

# Photophysical study of meso-phenothiazinyl-porphyrins metallocomplexes

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**Abstract.** Photophysical parameters of a set of metallocomplexes of meso-phenylthiazinylporphyrins with Zn (II), Pd (II) and Cu (II) ions were studied in different organic solvents, solid solutions and polymeric matrices at room and liquid nitrogen temperatures. The dependence of the spectral and photophysical parameters on changing the molecular structure with increasing number of branched substituents attached to aryl groups in different positions of the porphyrin macrocycle has been established.

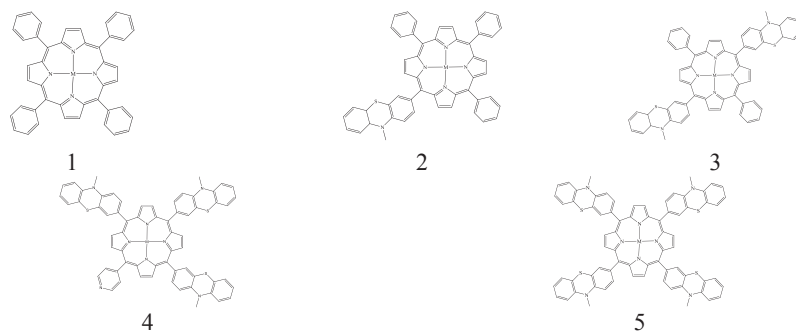
Macroheterocyclic compounds are widely used in medicine (compounds for photodynamic therapy and photodiagnostics) and as materials for design of electronics components (sensors, light emitting systems, solar cells and etc.), as well as systems for creation of optical memory, optical switches and etc. At the same time, increasing number of new applications of organic semiconductors in molecular electronics requires synthesis and studding of new molecular systems and optimization of their parameters.

The metallocomplexes of meso-phenylthiazinylporphyrins with Zn (II), Pd (II) and Cu (II) ions were studied in the current work. The synthesis of compounds was carried out by modified methods described in [1]. The structures of investigated compounds are shown on Fig. 1. The photophysical characteristics for newly synthesized metallocomplexes in various organic solvents and polymer films are presented (Tab. 1).

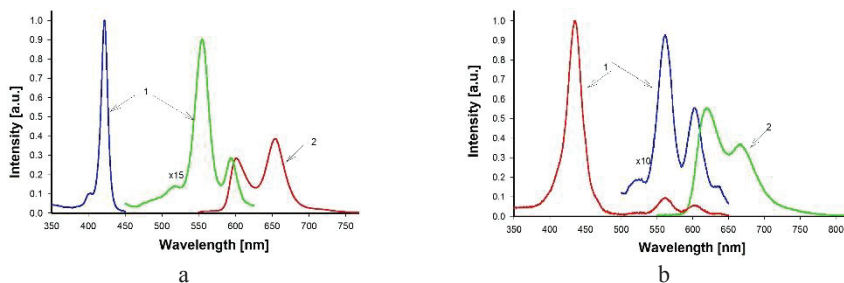
The progressive substitution with additional phenylthiazinyl (PTH) groups in the meso-positions of the porphyrin macrocycle leads to rather small but noticeable changes in the porphyrin absorption and fluorescence spectra (Fig. 2). It is well known [2] that with increasing of number of branched substituents in the meso-position of the porphyrin macrocycle the energy of the  $a_{2u}$  MO is changing, so that  ${}^1E(a_{2u}, e_g) < {}^1E(a_{1u}, e_g)$ . The substitution with PTH fragments in the meso-positions of the porphyrin macrocycle leads to the changes in the photophysical properties of the studied compounds. For example, in going from the parent unsubstituted Zn-TPP to the derivatives with increasing number of the PTH groups (Zn-TP2A, Zn-TP2B; Zn-TPy4PtzA, Zn-TP2D) the number of photophysical parameters was found to be altered (Fig. 2 and Tab. 1).

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**Fig. 1.** Structure of meso-phenylthiazinylporphyrins metallocomplexes (where M- Zn(II), Pd(II) and Cu(II)),: 1-M-5,10,15,20-tetraphenylporphyrin (M-TPP); 2- M-TP2A; 3-M-TP2B; 4- M-TPy4PtzA; 5 -M-TP2D.



**Fig. 2.** Absorption (1) and fluorescence (2) spectra of Zn-TPP (a) and Zn-TP2D (b) in 2-m-tetrahydrofuran at 300 K.

**Table 1.** Photophysical parameters of Zn-meso-phenylthiazinylporphyrins in 2-m-tetrahydrofuran at 300 K.

Compound	$\lambda_{\max}$ Sore, nm	$\lambda_{0-0}$ , nm	Fluorescence $\lambda_{0-0}$ , nm	$\phi_{F1}$	$\tau_{F1}$ , ns
Zn-TPP	422	594	601	0,028	1,82
Zn-TP2A	427	599	608	0,033	1,24
Zn-TP2B	428	599	611	0,034	1,26
Zn-TPy4tzA	430	602	615	0,03	1,10
Zn-TPP2D	435	602	619	0,025	1,02

First of all, the fluorescence quantum yield  $\phi_{F1}$  increases with increasing of number of attached PTH groups. A measurement of the fluorescence decay times demonstrates that decay becomes, as rule, also faster.

This work was supported by the BRFFI Grant No. F16RA-007 and H2020-MSCA-RISE-2014-RISE-645628 - METCOPH project.

## References

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