

## Supporting Information on

# Triplet-triplet annihilation upconversion through triplet energy transfer at a nanoporous solid-liquid interface

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### References

### S1. Curve fitting of phosphorescence decay

The decays of phosphorescence emission of the PtCP-fixed nano-porous glass immersed in neat toluene and in DPA solution in toluene are shown in Fig. S1(a) and Fig. S1(b), respectively.

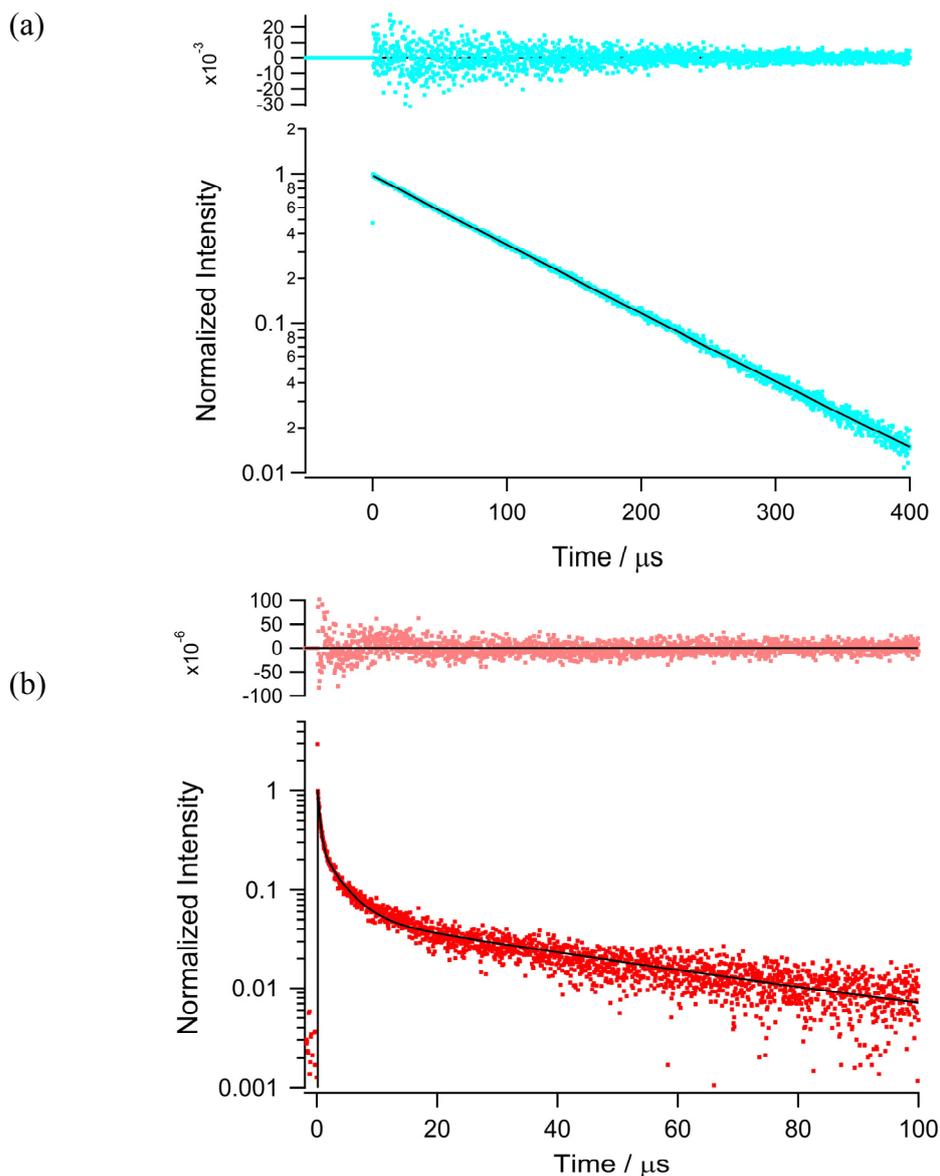


Fig. S1. Phosphorescence decay curves of the PtCP-fixed nano-porous glass immersed in neat toluene (a) and in DPA solution in toluene (b). Fitting curves based on  $y(t) = A \exp(-t/\tau)$  for (a) and  $y(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$  for (b) are shown in black curve. The residuals are shown on each top.

## S2. Curve fitting to the time-resolved upconversion (UC) emission data

The time profile of UC emission of PtCP-fixed nano-porous glass immersed in solution was analyzed by various kinetic models. The result of curve fitting with Eq. 11 in the main text was shown in Fig. S1. The values of  $\tau_{3S}$  and  $\tau_{3E}$  were obtained to be 0.57 and 75.2  $\mu\text{s}$ , respectively (Fig. S2(a)). However, the fitting curve failed to reproduce the rise part in the range of 0-2  $\mu\text{s}$  as shown in the wavy residual at the time range (Fig. S2(b)).

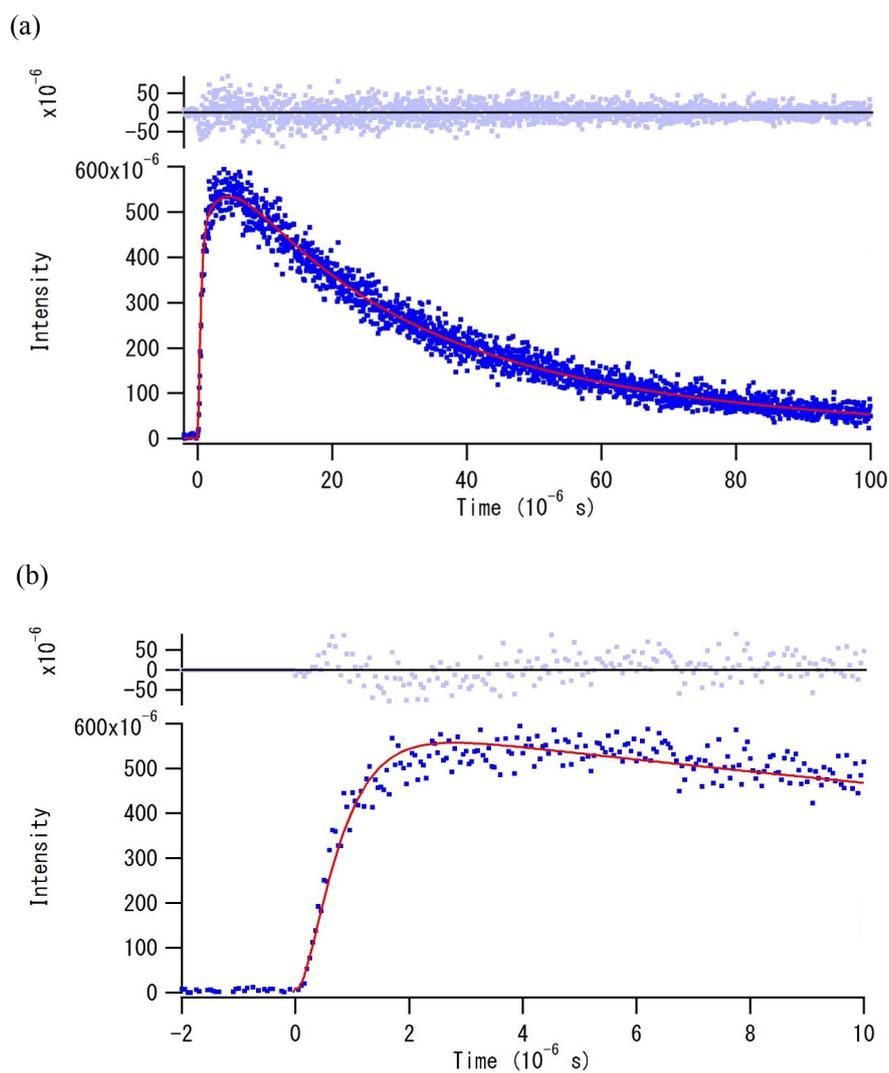


Fig. S2. Time-resolved UC emission profile of PtCP-fixed (150  $\mu\text{M}$ ) nano-porous glass immersed in DPA solution (15 mM) and the fitting curve based on Eq. 11 for (a) long time range (-2–100  $\mu\text{s}$ ) and (b) short time range (-2–10  $\mu\text{s}$ ) with the residuals (top of each plot in tint color).

The model was improved by introducing two TET paths (A and B) with Eqs. 12-14. The result of curve fitting (Fig. S3) successfully reproduced the observed data with flatter residual as in Fig. S3(b) in the time range of 0-2  $\mu\text{s}$ . The obtained lifetimes of the two rise components were  $\tau_{3SA} = 0.35 \mu\text{s}$  and  $\tau_{3SB} = 3.49 \mu\text{s}$ . The other parameters were obtained as  $\tau_{3E} = 165 \mu\text{s}$  and  $k_{TTA} = 1.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ . The same model but with a single rise component was also tried and then gave the deviation at the time range of 0-2  $\mu\text{s}$  as in Fig. S2(b).

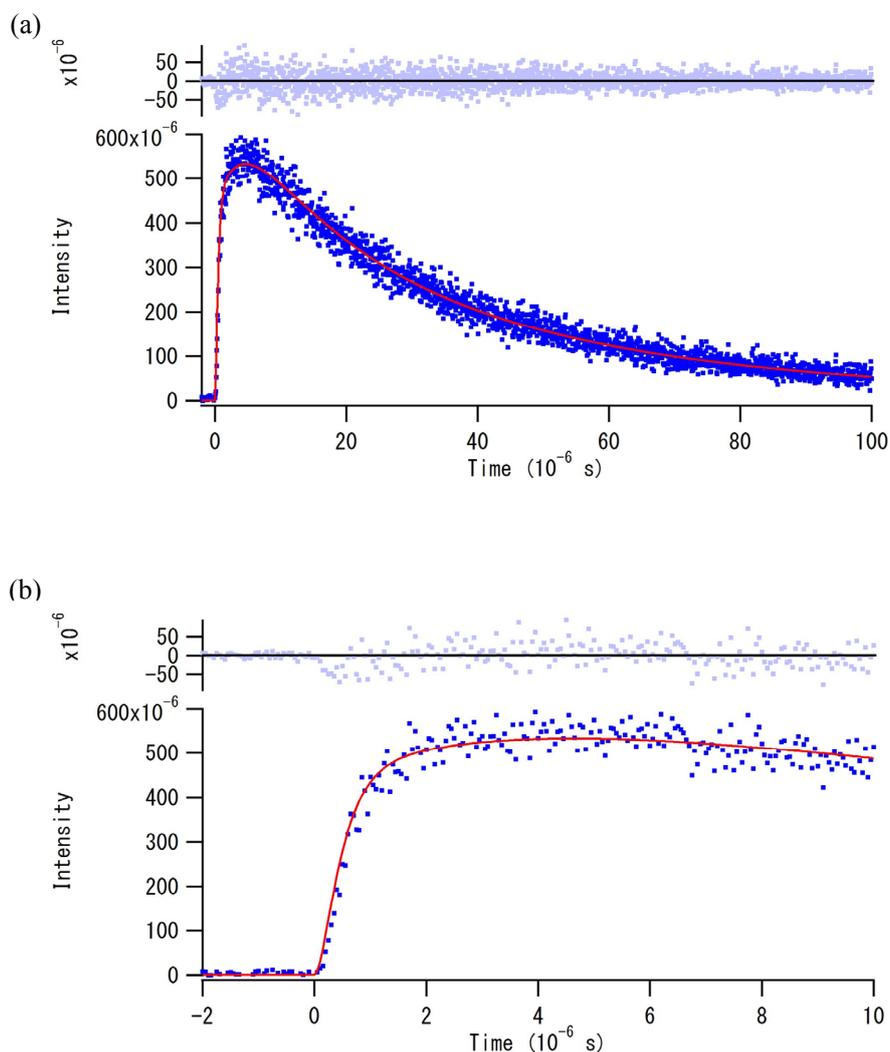


Fig. S3. Time-resolved UC emission profile of PtCP-fixed nano-porous glass immersed in DPA solution (The same data in Fig. S1) and the fitting curve based on Eqs. 12-14 for (a) long time range ( -2–100  $\mu\text{s}$ ) and (b) short time range (-2–10  $\mu\text{s}$ ) with the residuals (top of each plot in tint color).

The decay of phosphorescence and UC emission of the PtCP-fixed nano-porous glass in DPA solution obtained for the long-time range is shown in Fig. S4.

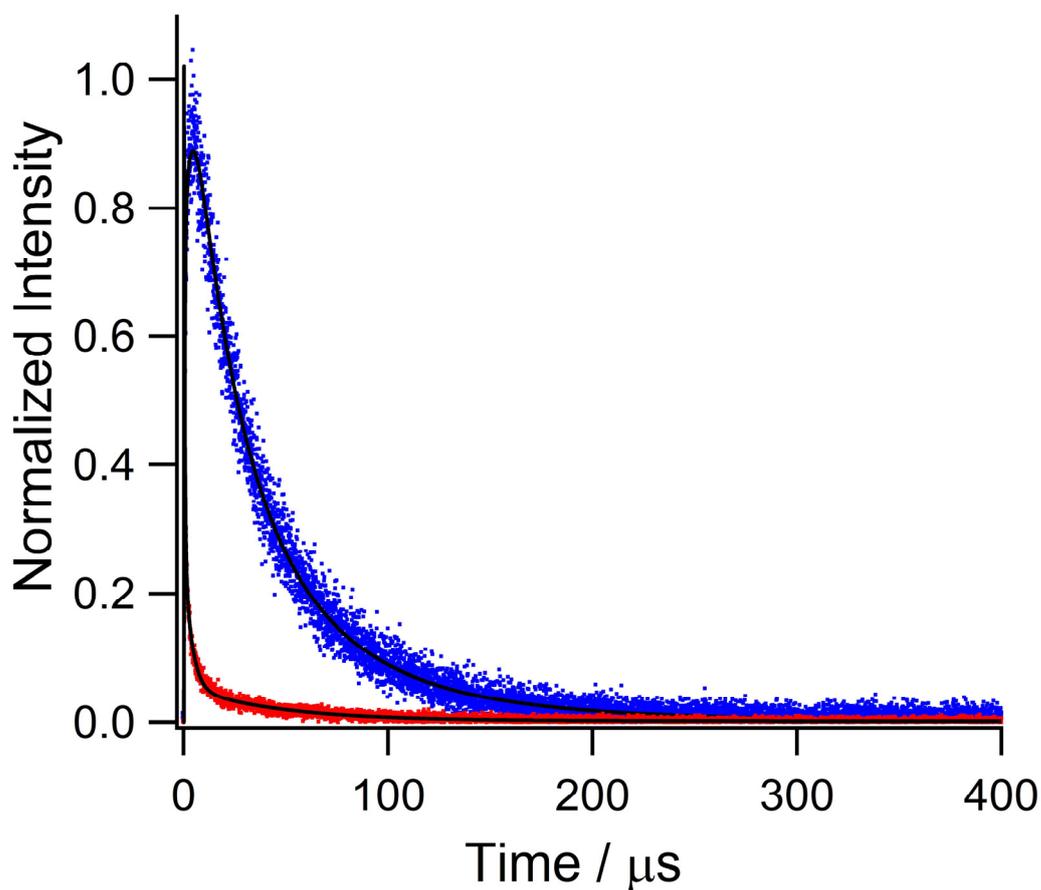


Fig. S4 Time profiles of phosphorescence (red dots) UC emission (blue dots) of the PtCP-fixed nano-porous glass in the DPA solution measured for long range with fitting curve (black line).

### S3. Monomer and dimer phosphorescence of PtCP fixed on the porous glass

The PtCP-fixed nano-porous glass (66  $\mu\text{M}$ ) was hold in a 1-mm quartz cuvette and was measured, (1a) dry condition in air, (1b) in Ar, (2a) immersed in THF air saturated, (2b) Ar bubbling, (3a) immersed in DPA/toluene solution air saturated, and (3b) Ar bubbling. Ar-replacement/bubbling was performed 15 min for each. The DPA/toluene solution was used for the experiment. The concentration was 9.3 mM, estimated by measuring the UV-

vis absorption spectrum of the 10x diluted solution.

An experimental setup was described in “Steady-state spectroscopies section” in the main article.

Fig.S5 shows over all view of the emission spectrum of the sample in dry condition, in neat toluene, and in DPA/toluene solution. It seems that the dimer emission around 780 nm does not exist for the sample in dry and in neat toluene.

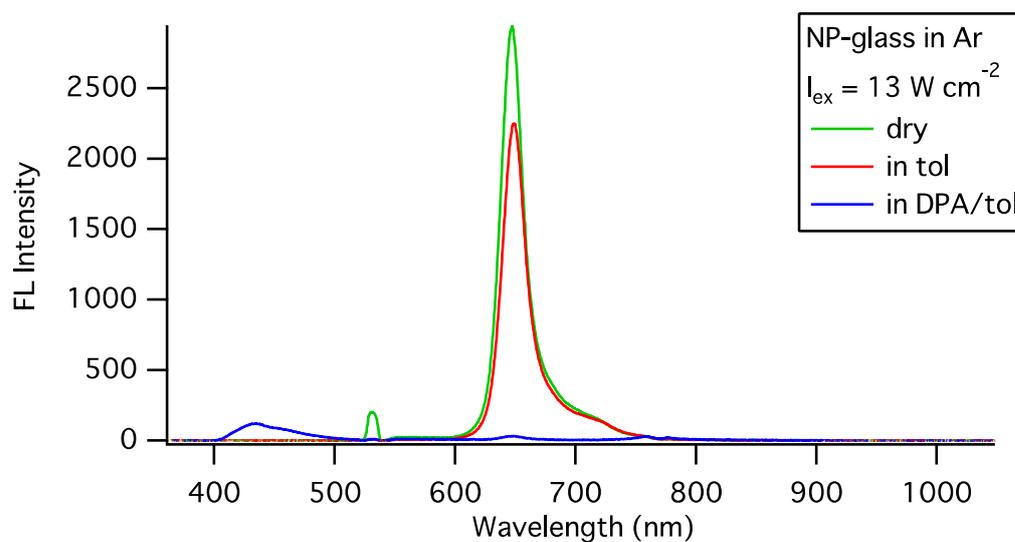


Fig. S5. Emission spectrum of the nano-porous glass sample excited at 532 nm in Ar atmosphere.

However, close look of the spectra (Fig. S6), the spectra in dry and in neat toluene shows a shoulder and a small peak at the same wavelengths of the dimer emission peaks (759 and 776 nm, respectively) in DPA/toluene solution, with the similar magnitudes.

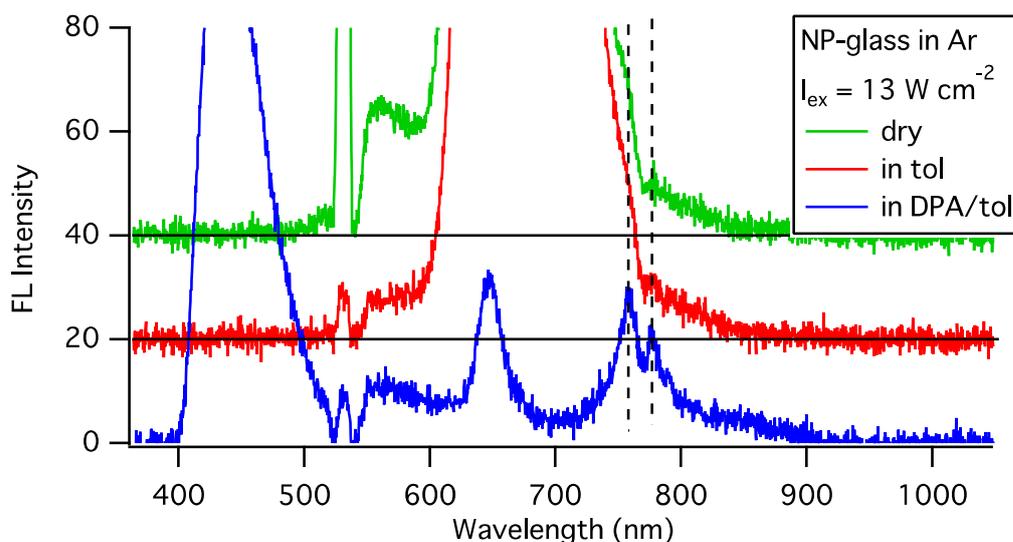


Fig. S6. Vertical magnification of the spectra in Fig. S5 shown with offsets.

This correspondence of the shoulder and peaks suggest that the dimer emission spectrum overlays the monomer spectrum. To confirm this hypothesis, spectral subtraction of the dimer emission from the spectra in dry condition (Fig. S7).

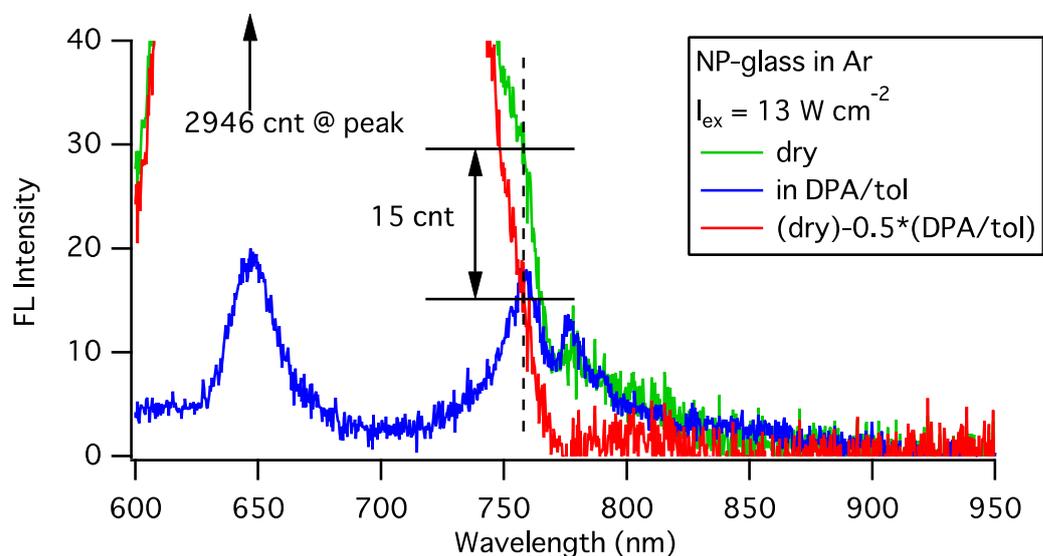


Fig. S7. Subtraction of the dimer emission from the spectrum in dry with a factor of 0.5.

The spectral edge of the obtained differential spectrum (red) was reasonably smooth. This strongly supports that the dimer emission overlays on the monomer emission. The ratio of peak intensities of the dimer emission to the monomer emission is estimated as 15 count: 2946 count (Fig. S7) =  $\sim 1:200$ . Here, the contribution of the dimer peak was calculated from the difference between the original spectrum in dry (monomer+dimer) and the differential spectrum (only monomer). Thus, it is concluded that the dimer emission exists even for the sample in dry and in toluene, but it is not significant because the intense monomer emission covered it. By adding DPA, quenching the monomer emission by TET, thus the dimer emission became prominent because the energy level of the dimer is too low to cause TET and quenching.

#### **S4. Self-absorption correction procedure of $\Phi_{UC}$**

In UC system, the emission wavelength is shorter than the absorption one; therefore, self-absorption correction was necessary for proper measurements of UC-QY [1, 2]. First, emission spectra containing UC emission and PtCP phosphorescence were measured with and without the integrating sphere. The obtained spectra were normalized for the dimer phosphorescence peak (775 nm), which were not affected by self-absorption. The self-absorption correction coefficient,  $a$ , was obtained from the ratio of the spectral areas with and without the integrating sphere. The corrected UC-QY ( $\Phi_{UC}^{crd}$ ) was calculated by using the following equation: [2]

$$\Phi_{UC}^{crd} \approx \frac{\Phi_{UC}^{obs}}{1 - a} \quad (1)$$

where,  $\Phi_{UC}^{obs}$  was as-observed QY.

UC quantum yield of a piece of PtCP-fixed glass in DPA/toluene solution and PtOEP in DPA/toluene solution (*i.e.* mixed solution) before and after self-absorption correction are shown in Figs. S8(a) and (b).

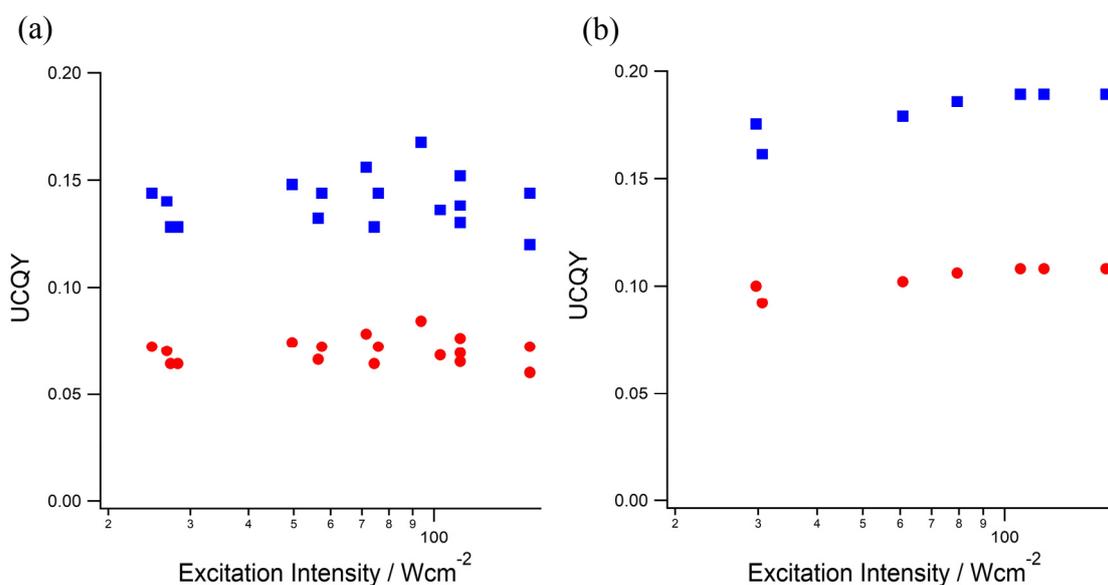


Fig. S8. Upconversion quantum yield (UC-QY) of (a) PtCP-fixed glass immersed in DPA solution in toluene and of (b) PtOEP-DPA solution in toluene (*i.e.* mixed solution) with different excitation light intensities at 532 nm in Ar before (red circles) and after (blue squares) self-absorption correction. The concentrations of PtCP, PtOEP and DPA were 180  $\mu\text{M}$ , 180  $\mu\text{M}$  and 18 mM, respectively.

### S5. Excitation intensity dependence of the phosphorescence and UC emission intensity of the all-solid hybrid system

Excitation intensity dependence of the phosphorescence and UC emission intensities of the all-solid hybrid system was shown in Fig. S9. The dependence of the phosphorescence and UC emission intensities were linear (slope = 1.0) and almost quadratic (slope = 1.9), respectively, between 2.9 and 11 W/cm<sup>2</sup>.

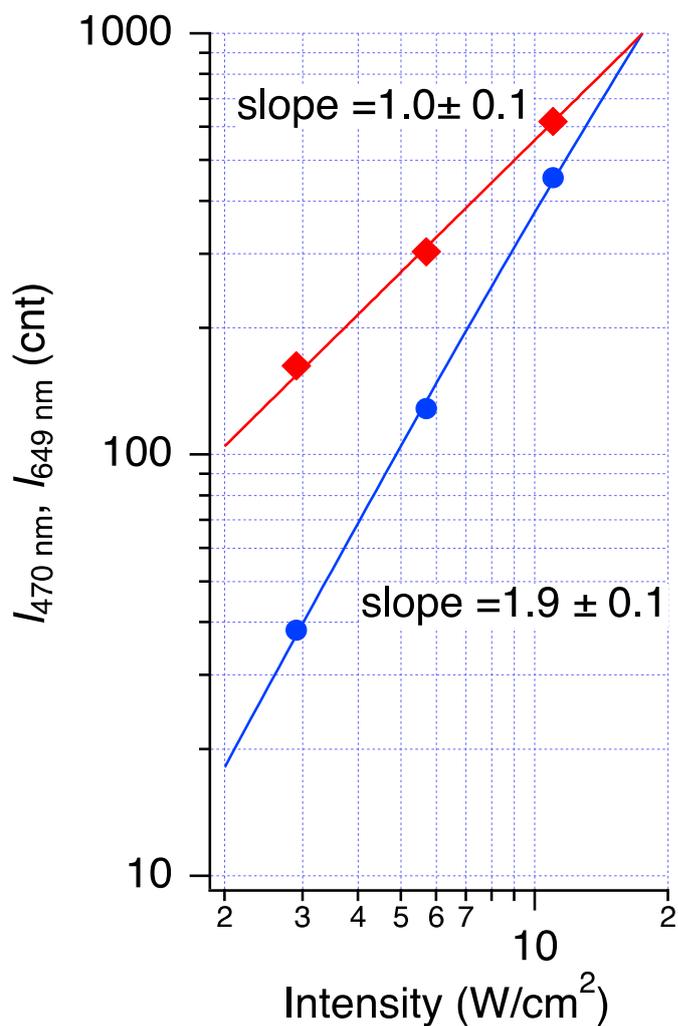


Fig. S9. Excitation intensity dependence of the phosphorescence (red diamond) and UC emission (blue circle) intensities of the all-solid hybrid system

### References

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- [2] N. Yanai, K. Suzuki, T. Ogawa, Y. Sasaki, N. Harada, N. Kimizuka, *J. Phys. Chem. A*, 2019, **123**, 10197.