



SYNTHESIS, SPECTROSCOPIC AND LUMINESCENT PROPERTIES OF ZINC COMPLEXES OF (4- OCTYLOXYPHENOXY)-SUBSTITUTED PHTHALOCYANINES

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The work is devoted to the preparation of zinc complexes of tetra(4-octyloxyphenoxy)phthalocyanines, as well as its sulfonated derivatives and the study of their properties, primarily spectroscopic and luminescent. The compounds were synthesized and characterized by IR and electron spectroscopy, MALDI-TOF mass spectrometry and elemental analysis. Absorption spectra were obtained in the visible range in chloroform, DMF, water (for the sulfonated analogue). It was shown that in the studied concentration range the complexes exist in monomeric form. Sulfonated phthalocyaninates turned out to be aggregated only in an aqueous medium, which made it possible to study the fluorescent properties in an organic medium (namely, in DMSO). The introduction of a sulfonate groups was found to lead to quenching of fluorescence in comparison with an organo-soluble phthalocyaninate.

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INTRODUCTION

Macrocyclic compounds are attracting more and more attention of researchers due to their unique properties closely related to the structure of the molecule.¹⁻³ Changing the nature of certain substituents in the molecular ensemble entails the possibility of highly specific adjustment of the properties of materials based on these compounds.⁴⁻⁷

Phthalocyanines and their metal complexes have proven to be one of the most promising classes of compounds in this direction. The possibility of varying the substituents in the peripheral and non-peripheral positions as well as the nature of the coordination center of the molecule opens a wide range of applications for these molecules. They are used as dyes and pigments,⁸⁻¹⁰ elements of optical and electronic devices, catalysts and sensitizers.¹¹⁻¹³ as components of solar cells¹⁴⁻¹⁶ etc.

One of the main problems in the study of phthalocyanines and their complexes is the low solubility (or lack thereof) in most organic and inorganic solvents due to their high aromaticity. This issue is solved by introducing suitable substituents on the periphery, which, on the one hand, would facilitate the solvation of the phthalocyanine macro-ring and, on the other hand, would not lead to the aggregation of compounds in the liquid phase or deterioration of the spectral properties.

Substitution with alkoxyphenoxy- fragments imparts substantial solubility to phthalocyanine molecules in organic media and, due to the relative flexibility of the introduced

groups, does not lead to aggregation consequences in the concentration ranges of interest. Thus, it becomes possible to use compounds of this class, to create hybrid materials^{17,18} and thin films^{19,20} with prospects for further use.

The next important point is the possibility of modifying the structure to make the compounds soluble in aqueous and aqueous-alkaline media. In combination with the possibility of selecting suitable substituents and a luminescent active central metal atom, it becomes possible to use the complexes in the field of medicine as elements for photodynamic therapy of cancer diseases.^{21,22}

Macrocyclic compounds are used as photosensitizers due to the possibility of intense absorption of light in the visible region. Giving such compounds solubility in aqueous media opens up simple ways for introducing a sensitizer into a living organism in order to further destroy cancer cells.²³ This work presents the results of obtaining and studying the spectral-luminescent properties of zinc tetra[4-octyloxyphenoxy]phthalocyaninate and its sulfonated derivatives.

EXPERIMENTAL

Elemental analysis of the synthesized compounds was carried out on a CHNS-OFlashEA, 1112 series analyzer. Electronic absorption spectra were recorded on a UNICO2800 UV-VIS spectrophotometer in organic solvents, in water, and sulfuric acid at room temperature at wavelength range of 350-900 nm. IR spectra were recorded on an IRAffinity-1s spectrometer in the region of 400-4000 cm⁻¹ in a potassium bromide matrix and thin films (chloroform).

The determination of the quantum yields of fluorescence was carried out using the comparative method described earlier⁹ using pyridine solution of unsubstituted zinc phthalocyanine as a standard ($\Phi_{\text{fluor}} = 0.3$).

The fluorescence lifetime was measured on a Fluorescence Lifetime Spectrometer FluoTime 300 (Germany). The fluorescence lifetimes were calculated using the EasyTau software package.

MALDI-TOF mass spectra were obtained on a Shimadzu Biotech Axima Confidence mass spectrometer in positive ion mode. 2,5-Dihydroxybenzoic acid was used as a matrix. Samples were prepared by dissolving the compounds in chloroform and ethanol (10^{-4} - 10^{-5} mol L $^{-1}$), then mixed in a 1 : 1 ratio (v/v) with a solution of the matrix (30 mg mL $^{-1}$) in THF. Before elemental analysis, the samples of the studied compounds were subjected to heat treatment at 110 °C for 2 h.

(4-Octyloxyphenoxy)phthalonitrile (2)

4-nitrophthalonitrile (1 mmol) (**1**) and 4-octyloxyphenol (1 mmol) were dissolved in 30 mL of DMF, a solution of K₂CO₃ (2 mol) in 5 mL of water was added to the resulting solution, and stirred at 100 °C for 3 h. The precipitate obtained was filtered off, washed with water to pH 7 and dried in air at 70-80 °C. Yield: 0.322 g (64%). FT-IR, ν = 2985, 2948, 2897 (C_{ar}-H), 2235-2220 (C≡N) 1583, 1541, 1489 (C_{ar}-C_{ar}), 1278 (Ar-O-Ar) cm $^{-1}$. Anal. Calcd. for C₂₂H₂₄N₂O₂: C, 75.83; H, 6.94; N, 8.04; O, 9.18. Found: C, 75.84; H, 6.95; N, 8.02; O, 9.18.

Zinc tetra[4-octyloxyphenoxy]phthalocyaninate (3)

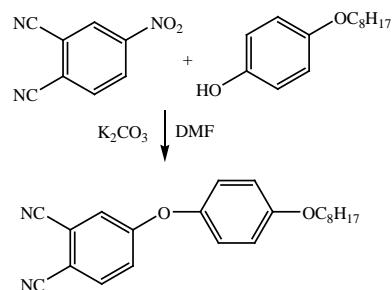
A ground mixture of compound **2** (0.1 mmol) and zinc (II) acetate (0.3 mmol) was heated to 180 °C until complete melting. Then, after solidification of the mixture, the resulting complex was precipitated on ice, the precipitate was washed with distilled water to neutral pH and dried. Final purification was carried out by column chromatography on silica gel M60 eluting with chloroform. Yield: 0.21 g (78%). MALDI-TOF, m/z : 1459.17 [M] $^{+}$. FT-IR, ν = 3070-2850 (C_{ar}-H), 1596-1480 (C_{ar}-C_{ar}), 1248 (Ar-O-Ar) cm $^{-1}$. Anal. Calcd. for C₈₈H₉₆CN₈O₈Zn: C, 72.44; H, 6.63; N, 7.68; O, 8.77; Zn, 4.48. Found: C, 72.42; H, 6.64; N, 7.68; O, 8.78; Zn, 4.48.

Zinc tetra[4-octyloxy-(2-sulfophenoxy)]phthalocyaninate (4)

Complex **3** (0.1 mmol) was mixed with chlorosulfonic acid (30 mmol) and thionyl chloride (30 mmol) and refluxed under constant stirring at 20 °C for 2 h. At the end of the time, the reaction mixture was poured onto an ice-salt mixture. The formed precipitate was filtered off and dried. Next, the sulfonyl chloride was extracted with acetone, after which the solvent was distilled off. The resulting substance was boiled in water until complete dissolution, after which the water was removed. Final purification was carried out by column chromatography eluting with DMF on silica gel. Yield: 0.173 g (84%). MALDI-TOF, m/z : 1779.37 [M] $^{+}$. FT-IR, ν = 3300-3100 (O-H), 3070-2850 (C_{ar}-H), 1596-1480 (C_{ar}-C_{ar}), 1248 (Ar-O-Ar), 1200-1150 (S=O), 1060-1025 (C-S) cm $^{-1}$. Anal. Calcd. for C₈₈H₉₆N₈O₂₀S₄Zn: C, 59.40; H, 5.44; N, 6.30; O, 17.98; S, 7.21; Zn, 3.67. Found: C, 59.38; H, 5.45; N, 6.30; O, 17.99; S, 7.20; Zn, 3.68.

RESULTS AND DISCUSSION

At the beginning of the work, for the synthesis of target metal complexes, **2** was obtained by nucleophilic substitution in **1** by interaction with 4-octyloxyphenol in DMF medium in the presence of potassium carbonate as the main agent (Scheme 1).



Scheme 1. Synthesis of 4-(4-octyloxy)phenoxy)phthalonitrile (2).

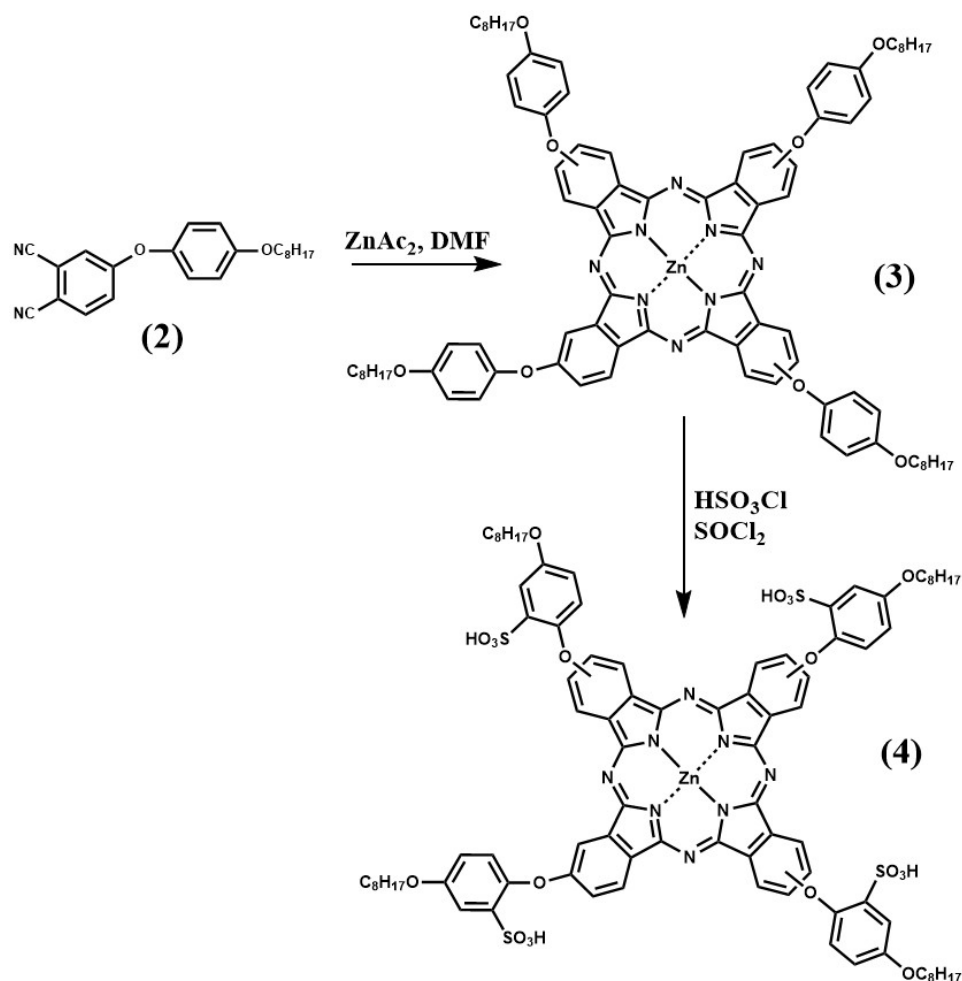
Next, using the reported nitrile method²⁴, which consists of high-temperature fusion of the corresponding phthalonitrile (**2**) and a metal salt (in this case zinc acetate) in a molar ratio of 1:3, in the absence of a solvent, zinc tetra[4-octyloxyphenoxy]phthalocyaninate (**3**) (Scheme 2) was synthesized.

The IR spectrum of complex **3** is characterized by the absence of vibrations in the range of 2220-2235 cm $^{-1}$, corresponding to the vibrations of cyano groups in the starting phthalodinitrile. This fact indicates the successful course of the synthesis and purification of the compound. At the same time, there are bands 3070-2850 (C_{ar}-H), 1596-1480 (C_{ar}-C_{ar}), 1248 (Ar-O-Ar). The mass spectrum recorded a molecular peak for ion 1459.17, corresponding to the molar mass of the complex.

To obtain a water-soluble derivative, a sulfonation reaction was carried out with chlorosulfonic acid and thionyl chloride. This method is characterized by higher selectivity and mild conditions compared to sulfonation with oleum. Sulfochloride obtained 2 h after adding sulfonating agents to the reaction mass and subsequent filtration, was converted to the target sulfonic acid (**4**) by boiling (Scheme 2). Purification was carried out using silica gel column chromatography with DMF as eluent.

The FT-IR spectrum of the obtained phthalocyaninate also contains all vibrations characteristic of phthalocyanane (Ar-O-Ar, C_{ar}-H, C_{ar}-C_{ar}). In addition, new bands were found in the range of 1200-1150 cm $^{-1}$ (S=O) and 1060-1025 cm $^{-1}$ (C-S), describing the vibrations of sulfonate groups, as well as a broadened band at 3300-3100 cm $^{-1}$, describing the vibration of the O-H sulfonic acid group.

The introduction of substituents gave the complexes significant solubility in organic or aqueous media, which made it possible to study their spectral-luminescent properties. The electronic absorption spectra of phthalocyaninates are characterized by the presence of an intense absorption band in the 650-700 nm range (depending on the medium) associated with π - π^* transitions in the phthalocyanine molecule (Table 1).



Scheme 2. Template tetramerization of phthalonitrile (1st step) and sulfochlorination reaction (2nd step).

Zinc tetra[4-octyloxyphenoxy]phthalocyaninate exhibited higher extinction coefficients compared to its sulfonated counterpart. The largest bathochromic shift was observed in the case of chloroform, which is probably due to its lowest coordination ability. Complexes **3** and **4** showed high aggregation stability, being monomers in all studied media, except for water (Figures 1 and 2).

Table 1. Spectroscopic characteristic of complexes **3** and **4** in various solvents.

Compound	Solvent/ λ_{\max} , nm ($\lg \epsilon$)				
	CHCl ₃	DMF	EtOH	DMSO	H ₂ O
3	683 (4.20)	680 (4.12)	-	-	-
4	-	-	678 (3.72)	682 (3.79)	aggregated

Shift from ethanol to DMSO resulted in a bathochromic shift for complex **4**. In contrast, in an aqueous medium the complex existed in an aggregated form over the entire studied concentration range (2.33×10^{-6} - 1.12×10^{-5} mol L⁻¹).

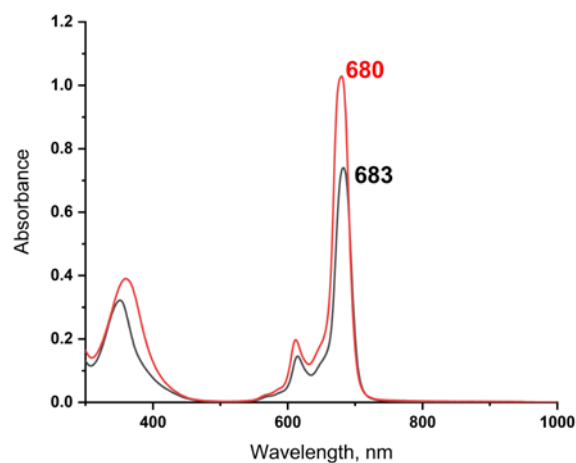


Figure 1. UV-vis spectra of **3** in CHCl₃ (black) and DMF (red).

At the next stage, the fluorescent properties of complexes **3** (in DMF) and **4** (in DMSO and ethanol) as potential PDT elements were studied. Fluorescent decays were obtained for all studied media, which made it possible to determine the fluorescence lifetimes of the complexes (Table 2).

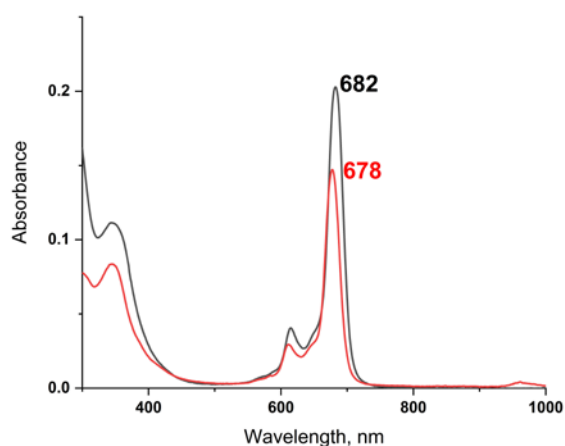


Figure 2. UV-vis spectra of **4** in DMSO (black) and EtOH (red).

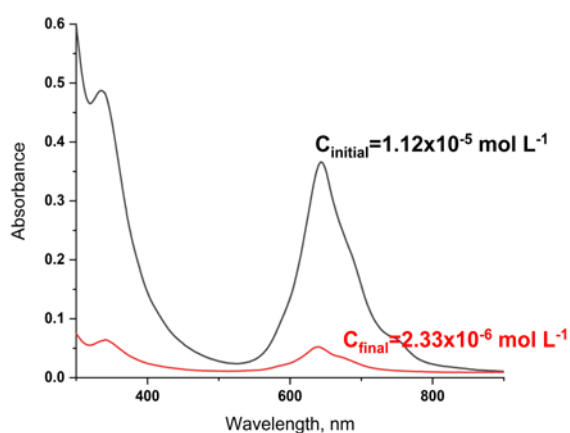


Figure 3. UV-vis spectra of **4** in H₂O at different dilutions ($C_{\text{initial}} = 1.12 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{final}} = 2.33 \times 10^{-6} \text{ mol L}^{-1}$).

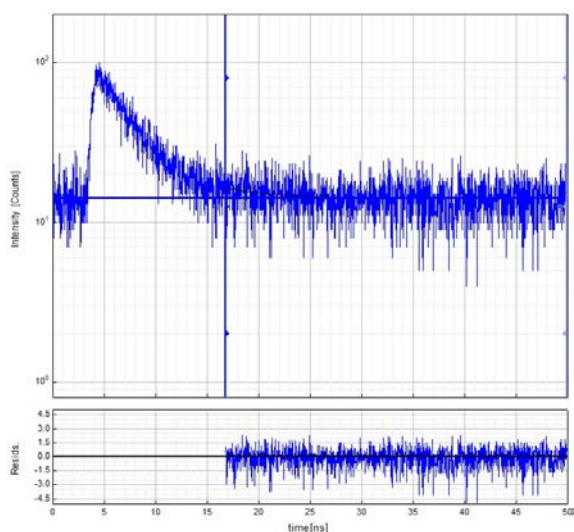


Figure 4. Fluorescent decay of **3** in DMF (Internal standard – ludox in water).

The lifetimes for both complexes **3** and **4** turned out to be longer than that of the reference object (unsubstituted zinc phthalocyaninate), based on which it can be concluded the fluorophore is stabilized by the introduction of

octyloxyphenoxy substituents into the peripheral fragments of the molecule (Figures 4–6). The fluorescence lifetimes for sulfo-substituted phthalocyaninate turned out to be 1.5–2 times lower than for unsubstituted phthalocyaninate.

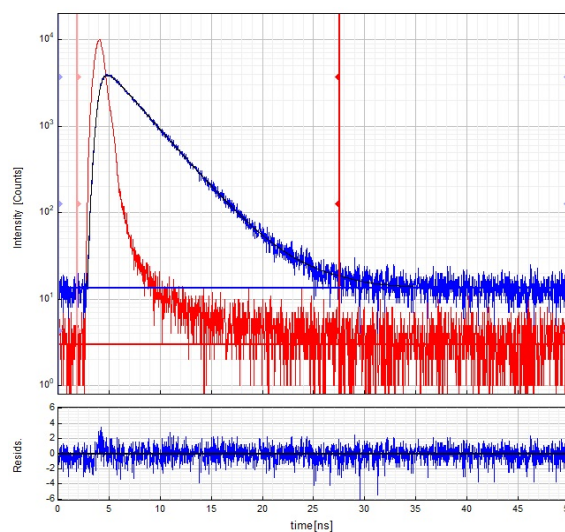


Figure 5. Fluorescent decay of **4** in DMSO (Internal standard – ludox in water).

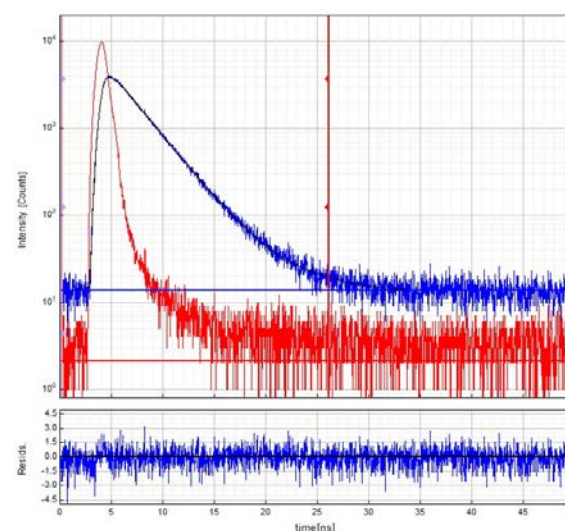


Figure 6. Fluorescent decay of **4** in ethanol (Internal standard – ludox in water).

Comparing the values of the fluorescence quantum yields, a correlation between the complexes is also observed. For complex **4**, the values turned out to be lower, which is likely due to the quenching of fluorescence upon the introduction of the sulfo- group.

CONCLUSIONS

In this work, new zinc tetra[4-octyloxyphenoxy]- and tetra[4-octyloxy-(2-sulfophenoxy)]phthalocyaninates have been obtained and characterized. The spectroscopic properties in various solvents are studied, the extinction coefficients of the complexes are determined, and the dependence of the absorption maximum on the medium under study is shown. The fluorescent properties of the

compounds have been studied for potential usage in PDT purposes. It was shown the transition to a sulfonate-substituted complex is accompanied by quenching of fluorescence and a decrease in its lifetime.

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