Fotonų konversijos našumo didinimas sluoksniuose apjungiant medžiagų gryninimo bei gamybos iš lydalo metodą

Boost in solid-state photon upconversion efficiency through combined approach of melt-processing and purification

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Low-to-high photon energy conversion, also designated as photon upconversion (UC), can be achieved in smartly designed organic systems under low densities of non-coherent excitation (~mW/cm^2, e.g. irradiation by the sunlight),[1,2] which opens up a variety of fascinating applications such as targeted drug delivery, bioimaging, photocatalysis, labeling, stress sensing, solar energy harvesting, etc. The UC is accomplished via triplet-triplet annihilation (TTA) process in emitter (annihilator) species, where the energy of two triplets is combined to create one singlet excitation (Fig. 1). Since the direct triplet state absorption by an emitter is extremely low due to the spin-forbidden nature of the transition, TTA-UC is usually realized in bi-component systems consisting of a triplet sensitizer and an emitter. Upon absorption of incident light by the triplet sensitizer, its singlet excitation is converted into a triplet via intersystem crossing (ISC). Triplet excitons then undergo triplet energy transfer (TET) to the emitter, where triplets migrate until they encounter and annihilate. Triplet migration in solution/liquid or "soft" solids featuring low glass transition temperature is accomplished through molecular diffusion of emitter species, whereas in a true solid state with molecule position fixed it can only occur via exciton hopping mechanism [3].

In this report we address the long-standing issue of low TTA-UC efficiency in a solid state, even though order of magnitude higher efficiencies are routinely reported in a solution/liquid state. The issue is indeed topical and urgent as it hampers utilization of TTA-UC for practical applications.

Conversely to the previous, yet so far unsuccessful attempts, our combined approach enables to deliver record-high UC quantum yields (Φ_{UC} = 8±1%, out of maximum 50%) across a centimeter-sized area amorphous films of the widely-exploited benchmark TTA-UC system DPA/PtOEP. The boost in Φ_{UC} is almost 3-fold compared to previously reported maximal Φ_{UC} values of the analogous films based on the DPA-derived compounds.

The introduced combined approach relies on i) thorough emitter purification for reduced exciton quenching and ii) UC film fabrication via melt-processing for attaining large emitter concentrations with suppressed aggregation. Emitter purification via vacuum sublimation is shown to reduce the number of both singlet and triplet quenchers as confirmed by fluorescence and UC emission quantum yield measurements along with the respective transient measurements performed on nanosecond- and millisecond-time domains. Importantly, such high efficiency is accomplished in large-area amorphous films, the most preferred for practical applications, and featuring low UC threshold (≈5 mW/cm^2) that is close to the solar irradiance.

The presented approach describes the guidelines for boosting TTA-UC performance in the solid state, and generally is applicable to any conventional TTA-UC system. This is believed to accelerate the development and applications of many solid-state TTA-UC systems created so far.

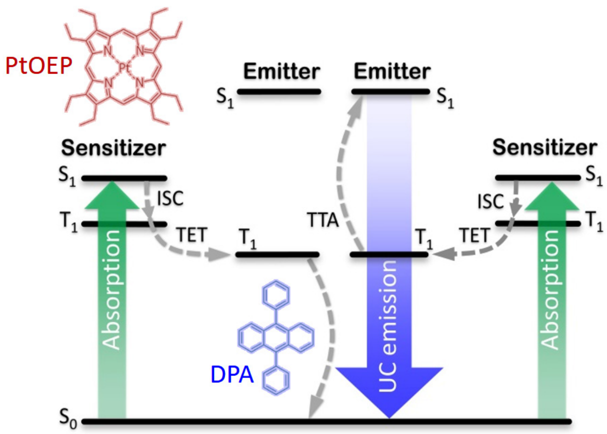

Fig. 1. TTA-UC energy scheme for the emitter/sensitizer model system DPA/PtOEP.

Keywords: photon upconversion, triplet-triplet annihilation, quantum yield, melt-processing.

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