【Grant-in-Aid for Scientific Research (S)】

Broad Section E

Title of Project : Molecular Systems Chemistry for the Efficient Utilization of Photon Energy

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Research Project Number: 20H05676 Researcher Number : 90186304
Keyword : Self-Assembly, Molecular System's Chemistry, Singlet Fission, Photon Upconversion

【Purpose and Background of the Research】

Photon energy conversion materials and devices - such as semiconductor photocatalysts and solar cells- suffer from the limitation in the wavelength of sunlight that can be used. As a method for solving this problem, (1) singlet fission (SF) and (2) photon upconversion based on the triplet-triplet annihilation (TTA-UC) mechanism have been attracting attention.

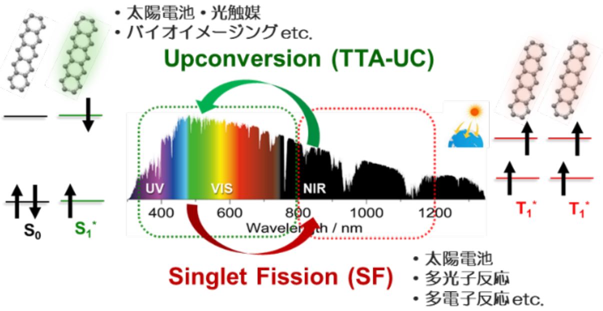

Figure 1 Photon upconversion and Singlet fission.

The study of TTA-UC phenomena has been conducted in organic media by taking advantage of molecular diffusion of the donor (D) and acceptor (A) molecules. However, the use of volatile organic solvents limits their applications. To overcome this issue, we have developed TTA-UC based on the self-assembly of acceptor molecules that harvest singlet and triplet excited energies by energy migration. We have pioneered the molecular self-assembly based TTA-UC in the visible light region in various molecular systems. On the other hand, TTA-UC from the near-infrared light (NIR) region to the visible light (VIS) region is more important, which has not yet been obtained by the molecular organization. In addition, "molecular-organized SF" based on the self-assembly of designed molecules remains an undeveloped field. In this project, we aim to achieve (1) singlet fission in well-designed, self-assembled molecular systems, and (2) NIR-to-Vis TTA-UC in self-assembled molecular systems on nanoplasmonic surfaces.

【Research Methods】

In this study, we mainly examine the following items.

(1) The concept of molecular self-assembly is introduced to the field of singlet fiction (SF). More specifically, we develop a methodology to promote SF by precisely aligning chromophores in self-assemblies. In order to improve the efficiency of SF, it is essential to simultaneously achieve (i) "asymmetric chromophore arrangement" for the efficient formation of triplet pairs and (ii) to facilitate separation of the two excited triplet states so that their recombination is avoided. To achieve both of these issues, we propose a chiral molecular organization. The SF characteristics of the chiral chromophore arrays will be evaluated by ultrafast spectroscopy, and the effect of the chiral organization on SF will be elucidated.

In addition, we will introduce nano-gap plasmonics to the field of self-assembly-based UC, and a methodology for enhancing low-intensity excitation light for NIR-To-Vis UC will be developed. The relative arrangement of D and A is defined by immobilizing Os complexes and stable organic radicals on the surface of metal nanocrystal arrays arranged at nano-gap intervals, and by depositing the acceptor self-assemblies on them.

【Expected Research Achievements and Scientific Significance】

Through the realization of molecular self-assembly-based SF and TTA-UC in the NIR-to-Vis region, a field of molecular systems chemistry will emerge that contributes to the control of the dynamics and functions of excited triplet states and the advanced utilization of light energy. It will lead to a paradigm shift in supramolecular chemistry and in photofunctional materials chemistry

【Publications Relevant to the Project】

・ Y. Yanai, N. Kimizuka, *Acc. Chem. Res.*, **50**, 2487-2495 (2017).
・ P. Bharmoria, S. Hisamitsu, Y. Yanai, N. Kimizuka et al, *J. Am. Chem. Soc.*, **140**, *34*, 10848-10855 (2018).
・ Y. Sasaki, A. H-Takagi, I. Ajioka, N. Yanai, N. Kimizuka et al, *Angew. Chem. Int. Ed.*, **49**, 17827-17833 (2019).

【Term of Project】 FY2020- 2024

【Budget Allocation】 149,900 Thousand Yen

【Homepage Address and Other Contact Information】

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