# Near-infrared-to-visible photon upconversion via triplet-triplet annihilation of a solid-state system fabricated by rapid drying casting

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### 1. Introduction

Photon upconversion is a photophysical process of two low-energy long-wavelength photons into a high-energy photon of a shorter wavelength. Among the various methods, triplet-triplet annihilation photon upconversion (TTA-UC) have attracted substantial interest due to its potential applications in a variety of novel and active research fields, such as spectral management of sunlight for solar cells and cancer bioimaging *in vivo* [1].

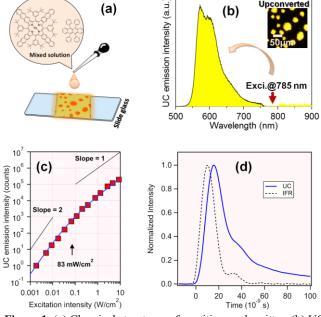
On the other hand, near-infrared-to-visible (NIR-to-Vis) TTA-UC in a solid material is an important research goal for optimizing the use of solar energy by boosting the effective efficiency of the photonic devices. In this study, we demonstrated for the first time that the  $\pi$ -extended Pd-porphyrin used NIR-to-Vis TTA photon up-conversion in binary solid by applying the rapid drying casting method.

#### 2. Results and discussion

Microparticles of the binary solid were fabricated by using the rapid drying solution casting method from the mixed solution of NIR sensitizer (PdTPTAP, Fig. 1a, 11  $\mu$ M) and emitter (rubrene, 11 mM) in tetrahydrofuran onto a flat slide glass under Ar environment. After drying, numerous spherical amorphous microparticles were obtained on the slide glass surface and were found to show yellow (~570 nm) UC emission by the NIR-continuous wave excitation at 785 nm (Fig. 1b). The threshold intensity  $(I_{th})$ , defined as the excitation intensity of the crossing point of the quadratic and first-order dependencies, it was characterized for individual particles under the microscope and revealed a low  $I_{\rm th}$  (~0.1W/cm<sup>2</sup>) as compared to the solution systems (Fig. 1c). The UC quantum yield (QY) of individual particles was measured under the same microscope and the UC-QY of particles was estimated to be  $(0.5\pm0.1)\%$  as the average of more than 40 individual microparticles [2].

The elementary processes (such as intersystem crossing (ISC), triplet energy transfer (TET), and fluorescence QY of solid-state rubrene) contributing to the UC-QY were investigated by time-resolved and/or steady-state spectroscopies. The ISC efficiency of PdTPTAP was found to be unity by femtosecond transient absorption spectroscopy [2]. The triplet lifetime with TET was determined by measuring the rise of the UC emission intensity. As shown in Fig. 1d, the time profile of UC emission of the microparticles excited by 800-nm, 13-ns laser pulses showed an extremely fast rise and decay in tens of nanoseconds. The fluores-

cence QY of amorphous rubrene was investigated by the relative method and found to be 1.5%. Above results clarified the fluorescence quantum yield of amorphous rubrene was responsible for limiting the UC-QY. The detailed discussion of the characterization of each photophysical process will be made on presentation.



**Figure 1.** (a) Chemical structures of sensitizer and emitter. (b) UC emission from the binary solid and UC microphotograph (insert). (c) The excitation-intensity dependence of the UC emission intensity. (d) Normalized time profile of the UC emission (blue) and the instrument response function (IRF, black dotted).

## 3. Conclusions

NIR-to-Vis (from 785 nm to  $\sim$ 570 nm) TTA photon upconversion was developed in a binary solid that was fabricated by the rapid drying casting. The UC characteristics of the individual microparticles of the system were evaluated under microscopy. The elementary processes were investigated by time-resolved/steady-state spectroscopies.

#### References

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