Supporting Information

Photon Upconversion through a Cascade Process of Two-Photon Absorption in $CsPbBr_3$ and Triplet-Triplet Annihilation in Porphyrin/Diphenylanthracene

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This supporting information presents the following contents.

Analysis of Quenching

The cause (i): the decrease of excitation light power due to the absorption of PtOEP was calculated by the following equation.

$$f(c) = \frac{\int_0^L A \cdot 10^{-(\alpha+\varepsilon c)x} dx}{\int_0^L A \cdot 10^{-\alpha x} dx} \qquad \text{(S1)}$$

A is the sensitivity factor associated with the photoluminescence experimental setup including the optical geometry and electric circuit, which is regarded as a constant. The L, α, ε, and c are the optical path of a quartz cell (1 cm in the present case), the linear absorption coefficient of PQD colloidal solution at the excitation wavelength (450 nm, 3.40 cm^{-1}), and the extinction coefficient of PtOEP at 450 nm (2.16×10^3 M^{-1} cm^{-1}, see Figure S5), and the concentration of PtOEP (M), respectively. Accordingly, eq S1 gives the fraction of excitation light intensity absorbed by PQD without the contribution from PtOEP. This equation is analytically solved as

$$f(c) = \frac{\alpha}{\alpha + \varepsilon c} \cdot \frac{1 - 10^{-(\alpha+\varepsilon c)L}}{1 - 10^{-\alpha L}} \quad . \qquad \text{(S2)}$$

Although the PtOEP absorption is less than 1% compared to that of PQD at c = 0.02 mM, the attenuation effect is not negligible at c = 0.5 mM (24%). The intensity of PQD photoluminescence in Figure 3a was divided by eq S2 and shown as the compensated SV plot in Figure 3b.

The cause (iii): trivial energy transfer (reabsorption of PtOEP) was calculated by the simple Beer-Lambert law as follows.

$$h(c) = 10^{-\varepsilon' cL/2} \qquad \text{(S3)}$$

The ε' is the extinction coefficient of PtOEP at the photoluminescence maximum of PQD (514 nm) and given by 5.09×10^3 M^{-1} cm^{-1} (Figure S5). The denominator of 2 for L means that the excitation light is exposed at the center of the cubic cell (1×1 cm^2) and the photoluminescence is monitored in the perpendicular direction, which leads to the average optical path length of 0.5 cm from the excitation to the escape from the cell.

Analysis of TPA quantum yield

Based on the wavelength (λ = 800 nm), the incident power (P = 0.7 W), the radius (R = 0.1 cm), the repetition rate (f = 1 kHz), and the pulse width (Δt = 130 fs) of the fs laser, the incident photon density (I_0) is calculated to be 1.11×10^{29} photon cm^{-2} s^{-1} through

$$I_0 = \frac{P}{f \cdot \frac{hc}{\lambda} \cdot \pi R^2 \cdot \Delta t}, \quad \text{(S4)}$$

where h and c are the Planck constant and the velocity of light, respectively. A Gaussian-shaped laser profile is simplified as a rectangular shape.

The concentration of $CsPbBr_3$ after centrifuge ($N_{CsPbBr3}$) was evaluated by measuring the change of the solution weights before and after centrifuge, affording $N_{CsPbBr3} = (2.37 \pm 0.14) \times 10^{-3}$ M (in a Pb base unit, averaged over eight time measurements). Assuming the size of cubic shaped PQD (L_{PQD} = 8 nm) and the averaged Pb-Pb distance (d_{Pb} = (0.8207+0.8255)/4 = 0.412 nm), the concentration of PQD (N_{PQD}) was calculated to be $(0.323 \pm 0.020) \times 10^{-3}$ M (in a PQD unit) through

$$N_{PQD} = \frac{N_{CsPbBr3}}{\left(\frac{L_{PQD}}{d_{PQD}}\right)^3}. \quad \text{(S5)}$$

The rate equation of TPA in the absence of the first-order absorption process (α = 0 for $h\nu < E_g$) is given by

$$\frac{dI}{dz} = -\beta I^2, \quad \text{(S6)}$$

where I, β, and z are the photon density (photon cm^{-2}), the TPA coefficient (cm photon^{-1}), and the distance from the front of a quartz cell (cm), respectively. The β is given by 10^{-3} N_A N_{PQD} σ_{TPA}, where the N_A is the Avogadro's number and the σ_{TPA} is the TPA cross section. Eq. (S6) is analytically solved, yielding

$$\frac{I(z)}{I_0} = \frac{1}{\beta I_0 z + 1}. \quad \text{(S7)}$$

By using $\sigma_{TPA} = \sim 1 \times 10^6$ GM ($= \sim 1 \times 10^{-44}$ cm^4 s photon^{-1}) at 800 nm (W. Chen et al. *Nat. Commun.* **2017**, *8*, 15198) and optical length ($z = L$ = 1 cm), the TPA quantum yield (φ_{TPA}) in the optimal solution at the given excitation power was calculated to be 0.30 via

$$\varphi_{TPA} \equiv \frac{\Delta I}{2I_0} = \frac{I(z) - I_0}{2I_0} = \frac{1}{2} \cdot \frac{\beta I_0 z}{\beta I_0 z + 1}. \quad \text{(S8)}$$

The denominator 2 is arisen from the two photon process (the mathematical maximum of φ_{TPA} is 0.5). The $\Delta I/(2I_0)$ was experimentally measured to be 0.21, which is in reasonable agreement with the calculated φ_{TPA}. Note that emission quantum yield of PQD is not included in the φ_{TPA}.

Supporting Table

Table S1. Tri-exponential analysis of picosecond lifetime spectroscopy of PQD with PtOEP in degassed toluene (λ_{ex} = 377 nm).[a]

PtOEP / mM	τ_1 (ratio) / ns	τ_2 (ratio)/ ns	τ_3 (ratio)/ ns	τ_{ave} / ns [b]	χ^2
0	28.3 (32.9%)	6.64 (29.4%)	225 (37.7%)	96.1	4.73
0.01	27.4 (34.3%)	6.43 (29.1%)	217 (36.5%)	90.4	4.08
0.02	26.1 (34.5%)	6.16 (30.4%)	202 (35.1%)	81.9	3.60
0.05	26.3 (34.7%)	5.98 (32.0%)	199 (33.4%)	77.5	3.28
0.1	25.2 (34.8%)	5.82 (31.9%)	193 (33.3%)	74.8	3.12
0.2	24.3 (35.0%)	5.43 (32.8%)	187 (32.2%)	70.7	2.86

[a] $B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$.

[b] $\tau_{ave} = (B_1 \cdot \tau_1 + B_2 \cdot \tau_2 + B_3 \cdot \tau_3)/(B_1 + B_2 + B_3)$

Table S2. Laser intensity (I_0) dependence of picosecond lifetime spectroscopy of PQD in degassed toluene (λ_{ex} = 377 nm).[a]

I_0 / nJ cm^{-2}	τ_1 (ratio) / ns	τ_2 (ratio)/ ns	τ_3 (ratio)/ ns	τ_{ave} / ns [b]	χ^2
3.18	70.4 (32.1%)	16.5 (50.7%)	343 (17.2%)	90.1	1.31
2.05	74.7 (31.0%)	17.7 (52.3%)	365 (16.7%)	93.4	1.56
1.55	75.6 (31.0%)	18.0 (52.5%)	367 (16.5%)	93.6	1.68
1.00	74.8 (30.8%)	18.0 (52.6%)	363 (16.6%)	92.8	1.67
0.32	76.6 (30.5%)	18.6 (53.2%)	372 (16.3%)	93.8	1.74

[a] $B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$.

[b] $\tau_{ave} = (B_1 \cdot \tau_1 + B_2 \cdot \tau_2 + B_3 \cdot \tau_3)/(B_1 + B_2 + B_3)$

Supporting Figures.

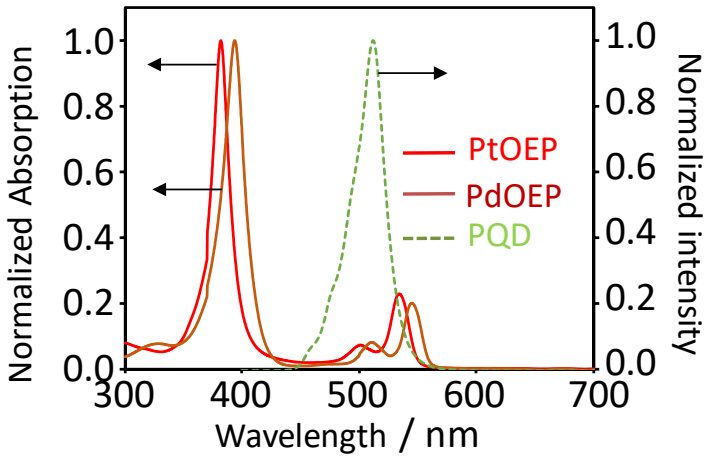


Figure S1. Normalized photoabsorption spectra of PtOEP (red line) and PdOEP (brown line) in toluene. The green dotted line is the photoluminescence spectrum of $CsPbBr_3$ PQDs in toluene (λ_{ex} = 340 nm).

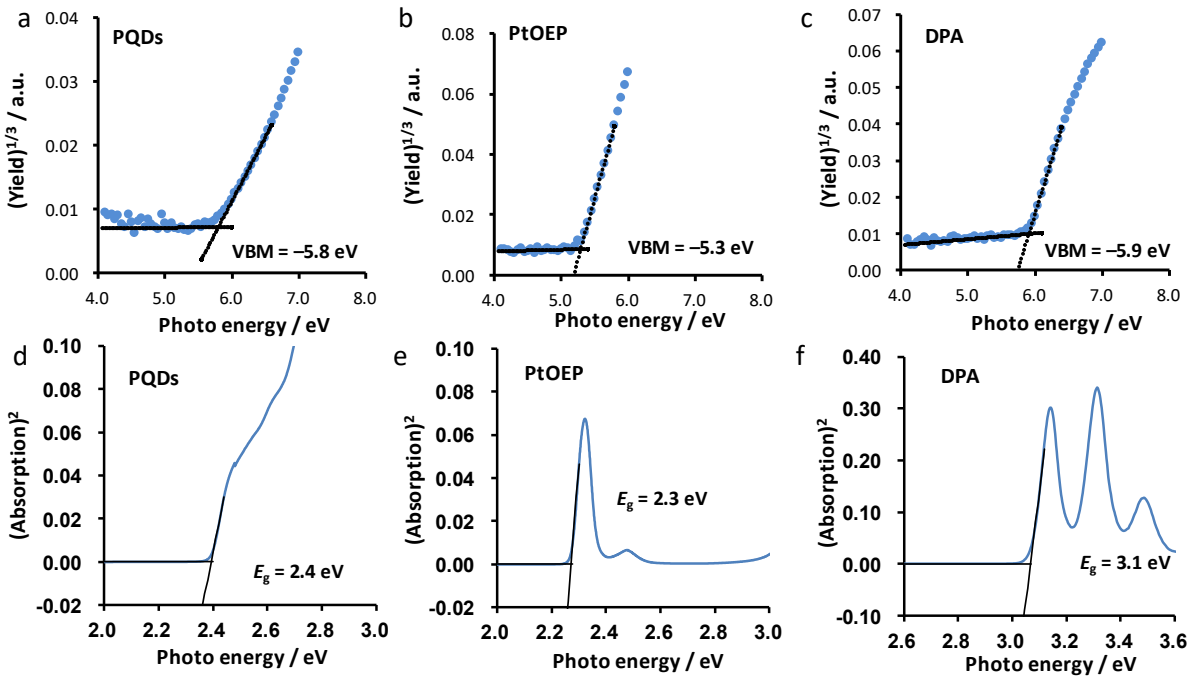
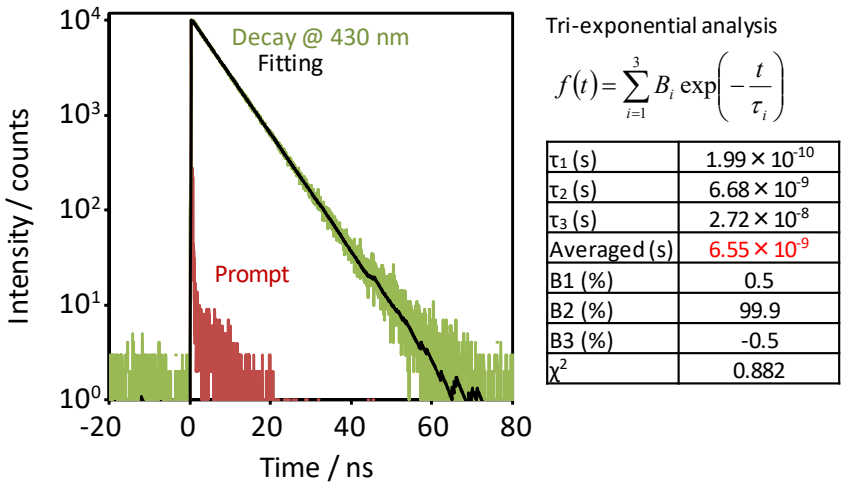


Figure S2. PYS spectra of (a) $CsPbBr_3$ PQDs, (b) PtOEP, and (c) DPA in solid states. The lower panel shows the absorption spectra of (d) PQDs, (e) PtOEP, and (f) DPA in toluene to evaluate the bandgap. The black lines are interpolated lines, the cross point of which is the bandgap.



τ_1 (s)	1.99×10^{-10}
τ_2 (s)	6.68×10^{-9}
τ_3 (s)	2.72×10^{-8}
Averaged (s)	6.55×10^{-9}
B1 (%)	0.5
B2 (%)	99.9
B3 (%)	-0.5
χ^2	0.882

Figure S3. Picosecond lifetime spectroscopy of 5 μM DPA in toluene (λ_{ex} = 377 nm). The green, red, and black lines are the experimental decays, the prompt (instrumental response function: IRF), and the analytical fit of tri-exponential function. The analysis result is shown in the table.

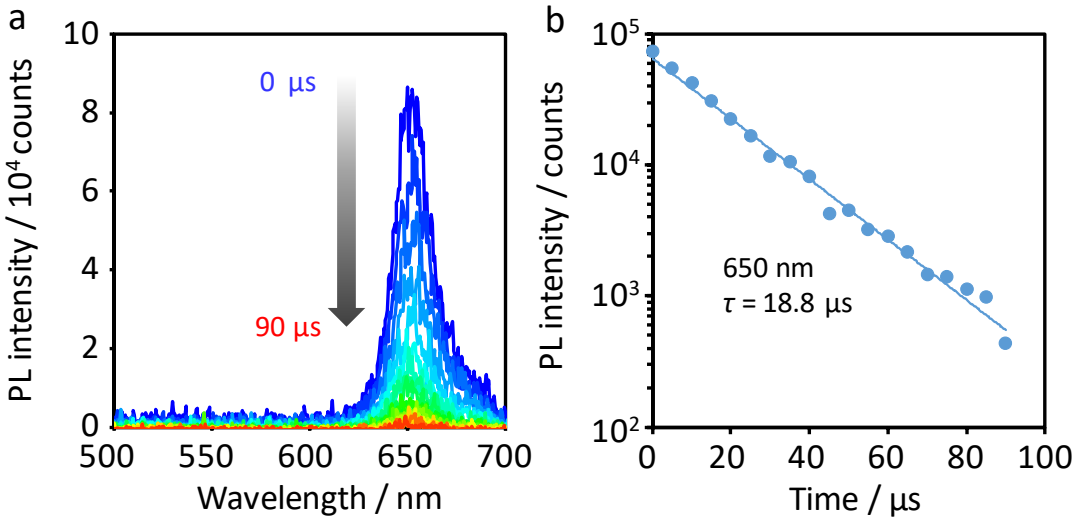


Figure S4. (a) Transient spectra from 0 (blue) to 90 μs (red) and (b) kinetics at 650 nm of 10 mM PtOEP in toluene. The nanosecond pulse at 532 nm (0.5 mJ cm^{-2}) was used as the excitation. The solid line in (b) is the least-mean-square fit of a single exponential function (τ = 18.8 μs) that corresponds to the lifetime of PtOEP triplet excited state (T_1).

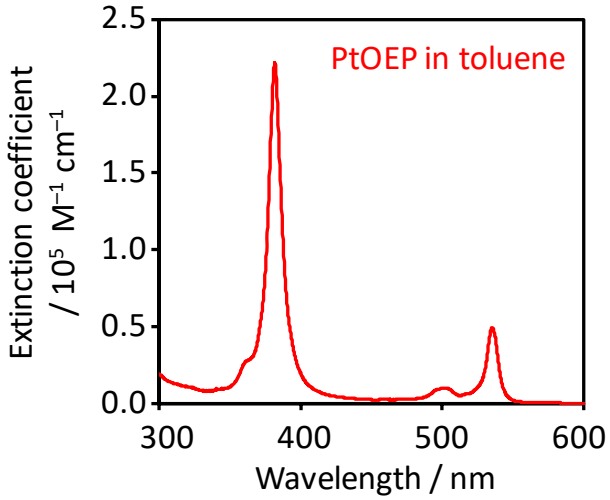


Figure S5. Steady-state photoabsorption spectrum of PtOEP in toluene (4.58 μM).

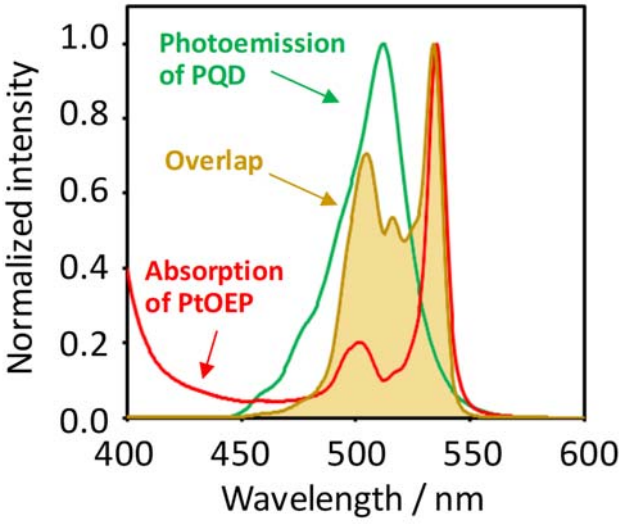


Figure S6. Normalized photoluminescence spectrum of PQD in toluene (green line), photoabsorption spectrum of PtOEP in toluene (red line), and the overlap of these spectra (yellow line and yellow-colored area). The calculated overlap integral J is 2.82×10^{14} M^{-1} cm^{-1} nm^4.

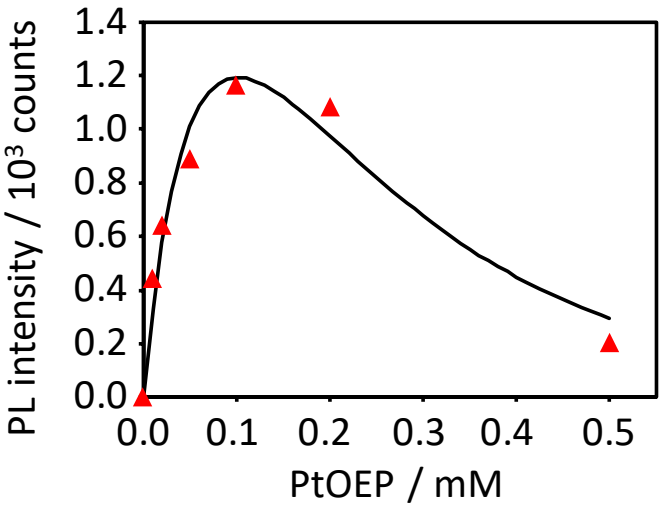


Figure S7. Steady-state photoluminescence peak intensities at 646 nm (attributed to T_1 of PtOEP) observed in a toluene solution of PQD with PtOEP (0–0.5 mM, red triangles) excited at 450 nm. The black solid line is the theoretical fit of $B(1 - (g(c)/h(c))^{-1}) \exp(-K_{CQ}\, c)$, where B is the scaling factor, $g(c)$ is the dynamic and static quenching function determined from the quenching of PQD (see eq 1 in the main text), $h(c)$ is the reabsorption function (see eq S3 in Supporting Information), c is the concentration of PtOEP, and K_{CQ} is the rate constant of concentration quenching. In the fitting, B and d K_{CQ} are varied to decrease the residual.

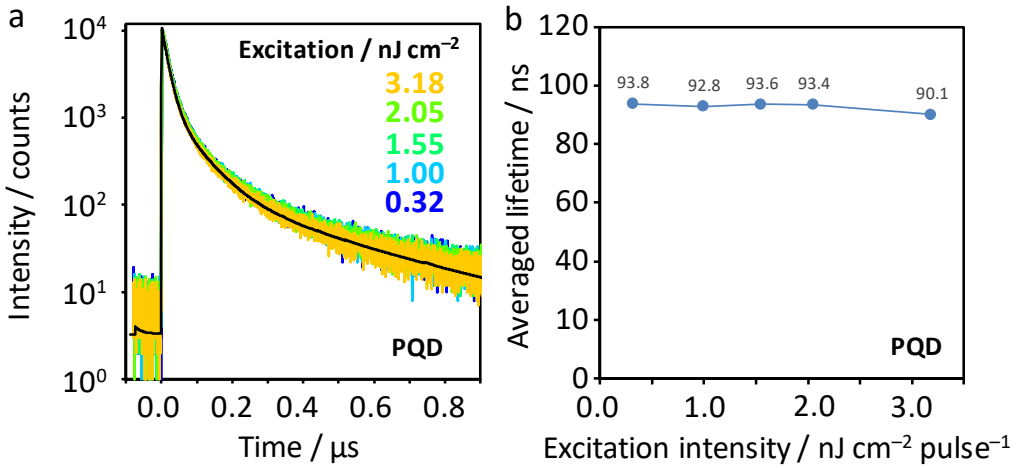


Figure S8. (a) Picosecond lifetime spectroscopies of PQD in toluene (λ_{ex} = 377 nm). The excitation intensity was changed from 0.32 (blue) to 3.18 nJ cm^{-2} (orange) using UV-compatible neutral density filters. The black solid line is the tri-exponential fit of the 3.18 nJ cm^{-2} decay. The averaged lifetimes are summarized in (b).

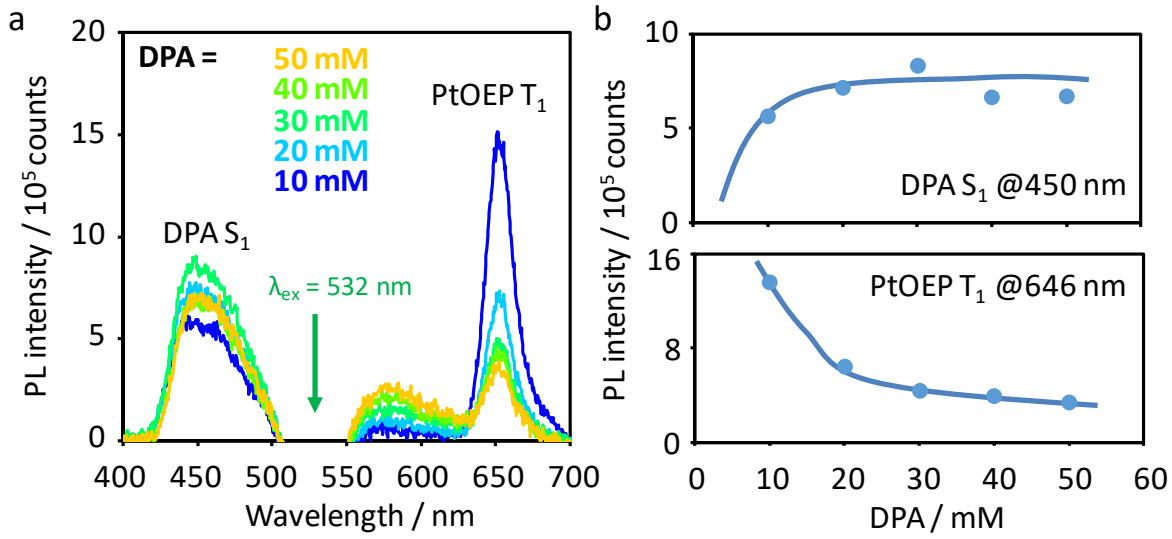


Figure S9. (a) Photoluminescence spectra of 0.1 mM PtOEP and 10–50 mM DPA in toluene (λ_{ex} = 532 nm, a nanosecond laser, 0.5 mJ cm^{-2}). (b) Photoluminescence intensities at 450 nm (upper panel, attributed to DPA S_1) and 646 nm (lower panel, attributed to PtOEP T_1). The solid line is an eye-guide.

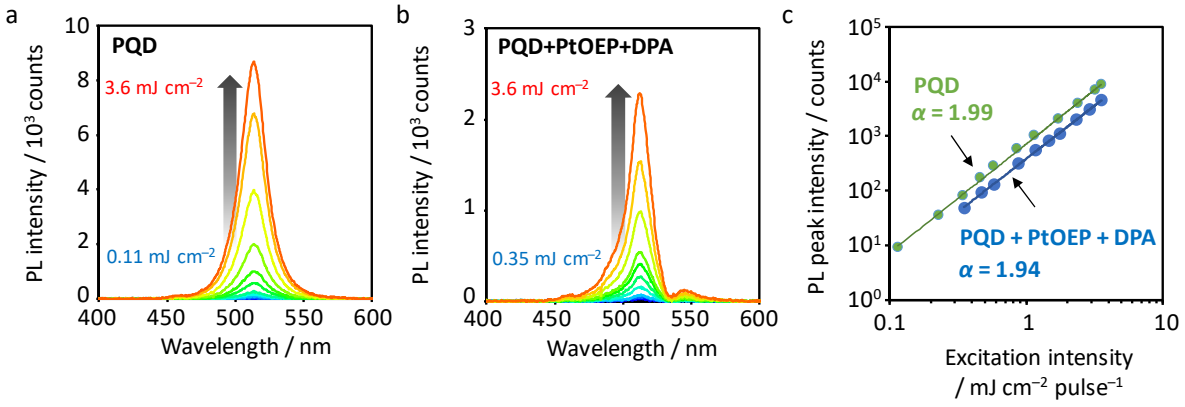


Figure 10. Photoluminescence spectra of (a) PQD and (b) PQD with 0.1 mM PtOEP and 10 mM DPA in toluene (λ_{ex} = 800 nm, a femtosecond laser *without focus*) with changing the excitation intensity (I_{ex}) from 0.11 (blue) to 3.6 mJ cm^{-2} (red). (c) Logarithmic plots of photoluminescence intensities at 514 nm vs I_{ex}. The solid lines are the least-mean-square fit of B $(I_{ex})^{\alpha}$, where B and α are the scaling factor and the power factor, respectively. The α corresponds to the slope of this plot.

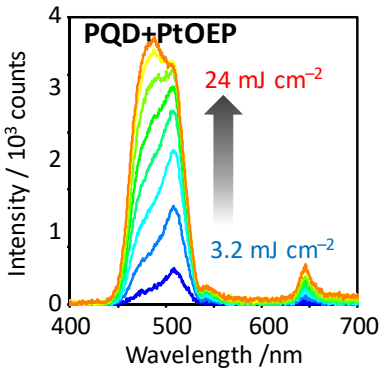


Figure S11. Photoluminescence spectra of PQD with 0.3 mM PtOEP in toluene (λ_{ex} = 800 nm, a focused femtosecond laser) with changing the excitation intensity (I_{ex}).

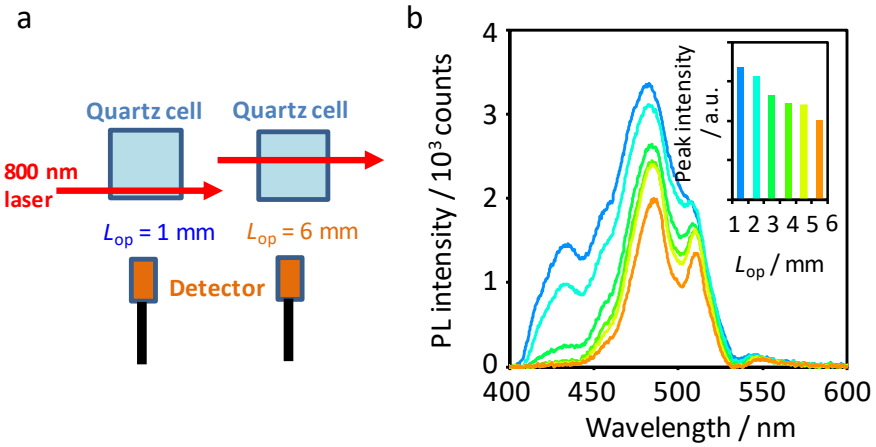


Figure S12. Experimental geometry of TTA-TPA process in PQD + PtOEP + DPA in toluene at different optical depth using a fused femtosecond laser pulse at 800 nm (the laser diameter is 2 mm and the quartz cell size is 1 × 1 cm^2). L_{op} is the optical path length from the side of the quartz cell in the direction of a detector. (b) Observed photoluminescence spectra at different L_{op} (blue: 0 mm to orange: 6 mm). The inset shows the intensity of the peak at ~485 nm.