

Study on Designed Molecular Self-Assemblies for Photon Upconversion

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<https://hdl.handle.net/2324/2236177>

出版情報 : Kyushu University, 2018, 博士 (工学) , 課程博士
バージョン :

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論 文 名 : Study on Designed Molecular Self-Assemblies for Photon
Upconversion
(フォトン・アップコンバージョン機能を有する分子集合体の設計に関する研究)

区 分 : 甲

論 文 内 容 の 要 旨

Molecular self-assembly is a spontaneous association of molecules through specific and local non-covalent interactions, which ultimately lead to a structural order from the nano to macroscopic levels. Although chemists have developed numerous molecular assembled architectures, it is one of great challenging to establish molecular systems chemistry which aims to conjugate molecular self-assembly and chemical- and physical phenomena that produce useful work.

Meanwhile, triplet-triplet annihilation-based photon upconversion (TTA-UC) has attracted much attention as the promising wavelength-upshifting technology. TTA-UC consists of multi-component molecules, a donor (sensitizer) and an acceptor (emitter). Donor-to-acceptor triplet-triplet energy transfer and inter-acceptor TTA processes take place according to the electron exchange Dexter mechanism, resulting in upconverted delayed fluorescence from acceptor. As an approach to achieve efficient energy transfer processes between molecules for TTA-UC, triplet energy migration-based UC have been exploited in molecular assembly, which utilizes the diffusion triplet excitons in densely chromophore arrays. However, it remains challenging to manage for the organization of diverse multiple chromophore molecules with precise control on distance and orientation towards maximizing the use of light energy.

The main purpose of this thesis is to establish a rational design of molecular self-assembly for the triplet energy migration-based UC systems. This thesis consists of five chapters. The outline of chapter 2 and later are described below.

In Chapter 2, the strategy to solve the problems of phase separation of donors in acceptor crystals is described. In this system, a rational molecular design to molecularly disperse donor molecules in acceptor crystals was developed. A series of multiple alkyl chains modified crystalline acceptors was developed that provide both of regular acceptor alignment and soft domain of alkyl chains, which accommodates donor molecules without segregation. As a result, efficient TTET from the donor to the acceptor and diffusion of triplet excitons among regularly aligned anthracene chromophores occurred. It resulted in TTA-UC emission at low excitation intensity, comparable to the solar irradiance.

Chapter 3 describes the synthesis and TTA-UC properties of molecular cage containing anthracene chromophores. Condensation from tetraaldehyde anthracene derivatives with chiral diamine gave molecular cages by means of dynamic imine chemistry, which allow spatially arrangements of chromophore with high precision and highly emission property. Moreover, molecular cage covalently linking porphyrin as a triplet sensitizer was also synthesized, which was achieved UC emission within each single cage molecules for the first time.

In Chapter 4, the method of synthesizing coordination nanofibers by extracting the structural motif of metal-organic frameworks (MOFs) was demonstrated for the first time. The morphology of coordination nanofibers revealed clearly by direct observations using high-speed atomic force microscopy. The design approach for coordination nanofibers allows the homogeneous integration of multiple chromophores with totally different size and shape assemblies at desired compositions. Moreover, the coordination nanofibers show the appropriate molecular arrangements of diverse chromophores that effectively avoid concentration quenching and achieve efficient triplet energy migration, resulting in efficient TTA-UC emission even at the low concentration condition.

Chapter 5 summarizes the whole thesis work.