Palladium complex of octaphenyl-substituted pyrazinoporphyrazine: synthesis, photochemical and photophysical properties

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Abstract. Novel palladium (II) tetrapyrazinoporphyrazinate, bearing eight peripheral phenyl groups, was obtained via metallation of the corresponding porphyrazine ligand. Target complex was identified using mass spectrometry, Fourier transform infrared and UV-Vis spectroscopy. Luminescence properties of palladium complex were investigated. Phosphorescence maximum of target compound was observed in the near IR region (828 nm). Singlet oxygen quantum yield (\(\phi_\Delta\)) was measured using the 1,3-diphenylisobenzofuran (DPBF) as the singlet oxygen trap. Value of \(\phi_\Delta\) (0.35) is in a good agreement with literature data for porphyrazine complexes.

1. Introduction
Palladium complexes of porphyrins and their analogues are of increasing importance due to their possible applications in optical oxygen sensors¹,². They possess luminescence and absorption of visible light and can be applied in organic light-emitting diodes (OLEDs), chemical and biological sensing, photovoltaic devices, bioimaging³. Additionally, Pd (II) central ion enhances spin-orbit coupling, so that triplet state \(\tau_0\) is not so long-lived as to be totally quenched by environmental exposure or trace quenchers². Interesting example of reversible oxygen binding by palladium complex of antracocyanine as a prospective agent for photodynamic therapy was described⁴. However, only little attention has been paid to tetrapyrazinoporphyrazine complexes of palladium⁵-⁷. The purpose of this work was to investigate spectral and photochemical properties of novel phenyl substituted tetrapyrazinoporphyrazine complex of palladium. Introduction of eight phenyl groups onto peripheral positions of porphyrine macrocycle results in increasing of solubility of target complex comparing to unsubstituted or methylsubstituted⁸ analogues.

2. Results and discussion
2.1. Synthesis and identification
Initial 5,6-diphenylpyrazine-2,3-dicarbonitrile 1 was obtained by the reaction between benzil and diaminomaleonitrile using ethanol as a solvent⁹-¹¹ (See Experimental section).
Palladium pyrazinoporphyrazinates, which were described earlier, were obtained by template cyclotetramerization of corresponding pyrazines. Pyridyl-substituted compound was obtained in a boiling DMSO in a high yield (80%)\(^5\). However, in the case of octapropyl-substituted complex this approach results in target palladium complex in a very low yield (11%)\(^6\).

In the present work, alternative multi-step approach was realized (Scheme 1). Firstly, dilitium complex 2 was obtained by template synthesis in the presence of p-hydroquinone under MW irradiation. Compound 2 was further demetallated by freshly obtained polyphosphoric acid to give ligand 3. The following synthesis of palladium complex 4 was performed in a boiling 1,2-dichlorobenzene (o-DCB) in the presence of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) as a base and catalytic amounts of ammonium acetate. Total yield of three stages (dilithium complex formation, demetallation, and metallation) of the multi-step approach was 43% (Scheme 1).

All compounds were identified by mass spectrometry. Palladium complex was also characterized using high-resolution MALDI-TOF mass spectrometry (Table 1). The high resolution spectrum demonstrates good agreement between the observed mass and the monoisotopic mass calculated. The isotopic distribution of the molecular ion peak is almost equal to the theoretically calculated one (Figure 1). Besides the peak of molecular ions, peak of adducts with Na was also detected in the positive mode mass spectrum.

![Scheme 1. Synthesis of phenyl-substituted tetrapyrazinoporphyrazine complex of palladium.](image)

![Figure 1. MALDI TOF of palladium complex 4, isotopic pattern for the peak of [M+H]\(^+\) ion (A) and simulated MS pattern (B).](image)
Table 1. High-resolution MALDI TOF/TOF mass spectrometry data.

| Compound      | Ion              | Mass calculated | Mass found  |
|---------------|------------------|-----------------|-------------|
| $\text{C}_{30}\text{H}_{41}\text{N}_{16}\text{Pd}$ | $[\text{M}+\text{H}]^+$ | 1235.2735       | 1235.2731   |

In FT-IR spectra of complex 4 (Figure 2), skeletal vibrations of the pyrrole and pyrazine fragments occupy the region from 1345 to 1635 cm$^{-1}$.

Figure 2. IR spectra of palladium complex 4 on the working surface of the internal reflection (ATR) diamond element.

2.2. **UV-Vis spectroscopy and luminescence properties**

In the UV-Vis spectrum of palladium complex 4 two main peculiarities were observed: $B$ band (351 nm) in UV region and $Q$ band (664 nm) in visible region (Figure 2). In comparison with phenyl-substituted phthalocyanine complexes, a hypsochromic shift of the $Q$ band of about 30 nm is observed$^{12,13}$.

Figure 3. UV-Vis (solid line) and fluorescence (dashed line, $\lambda_{ex}=635$ nm) spectra of palladium complex 4 in pyridine.
Fluorescence spectrum was also measured for target complex (Figure 3). The Stokes shift for $Q$ band is very small (11 nm). This peculiarity is typical for porphyrin complexes. For instance, in the case of methyl-substituted pyrazinoporphyrzines, Stokes shift is about 6 nm. The phosphorescence spectrum of the palladium complex was measured for deoxygenated acetone solution at 77 K (Figure 4). The main maximum of emission for compound 4 is observed at 828 nm. In comparison with $Q$ band position in acetone solution (656 nm), the phosphorescence maximum is characterized by 172 nm bathochromic shift.

![Figure 4. Phosphorescence spectrum of the complex 4 (77 K, acetone).](image)

Similar large shift of the phosphorescence maximum to the near IR region was observed for platinum and palladium phthalocyaninates described in literature $^1, 14, 15$.

### 2.3. Study of the quantum yield of singlet oxygen generation

Singlet oxygen quantum yield ($\phi_{\Delta}$) was measured using the 1,3-diphenylisobenzofuran (DPBF) as the singlet oxygen trap. *meso*-Tetraphenylporphyrin (TPP) was chosen as a standard compound. According to the literature data, the value of the quantum yield of singlet oxygen generation by this porphyrin in acetone is $0.65 \pm 0.05$ $^{16, 17}$. The interaction between the trap and singlet oxygen is determined by the chemical reaction, which is presented in the scheme 2 $^{18}$. The reaction products do not absorb visible light. Therefore, the amount of singlet oxygen formed during the photoreaction can be judged by the loss of optical density in the region of the maximum absorption of DPBF.

![Scheme 2. The reaction between chemical trap and singlet oxygen.](image)
To determine the quantum yields of singlet oxygen generation, solutions of the test compound and DPBF were mixed in a fixed volume of solvent. The wavelength of the light irradiated was chosen according to the position of the maximum of the most red shifted band for the compound investigated.

The calculation was made according to the following formula:

\[
\phi_{\Delta} = \phi_{\Delta St} \cdot \frac{\Delta D_C \cdot t_{irrSt} \cdot I_{St} \cdot (1 - 10^{-D_{St}}) \cdot \lambda_{St}}{\Delta D_{St} \cdot t_{irrC} \cdot I_C \cdot (1 - 10^{-D_C}) \cdot \lambda_C},
\]

where \( \phi_{\Delta St} \) - is the quantum yield of singlet oxygen generation for the standard compound; \( \Delta D_C \) - the average loss of optical density of DPBF in experiments with the test compound, \( \Delta D_{St} \) - the average decrease in optical density of DPBF in experiments with a standard, \( t_{irrC} \) - the duration of irradiation of a mixture of DPBF with a test compound in s, \( t_{irrSt} \) - the duration of irradiation of a mixture of DPBF with a standard compound in s, \( I_C \) and \( I_{St} \) flux from a xenon lamp in experiments with a test compound and a standard compound in mW, \( D_C \) and \( D_{St} \) the optical densities of the compound studied and a standard compound corresponding to the wavelengths of booming light \( \lambda_C \) and \( \lambda_{St} \) (in nm).

Data obtained are summarized in Table 2. The value of \( \phi_{\Delta} \) for target palladium complex is comparable with substituted phthalocyanine analogs, described in literature. For e.g. for zinc tetrakis(benzylmercapto)phthalocyanine and for thiopheneethoxy-substituted zinc phthalocyanine \( \phi_{\Delta} = 0.33 \). Thus the palladium phenyl-substituted tetrapyrazinoporphyrazine \( 4 \) is a prospective photosensitizer.

### Table 2. Experimental data for photochemical measurements.

| Compound | \( \lambda_{irr} \) (nm) | I (mW) | \( t_{irr} \) (s) | Optical densities | \( \Delta D \) (DPBF) | \( \phi_{\Delta} \) |
|----------|-------------------------|-------|------------------|------------------|-------------------|----------------|
| 4        | 660                     | 98    | 120              | 0.134            | 0.180             | 0.35±0.05      |
| TPP      | 512                     | 105   | 600              | 0.026            | 0.113             | 0.65±0.05      |

### 3. Experimental

#### 3.1. Materials and methods

All reagents and solvents were obtained or distilled according to standard procedures. All reactions were TLC and UV/Vis controlled until complete disappearance of the starting reagents if not additionally specified. Thin-layer chromatography was performed using Merck Aluminium Oxide F254 neutral flexible plates.

The synthesis under microwave irradiation was performed using Samsung microwave oven. UV-Vis absorption spectra were recorded on a ThermoSpectronic Helios-\( \alpha \) spectrophotometer using quartz cells (1×1 cm). Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass-spectra were taken on a Bruker Autoflex II mass spectrometer with 2,5-dihydroxybenzoic acid (DHB) as the matrix. High-resolution MALDI mass spectra were registered on a Bruker ULTRAFLEX II TOF/TOF instrument.

IR spectra were recorded on IR spectrometer with Fourier transform IR 200 produced by Thermo Nicolet. Registration of spectra was carried out at a resolution of 4 cm\(^{-1}\), the number of scans 20. Samples were placed on the working surface of the internal reflection (ATR) diamond element with
the angle of incidence of 45°. Phosphorescence was excited by a focused light of a xenon lamp of 1 kW through a red border filter KS-11 (λ ≥ 660 nm). The phosphorescence spectrum was measured using a monochromator with a replica of a diffraction grating. The gap width corresponded to 8 nm. The fluorescence spectra were recorded on a Hitachi F-2700 spectrometer in quartz cells (1×1 cm). The quantum yield of singlet oxygen generation by this compound was determined by the relative method using a chemical trap. 1,3-Diphenylisobenzofuran (DPBF) was used as a chemical trap. The measurements were carried out in a quartz cell with an optical path length of 1 cm. The solutions were irradiated for a certain time with light passing through a monochromator from a xenon lamp of a Perkin Elmer MPF-44B fluorimeter, its power was measured using a Thorlabs PM-100D instrument with a SI20VC sensor head. Optical density was determined using a Hitachi U-3400 dual-beam spectrophotometer.

3.2. Synthetic procedures

3.2.1 5,6-Diphenylpyrazine-2,3-dicarbonitrile (1). Benzil (1.06 g, 5.00 mmol) and diaminomaleonitrile (0.54 g, 5.00 mmol) were refluxed in 100 mL ethanol for 6h (TLC-control: SiO2, ethyl acetate:hexane (1:2)). Then the reaction mixture was cooled to room temperature. The resulting residue was filtered off, washed with cold C2H5OH (3×30 mL) and dried at room temperature to give compound 1 (1.24 g, 88%). m.p. 244-246°C (lit. 246°C). 1H NMR (400.13 MHz, [D6]Py) δH ppm: 7.35-7.39, 7.43-7.47 and 7.65-7.67 (m, Ph). The fluorescence spectra were recorded on a Hitachi F-2700 spectrometer in quartz cells with an optical path length of 1 cm.

3.2.2 [2,3,9,10,16,17,23,24-Octaphenyl-1,4,8,11,15,18,22,25-octaazaphthalocyaninato]dilithium (2). A mixture of compound 1 (0.40 g, 1.42 mmol), MeOLi (0.11 g, 2.89 mmol) and p-hydroquinone (0.080 g, 0.73 mmol) was placed into a glass tube. The resulting mixture was irradiated in a microwave oven (600 W) during 15 min. Then the reaction mixture was cooled to room temperature and a MeOH-H2O (20:1 v/v) mixture was added. The precipitate was filtered and washed with H2O, MeOH, and acetone. This yielded complex 3 (0.31 g, 76%). MS (MALDI-TOF) m/z: 1132 ([M-2Li+3H]+, 30%), 1154 ([M-2Li+Na+2H]+, 100%), 1176 ([M-2Li+2Na+H]+. UV-Vis λmax (Py)/nm 370 (lgε 4.56) and 660 (4.66). IR (ZnSe): ν (cm−1): 1377-1612 (γ pyrrole and pyrazine). 3.2.3 [2,3,9,10,16,17,23,24-Octaphenyl-1,4,8,11,15,18,22,25-octaazaphthalocyanine (3). Complex 2 (0.31 g, 0.27 mmol) was dissolved in polyphosphoric acid (30ml) and stirred at 110°C for 2 h. Then the mixture was cooled to room temperature, and distilled H2O was added. Ammonium carbonate was added until neutral medium of the reaction mixture was reached. The precipitate was filtered and washed with H2O, MeOH, and acetone. This yielded compound 3 (0.25 g, 82%). MS (MALDI-TOF) m/z: 1131 ([M+H]+, 100%). UV-Vis λmax (CHCl3)/nm 363 (lgε 3.98), 639 (4.56) and 672 (4.63). IR (ZnSe): ν (cm−1): 1346-1600 (γ pyrrole and pyrazine). 3288 (st NH).

3.2.4 [2,3,9,10,16,17,23,24-Octaphenyl-1,4,8,11,15,18,22,25-octaazaphthalocyaninato]palladium (4). Compound 3 (0.050 g, 0.045 mmol), PdCl2 (0.020 g, 0.135 mmol) were refluxed in o-dichlorobenzene (3 mL) (after complete dissolution catalytic amounts of NH4OAc were added) in the presence of DBU (0.10 g, 6.00 mmol) for 2 h. Then the reaction mixture was cooled to room temperature and a MeOH-H2O (20:1 v/v) mixture was added. The precipitate was filtered and washed with H2O, MeOH, and acetone. This yielded complex 4 (0.039 g, 69%). MS (MALDI-TOF) m/z: 1235 ([M+H]+, 100%), 1257 ([M+Na]+, 60%). IR (diamond): ν (cm−1): 1345-1635 (γ pyrrole and pyrazine). UV-Vis λmax (Py)/nm 351 (I/Imax 1.00) and 664 (0.65).

4. Conclusions

Novel octaphenyl-substituted palladium tetrapyrazinoporphyrazinate was obtained in a high yield using the modified multi-step synthesis including the stage of formation of the porphyrazine ligand. Target complex was identified by high resolution MALDI-TOF mass-spectrometry, FTIR spectroscopy. In its UV-Vis spectrum, two main peculiarities were observed: B band (351 nm) in UV region and Q band (664 nm) in visible region. In comparison with phenyl-substituted phthalocyanine complexes, a hypsochromic shift of the Q band of about 30 nm is observed. Target complex possess phosphorescence at 828 nm. The value of singlet oxygen quantum yield φO2=0.35±0.05 for title
compound is comparable with substituted phthalocyanine analogs, described in literature. Thus, the investigated palladium tetrapyrazinoporphyrazine can be considered as a prospective photosensitizer.

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