Mendeleev Commun., 2027, **37**, JUST ACCEPTED

Received 02.06.26
Revised 28.09.26

26/8106

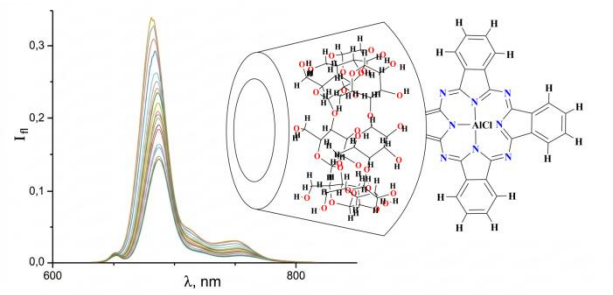
Supramolecular complex in the aluminum phthalocyanine chloride–β-cyclodextrin system: formation, spectral properties and stabilization mechanisms

Edgar S. Nersesyan,[a] Inna V. Klimenko,[a] Anton V. Lobanov [a,b] and Sergey B. Bibikov [a]

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

DOI: 10.71267/mencom.8106

Supramolecular inclusion complexes based on aluminum phthalocyanine chloride (AlClPc) and β-cyclodextrin (β-CD) were prepared via incremental titration in a N,N-dimethylformamide–water (DMF-water) binary system. The host–guest assembly process was characterized by UV-Vis and fluorescence spectroscopy, demonstrating a robust 7 nm bathochromic shift of the Q-band and pronounced fluorescence quenching. The structural parameters of the complex and solid-state intermolecular interactions were confirmed by Attenuated Total Reflectance (ATR) IR spectroscopy.

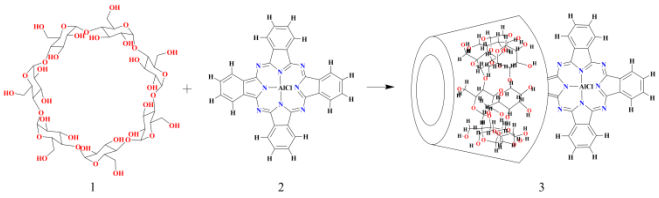


Keywords: cyclodextrins, phthalocyanines, host–guest molecules, inclusion complexes, monomer stabilization, ATR IR spectroscopy, fluorescence.

The characterization of supramolecular architectures based on macrocyclic tetrapyrroles represents a key frontier in modern physical chemistry[1–4]. These systems undergo self-assembly into host–guest complexes, altering the photophysical pathways of encapsulated molecules[5–10]. Phthalocyanines possess extended π-conjugated networks providing exceptional stability and intense far-red absorption[4, 11–12]. However, their application is limited by spontaneous self-association into non-fluorescent H-type aggregates in aqueous media, which causes fluorescence quenching[13–16].

The use of β-CD as a hydrophobic molecular container in various supramolecular systems isolates monomeric macrocycles and prevents their aggregation[17–23]. Phthalocyanines contain isoindole units and nitrogen meso-bridges, yielding intense Q-band absorption and susceptibility to macrocycle deformation[24]. The presence of an axial chloride extraligand provides a unique coordination geometry, necessitating dedicated insights into the stabilization mechanisms[24]. Currently, AlClPc–β-CD systems are evaluated for photodynamic therapy[25–28], cutaneous drug delivery[29], and antimicrobial treatments[30]. This work explores the synthesis, stability, and intermolecular interactions of AlClPc–β-CD complexation in a binary DMF–water solution (Scheme 1).

The supramolecular host–guest inclusion complexes were successfully synthesized via steps of incremental titration using a fixed concentration of AlClPc (C = 2.16×10^{-6} mol/L) in DMF and sequential additions of aqueous β-CD (C = 2.71×10^{-4} mol/L). The full synthetic preparation criteria, chemical source purities, and explicit instrument parameters are detailed in the Electronic Supplementary Materials.



Scheme 1 Reagents and products: aluminum phthalocyanine chloride (1), β-cyclodextrin (2), host-guest inclusion complex (3).

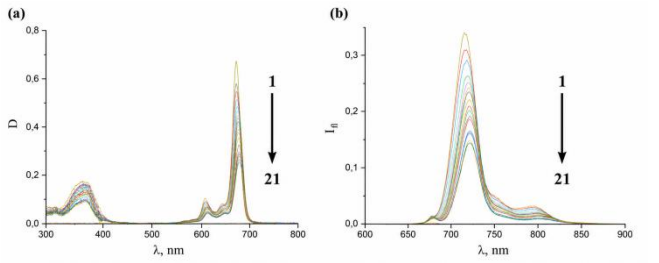


Figure 1 (a) Electronic absorption and (b) fluorescence emission spectra of AlClPc upon titration with β-CD. Arrow indicates the direction of increasing β-CD concentration. Spectrum 1 — pure AlClPc; spectra 2–21 — AlClPc + β-CD (0.1 mL × n, n ∈ [1; 20]).

The initial UV-Vis profile of AlClPc in DMF is dominated by a sharp monomeric Q-band maximum at λ = 673 nm. Sequential introduction of the aqueous β-CD phase triggers a steady hypochromic effect accompanied by a progressive bathochromic displacement of the Q-band by 7 nm ($\lambda_{max} \rightarrow 680$ nm) (Figure 1a). These developments reflect the encapsulation of the phthalocyanine framework inside the hydrophobic cavity of the

© Mendeleev Communications.

host macrocycle, leading to structural stabilization and altered microenvironment polarity. Mathematical evaluation via the Benesi–Hildebrand expression confirmed a 1:1 complex stoichiometry[30–35]. The logarithmic binding constant $\log K_b$ was calculated to be 5.26 (R^2_{adj} = 0.999), indicating high thermodynamic stability governed by hydrophobic interactions, Van der Waals forces, and peripheral π–π interactions. Fluorimetric data correlated well with the absorption trends: the emission intensity of the Q-band maximum at λ = 718 nm systematically decreased upon the addition of β-CD (Figure 1b). This fluorescence quenching predominantly follows a static mechanism[36-37], which is clearly evidenced by the concurrent ground-state alterations (a 7 nm bathochromic shift and hypochromicity) observed in the UV-Vis absorption spectra. The linear dependency of the relative fluorescence intensity (I_0/I_i) on the host concentration confirms a controlled, stoichiometric binding process. The Stern–Volmer constant K_{SV}[38] was determined to be 5.86×10^6 L/mol (R^2_{adj} = 0.983), further verifying the high efficiency of the macrocycle encapsulation process into the cyclodextrin cavity.

Solid-state ATR IR analysis verified the host–guest spatial relationship. Upon complexation, the prominent, broad stretching envelope of the β-CD hydroxyl units (3200–3500 cm^{-1}) undergoes a noticeable low-frequency shift combined with contour restructuring. This behavior, coupled with sharp intensity realignments of the core skeletal ring vibrations within the 1400–1650 cm^{-1} interval, points to the generation of systemic intermolecular hydrogen bonds involving the carbohydrate hydroxyl groups and peripheral nitrogen/carbon centers of the core macrocycle. The data confirm steric immobilization of the guest molecule within the inner portal, completely separating this mechanism from superficial surface adsorption phenomena. In conclusion, stable supramolecular host–guest assemblies based on AlClPc and β-CD in DMF-water environment were successfully realized. The integration of spectroscopic methodologies proved a high-affinity binding model where the cooperative net of peripheral hydrogen bonds effectively preserves the active monomeric state of the photosensitizer.

This work was supported by the state assignment of IBCP RAS (theme No. 125020401357-4).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.8106.

References

1 O. I. Koifman, T. A. Ageeva, N. S. Kuzmina, V. F. Otvagin, A. V. Nyuchev, A. Yu. Fedorov, D. V. Belykh, N. Sh. Lebedeva, E. S. Yurina, S. A. Syrbu, M. O. Koifman, Y. A. Gubarev, D. A. Bunin, Yu. G. Gorbunova, A. G. Martynov, A. Yu. Tsivadze, S. V. Dudkin, A. V. Lyubimtsev, L. A. Maiorova, M. V. Kishalova, M. V. Petrova, V. B. Sheinin, V. S. Tyurin, I. A. Zamilatskov, E. I. Zenkevich, P. K. Morshnev, D. B. Berezin, E. A. Drondel, A. V. Kustov, V. A. Pogorilyy, A. N. Noev, E. A. Eshtukova-Shcheglova, E. A. Plotnikova, A. D. Plyutinskaya, N. B. Morozova, A. A. Pankratov, M. A. Grin, O. B. Abramova, E. A. Kozlovtseva, V. V. Drozhzhina, E. V. Filonenko, A. D. Kaprin, A. V. Ryabova, D. V. Pominova, I. D. Romanishkin, V. I. Makarov, V. B. Loschenov, K. A. Zhdanova, A. V. Ivantsova, Yu. S. Bortnevskaya, N. A. Bragina, A. B. Solovieva, A. S. Kuryanova and P. S. Timashev, *Macroheterocycles* 2022, **15**, 207; https://doi.org/10.6060/mhc224870k.

2 R. C. Soy, B. Babu, D. O. Oluwole, N. Nwaji, J. Oyim, E. Amuhaya, E. Prinsloo, J. Mack and T. Nyokong, *J. Porphyrins Phthalocyanines* 2019, **23**, 34; https://doi.org/10.1142/S1088424618501146.

3 M. A. Rajora, J. W. H. Lou and G. Zheng, *Chem. Soc. Rev.* 2017, **46**, 6433; https://doi.org/10.1039/C7CS00525C.

4 B. D. Berezin, Coordination compounds of porphyrins and phthalocyanine, John Wiley & Sons, New York-Toronto, 1981;

5 L. S. Kudin, A. M. Dunaev, V. B. Motalov, L. Cavallo and Y. Minenkov, *J. Chem. Thermodyn.* 2020, **151**, 106244; https://doi.org/10.1016/j.jct.2020.106244.

6 J. M. Park, K. I. Hong, H. Lee and W. D. Jang, *Acc. Chem. Res.* 2021, **54**, 2249; https://doi.org/10.1021/acs.accounts.1c00114.

7 M. Chen, S. Ji, X. Liu, X. Zheng, M. Zhou and W. Wang, *Mol. Pharmaceutics* 2025, **22**, 2765; https://doi.org/10.1021/acs.molpharmaceut.4c01359.

8 S. Bandyopadhyay, J. A. Forzano, M. Dirak and J. Chan, *JACS Au* 2025, **5**, 42; https://doi.org/10.1021/jacsau.4c01108.

9 I. V. Klimenko and A. V. Lobanov, *Macroheterocycles* 2020, **13**, 142; https://doi.org/10.6060/mhc200390k.

10 X. Xue, A. Lindstrom and Y. Li, *Bioconjugate Chem.* 2019, **30**, 1585; https://doi.org/10.1021/acs.bioconjchem.9b00231.

11 A. A. Fadda, R. E. El-Mekawy, A. El-Shafei, H. S. Freeman, D. Hinks and M. El-Fedawy, *J. Chem.* 2013, **2013**, 340230; https://doi.org/10.1155/2013/340230.

12 I. V. Klimenko, M. A. Gradova, O. V. Gradov, S. B. Bibikov and A. V. Lobanov, *Russ. J. Phys. Chem.* B 2020, **14**, 436; https://doi.org/10.1134/s1990793120030070.

13 I. V. Klimenko, E. A. Trusova and A. V. Lobanov, *Macroheterocycles* 2024, **17**, 224; https://doi.org/10.6060/mhc245851k.

14 L. H. Madkour, *RETRACTED BOOK Nanoparticles Induce Oxidative and Endoplasmic Reticulum Stresses*, *Springer Cham.* 2020; https://doi.org/10.1007/978-3-030-37297-2_4.

15 D. B. Berezin, V. V. Makarov, S. A. Znoyko, V. E. Mayzlish and A. V. Kustov, *Mendeleev Commun.* 2020, **30**, 621; https://doi.org/10.1016/j.mencom.2020.09.023.

16 S. V. Kurmaz, I. V. Ulyanov, N. S. Emelyanova, V. A. Kurmaz, A. V. Kozlov, L. R. Sizov and A. Y. Rybkin, *Mendeleev Commun.* 2024, **34**, 492; https://doi.org/10.1016/j.mencom.2024.06.007.

17 G. Crini, S. Fourmentin, É. Fenyvesi, G. Torri, M. Fourmentin, and N. Morin-Crini, in *Cyclodextrin Fundamentals, Reactivity and Analysis*, ed. S. Fourmentin, G. Crini and E. Lichtfouse, *Springer Cham*, 2018, 1–56; https://doi.org/10.1007/978-3-319-76159-6.

18 T. Loftsson, D. Hreinsdóttir and M. Másson, *Int. J. Pharm.* 2005, **302**, 18; https://doi.org/10.1016/j.ijpharm.2005.05.042.

19 N. V. Kutyasheva, G. I. Kurochkina, K. K. Ilinich and M. K. Grachev, *Macroheterocycles* 2022, **15**, 123; https://doi.org/10.6060/mhc224126g.

20 F. M. Bezerra, M. J. Lis, H. B. Firmino, J. G. Dias da Silva, R. D. C. S. Curto Valle, J. A. Borges Valle, F. A. P. Scacchetti and A. L. Tessaro, *Molecules* 2020, **25**, 3624; https://doi.org/10.3390/molecules25163624.

21 N. Molupe, B. Babu, E. Prinsloo, A.Y. Kaassis, K. Edkins, J. Mack and T. Nyokong, *J. Porphyrins Phthalocyanines* 2019, **23**, 1486; https://doi.org/10.1142/s1088424619501633.

22 A. Puglisi, R. Purrello, E. Rizzarelli, S. Sortino and G. Vecchio, *New J. Chem.* 2007, **31**, 1499; https://doi.org/10.1039/b703680a.

23 L. R. Kopnova, D. E. Grigoryan and E. V. Kudryashova, *Mendeleev Commun.* 2026, **36**, 407; https://doi.org/10.71267/mencom.8002.

24 I. M. Soliman, M. M. El-Nahass, K. M. Eid and H. Y. Ammar, *Physica B: Condensed Matter* 2016, **491**, 98–103; https://doi.org/10.1016/j.physb.2016.03.023.

25 E. Georgiopoulou, E. Kavetsou, E. Alexandratou, A. Detsi and K. Politopoulos, *J. Biomater. Appl.* 2025, **39**, 933; https://doi.org/10.1177/08853282241306858.

26 E. Kavetsou, C. Tsoukalas-Koulas, A. Katopodi, A. Kalospyros, E. Alexandratou and A. Detsi, *Bioengineering* 2023, **10**, 244; https://doi.org/10.3390/bioengineering10020244.

27 X. Dai, M. Huo, B. Zhang, Z. Liu and Y. Liu, *Biomacromolecules* 2022, **23**, 3549; https://doi.org/10.1021/acs.biomac.2c00276.

28 A. Ben Mihoub, L. Larue, A. Moussaron, Z. Youssef, L. Colombeau, F. Baros, C. Frochot, R. Vanderesse and S. Acherar, *Molecules* 2018, **23**, 1936; https://doi.org/10.3390/molecules23081936.

29 T. A. Reis, A. E. Jaculi, K. L. Ramos, P. E. N. Souza, F. H. Veiga-Souza, G. A. Joanitti, R. B. Azevedo, T. Gratieri, M. Cunha-Filho and G. M. Gelfuso, *Eur. J. Pharm. Sci.* 2019, **139**, 105056; https://doi.org/10.1016/j.ejps.2019.105056.

30 A. Galstyan, U. Kauscher, D. Block, B. J. Ravoo and C. A. Strassert, *ACS Appl. Mater. Interfaces* 2016, **8**, 12631; https://doi.org/10.1021/acsami.6b02132.

© Mendeleev Communications.

31 M. Dong, T. H. Ma, A. J. Zhang, Y. M. Dong, Y. W. Wang and Y. Peng, *Dyes Pigm.* 2010, **87**, 164; https://doi.org/10.1016/j.dyepig.2010.03.015.
32 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.* 1949, **71**, 2703; https://doi.org/10.1021/ja01176a030.
33 R. Wang and Z. Yu, *Acta Physico-Chimica Sinica* 2007, **23**, 1353; https://doi.org/10.1016/S1872-1508(07)60071-0.
34 D. B. Berezin, A. V. Kustov, M. A. Krest'yaninov, O. V. Shukhto, D. V. Batov and N. V. Kukushkina, *J. Mol. Liq.* 2019, **283**, 532; https://doi.org/10.1016/j.molliq.2019.03.091.
35 D. Roy, A. Chakraborty and R. Ghosh, *RSC Adv.* 2017, **7**, 40563; https://doi.org/10.1039/c7ra06687b.
36 B. T. Huy, D. T. Thangadurai, M. Sharipov, N. N. Nghia, N. Van Cuong and Y. I. Lee, *Microchem. J.* 2022, **179**, 107511; https://doi.org/10.1016/j.microc.2022.107511.
37 A. A.Skuredina and E. V. Kudryashova, *Mendeleev Commun.* 2025, **35**, 76; https://doi.org/10.71267/mencom.7555.
38 M. H. Gehlen, *J. Photochem. Photobiol., C* 2020, **42**, 100338; https://doi.org/10.1016/j.jphotochemrev.2019.100338.

Received: 2nd June 2026; Com. 26/8106

© Mendeleev Communications.