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# Studies on near-infrared-to-visible photon upconversion materials

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https://hdl.handle.net/2324/4475066

出版情報：Kyushu University, 2020, 博士（工学）, 課程博士
バージョン：
権利関係：

KYUSHU UNIVERSITY

（様式２）

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論 文 名　：Studies on near-infrared-to-visible photon upconversion materials

(近赤外－可視フォトン・アップコンバージョン材料に関する研究)

区　　分　：　甲

## 論　文　内　容　の　要　旨


The efficient utilization of near-infrared (NIR) photons has been coveted for energy and biological applications. As a means to produce useful high potential energy photons from the low energy photons in the NIR spectral region, tremendous effort has been devoted to the development of photon upconversion (UC) materials. Particularly, triplet-triplet annihilation-based photon upconversion (TTA-UC) is a promising strategy since it works at relatively low excitation intensity such as sunlight. However, in the conventional process, NIR-to-visible(vis) TTA-UC has been difficult due to energy losses during triplet sensitization processes. In this thesis, strategies to realize efficient triplet sensitization under NIR light irradiation are discussed.

The first chapter of this thesis overviews the important parameters for TTA-UC and the recent progress of NIR light-absorptive triplet sensitizers. Since 2015, much effort has been devoted to reduction of thermal energy loss associated with a spin-flip process of intersystem crossing (ISC). To minimize or circumvent the energy loss, new types of triplet sensitizers such as quantum dots, perovskites, and heavy metal complexes have been developed. These sensitizers successfully enabled NIR-to-vis TTA-UC both in solution-state and in solid-state. The general properties, design principles, and applications of these sensitizers are summarized.

Chapter 2 shows the first example of NIR-to-blue TTA-UC based on singlet-to-triplet (S-T) direct transition of an osmium complex. Since NIR light ($\lambda$>700 nm) shows good tissue transparency and blue light can induce chemical reactions, NIR-to-blue TTA-UC materials are expected to expand the scope of biological applications such as bioimaging, photodynamic therapy, and drug release. The energy level of an osmium complex was tuned to a blue emissive triplet acceptor, and NIR-to-blue TTA-UC was achieved for the first time. The obtained anti-Stokes shift of 0.97 eV was much larger than values obtained by the conventional TTA-UC scheme, illustrating the merit of the S-T transition.

Chapter 3 describes improvement of triplet energy transfer efficiency of an osmium complex and optogenetic genome engineering based on NIR-to-blue TTA-UC hydrogels. Excited-state lifetimes of NIR triplet sensitizers are often too short for achieving efficient TET to neighboring acceptors. A NIR-absorbing Os complex was covalently linked with energy-pooling acceptor chromophores, which significantly elongated the donor triplet excited-state lifetime and maximized the TET efficiency in an organic solvent. Importantly, TET was observed even in a viscous hydrogel. The NIR-to-blue UC dyes were hybridized with biocompatible pluronic F127, and air-stable TTA-UC hydrogels were developed. By combining Cre recombinase technology, NIR light excitation-based optogenetic genome engineering was demonstrated for the first time.

In chapter 4, heavy atom effect in osmium complexes showing S-T transition is discussed. Whereas there have been many reports on prolonged excited-state lifetimes of chromophore-combined metal complexes, heavy atom effects of the central metal on the photophysical properties of the complexes have rarely been discussed. In this work, we investigated the relationship between the structure of 3-perylenyl group-combined Os and Ru bis(terpyridine) complexes and excited-state lifetimes to understand the heavy atom effect. Importantly, we found that use of phenylene bridges effectively suppress the electronic interaction between each unit, and a complex with long phosphorescence lifetime of 80 microseconds was developed. This work offers a guide to manipulate the heavy atom effect in chromophore-combined heavy metal complexes for triplet sensitization under NIR light irradiation.

In chapter 5, recent advance in S-T transition-based TTA-UC is described. It provides a new perspective to create efficient NIR-to-vis TTA-UC materials that would boost the efficiency of sunlight-powered devices or open new classes of biological applications driven under NIR light irradiation.

In chapter 6, a summary of this thesis and future remarks were provided.