1-4-4. Triplet-Triplet Annihilation Photon Upconversion and Singlet Fission

Overview

Triplet-triplet annihilation-based photon upconversion (TTA-UC) was observed in the 1960s and has regained attention in the 2000s from the perspective of effective utilization of solar energy. In TTA-UC, two photosensitized excited triplets exothermically produce one excited singlet. On the other hand, singlet fission (SF), the reverse process of TTA, was also observed in the 1960s and has been the subject of extensive research since the 2000s aimed at improving the efficiency of solar cells. Recently, triplet pairs, which are intermediates in SF, have also attracted attention as qubits.

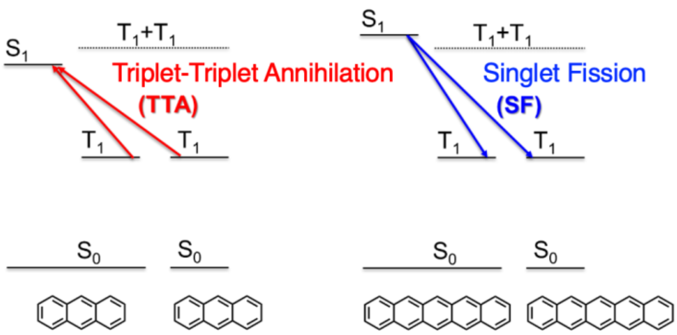

Figure 1. Mechanism of TTA and SF.

Current Status and Frontiers

Photon upconversion is a phenomenon in which low-energy light of long wavelengths is converted into high-energy light of short wavelengths. TTA-UC has attracted attention because it can utilize low-intensity excitation light, such as sunlight. While high-efficiency TTA-UC has been achieved within the visible light spectrum, such as converting green light to blue light, TTA-UCs from visible light to ultraviolet light and from near-infrared light to visible light are essential, as well, for a wide variety of applications,. In recent years, the development of superior triplet sensitizers and ultraviolet emitters has progressed, enabling the generation of ultraviolet light even from weak visible light sources such as sunlight or indoor lighting (Yanai, Kimura et al.). Additionally, examples of utilizing the high ultraviolet light energy generated by TTA-UC in photochemical reactions have also emerged (Yanai, Kerzig et al.).

TTA-UC from near-infrared light to visible light is attracting attention not only for its application in energy fields such as improving the efficiency of solar cells but also for its potential in biofields such as imaging and photodynamic therapy. An excellent sensitizer that suppresses energy loss due to intersystem crossing without using heavy

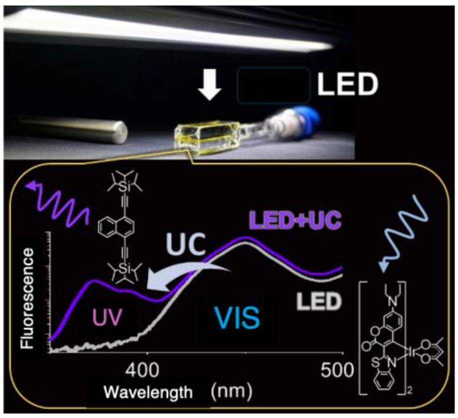

Figure 2. TTA-UC in the ultraviolet range.

metals has been developed, and by nanoparticle-izing this dye, TTA-UC-based optogenetics in vivo has been demonstrated for the first time (Yanai, Ajioka, Kimizuka et al.).

SF is a process that generates two triplets from one exciton produced by single-photon excitation, and it holds the potential to achieve a light energy conversion efficiency of 200%. Detailed analyses of the generation and annihilation of quintet excitons and spin-correlated triplet pairs, which are crucial processes for efficiency enhancement, were conducted using magnetic field effect and ESR measurements on molecular assemblies and linked dimers (Yago et al.; Nagashima, Kobori et al.; Matsui, Ikeda, Kobori et al.; Hasobe, Kobori et al.). Time-resolved ESR measurements were also performed in TTA-UC, revealing a spin conversion mechanism caused by the rapid motion of excitons (Okamoto, Sakuda, Kobori et al.).

Furthermore, using pulse ESR, it has been revealed that the triplet pairs, which are intermediates in SF, behave as qubits at room temperature (Yanai, Kobori et al.), attracting significant attention.

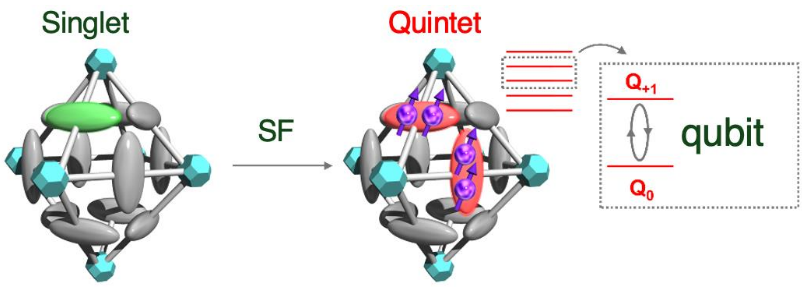

Figure 3. Generation of triplet pairs and quantum coherence at room temperature.

References

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Future Perspectives and Directions

Issues to be resolved or realized within the next 10 years: Further efficiency improvement and social implementation of TTA-UC. Development of stable singlet fission materials and their application to solar cells. Multi-spin quantum operations using light for input and readout, quantum sensing, and their expansion into the life sciences and medical fields.

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