

Supplementary Information

Photon upconversion utilizing energy beyond the band gap of crystalline silicon
with a hybrid TES-ADT/ PbS quantum dots system

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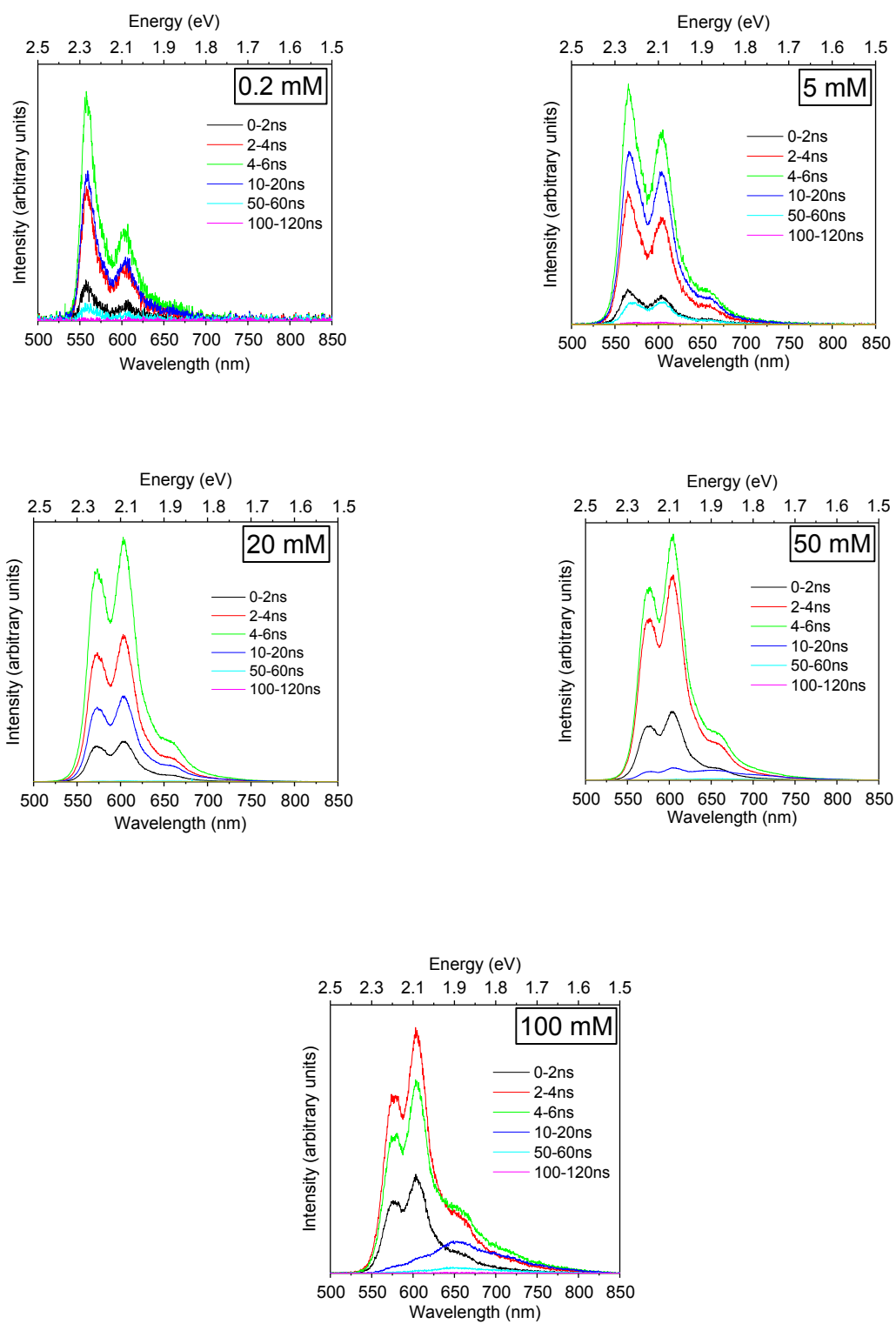


Figure S1. Time resolved emission spectra of TES-ADT solution with various concentrations (0.2, 5, 20, 50, 100 mM)

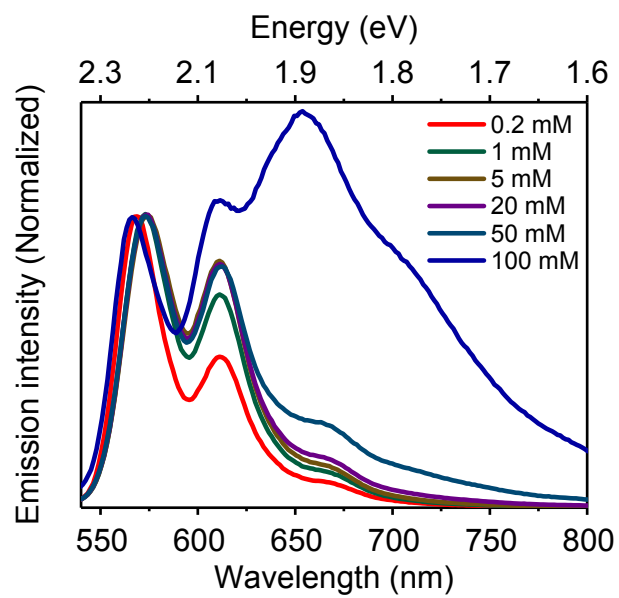


Figure S2. Dependency of TES-ADT concentration on the steady state emission spectra with an excitation of 0.4 mW cm^{-2} at 520 nm

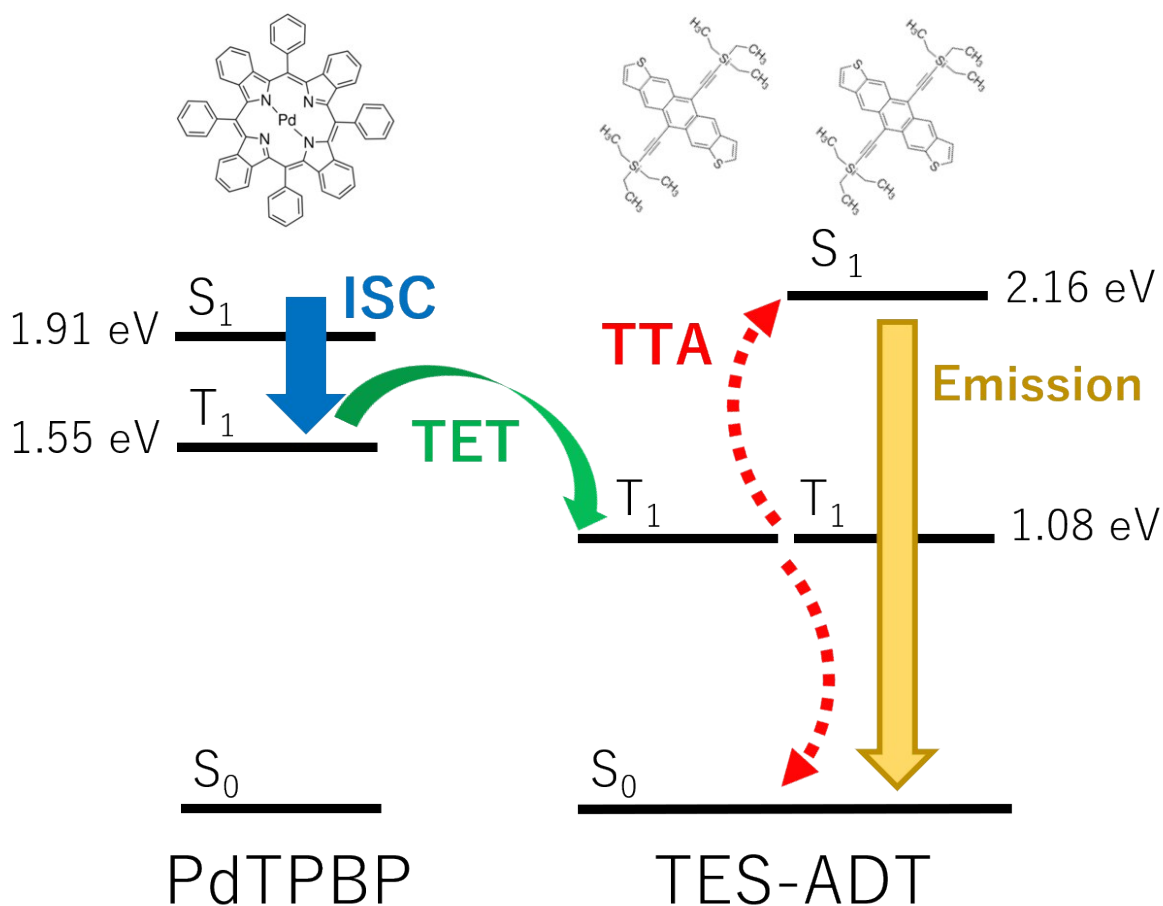


Figure S3. Energy diagram of PUC system consisting of TES-ADT and PdTPBP and scheme of the PUC process: S₁ state of PdTPBP is excited by an irradiation, followed by inter system crossing converting S₁ to T₁ in PdTPBP. After that, the triplet exciton in PdTPBP transfers to TES-ADT (TET), then TTA proceeds occasionally when two TES-ADT molecules whose T₁ states are excited collision each other, and finally TES-ADT whose S₁ state is excited via TTA emits.

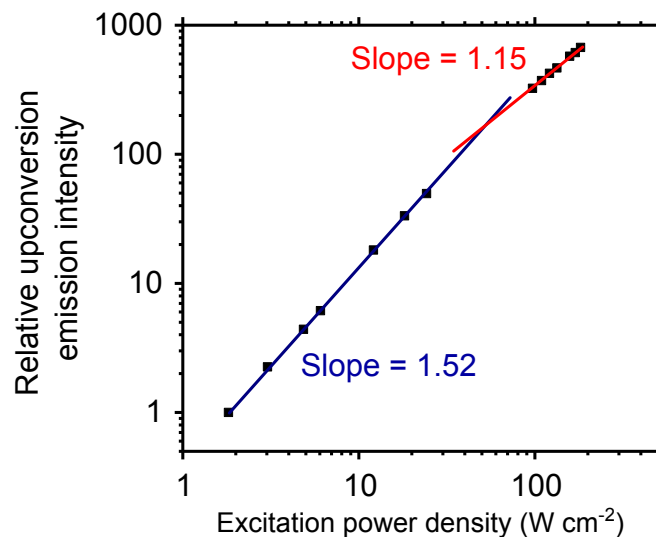


Figure S4. Relationship between PUC emission intensity from a solution consisting of 1 mM TES-ADT and 20 μ M PdTPBP and the excitation power density

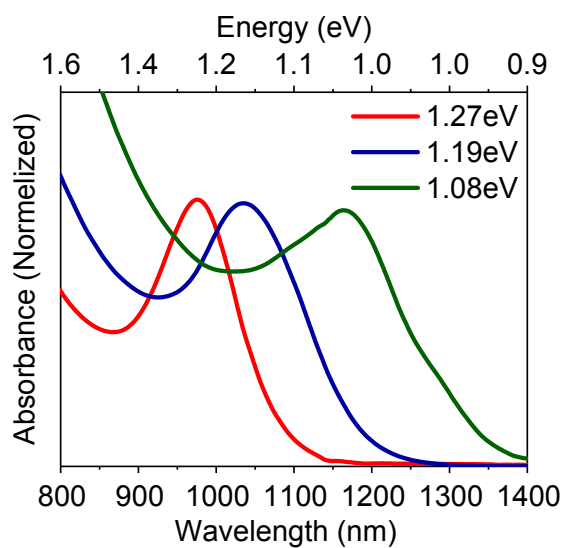


Figure S5. Absorption spectra of PbS QDs with excitonic energy of 1.27 ± 0.07 , 1.19 ± 0.08 , 1.08 ± 0.07 eV.

Effects of PbS QDs concentration on PUC emission QY

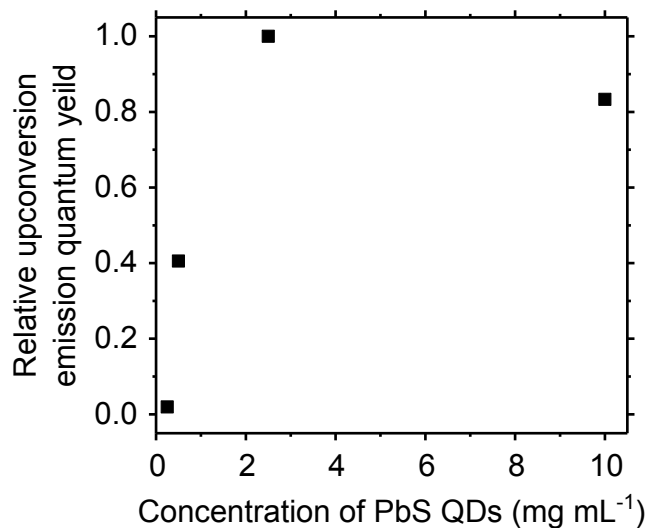


Figure S6. PbS QDs (1.27eV) concentration dependency on PUC emission intensity with the PUC system excited at 1064 nm

With an increase in a concentration of the QDs to 2.5 mg mL⁻¹ (O.D.: 0.04 at 1064 nm), the QY significantly increased, then it became a plateau. The steep increase in QY with the low concentrations was probably due to an insufficient concentration of the triplet, and the saturation of QY beyond 2.5 mg mL⁻¹ may reflect the enough triplet concentration to proceed TTA efficiently.

Effects of the population of excited states on emission spectra from concentrated TES-ADT

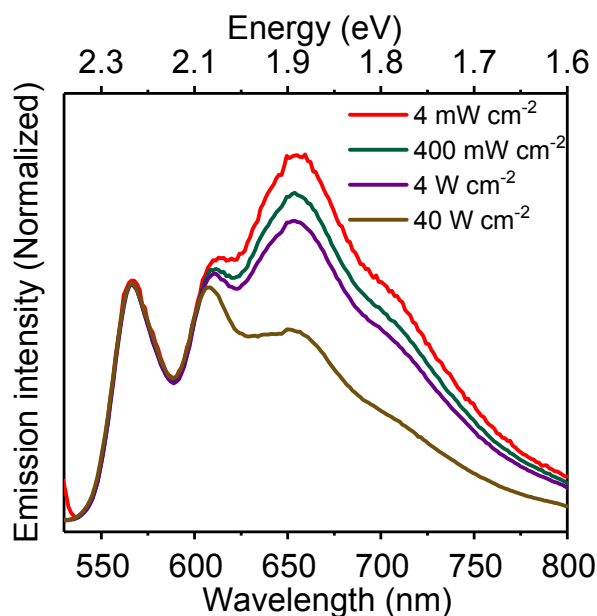


Figure S7. Effects of excitation power on emission spectra from 100 mM TES-ADT solution with an excitation by 520 nm CW laser

Relative emission intensities at 660 nm corresponding to emission from the (TT)¹ state increased with a decrease in the excitation power density from 40 W cm⁻² to 4 mW cm⁻². Under continuous excitation as the experiment condition in Figure S7, quasi-equilibrium can be provided between kinetically connected excited states which are the S₁ state and the (TT)¹ state in this case. Life time of (TT)¹ state is greatly longer than S₁ state: life times of the S₁ state and the (TT)¹ state were ~10 ns and ~100 ns, respectively. (Figure S1) With a continuous and strong excitation, hence, this difference in the life time leads to accumulation of (TT)¹ state, resulting in a higher population of the (TT)¹ state than that of the S₁ state. This change in the population occurs a shift of the quasi-equilibrium toward the S₁ state, blocking transition from the S₁ state to the (TT)¹ state, so that with an increase in the

excitation power density the relative intensity of the emission from (TT)¹ state becomes lower. Accordingly, the change in the emission spectrum in Figure S7 was attributed to a change in population of the excited states under the continuous excitation, which may also affect the PUC emission. (Figure 4B) We note that effect of the excitation power density on QY of 100 mM TES-ADT was also investigated, yet the power density was not significant for the QY as the results of 2.6 % at 20 W cm⁻² and 3.0 % at 200 mW cm⁻².

TA features of pristine 100mM TES-ADT

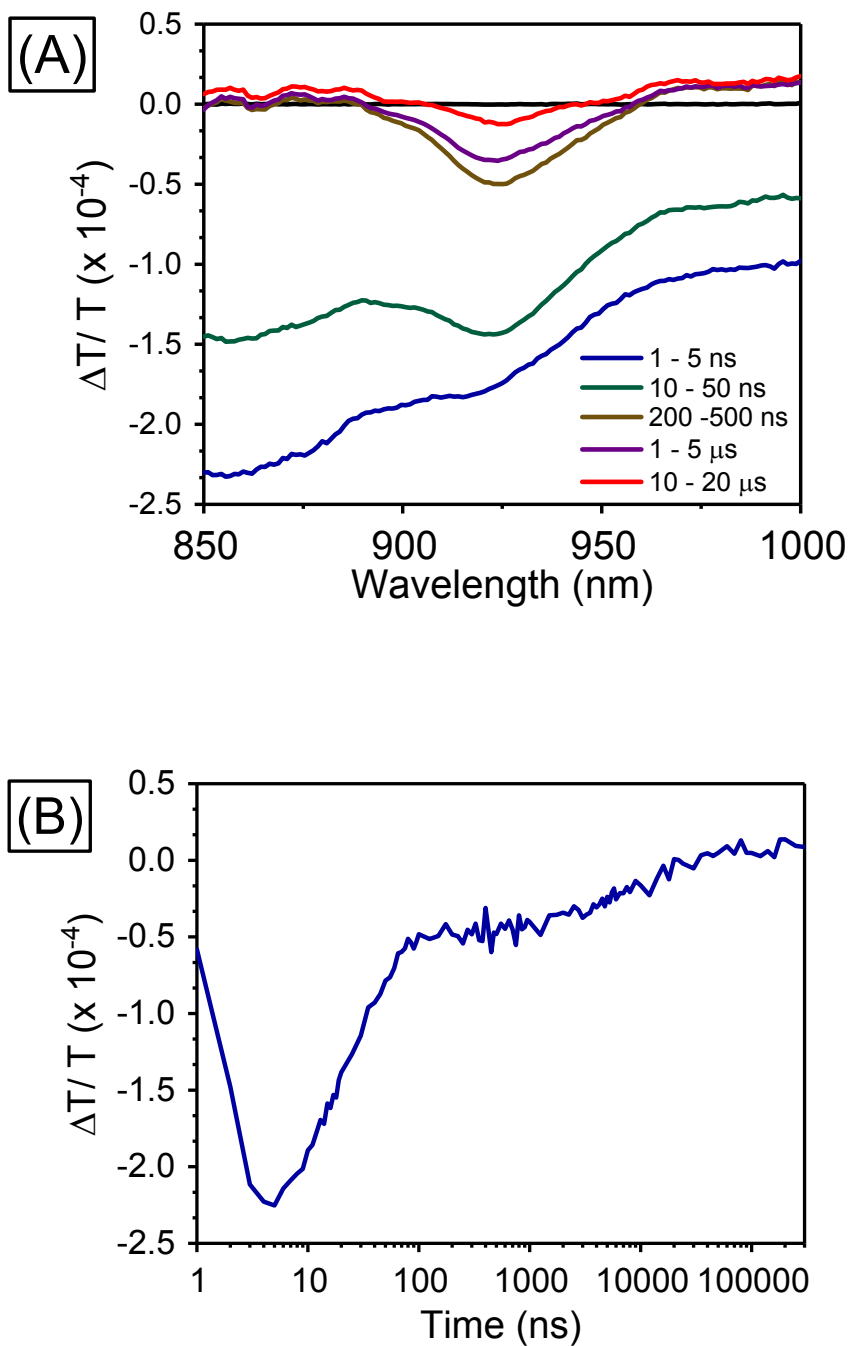


Figure S8. (A) TA spectra of 100 mM TES-ADT solution, (B) Kinetics at 920 - 930 nm in the TA spectra of 100 mM TES-ADT solution

To verify the triplet features of TES-ADT, TA spectra of 100 mM TES-ADT in toluene excited at 532 nm were measured, as shown in Figure S8. Overall, main features were divided into three types in the time range: up to several ns, up to around 100 ns, and up to several ten μ s, assigned as singlet states, coupled triplet states ((TT)¹ state), isolated triplet states, respectively, according to the previous study on diF-TES-ADT.¹ In terms of features in isolated triplet state, photo induced absorption (PIA) derived from $T_1 \rightarrow T_n$ transition was observed at around 920 - 930 nm where is red-shifted from that of diF-TES-ADT at around 890 nm in the previous report,¹ likely due to absence of fluorines in the structure of the molecule. The triplet decay was estimated as 10.6 μ s with a mono exponential fitting.

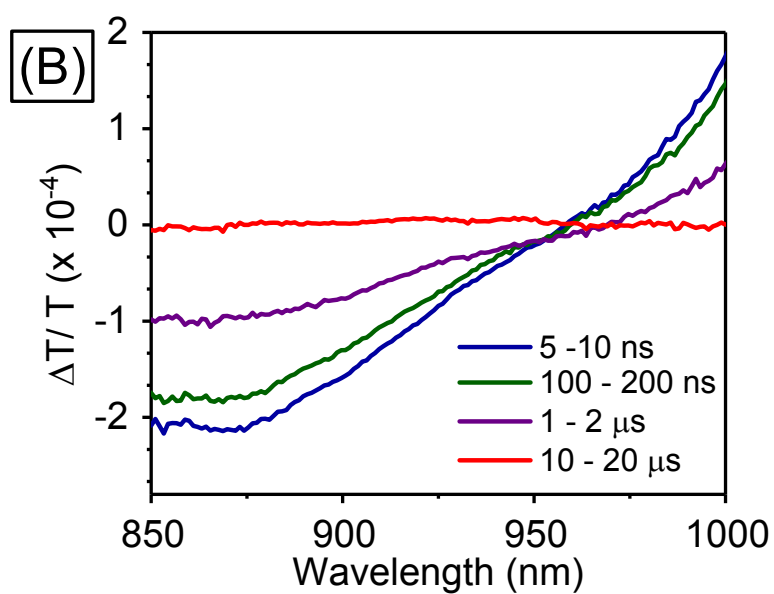
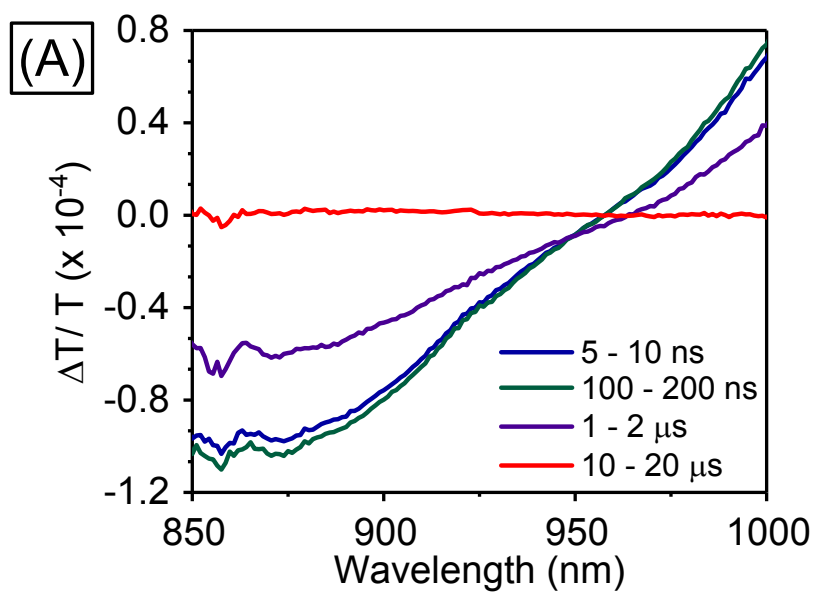


Figure S9. TA spectra of (A) PbS QDs (1.08 eV), (B) with 50 mM TES-ADT

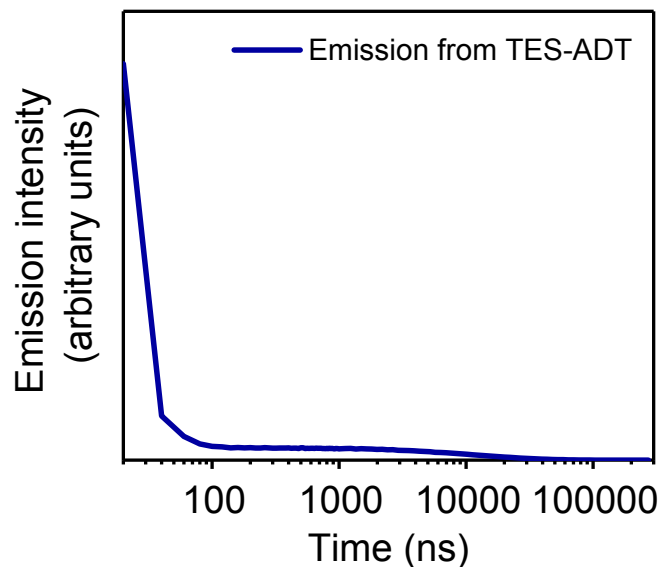


Figure S10. Kinetics of time resolved emission (traced at 570 - 600 nm) from a solution consisting of 100 mM TES-ADT and 2 mM PdTPBP with an excitation at 635 nm

The solution consisting of 100 mM TES-ADT and 2 mM PdTPBP generated long life-time emission after 100 ns, assigned as TTA emission. We note that the initial strong emission in Figure S10 was derived from two photon absorption, due to short pulse duration (~ 100 fs) in the excitation. Although the emission due to two photon absorption hindered to observe generation feature of the TTA emission in the initial time scale (< 100 ns), the intensity of TTA emission had been saturated within 100 ns, indicating that rate constant of the TTA is greatly faster than the rate determining step of PUC emission from TES-ADT/ PbS QDs system ($k \approx 5 \times 10^5 \text{ s}^{-1}$). Thus, the TTA process was not the rate determining process in the PUC process with TES-ADT/ PbS QDs system.

(Reference)

1. C. K. Yong, A. J. Musser, S. L. Bayliss, S. Lukman, H. Tamura, O. Bubnova, R. K. Hallani, A. Meneau, R. Resel, M. Maruyama, S. Hotta, L. M. Herz, D. Deljone, J. E. Anthony, J. Clark, H. Sirringhaus, *Nature Communications*, 2017, **8**,15953.

