Studies on Triplet Sensitization Processes for Photon Upconversion

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https://doi.org/10.15017/4060108

出版情報：九州大学, 2019, 博士（工学）, 課程博士
バージョン：
権利関係：

（様式２）

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論 文 名　：　Studies on Triplet Sensitization Processes for Photon Upconversion
(フォトン・アップコンバージョンにおける三重項増感過程に関する研究)

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論　文　内　容　の　要　旨

Photon upconversion (UC), converting two or more photons into one higher-energy photon, has attracted fundamental and practical interests for a broad range of application from energy to biology. Among other UC mechanisms based on multistep excitation of rare-earth elements or two-photon absorption of organic molecules, triplet-triplet annihilation-based UC (TTA-UC) is immensely promising because it works with low-intensity, noncoherent incident light such as sunlight. In the conventional TTA-UC system, excited triplet states of emitter molecule are populated by triplet energy transfer (TET) from molecular sensitizers with high intersystem crossing (ISC) efficiency. This is followed by annihilation between two triplets of emitter, which produces a higher-energy excited singlet state of emitter that shows upconverted delayed fluorescence.

There are some fundamental problems related to the triplet sensitizers. The conventional sensitizer molecules harvest only a limited range of light due to their narrow absorption bands. Additionally, laborious molecular design and organic syntheses are required to obtain the sensitizer molecule with appropriate photophysical properties. Moreover, large intrinsic energy loss in triplet sensitization processes, namely ISC and TET, reduces attainable anti-Stokes shifts. The anti-Stokes shift, defined as the energy difference between excited and emitted light, is an important parameter in UC systems for practical applications.

The main focus of this thesis is to develop TTA-UC systems with new triplet sensitization processes to solve the intrinsic problems in conventional systems sensitized by common molecular sensitizers. This thesis consists of five chapters. The outlines of chapter 2 and later are described below.

Chapter 2 describes the triplet sensitization by CdSe/ZnS core-shell quantum dots (QDs) for TTA-UC. The QDs-based mechanism involves absorption of incident light by QDs, interfacial energy transfers from QDs to the triplet states of an emitter, followed by TTA. There is no significant energy loss resulting from ISC of sensitizers, which has potential to realize larger anti-Stokes shifts than that in the conventional TTA-UC systems sensitized by molecular sensitizers. In this system, a large anti-Stokes of 0.91 eV was

achieved in both solution and solid state. The surface modification of QDs with energy transmitter molecules played a key role in the efficient relay of the excited energy of QDs to emitter molecules. Interestingly, UC properties were improved with CdSe/ZnS core-shell QDs compared to CdSe core-only QDs, which should be derived from the reduced surface traps on core-shell QDs.

Chapter 3 describes the first example of visible-to-UV TTA-UC sensitized by $CsPb(Cl/Br)_3$ perovskite nanocrystals (PNCs). The mechanism and advantage of this system is similar to QDs-sensitized system. As is the case with triplet sensitization by QDs, efficient sensitization was possible only in the presence of surface-anchored transmitter molecules, resulting in high TTA-UC efficiency. The observed anti-Stokes shift reached 0.88 eV at maximum. The control experiments clarified that the appropriate triplet energy level and its binding to PNC surface are essential for transmitters to mediate interfacial TET.

Chapter 4 describes a new concept of sensitizer-free TTA-UC, where excited triplet states of emitter molecules are generated by direct singlet-to-triplet (S-T) absorption. In this system, energy-loss processes of ISC and TET are eliminated, which would further extend the attainable anti-Stokes shifts. Although the S-T absorption is spin-forbidden, modification of chromophores with heavy bromine atoms and their crystal formation allowed the population of excited triplets at incident light intensities of ~W cm^{-2}.The sensitizer-free TTA-UC was observed for crystals of brominated anthracene and perylene derivatives, which showed NIR-to-visible UC with remarkably large anti-Stokes shifts (0.96 eV at maximum).

Chapter 5 summarizes this thesis.