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Protonation of the TPPS₄ center due to Interactions with L-Ascorbic acid. Simulations using the DFT approach

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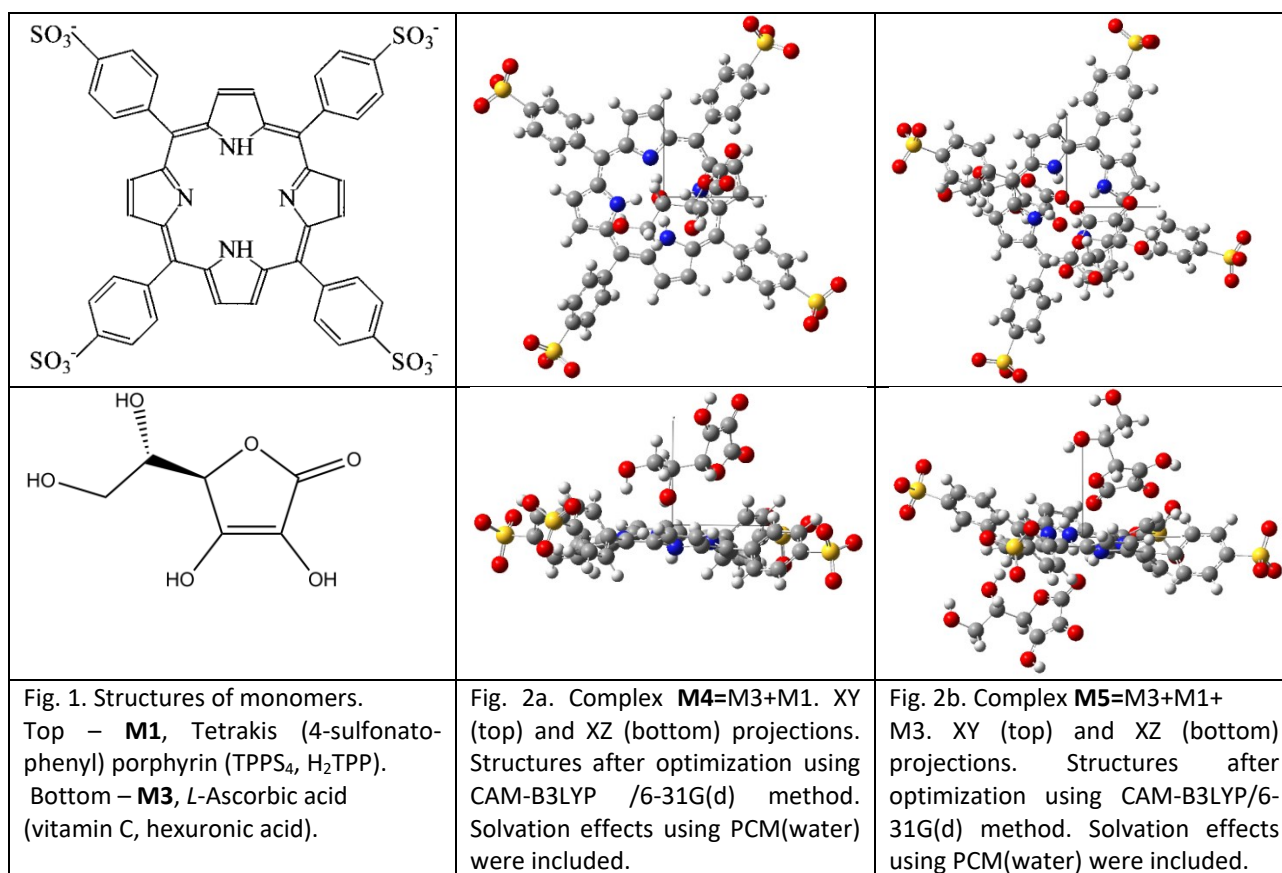
In the class of naturally occurring porphyrins, tetrakis (4-sulfonatophenyl) porphyrin (TPPS₄, H₂TPP, see Fig. 1, top, M1) represents heterocyclic compound which is important as a potential photosensitizer for production of the singlet oxygen [1] (cancer photodynamic therapy). Modeling results presented in Ref. [2] showed that geometry of TPPS₄ molecule changes from flat (ionic form at neutral pH), to saddle-shaped (protonated core at moderate acidity) ionic forms (H₂TPPS₄⁴⁻, H₄TPPS₄²⁻, H₆TPPS₄⁰, and H₈TPPS₄²⁺). L-Ascorbic acid (vitamin C, hexuronic acid, see Fig. 1, bottom, M3) represents well-known organic material of high biological importance. L-Ascorbic acid could be used as antioxidant for help protect against oxidative stress in tissues and inflammation [3]. This work is dedicated to the study of modeling the interaction of TPPS₄ (M1) and L-ascorbic acid (M3).

Simulations. Several complexes such as M4 and M5 were used for simulations.



Gaussian16 [4] package was used to establish the ground state complex structure and corresponding electronic excitations. Optimization in the ground electronic state has been provided using semiempirical CAM-B3LYP method and 6-31G(d) basis set consisting of polarization function (d). Electronic excitations were calculated using semiempirical TD method for singlets only. Environmental effects were included using PCM (water) routine for structure simulations as well as for excitations. Fig. 2a and b represents M4 complex and M5 complex respectively. Both structures are presented in two projections after optimization using CAM-B3LYP/6-31G(d) method. Solvation effects using PCM(water) were included. Firstly, for M4 and M5 complexes, M1 monomer was presented in centre-unprotonated flat form (two protons at centre only) which corresponds to case of neutral surrounding at pH=7. M3 monomer was presented as L-ascorbic acid (two protons in positions 4 and 5). Successful optimization in the ground electronic state allows obtaining the weak associate without geometry change (M1 flat, centre protonated by two native protons) and without proton transport (M3 in form of L-ascorbic acid, reduced form). Secondly, additional structure optimization in the first excited electronic state allows obtaining weak associate with geometry change (M1 saddle-shaped, centre fully protonated, four protons) and proton transport is present (M3 in form of L-dehydroascorbic acid, oxidized form). This final situation is depicted in Fig. 2. In case of M4 complex (one L-ascorbic acid), protons of L-Ascorbic acid from position 4 and 5 (two per one molecule) must be shared between L-Ascorbic acid and TPPS₄. In case of M5 complex (two L-ascorbic acids), two necessary protons (one per each molecule) were present in proton transfer.

Conclusions. Simulation of the molecular structures using quantum chemical methods allows to estimate most probable structures of separate monomers L-Ascorbic acid and TPPS₄ as well as the complexes. Initial hypothesis about the role of L-Ascorbic acid as reducing agent when neighbour contact to TPPS₄ is present was approved. In complex [L-Ascorbic acid + TPPS₄ + L-Ascorbic acid], intermolecular charge transfer takes place. Protonation of centre of TPPS₄ could be provided using two L-Ascorbic acids as the proton sources. Presence of L-Ascorbic acid in the solvent allows protonation reaction in form of TPPS₄ → H₂TPPS₄.



REFERENCES

- [1] Pfoertner, K.-H. (2000). Photochemistry. In Ullmann's Encyclopedia of Industrial Chemistry, (Ed.). https://doi.org/10.1002/14356007.a19_573
- [2] Poderys, V.; Gruodis, A.; Tamoliunaite, G.; Kalnaityte-Vengeliene, A.; Bagdonas, S.; Rotomskis, R. (2026) Spectroscopy and structural modelling of TPPS4 in aqua interactions: Role of protonation and concentration, *Journal of Molecular Structure*, 1355, 2026, 145073, <https://doi.org/10.1016/j.molstruc.2025.145073>.
- [3] Abdulhameed, Elaf Akram; Rani, K.G. Aghila; AlGhalban, Fatima Mousa; Abou Neel, Ensanya A.; Khalifa, Nadia; Khalil, Khalil Abdelrazek; Omar, Marzuki; Samsudin, Ab Rani (2025) Managing Oxidative Stress Using Vitamin C to Improve Biocompatibility of Polycaprolactone for Bone Regeneration In Vitro *ACS Omega* 29(2024)31776-31788 - doi: 10.1021/acsomega.4c02858
- [4] *Gaussian 16, Revision C.01*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.