2019年度 物質生命理工学科コロキウム

上智大学 理工学部 物質生命理工学科 主催

理工学部・理工学振興会 共催

“Host-guest Complexes of Chiral & Achiral Metalloporphyrin Dimers: Stereochemical Structure & Application by MD, ECD, 1H-NMR”

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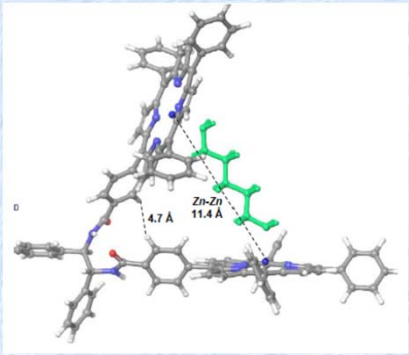
2019年4月22日（月曜日）　13：30～15：00　　場所：L－821

Metalloporphyrin dimers continue to attract a great attention due to growing interest for development of more versatile chiroptical sensors at supramolecular level. In most cases two metalloporphyrin macrocycles (Zn(II)P) are attached to achiral linker, thus forming an achiral tweezer receptor. If their coordination to chiral bidentate substrate proceeds as the stereodifferentiating process two porphyrins adopt a chiral mutual disposition and are able to interact through the space. In response to this situation it may appear an exciton split electronic CD (couplet), usually very intense and observable on a submicroscale level. Such ECD profile possesses a great diagnostic power regarding the absolute configuration of chiral natural products, drugs and other synthetic substrates. However, sometimes the metal coordination results to a mixture of chiral host-guest complexes of great conformational diversity. In such case a theoretical conformational analysis and ECD simulations are desirable in order to rationalize the experimental results. More recent studies also on chiral tweezers hosts and achiral guests revealed that the conformational analysis in these cases might be more challenging task than expected, since even subtle spatial changes either in the guest molecule or in chiral host, or in both, may profoundly affect the ECD response. It is not surprising therefore, that the versatile porphyrin-based receptors continue to stimulate more studies towards chiral sensing and development of new stereodynamic probes.



In the lecture we will also discuss an intriguing chiral switch, namely a two-step helicity inversion upon complexation between a chiral tweezer host, the Zn(II)bisporphyrin derivative of (1*R*, 2*R*)- diphenylethylenediamine, and achiral aliphatic diamines of different length and stoichiometry. We will present as well some unpublished results. They are based on Molecular Dynamics (MD) simulations, *ab initio* geometry optimization and theoretical calculations of electronic CD (ECD) by TD-DFT along with 1H-NMR experimental analysis and interpretation in the light of porphyrin ring-current effect phenomenon.

学外の方の聴講歓迎・申込不要・参加無料

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