

MERIT Long-Term Overseas Research Report

MERIT 11th Cohort

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Research Topic: Study on Two-Electron Excited States in Phthalocyanine Oligomers

«Background»

Multiphoton absorption is a fundamental concept underpinning next-generation photo technologies such as optical communication and 3D imaging. In particular, π -conjugated molecular aggregates have been actively studied as promising candidates for two-photon absorption materials. However, the mechanisms of such two-photon absorption processes have not been fully understood yet. Recently, our laboratory has demonstrated the formation of the two-electron excited states in phthalocyanine (Pc) oligomers, aggregates of Pc molecules, via two-photon absorption. By using transient absorption measurements, we have revealed the absorption spectra of unexcited Pc units within oligomers in the triplet excited state. Since the excitation energy of unexcited units in the triplet state differs from that in the ground state, understanding the electronic structure of the two-electron excited states is essential for elucidating the two-photon absorption process.

Previous studies have proposed wavefunction models for the singly excited states of Pc dimers, describing delocalized electronic structures in terms of localized configurations on each Pc unit. However, such wavefunction-based models for two-electron excited states in dimer molecules have yet been proposed. Moreover, the semi-empirical methods reported in earlier studies are not suitable for accurate analysis of Pc oligomers, where strong inter-unit interactions lead to multi-configurational wavefunctions.

«Research Objective»

This study aims to elucidate the two-photon absorption process in Pc oligomers by analyzing their electronic structures in the excited states using ab-initio (first-principles) quantum chemical methods based on wavefunction theory.

«Method»

In this study, we focused on the phthalocyanine (Pc) dimer, a molecular aggregate composed of two Pc units. By using CAS-SCF (Complete Active Space Self-Consistent Field) method implemented in the ab-initio quantum chemistry software MOLCAS, the ground and excited states of the Pc dimer were calculated. The multi-configurational excited-state wavefunctions described in terms of delocalized molecular orbitals spreading in both Pc units and their energies were obtained. Subsequently, by using Procrustes rotation procedure, these delocalized molecular orbitals were transformed into localized orbitals on each Pc unit (see Figure). This method enabled the excited-state wavefunctions of the Pc dimer to be analyzed in terms of localized electronic structures.

To improve the accuracy of the calculations, dynamic correlation was introduced to the CAS-SCF calculation. Specifically, two methods were employed: the CAS-PT2 (Complete Active Space Second-Order Perturbation Theory) method, which introduces second-order perturbation corrections, and the MCP-DFT (Multiconfiguration Pair-Density Functional Theory) method, which applies density functional theory to multi-configurational wavefunctions.

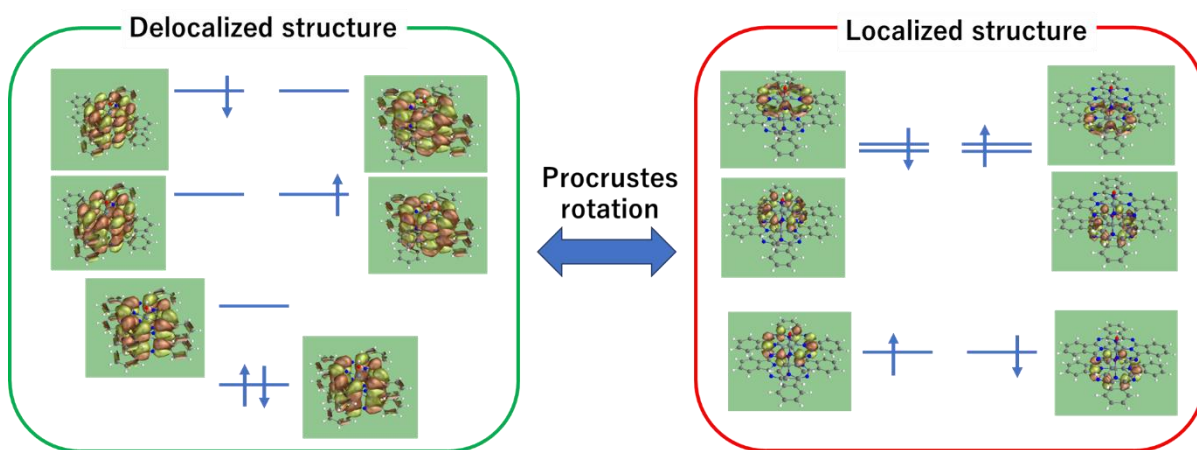


Figure: Transformation from delocalized electronic structure to the localized one

«Results and Discussion»

By calculating the configuration interaction using the localized molecular orbitals obtained through Procrustes transformation, we found that the excited-state wavefunctions of the Pc dimer consist of the linear combination of multi-configurational linear combination of localized exciton and charge-transfer electronic configurations. Notably, the wavefunction of the singly excited state was consistent with the wavefunction model reported in previous studies. This result demonstrates that combining the CAS-SCF method with Procrustes localization procedure is a novel and effective approach for analyzing localized electronic structures in the excited states of molecular dimers.

Using this computational protocol, we proceeded to calculate the two-electron excited states. At the CAS-SCF level, the computed excitation energies deviated significantly from experimental values, and the ordering of electronic configurations did not align with chemical intuition. However, by

introducing dynamic correlation through the CAS-PT2 method and the MCP-DFT method, the ordering of excited states was corrected, and the excitation energies became closer to experimental observations. These results revealed the importance of dynamic correlation effects in large molecular systems such as Pc dimers.

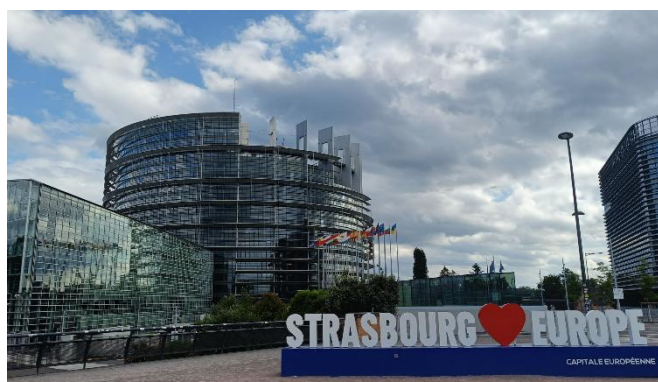
Finally, we have successfully established a quantum chemical methodology that enables both quantitative and qualitative analysis of the excited states of Pc dimers based on ab-initio wavefunction theory. Further improvements for calculation accuracy are expected by expanding the active space and basis sets for aiming well-reproducing experimental values.

«Life at Strasbourg»

Strasbourg is a city located in the Alsace region near the border between France and Germany. It is rich in both cultural heritage and natural beauty. The city is clean, safe, and well-organized, with highly convenient public transportation, making it a comfortable place to live even for Japanese. Additionally, as the seat of the European Parliament, Strasbourg holds significant political importance within Europe.

The University of Strasbourg is located near the city center, surrounded by variety of restaurants and supermarkets, which made daily life convenient. However, most signage and communication were in French, and English was not always understood. As a result, I often relied on recommendations from laboratory members in host institute and enjoyed the process of discovering and trying new items—an experience that felt like a kind of “treasure hunt”.

During the summer, Strasbourg has long daylight hours, with the sun rising around 6 a.m. and setting around 10 p.m., allowing us to live relax and extend daily time. A large natural park was located near my dormitory, and I developed a habit of going for a run almost every morning before going to the lab. My research schedule was generally healthy and consistent, starting around 8–9 a.m. and finishing by 7 p.m. The lab, being focused on theoretical calculations, fostered active discussions involving mathematical formulations, which was both new



and fascinating for me. For meals, I often used the university cafeteria, which offered nutritious and filling dishes for just 3 €.

During my stay, I had the opportunity to begin a collaborative research project with Dr. Giovanni Li Manni at the Max Planck Institute in Stuttgart. I also participated in local conference organized by my host laboratory. These experiences allowed me to build valuable connections within the European research community, making this long-term overseas research program a highly meaningful and beneficial step in my academic career.

Acknowledgements

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