Triplet-triplet annihilation upconversion in binary solids fabricated by solution casting

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Triplet–triplet annihilation upconversion (TTA-UC) has attracted considerable attention because of its high quantum yield at low excitation intensity close to sunlight. TTA-UC in solid state is important for future device applications although the UC emission quantum yield (Φ_{UC}) is still low and high excitation intensity is needed compared to the solution system where molecular diffusion plays a crucial role for triplet energy transfer (TET) from the sensitizer to emitter and TTA between emitter triplets [1]. This is true especially for binary crystal systems where sensitizer is involved in the matrix of emitter. Previously, binary solid fabricated by deposition [2] and co-crystallization [3] were reported to show poor UC performance because of segregation of sensitizer from the emitter matrix, which spoiling TET from sensitizer to emitter. If the segregation problem is overcome, binary crystal can be an ideal system for TTA because fast triplet exciton migration due to the crystal regularity and dense packing lead efficient TTA. To the end, we applied *rapid-drying solution casting* from mixed solution containing dilute sensitizer (Pt-octaethylporphyrin, PtOEP**)** and nearly saturated emitter (9,10-diphenyanthracene, DPA or its cyclic alkyl derivative, C7-sDPA, Fig. 1). This nonequilibrium approach is expected to inhibit macroscopic segregation because of fast crystallization of emitter matrix before the sensitizer segregates. C7-sDPA was selected because of its excellent photostability [4] and superior TTA yield than DPA in solution.

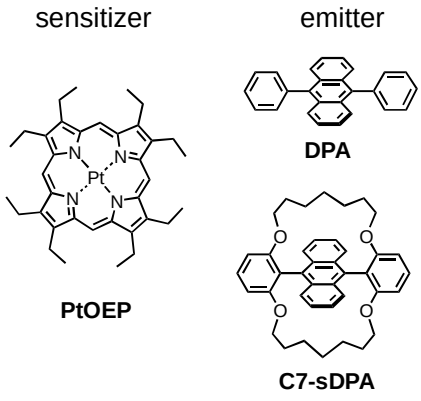

Figure 1. Chemical structures.

Binary crystal sample was prepared by the drop casting on a glass plate from the mixed solution with molar ratio around [sensitizer]:[emitter]=1:1000 in tetrahydrofuran. The cast sample consisted of microcrystals in different shape and characteristic, so all spectroscopic

measurements were carried out under an optical microscope (20× objective lens).

Among the microcrystals formed, some showed clear blue emission by 6-W/cm^2 excitation at 532 nm (Fig. 2) under air for both PtOEP:DPA and PtOEP:C7-sDPA systems. The emission spectra (not shown) match with the fluorescence spectra of the emitters in powder form, demonstrating efficient TTA-UC in binary crystals.

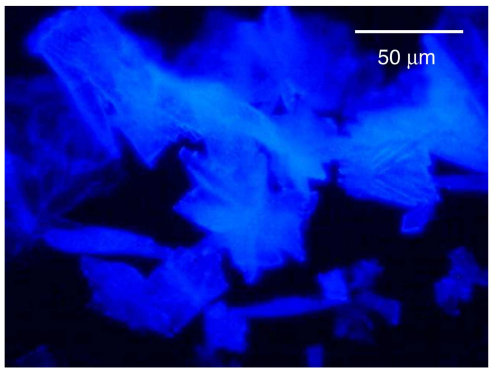

Figure 2. Upconverted emission from PtOEP:C7-sDPA binary microcrystal under cw excitation (532 nm).

Excitation-intensity (I_{ex}) dependence measurement of the upconverted emission of single microcrystal clarified the threshold intensities (I_{th}) at which the quadratic and linear dependences are crossing. The I_{th} obtained by using the curve fitting was 0.2–7 W/cm^2 for PtOEP:DPA and 5–24 mW/cm^2 for PtOEP:C7-sDPA (Fig. 3), depending on the microcrystals[5]. The I_{th} of PtOEP:C7-sDPA close to sunlight (~1 mW/cm^2 for 532±5 nm).

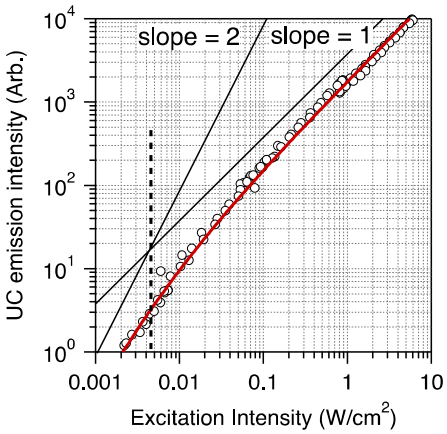

Fig. 3. Excitation-intensity dependence of the upconverted emission from a microcrystal of PtOEP:C7-sDPA (circle) with the curve fit (I_{th} = 4.6 ± 2.2 mW/cm^2). The slope lines are eye guides.

The Φ_{UC} of individual microcrystals was characterized under the microscope by using rhodamine 101 in ethylene glycol (Φ_f 0.94) as reference. We use the definition of Φ_{UC} in which 100% means the full conversion. The Φ_{UC} was ~2% for PtOEP:DPA and ~20% for PtOEP:C7-sDPA. These Φ_{UC} did not vary under Ar and air, suggesting oxygen cannot penetrate into the microcrystals. This very high value of Φ_{UC} for PtOEP: C7-sDPA as solid state, comparable to those in degased solution systems, was achieved by better dispersion of PtOEP in the matrix, supported by absorption spectroscopy, high-resolution spectrograph, and transmission electron microscopy. These results demonstrate that the dispersion of the sensitizer is crucial issue and can be achieved by a simple technique such as rapid-drying solution casting. Other derivatives of emitter will also be reported at the presentation.

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