

4-Carboxyphenyl Substituted Porphyrazine, Its Ester and Their Zinc(II) Complexes

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The porphyrazines bearing eight 4-carboxyphenyl and 4-butoxycarbonylphenyl groups ($H_2Pz(PhCOOH)_8$ and $H_2Pz(PhCOOBu)_8$), as well as their Zn(II) complexes were obtained and characterized by spectral methods. The conversion of carboxyl derivatives into their anionic forms $H_2Pz(PhCOO^-)_8$ and $ZnPz(PhCOO^-)_8$ in the presence of alkali leads to water-soluble species. $ZnPz(PhCOOH)_8$ and $ZnPz(PhCOOBu)_8$ possess the high ability to generate singlet oxygen in DMF solutions ($\Phi_\Delta = 80-83\%$), while their metal free analogues are weak photosensitizers due to their aggregation tendency.

Keywords: Porphyrazines, zinc complexes, carboxyl groups, photosensitizers, ligands for HOFs.

4-Карбоксифенилзамещенный порфиразин, его эфир и их комплексы с Zn(II)

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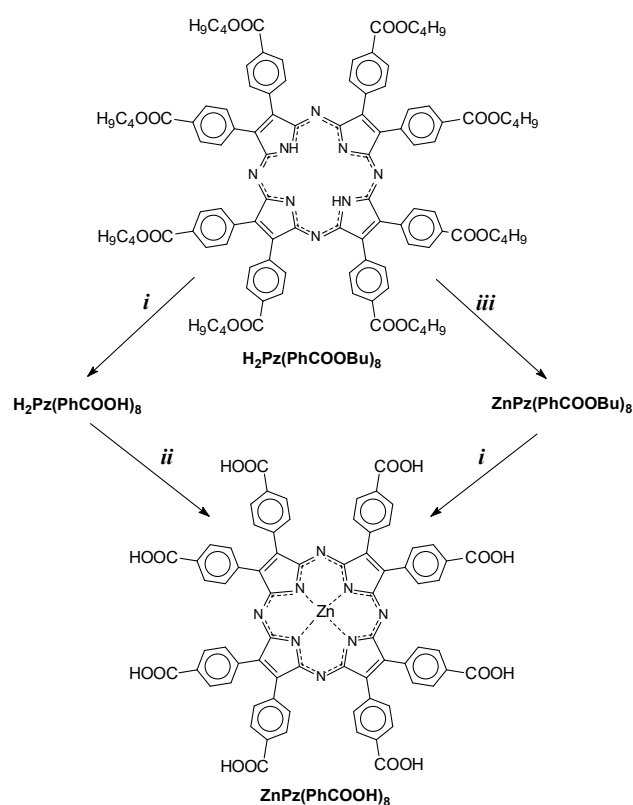
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Получены окта(4-карбоксифенил)- и окта(4-бутоксикарбонилфенил)замещенные порфиразины ($H_2Pz(PhCOOH)_8$ и $H_2Pz(PhCOOBu)_8$), а также их комплексы с цинком(II), и изучены их спектральные свойства. В щелочной среде карбоксильные производные образуют растворимые в воде анионные формы $H_2Pz(PhCOO^-)_8$ и $ZnPz(PhCOO^-)_8$. В то время как комплексы $ZnPz(PhCOOH)_8$ и $ZnPz(PhCOOBu)_8$ обладают высокой способностью к генерации синглетного кислорода в растворах ДМФА ($\Phi_\Delta = 80-83\%$), соответствующие им безметалльные макроциклы из-за склонности к агрегации являются слабыми фотосенсибилизаторами.

Ключевые слова: Порфиразины, комплексы цинка, карбоксильные заместители, фотосенсибилизаторы, органические каркасные соединения с водородными связями.

Due to their unique spectral and photochemical properties phthalocyanine (Pc)-type dyes are actively studied as perspective materials for various fields.^[1,2, etc.] Their solubility in aqueous medium which is often desirable for catalytic or biomedical applications can be most easily achieved by introduction of solubilising substituents in the peripheral positions of the macrocycle.^[3] Among the peripheral substituents used for design of anionic water-soluble phthalocyanines and their analogues the carboxylic (COOH) groups are widely used. Carboxy substituted phthalocyanines are interesting as water-soluble photo-

sensitizers^[4-6] and catalysts.^[7] Moreover COOH groups can form intermolecular hydrogen bonds and participate in complexation of metal ions, and, therefore, they are suitable for the construction of hydrogen-bonded and metal organic frameworks (HOF and MOFs).^[8-10] Among Pc and its analogues synthesis of octacarboxylated phthalocyanines,^[11] tetrapyrzainoporphyrazines,^[12,13] and tetraquinoxalinoporphyrazine^[14] were reported. In the present work we have prepared 4-carboxyphenyl substituted porphyrazine and its Zn^{II} complex and studied their spectral and photophysical properties (Scheme 1).



Scheme 1. Synthesis of Zn octa(4-carboxyphenyl)porphyrazine from octa(4-butoxycarbonylphenyl)porphyrazine by two routes: *i* – a) THF / NaOH saturated MeOH:H₂O (5:1, v/v) solution, 40 °C, 1 h, b) H₂O, HCl; *ii* – ZnAc₂·2H₂O (2 eq.), DMF, reflux, 1 h; *iii* – ZnAc₂·2H₂O (2 eq.), THF, reflux, 50 min.

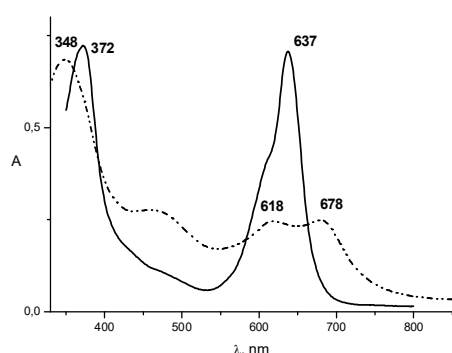


Figure 1. The UV-vis spectra of H₂Pz(PhCOONa)₈ (dashed line) and ZnPz(PhCOONa)₈ (solid line) in water.

Table 1. Spectral and photophysical parameters in DMF.

Compound	Stokes shift, ν_{ss} , cm ⁻¹	Φ_F , %	Φ_{Δ} , %
H ₂ Pz(PhCOOBu) ₈		0.1	1.8±0.1
H ₂ Pz(PhCOOH) ₈	201	<0.1	3.5±0.5
ZnPz(PhCOOBu) ₈	378	2.2±0.1	80±8
ZnPz(PhCOOH) ₈	356	2.9±0.1	83±4
ZnPc ^[16,17]		30	56
ZnPc(COOH) ₈ (in DMSO) ^[18]			57
ZnQPz(COONa) ₈ (in DMSO/water, 9:1 v/v) ^[14]		17	67

The starting octa(4-butoxycarbonylphenyl) substituted porphyrazine H₂Pz(PhCOOBu)₈ was prepared according to ^[15]. Hydrolysis of ester group was conducted closely as described in ^[14] by treatment with methanol-water (5:1, v/v) solution saturated with NaOH. The formed octasodium salt H₂Pz(PhCOONa)₈ was dissolved in water (Figure 1) and following acidification with HCl leads to precipitation of octacarboxylic acid H₂Pz(PhCOOH)₈. Its following heating with two-fold excess of zinc acetate in DMF leads according to the spectral data (Figure 2) to the Zn(II) complex. The complete complexation and formation of ZnPz(PhCOOH)₈ requires 2 h, in contrast to the pyrazine annulated analogue for which much longer treatment was needed (12 h^[14]). After evaporation of DMF, the residue was washed with water, ethanol, acetone and dried. The dry product prepared in such way has lost solubility in water and can't be transformed to the octaanionic water soluble species in the alkaline medium. Presumably, it is a result of coordination of zinc cations, presenting in excess, with carboxylic groups with formation of polymeric form, *i.e.* MOF-type compound.

In the alternative synthetic route for preparation of ZnPz(PhCOOH)₈ the free carboxylic groups were preserved. First, the H₂Pz(PhCOOBu)₈ was converted to Zn complex by refluxing its THF solution with Zn acetate (Scheme 1). The better solubility of octabutyl ester as compared to octacarboxylic acid makes the procedure of synthesis and isolation of the product much easier. The formed ZnPz(PhCOOBu)₈ was purified by column chromatography (silica, CH₂Cl₂:MeOH, 99:1, v/v) and isolated in 68% yield. The alkaline hydrolysis of its ester groups with following acidification, which was carried out as described above for corresponding metal-free derivative, resulted in formation of ZnPz(PhCOOH)₈ with a good yield (75%). The obtained compound is easily soluble in water after addition of alkali converting it to the octaanionic form (Figure 1). It is noteworthy, that in the case of porphyrazine analogue with annulated electron deficient pyrazine rings the degradation of the macrocycle upon alkaline hydrolysis was observed and ZnPyzPz(COOH)₈ could not be obtained in a such way.^[14]

The characterization (mass-spectrometry, IR, ¹H NMR data) of the obtained compounds are presented in the Supporting Information.

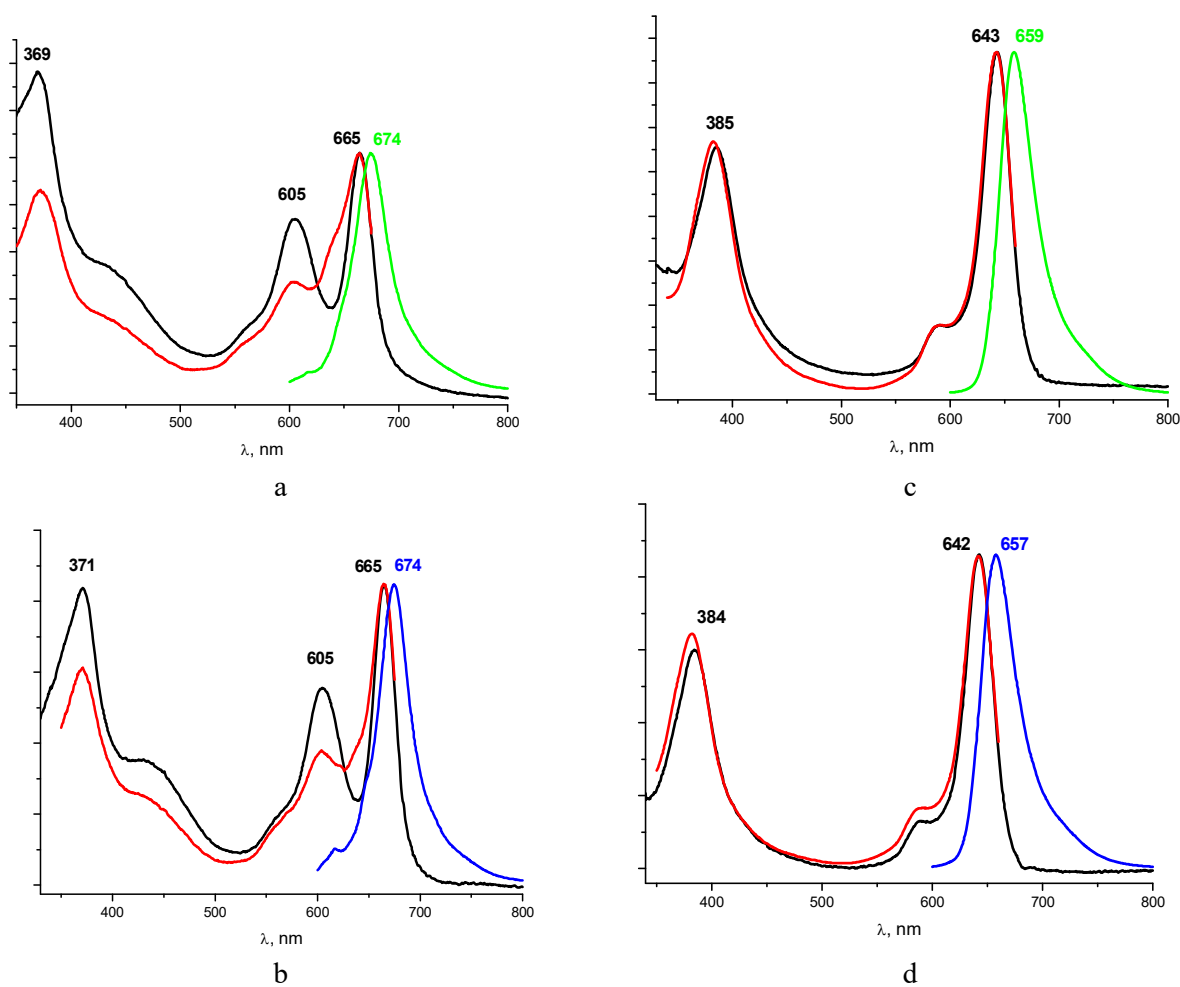


Figure 2. The electronic absorption spectra (black), fluorescence emission (red) ($\lambda_{\text{ex}}=590$ nm) and excitation (green or blue) ($\lambda_{\text{em}}=685$ nm) spectra of $\text{H}_2\text{Pz}(\text{PhCOOBu})_8$ (a), $\text{H}_2\text{Pz}(\text{PhCOOH})_8$ (b), $\text{ZnPz}(\text{PhCOOBu})_8$ (c) and $\text{ZnPz}(\text{PhCOOH})_8$ (d) in DMF.

The electronic absorption spectra, fluorescence emission and excitation spectra are presented in Figure 2. The UV-vis spectra of both metal free macrocycles, $\text{H}_2\text{Pz}(\text{PhCOOBu})_8$ and $\text{H}_2\text{Pz}(\text{PhCOOH})_8$, contain unlike their Zn(II) complexes, the broadened and more intense Soret band at ~ 370 nm, what may evidence the association process in their solutions. Thus, the excitation spectra of Zn porphyrines coincide in shape of their electronic absorption spectra and confirm the monomeric state of the molecules in the solution in contrast with the metal-free analogs (Figure 2). Fluorescence quantum yields (Φ_{F}) were determined in DMF using zinc phthalocyanine (ZnPc) as a reference as described in [19]. The aggregation diminishes the fluorescence ability in the DMF solution of the both metal free macrocyclic ligands and the values of fluorescence quantum yields (Φ_{F}) are close to zero (Table 1). For the non-aggregated Zn(II) complexes the fluorescence is higher, but remains low ($\Phi_{\text{F}} \sim 2\text{--}3\%$).

Values of the singlet oxygen quantum yields (Φ_{Δ}) were determined following the kinetics of decomposition of 1,3-diphenylisobenzofuran (DPBF) using zinc phthalocyanine as a reference compound.[19] The both zinc(II) complexes reveal very high ability to generate singlet oxygen ($\Phi_{\Delta} \sim 80\%$) which is even higher than for the Zn(II) phthalocyanine derivatives (Table 1). The metal free porphyrines are rather weak photosensitizers ($\Phi_{\Delta} \sim 2\text{--}4\%$), possibly due to their aggregation in the solutions.

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References

1. Wöhrle D., Schnurpfeil G., Makarov S.G., Kazarin A., Suvorova O.N. *Macromolecules* **2012**, *5*, 191–202, doi: 10.6060/mhc2012.120990w.
2. Lukyanets E.A. *J. Porphyrins Phthalocyanines* **1999**, *3*, 424–432, doi: 10.1002/(SICI)1099-1409(199908/10)3:6/7<424::AID-JPP151>3.3.CO;2-B.
3. Dumoulin F., Durmus M., Ahsen V., Nyokong T. *Coord. Chem. Rev.* **2010**, *254*, 2792–2847, doi:10.1016/j.ccr.2010.05.002.
4. Kuznetsova N.A., Shevchenko E.N., Makarov D.A., Slivka L.K., Solovyova L.I., Kaliya O.L., Lukyanets E.A. *J. Porphyrins Phthalocyanines* **2012**, *16*, 1244–1251, doi: 10.1142/S1088424612501301.
5. Kaliya O.L., Kuznetsova N.A., Bulgakov R.A., Solovyova L.I., Shevchenko E.N., Slivka L.K., Lukyanets E.A. *Macromolecules* **2016**, *9*, 186–192, doi: 10.6060/mhc160646k.
6. Kuznetsova N.A., Bulgakov R.A., Solovyova L.I., Shevchenko E.N., Kaliya O.L., Lukyanets E.A. *Macromolecules* **2015**, *8*, 143–149, doi: 10.6060/mhc150353k.

7. Kuznetsova N.A., Fedorova T.M., Solovyova L.I., Shevchenko E.N., Bordaev E.B., Bulgakov R.A., Kaliya O.L., Lukyanets E.A. *Macroheterocycles* **2018**, *11*, 21–28, doi: 10.6060/mhc171152k.
8. Zhang Y., Tian M., Majeed Z., Xie Y., Zheng K., Luo Z., Li C., Zhao C. *Separations* **2023**, *10*, 196, doi: 10.3390/separations10030196.
9. Gorbunova Yu.G., Enakieva Yu.Yu., Volostnykh M.V., Sinelshchikova A.A. *Russ. Chem. Rev.* **2022**, *91*(4), RCR5038, doi: 10.1070/RCR5038?locatt=label:RUSSIAN.
10. Han B., Ding X., Yu B., Wu H., Zhou W., Liu W., Wei Ch., Chen B., Qi D., Wang H., Wang K., Chen Y., Chen B., Jiang J. *J. Am. Chem. Soc.* **2021**, *143*, 7104–7113, doi: 10.1021/jacs.1c02145.
11. Opris D.M., Nuesch F., Lowe Ch., Molberg M., Nagel M. *Chem. Mater.* **2008**, *20*, 6889–6896, doi: 10.1021/cm801871t.
12. Kudrevich S.V., Galpern M.G., van Lier J.E. *Synthesis* **1994**, *08*, 779–781, doi: 10.1055/s-1994-25571.
13. Yagodin A.V., Mikheev I.A., Dolgushin F.M., Martynov A.G., Gorbunova Yu.G., Tsivadze A.Yu. *Macroheterocycles* **2023**, *16*, 218–224, doi: 10.6060/mhc235129m.
14. Yagodin A.V., Mikheev I.A., Bunin D.A., Sinelshchikova A.A., Martynov A.G., Gorbunova Yu.G., Tsivadze A.Yu. *Dyes Pigm.* **2023**, *216*, 111326, doi: 10.1016/j.dyepig.2023.111326.
15. Sakellariou E.G., Montalman A.G., Beall S.L., Henderson D., Meunier H.G., Phillips D., Suhling K., Barrett A.G.M., Hoffman B.M. *Tetrahedron* **2003**, *59*, 9083–9090, doi: 10.1016/j.tet.2003.09.060.
16. Seybold P.G., Gouterman M. *J. Mol. Spectrosc.* **1969**, *31*, 1–6, doi: 10.1016/0022-2852(69)90335-X.
17. 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.
18. a) Bulgakov R.A., Kuznetsova N.A., Dolotova O.V., Solovieva L.I., Mack J., Chidawanyika Wadzanai J.U., Kaliya O.L., Nyokong T. *J. Porphyrins Phthalocyanines* **2012**, *16*, 1217–1224, doi: 10.1142/S1088424612501209; b) Patent RF 2193563, **2000**.
19. Ivanova S.S., Salnikov D.S., Knorr G., Ledovich O., Sliznev V., Kubat P., Novakova V., Stuzhin P.A. *Dalton Trans.* **2022**, *51*, 1364–1377, doi: 10.1039/D1DT02453A.

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