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学 位 論 文 内 容 の 要 旨

博士 (環境科学)

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学 位 論 文 題 名

Spectroscopic investigations of photothermal and photochemical activities of electron donor-acceptor molecular dyads

(電子ドナー・アクセプター連結分子による光熱変換および光化学反応についての分光学的研究)

This thesis emphasizes on the regulation and control of photochemical and photothermal functions of simple electron Donor-Acceptor (D-A) molecular dyads. Electron transfer is one of the extensively investigated phenomena in basic science, which is by considering its vital role in natural and artificial photosynthesis. Despite, several complex electron transfer systems developed for light-harvesting by mimicking the natural photoinduced electron transfer process, simple electron transfer systems are continuously sought after for improving the efficiency of solar energy harvesting and developing molecular sensors. In this work, I design and synthesize two classes of novel electron D-A dyads; one for the efficient photothermal energy conversion, and the other for the efficient sensing of singlet oxygen ($^1\text{O}_2$) in the homogenous solution phase and in the cell microenvironment.

This thesis consists of five chapters, including the introduction to photoinduced electron transfer (chapter 1), where I summarize photoinduced electron transfer occurring in natural photosynthesis and its efficient mimicking toward the construction of various artificial solar energy harvesting systems. In the introduction chapter, I explain the classical theories of electron transfer in the designing of simple D-A dyads with efficient intramolecular electron transfer. In chapter 2, I discuss the synthesis of novel D-A systems, methods of characterization of D-A systems, and spectroscopic methods employed in the investigation of electron transfer and photothermal and sensing studies.

In chapter 3, I demonstrate the upgraded photothermal energy conversion by acridinium-based D-A dyads. Even though the conventional photothermal agents offer high energy conversion efficiency, most of them have narrow absorption bands. Therefore, broad band solar energy absorbing molecules and materials are continuously sought after. The general approach for the extension of light absorption by molecules to the entire UV-Visible-Near Infrared (UV-Vis-NIR) region is to extend the π -conjugation, which is tedious and time consuming. Thus, in this chapter, I employ a novel acridinium-based D-A dyad with highly-efficient electron transfer. The UV to blue absorbing dyad undergoes photoinduced electron transfer, followed by excited-state deprotonation to

generate its betaine form. The betaine shows appreciably long half-life and extended absorption in the UV-Vis-NIR region. The photothermal energy conversion efficiency of the dyad under blue light excitation is enhanced by illumination with long wavelength light. The dyad shows excellent photostability, making the dyad-betaine combination promising for photothermal energy conversion applications.

In chapter 4, I demonstrate the applications and principles of D-A systems to the sensing of $^1\text{O}_2$. Reactive oxygen species offer positive and negative impacts on our life-routine, among which $^1\text{O}_2$ attracts considerable attention owing to its significance to various chemical, biological, and biochemical processes. Therefore, the sensitive and efficient detection of $^1\text{O}_2$ is relevant in our daily life. The conventional fluorescence sensors of $^1\text{O}_2$ are anthracene-based electron D-A systems to which many fluorogenic sensors based on substituted anthracene are reported. However, the roles of substituents on the sensing efficiency remain largely unknown. Therefore, in chapter 4, I investigate the substituent effects on the $^1\text{O}_2$ sensing efficiency, which is with the intention to improve the efficiency and speed of $^1\text{O}_2$ detection. Here, I examine the rate of $^1\text{O}_2$ sensing by three anthracene-based electron D-A dyads, aminocoumarin-anthracene conjugates (**S1** and **S2**), a rhodamine-anthracene conjugate (**S3**) and a model compound. The second-order rate of reaction of the sensors with $^1\text{O}_2$ is an order of magnitude less than 9-methylanthracene. The reduced reactivity of **S1** suggests the role of the substituent on the rate of sensing.

During $^1\text{O}_2$ sensing studies involving **S1** as the sensor, I found an anomalous increase in the fluorescence intensity of **S1** under the illumination with UV light, which is after co-sensitization with a porphyrin molecule or Rose Bengal. This abrupt and colossal enhancement of fluorescence intensity suggests the formation of an intermediate complex which is UV-active. The intermediate complex shows stability against $^1\text{O}_2$ scavengers. To verify the existence of the intermediate complex between **S1** and $^1\text{O}_2$, I employ electron paramagnetic resonance spectroscopy (EPR) and nuclear magnetic resonance spectroscopy (NMR) and rationalize the crucial role of coumarin to form the complex. The steady-state absorption, fluorescence, EPR, and NMR studies suggest that the reaction of $^1\text{O}_2$ to **S1** leads to the trapping of $^1\text{O}_2$ inside **S1**. The UV stimulation activates the intermediate complex to form the end product endoperoxide efficiently and swiftly. Finally, I test the potentials of the sensors to detect the intracellular $^1\text{O}_2$ by cell imaging.