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Interaction of Cationic Porphyrin with Cobalt Tetracarboxyphthalocyaninate in a Solution

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The preparation of a heterocomplex based on 5,10,15,20-tetrakis(1-hexylpyridinium-4-yl)porphine tetrabromide and cobalt tetracarboxyphthalocyaninate is described in the work. The porphyrin-phthalocyanine complex has been obtained by homogeneous and heterogeneous methods. The donor-acceptor nature of the interaction between macroheterocycles has been confirmed by electron spectroscopy and fluorescence. Carrying out a catalytic experiment in the oxidation reaction of 4-tert-butylpyrocatechol with atmospheric oxygen confirms the occurrence of the charge transfer process. The resulting complex is characterized by inhibition of the redox activity of cobalt phthalocyaninate in its composition. The acceptor nature of cobalt tetra-carboxyphthalocyaninate in relation to the cationic porphyrin in the heterocomplex is shown by quantum chemical modeling.

Keywords: Carboxyphthalocyanines, cationic porphyrins, donor-acceptor complex, quantum chemical calculations.

Взаимодействие катионного порфирина с *тетра*-карбоксифталоцианинатом кобальта в растворе

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В работе описано получение гетерокомплекса на основе 5,10,15,20-тетракис(1-гексилпиридиний-4-ил)порфина тетрабромида и тетра-карбоксифталоцианината кобальта. Комплекс порфирин-фталоцианин был получен гомогенным и гетерогенным способами. Донорно-акцепторный характер взаимодействия между макрогетероциклами подтвержден с помощью электронной спектроскопии и флуоресценции. Проведение каталитического эксперимента в реакции окисления 4-трет-бутилпирокатехина кислородом воздуха подтверждает протекание процесса переноса заряда. Для полученного комплекса характерно ингибирование redox-активности фталоцианината кобальта в его составе. Методом квантово-химического моделирования показана акцепторная природа тетра-карбоксифталоцианината кобальта по отношению к катионному порфирину в составе гетерокомплекса.

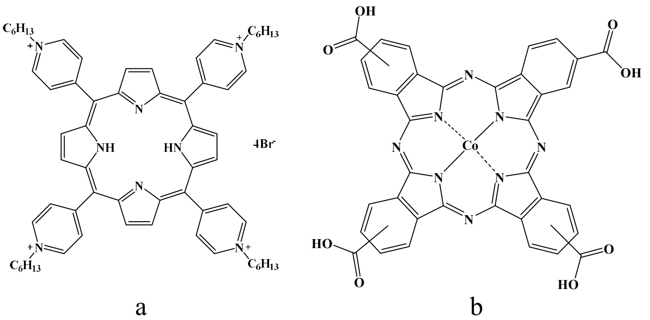
Ключевые слова: Карбоксифталоцианины, катионные порфирины, донорно-акцепторный комплекс, квантово-химические расчеты.

Among tetrapyrrole macroheterocyclic compounds, porphyrins and phthalocyanines, as well as their metal complexes, are most widely used in fundamental and applied research.[1] For such compounds, a large number of methods for synthesis and subsequent modification of their structure have been developed, which makes it possible to obtain compounds with desired properties.[2-4] Today, phthalocyanines and porphyrins have found wide application in many fields of science, technology, and also in industry. They are actively used as photosensitizers,[5] catalysts,[6-8] sensors.[9,10]

Tetrapyrrole macroheterocyclic compounds capable of dissolving in aqueous media due to the presence of ionogenic groups in their structure are of particular interest. Among phthalocyaninates, the most widespread are sulfo- and carboxy- derivatives,[11] which are available. One of the methods for obtaining of the water-soluble porphyrins is the quaternization of peripheral nitrogen atoms, which makes it possible to synthesize a variety of the cationic macroheterocycles.[12-16] Due to electrostatic and π–π interactions of differently charged macroheterocycles, it is possible to receive mixed assemblies with unique characteristics.[17-19] Currently, the literature provides data on the preparation of the complexes based on anionic and cationic homonuclear macroheterocycles.[17-21] However, the heterocomplexes containing opposite charge porphyrins and phthalocyanines have been studied less.

In this work, the interaction of the cationic *tetra*-pyridylporphyrin with cobalt *tetra*-carboxyphthalocyaninate has been studied, the spectral and catalytic properties of the resulting heterocomplex have been investigated, and quantum chemical modeling of the initial macroheterocycles has been carried out by the DFT method.

To obtain the heterocomplex cobalt *tetra*-carboxyphtha-locyaninate (CoPc(COOH)$_4$) and 5,10,15,20-tetrakis(1-hexylpyridinium-4-yl)porphine tetrabromide ([T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$) were used (Chart 1). Cobalt *tetra*-carboxyphthalocyaninate was synthesized by the urea method from trimellitic anhydride similar to the method described in the work.[22] 5,10,15,20-Tetrakis(1-hexylpyridinium-4-yl)porphine tetrabromide ([T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$) was synthesized by quaternization reaction from *tetra*-pyridyl-substituted porphyrin and bromohexane.[23]



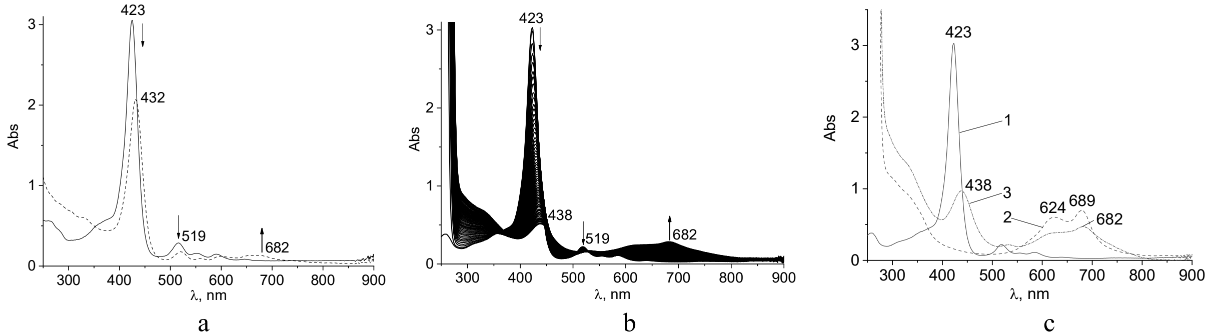
a b

Chart 1. The structure of the initial compounds:
a) [T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$, b) CoPc(COOH)$_4$.

The [T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$–CoPc(COOH)$_4$ heterocomplex was prepared by two methods. In the heterogeneous method, dry cobalt phthalocyaninate (1.08 mmol), insoluble in methanol, was added to a solution of [T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$ in methanol ($5\cdot10^{-5}$ mol/L). The formation of the complex occurred within 24 h, which was a consequence of the process occurring at the interface. The constancy of the UV-Vis spectra (Shimadzu UV-2550 spectrophotometer) in two subsequent measurements indicated the end of the process. Spectral changes showed that unreacted porphyrin remained in the system (Figure 1a).

In a homogeneous method, an aqueous-pyridyl (H$_2$O-Py, 5 vol. %) solution of cobalt phthalocyaninate (initial concentration 10^{-4} mol/L) was gradually added to an aqueous solution of [T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$ (initial concentration 10^{-4} mol/L). The heterocomplex formation was monitored by changes in the UV-vis spectra of the solution (Figure 1b). In this case, the process occurred almost instantly.

The same pattern of changes in the UV-vis spectra is observed for homogeneous and heterogeneous interaction methods of differently charged macroheterocycles. There is a decrease in the intensity of the porphyrin Soret band and its bathochromic shift by 9–15 nm (Figure 1a,b). Moreover, the solution color changes to green (Supplement 1). The resulting spectrum differs from the sum of the spectra of the individual macroheterocycles, which indicates the formation of a new heterocomplex in a solution (Figure 1c). Similar changes were observed by the authors in the works.[24-26]



a b c

Figure 1. UV-vis spectra: a) during the formation of the [T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$–CoPc(COOH)$_4$ complex in MeOH; b) during the formation of the [T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$–CoPc(COOH)$_4$ complex in H$_2$O-Py; c) 1 – T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$ solution in H$_2$O, 2 – CoPc(COOH)$_4$ solution in H$_2$O-Py, 3 – [T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$–CoPc(COOH)$_4$ complex solution in H$_2$O-Py, C([T$_4$(C$_6$H$_{13}$Py)P][Br]$_4$) = C(CoPc(COOH)$_4$) = $5\cdot10^{-5}$mol/L.

As is known, porphyrins and phthalocyanines with peripheral differently charged substituents are capable of interacting with each other in solutions to form dyads, triads or aggregates of a higher order.[27,28] Determination of the structure of heteroaggregates formed by $[T_4(C_6H_{13}Py)P][Br]_4$ and $CoPc(COOH)_4$ are planned to be performed in further studies.

The fluorescent properties of solutions of the original porphyrin and cobalt phthalocyanate, as well as their heterocomplex, were also studied. 3D fluorescence spectra were recorded by a Shimadzu RF-6000 spectrofluorimeter in the region 250–900 nm. The fluorescence spectra of the aqueous solutions of the original porphyrin and the resulting heterocomplex are presented in Figure 2. UV-vis spectrum, 2D fluorescence spectrum as well as fluorescence excitation spectrum of the $[T_4(C_6H_{13}Py)P][Br]_4$ porphyrin are given in the supporting information (Supplement 2). During the fluorescence study, it was found that cobalt phthalocyaninate does not exhibit luminescent properties in an aqueous solution with the addition of pyridine (5 vol.%), which is consistent with the data described in the literature.[29]

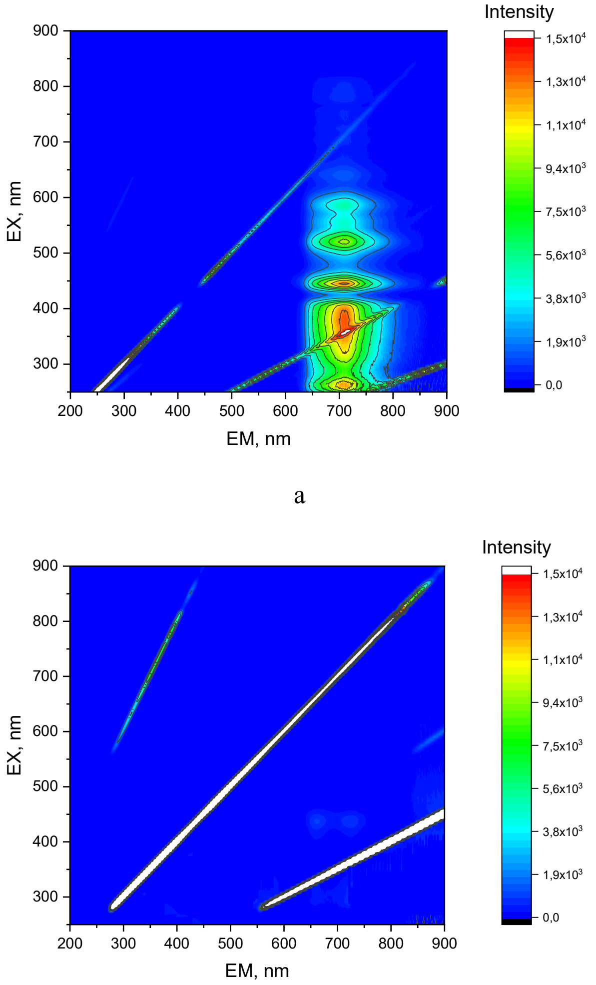


Figure 2. Fluorescence spectra of: a) $T_4(C_6H_{13}Py)P][Br]_4$ solution in H_2O; b) $[T_4(C_6H_{13}Py)P][Br]_4$–$CoPc(COOH)_4$ complex solution in H_2O-Py (5 vol. %).

For an aqueous solution of porphyrin, a strongly broadened fluorescence band is observed with a maximum at 700 nm (Figure 2a). For porphyrins in weakly polar organic solvents, as a rule, two fluorescence bands are detected.[30,31] Strong broadening and merging of two fluorescence bands probably occurs due to the aggregation of the porphyrin molecules, as well as strong dipole-dipole interaction between the charged centers of the porphyrin molecule and water molecules. Fluorescence quenching was observed for the heterocomplex solution (Figure 2b), which is consistent with the data presented in work[32] about fluorescence quenching during the formation of a heterocomplex from differently charged porphyrin and cobalt phthalocyaninate.

The combination of electron spectroscopy and fluorescence data confirms the formation of a new charge transfer heterocomplex.

The presence of two catalytically active structural units in the heterocomplex suggests the participation of these components in redox processes. Cobalt phthalocyaninate exhibits catalytic activity in the oxidation reaction of 4-*tert*-butylpyrocatechol with atmospheric oxygen with the release of hydrogen peroxide.[33,34] And some porphyrins are capable of catalyzing redox reactions involving peroxides.[35] The simultaneous presence of porphyrin and cobalt phthalocyaninate in the catalytic system in the absence of their interaction with each other could lead to a synergistic effect. In turn, the absence of catalytic activity will indicate the formation of a charge transfer complex. It has been shown that the $[T_4(C_6H_{13}Py)P][Br]_4$–$CoPc(COOH)_4$ heterocomplex does not exhibit catalytic activity in the oxidation of 4-*tert*-butylpyrocatechol with atmospheric oxygen. This indicates the formation of a donor-acceptor complex.

To study the process of charge transfer inside the heterocomplex, quantum chemical modeling of its structural units was carried out. Geometry optimization were done with ORCA 5.0.4 method DFT/M06L/TZVP and visualized with Avogadro 1.2.0 on a Ryzen 9 3900X computer equipped with Microsoft Windows, 24 GB of memory. The data obtained are shown in Figure 3.

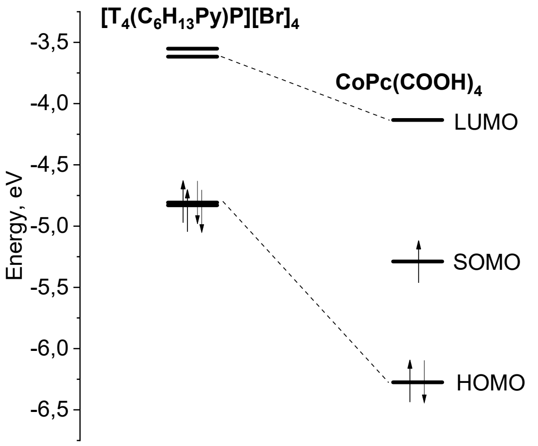


Figure 3. Energy diagram of the boundary electronic levels of $[T_4(C_6H_{13}Py)P][Br]_4$ and $CoPc(COOH)_4$.

The presented diagram (Figure 3) shows that the interaction of $[T_4(C_6H_{13}Py)P][Br]_4$ and $CoPc(COOH)_4$ leads to non-radiative relaxation of the excited state of the system, which is due to the presence of several energy levels with narrow gaps. An electron smoothly transitions from an excited state to a ground state in several steps, while emitting low-energy quanta that can't be detected by a spectrofluorimeter. The ground state is characterized by electron transfer from the HOMO porphyrin molecule to the SOMO molecule of cobalt phthalocyaninate. In this case, electron pairing occurs on the SOMO of cobalt phthalocyaninate, which leads to the loss of the ability of $CoPc(COOH)_4$ to grab triplet oxygen. This confirms the lack of catalytic activity of the heterocomplex in the oxidation of pyrocatechol with atmospheric oxygen.

In conclusion, a heterocomplex has been obtained based on cationic *tetra*-pyridyl-substituted porphyrin and cobalt *tetra*-carboxyphthalocyaninate. The interaction of differently charged macroheterocycles exhibits a donor-acceptor character, which is confirmed by fluorescence quenching, the absence of catalytic activity, and quantum chemical calculations.

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Conflict of interests. The authors declare no conflict of interests.

References

1. Tomilova L.G., Pushkarev V.E., Dubinina T.V., Tolbin A.Yu. *Advances in the Synthesis and Study of the Properties of Phthalocyanines and Their Analogues* (Tomilova L.G., Ed.). Moscow, **2019**. 240 p. [Достижения в синтезе и исследовании свойств фталоцианинов и их аналогов (Томилова Л.Г., ред.), **2019**. 240 с. ISBN: 978-5-19-011411-9].
2. Dubinina T.V., Tomilova L.G., Zefirov N.S. *Russ. Chem. Rev.* **2013**, *82*, 865–895. DOI: 10.1070/RC2013v082n09ABEH004353.
3. Tolbin A.Yu., Tomilova L.G., Zefirov N.S. *Russ. Chem. Rev.* **2008**, *77*, 435–449. DOI: 10.1070/RC2008v077n05ABEH003769.
4. Tolbin A.Yu., Tomilova L.G., Zefirov N.S. *Russ. Chem. Rev.* **2007**, *76*, 681–692. DOI: 10.1070/RC2007v076n07ABEH003698.
5. Koifman O.I., Ageeva T.A., Beletskaya I.P., Averin A.D., Yakushev A.A., Tomilova L.G., Dubinina T.V., Tsivadze A.Yu., Gorbunova Yu.G., Martynov A.G., Konarev D.V., Khasanov S.S., Lyubovskaya R.N., Lomova T.N., Korolev V.V., Zenkevich E. I., Blaudeck T., von Borczyskowski C., Zahn D.R.T., Mironov A.F., Bragina N.A., Ezhov A.V., Zhdanova K.A., Stuzhin P.A., Pakhomov G.L., Rusakova N.V., Semenishyn N.N., Smola S.S., Parfenyuk V.I., Vashurin A.S., Makarov S.V., Dereven'kov I.A., Mamardashvili N.Zh., Kurtikyan T.S., Martirosyan G.G., Burmistrov V.A., Aleksandriiskii V.V., Novikov I.V., Pritmov D.A., Grin M.A., Suvorov N.V., Tsygankov A.A., Fedorov A.Yu., Kuzmina N.S., Nyuchev A.V., Otvagin V.F., Kustov A.V., Belykh D.V., Berezin D.B., Solovieva A.B., Timashev P.S., Milaeva E.R., Gracheva Yu.A., Dodokhova M.A., Safronenko A.V., Shpakovsky D.B., Syrbu S.A., Gubarev Yu.A., Kiselev A.N., Koifman M.O., Lebedeva N.Sh., Yurina E.S. *Macroheterocycles* **2020**, *13,* 311–467. DOI: 10.6060/mhc200814k.
6. Öztürmen B.A., Akkol Ç., Saka E.T., Biyiklioglu Z. *Inorg. Chem. Commun.* **2023**, *158,* 111647. DOI: 10.1016/j.inoche.2023.111647.
7. Nakazono T., Amino N., Matsuda R., Sugawara D., Wada T. *Chem. Commun.* **2022**, *58,* 7674–7677. DOI: 10.1039/D2CC01985J
8. Costa e Silva R., Oliveira da Silva L., de Andrade Bartolomeu A., Brocksom T.J., de Oliveira K.T. *J. Org. Chem.* **2020**, *16*, 917–955. DOI: 10.3762/bjoc.16.83.
9. Ivanova V., Şenocak A., Klyamer D., Demirbas E., Makhseed S., Krasnov P., Basova T., Durmuş M. *Sens. Actuators, B* **2024**, *398*, 134733. DOI: 10.1016/j.snb.2023.134733.
10. Norvaiša K., Kielmann M., Senge M.O. *ChemBioChem* **2020**, *21*, 1793–1807. DOI: 10.1002/cbic.202000067.
11. Shaposhnikov G.P., Maizlish V.E., Kulinich V.P. *Russ. J. Gen. Chem.* **2005**, *75,* 1480–1488. DOI: 10.1007/s11176-005-0450-4.
12. Li K., Titi H.M., Berton P., Rogers R.D. *ChemistryOpen* **2018**, *7*, 659–663. DOI: 10.1002/open.201800166.
13. Tovmasyan A., Babayan N., Poghosyan D., Margaryan K., Harutyunyan B., Grigoryan R., Sarkisyan N., Spasojevic I., Mamyan S., Sahakyan L., Aroutiounian R., Ghazaryan R., Gasparyan G. *J. Inorg. Biochem.* **2014**, *140*, 94–103. DOI: 10.1016/j.jinorgbio.2014.06.013.
14. Caruso E., Malacarne M.C., Banfi S., Gariboldi, M.B. Orlandi V.T. *J. Photochem. Photobiol., B* **2019**, *197*, 111548. DOI: 10.1016/j.jphotobiol.2019.111548.
15. Shorokhova T.V., Plotnikova A.O., Ivanova Yu.B., Lyubimova T.V., Lyubimtsev A.V., Kruk N.N., Syrbu S.A. *ChemChemTech* **2023**, *66*, 65–75. DOI: 10.6060/ivkkt.20236612.6819.
16. Lyubimtsev A.V., Semeikin A.S., Koifman M.O., Koifman O.I. *Dokl. Chem.* **2023**, *508*, 13–22. DOI: 10.1134/S0012500823600128.
17. Locklin J., Shinbo K., Onishi K., Kaneko F., Bao Zh., Advincula R.C. Chem. Mater. 2003, *15*, 1404–1412. DOI: 10.1021/cm021073f.
18. Enoki O., Imaoka T., Yamamoto K. *Macromol. Symp.* **2003**, *204*, 151–158. DOI: 10.1002/masy.200351413.
19. Tran-Thi T.-H. *Coord. Chem. Rev.* **1997**, *160,* 53–91. DOI: 10.1016/s0010-8545(96)01341.
20. Koposova E.A., Ermolenko Y.E., Offenhausser A., Mourzina Y.G. *Colloids Surf., A* **2018**, *548*, 172–178. DOI: 10.1016/j.colsurfa.2018.03.053
21. Medforth C.J., Wang Zh., Martin K.E., Song Yu., Jacobsen J.L., Shelnutt J.A. *Chem. Commun.* **2009**, *47*, 7261–7277. DOI: 10.1039/b914432c.
22. McKeown N.B. In: *Science of Synthesis, 17: Category 2, Hetarenes and Related Ring Systems* (Weinreb S.M., Schaumann, E., Eds.) Stuttgart. **2004**. p. 1237–1368.
23. Efimova E.A., Pechnikova N.L., Lyubimtsev A.V., Aleksandriiskii V.V., Ageeva T.A. *Russ. J. Gen. Chem.* **2023**, *93*, 1574–1578. DOI: 10.1134/S1070363223060300.
24. Mao H.-F. Tian H.-J., Xu H.-J. *Chin. J. Chem.* **1995**, *13*, 223–230. DOI: 10.1002/cjoc.19950130306.
25. Mao H., Sun Y., Li H., Zhou Q., Zhang X., Shen J., Xu H. *Sci. China, Ser. B* **1998**, *41*, 449–454. DOI: 10.1007/bf02882797.
26. Chen J., Lever A.B.P. *J. Porphyrins Phthalocyanines* **2007**, *11*, 151–159. DOI: 10.1142/s1088424607000199.
27. Ribeiro M.G., Azzellini G.C. *J. Brazil. Chem. Soc.* **2003**, *14*, 914–921. DOI: 10.1590/s0103-50532003000600008.
28. Tasso T.T., Moreira W.C. *J. Porphyrins Phthalocyanines* **2012**, *16*, 244–249. DOI: 10.1142/s1088424612004586.

29. Kuzmitsky V.A., Soloviev K.N., Tsvirko M.P. In: *Porphyrins: Spectroscopy, Electrochemistry, Application* (Enikolopyan N.S., Ed.) Moscow, **1987**. pp. 7–126. [В кн.: *Порфирины: спектроскопия, электрохимия, применение* (Ениколопян Н.С., ред.), М.: Наука, **1987**. с. 7–126].
30. Zheng W., Shan N., Yu L., Wang X. *Dyes Pigm.* **2008**, *77,* 153–157. DOI: 10.1016/j.dyepig.2007.04.00.
31. Lourenço L.M.O., Resende J., Iglesias B.A., Castro K., Nakagaki S., Lima M.J., da Cunha A.F., Nevesa M.G.P.M.S., Cavaleiro J.A.S., Tomé J.P.C. *J. Porphyrins Phthalocyanines* **2014**, *18*, 967–974. DOI: 10.1142/s1088424614500783.
32. Gaspard S., Tran-Thi T.-H. *J. Chem. Soc., Perkin Trans. 2* **1989**, *5*, 383–389. DOI: 10.1039/P29890000383.
33. Selmeczi K., Réglier M., Giorgi M., Speier G. *Coord. Chem. Rev.* **2003**, *245*, 191–201. DOI: 10.1016/j.cct.2003.08.002.
34. Pinnataip R., Lee B.P. *ACS Omega* **2021**, *6,* 5113–5118. DOI: 10.1021/acsomega.1c00006.
35. Liu Q., Chen P., Xu Zh., Chen M., Ding Ya., Yue K., Xu J. *Sens. Actuators, B* **2017**, *251,* 339–348. DOI: 10.1016/j.snb.2017.05.069.

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