Supporting Information for:

Triplet Energy Transfer from Perovskite Nanocrystals Mediated by Electron Transfer

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respectively. Note that the absorption spectra of CsPbBr₃ NCs are slightly blue-shifted upon RhB adsorption, because of anion exchange between Br⁻ in the lattice and Cl⁻ in the RhB molecule. The molecular structure of RhB is shown in (d).



Figure S3. (a) TEM image of CdS NCs used in the main text. (b) Statistic histogram of the diameters of the NCs in (a).



Figure S4. (a) TA spectra of RhB in ethanol excited at 540 nm. The excited state absorption (ESA), ground state bleach (GSB) and stimulated emission (SE) features are indicated. (b) TA kinetics probed at the ESA, GSB and SE features.



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Figure S6. TA results for CsPbBr₃-1. (a,b) TA spectra of (a) CsPbBr₃-1 NCs and (b) NC-RhB complexes probed at indicated time delays following 330 nm excitation. (c) The enlarged TA spectra in the spectral features of RhB (dashed in panel b). (d) 2D pseudocolor TA spectrum of NC-RhB complexes zooming in the spectral features of RhB (dashed in panel b). The GSB of RhB and absorptions of ³RhB* are indicated. (e) TA kinetics of CsPbBr₃-1 NCs and NC-RhB complexes probed at XB peaks. (f) TA kinetics of NC-RhB complexes probed at the GSB (550-560 nm, balck) and ³RhB* (610-630 nm, green). The kinetics of ³RhB* is amplified by a factor of 4 for clear comparison.



Figure S7. TA results for CsPbBr₃-2. (a,b) TA spectra of (a) CsPbBr₃-2 NCs and (b) NC-RhB complexes probed at indicated time delays following 330 nm excitation. (c) The enlarged TA spectra in the spectral features of RhB (dashed in panel b). (d) 2D pseudocolor TA spectrum of NC-RhB complexes zooming in the spectral features of RhB (dashed in panel b). The GSB of RhB and absorptions of ³RhB* are indicated. (e) TA kinetics of CsPbBr₃-2 NCs and NC-RhB complexes probed at XB peaks. (f) TA kinetics of NC-RhB complexes probed at the GSB (550-560 nm, balck) and ³RhB* (610-630 nm, green). The kinetics of ³RhB* is amplified by a factor of 4 for clear comparison.



Figure S8. Absorption spectra of another two CdS NC samples, (a) CdS-2 and (b) CdS-3.



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³RhB* are indicated. (e) TA kinetics of NC-RhB complexes probed at the GSB (545-555 nm, magenta), RhB⁻ (420-440 nm, green; also contains ³RhB*) and ³RhB* (635-645 nm, blue).



Figure S10. TA results for CdS-3. (a,b) TA spectra of (a) CdS-3 NCs and B) NC-RhB complexes probed at indicated time delays following 330 nm excitation. (c) TA kinetics of CdS-3 NCs and NC-RhB complexes probed at XB peaks (375 nm). (d) 2D pseudocolor TA spectrum of NC-RhB complexes. The XB of NC, GSB of RhB and absorptions of RhB⁻ and ³RhB* are indicated. (e) TA kinetics of NC-RhB complexes probed at the GSB (545-555 nm, magenta), RhB⁻ (425-440 nm, green; also contains ³RhB*) and ³RhB* (630-640 nm, blue).



Figure S11. Energy level alignment in CdS NC-RhB, with the unit of eV vs vacuum. The triplet oxidation potential energy of RhB (-5.81 eV) is obtained by subtracting the triplet energy (1.86 eV) from the LUMO. The PL spectrum of CdS NCs is used to derive the hole trap state energy distribution. This is done by aligning the band-edge emission peak center to the valence band edge (-6.50 eV). Because the band-edge and trap-state emissions share the same conduction band energy level, the trap-state emission spectral shape directly reflects the hole trap state energy distribution. From the drawing, -5.81 eV is roughly at the peak position of the trap-state emission band, indicating that half of the trap states are below -5.81 eV while the other half is above -5.81 eV. The latter does not have sufficient driving force for hole transfer from the trap states to RhB⁻ for 3 RhB* formation. Thus, the partition ratio between charge recombination and triplet formation pathways is ~1:1.



Figure S12. Singlet oxygen generation using CsPbBr₃ NC-RhB complexes. (a,b) Absorption spectra and molecular structures of (a) 1,3-diphenylisobenzofuran (DPBF) and (b) Rose Bengal (RB) that are used as the ¹O₂ scavenger and the standard sensitizer, respectively. (c) Representative time-dependent absorption spectra of CsPbBr₃ NC-1-RhB complexes in the presence of DPBF in aerated hexane excited at 460 nm. (d) Time-dependent absorbance of DPBF at 410 nm for RB (red squares) and CsPbBr₃ NC-1-RhB sensitizers. The black solid lines are linear fits to the data.



Figure S13. Integrated TTA-UC emission intensities as a function of the excitation power density for (a) NC-1-RhB and (b) NC-2-RhB samples. NC-1 and NC-2 refer to CsPbBr₃ NCs with their first absorption peaks at ~460 and 495 nm, respectively. The violet squares are experimental data points. The red solid lines are their power fits which change from quadratic to linear dependences. The UC threshold (I_{th}) and quantum efficiency (Φ_{UC}) are labeled.

Experimental Methods

Chemicals. The following reagents were used to prepare nanocrystal (NC)-molecule complexes: cesium carbonate (Cs₂CO₃, Sigma-Aldrich, 99.9%), lead(II) chloride (PbCl₂, Sigma-Aldrich, 99.999%), lead(II) bromide (PbBr₂, Alfa Aesar, 98+%), zinc bromide (ZnBr₂, Alfa Aesar, 99.9%), cadmium oxide (CdO, Sigma-Aldrich, 99.99%), oleic acid (OA, Sigma-Aldrich, 90%), oleylamine (OAm, Acros Organics, 80–90%), 1-octadecene (ODE, Sigma-Aldrich, 90%), rhodamine B (RhB, Sigma-Aldrich, \geq 95%), 9-anthracene carboxylic acid (ACA, Sigma-Aldrich, 99%).

Synthesis of CsPbCl₃ and CsPbBr₃ NCs. CsPbCl₃ perovskite NCs were synthesized as described by Protesescu *et al*². Briefly, 0.40 g Cs₂CO₃, 1.75 mL OA, and 15 mL ODE were degassed for 30 min under vacuum at 60 °C, and heated under Ar atmosphere to 150 °C until all the Cs₂CO₃ powders were dissolved. This Cs-oleate precursor solution was kept at 100 °C for use. Then, 0.1 mmol of PbCl₂, 5 mL ODE, 0.5 mL OA, and 0.5 mL OAm were loaded in a 25 mL three-neck flask and dried under vacuum for 1 h at 120 °C. After degassing, the temperature was raised to 180 °C and 0.4 mL of previously synthesized Cs-oleate precursor was swiftly injected. 30 seconds after the injection, the NC solution was quickly cooled down to room temperature with an ice bath. The NCs were separated from the crude solution by centrifuging at 3000 rpm for 30 mins. The precipitant was re-dispersed in 5 mL hexane by shaking and sonication, followed by centrifugation at 7830 rpm for 2 mins in order to remove larger NCs and agglomerates.

CsPbBr₃ perovskite NCs were synthesized by using a hot injection approach with modifications³. The synthesis started with preparation of Cs-oleate precursors ($0.25 \text{ g Cs}_2\text{CO}_3$)

was degassed in 0.8 g OA and 7 g ODE at 150 °C for 1 h, and then kept at 100 °C for use). In another 250 mL 3-neck flask, the precursor solution of Pb and Br was prepared by dissolving 0.45 g PbBr₂ and 1.10 g ZnBr₂ in a mixture of OA (16 mL), OAm (16 mL) and ODE (26 mL). Then, the precursor solution was vacuum-dried for 1 h at 110 °C, and heated under Ar atmosphere to 140 °C until all the powders were dissolved. After the solution was cooled and kept at 110 °C, 2.4 mL of Cs-oleate precursor was injected to initiate the reaction. The reaction was quenched after 6 mins by cooling the flask in an ice bath. The product was centrifuged at 4000 rpm for 15 min to remove the unreacted salts as the precipitate, and the perovskite NCs dispersed in the supernatant were collected. 10 mL of acetone was directly added into the supernatant to precipitate the NCs followed by centrifuging at 4000 rpm for 5 mins. The dried NCs were collected and dissolved in hexane. The lowest energy absorption peak of as-prepared CsPbBr₃ NCs is situated at ~460 nm (CsPbBr₃-1 sample). Another CsPbBr₃ NCs (CsPbBr₃-2 sample) were obtained by tuning the reaction temperature and time (the lowest energy absorption peak at ~490 nm), as detailed in refs^{4,5}.

Synthesis of CdS NCs. CdS NCs were synthesized according to a literature method⁶. Briefly, 0.077 g CdO, a varying amount of OA (1.8 mL, 1.2 mL and 1.5 mL for CdS, CdS-2 and CdS-3 samples, respectively) and 15 mL ODE were degassed under vacuum for 10 mins at 90 °C. The solution was then heated to 270 °C in 30 mins under Ar atmosphere until all the CdO powders were dissolved. Then, 3 mL of sulfur (S) stock solution (0.1 M of S in ODE) was swiftly injected. The reaction was stopped after 30 s by injecting 7 mL room-temperature ODE and removing the heating mantle. The CdS NCs were purified several times at 7800 rpm for 5 mins with ethanol and finally dispersed in hexane for use.

Preparation of NC-RhB complexes. The NC-RhB complexes were prepared by adding RhB powders into a NC solution in hexane, followed by sonication for controlled time (5-30 mins). The mixture was filtered to obtain a clear solution containing NC-RhB complexes; because the solubility of RhB in hexane is negligible, all the RhB molecules were believed to be anchored to NC surfaces. On the basis of the molecular structure of RhB (Fig. S2d), there should be a large steric hindrance for the carboxyl group to access NC surface. Nonetheless, we believe the carboxyl group still plays a key role in anchoring the molecule on to NC surface. This is because we found it very difficult to attach another molecule with a similar ammonium inner salt structure but no carboxyl group, methylene blue, onto the surface of perovskite NCs.

On the basis of the extinction coefficients of CsPbCl₃ NCs (ϵ_{400nm} =6.3×10⁵ M⁻¹cm⁻¹)⁷, CdS NCs (ϵ_{382nm} =2.5×10⁵ M⁻¹cm⁻¹)⁸ and RhB molecule (ϵ_{543nm} =106000 M⁻¹cm⁻¹)⁹, on average 3 and 3.5 molecules were bound to CsPbCl₃ and CdS NCs, respectively.

TEM measurements. TEM images were acquired on a JEOL JEM-2100 TEM at 200 KV (line resolution of 0.14 nm) by drop casting the NC-hexane dispersions on carbon-coated Cu grids and drying under ambient conditions.

Transient absorption (TA). The femtosecond pump-probe TA measurements were performed using a regenerative amplified Ti:sapphire laser system (Coherent; 800 nm, 70 fs, 6 mJ/pulse, and 1 kHz repetition rate) as the laser source and a HELIOS Fire spectrometer (Ultrafast Systems LLC). Briefly, the 800 nm output pulse from the regenerative amplifier was split in two parts with a 50% beam splitter. The transmitted part was used to pump a TOPAS Optical Parametric Amplifier (OPA) which generated a wavelength-tunable laser

pulse from 250 nm to 2.5 µm as pump beam. The reflected 800 nm beam was split again into two parts. One part with less than 10% was attenuated with a neutral density filter and focused into a crystal to generate a white light continuum (WLC) used for probe beam. The probe beam was focused with an Al parabolic reflector onto the sample. After the sample, the probe beam was collimated and then focused into a fiber-coupled spectrometer with CMOS sensors and detected at a frequency of 1 KHz. The intensity of the pump pulse used in the experiment was controlled by a variable neutral-density filter wheel. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump pulses were chopped by a synchronized chopper at 500 Hz and the absorbance change was calculated with two adjacent probe pulses (pump-blocked and pump-unblocked). The samples were placed in 1 mm airtight cuvettes in a N₂-filled glove box and measured under ambient conditions. 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).

Time-resolved PL. For an 8 ns time window, the PL decay was measured using a time-resolved fluorescence upconversion set-up (Chimera, Light conversion) and a Pharos laser (1030 nm,100 kHz, 230 fs pulse-duration; Light conversion). Briefly, the fundamental 1030 nm laser pulse was split into two parts. One part was used to pump a TOPAS OPA to generate wavelength-tunable excitation pulses; the other was used as the gate pulse. The

emitted light was collected by lens and focused into a BBO crystal together with the 1030 nm gate pulse to generate the up-converted signal via sum-frequency-generation (SFG). The up-converted photons were focused onto the entrance slit of a monochromator and then detected by the spectrometer. The fluorescence decay curve was obtained by delaying the gate pulse using a mechanical delay stage. For a 100 ns time window, the time-resolved PL decay was measured using time-correlated single-photon counting (TCSPC) set-up, which uses the same excitation source and camera as the fluorescence upconversion set-up and has a temporal resolution of 100 ps. All samples were placed in 1 mm airtight cuvettes in a N_2 -filled glove box and were vigorously stirred in all the measurements.

Singlet Oxygen generation. The singlet oxygen (${}^{1}O_{2}$) generation experiments were performed for air equilibrated samples. In brief, CsPbBr₃ NC-RhB complexes were mixed with 1,3-diphenylisobenzofuran (DPBF) in hexane. DPBF was used as ${}^{1}O_{2}$ scavenger because it can trap the generated ${}^{1}O_{2}$ through oxidation¹⁰. The as-prepared samples were irradiated with a 460 nm laser light (30 mW; from the Pharos laser) with variable excitation time. The ${}^{1}O_{2}$ production sensitized by NC-RhB was monitored by following the absorbance of DPBF at 410 nm. We calculated ${}^{1}O_{2}$ quantum yield (Φ_{Δ}) using a relative method with Rose Bengal (RB) as the standard sensitizer (sensitization quantum yield $\Phi_{std} = 80\%$ in methanol)¹¹. The Φ_{Δ} of the NC-RhB sensitizer was calculated according to the following equation¹²:

$$\Phi_{\Delta} = \Phi_{\text{std}} \times \left(\frac{N_{\text{std}}}{N_{\text{sam}}} \times \frac{1 - 10^{-A_{\text{std}}}}{1 - 10^{-A_{\text{sam}}}}\right) \times \left(\frac{m_{\text{sam}}}{m_{\text{std}}}\right) \times \left(\frac{n_{\text{sam}}}{n_{\text{std}}}\right)^2 \tag{S1}$$

where "sam" and "std" represent the sample and the standard. Φ , N, A, m, and n are the singlet oxygen quantum yield, the total number of incident photons, the absorbance at excitation wavelength, the slope of the absorbance of DPBF changing over time, and the

refractive index of the solvent used for measurement, respectively.

Triplet-triplet annihilation photon upconversion (TTA-UC). TTA-UC measurements were performed with a 447 nm *cw* laser under deaerated conditions. In brief, CsPbBr₃ NC-RhB complexes were mixed with diphenyl anthracene (DPA) in hexane. The as-prepared samples were irradiated with *cw* laser light with variable excitation intensity. The laser beam was focused by a quartz lens. The focal point was at the air-free cuvettes with the samples. Along the axis perpendicular to the excitation laser, a lens system was used to collect the fluorescence and couple it into a fiber. The other side of the fiber was connected to a spectrometer (Maya2000 pro; Ocean Optics). The upconversion quantum yield (Φ_{UC} ') was calculated using Coumarin 503 as a reference with quantum yield of 0.75 in ethanol. The Φ_{UC} ' was calculated according to the following equation:

$$\Phi_{\rm UC}' = 2 \times \Phi_{\rm std} \times (\frac{1 - 10^{-A_{\rm std}}}{1 - 10^{-A_{\rm sam}}}) \times (\frac{F_{\rm sam}}{F_{\rm std}}) \times (\frac{n_{\rm sam}}{n_{\rm std}})^2$$
(S2)

where "sam" and "std" represent the sample and the standard. Φ , A, F, and n are the photoluminescence quantum yield, the absorbance at the excitation wavelength, the integrated photon number, and the refractive index of the solvent used for measurement, respectively.

Kinetics fitting

Model for CsPbCl₃ NC-RhB complexes. According to the TA and PL measurements, a kinetic fitting model is proposed as follows: upon selective photoexcitation CsPbCl₃ NCs in NC-RhB complexes, the band-edge electrons transfer (ET) from NC to RhB within ~20 ps to form charge separated states (NC⁺-RhB⁻) with a rate of k_{ET} (Stage I). From ~20 ps to 10 ns timescale, the band-edge holes in NC⁺ are injected into the RhB⁻ to form NC-³RhB* with a rate of k_{HT} , while the absorptive signal of ³RhB* grows in and the ground state bleach (GSB) signal of RhB maintains constant (Stage II). From 10 ns to μ s timescale, the generated triplets (³RhB*) decay out to form to NC-RhB (Stage III).

The formation kinetics of RhB GSB and RhB⁻ are simultaneously fitted using a mono-exponential decay function $(S(t) \propto A \cdot e^{-(k_{ET}+k_{ET})t})$. Here k_{Etr} is the rate constant for the electron trapping process that competes with electron transfer, which is ~0.045 ps⁻¹ from the kinetics of free CsPbCl₃ NCs. The ensuing hole transfer and ³RhB* formation kinetics are simultaneously fitted using two-exponential decay functions $(S(t) \propto A_1 \cdot e^{-k_t t} + A_2 \cdot e^{-k_2 t})$, where we have assumed that the hole in the charge separated state has a much longer intrinsic lifetime than the hole transfer process. Lastly, the ³RhB* decay is fitted using three-exponential decay functions $(S(t) \propto A_1 \cdot e^{-k_t t} + A_2 \cdot e^{-k_2 t} + A_3 \cdot e^{-k_2 t})$. Note that the criterion for the choice of the number of exponential components is to use the fewest components while ensuring fitting convergence. The fitting parameters are listed in Table S1, and the rate constants are converted to time constants in the table. The average lifetime τ_{ave} was calculated according to the following equation:

$$\tau_{ave} = \frac{\sum_{i}^{i} A_{i} \tau_{i}}{\sum_{i}^{i} A_{i}}$$
(S3)

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

Probe	Electron	Hole transfer			Triplet lifetime			
wavelength	transfer							
(nm)	$ au_{\mathrm{ET}}$ (ps)	τ_1 (ps)	$ au_2$ (ps)	$ au_{ m ave,HT}$	$ au_1$ (µs)	$ au_2$ (µs)	τ ₃ (μs)	$ au_{\mathrm{ave,T}}$
	A (%)	A ₁ (%)	$A_{2}(\%)$	(ps)	$A_{1}(\%)$	$A_{2}(\%)$	A ₃ (%)	(µs)
430-440	6.6±0.3	359±27	8856±1056	2993±346	0.54±0.03	16.5±2.1	198±23.3	54.9±6.5
(RhB ⁻ +	(100)	(69)	(31)		(44)	(31)	(25)	
³ RhB*)								
555-565	6.6±0.3	-	-	-	0.54±0.03	16.5±2.1	198±23.3	54.9±6.5
(GSB)	(100)				(44)	(31)	(25)	
610-630	-	359±27	8856±1056	2993±346	0.54±0.03	16.5±2.1	198±23.3	54.9±6.5
(³ RhB*)		(69)	(31)		(44)	(31)	(25)	

Table S1. Fitting parameters for CsPbCl₃ NC-RhB complexes.

Model for CdS NC-RhB complexes. According to the TA and PL measurements, a kinetic fitting model is proposed as follows: upon selective photoexcitation CdS NCs in NC-RhB complexes, the band-edge electrons quickly transfer from NC to RhB within ~10 ps to form RhB⁻ with a rate of k_{ET} , while a sub-ensemble of band-edge holes are quickly trapped in several picoseconds through ultrafast hole trapping (HTr). In addition, the RhB GSB and

absorptive signal of RhB⁻ grow in a simultaneous way. From ~10 ps to 10 ns timescale, a fraction of RhB⁻ decay via charge recombination (CR) to form ground state NC-RhB, along with a simultaneous decay of RhB GSB signal with a rate of k_{CR} . On the other hand, a part of trapped holes are injected into the rest RhB⁻ to form NC-³RhB* with a rate of k_{HT} , while the absorptive signal of ³RhB* grows in. From ~10 ns to μ s timescale, the generated triplets (³RhB*) decay out to form to NC-RhB.

The formation kinetics of RhB GSB are fitted using a mono-exponential decay function $(S(t) \propto A \cdot e^{-k_{ET}t})$. The intrinsic decay rate of electrons is ignored in this equation because band edge electrons in CdS are long-lived. The ensuing hole transfer kinetics are fitted using a mono-exponential decay function $(S(t) \propto A \cdot e^{-k_{HT}t})$, and charge recombination kinetics are fitted using two-exponential decay functions $(S(t) \propto A_1 \cdot e^{-k_{t}t} + A_2 \cdot e^{-k_2t})$. Lastly, the ³RhB* decay is fitted using another two-exponential decay functions $(S(t) \propto A_1 \cdot e^{-k_{t}t} + A_2 \cdot e^{-k_2t})$. Again, the criterion for the choice of the number of exponential components is to use the fewest components while ensuring fitting convergence. The fitting parameters are listed in Table S2, and the rate constants are converted to time constants in the table. The average lifetime τ_{ave} was calculated according to the equation S3.

 Table S2. Fitting parameters for CdS NC-RhB complexes.

Probe	Electron	Hole	Charge recombination			Triplet lifetime		
wavelength	transfer	transfer						
(nm)	$ au_{\mathrm{ET}}$ (ps)	$ au_{ m HT}$ (ps)	$ au_1$ (ps)	$ au_2$ (ps)	$ au_{ m ave,CR}$	$ au_1$ (µs)	$ au_2$ (µs)	$ au_{\mathrm{ave,T}} (\mu \mathrm{s})$
	A (%)	A (%)	A ₁ (%)	$A_{2}(\%)$	(ps)	A ₁ (%)	A_2 (%)	

550-560	1.4±0.1	-	707±52	10064±304	6976±221	7.2±0.7	182±7	128±5.0
(GSB)	(100)		(33)	(67)		(31)	(69)	
630-640	-	2955±520	-	-	-	7.2±0.7	182±7	128±5.0
(³ RhB*)		(100)				(31)	(69)	

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