九州大学学術情報リポジトリ Kyushu University Institutional Repository

Studies on Triplet Energy Migration-based Photon Upconversion in Self-Assembled Molecular Systems

小川, 卓

https://doi.org/10.15017/1931868

出版情報:Kyushu University, 2017, 博士(工学), 課程博士 バージョン: 権利関係: 氏 名 : 小川 卓

論 文 名 : Studies on Triplet Energy Migration-based Photon Upconversion in Self-Assembled Molecular Systems (自己組織化分子システムにおける三重項エネルギー拡散に基づく フォトン・アップコンバージョンに関する研究)

区 分:甲

## 論文内容の要旨

Triplet-triplet annihilation-based photon upconversion (TTA-UC) has attracted much attention as the promising wavelength-upshifting technology due to its occurrence at much lower excitation intensity compared with other conventional mechanisms. In the typical TTA-UC scheme, donor (sensitizer) molecules absorb light and undergo intersystem crossing to become triplet excited state, which is followed by triplet energy transfer to acceptor (emitter) molecules. The sensitizer acceptor triplets collide to show TTA, and resulting acceptor excited singlets exhibit upconverted delayed fluorescence. For the most of applications of TTA-UC to the real-world devices, solid-state systems are highly preferable since they are free from volatile and toxic organic solvents. In such solid systems, molecules involved in TTA would not be able to diffuse freely as the ones in solution. Therefore, in order to achieve the ideal conditions, a strategy different from the conventional way is required.

In this thesis, the triplet-energy-migration-based TTA-UC (TEM-UC) in the supramolecular systems instead of the conventional molecular-diffusion-based mechanism was proposed. The main purpose of this thesis is to establish a rational design for the TEM-UC systems by utilizing molecular self-assembly.

Chapter 2 describes that the first supramolecular triplet-energy-harvesting system that shows energymigration-based TTA-UC. A newly developed lipophilic 9,10-diphenylanthracene-based emitter molecule functionalized with multiple hydrogen-bonding moieties spontaneously coassembled with a triplet sensitizer in organic media, showing efficient triplet sensitization and subsequent triplet energy migration among the preorganized chromophores. This supramolecular light-harvesting system shows the high UC quantum yield of 30% optimized at low excitation power in deaerated conditions. Significantly, the UC emission largely remains even in an air-saturated solution, and this approach is facilely applicable to organogel and solid-film systems. Chapter 3 describes that a kinetically-controlled crystal growth approach which improved the dispersibility of donors in acceptor crystals and consequently increased the efficiency of TEM-UC. We applied the kinetic control concept to improve the miscibility of donor PtOEP and acceptor DPA in nanocrystals. For this, we adopted a colloid chemistry approach; different condition of tetrahydrofuran (THF) solutions of DPA-PtOEP was injected into aqueous cetyltrimethylammonium bromide (CTAB). Upon the diffusion of injected THF solution into the aqueous phase, nucleation of water-insoluble aromatic crystals occurred. Absorption of CTAB molecules on the resulting crystal surfaces during the crystal growing process would reduce their interfacial energy, thus enhancing the dispersion stability of the crystals. It was found that increasing the concentration of DPA-PtOEP caused faster crystallization of DPA, which allowed the PtOEP molecules to be kinetically trapped in the DPA crystals with improved dispersibility.

Chapter 4 describes that ionic interactions can realize aggregation-free dispersion of donor molecules in acceptor ionic crystals without losing the high crystal regularity. As a proof-of-concept, one of the simplest anionic acceptors 9,10-anthracenedicarboxylate (ADC) was combined with dicyclohexyl ammonium (DCA) cations to form ionic crystals (DCA)<sub>2</sub>ADC. When the ionic crystals were prepared in the presence of an anionic donor, palladium mesoporphyrin (PdMesoP), the donor molecules were successfully introduced into the crystals. Remarkably, accommodated donor molecules were found to be molecularly dispersed, resulting in quantitative donor-to-acceptor TET. The impact of the crystal defects upon TTA-UC properties was proven for the first time by comparing the UC efficiency and the emission decay profiles of single crystals and mechanically-ground powder samples. This work offers a clear answer to the long-standing questions; what makes the UC efficiency in crystalline systems low, and how to rationally achieve efficient UC in solid crystals.

Chapter 5 describes that the UC efficiency can be largely improved by the introduction of a third component, highly fluorescent singlet energy collector, to the lipophilic acceptor A2 and PtOEP combination for improving the fluorescence quantum yield and avoiding the back energy transfer to the donor. In this work, we introduced, 2,5,8,11-tetra-*tert*-butylperylene (TTBP) an energy collector, whose absorption has a larger spectral overlapping with the acceptor fluorescence than that of the donor-acceptor two-component system. By the addition of TTBP, the UC efficiency was successfully improved from 4.2% to 9.0%. To understand this observation, we carried out various experiments to study the basic behavior of excitons in the condensed films. By analyzing the dynamics of acceptor singlet state, we found that the delocalized singlet excitons with a long lifetime of 29.7 ns give a significantly long singlet diffusion length of 26.1 nm. Furthermore, since the donor PtOEP and the collector TTBP are fixed in a spatially separated manner in the A2 film, the singlet back energy transfer from TTBP to PtOEP was completely suppressed, which has been difficult to achieve with the previous donor-acceptor two-component systems.

Chapter 6 summarizes this thesis and describes future prospects.