

論文審査の結果の要旨および担当者

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氏 名 臼 井 孝 介

論 文 題 目 Theoretical Investigation of Fluorescence Mechanisms in
Photoactive Molecules Aimed at Their Improved Design
(先進的光活性分子デザインに向けた蛍光メカニズムに関する理論的研究)

論文審査担当者

主 査 名古屋大学トランスフォーメティブ生命分子研究所

教授 Ph.D. IRLE Stephan

委 員 名古屋大学トランスフォーメティブ生命分子研究所

教授 博士(工学) 山口 茂弘

委 員 京都大学大学院工学研究科

教授 博士(理学) 佐藤 啓文

論文審査の結果の要旨

別紙 1 - 2

From his time as a Master Course student in the group of Professor Shigehiro Yamaguchi, Mr. Kosuke Usui was involved in the application of quantum chemical methods to the study of large organic molecules in their electronically excited states. When the candidate moved to our lab to conduct his PhD studies in our Quantum Chemistry Laboratory, he sincerely studied theoretical excited state formalisms and became involved in developing novel theoretical methods, especially for the treatment of molecules in their excited states in a biological context. Doing so requires the understanding and calculation of i) the electronic structure, ii) the geometrical relaxation in the excited state, and iii) the solvation effect on structures and dynamics of excited molecules in aqueous solution, as will be explained in greater detail below.

In topic i), Mr. Usui chose an interesting biradical system containing a trimethylenemethane (TMM) unit, which was first discovered by the group of Professor Hiroshi Ikeda at Osaka Prefectural University. This molecule strongly emits red, green, or blue light, depending on the nature of the choice of ligands. The candidate carried out calculations of ground and first excited triplet states, using post-Hartree-Fock *ab initio* and various first principles density functional theory methods. Analysis of optimized geometries including bond alternations and spin distributions indicates that the triplet ground and excited states of these biradicals have aromatic and quinoidal characteristics, respectively. Inspection of their calculated electronic structures shows that, in comparison the triplet ground state, one of the spins in the triplet excited state is more delocalized on arene-rings linked to the TMM framework.

In topic ii), the candidate elucidated the on-off switching mechanism in cationic tetravalent group V-based fluoride molecular sensors based on *ab initio* calculations. Although many on-off switching dyes have been synthesized experimentally, it remains unclear in many cases how these molecules can switch between radiative and non-radiative excitation decay pathways. In his work, Usui-san precisely analyzed excited state of the cationic tetravalent group V-based fluoride molecular sensor by time-dependent density functional theory and orbital analysis, and showed that the on-off switching is subtly controlled by the distance between central element and anthracene group, which may be tuned by synthetic techniques.

In topic iii), Mr. Usui has proposed an approach to treat the multi-dimensional solvent fluctuation for the simultaneous treatment of ground and multiple excited states, based on the reference interaction site model.

In the thesis defense presentation on February 22, the candidate explained his research results well and was able to explain detailed questions to the satisfaction of the reviewers.