Supporting Information

CdSe Nanocrystal Sensitized Photon Upconverting Film

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1. Materials

Cadmium oxide (CdO, 99.99%), oleic acid (OA, tech. grade, 90%), and 1-octadecene (ODE, 90%) were purchased from Aldrich. Selenium (Se, 99.9%) was purchased from Strem Chemicals, and toluene was purchased from Fisher, dried and degassed using a JC Meyer's solvent purification system.

2. Instrumentation

Linear absorption spectra were recorded on a Cary 5000 UV-Vis absorption spectrophotometer. Photoluminescence (PL) of CdSe nanocrystals (NCs) were recorded on Spex Fluorolog Tau-3 fluorescence spectrophotometer. Photoluminescence quantum yields were obtained using a standard of rhodamine 6G in ethanol.

Upconversion fluorescence spectra were recorded at right angles to the excitation with an Ocean Optics Inc. Maya Pro 2000 spectrometer. A 532 nm Coherent Sapphire laser with an output power of 10.0 mW and power density of 12.7 W/cm^2 is focused to a spot with a diameter of 120.9 μm. In front of the detector, a 532 nm StopLine single-notch filter (part number NF01-532U-25) is used to block the scattered laser light. The upconverted light was collected from the side of the cuvette and focused into a PAF-SMA-11-A (Thor Labs) fiberport through an Ocean Optics QP400-2-SR fiber connected to the Maya Pro 2000 spectrometer. The upconversion sample is prepared in air tight Starna cuvettes with screw tops in a nitrogen glove box. Upconversion quantum yields were calculated with a rhodamine 6G reference excited with the 532 nm laser.

Nanosecond transient absorption measurements were made using an enVISion spectrometer from Magnitude Instruments using 532 nm excitation, with a repetition rate varying from 1.2 to 12 kHz (depending on the time window). The excitation energy density was 87 μJ/cm^2 for a 10 kHz repetition rate.

3. Synthesis of CdSe NCs

2.3 nm diameter zinc blende CdSe NCs were synthesized following the modified method of Zhang et al:[1] 230 mg CdO, 1.6 mL oleic acid and 14.25 mL 1-octadecene were added into a 50 mL 3-necked round bottom flask and heated at 100 °C for 1 hour under vacuum. The flask was then filled with argon and was then heated to 260 °C. Once the solution turned clear, the temperature was reduced to 226 °C. Once the injection temperature was reached, 2.5 mL of a 0.4 M suspension of Se powder in ODE was injected and the reaction flask was cooled to room temperature with compressed air. Nanocrystals were washed three times by precipitation/redispersion with ethanol/hexane and stored in toluene in the dark.

4. Ligand loading and fabrication of thin film samples for upconversion, transient absorption, and upconversion measurements

Ligand exchange was performed by mixing CdSe NCs with 9-ACA at different concentrations in THF and then stirring overnight. The total volume of the ligand exchange solution was 190 μL. After ligand exchange, 1 mL acetone was added as a bad solvent to precipitate out nanocrystals, and the CdSe/9-ACA complex was precipitated by centrifuging for at least 10 min at 7830 rpm. The clear supernatant containing excess 9-ACA ligand was discarded.

To test for optimal loading, an upconversion measurement was performing by redispersing the CdSe/9-ACA pellet in 2 mL of a 3 mM DPA/toluene solution and then transferred to a 1 cm path length Starna cuvette. The ligand loading which produced the highest upconversion QY was then used throughout the rest of the thin film fabrication experiments.

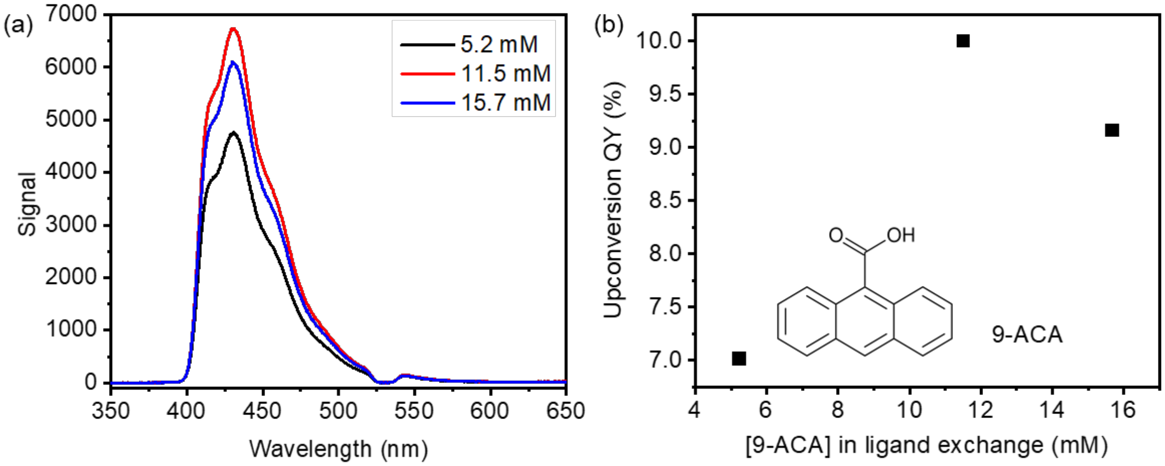

Figure S1. Ligand loading optimization for CdSe nanocrystals. (a) Upconversion emission for three different ligand loading concentrations. (b) Upconversion QY vs concentration of 9-ACA ligand in the ligand exchange solution.

Thin film samples were drop cast from a 20 wt% DPA in PVK solution in 1,2-dichlorobenzene. 0.4 mL of each solution was dropped onto a uniform, clean glass coverslip and allowed to completely dry overnight. Dry samples were sealed onto a clean glass microscope slide using UV curing epoxy. To protect the UV sensitive DPA molecules and CdSe surface, a small disk covered in aluminum foil was used to cover and protect the center of the film during the UV curing process, leaving only the edge of the coverslip exposed to the UV light. All samples were prepared in a nitrogen glovebox.

The R6G reference thin film was fabricated by adding R6G to a sample of 8 mg PVK dissolved in 1 mL *o*-DCB in a nitrogen glovebox. 400 μL of the final solution was drop cast onto a 25 mm glass coverslip. The R6G concentration was designed so that the resulting thin film absorbance was within 0.05 of the absorption of the upconverting thin films at 532 nm.

5. Profilometry experiments

Profilometry experiments were performed using a Dektak8, Bruker profilometer using a standard scan and 5 micrometer radius stylus. Twenty second scans were performed for 17-22 mm depending on the sample with a force of 5 mg and a measurement range of 655 kAngstrom.

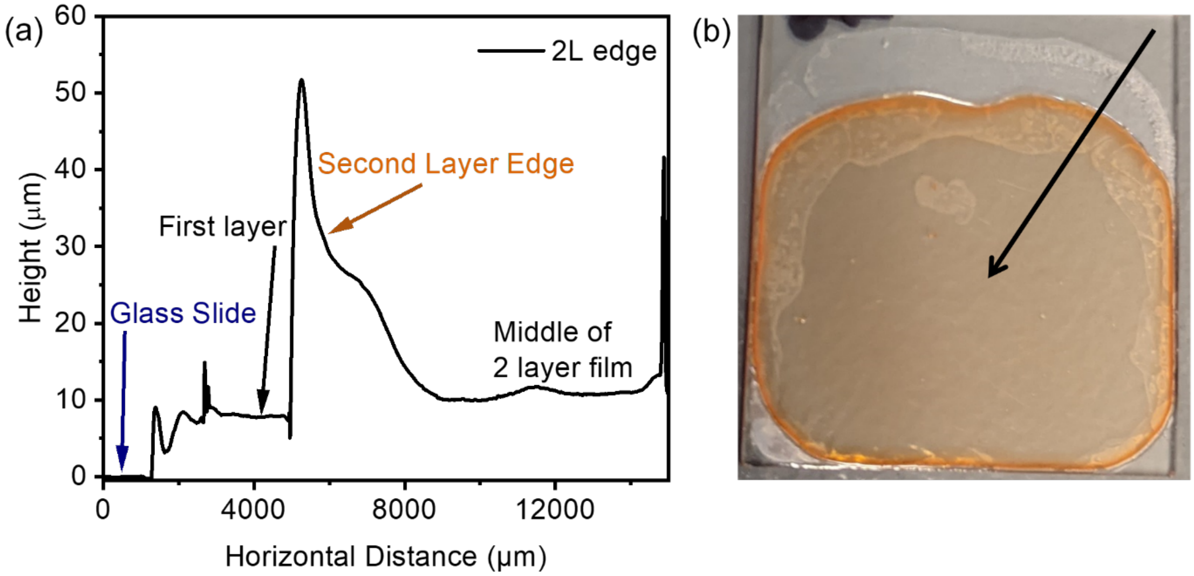

Figure S2. Profilometry shows the height of the dropcast film with respect to the glass slide. The initial jagged peaks correspond to bubbles formed on the outer edge of the first layer of epoxy. The sharp edge of the second CdSe/9ACA/OA+DPA in PVK layer is due to the drop-cast film drying faster at the edges. The middle of this film corresponding to the tip of the black arrow in (b) is labelled.

6. Concentration of DPA and CdSe in blended and layered film morphologies

The concentration, c, of DPA and CDSe/9-ACA in PVK was determined by the Beer-Lambert law, $A = \varepsilon c t$, where A is the absorption of the film, ε is the molar extinction, and t is the thickness of the film.

Table S1. Summary of film thickness, concentration of DPA and CdSe/9-ACA in the film. The molar absorptivity of DPA at 372.5 nm is 1.40 x10^4 M^{-1}cm^{-1}; CdSe at 523 nm is 6.67 x10^4 M^{-1}cm^{-1}.[2-3]

	Thickness (cm)	[DPA]	[CdSe]	DPA/CdSe
Drop cast film	5.84×10^{-4}	5.74×10^{-1}	1.05×10^{-3}	546.1

7. Upconversion quantum yield measurements

The photon upconversion (UC) QY, Φ_{UC} is defined as:

$$\Phi_{UC} = 2 \times \Phi_{ref} \times \frac{(\text{photons absorbed by reference})}{(\text{photons absorbed by UC sample})} \times \frac{\text{PL signal}(\text{UC sample})}{\text{PL signal}(\text{reference})} \qquad \text{Eq S1}$$

where Φ_{ref} is the photoluminescence QY of the rhodamine 6G reference, which is 95% in ethanol.

The quantum yield is defined as the ratio of emitted photons to absorbed photons, meaning that the theoretical maximum upconversion quantum efficiency is 50% as the absorption of a minimum of two photons is required to generate one upconverted photon. All upconversion measurements were performed with an incident laser power in the linear regime for photon upconversion, meaning that triplets decay primarily by TTA.

The PL quantum yield of the reference R6G in PVK thin film was determined from an absolute quantum yield measurement using a Labsphere RT-060 integrating sphere, exciting with a continuous wave (CW) 532 nm laser with a beam radius of 89.5 µm and detecting with a Maya Pro 2000 spectrometer.[4]

8. Photoluminescence mapping of blended and layered films

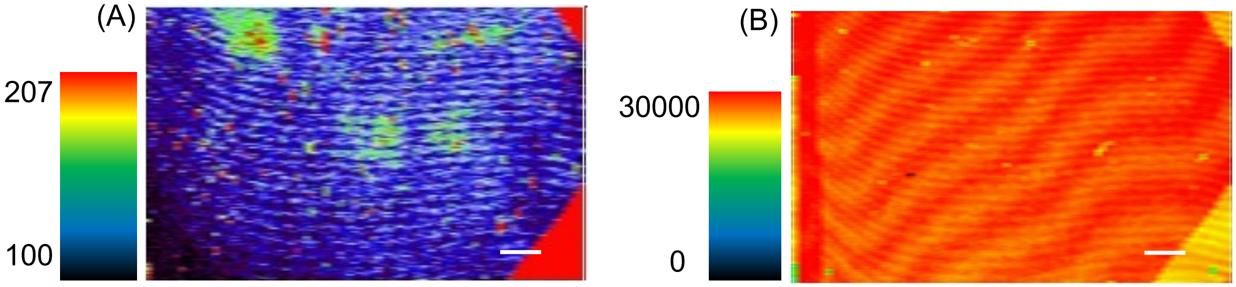

Fig. S3. Photoluminescence mapping of CdSe 9ACA/OA and DPA film (A) excited at 532 nm, collected at 550 nm and (B) excited at 405 nm and collected at 440 nm showing the CdSe NC and DPA PL respectively. In (A), only CdSe emits, thus the distribution of CdSe is shown, while in (B), both the CdSe and DPA signals are presented. Scale bar is 1 mm.

9. Beam radius and power dependence measurements

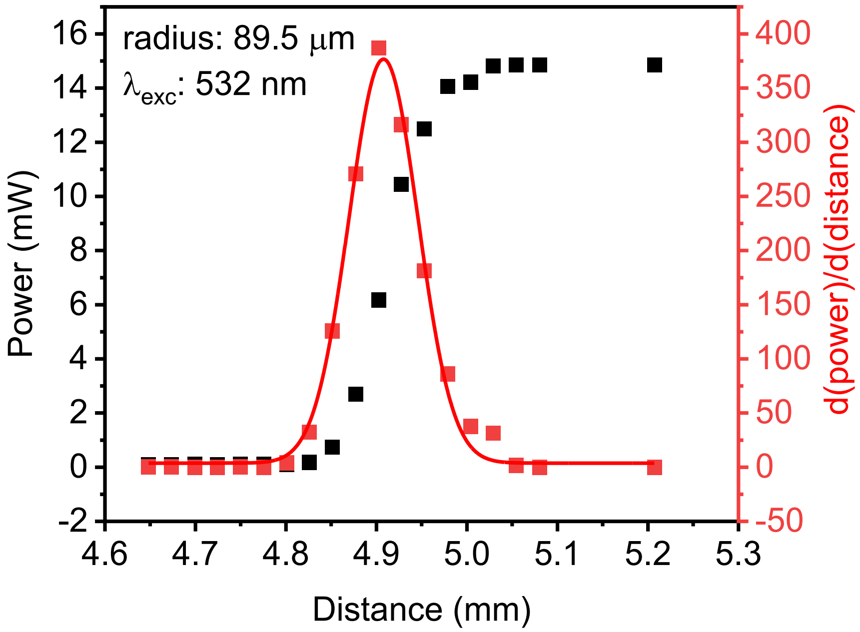

Figure S4. Laser intensity (black squares) decreases as a razor blade is translated across the excitation source. The first derivative of the laser intensity (red squares) with respect to distance, $d(power)/d(distance)$. The radius of the excitation light is obtained with a Gaussian fit (red curve).

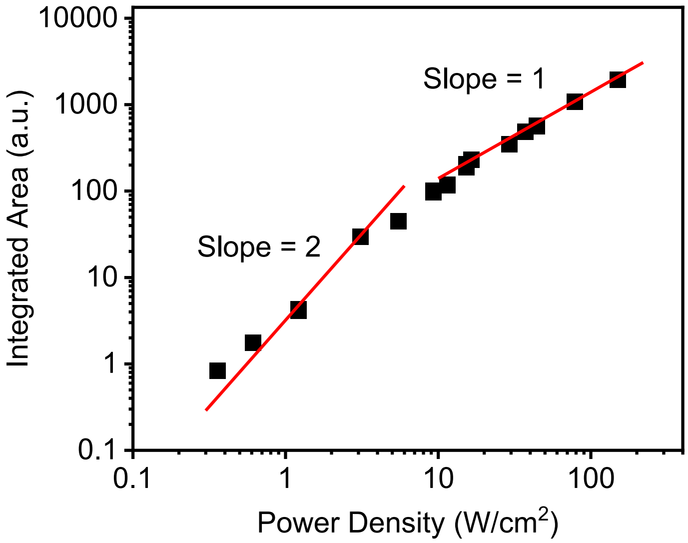

Figure S5. Power dependence on best upconverting spot in the film, excited with 532 nm CW laser. The signal is measured in front face geometry and integrating from 380-513 nm.

10. PL spectra of film upconversion vs DPA in toluene

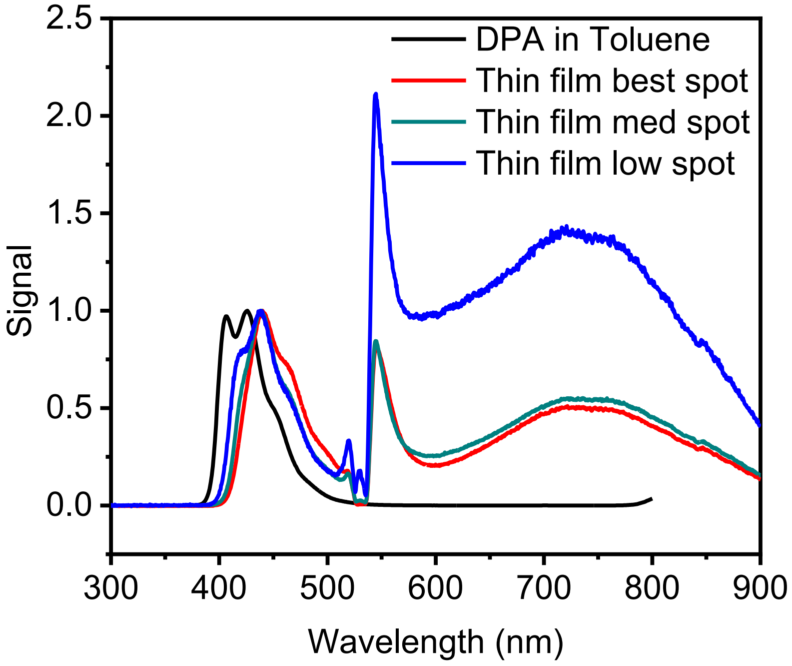

Figure S6. Normalized photoluminescence for DPA in toluene (black trace) compared to the best, average, and low quantum yield samples during photon upconversion in the blended film.

11. Transient absorption spectra of films

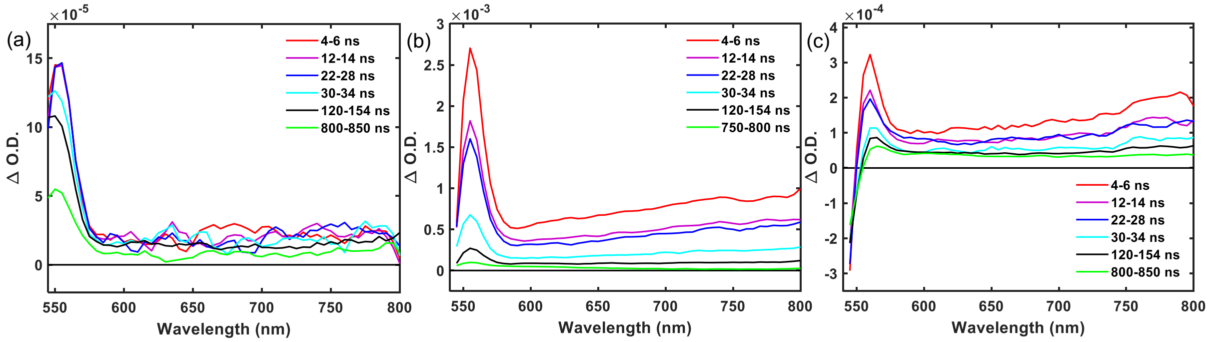

Figure S7. Transient absorption spectra from 545 nm to 800 nm for films of (a) CdSe OA, (b) CdSe 9ACA/OA and (c) CdSe 9ACA/OA and DPA in PVK using 532 nm excitation.

12. Fitting excited state kinetics

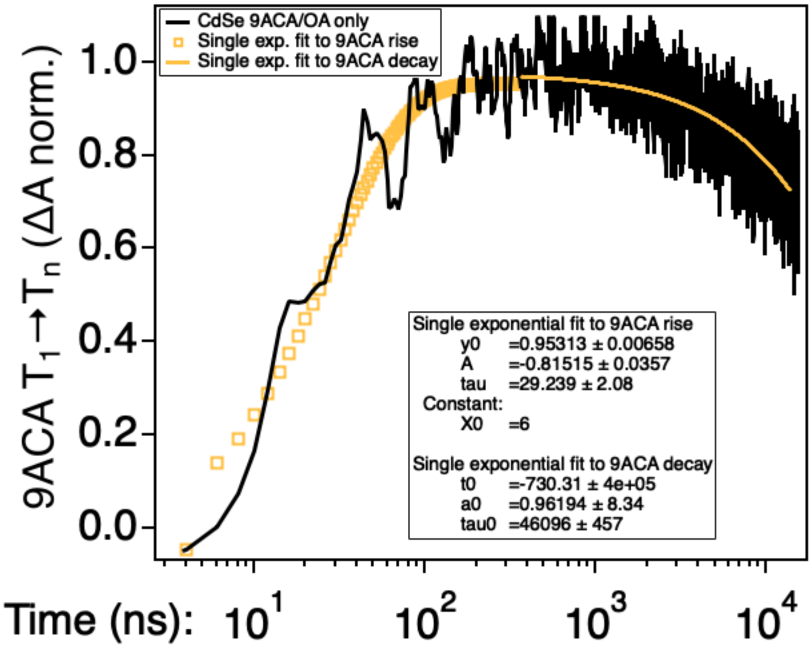

Figure S8. The triplet kinetics centered from 440-455 nm obtained from the double difference (dd) spectra of the CdSe 9ACA/OA in PVK sample (Fig. 4a) are monoexponentially fit to a triplet rise of 29.2 ± 2.1 ns and 9ACA lifetime of 46.1 ± 0.5 μs after subtracting the CdSe component.

The rise (open yellow squares), is fit to:

$$I(t) \ = \ y_0 + Aexp\left(-\frac{\{t - x_0\}}{tau}\right) \qquad \text{Eq S2}$$

The decay (yellow line), is fit to:

$$I(t) \ = \ a_0 exp\left(-\frac{\{t - t_0\}}{tau_0}\right) \qquad \text{Eq S3}$$

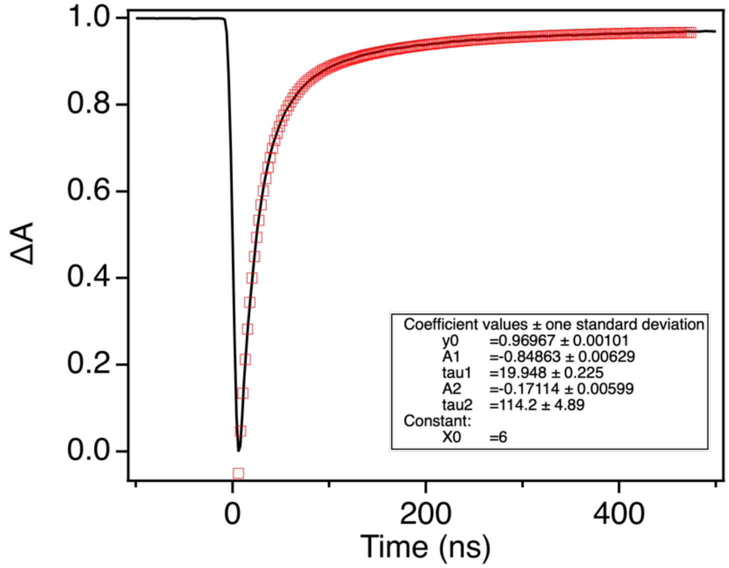

Figure S9. The recovery of the ground state bleach from the CdSe nanocrystal in the CdSe/OA in PVK sample is obtained by averaging the signals between 505-520 nm (black line) and fit (open red squares) to obtain the amplitude averaged lifetime using a biexponential:

$$I(t) = y_0 + A_1 exp\left(-\frac{\{t-t_0\}}{\tau_1}\right) + A_2 exp\left(-\frac{\{t-t_0\}}{\tau_2}\right) \qquad \text{Eq S4}$$

Since we are considering triplet energy transfer, the lifetime of CdSe/OA is calculated from the amplitude weighted lifetime:

$$\bar{\tau} = \frac{\sum_i A_i * \tau_i}{\sum_i A_i} = 35.77ns$$

Φ_{TET1} is the efficiency of triplet energy transfer from the CdSe NC absorber and the bound 9-ACA ligand.

$$\phi_{TET1} = \frac{{}^{1}/_{\tau_{TET1}}}{{}^{1}/_{\tau_{TET1}} + {}^{1}/_{\tau_{CdSe-OA}}} = \frac{{}^{1}/_{158}}{{}^{1}/_{158} + {}^{1}/_{35.77}} = 0.18 \qquad \text{Eq S5}$$

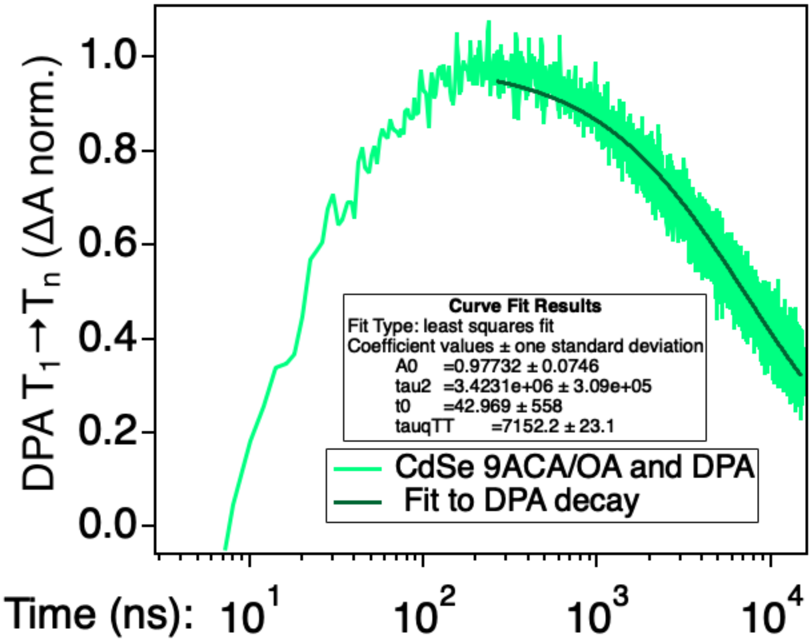

Figure S9. The triplet kinetics centered from 440-455 nm obtained from the dd spectra of the CdSe 9ACA/OA and DPA in PVK sample (Fig. 4b) are fit after subtracting the CdSe component to Equation 3 in the main manuscript:

$$[^3A^*]_t = [^3A^*]_0 \frac{1-\beta}{e^{k_1 t}-\beta} \text{ where } \beta = \frac{k_{TT}^{q}[^3A^*]_0}{k_1 + k_{TT}^{q}[^3A^*]_0} \qquad \text{(Equation 3)}$$

References

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4. Leyre, S.; Coutino-Gonzalez, E.; Joos, J. J.; Ryckaert, J.; Meuret, Y.; Poelman, D.; Smet, P. F.; Durinck, G.; Hofkens, J.; Deconinck, G.; Hanselaer, P., Absolute determination of photoluminescence quantum efficiency using an integrating sphere setup. *Review of Scientific Instruments* **2014,** *85* (12), 123115.