в присутствии $SiCl_4$. При кипячении в сухом пиридине в присутствии трибутилхлорсилана ($Bu_3SiCl$) и трибутиламина в качестве основания наблюдается аксиальное замещение с образованием $(Bu_3SiO)_2SiPzPh_8$. Под действием системы Mg–$Bu_3SiCl$ порфиразиновый макроцикл претерпевает восстановительное сжатие с образованием корролазина $(Bu_3SiO)SiCzPh_8$. Обработка комплексов корролазина $(Alk_3SiO)SiCzPh_8$ и $(Alk_3SiO)SiCz(^tBuPh)_8$ (Alk=Pr или Bu) плавиковой кислотой приводит к образованию соответствующих фторпроизводных. При попытке их разделения методом колоночной хроматографии на оксиде алюминия ($CH_2Cl_2$:$CH_3OH$ = 98:2) образуются μ-оксодимеры $O[SiAr_8]_2$.*

**Ключевые слова:** Порфиразин (тетраазапорфирин), корролазины (триазакоррол), кремний, синтез, аксиальные фторидные лиганды, μ-оксодимеры.

## Introduction

Tetrapyrrolic macrocycles find an increasing number of application areas: from medicine and catalysis to alternative energy sources and energy storage devices.[1,2] Silicon complexes with phthalocyanines, as well as their analogs lacking one of the *meso*-nitrogen atoms – tetrabenzotriazacorrolles – have attracted the attention of researchers due to the possibility of varying not only the periphery of these macrocyclic ligands, but also the axial substituents at the central hexacoordinated silicon atom and, thereby, adjusting the required physicochemical properties.[3,4] Thus, when searching for optimal structural modifications of SiPc and SiTBC for their potential application as the gas sensors, organic electronic devices and photosensitizers, cases where the axial ligand is bound to the silicon via oxygen atom are most often used.[e.g. 5-8] Alternative ligand functionalization via axial Si-C bonds is comparatively difficult to realize. It was shown, that halide substitution at the axial position in $(Hal)_2SiPc$ (Hal=Cl, F) changes the decomposition and sublimation temperature,[9] what is important to consider when developing photovoltaic cells.

Recently, we have obtained silicon complexes with octaaryl substituted porphyrazines ($L_2SiPzAr_8$) and corollazines ($LSiCzAr_8$; L=OH, $OSiPr_3$; Ar=Ph, $^t$BuPh) and analyzed the effect of benzoannulation on their physicochemical properties.[10] Thus, silicon corrolazine $(Pr_3SiO)SiCzPh_8$ ($\Phi_\Delta$ = 0.76 in DMF) proved to be a more effective photosensitizer than Si(IV) phthalocyanines and tetrabenzotriazacorrole. Furthermore, it was shown that preparation process of Si(IV) octaphenylporphyrazine by template cyclotetramerization of crude 3,4-diphenyl-1H-pyrrole-2,5-diimine with $SiCl_4$ leads to, along with the expected complex, an unusual side-product – a silicon(IV) tetraazachlorin containing a fused pyrrolo[1,2-a]imidazolone moiety.[11]

Herein it is demonstrated that an alternative complexation method can be used to obtain silicon porphyrazine $(HO)_2SiPzPh_8$, which is compared with the previously used tetramerization approach. Both the resulting porphyrazine and related corrolazines $(Alk_3SiO)SiCzAr_8$ (Ar=Ph, $^t$BuPh) can be axially modified by tributylsiloxy groups and/or fluoride anions, with fluoride corrolazines tending to form μ-oxodimers.

## Experimental

### General

$^1$H NMR spectra were measured with Bruker Avance 500 spectrometer. Mass spectra were recorded on a MALDI TOF Shimadzu Biotech Axima Confidence mass-spectrometer in negative and positive modes using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT. Electronic absorption spectra were recorded using Agilent Cary 60 and Jasco V-770 UV-Visible/NIR spectrophotometer. Infrared spectra were taken on an IR-spectrometer Cary 630 FT-IR. Photoluminescence spectra were collected using a Fluorescence Spectrometer Jasco FP-8350. For the emission measurements, the excitation wavelength was set at 600 nm. The emission in the excitation spectra was registered at 660 or 670 nm.

Fluorescence quantum yields ($\Phi_F$) and the singlet oxygen quantum yields ($\Phi_\Delta$) were determined using zinc phthalocyanine as a reference (ZnPc; $\Phi_F$ = 0.17 in DMF and 0.07 in toluene;[12] $\Phi_\Delta$ = 0.56 in DMF and 0.58 in toluene[13]) as described in.[8]

The basicity of *meso*-nitrogen atoms in the $CH_2Cl_2$-trifluoroacetic acid (TFA) medium was determined as stability constant of the mono- ($pK_{s1}$) and diprotonated forms ($pK_{s2}$) using the equation: $pK_s = \log I - \log[TFA]$, where $I$ is the indicator ratio of i protonated and previous (i-1) forms, $I^i = C^i/C^{i-1}$, determined spectrophotometrically at the wavelengths corresponding to the maximum absorption.[14]

### Solvents and reagents

Commercially available reagents were used without any additional purification. Dimethylformamide (DMF) was used after distillation; dichloromethane was distilled over $K_2CO_3$, pyridine - over KOH. Aluminium oxide was used for column chromatography. Purity of the synthesized complexes was controlled by TLC on ALUGRAM ALOX N plates. Diphenylfumarodinitrile (DPhFN) obtained from the corresponding arylacetonitriles (commercially available or prepared as earlier described[15]). Octaphenylporphyrazine $H_2PzPh_8$ was obtained by demetallation of $MgPzPh_8$[16] by acetic acid or by demetallation of $InPzPh_8$ by original methology.[17] Dihydroxy silicon(IV) octa(*tert*-butylphenyl)-porphyrazine, $(HO)_2SiPz(^tBuPh)_8$, and tripropylsiloxy silicon(IV) octaphenylcorrolazine, $(Pr_3SiO)SiCzPh_8$, were obtained as described earlier.[10]

### Synthesis

*Dihydroxysilicon(IV) octaphenylporphyrazine, $(HO)_2SiPzPh_8$.* $H_2PzPh_8$ (200.0 mg, 0.2 mmol) and $Bu_3N$ (0.5 mL, 2.0 mmol) were dissolved in freshly distilled dry pyridine (10 mL). Then $HSiCl_3$ (0.44 mL, 4.3 mmol) was added dropwise through a syringe and the mixture was refluxed during 1 h. Then, the isolation of the pure desired complex was carried out using two methods. *Method A*: The obtained mixture was dried and the product was separated by using Soxhlet extraction in pyridine. The target complex was isolated by column chromatography ($Al_2O_3$, eluent $CH_2Cl_2$:MeOH, 9:1 v/v). Yield: 135 mg (64%). *Method B:* The obtained mixture was dried and the resulting solid residue was treated with a saturated NaOH solution. The precipitate was filtered, washed with water, dried, and purified by column chromatography ($Al_2O_3$, eluent $CH_2Cl_2$:MeOH, 9:1 v/v). Yield: 147 mg (75%). The identification characteristics of $(HO)_2SiPzPh_8$ are the same as for the complex obtained previously by the template tetramerization method.[10]

*Bistributylsiloxy silicon(IV) octaphenylporphyrazine, $(Bu_3SiO)_2SiPzPh_8$.* To the mixture of $(HO)_2SiPzPh_8$ (1.0 g, 1.0 mmol) and $Bu_3N$ (1.2 mL, 5 mmol) in 30 mL of anhydrous pyridine, chlorotributylsilane (1.3 mL, 5 mmol) was added using a syringe. The mixture was refluxed under argon atmosphere during 5 h. Then it was concentrated under reduced pressure and the residue was chromatographed ($Al_2O_3$, eluent $CH_2Cl_2$: *n*-hexane, 1:1 v/v). Yield: 1.2 g (90%) $R_f$ = 0.84 ($Al_2O_3$, $CH_2Cl_2$:*n*-hexane, 1:1 v/v). UV-Vis ($CH_2Cl_2$) λ nm: 621 (1.00), 569 (0.18), 451 (0.14), 374 (0.72). IR (KBr) ν cm$^{-1}$: 3055w (Ph), 2955m (νCH), 2920m (νCH), 2871m (νCH), 2850m (νCH), 1372m, 1210w, 1182w, 1142m, 1034s (Si-O-Si), 1005vs, 992s, 914w, 890w, 831w, 775m, 741m, 690s (γPh), 624m (Si-O), 609m, 537m, 517w, 463w. $^1$H NMR (500 MHz, benzene-$d_6$) δ ppm: 8.62 (d, $J$ = 7.0 Hz, 16H, *ortho*-H), 7.44 (t, $J$ = 7.5 Hz, 16H, *meta*-H), 7.36 (t, $J$ = 7.4 Hz, 8H, *para*-H), 0.56 (p, $J$ = 7.3 Hz, 12H, -C*H*$_2$-CH$_3$), 0.46 (t, $J$ = 7.2 Hz, 18H, -CH$_3$), -0.73 (p, $J$ = 7.8 Hz, 12H, Si-CH$_2$-C*H*$_2$-), -1.96 – -2.05 (m, 12H, Si-CH$_2$-). MS (MALDI-TOF) *m/z*: 1163.5 [M–$Bu_3SiO$]$^+$ calculated for $C_{76}H_{67}N_8OSi_2$ 1163.5. $(Bu_3SiO)_2SiPzPh_8$ is formed also as a byproduct during the $(Bu_3SiO)SiCzPh_8$ corrolazine synthesis with 2% yield.

*Tributylsiloxy silicon(IV) octaphenylcorrolazine, $(Bu_3SiO)SiCzPh_8$.* $(HO)_2SiPzPh_8$ (1.0 g, 1.0 mmol) was mixed with magnesium turnings (122.5 mg, 5.0 mmol) in 30 mL anhydrous pyridine under argon atmosphere. The reaction mixture was

then heated to 100 °C. Chlorotributylsilane (1.4 mL, 5.0 mmol) was then added to the mixture using a syringe. Complete conversion was confirmed using UV-vis spectroscopy after 24 h. The obtained mixture was dried. The target complex was isolated by column chromatography ($Al_2O_3$, eluent $CH_2Cl_2$:*n*-hexane, 1:9 v/v) as a second fraction; the first fraction contained porphyrazine $(Bu_3SiO)_2SiPzPh_8$. Yield of $(Bu_3SiO)SiCzPh_8$: 203 mg (17.4 %). $R_f$ = 0.74 ($Al_2O_3$, $CH_2Cl_2$:*n*-hexane, 1:1 v/v). UV-Vis ($CH_2Cl_2$) λ nm: 637 (0.68), 591 (0.15), 531 (0.08), 436 (1.00). IR (KBr) ν $cm^{-1}$: 2959m (νCH), 2926m (νCH), 2850m (νCH), 1267w, 1214w, 1161m, 1055w (Si-O-Si), 1010s, 997m, 914w, 881w, 864w, 834w, 780w, 762w, 750w, 691s (γPh), 670w, 631w, 577w, 528w, 507w, 484w, 463w. $^1$H NMR (500 MHz, benzene-$d_6$), δ, ppm: 8.71 (dd, *J* = 16.5, 7.6 Hz, 8H, Ph), 8.52 (d, *J* = 7.6 Hz, 4H, Ph), 7.53 (t, *J* = 7.6 Hz, 12H, Ph), 7.48 – 7.34 (m, 8H, Ph), 7.33 – 7.25 (m, 4H, Ph), 6.89 (t, *J* = 7.5 Hz, 4H, Ph), 0.60 (p, *J* = 6.6, 5.8 Hz, 6H, -C$H_2$-$CH_3$), 0.54 (t, *J* = 6.9 Hz, 9H, -$CH_3$), -0.41 (p, *J* = 7.3 Hz, 6H, Si-$CH_2$-C$H_2$-), -1.46 – -1.55 (m, 6H, Si-$CH_2$-). MS (LDI-TOF), *m/z*: 1150.5 $[M]^+$ calculated for $C_{76}H_{68}N_7OSi_2$ 1150.5.

*General method of fluorination of $SiCzAr_8$ and $SiPzAr_8$.* $(HO)_2SiPzAr_8$ or $LSiCzAr_8$ (Ar = Ph or $^t$BuPh, L = $Pr_3SiO$ or $Bu_3SiO$) was dissolved in minimal amount of acetone in a plastic flask. Aqueous HF solution (40%) was added and the mixture was stirred at the room temperature for 1 h. Then $H_2O$ was added and obtained precipitate was filtered off, washed with water and dried. The following purification by column chromatography at $Al_2O_3$ (eluent $CH_2Cl_2$:MeOH, 98:2 v/v) results in strong association in the case of porphyrazine derivatives and dimerization in the case of corrolazines.

*Difluoro silicon(IV) octaphenylporphyrazine, $F_2SiPzPh_8$,* and *Difluoro silicon(IV) octa(tert-butylphenyl)porphyrazine, $F_2SiPz(^tBuPh)_8$* were detected in the corresponding reaction mixtures, but not isolated. $F_2SiPzPh_8$: MS (LDI-TOF), *m/z*: 968.2 $[M-F+H]^+$ calculated for $C_{64}H_{40}FN_8Si$ 967.31. $F_2SiPz(^tBuPh)_8$: MS (LDI-TOF) *m/z*: 1416.9 $[M-F+H]^+$ calculated for $C_{96}H_{104}FN_8Si$ 1415.81; 1435.0 $[M]^+$ calculated for $C_{96}H_{104}F_2N_8Si$ 1434.81.

*Fluoro silicon(IV) octaphenylcorrolazine, $FSiCzPh_8$,* instead of column chromatography was washed with methanol and dried. Yield 95 %. UV-vis ($CH_2Cl_2$) λ nm: 636 (0.65), 589 (0.14), 437 (1.00). IR (KBr) ν $cm^{-1}$: 3058w (Ph), 3030w, 1489m, 1451m, 1214w, 1158m, 1116w, 1073w, 1055w, 1038w, 1010s, 966w, 948w, 917w, 881w, 848w, 778w, 760m, 739w, 694vs (Ph), 633w, 613w, 580w, 559w, 525w, 504w. MS (LDI-TOF) *m/z*: 953.9 $[M+H]^+$ calculated for $C_{64}H_{40}FN_7Si$ 954.32.

*Fluoro silicon(IV) octa(tert-butylphenyl)corrolazine, $FSiCz(^tBuPh)_8$,* was detected in a reaction mixture. MS (LDI-TOF) *m/z*: 1402.8 $[M+H]^+$ calculated for $C_{96}H_{104}FN_7Si$ 1402.8.

*μ-Oxo complex $O[SiCzPh_8]_2$.* Yield 85%. $R_f$ = 0.38 (Silica, $CH_2Cl_2$:*n*-hexane, 1:1 v/v). UV-Vis ($CH_2Cl_2$) λ nm: 640, 601, 425. IR (KBr) ν $cm^{-1}$: 3049w (Ph), 1481m, 1444w, 1379w, 1361w, 1312w, 1280w, 1262w, 1225w, 1210w, 1160m, 1106m(Si-O-Si), 1073w, 1038w, 1008vs, 999m, 966w, 920w (δPh), 882w, 867w, 840w, 802w,780m, 756w, 724w, 692s (γPh), 666w, 633m, 615w, 573w, 526w. MS (LDI-TOF) *m/z*: 1886.8 $[M+H]^+$ calculated for $C_{128}H_{80}N_{14}OSi_2$ 1886.2.

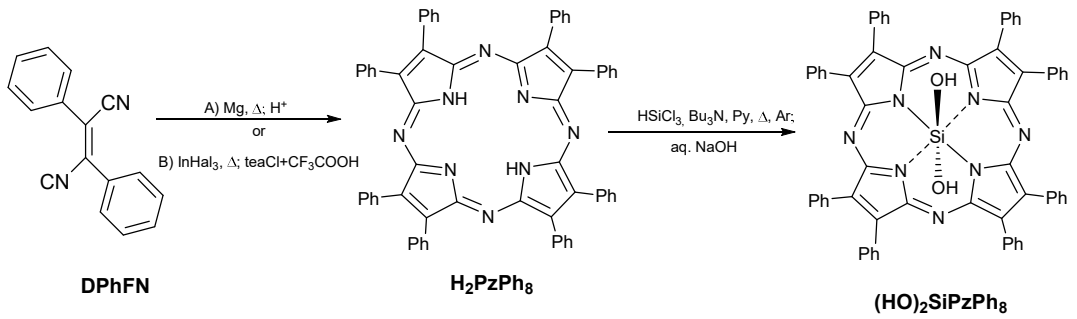
*μ-Oxo complex $O[SiCz(^tBuPh)_8]_2$.* Yield 72%. $R_f$ = 0.69 (Silica, $CH_2Cl_2$:*n*-hexane, 1:1 v/v). UV-Vis ($CH_2Cl_2$) λ nm: 644, 605, 431. IR (KBr) ν $cm^{-1}$: 2961vs (νCH), 2919vs (νCH), 2848vs (νCH), 1495w, 1463m, 1384m, 1363w, 1285m, 1270m, 1204w, 1187w, 1169w, 1115m, 1070m, 1032w, 1005m, 963w, 947w, 845w, 822w, 743w. MS (LDI-TOF) *m/z*: 2785.3 $[M+H]^+$ calculated for $C_{192}H_{208}N_{14}OSi_2$ 2785.0.

## Results and Discussion

### *Complexation approach for obtaining of silicon(IV) porphyrazine*

Tetramerization of appropriate diimiisoindoline, obtained from corresponding phthalonitrile, with silicon tetrachloride as a template is considered to be the most convenient pathway for construction of silicon phthalocyanines SiPcs.[3] Recently, similar methodology allowed to obtain nonannulated silicon porphyrazines with various aryl substituents at the periphery of the macrocycle $(HO)_2SiPzAr_8$.[8,18] Though alternative complexation method is used much less frequently (*e.g.* in[19]) it seemed to be good for synthesis of the pyrazine annulated silicon porphyrazinates by reaction of corresponding macrocyclic ligand with excess of trichlorosilane in the presence of tributylamine as a base with 12–29% yields.[20] Here, we have adopted this methodology for preparation of $(HO)_2SiPzPh_8$ with 64 % yield according to Scheme 1. At the same time, the isolation procedure is complicated by hydrolysis of silane after contact of the reaction mixture with air moisture and formation of some amount of silicon dioxide which adsorbs strongly the target Si(IV) porphyrazinate, and the product losses are quite noticeable. So, the separation of the target dihydroxidosilicon complex was carried out by treatment of reaction mass by the saturated alkali solution using an idea described in work.[21] This allowed to increase the product yield up to ~75%, which is much higher than for tetra(benzo/pyrazine) annulated analogs.[3,19,20]

The comparison assessment of two synthetic approaches to the $(HO)_2SiPzPh_8$ starting from the common precursor – diphenylfumarodinitrile DPhFN, speaks in favour of complex formation methodology. Although the procedure, based on cyclotetramerization, includes less synthetic steps, the whole yield of $(HO)_2SiPzPh_8$ is only *ca*. 7% relatively DPhFN. The use of complex formation approach is little more time-consuming, but at the same time it is more productive, giving *ca*. 30% of the silicon complex.

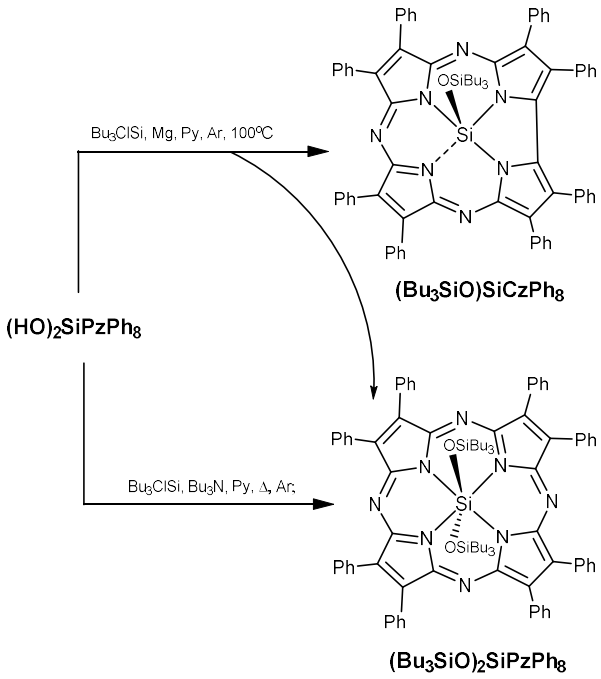



**Scheme 1.** Synthesis of Si(IV) porphyrazine $(HO)_2SiPzPh_8$ by complexation method.

It is noteworthy that in the case of preparation of Si phthalocyanines, the use of $SiCl_4$ by tetramerization or $HSiCl_3$ by complexation method leads to the formation of dichlorosilicon phthalocyanines, which can be isolated with the Si-Cl bond preserved. Only targeted hydrolysis of axial chloride ligands leads to the dihydroxyl $(HO)_2SiPc$ derivative.[3] In the case of the nonannulated complex $L_2SiPzAr_8$, the Si-Cl bond is not so stable to hydrolysis than that of phthalocyanine, and already during the chromatographic purification the initially formed chloride complex $Cl_2SiPzAr_8$ is converted to $(HO)_2SiPzAr_8$. The dihydroxy form is prone to the formation of associates in solution, and at the same time, it readily interacts with the adsorbent and is difficult to be isolated by chromatography, becoming stuck on the chromatographic column. Axial modification could reduce these negative features.

### *Corrolazine formation*

When refluxing in dry pyridine in the presence of trialkylchlorosilane ($Alk_3ClSi$, Alk = Pr, Bu) and magnesium, porphyrazine macrocycle of $(HO)_2SiPzAr_8$ undergoes reductive contraction with formation of corresponding corrolazine complex $(Alk_3SiO)SiCzAr_8$ (Scheme 2). This reaction with $Pr_3ClSi$ was described earlier in detail.[10] It was shown, that Pz→Cz transformation at these conditions occurs only partially and porphyrazine macrocycle retains unchanged in the form of disiloxylated derivative $(Pr_3SiO)_2SiPzAr_8$. Here, the same reaction using tributylchlorosilane – magnesium reductive system and $(HO)_2SiPzPh_8$ also gave both the corrolazine $(Bu_3SiO)SiCzPh_8$ (yield *ca.* 17%) and porphyrazine $(Bu_3SiO)_2SiPzPh_8$ (2%). The formation of ring-contracted derivative may be easily identified by characteristic UV-Vis spectrum, containing more intensive and bathochromically shifted Soret band if compared with appropriate porphyrazine (Figure 1).




**Scheme 2.** Synthesis of Si(IV) octaphenyl substituted corrolazine and porphyrazine with axial tributylsiloxy groups.

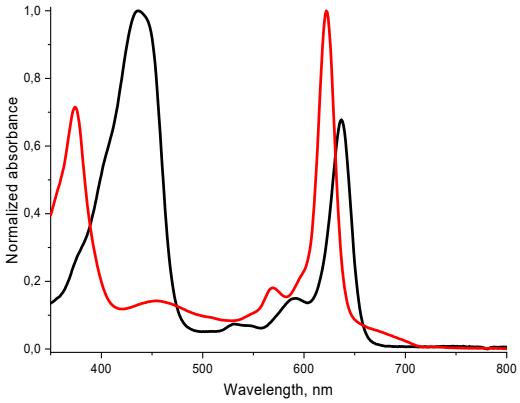



**Figure 1**. UV-Vis spectra of $(Bu_3SiO)_2SiPzPh_8$ (red) and $(Bu_3SiO)SiCzPh_8$ (black) in $CH_2Cl_2$.

IR and $^1H$ NMR spectra of tributylsiloxy Si porphyrazine and corrolazine are similar to propylsiloxy derivatives described earlier.[10] Thus their IR spectra contain, besides of typical vibrations of octaphenyl substituted macrocycle, vibrations of Si-O-Si bridge at 1030–1100 $cm^{-1}$ and stretching vibrations of tributylsiloxy groups at 2800–3000 $cm^{-1}$ (Figure S1). In the $^1H$ NMR spectra, the peripheral phenyl groups give multiplets in the 6.8 – 8.6 region, while the proton signals of butyl groups of the axial $Bu_3SiO$-ligands are observed in high field in the -2 – 0.6 ppm range (Figures S2, S3).

Previously, in the case of silicon octaarylporphyrazine and phthalocyanine, the important role of acid addition in the transformation of their macrocycle into the corresponding corrolazine under the conditions of the magnesium-trialkyl(aryl)chlorosilane reducing system was noted.[10,22] A detailed study of the basic properties of porphyrazine $(Pr_3SiO)_2SiPzAr_8$ in a trifluoroacetic acid–dichloromethane medium showed that a small amount of acid leads to the cleavage of one of the axial ligands with formation of positively charged particle $[(Pr_3SiO)Si^+PzAr_8]$, which is more easily subjected to reductive contraction of the macrocycle.[10]

The behavior of silicon octaphenyl substituted porphyrazine and corrolazine with tributylsiloxy axial groups in the presence of trifluoroacetic acid, studied by spectrophotometric titration, is rather similar to that of the tripropylsiloxy derivatives. In weakly acidic solutions of $(Bu_3SiO)_2SiPzPh_8$, a slight bathochromic shift of the Q-band and an increase in the intensity of the charge-transfer (CT) band, associated with the loss of one tributylsiloxy group, are observed (Figure 2a, 1st stage inset). A further increase in acidity leads to the protonation of one of four *meso*-nitrogen atoms, which is typically indicated by a significant shift of the Q-band to the long-wavelength region (635 → 693 nm, Figure 2a). The concentration stability constant of this monoprotonated form $pK_s$ was determined to be 0.25±0.01. In the case of related corrolazine, $(Bu_3SiO)SiCzPh_8$, with an increase in the acid concentration, consequent stages of protonation of two *meso*-nitrogen atoms are observed (637 → 677 → 705 nm, Figure 2b), which allowed to determine the $pK_{s1}$=1.8±0.2 and $pK_{s2}$ = =0.92±0.08. A similar tendency of increasing the basic properties of the *meso*-nitrogen atoms in corrolazine compared to porphyrazine was observed for the tripropylsiloxy derivatives.[10]

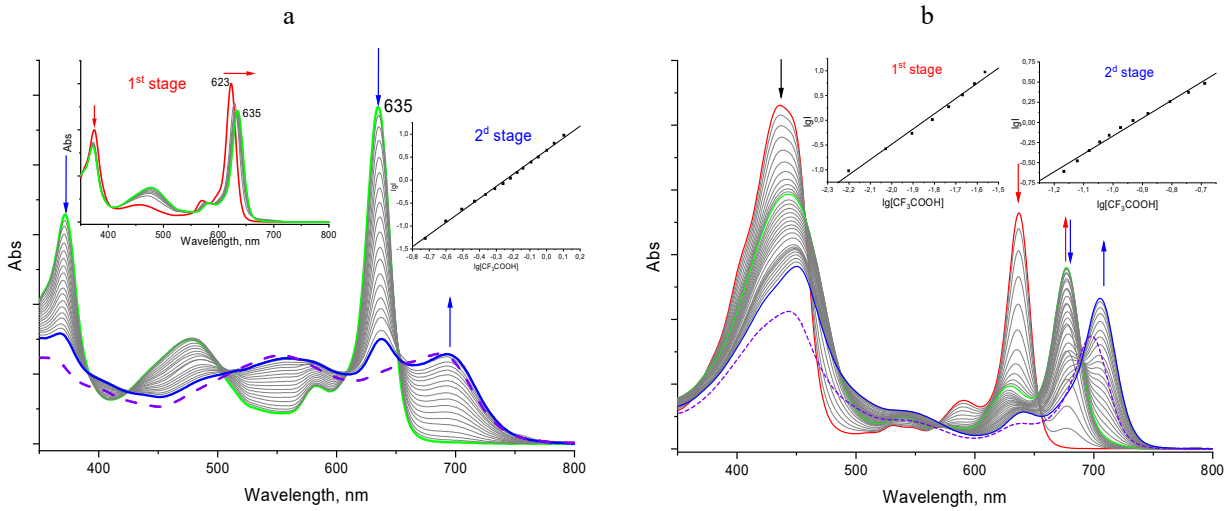



**Figure 2.** UV-Vis spectral changes of porphyrazine $(Bu_3SiO)_2SiPzPh_8$ (a) and corrolazine $(Bu_3SiO)SiCzPh_8$ (b) solutions in $CH_2Cl_2$ upon titration by trifluoroacetic acid (the dotted line – in 100% $CF_3COOH$). Insets show the logarithmic dependences of indicator ratio on acid concentration.

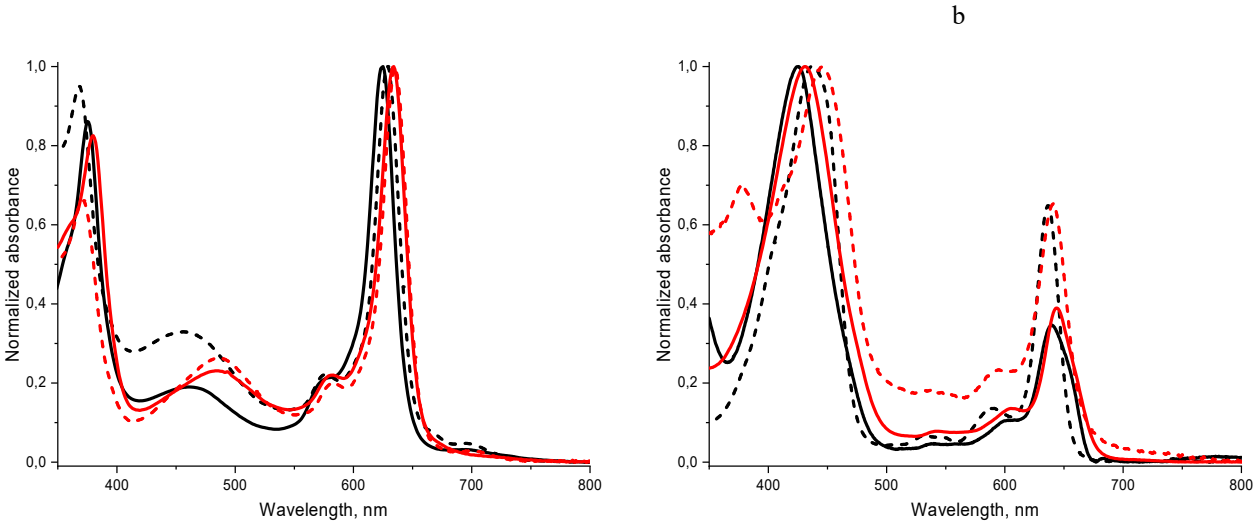



**Figure 3.** UV-vis spectra in $CH_2Cl_2$ of (a) $(HO)_2SiPzPh_8$ (black solid line), $(HO)_2SiPz(^tBuPh)_8$ (red solid line) and their derivatives after fluorination: $SiPzPh_8$ (black dashed line), $SiPz(^tBuPh)_8$ (red dashed line); (b) $FSiCzPh_8$ (black dashed line), $FSiCz(^tBuPh)_8$ (red dashed line) and μ-oxo dimers $O[SiCzPh_8]_2$ (black solid line) and $O[SiCz(^tBuPh)_8]_2$ (red solid line)

### *Axial modification*

If magnesium is not used when $(HO)_2SiPzPh_8$ is allowed to react with trialkylchlorosilane in the presence of excess amount of a base (tributylamine), the porphyrazine ring contraction reaction is excluded and only the axial substitution is observed (Scheme 2). The complexes $(Pr_3SiO)_2SiPzAr_8$ (Ar = Ph, $^t$BuPh)[10] and $(Bu_3SiO)_2SiPzPh_8$ obtained in such a way possess high stability in solutions, low tendency to hydrolysis and can be easily isolated by column chromatography in contrast to their dihydroxy precursors.

Fluorination of silicon atom is one of the methods for forming complexes with non-bulky and compact axial substituents. Treatment of acetone solutions of $(HO)_2SiPzAr_8$ and $(Alk_3SiO)SiCzAr_8$ with hydrofluoric acid was used for substitution of axial groups in for fluorine atoms.

The mass spectra of the reaction mixtures for the fluorination of silicon octaphenyl and octa(*tert*-butylphenyl) substituted porphyrazines show signals of the fluorinated complexes $[M]^+$, $[M\text{-}F+OH]^+$ (Figure S4). In the case of $(HO)_2SiPz(^tBuPh)_8$ substitution of the axial ligand with F has little effect on the position of the Q band, causing a slight hypsochromic shift of the Soret band. The charge transfer band from the phenyl rings with electron-donating *tert*-butyl groups to the central atom with electronegative fluoride at approximately 490 nm is slightly more pronounced (Figure 3). The increase and broadening of the Soret band in the electronic absorption spectrum of Si octaphenylporphyrazine treated by HF indirectly confirms the presence of associates in the reaction mixture (Figure 3). Unfortunately, it was not possible to isolate the fluorination products by chromatography due to their blocking by adsorbent.

Treatment of corrolazine complexes with axial trialkylsiloxy groups $(Alk_3SiO)SiCzAr_8$ (Ar = Ph, $^t$BuPh; Alk=Pr or Bu) by hydrofluoric acid results in formation of corresponding fluoride derivatives. Unlike the initial corrolazines, the IR spectra of the fluorination products lack the band of trialkylsiloxy group stretching vibrations in the region of 2850–3000 $cm^{-1}$ (Figure S6). The MALDI-TOF

mass spectra of the reaction mixtures contain $[M+H]^+$ molecular ion peaks with *m/z*=953.9 and 1402.8, corresponding to $FSiCzPh_8$ and $FSiCz(^tBuPh)_8$, respectively (Figure 4a). It is noteworthy, that in both cases additional peaks with *m/z*=1886.8 and 2785.3 are observed, that could be assigned, presumably, to the appropriate μ-oxo dimers.

In contrast to porphyrazine analogues, the products of corrolazine fluorination are highly soluble. When attempting to separate them by column chromatography on aluminum oxide ($CH_2Cl_2$:$CH_3OH$ = 98:2), oligomerization of fluoride complexes most likely occurs (Scheme 3), and in the mass spectra of the fractions isolated after chromatography, only peaks corresponding to μ-oxo dimers are observed (Figure 4b).

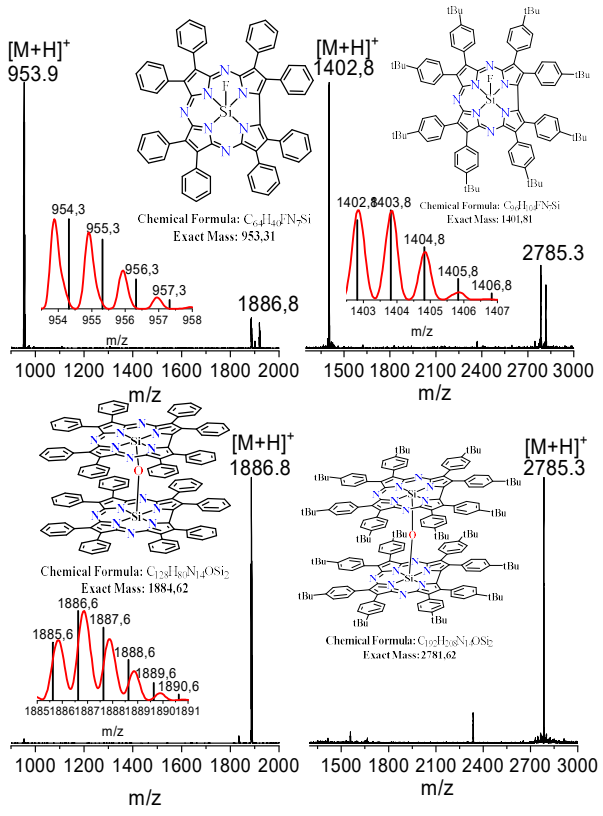



**Figure 4.** MALDI-TOF mass spectra of fluorination products of Si(IV) corrolazines before (a) and after (b) chromatography on aluminum oxide.

The formation of μ-oxo dimers of silicon complexes of phthalocyanines and corrolazines from monomers during chromatography was observed also earlier.[23,24]

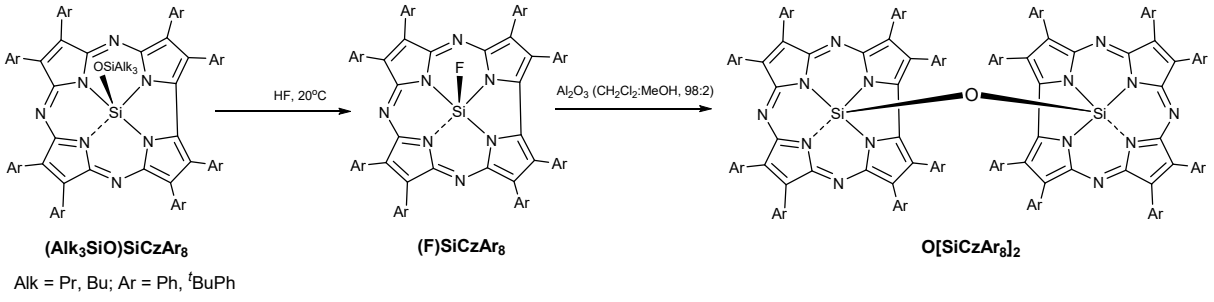
The Q-band in the electronic absorption spectra of dimers seems to be asymmetrical due to π–π-interaction of two macrocycles bound through an oxo-bridge. It is observed at a longer wavelength (by ~5 nm) if compared with that of monomer, while Soret band is shifted hypsochromically (by~12 nm) (Figure 3, right). These spectral changes are similar to those observed earlier for the μ-oxo dimers of Si corrole,[25] as well as of Si corrolazine.[23] The IR spectra of the obtained dimers contain additional rather intensive broad bands at *ca*. 1100 $cm^{-1}$, which is absent in the case of monomeric $FSiCzAr_8$ and may be assigned to the Si-O-Si stretching vibrations (Figure S6).

### *The photophysical properties*

The fluorescence excitation spectra of tributylsiloxilated porphyrazine $(Bu_3SiO)_2SiPzPh_8$ and corrolazine $(Bu_3SiO)SiCzPh_8$ in DMF solutions are almost identical to absorption spectra, indicating the presence of the single fluorescence species in the nonagregated form (Figure S7). The quantum yield of fluorescence $\Phi_F$ upon lengthening the alkyl chain by one carbon atom in the axial ligand increases twofold, although it remains quite low (Table 1).

The fluorescence measurements of μ-oxo corrolazine complexes were performed in toluene, in which they dissolve better. The Q-band position in their fluorescence excitation spectra is shifted bathochromically by 8–9 nm relatively absorption spectra and does not coincide with those of monomers (Figure 5, Table 1). Dimers practically lose their fluorescence ability and have the $\Phi_F$ values close to zero (Table 1). These observations are probably associated with the fact that in the case of μ-oxo dimers, only one of all possible conformers with a smaller π-interaction of corrolazine macrocycles is capable of fluorescence; its proportion in the solution being insignificant.

The quantum yields of singlet oxygen $\Phi_\Delta$ were determined by measuring of kinetics of 1,3-diphenylisobenzofuran decomposition upon $^1O_2$ produced by Si complexes using ZnPc as a reference (Figure S8). In contrast to fluorescence, the $\Phi_\Delta$ value is lower for butylsiloxy than for propylsiloxy derivatives. In any case, silicon corrolazines, even in dimeric form, generate singlet oxygen better than porphyrazine complexes (Table 1).




**Scheme 3.**

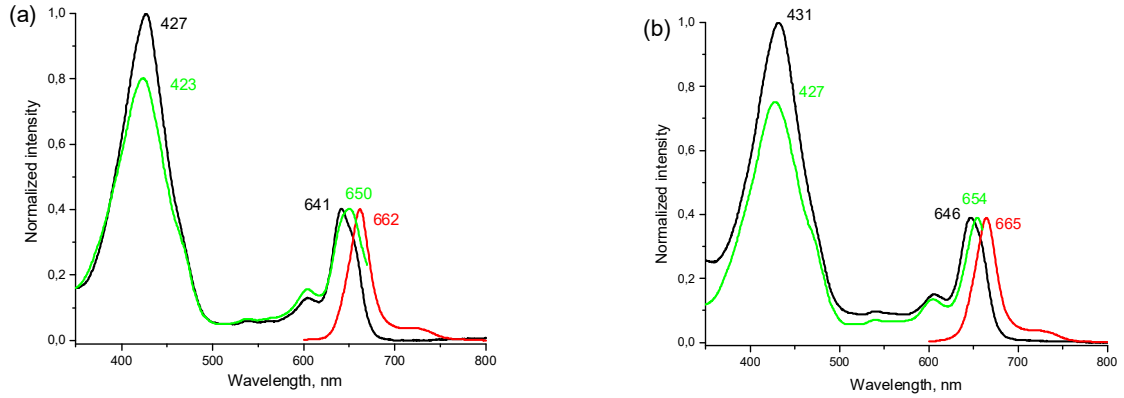



**Figure 5.** Normalized absorption (black), fluorescence emission (red) and excitation (green) spectra of corrolazine μ-oxo dimers $O[SiCzPh_8]_2$ (a) and $O[SiCz(^tBuPh)_8]_2$ (b) in toluene; $\lambda_{ex}$ = 590 nm, $\lambda_{em}$ = 660 and 670 nm.

**Table 1.** Some spectral and photophysical parameters of Si monomer and dimer complexes.

| Compound | Solvent | $\lambda_{abs}$, nm | $\lambda_f$, nm | Stokes shift, $cm^{-1}$ | $\Phi_F$±0.02 | $\Phi_\Delta$±0.02 |
|---|---|---|---|---|---|---|
| $(Bu_3SiO)_2SiPzPh_8$ | DMF | 621 | 630 | 230.0 | 0.05 | 0.10 |
| $(Bu_3SiO)SiCzPh_8$ | DMF | 636 | 647 | 267.3 | 0.14 | 0.66 |
| $(Pr_3SiO)_2SiPzPh_8$ [10] | DMF | 621 | 629 | 205 | 0.03 | 0.15 |
| $(Pr_3SiO)$-$SiCzPh_8$ [10] | DMF | 636 | 645 | 220 | 0.07 | 0.76 |
| $O[SiCzPh_8]_2$ | toluene | 641 | 662 | 278.9* | 0.02 | 0.56 |
| $O[SiCz(^tBuPh)_8]_2$ | toluene | 646 | 665 | 252.9* | 0.02 | 0.45 |

*relative $\lambda_{max}$ in fluorescence excitation spectra.

## Conclusion

Silicon complex of octaphenylporphyrazine was prepared by the reaction of $H_2PzPh_8$ and trichlorosilane via complexation. The yield of $(HO)_2SiPzPh_8$ relative to the starting precursor diphenylfumarodinitrile was approximately 30%, while the previously used cyclic tetramerization method yielded only approximately 7% of the target silicon complex. Corrolazine $(Bu_3SiO)SiCzPh_8$ was obtained by reductive contraction of the porphyrazine macrocycle. Treatment of Si(IV) porphyrazines and corrolazines with hydrofluoric acid results in substitution of the axial ligand by fluoride. However, isolation of the fluoride porphyrazines was unsuccessful due to the formation of polymerization products. In the case of corrolazines, fluoride complexes are transformed into μ-oxo dimers after their passing through a column of aluminum oxide. Silicon corrolazines, even in dimeric form, generate singlet oxygen better than porphyrazine complexes, but are not capable of fluorescence.

Looking to the future, the complexation method for preparing silicon(IV) octaphenylporphyrazine developed here should be more suitable for the synthesis of porphyrazines with peripheral active groups (*e.g.* carboxy groups) than the tetramerization method. Moreover, the observed dimer formation via the μ-oxo bridge can be used to design 3D covalent organic frameworks on the basis of carboxylated silicon porphyrazines.

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## References

1. Ding X., Zhou Z., Chufarin A. *et al.Chem. Engin. J.* **2025**, 518, 164913. DOI: 10.1016/j.cej.2025.164913
2. a) Koifman O.I., Ageeva T.A., Beletskaya I.P., *et al. Macroheterocycles* **2020**, *13*, 311–467. DOI: 10.6060/mhc200814k; b) Znoyko S.A., Maizlish V.E., Koifman O.I. *ChemChemTech* **2023**, *67*(1), 6–35. DOI: 10.6060/ivkkt.20246701.6859.
3. Mitra K., Hartman M.C.T. *Org. Biomol. Chem.* **2021**, *19*, 1168–1190. DOI: 10.1039/D0OB02299C
4. Zhang X.-F. *Coord. Chem. Rev.* **2015**, *285*, 52–64. DOI: 10.1016/j.ccr.2014.11.002
5. Ivanova V., Basova T., Klyamer D., Sukhikh A., Buyukeks-I S.I., Atilla D., Gu¨l Gu¨rek A. *New J. Chem*. **2025**, *49*, 8279. DOI: 10.1039/d5nj00507h.
6. Cranston R.R., Mauthe J., Wang T., Thapa G.J., Amassian A., Lessard B.H. *Adv. Electron. Mater*. **2025**, *11*, 2400500. DOI: 10.1002/aelm.202400500.
7. Lessard B.H. *ACS Appl. Mater. Interfaces* **2021**, *13*, 31321−31330. DOI: 10.1021/acsami.1c06060
8. Atmaca G.Y., Karanlık C.C., Erdogmus A. *J. Photochem. Photobiol., A: Chem*. **2023**, *436*, 114365. DOI: 10.1016/j.jphotochem.2022.114365
9. Grant T.M., Victoria McIntyre V., Vestfrid J., Raboui H., White R.T., Lu Zh.-H., Lessard B.H., Bender T.P. *ACS Omega* **2019**, *4*, 5317−5326. DOI: 10.1021/acsomega.8b03202
10. Rychikhina E.D., Ivanova S.S., Novakova V., Stuzhin P.A. *Dalton Trans.* **2023**, *52*, 6831–6840. DOI: 10.1039/d3dt00319a.
11. Rychikhina E.D., Ivanova S.S., Somov N.V., Lazovskiy D.A., Stuzhin P.A. *Dalton Trans*. **2025**, *54*, 11822–11827. DOI: 10.1039/D5DT01113B
12. Ogunsipe A., Maree D., Nyokong T. *J. Mol. Struct*. **2003**, 650, 131–140. DOI: 10.1016/s0022-2860(03)00155-8.

13. Spiller W., Kliesch H., Wöhrle D., Hackbarth S., Röder B., Schnurpfeil G. *J. Porphyrins Phthalocyanines* **1998**, *2*, 145–158. DOI: 10.1002/(SICI)1099-1409(199803/04)2:2<145::AID-JPP60>3.0.CO;2-2
14. Ivanova S.S., Stuzhin P.A. *Russ. J. Coord. Chem*. **2004**, *30*, 765–773 [*Koord. Khimiya* **2004**, *30*, 813–821]. DOI: 10.1023/b:ruco.0000047462.95197.26.
15. a) Baumann T.F., Barrett A.G.M., Hoffman B.M. *Inorg. Chem*. **1997**, *36*, 5661. DOI: 10.1021/ic9701367; b) Kozlov A.V., Stuzhin P.A. *Zh. Org. Khim.* **2013**, *49*, 928–935.
16. Cook A.H., Linstead R.P. *J. Chem. So. (Resumed)* **1937**, *189*, 929. DOI: 10.1039/jr9370000929.
17. Ivanova S.S., Stuzhin P.A. *J. Porphyrins Phthalocyanines* **2011**, *15,* 1299–1309. DOI: 10.1142/S108842461100421X.
18. Kanamori R., Iguchi M., Tsutsumi T., Ehara T., Onda K., Miyata K., Mori Sh., Kamada K., Shimizu S. *Chem. Eur. J.* **2025**, e02913. DOI: 10.1002/chem.202502913.
19. a) Bergkamp J.J., Sherman B.D., Marino-Ochoa E., Palacios R.E., Cosa G., Moore T.A. *et al. J. Porphyrins Phthalocyanines* **2011**, *15*, 943–950. DOI: 10.1142/S1088424611003847; b) Biyiklioglu Z., Alp H. *Dalton Trans.* **2015**, *44*, 18993–9. DOI: 10.1039/C5DT03421C
20. Kolarova M., Zimcik P., Ivanova S., Miletin M., Novakova V. *J. Porphyrins Phthalocyanines* **2023**, *27*, 445–451. DOI: 10.1142/S108842462350013X
21. Marriott P.J., Gill J.P., Evershed R.P., Hein C.S., Eglinton G. *J. Chromatography A* **1984**, *301*, 107–128. DOI: 10.1016/s0021-9673(01)89182-2.
22. Raboui H., Lough A.J., Szawiola A.M., Bender T.P. *Inorg. Chem.* **2018**, *57*, 5174–5182. DOI: 10.1021/acs.inorgchem.8b00181
23. Kobayashi N., Yokoyama M., Muranaka A., Ceulemans A. *Tetrahedron Lett.* **2004**, *5*, 1755–1758. DOI: 10.1016/j.tetlet.2003.12.083
24. Esposito J.N., Lloyd J.E., Kenney M.E. *Inorg. Chem.* **1966**, *5*, 11, 1979–1984. DOI: 10.1021/ic50045a031.
25. Ueta K., Fukuda M., Kim G., Shimizu S., Tanaka T., Kim D., Osuka A. *Chem. Eur. J.* **2018**, *24*, 7637–7646. DOI: 10.1002/chem.201800165

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