

Supporting information for article

Synthesis and Characterization of Tetrakis(allyloxy) -substituted Zn(II), Pt(II) and Pd(II) Phthalocyanines

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Синтез и характеристика тетракис(аллилокси) -замещенных фталоцианинов Zn(II), Pt(II) и Pd(II)

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1. General Considerations

All reagents and solvents were obtained or distilled according to standard procedures. The reagents used for experiments were purchased from Sigma-Aldrich Co. and used as received unless otherwise noted. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 under argon, tetrahydrofuran (THF) was distilled from Na under argon and solvents were stored under argon.

N,N-dimethylformamide (DMF), dimethylaminoethanol (DMAE), benzonitrile (PhCN), chloroform (CHCl_3), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), zinc acetate $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, platinum(II) chloride (PtCl_2) were purchased from commercial sources (Sigma-Aldrich).

Preparation of zinc and platinum(II) complexes was monitored by thin-layer chromatography (TLC) and UV-Vis until complete disappearance of the starting reagents. TLC was performed using Merck Silica on Alu Foil F₂₅₄ neutral flexible plates. Electronic absorption spectra were recorded on a Jasco V-770 spectrophotometer using quartz cells (1×1 cm). MALDI-TOF mass spectra were taken on a ULTRAFLEX II mass-spectrometer. ¹⁹⁵Pt NMR (129.009 MHz) spectra were obtained on Bruker Ascend 600 MHz spectrometer with CDCl_3 as solvent and Na_2PtCl_6 in D_2O as internal standard. Chemical shifts were reported in units (ppm) by assigning Na_2PtCl_6 in D_2O resonance in the ¹⁹⁵Pt NMR spectra as 0.00 ppm.

2. Synthesis of Phthalocyanine Complexes

Zinc 2,9,16,23-tetrakis(prop-2-enoxy)phthalocyaninate. 100 mg (0.136 mmol) of 2,9,16,23-tetrakis(prop-2-enoxy)phthalocyanine and 31 mg (0.813 mmol) of MeOLi were dissolved in 4 ml of isoamyl alcohol. After the receiving of dianion form (UV-Vis control in CHCl_3), 36 mg (0.163 mmol) of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was added. The mixture was stirred with heating for 1.5 hours. After the reaction, the mixture was diluted with MeOH- H_2O (9:1) and filtered. The residue was purified by flash-chromatography (silica, CH_2Cl_2 -THF 20:1). Product was obtained as a dark green-blue powder with 90 % yield. MALDI-TOF (*m/z*): 800.066 (M^+). UV-Vis (CHCl_3) λ_{max} nm: 682, 619, 350.

Platinum(II) 2,9,16,23-tetrakis(prop-2-enoxy)phthalocyanine. 54 mg (0.204 mmol) of PtCl_2 was dissolved in 5 ml of benzonitrile while heating. Then, 100 mg (0.136 mmol) of 2,9,16,23-tetrakis(prop-2-enoxy)phthalocyanine and 5 drops of DBU were added. The mixture was stirred with heating for 8 hours. After the reaction, the mixture was diluted with MeOH- H_2O (9:1) and filtered. The residue was purified by flash-chromatography (silica, CH_2Cl_2 -THF 20:1). Product was obtained as a dark blue powder with 85 % yield. MALDI-TOF (*m/z*): 931.106 (M^+). UV-Vis (CHCl_3) λ_{max} nm: 691.8, 625, 343. ¹⁹⁵Pt NMR (CDCl_3 , 129.009 MHz, 25 °C) δ_{H} ppm: -3200.664.

3. Copies of Spectra

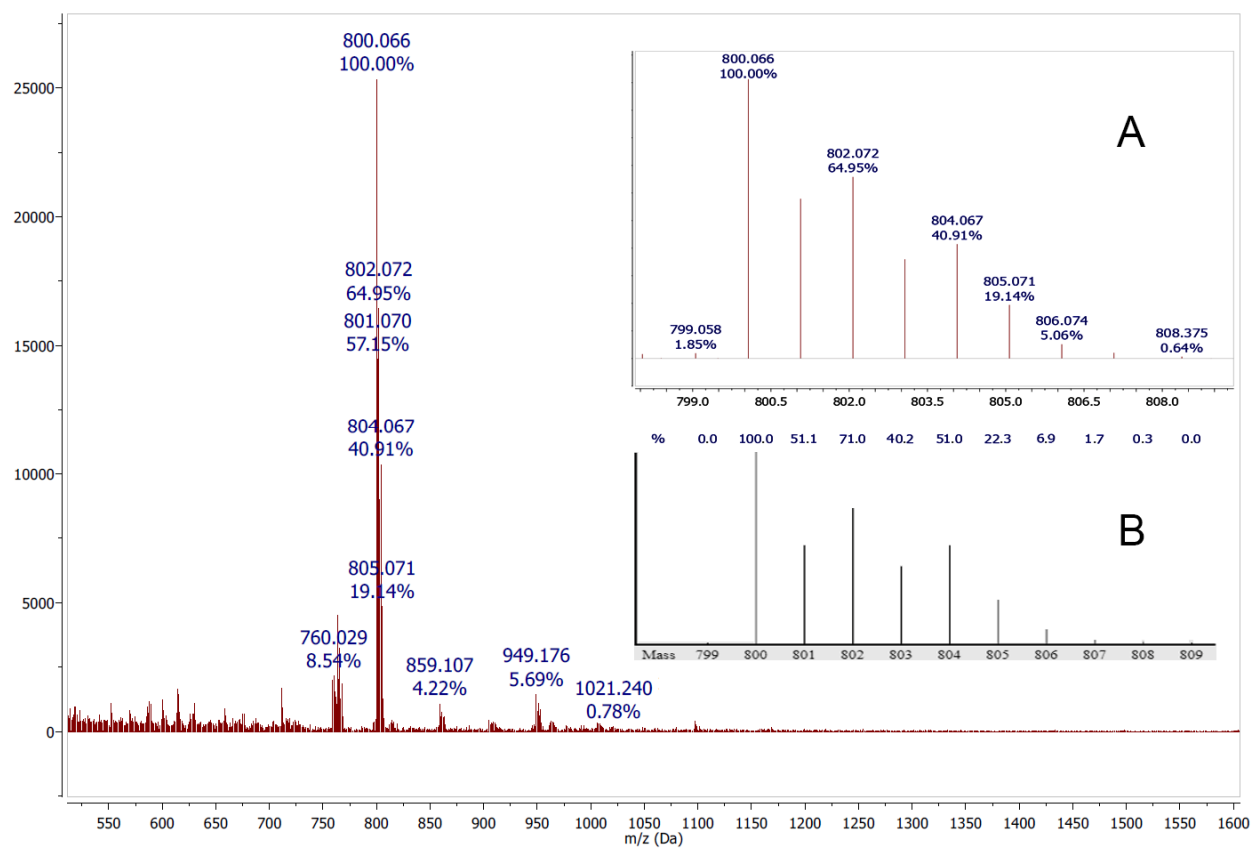


Figure S1. MALDI-TOF mass spectrum of $O\text{-AllylPcZn}$ complex and isotopic patterns for particle $O\text{-AllylPcZn}$: observed peak (insert A), theoretically calculated peak (insert B).

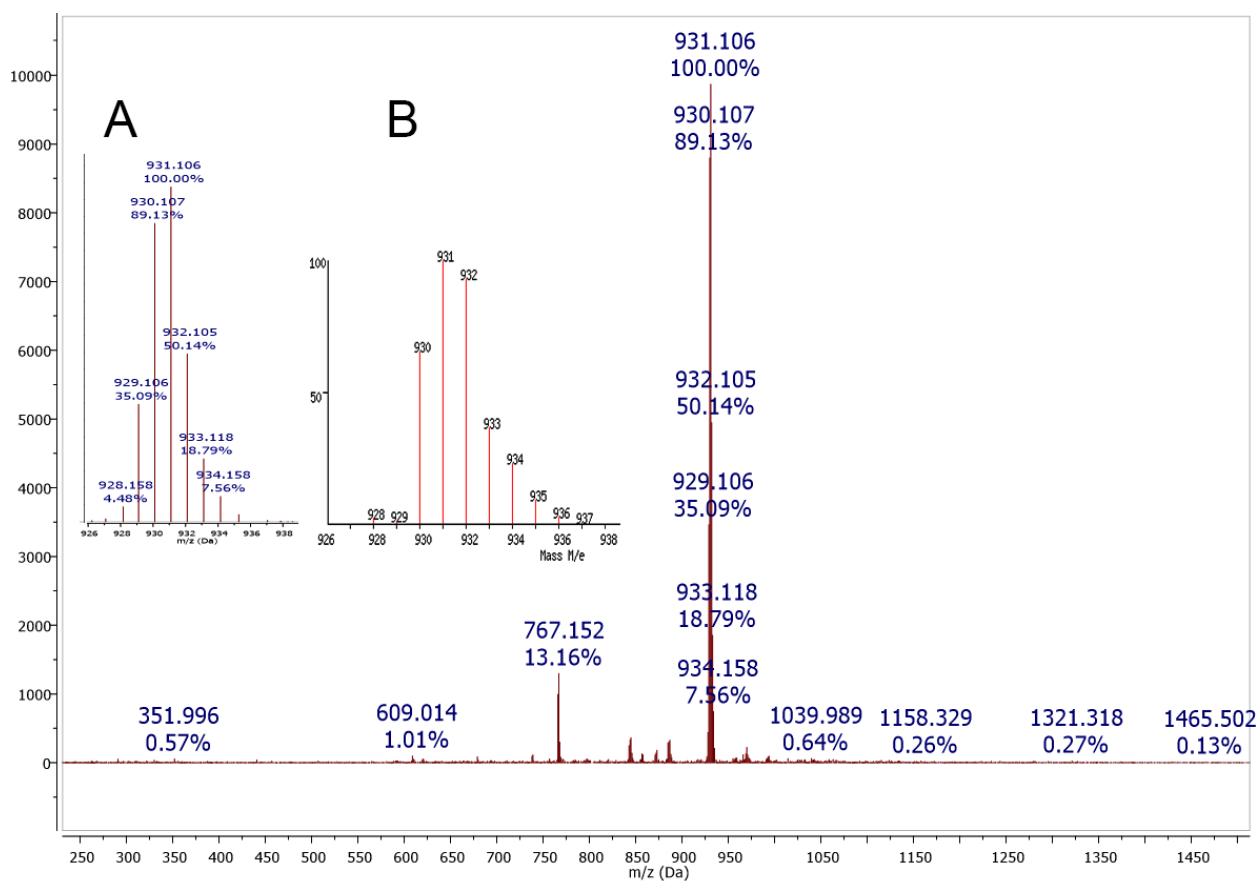


Figure S2. MALDI-TOF mass spectrum of ^{O-Allyl}PcPt complex and isotopic patterns for particle ^{O-Allyl}PcPt: observed peak (insert A), theoretically calculated peak (insert B).

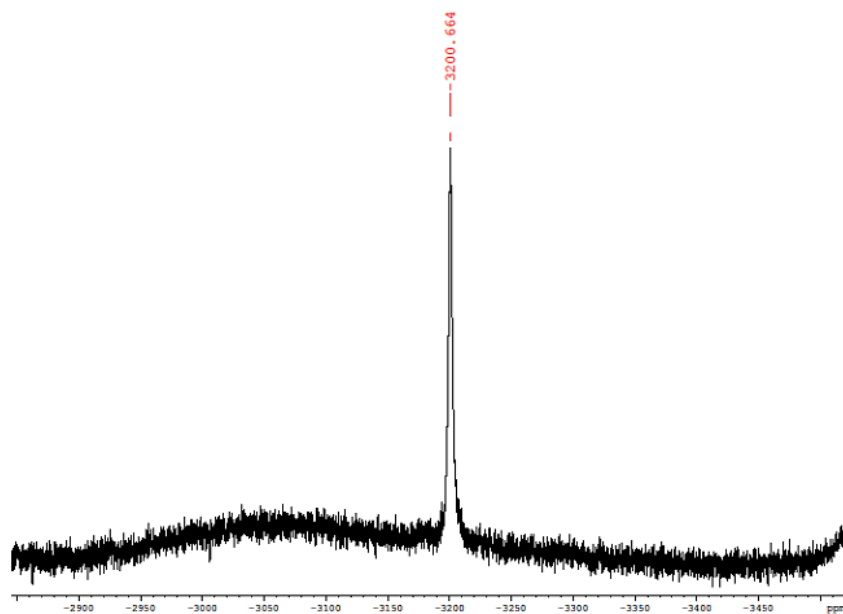


Figure S3. ¹⁹⁵Pt-NMR spectrum of ^{O-Allyl}PcPt in CDCl₃.

4. Photochemical Research

For photochemical research the solvent used was acetone ("Himmed"), in which platinum(II) phthalocyanine $^{0-}$ $^{Allyl}PcPt(II)$ is highly soluble.

The phosphorescence of the studied compound was measured at 77 K on a device with a mechanical phosphoroscope, described in literature.^[1] Freshly prepared solution of metal complex in acetone was frozen in special metal frames with a thickness of 5 mm in liquid nitrogen. Sample in frame was placed in Dewar quartz vessel filled with liquid nitrogen, fixed with special holders inside the phosphoroscope. The optical density of the solution before cooling was 0.15 in 5 mm at the long-wave absorption maximum (692 nm). Phosphorescence was excited by the focused light of a xenon lamp (1 kW) through a red boundary light filter KS-11 ($\lambda \geq 690$ nm). The phosphorescence spectra were measured using a monochromator with a replica of a diffraction grating. The width of the gap corresponded to 10 nm.

For determination of quantum yields of singlet oxygen generation TPP (*meso*-tetraphenylporphine) was used as the standard compound. According to the literature, the most probable value of the singlet oxygen quantum yield of this porphyrin in acetone is 0.65 ± 0.05 .^[2,3] 1,3-Diphenylisobenzofuran (DPBF) was used as a chemical trap. The products of interaction of this trap with singlet oxygen^[4] do not have absorption bands in the visible range of the spectrum. Therefore, the amount of singlet oxygen formed during the photoreaction can be judged by the decrease in the optical density in the region of the maximum absorption of DPBF.

To determine the quantum yields of singlet oxygen generation, mixed solutions of the studied compounds and DPBF were prepared in a fixed volume of solvent. Measurements were made in square quartz fluorescent cuvettes 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 the Perkin Elmer MPF-44B fluorimeter, its power was measured using a ThorLabs PM-100D device with a S120VC sensor head (Germany). The wavelength of light that irradiated the samples was selected from the position of the maximum long-wave band of the compound under study (692 nm). The spectral width of the gap of the fluorimeter monochromator corresponded to 5 nm. During irradiation, not only changes in the optical density in the region of the maximum absorption of DPBF were controlled, but also at the wavelength of the exciting light. During irradiation, the absorption band of the sensitizer did not fade, *i.e.* the optical density of the sensitizer did not change at the wavelength of the exciting light. The optical density was determined using a Hitachi U-3400 bi-beam spectrophotometer. The concentration of DPBF in the sample was selected so that its optical density in the region of maximum absorption was 0.80-1.20.

When calculating the quantum yield, the relative method compares the loss of the optical density of the DPBF and the irradiation time in experiments conducted for the studied compounds and the standard compound. Three experiments were performed with the standard compound, and four experiments were performed with the studied compounds.

The calculation was made using 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 $\phi_{\Delta St}$ – singlet oxygen quantum yield of the standard compound; ΔD_C – average decay of the optical density of DPBF, ΔD_{St} – average decay of the optical density of DPBF in experiments with standard, t_{irrC} – time of irradiation of the DPBF and studied compound mixture, t_{irrSt} – time of irradiation of the DPBF and standard compound mixture, I_C and I_{St} – the intensity of the light flux from a xenon lamp in experiments with the studied compound and the standard compound, D_C and D_{St} – optical densities of the studied compound and standard compound, which corresponds to the wavelength of the exciting light λ_C and λ_{St} . Calculations were performed in MS Excel.

References

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