# Development of photo/excited triplets based functional materials for aqueous systems

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(励起三重項状態を利用した機能性材料の水系への展開)

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## 論　文　内　容　の　要　旨

全体の概要

Recently, the interesting properties of photo-excited triplet states have attracted much attention, e.g., triplet-triplet annihilation-based photon upconversion (TTA-UC), triplet dynamic nuclear polarization (triplet-DNP), singlet fission (SF), organic light emitting diodes (OLED), and nitrogen vacancy centers (NVC). The unique properties of triplet excited states of functional molecular materials are promising for the development of novel materials. This thesis focused on the development of functional materials based on photo-excited triplet states, especially TTA-UC and triplet-DNP, for aqueous systems.

The first chapter of this thesis provided the introduction of the intriguing phenomena using photo-excited state, especially TTA-UC and triplet-DNP, and their research histories. A lot of physicists have developed fundamental researches for TTA-UC and triplet-DNP. On the other hand, a few researchers have designed molecules in terms of giving functions. The work presented in this thesis discussed the concept of developing self-assembly molecular systems with the ability to work in aqueous media. A molecular design being able to suppress the strong hydrogen bonding between water molecules is necessary to expand the applications of functional materials into aqueous media. In particular, it is important to control the interfaces between water and functional molecules to establish functional materials. In this thesis, the concept of developing self-assembled molecular systems with the ability to work in aqueous media is investigated.

Chapter 2 described the first example of an air-saturated aqueous triplet energy migration-based TTA-UC system. We made the assumption that ordered aqueous molecular self-assemblies with extended molecular networks containing interactions such as hydrogen bonding can prevent the intrusion of $O_2$ from the bulk water into the hydrophobic interior of the molecular assemblies. As a proof of concept, a novel amphiphilic acceptor was designed. Co-assemblies of this acceptor with an anionic donor show efficient triplet energy migration-based TTA-UC emission in deaerated aqueous dispersions, which was largely preserved even in the air-saturated aqueous systems

In chapter 3, a method to avoid oxygen quenching in aqueous media was discussed. This chapter introduced a simple strategy to achieve air-stable TTA-UC in water. Amphiphilic acceptor molecules and anions with long alkyl chains were co-assembled in water. The assemblies with hydrophobic donor maintained 80% of their TTA-UC efficiency in aqueous dispersion compared with that under deaerated conditions. This work demonstrated a new promising potential of supramolecular chemistry to achieve photophysical and photochemical functions with oxygen-sensitive species.

Chapter 4 described the potential of diaza-substituted acenes as air-stable and high-performance triplet polarizing agents. The introduction of electron-withdrawing diaza substituents onto pentacene and tetracene lowered the lowest unoccupied molecular orbital level and provided much improved stability under ambient conditions. Importantly, the diaza-substituted pentacene and tetracene offered similar, or even slightly better, $^1$H NMR signal enhancement to that of pentacene in a prototypical triplet-DNP test using *p*-terphenyl crystals. This work removed one of the largest obstacles in the use of triplet-DNP for the hyperpolarization of biological molecules.

In chapter 5, we demonstrated the first example of $^1$H NMR signal enhancement in pure ice state by triplet DNP with a novel water-soluble triplet polarizing agent. The ion-pairing of a triplet polarizing agent with carboxylic acid groups and hydrophilic amine is a simple method to achieve dispersibility even in an ice matrix. This concept of hyperpolarization in ice provides an important initial step towards the hyperpolarization of various biomolecules in water and even in vivo.

Chapter 6 provided a summary of this thesis and future remarks.