Макрогетероциклы
http://mhc-isuct.ru

DOI: 10.6060/mhc256733n

Supramolecular Complexes Based on a Dimeric β-Cyclodextrin Derivative and 5,10,15,20-Tetraphenylporphyrin: Synthesis and Photophysical Properties

E. S. Nersesyan,[a@] I. V. Klimenko,[a] A. V. Lobanov,[a,b] N. V. Kutyasheva,[b] G. I. Kurochkina,[b] and M. K. Grachev[b]

[a]*N.M. Emanuel Institute of Biochemical Physics of Russian Academy of Sciences, 119334 Moscow, Russian Federation*
[b]*Moscow Pedagogical State University, 119991 Moscow, Russian Federation*
[@]*Correspondong author E-mail: Edgar.S.Nersesyan@gmail.com*

Supramolecular complexes based on 5,10,15,20-tetraphenylporphyrin (TPP) and β-cyclodextrin (β-CD), and its dimeric derivative – di-6,6'-dideoxy-6,6'-(hexane-1,3-diyl diamine)-β-cyclodextrin iodide (HDβ-CD), were synthesized using the drop-titration method in an aqua-organic medium. N,N-Dimethylformamide was used as the organic solvent. Complex formation was confirmed and comparatively studied using absorption and fluorescence spectroscopy. The stability of the obtained supramolecular complexes and the binding capacity of the system components were assessed. The role of the structural features of β-CD and HDβ-CD during their interaction with TPP was investigated.

Keywords: Tetraphenylporphyrin, β-cyclodextrin, dimeric β-cyclodextrin, supramolecular complexes, photophysical properties, binding constant, Stern-Volmer constant, absorption spectra, fluorescence spectra.

Супрамолекулярные комплексы на основе димерного производного β-циклодекстрина и 5,10,15,20-тетрафенилпорфирина: получение, фотохимические свойства

Э. С. Нерсесян,[a@] И. В. Клименко,[a] А. В. Лобанов,[a,b] Н. В. Кутяшева,[b] Г. И. Курочкина,[b] М. К. Грачев[b]

[a]*ФГБУН Институт биохимической физики им. Н.М. Эмануэля Российской академии наук, 119334 Москва, Россия*
[b]*ФГБОУ ВО «Московский педагогический государственный университет», 119991 Москва, Россия*
[@]*E-mail: Edgar.S.Nersesyan@gmail.com*

Супрамолекулярные комплексы на основе 5,10,15,20-тетрафенилпорфирина (ТФП), β-циклодекстрина (β-ЦД) и его димерного производного – ди-6,6'-дидезокси-6,6'-(гексан-1,3-диил диамин)-β-циклодекстрин йодида (ГДβ-ЦД) были получены методом капельного титрования в водно-органической среде. В качестве органического растворителя был использован N,N-диметилформамид. Образование комплексов было подтверждено и сравнительно изучено методами абсорбционной спектроскопии и флуоресценции. Были оценены стабильность полученных супрамолекулярных комплексов и связывающая способность компонентов системы. Исследована роль структурных особенностей β-ЦД и ГДβ-ЦД в процессе их взаимодействия с ТФП.

Ключевые слова: Тетрафенилпорфирин, β-циклодекстрин, димерный β-циклодекстрин, супрамолекулярные комплексы, фотофизические свойства, константа связывания, константа Штерна-Фольмера, спектры поглощения, спектры флуоресценции.

Introduction

Porphyrin derivatives attract increasing attention from researchers for their potential uses in a variety of fields, including medicine, ecology, agriculture, and optics, due to their diverse applications in the natural environment. Particular attention is focused on the study of assembly processes of supramolecular systems based on natural porphyrins (*e.g.* etioporphyrins, proto-, meso-, hemato-, deutero-, copro-, uro-, phyllo- and pyrroporphyrins and their analogues such as azaporphyrins, chlorins, bacteriochlorins and porphyrinogens), which participate in many biological processes in living organisms. These natural porphyrins are components of pigments and transport proteins that play an important role in oxygen transport and photosynthesis. Synthetic analogues of natural porphyrins, which form systems based on noncovalent interactions, have already led to the creation of materials for photovoltaics and photocatalysis.[1-8] Furthermore, natural porphyrins and their synthetic analogues efficiently promote the generation of reactive oxygen species ($O_2^{-\bullet}$, $OH^{\bullet}$, H_2O_2, $^1O_2$ and others) and can be utilized as photosensitizers for photodynamic therapy.[9-11]

Chemical design methods allow for the deliberate creation of materials with predetermined properties and control of their physicochemical characteristics. Porphyrins are macrocyclic molecules of high symmetry that possess a wide range of optical, electrochemical and electronic properties making them promising materials for constructing supramolecular ensembles.[12-14]

Synthetic analogues of natural porphyrins, including the first synthesized in the middle of 20th century 5,10,15,20-tetraphenylporphyrin (TPP, Figure 1a), possess a macrocyclic structure similar to that of natural porphyrins, including four pyrrole rings connected in the α position by a methine unit.[1,15,16] TPP, whose electronic system has been described by the four-orbital Guterman model,[14,17,18] is often used as a model compound in studies of the biochemical and physicochemical properties of porphyrins, because the positions and intensities of the TPP absorption bands depend on external factors such as temperature and environment.[18]

TPP, akin to the majority of porphyrins, exhibits a propensity to spontaneously form H-type aggregates and, under specific conditions, J-aggregates. However, obtaining of functional porphyrin-based materials necessitates their effective stabilization in monomeric molecular form, given the significant influence of molecular architecture, morphology and size on photochemical activity.

The nature of the solvent is one of the factors that affect the capacity of TPPs to aggregate, and consequently facilitate the rapid recombination of photoinduced electron-hole pairs. A universal organic solvent for TPP is N,N-dimethylformamide (DMF), an aprotic polar solvent that is miscible with water and is used in small quantities in pharmaceuticals for the synthesis of active pharmaceutical substances, improving solubility and accelerating the rate of reactions.[19-21]

Supramolecular complexes based on TPP and its derivatives with various auxiliary substances are of particular interest. These substances modify and, in some cases, functionalize porphyrins, protecting them from degradation and increasing their bioavailability. Such supramolecular complexes can be utilized in targeted drug delivery systems, where it is necessary to overcome the undesirable properties of a drug, such as its low water solubility. It is important to note that the optimal «carrier» should exhibit the necessary functional properties and be sufficiently simple and technologically easy to synthesize.

Promising complex-forming agents are derivatives of β-cyclodextrin (β-CD) (Figure 1b). These unique water-soluble nanostructures consist of cyclic oligosaccharides with a rigid D-glucopyranose structure. They are stabilized by hydrogen bonds between hydroxyl groups and their lack of free rotation due to α-(1-4)-bonds, possessing a hydrophobic inner cavity and a hydrophilic exterior.[22-26]

Currently, TPP–β-CD inclusion complexes are being extensively studied as promising functional materials for various applications. Firstly, significant research has focused on the fundamental physical chemistry of inclusion complexes involving β-cyclodextrin and various tetrapyrroles, such as porphyrin derivatives and chlorins (*e.g.*, meta-tetra(hydroxyphenyl)chlorin, mTHPC or Temoporfin). Such studies are crucial for understanding their dynamic behavior, including the comparative analysis of dissociation kinetics from both monomeric and polymeric cyclodextrin derivatives.[27] Specifically, the distribution of photosensitizers like mTHPC between β-cyclodextrin nanocarriers and serum proteins has been determined using optical methods (fluorescence anisotropy, Soret band analysis).[28,29] Based on these fundamental achievements, the potential applications of TPP–β-CD complexes and related systems in several domains are actively pursued. Data on their use as stable polymer nanowires, systems for effective detection of tumor cells, multifunctional carriers for synergistic cancer therapy and emerging delivery platforms (nanosponges, micelles, hydrogels, nanogels, and dendrimers)[30,31,33,36,37] are already known. Furthermore, these complexes have been studied as antidotes against carbon monoxide and cyanide poisoning,[32,34] and as antimicrobial agents.[35]

In the present work, we conducted a series of studies on the synthesis and photochemical properties of new inclusion complexes, whose composition was previously unknown, based on dimeric β-CD derivative and TPP. The aim was to synthesize and investigate the physicochemical and photophysical properties of these complexes, and to evaluate the role of the structural features of the cyclodextrins in the complexation process. For comparison, a TPP–β-CD complex was synthesized and examined in parallel.

Experimental

Host-guest supramolecular complexes were synthesized using 5,10,15,20-tetraphenylporphyrin (Sigma-Aldrich), β-cyclodextrin (Sigma-Aldrich), di-6,6-dideoxy-6,6'-(propane-1,3-diyl diamine)-β-cyclodextrin iodide (PDβ-CD), di-6,6-dideoxy-6,6'-(butane-1,3-diyl diamine)-β-cyclodextrin iodide (BDβ-CD) and di-6,6-dideoxy-6,6'-(hexane-1,3-diyl diamine)-β-cyclodextrin iodide (HDβ-CD). The synthesis process for the latter is outlined in [38]. Distilled water and N,N-dimethylformamide (DMF, Reakhim, Russia, double-distilled) were utilized as solvents.

A TPP solution was prepared by adding pure TPP to DMF at room temperature with stirring. The PDβ-CD, BDβ-CD and HDβ-CD solutions was subjected to a temperature of 80°C for one hour to achieve complete dissolution.

The synthesis of inclusion complexes was performed by dropwise titration, whereby 0.1 mL aliquots of an aqueous solution of β-CD (C=2.71·10^{-4} mol/L), PDβ-CD (C=2.09·10^{-4} mol/L), BDβ-CD (C=2.25·10^{-4} mol/L) and HDβ-CD (C=2.15·10^{-4} mol/L) were added sequentially to 2 mL of a TPP solution in DMF (C=5.18·10^{-6} mol/L) 10 times. All experiments were conducted in triplicate, and the obtained data showed high reproducibility.

The electronic absorption spectra in the wavelength range of 200–900 nm were measured using a TU-1901 UV–Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). Fluorescence spectra within the wavelength range of 400–860 nm were measured utilizing a «Fluorat-02 Panorama» spectrofluorometer (Lumex). The excitation wavelength was λ=430 nm. The measurements were conducted at room temperature using standard quartz cuvettes (K10) with a 1 cm optical path.

The absorption spectra were analyzed by decomposing them into Gaussian components. All spectrophotometric data obtained following the addition of β-CD, PDβ-CD, BDβ-CD and HDβ-CD solutions were converted to the initial volume of TPP–DMF by recalculation according to the following formula:

$$A_i = \frac{A_0}{\frac{V_1}{(V_1+V_2)}}, \quad (1)$$

where A_i and A_0 are corrected and experimental optical density of the solution, respectively; V_1=2 mL – the initial volume of the TPP–DMF solution; V_2 – the volume of β-CD–water, PDβ-CD–water, BDβ-CD–water or HDβ-CD–water solution added to the cuvette (from 0.1 to 1 mL).

Results and Discussion

The advantage of the dimeric «host» structure is the presence of two linked β-CD cavities, which may lead to stronger and sterically favorable binding with the TPP molecule. To select the optimal dimeric «hosts», several dimeric derivatives were investigated, differing in the length of the diamino cationic linker connecting the two β-CD molecules (propane, butane, and hexane-1,6-diaminecationic linkers). The length and conformation of the linker must be considered to facilitate the efficient binding of the «guest».

Preliminary experiments demonstrated that the propane PDβ-CD and butane BDβ-CD derivatives formed complexes with significantly lower stability; for instance, their binding constants K_B (calculated by the Benesi–Hildebrand equation) were less than $10^{1.3}$ L/mol, and their Stern–Volmer constants K_{SV} were below $10^{1.2}$ L/mol. These values, wich are substantially lower than those observed for the β-CD and HDβ-CD systems, confirmed that the HDβ-CD has the most optimal structure for complexation. This can be attributed to the absence of steric hindrance, allowing it to encapsulate two phenyl substituents of porphyrin simultaneously, forming a «molecular container» that is capable of holding non-polar molecules of the «guest» in the inner cavity.

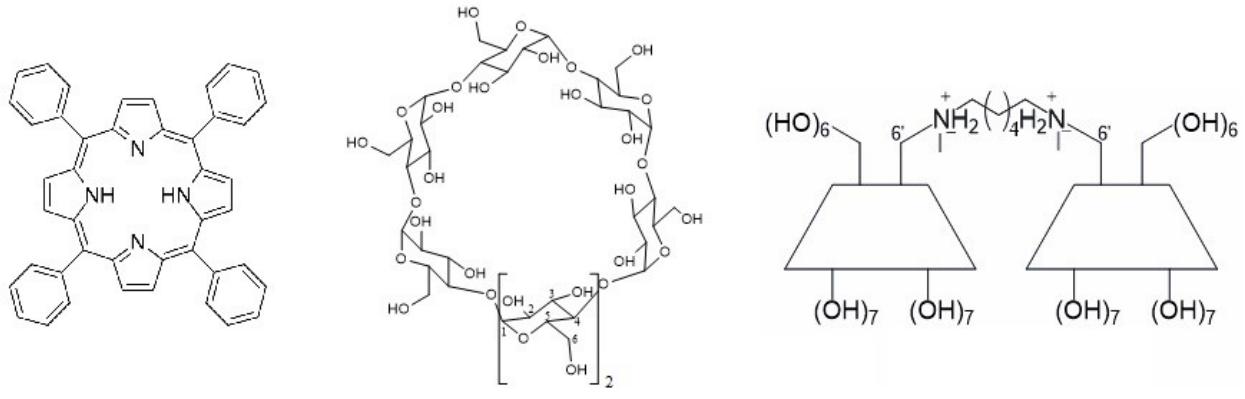
It is known that the formation of an inclusion complex with β-CD results in the stabilization of the «guest» molecule and an increase in its solubility in aqueous and physiological solutions. This is an essential step in the development of pharmaceuticals for biomedical applications.[39] Moreover, the utilization of β-CD as a «molecular container» facilitates the synthesis of microcrystalline powders from solutions, while simultaneously preventing the interaction between drug components, thereby reducing the potential for irritation of the gastrointestinal tract.

Figure 2 illustrates the absorption spectra of the TPP–DMF system during titration with aqueous solutions of β-CD (a) and HDβ-CD (b). The original TPP absorption spectrum is characterized by an intense Soret band with a maximum at λ≈397 nm and weaker Q bands in the region of 500–700 nm. As successive aliquots of each cyclodextrin solution are added, a consistent drop in the intensity of the Soret band is observed, without a significant shift in its maximum. This indicates the absence of TPP aggregation in the presence of water in solution. In both the β-CD and HDβ-CD cases, the interaction with TPP and the subsequent complex formation manifests as stabilization of the porphyrin molecules and changes in their spectral characteristics.

To determine the stability and binding strength of the obtained supramolecular complexes, their binding constants K_b were determined using the Benesi-Hildebrand equation (2):[40-44]

$$\lg\frac{A_i - A_0}{A_f - A_0} = \lg[C] + \lg K_b\,, \quad (2)$$

where A_0, A_i, A_f are the optical densities of the solution in the absence, at an intermediate concentration, and at saturation of the quencher, respectively; C is the intermediate equilibrium concentration of the added quencher; K_b is the binding constant.



a b c

Figure 1. Structures TPP (a), β-CD (b) and HDβ-CD (c).

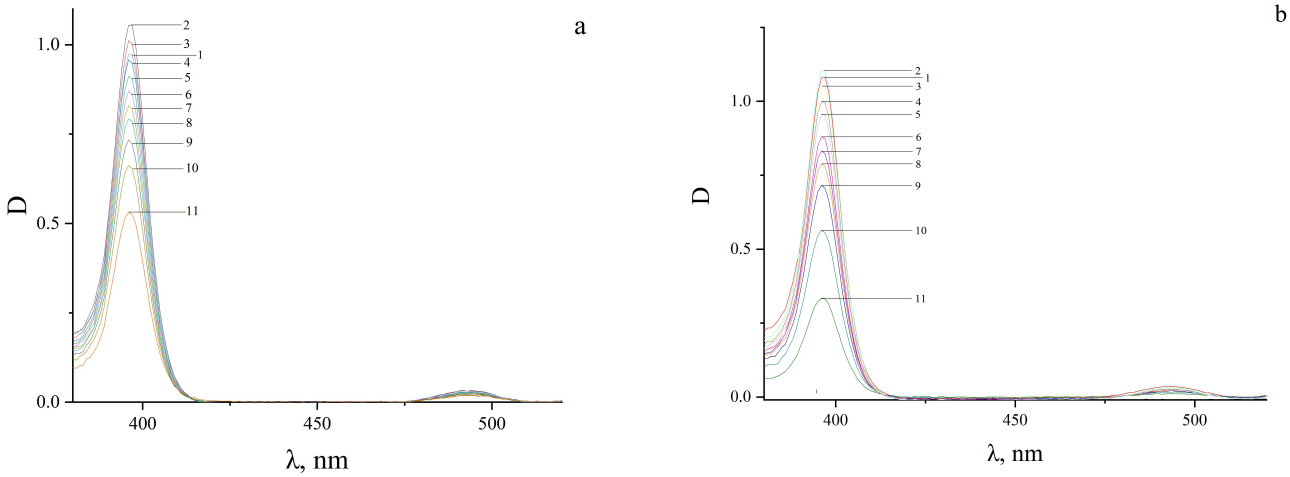


Figure 2. Absorption spectra of TPP upon titration with β-CD (a) and HDβ-CD (b). In system a: 1 – TPP without any quencher; 2–11 – TPP + β-CD (0.1 mL × n, n ∈ [1; 10]); in system b: 1 – TPP without any quencher; 2–11 – TPP + HDβ-CD (0.1 mL × n, n ∈ [1; 10]).

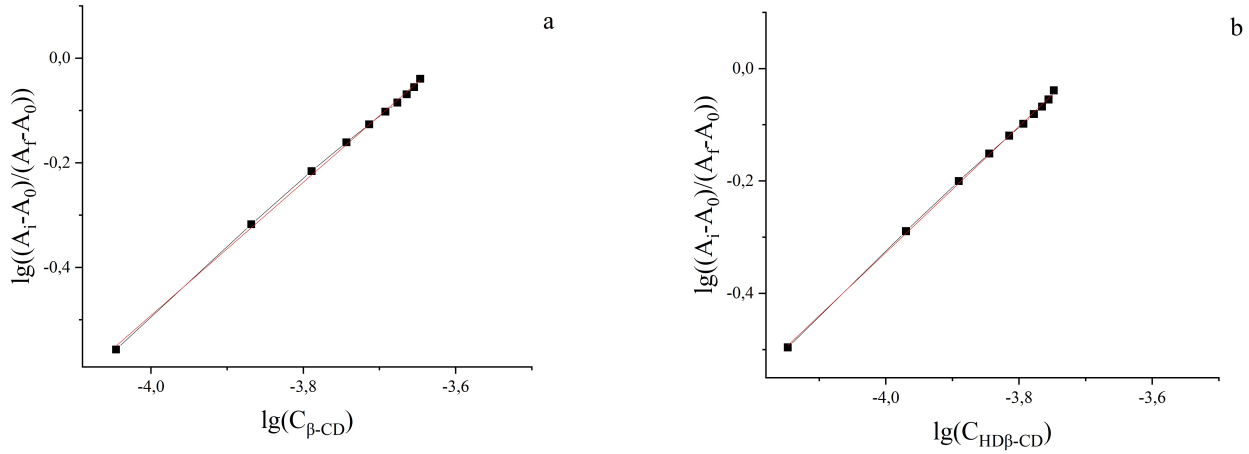


Figure 3. Linear Benesi–Hildebrand plots (Equation 2) for TPP titrated with β-CD (a) and HDβ-CD (b).

The values of K_b were determined by plotting linear dependences of lg((*A*$_i$–*A*$_0$)/(*A*$_f$–*A*$_0$)) versus lg[*C*] (Figure 3). In this instance, K_b, which is a measure of complex stability, indicates the equilibrium between the bound and unbound forms. The magnitude of K_b is directly proportional to the strength of the interaction.

The approximation function *f*(x)=1.28x+4.65, obtained for the TPP–β-CD system (coefficient of determination R^2_{adj}=0.998), was utilized to calculate the logarithm of the binding constant, lgK_b, which was found to be 4.65. This value indicates a strong binding between the TPP and β-CD molecules. A similar function *f*(x)=1.15x+4.29 (coefficient of determination R^2_{adj}=0.997) and logarithm of the binding constant lgK_b=4.29 were obtained for the TPP–HDβ-CD system. This value is comparable to that observed for the TPP–β-CD system. The similarity of these values for both complexes indicates that the structural change of cyclodextrin from β-CD to HDβ-CD did not have a significant effect on the strength of TPP binding. This finding indicates that, in both cases, the interactions of the compounds are driven by the same fundamental binding forces, including Van der Waals interactions, π–π stacking, and the hydrophobic effect. Alternatively, HDβ-CD compensates for the alterations in structure compared to β-CD, thereby maintaining a constant overall binding energy.

Figure 4 shows the fluorescence spectra of the corresponding TPP complexes with β-CD (a) and HDβ-CD (b). The fluorescence spectrum of free TPP comprises two principal bands at wavelengths of λ≈653 nm and λ≈716 nm. The sequential addition of cyclodextrins leads to a decrease in the intensity of the porphyrin fluorescence maxima, which is characteristic of the formation of a non-fluorescent or weakly fluorescent supramolecular complex.

The spectral data were transformed into coordinates of the Stern–Volmer equation to calculate the corresponding constant K_{SV},[45] both for the TPP–β-CD complex (Figure 5a) and for the TPP–HDβ-CD complex (Figure 5b).

$$\frac{I_0}{I_i} = 1 + [C] \cdot K_{SV}\,, \qquad (3)$$

where I_0 and I_i are the fluorescence intensities in the absence and at intermediate the quencher concentration of quencher in the solution, respectively; [*C*] is the intermediate equilibrium concentration of the added quencher; K_{SV} is the Stern-Volmer constant.

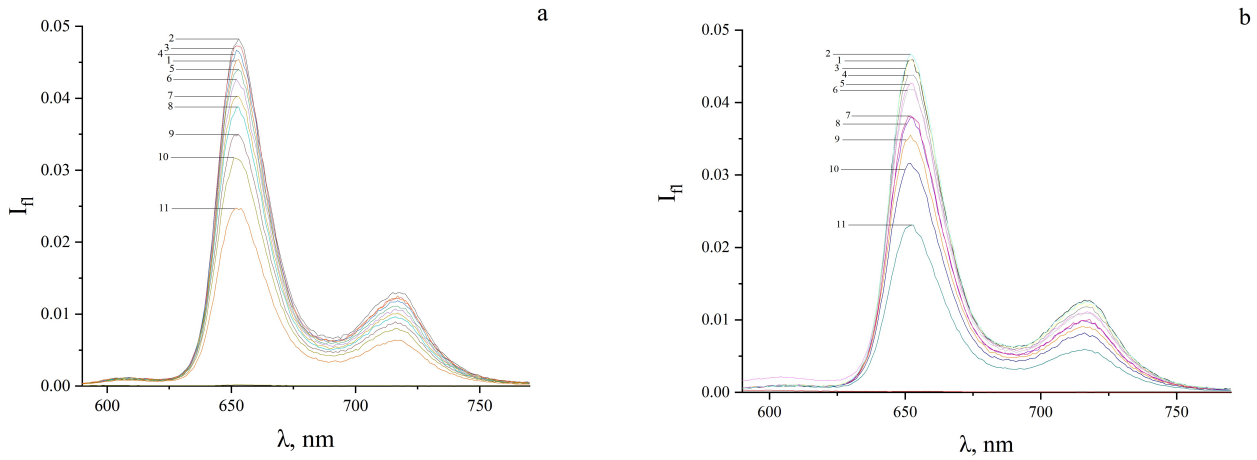


Figure 4. Fluorescence spectra of TPP upon titration with β-CD (a) and HDβ-CD (b). In system a: 1 — TPP without any quencher; 2–11 — TPP + β-CD (0.1 mL × n, n ∈ [1; 10]); in system b: 1 — TPP without any quencher; 2–11 — TPP + HDβ-CD (0.1 mL × n, n ∈ [1; 10]).

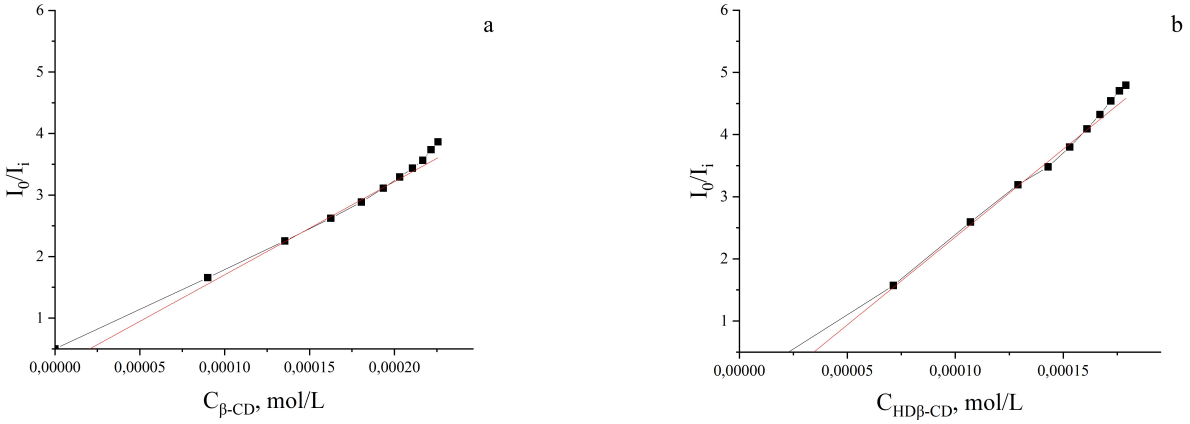


Figure 5. Stern-Volmer plots (Equation (3)) for TPP titrated with β-CD (a) and HDβ-CD (b).

For the TPP–β-CD system, the Stern-Volmer constant K_{SV} (coefficient of determination R^2_{adj}=0.988), was determined to be approximately equal to $1.46 \cdot 10^4$ L/mol, thereby confirming the formation of the inclusion complex.

In a similar manner, the TPP–HDβ-CD complex demonstrated a comparable K_{SV} (coefficient of determination R^2_{adj}=0.991), which was equal to $2.7 \cdot 10^4$ L/mol. The close values for both systems further confirm that the binding strength of the obtained complexes is similar.

Apparently, the binding mechanism of the obtained complexes is based on a typical «host» and «guest» interaction, where the hydrophobic effect prevails. The phenyl substituents of the porphyrin, being hydrophobic functional groups, are encapsulated from the polar aqueous environment into the hydrophobic cavities of the cyclodextrins.

The stoichiometric composition of the complexes was determined from the slope (a) of the Benesi-Hildebrand plot (Equation (2)). For the TPP–β-CD system, the calculated slope (a=1.28 ≈ 1) confirms the formation of a simple 1:1 complex (β-CD:TPP), where the single β-CD cavity encapsulates one phenyl substituent.

The structure of the HDβ-CD with two linked cavities is optimized to form a 1:1 supramolecular container (HDβ-CD:TPP) by utilizing two cavities to encapsulate two phenyl substituents of a single TPP molecule. This interpretation is supported by the slope of the Benesi-Hildebrand plot (a = 1.15 ≈ 1).

The observed parallels in the obtained K_b and K_{SV} values for both systems may indicate that, although the dimeric «host» has the capacity for more complex binding, the initial stage of encapsulation of the first phenyl functional group is the decisive factor in the complexation process. The contribution of binding the second phenyl substituent is either negligible or compensated by steric hindrances.

Conclusions

This study successfully obtained supramolecular inclusion complexes based on the model porphyrin TPP, β-CD, and HDβ-CD, as confirmed by the absorption and fluorescence spectra of the complexes. It has been demonstrated that supramolecular systems, characterized by non-covalent interactions, exhibit high binding constants and enhanced stability. The cyclodextrin oligosaccharide functions as a protective shell for the porphyrin and as a solubilizer, thus enhancing the solubility of TPP in an aqueous environment. This method is promising for future targeted drug delivery applications of active tetrapyrrole derivatives, and creates new opportunities for increasing bioavailability and overcoming various barriers, such as the blood–brain barrier.

Acknowledgements. The work was performed within the framework of the State Assignment of IBCP RAS (No. 125020401357-4) and utilized β-CD and HDβ-CD provided by the staff of the Department of Organic Chemistry, Institute of Biology and Chemistry, Moscow Pedagogical State University.

Author contribution. E.S. Nersesyan: writing – original draft; formal analysis. I.V. Klimenko: methodology; writing – original draft. A.V. Lobanov: conceptualization; writing – review and editing. N.V. Kutyasheva: methodology; writing – review and editing. G.I. Kurochkina: writing – review and editing. M.K. Grachev: conceptualization; writing – review and editing.

References

1. Kudin L.S., Dunaev A.M., Motalov V.B., Cavallo L., Minenkov Y. *J. Chem. Thermodyn*. **2020**, *151*, 106244. doi: 10.1016/j.jct. 2020.106244.
2. Valiev R.R., Cherepanov V.N., Artyukhov V.Y., Sundholm D. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11508–11517. doi: 10.1039/c2cp40468k.
3. Park J.M., Hong K.I., Lee H., Jang W.D. *Acc. Chem. Res.* **2021**, *54*, 2249–2260. doi: 10.1021/acs.accounts.1c00114
4. Klimenko I.V., Lobanov A.V. *Macroheterocycles* **2020**, *13*, 142–146. doi: 10.6060/mhc200390k.
5. Xue X., Lindstrom A., Li Y. *Bioconjugate Chem.* **2019**, *30*, 1585–1603. doi: 10.1021/acs.bioconjchem.9b00231.
6. Tsolekile N., Nelana S., Oluwafemi O.S. *Molecules* **2019**, *24*, 2669. doi: 10.3390/molecules24142669.
7. Li L.L., Diau E.W.G. *Chem. Soc. Rev.* **2013**, *42*, 291–304. doi: 10.1039/c2cs35257e.
8. Ding Y., Zhu W.H., Xie Y. *Chem. Rev*. **2017**, *117*, 2203–2256. doi: 10.1021/acs.chemrev.6b00021.
9. Klimenko I.V., Trusova E.A., Lobanov A.V. *Macroheterocycles* **2024**, *17*, 224–230. doi: 10.6060/mhc245851k.
10. Madkour L.H. The Roles and Mechanisms of ROS, Oxidative Stress, and Oxidative Damage. In: *Retracted Book. Nanoparticles Induce Oxidative and Endoplasmic Reticulum Stresses. Nanomedicine and Nanotoxicology* (Madkour L.H., Ed.), Springer, Cham., **2020**, pp. 139–192. doi: 10.1007/978-3-030-37297-2_4.
11. Kustov A.V. *ChemChemTech* **2023**, *66*(12), 32–40. doi: 10.6060/ivkkt.20236612.6902
12. Koifman O.I., Ageeva T.A., Kuzmina N.S. et al. *Macroheterocycles* **2022**, *15*, 207–302. doi: 10.6060/mhc224870k.
13. Rajora M.A., Lou J.W.H., Zheng G. *Chem. Soc. Rev.* **2017**, *46*, 6433–6469. doi: 10.1039/C7CS00525C.
14. Berezin B.D. Coordination Compounds of Porphyrins and Phthalocyanine. New-York, Toronto: Wiley, **1981**. 280 p.
15. Taniguchi M., Lindsey J.S., Bocian D.F., Holten D. *J. Photochem. Photobiol. C: Photochem. Rev.* **2021**, *46*, 100401. doi: 10.1016/j.jphotochemrev.2020.100401.
16. Silvers S.J., Tulinsky A. *J. Am. Chem. Soc.* **1967**, *89*, 3331–3337. doi: 10.1021/ja00989a036.
17. Fadda A.A., El-Mekawy R.E., El-Shafei A., Freeman H.S., Hinks D., El-Fedawy M. *J. Chem.* **2013**, *2013*, 340230. doi: 10.1155/2013/340230.
18. Klimenko I.V., Gradova M.A., Gradov O.V., Bibikov S.B., Lobanov A.V. *Russ. J. Phys. Chem. B* **2020**, *14*, 436–442. doi: 10.1134/s1990793120030070.
19. Grodowska K., Parczewski A. *Acta Poloniae Pharmaceutica – Drug Research* **2010**, *67*(1), 3–12.
20. Alea-Reyes M.E., Rodrigues M., Serra A., Mora M., Sagristá M.L., González A., Durán S., Duch M., Plaza J.A., Vallés E., Russell D.A., Perez-Garcia L. *RSC Adv.* **2017**, *7*, 16963–16976. doi: 10.1039/C7RA01569K.
21. Vallecorsa P., Di Venosa G., Ballatore M.B., Ferreyra D., Mamone L., Sáenz D., Calvo G., Durantini E., Casas A. *BMC Cancer* **2021**, *21*, 547. doi: 10.1186/s12885-021-08286-6.
22. *Cyclodextrin Fundamentals, Reactivity and Analysis, Vol. 16* (Fourmentin S., Crini G., Lichtfouse E., Eds.), Springer, **2018**. 262 p. doi: 10.1007/978-3-319-76159-6.
23. Loftsson V., Hreinsdottir D., Masson M. *Int. J. Pharm.* **2005**, *302*(1–2), 18–28. doi: 10.1016/j.ijpharm.2005.05.042.
24. Kutyasheva N.V., Kurochkina G.I., Ilinich K.K., Grachev M.K. *Macroheterocycles* **2022**, *15*, 123–127. doi: 10.6060/mhc224126g.
25. Bezerra F.M., Lis M.J., Firmino H.B., Dias da Silva J.G., Curto Valle R.d.C.S., Borges Valle J.A., Scacchetti F.A.P., Tessaro A.L. *Molecules* **2020**, *25*, 3624. doi: 10.3390/molecules25163624.
26. Molupe N., Babu B., Prinsloo E., Kaassis A.Y., Edkins K., Mack J., Nyokong T. *J. Porphyrins Phthalocyanines* **2019**, *23*(11–12), 1486–1494. doi: 10.1142/s1088424619501633.
27. Kablov I.V., Kravchenko I.E., Zorina T.E., Kaskeh V., Zorin V.P. *J. Belarusian State University. Physics* **2024**, *2*, 30–37.
28. Yakavets I.V., Yankovsky I.V., Khludeyev I.I., Lassalle H.P., Bezdetnaya L.N. Zorin V.P. *J. Appl. Spectrosc.* **2018**, *84*, 1030–1036. doi: 10.1007/s10812-018-0582-z.
29. Yakavets I., Yankovsky I., Bezdetnaya L., Zorin V. *Dyes Pigm*. **2017**, *137*, 299–306. doi: 10.1016/j.dyepig.2016.11.007.
30. Fathalla M., Neuberger A., Li S.C., Schmehl R., Diebold U., Jayawickramarajah J. *J. Am. Chem. Soc.* **2010**, *132*, 9966–9967. doi: 10.1021/ja1030722.
31. Gu Z.Y., Guo D.S., Sun M., Liu Y. *J. Org. Chem.* **2010**, *75*, 3600–3607. doi: 10.1021/jo100351f.
32. Kitagishi H., Chai F., Negi S., Sugiura Y., Kano K. *Chem. Commun*. **2015**, *51*, 2421–2424. doi: 10.1039/c4cc09042j.
33. Grodner B., Napiórkowska M. *Molecules* **2021**, *26*, 993. doi: 10.3390/molecules26040993.
34. Mao Q., Zhao X., Kiriyama A., Negi S., Fukuda Y., Yoshioka H., Kawaguchi A.T., Motterlini R., Foresti R., Kitagishi H. *Proc. Natl. Acad. Sci.* **2023**, *120*, e2209924120. doi: 10.1073/pnas.2209924120.
35. Choi S.R., Talmon G.A., Britigan B.E., Narayanasamy P. *ACS Infect. Dis.* **2021**, *7*, 2299–2309. doi: 10.1021/acsinfecdis.0c00896.
36. Yi S., Liao R., Zhao W., Huang Y., He Y. *Theranostics* **2022**, *12*, 2560. doi: 10.7150/thno.70243.
37. 37. Spiridon I., Anghel N. *Molecules* **2025**, *30*, 3044. doi: 10.3390/molecules30143044.
38. Shipilov D.A., Kurochkina G.I., Akhlebinin A.K., Kutyasheva N.V., Grachev M.K. *Macroheterocycles* **2019**, *12*, 94–97. doi: 10.6060/mhc181110s.
39. Puglisi A., Purrello R., Rizzarelli E., Sortino S., Vecchio G. *New J. Chem*. **2007**, *31*, 1499–1506. doi: 10.1039/b703680a.
40. Dong M., Ma T.H., Zhang A.J., Dong Y.M., Wang Y.W., Peng Y. *Dyes Pigm.* **2010**, *87*, 164–172. doi: 10.1016/j.dyepig. 2010.03.015.
41. Benesi H.A., Hildebrand J.H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707. doi: 10.1021/ja01176a030.
42. Wang R., Yu Z. *Acta Phys.-Chim. Sinica* **2007**, *23*, 1353–1359. doi: 10.1016/S1872-1508(07)60071-0.
43. Berezin D.B., Kustov A.V., Krest'yaninov M.A., Shukhto O.V., Batov D.V., Kukushkina N.V. *J. Mol. Liq.* **2019**, *283*, 532–536. doi: 10.1016/j.molliq.2019.03.091.
44. Roy D., Chakraborty A., Ghosh R. *RSC Adv*. **2017**, *7*, 40563–40570. doi: 10.1039/c7ra06687b.
45. Gehlen M.H. *J. Photochem. Photobiol. C: Photochem. Rev.* **2020**, *42*, 100338. doi: 10.1016/j.jphotochemrev.2019.100338.

Received 22.09.2025
Accepted 09.12.2025