Development of triplet functional materials based on supramolecular chemistry

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（超分子化学に基づく三重項機能材料の開発）

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論　文　内　容　の　要　旨

In recent years, various functions based on the unique properties of photoexcited triplet states have attracted much attention. Photon upconversion based on triplet-triplet annihilation (TTA-UC), dynamic nuclear polarization based on triplet states (triplet-DNP), and singlet fission (SF) are typical examples. On the other hand, these functions require multiple components to appear in the system and their assembly structures to be controlled. In this paper, we focus on the supramolecular chemistry approach to assemble multiple molecules and describe the development of supramolecular functional materials exhibiting various functions of the excited triplet state.

Photon upconversion is a technique that converts low-energy light into higher-energy light, and it has the potential to solve a wide range of energy and biology problems. Conventional upconversion processes such as two-photon absorption and multi-step excitation of rare earths require very strong excitation light on the scale of 10 W/cm^2 to collect the photon energy. In TTA-UC, the long lifetime of the excited triplet state of an acceptor generated by the energy transfer from a donor with a large absorption coefficient is utilized to increase the probability of the meeting of the two excited species, thereby realizing upconversion emission with light as weak as sunlight. However, many problems remain to be solved in the practical application of this technology, such as quenching of the triplet state by oxygen molecules in air, and aggregation of donors in the acceptor solid.

Chapter 2 describes the TTA-UC from visible light to UV light based on supramolecular assembly under practical conditions of air-saturated water. We designed an amphiphilic acceptor with fluorescence in the UV region and co-assembled it with a fatty acid in water to make a dense structure that suppresses the diffusion of oxygen. To this aggregate, a donor with absorption in the visible region were added to form a ternary supramolecular aggregate. By irradiating the aggregate with a visible laser at 445 nm, upconversion emission was observed around 390 nm in the UV region. This emission was stable for more than one hour even in a sample prepared under atmospheric conditions.

Triplet DNP is a technique to increase the sensitivity of NMR by transferring the temperature-independent non-equilibrium electron spin polarization of the excited triplet state to the nuclear spins. This technique has attracted much attention in recent years because it does not require cryogenic temperatures, unlike the conventional DNP method, which uses electron spin polarization in the temperature-dependent thermal equilibrium state. In particular, the sensitization of the NMR signal of water molecules is expected to have applications in improving the performance of biological imaging using MRI. However, pentacene derivatives, which are mainly used as a polarizing agent in triplet-DNP, are insoluble in water, making it difficult to improve the NMR sensitivity of water molecules, which makes it difficult to apply triplet-DNP to protein NMR and MRI.

Singlet fission is a phenomenon in which two excited triplet states are generated from a single excited singlet state in a system where the dyes are close together, and enables a significant increase in the generation efficiency of excited triplet states. Therefore, it is expected to improve the efficiency of functions via the excited triplet state, such as photovoltaics and OLEDs. However, these applications have focused on the property of enhanced quantum yield. The application of the unique spin properties exhibited by the pairs of triplets with strongly correlated electron spins produced by SF remains unexplored. And there have been no demonstration of the enhancement of the NMR signal by using SF-derived electron spin polarization.

Chapter 3 describes the first example of nuclear spin polarization of water molecules by using the electron spin polarization generated by SF. The aggregation state of the polarizing agent molecules was controlled in various ways in aqueous solvents using supramolecular chemistry approach. Various spectroscopic measurements revealed that the pentacene derivatives that serve as polarizers in these supramolecular assemblies have different assembly structures, and simulation results based on MD calculations suggest that the SF properties can be controlled. Their SF properties were evaluated using pump-probe transient absorption and time-resolved ESR measurements. We have succeeded in enhancing the NMR signal of water molecules more than several tens of times by using the electron polarization of SF-generated triplet as well as quintet state. In the DNP using the quintet state, the high Rabi frequency of the quintet was utilized to drive the DNP at a weaker microwave power than that of ordinary triplet-based DNP.

Chapter 4 summarizes this thesis.