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Electronic Supplementary Information

Sensitizing Phosphorescent and Radical Emitters via Triplet Energy Translation from $CsPbBr_3$ Nanocrystals

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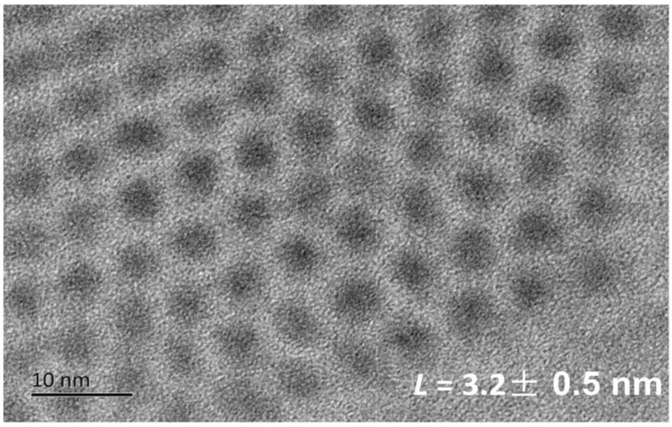


Fig. S1. Transmission electron microscope (TEM) image of CsPbBr3 NCs. Their average edge length (*L*) and standard deviation are labeled.

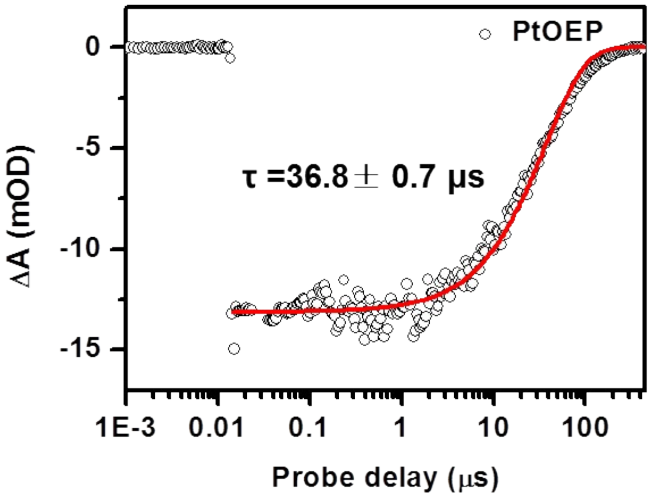


Fig. S2. TA kinetics of PtOEP probed at the ground bleach center (~535 nm). The red solid line is a single-exponential fit.

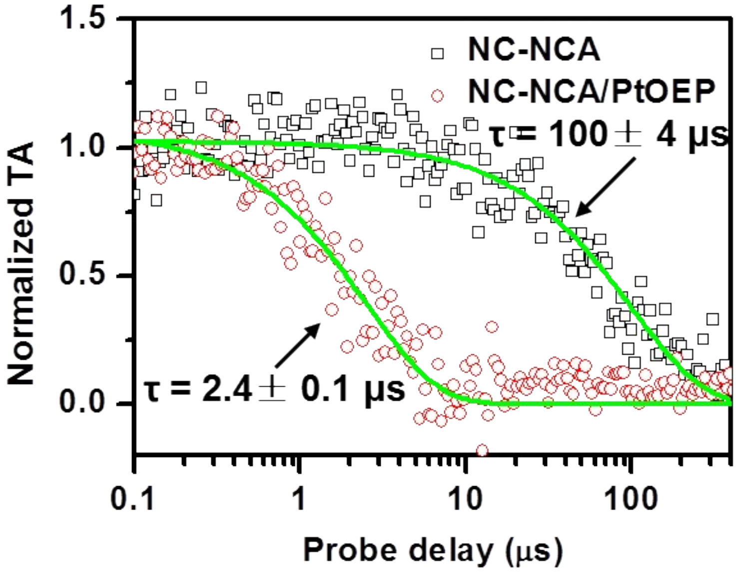


Fig. S3. TA kinetics probed at 470 nm (the absorption of ^{3}NCA*) for NC-NCA (black open square) and NC-NCA//PtOEP (red open circle). The green solid lines are single-exponential fits of them.

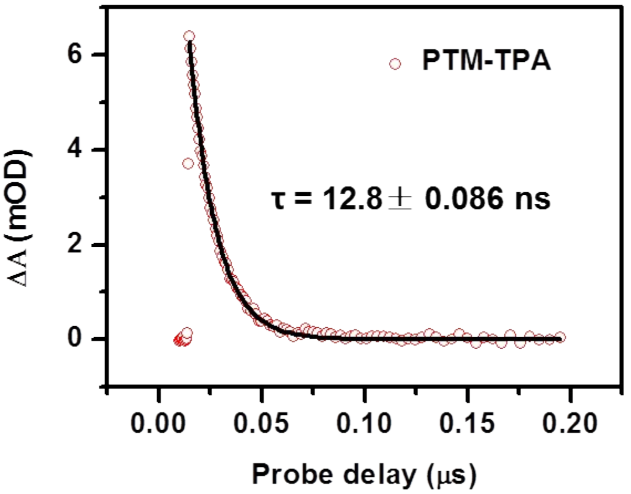


Fig. S4. TA kinetics of PTM-TPA probed at the excited state absorption feature (~630 nm). The black solid lineis a single-exponential fit.

Materials and Methods

Chemicals. Cesium carbonate (Cs_2CO_3, Sigma-Aldrich, 99.9%), lead(II) bromide ($PbBr_2$, Alfa Aesar, 98+%), zinc bromide ($ZnBr_2$, Alfa Aesar, 99.9%), oleic acid (OA, Sigma-Aldrich, 90%), oleylamine (OAm, Acros Organics, 80–90%), 1-octadecene (ODE, Sigma-Aldrich, 90%), 1-naphthalene carboxylic acid (NCA, Alfa Aesar, 98%); 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II) (PtOEP) was purchased from Sigma-Aldrich. (4-(4'-triphenylamine-yl)-tetrachlorophenyl)bis-(pentachlorophenyl)-methyl (PTM-TPA) was synthesized as described previously.[1]

Synthesis of $CsPbBr_3$NCs. $CsPbBr_3$ perovskite NCs were synthesized following previously reported procedure.[2] Briefly, 0.256g Cs_2CO_3, 0.9 mL oleic acid (OA), and 9 mL 1-octadecene (ODE) were loaded into a 25 mL 3-neck flask and vacuum-dried for 2 h at 120 °C using a Schlenk line. Then the mixture was heated to 140 °C under Ar atmosphere until all Cs_2CO_3 powders were dissolved. The Cs-oleate precursor was kept at 100 °Cto prevent Cs-oleate precipitation. In another 100 mL 3-neck flask, $PbBr_2$ (0.225 g) and $ZnBr_2$ (0.552 g) was dissolved in a mixture of OA (6 mL), ODE (15 mL), and oleylamine (OAm, 6 mL). The precursor solution of Pb and Br were vacuum-dried for 40 min at 120°C and cooled down to 90 °C under Ar atmosphere. Then 1.2 mL Cs precursor solution was injected to the initiate the reaction. The reaction was quenched after 2 min by cooling the flask in an ice bath. The crude solution was then cooled to the room temperature, and centrifuged at 3500 rpm for 10 min to remove the unreacted salts asthe precipitate. NCs were then precipitated by adding methyl acetate dropwise until the mixture turned turbid. The dried NCs were collected and re-dissolved in hexane and stored in glovebox. The concentrations of NCs can be estimated from $A=\varepsilon bc$, where A and εstand for absorbance and extinction coefficient, b stands for the thickness of the quartz cuvette. Using this equation, c is calculated to be 0.66 μM for $CsPbBr_3$ NCs.

Preparation of $CsPbBr_3$ NCs-NCA complexes. The $CsPbBr_3$ NC-NCA complexes were prepared by simply adding 1-naphthalene carboxylic acid (NCA) powders into the $CsPbBr_3$NCs solution followed by sonication and filtering. The average number of NCA ligands per NC (n) can be estimated from the absorption spectrum using the extinction coefficient reported for $CsPbBr_3$NCs of similar emission energy and that of NCA: $n=[A(\mathrm{NCA})/\varepsilon(\mathrm{NCA})]/[A(\mathrm{NC})/\varepsilon(\mathrm{NC})]=561$, where A and εstand for absorbance and extinction coefficient, respectively.

Preparation of $CsPbBr_3$NCs-NCA//(PtOEP, PTM-TPA) complexes. The $CsPbBr_3$ NC-NCA//(PtOEP, PTM-TPA) samples were prepared by adding PtOEP or PTM-TPA powders into the $CsPbBr_3$ NC-NCA complexes prepared above. The concentrations of PtOEP and PTM-TPA can also be estimated from $A = \varepsilon bc$, from which $C(\mathrm{PtOEP}) = 0.21$ mM, $C(\mathrm{PTM\text{-}TPA}) = 0.11$ mM.

Femtosecond pump-probe TA. The femtosecond pump-probe TA measurements were performed using a regenerative amplified Ti:sapphire laser system (Coherent; 800nm, 70 fs, 6 mJ/pulse, and 1 kHz repetition rate) as the laser source and a Femto-100 spectrometer (Time-tech spectra) as the spectrometer. The white-light continuum (350-650 nm) (WLC) probe pulse were generated by focusing the 800-nm beam (split from regenerative amplifier with a tiny portion) onto 2 mm thick CaF_2. The time delay (0-8 ns) between the pump and probe pulses were varied by a motorized optical delay line. A mechanical chopper operating at 500 Hz was used to modulate the pump pulses such that the fs-TA spectra with and without the pump pulses can be recorded alternately. The samples well dispersed in hexane were contained in a 1-mL air-free quartz cuvettes under a continuous magnetic stirring condition ensuring that the photoexcited volume of the sample was kept fresh during the course of the fs-TA measurements.

Nanosecond pump-probe TA. Nanosecond TA was performed with the EOS spectrometer (Ultrafast Systems LLC). The pump beam is generated in the same way as the femtosecond TA experiment described above. A different white light continuum (380-1700 nm, 0.5 ns pulse width, 20 kHz repetition rate) was used, which was generated by focusing a Nd:YAG laser into a photonic crystal fiber. The delay time between the pump and probe beam was controlled by a digital delay generator (CNT-90, Pendulum Instruments).

Kinetics fitting. The decay curve for free NCs can be fitted by a single-exponential decay function, whereas the NC-NCA sample needs to be fitted by a 2-exponential function. The average lifetime τ_{ave} was calculated according to equation below,

$$\tau_{ave} = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2}$$

A_i and τ_i are the amplitude and lifetime, respectively, of the i-th exponential component.

The lifetime of NCs is τ_{NC} and the decay rate can be described as $\frac{1}{\tau_{NC}}$. Similarly, the decay rate of NC-NCA can be described as $\frac{1}{\tau_{ave}}$. Therefore, for NC-NCA hybrid system, the TET rate is $\frac{1}{\tau_{ave}} - \frac{1}{\tau_{NC}}$ and TET yield is $1 - \frac{\tau_{ave}}{\tau_{NC}}$.

For $CsPbBr_3$NCs-NCA//(PtOEP, PTM-TPA) complexes, The lifetime of NCA is τ_{NCA} and the decay rate can be described as $\frac{1}{\tau_{NCA}}$. Similarly, the decay rate of NCs-NCA//(PtOEP, PTM-TPA) can be described as $\frac{1}{\tau'}$. Therefore, for $CsPbBr_3$NCs-NCA//(PtOEP, PTM-TPA) hybrid system, the energy transfer rate is $\frac{1}{\tau'} - \frac{1}{\tau_{NCA}}$ and the yield is $1 - \frac{\tau'}{\tau_{NCA}}$.

Photoluminescence quantum yield measurement. The samples were all prepared in a glovebox and sealed in air-free quartz cuvettes. $CsPbBr_3$ photoluminescence quantum yields were determined relative to Coumarin 307 in ethanol (75%). PtOEP and PTM-TPA photoluminescence quantum yields were determined relative to CV(cresyl violet) in ethanol (57.8%). The quantum yield was calculated according to equation below,

$$\Phi_x = \Phi_r \bullet \frac{1-10^{-A_r}}{1-10^{-A_x}} \bullet \frac{F_x}{F_r} \bullet \frac{\eta_x^2}{\eta_r^2}$$

where Φ_r is the quantum yield of the reference sample (C307 or CV). A_i is the absorption at the excitation wavelength, $F_i$is the integrated photon number, and η_x and η_r are the refractive indexes for hexane and ethanol, respectively.

Diffusion limited rate constant calculation. The diffusion coefficient can be expressed as:[3,4]

$$D_1 = \frac{k_B T}{6\pi\eta r_1}$$

, where k_B is the Boltzmann constant, T is the temperature, η is the solvent viscosity, $r_1(r_2)$ is the first (second) molecule's equivalent radius (the radius of sphere with the same collision volume of the molecule). The reaction rate constant is written as: $k = 4\pi N R_{12} D_{12}$, where N is the Avogadro constant, R_{12} is the sum of r_1 and r_2, D_{12} is the sum of D_1 and D_2.

Assuming η of 0.3mPa for toluene, $r_1$of 3.2 nm for $CsPbBr_3$QDs and r_2 of 0.5 nm for PtOEP, the diffusion constants are calculated to be:

$$D_1 = 2.3\times10^{-10} m^2 s^{-1} \qquad D_2 = 1.5\times10^{-9} m^2 s^{-1}$$

The diffusion limited reaction rate constant is calculated to be:$k_1=4.84\times10^{10}\ s^{-1}M^{-1}$.

For PtOEP concentration of 0.21 mM, the diffusion limited pseudo first order energy transfer rate can be estimated to be $k_{TET}=1\times10^7\ s^{-1}$, corresponding to a time constant of τ_{TET}= 100 ns.

In a similar way, assuming r_2 of 1 nm for PTM-TPA, D_2= 7.4 $\times10^{-10}m^2s^{-1}$,$k_2=3\times10^{10}\ s^{-1}M^{-1}$,For PTM-TPA concentration of 0.11 mM, the diffusion limited pseudo first order energy transfer rate can be estimated to be $k_{TET}=3.3\times10^6\ s^{-1}$, corresponding to a time constant of τ_{TET}= 300 ns.

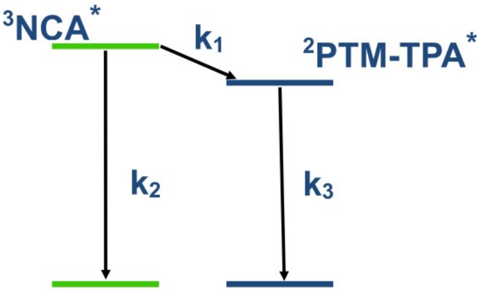
Detection of ^{2}PTM-TPA*feature. The kinetic equations are as follows:

$$\frac{d[^3NCA^*]}{dt} = -(k_1+k_2)[^3NCA^*]$$

$$\frac{d[^2PTM-TPA^*]}{dt} = k_1[^3NCA^*] - k_3[^2PTM-TPA^*]$$

$$[^3NCA^*] = [^3NCA^*]_{t=0}\times\exp[-(k_1+k_2)t]$$

$$[^2PTM-TPA^*] = \frac{k_1}{k_1+k_2\text{-}k_3}[^3NCA^*]_{t=0}\times\{-\exp[-(k_1+k_2)t]+\exp(-k_3t)\}$$



Using the corresponding experimental rate constants of k_1, k_2, and k_3 , we can obtain $\frac{k_1}{k_1+k_2\text{-}k_3}$ = 0.0052, which means the concentration of ^{2}PTM-TPA* is ~200-fold lower than the concentration of NCA*. This quantitatively explains why we cannot detect the signal of ^{2}PTM-TPA* in NC-

NCA/PTM-TPA system.

References

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