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Review

Towards efficient solid-state triplet–triplet annihilation based photon upconversion: Supramolecular, macromolecular and self-assembled systems

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ABSTRACT

Photon upconversion through sensitized Triplet–Triplet Annihilation (TTA-UC) has regained a lot of interest during the last decade mainly due to its potential for significantly increased solar energy harvesting. Other applications such as anti-Stokes fluorescence labels for bio-imaging and drug-targeting have also emerged. Considering practical large scale use of TTA-UC, solid state materials are required. The TTA-UC process depends on a sequence of energy transfer processes and it is a great challenge to maintain high efficiencies while solidifying these diffusion limited energy transfer steps. This review covers the basic, fundamental aspects of TTA-UC, but focuses on the current state of the art of the many attempts to develop solid state based TTA-UC systems. In particular, work aiming at overcoming the diffusion limit though supramolecular, macromolecular or self-assembly approaches are highlighted.

Contents

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1. Introduction

The mismatch between the solar spectrum and current day solar cell materials is one of the major reasons that photon upconversion through triplet–triplet annihilation (TTA-UC) has attracted much attention in recent years. If the low-energy range of the solar spectrum can be efficiently utilized in a photon upconversion process, this could increase the maximum efficiency for a single-junction photovoltaic device to ca 51% [1,2], well above the Shockley–Queisser limit of ca 32% found for single band-gap solar cells [3]. Thus, a photon upconversion system, incorporated in a photovoltaic device could make solar energy significantly more competitive. However, incorporation of such a system in working solar cells comes with additional design requirements, including the ability to work efficiently under natural light conditions and the need for solid state materials. This makes a photon upconversion scheme based upon TTA-UC particularly attractive, since it fulfils the diffuse light-condition. The aim of this review is to summarize the current state of the art, moving from the traditional liquid TTA-UC system relying on diffusion, towards solid state TTA-UC systems, and especially the current approaches to overcome the diffusion limit.

1.1. Triplet–triplet annihilation based photon upconversion (TTA-UC)

Triplet–triplet annihilation based photon upconversion is a bimolecular process, schematically illustrated in Fig. 1. The cascade of energy transfer reactions starts by absorption of a low energy photon by the sensitizer, which readily populates its first triplet excited state after intersystem crossing (ISC). The first energy transfer process is triplet energy transfer (TET) from the triplet excited sensitizer to a ground state annihilator, generating a triplet excited annihilator. Two triplet excited annihilators then interact in the second energy transfer process, namely triplet–triplet annihilation (TTA). Upon TTA the triplet energies are combined and a singlet excited annihilator is formed. From the singlet excited state the annihilator returns to the ground state through the emission of a photon. Overall, two low energy photons have been converted into one photon of higher energy. As such, TTA-UC utilizes long lived triplet states to temporarily store the photon energy. Since molecular oxygen effectively quenches triplet states in solution, TTA-UC systems must be thoroughly degassed to function efficiently.

When discussing and comparing TTA-based photon upconversion it is necessary to mention the most important figures of merit.

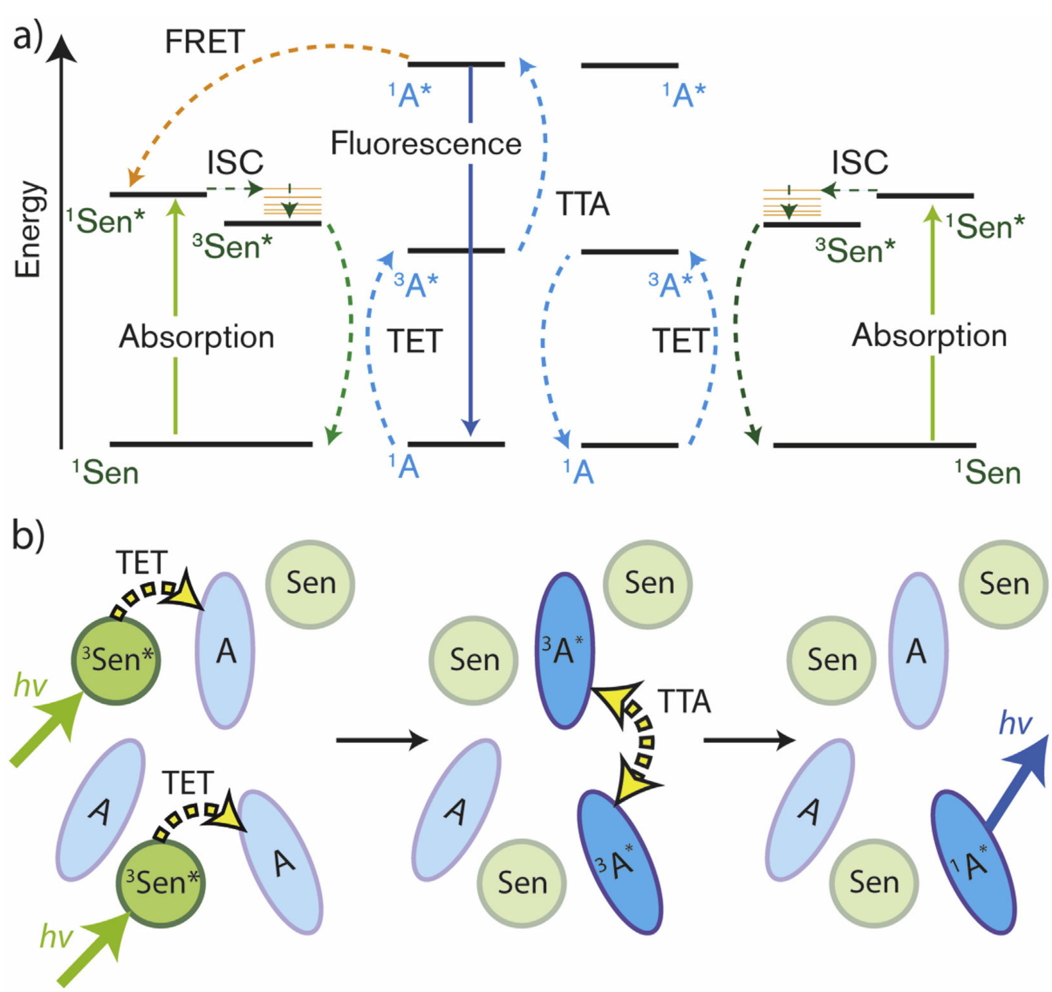

Fig. 1. The triplet–triplet annihilation (TTA) based photon upconversion process schematically illustrated in (a) a Jablonski energy level diagram and (b) a molecular representation. First a sensitizer (Sen) absorbs a low energy photon (green arrows) and populates its triplet excited state (^{3}Sen*) through intersystem crossing (ISC). Triplet energy transfer (TET) from ^{3}Sen* to a ground state annihilator generates a triplet excited annihilator (^{3}A*). Two ^{3}A* then interact through triplet–triplet annihilation (TTA), generating a singlet excited annihilator ^{1}A*, which can emit a high energy photon (blue arrow) upon relaxation back to its ground state. A possible quenching mechanism, especially relevant for many solid state systems, is singlet energy transfer from ^{1}A* to a sensitizer, often through Förster resonance energy transfer (FRET, orange dashed arrow).