Supplementary Information for

Electron transfer-mediated triplet sensitization from CsPbI3 nanocrystals to fullerene for photon upconversion

Materials

The raw materials required for preparing perovskite nanocrystals such as $Pb(CH_3COO)_2 \cdot 3H_2O$ (99.99%) and Cs_2CO_3 (99.99%) were purchased from TCI Chemicals. 1-Octadecene (ODE, 90%) was purchased from Acros. Diethyl bromomalonate (90 %), Fullerene C_{60} (99.5 %) and Oleic acid (OA, 90%), oleylamine (OAm, 90%), benzoyl bromide and benzoyl chloride were purchased from Innochem. Spectrophotometric grade toluene was purified by redistilling. Other materials were purchased without further purified.

Synthesis of CsPbI$_3$ NCs

CsPbI$_3$ NCs were prepared according to the recent report.[1-2] In a typical synthesis, 0.5 g of Cs_2CO_3, 2 mL OA and 50 mL ODE were added to a 100 mL Schlenk flask and the flask was purged with N_2 for 3 min and then placed back under vacuum. This process of alternately applying vacuum and N_2 was repeated for 3 times. Then the flask was stirred under vacuum for 60 min at 120 °C to remove moisture. The reaction was considered complete when the solution was clear, indicating that the Cs_2CO_3 had reacted with the OA. The Cs-oleate solution in ODE was stored in N_2 and keep the temperature above 100 °C. In another Schlenk flask, 1 g PbI$_2$ precursor, 5 mL oleylamine, and 50 mL 1-octadecene were loaded into a 250-mL Schlenk flask and degassed for 60 min at 120 °C to remove water. The flask was purged with N_2 for 3 min and then placed back under vacuum. This process of alternately applying vacuum and N_2 was repeated for a total of 3 times to remove moisture and O_2. The flask was then filled with N_2 and heated to140 °C under constant N_2 flow. When the temperature is stable, 8 mL Cs-oleate precursor was rapidly injected into the reaction mixture. The

mixture turned dark red swiftly, and after 5 s the reaction was quenched by an ice bath.

MeOAc was used to extract cubic-phase NCs. At first, the synthesized NCs were separated into eight parts and each one precipitated by adding ~25 mL MeOAc (ratio of QD reaction solution: MeOAc is 1:3), then centrifuged at 8,000 rpm for 5 min. The precipitation in each centrifuge tube was re-dispersed in 3 mL anhydrous hexane, precipitated again with adding ~6 mL MeOAc slowly until it turns cloudy and centrifuged at 10,000 rpm for 3 min. The NCs were then re-dispersed in 20 mL hexane total, and centrifuged again at 4,000 rpm for 5min to remove excess PbI_2 and Cs-oleate. The supernate was kept at 4 °C overnight in the dark to precipitate excess Cs-oleate and Pb-oleate. After cooling subsidence, the NCs solution needs to be centrifuged again at 4,000 rpm for 5 min to obtain the final product.

Synthesis of $C_{61}(COOH)_2$
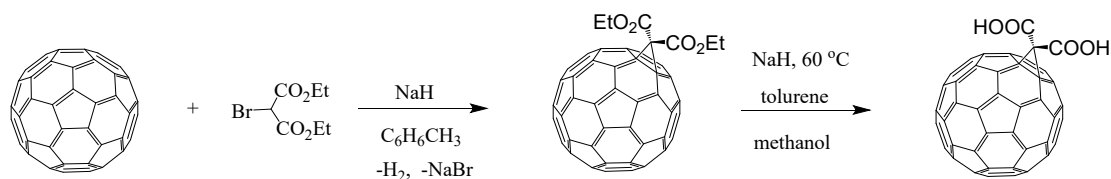
Scheme S1. Synthesis route of $C_{61}(COOH)_2$

$C_{61}(COOH)_2$ were synthesized according to the recent report.[3-6] $C_{61}(COOEt)_2$ was prepared firstly. 610 mg fullerene, 0.315 mg diethyl bromomalonate (96%) and 0.232 g NaH were added to 280 mL toluene and stirred at room temperature for 6.5 h. About 5 mL of 1M dilute sulfuric acid was added to the reaction solution and stirred. Anhydrous magnesium sulfate was used to dry the reaction solution. After filtration, about 10 g silica gel was mixed into the reaction solution and the crude products were separated by column chromatography (toluene: hexane=1:1). After the separation, the product was dried overnight in a vacuum oven. The product was 230 mg and the yield was 31 %.

230 mg $C_{61}(COOEt)_2$ and 150 mg NaH were added to 130 mL toluene, stirred in N_2 atmosphere at 60 °C for 3 h, then 3 mL methanol was injected into the reaction system, and continued stirring. Brown solid precipitated out of the reaction system. The reaction

liquid was cooled to room temperature and centrifugated at 4000 rpm for 5min. The supernatant was poured away, and the precipitates were washed with toluene, 1 M sulfuric acid and water, respectively, and then dried in vacuum oven at 60 $^{\circ}$C overnight.

Instrumentation

Ultraviolet photoelectron spectroscopy (UPS) was performed on Thermo Scientific ESCALab 250Xi. The gas discharge lamp was used for UPS, with Helium gas admitted and the He I emission line at 21.22eV employed. The Helium pressure in the analysis chamber during analysis is about 3×10^{-8} mbar. X-ray powder diffraction (XRD) patterns were measured by using a Bruker D8 Focus X-ray diffractometer equipped with $Cu_{K\alpha}$ radiation (λ = 1.54050 Å). UV-Vis absorption spectra of NCs, $C_{61}(COOH)_2$ and perylene in toluene were measured by using a Shimadzu 2550-PC spectrometer. Emission spectra of NCs, $C_{61}(COOH)_2$ and perylene were measured by using a Hitachi F-4600 spectrometer. Upconversion emission spectra was measured by a Princeton Instrument Acton SP2500 spectrograph and a SPEC-10 liquid nitrogen-cooled CCD excited by a continuous-wave laser (MRL-III-635L, 635 nm). The laser was purchased from Changchun New Industries Optoelectronics Tech. Co. Ltd. The incident laser power was measured with an Ophir Nova II powermeter with a PD300-3W photodetector. Morphology and lattice fringes were recorded on a JEM 2100F transmission electron microscope (TEM). Luminescence decay processes were recorded on an Edinburgh FLS1000 photoluminescence lifetime system with single photon counting technique. Nanosecond-to-microsecond transient absorption experiments were performed using a commercial nanosecond laser flash photolysis spectrometer (LP980-KS, Edinburgh Instruments Ltd., Livingston, UK) at ambient temperature. The pump laser pulse was obtained from Optical Parametric Oscillator (PrimoScan ULD400, Spectra-Physics, US) at 635 nm, with the FWHM around 10 ns. The probe light was provided by a 150 W Pulsed xenon arc lamp. Liquid samples were excited by the pump, subsequently the probe light from the xenon lamp passed through the sample in a in a crossbeam geometry holder. The transmitted probe light was measured by a single PMT detector (Hamamatsu R928), using a Tektronix Model MDO3052 (100 MHz, 1.25 GS s-1) digital oscilloscope, at 510 nm for kinetic analysis.

The femtosecond transient absorption data of visible and NIR light region is Light Conversion Ltd. Liquid samples were excited by PHAROS (10 W-33 kHz-300 μJ-190 fs). The optical amplifier is ORPHEUS HP and the signal were detected by HARPIA. TR-PL date were acquired by a Streak camera (Hamamatsu Photonics) combined with Astrella Opera Solo-Femtosecond Laser (The United States Coherent).
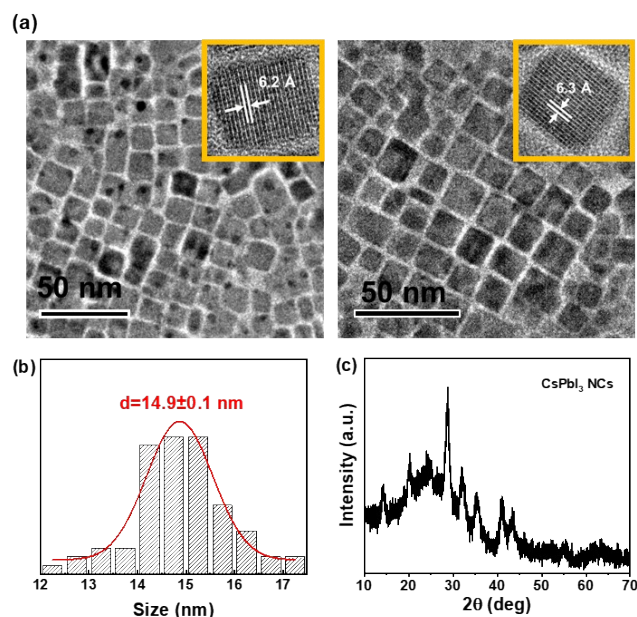

Figure S1. TEM of **(a)** NCs (left) and NCs-$C_{61}(COOH)_2$ (right). Insert: HRTEM of NCs and NCs-$C_{61}(COOH)_2$ complex. **(b)** Size distribution of NCs. **(c)** XRD of NCs.

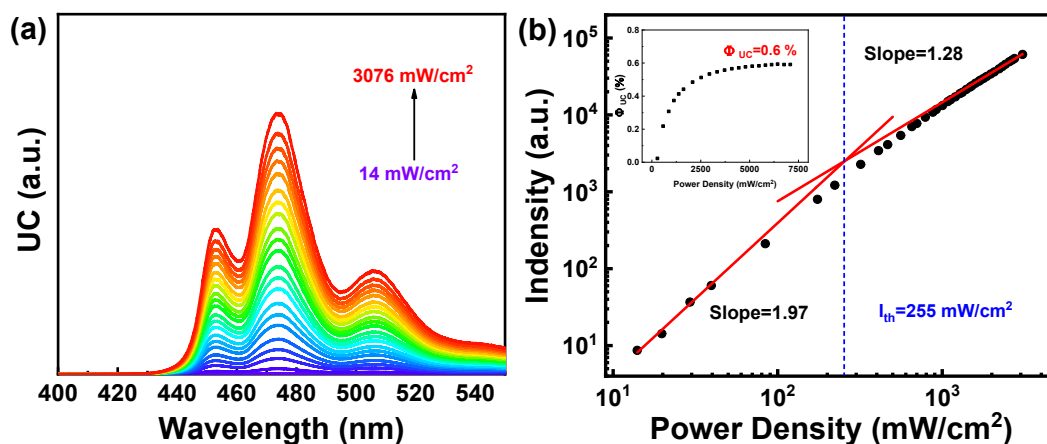**Figure S2. (a)** UC emission spectra of $CsPbI_3$-$C_{61}(COOH)_2$-Perylene with various excitation intensity from 14 mW/cm^2 to 3076 mW/cm^2 (λ_{ex}=635 nm). **(b)** Dependence of the UC intensity on the various incident power densities. Insert: Dependence of the UC quantum yield on the various

incident power densities. (λ_{ex} = 653 nm). The lines that have slopes of 1.97 and 1.28 are the fitting in the low-and high-power regions, respectively, giving I_{th} is 255 mW/cm^2.
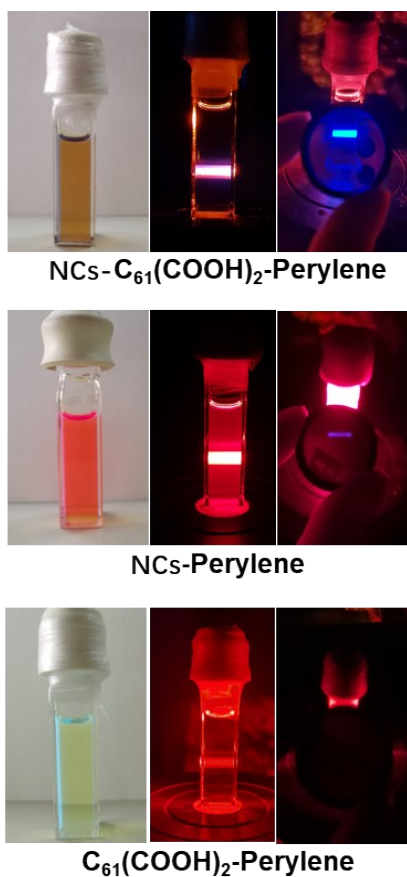

Figure S3. Photos of NCs-C$_{61}$ (COOH)$_2$-Perylene (top), NCs-Pyrene (middle) and C$_{61}$(COOH) $_2$-Perylene (bottom) in daylight (left), under 635 nm laser excitation (middle) and observed through a 470 nm bandpass filter (right) (λ_{ex} = 635 nm, 1.32 W/cm^2).

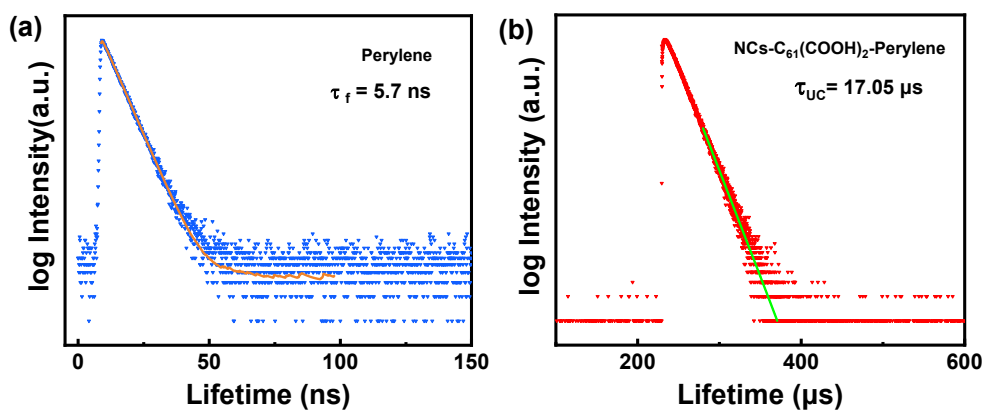**Figure S4. (a)** Time-resolved luminescence spectra at 470 nm of Perylene (λ_{ex} = 405 nm) and **(b)** Time-resolved UC intensity at 470 nm of NCs-C$_{61}$(COOH)$_2$-Perylene (λ_{ex} = 635 nm).
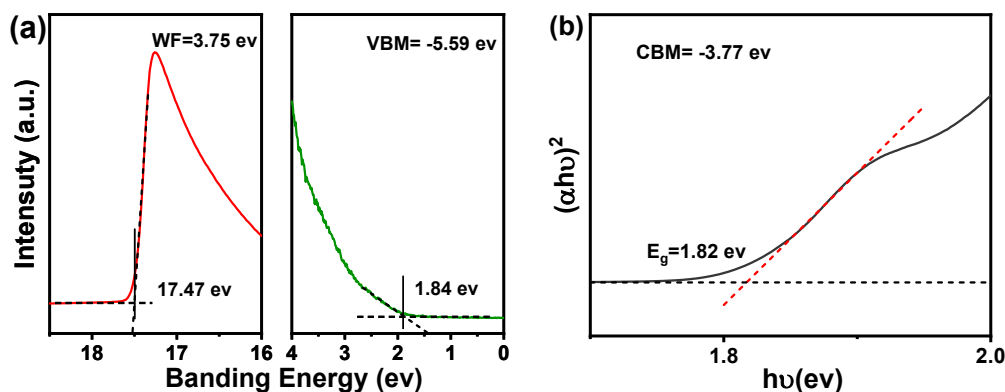
Figure S5. (a) UPS spectra of NCs. The dashed black lines mark the baseline and the tangents of the curve. The intersections of the tangents with the baseline give the edges of the UPS spectra from which the UPS width is determined. **(b) (a**hυ**)^2** versus **h**υ curve of NCs. The horizontal dashed black line marks the baseline; the other dashed lines are the tangents of the curves. The intersection value is the band gap.

The optical band gap of NCs was measured from the Tauc plot that is the curve of converted $(\alpha h\nu)^r$ versus $h\nu$ from the UV-vis spectrum (α, h, and ν are the absorption coefficient, Planck constant, and light frequency, respectively, and r = 2 for a direct band gap material and r =1/2 for an indirect band gap material). It has a good liner fit when using r = 2 which is consist with previous work claiming perovskite to be a direct band gap material.[7] By measuring the x-intercept of the line extrapolated from the linear state of the curve, the E$_g$ value of this NCs is 1.82eV (Figure S5b, red dotted line). As shown in Figure S5a, the work function of NCs was determined to be 3.75 eV by ultraviolet photoelectron spectroscopy (UPS), and the ionization potential (i.e. valence band energy, E_{VB}) was calculated to be -5.59 eV by subtracting the width of the He I UPS from the excitation energy (21.22 eV). The conduction band energy (E_{CB})of NCs was determined to be -3.77 eV. E_{VB} and E_{CB} are both values relative to the vacuum energy level.
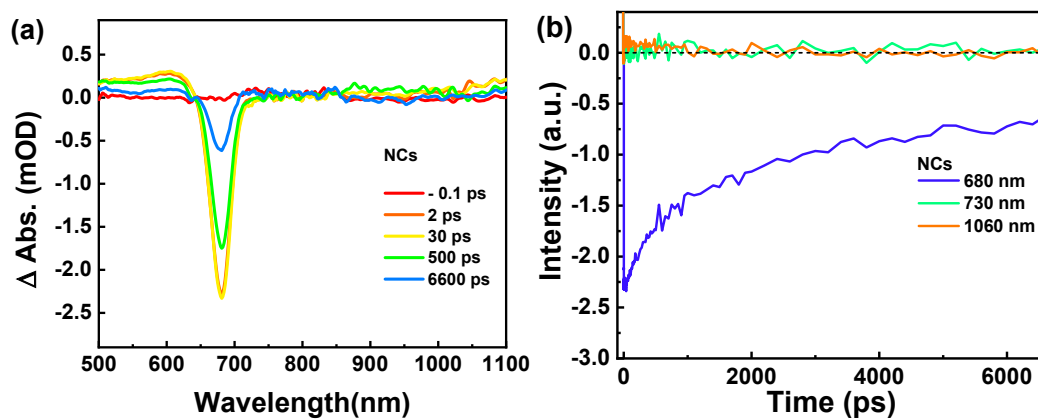
Figure S6. (a) TA spectra at indicated time delays and **(b)** TA kinetics of CsPbI$_3$ NCs probed at the indicated wavelength after excitation by a 635 nm pulse.
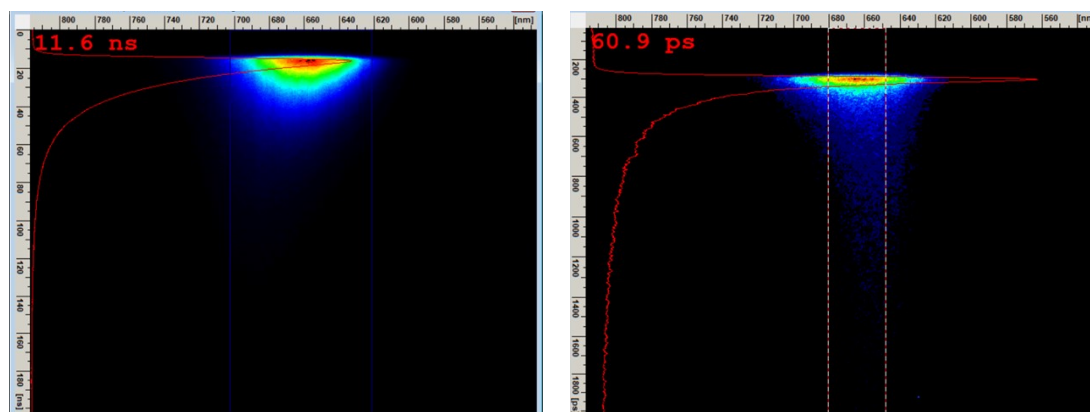

Figure S7. Streak camera images of the time-evolution of the photoluminescence of NCs (left) and NCs- C$_{61}$(COOH)$_2$ (right) (λ_{ex}=550 nm).
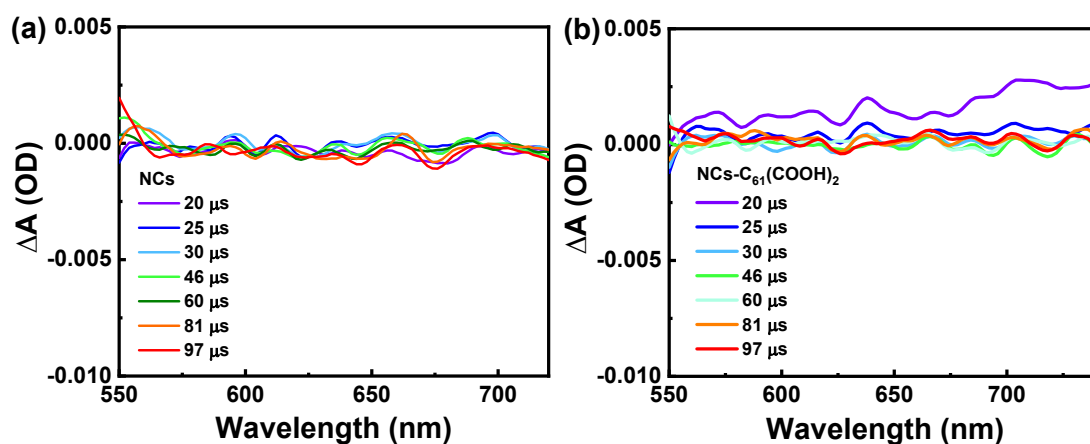

Figure S8. TA spectra of **(a)** NCs at indicated time delays following the excitation by a 420 nm pulse laser and **(b)** NCs-C$_{61}$(COOH)$_2$ at indicated time delays after the excitation by a 635 nm

pulse laser which selectively excites NCs.

The calculated triplet quantum yield of $C_{61}(COOH)_2$

We obtained the triplet state quantum yields of $C_{61}(COOH)_2$ in NCs-$C_{61}(COOH)_2$ by the comparative method as described in the literature.[8-9] Briefly, measurements were obtained by excitation of deoxygenation solutions at 355 nm ($C_{61}(COOH)_2$) and 635 nm (NCs/$C_{61}(COOH)_2$) and the initial intensity of the triplet absorbance (ΔOD) of NCs-$C_{61}(COOH)_2$ and $C_{61}(COOH)_2$ were obtained under identical experimental conditions. The triplet quantum yield (Φ_T) of NCs-$C_{61}(COOH)_2$ was calculated using $C_{61}(COOH)_2$ ($\Phi_T = 0.95$)[9] as a reference (eq 1).

$$\frac{\Delta\varepsilon_{T-T, sample}\, \Phi_{T, sample}}{\Delta\varepsilon_{T-T, reference}\, \Phi_{T, reference}} \times \frac{\text{photons absorbed by sample}}{\text{photons absorbed by reference}} = \frac{\Delta OD_{sample}}{\Delta OD_{reference}} \qquad \text{eq 1}$$

Where $\Delta\varepsilon_{T-T, sample}$ and $\Delta\varepsilon_{T-T, reference}$ are triplet-triplet extinction coefficients of NCs-$C_{61}(COOH)_2$ and $C_{61}(COOH)_2$ respectively. $\Phi_{T, sample}$ and $\Phi_{T, reference}$ are triplet quantum yield of NCs-$C_{61}(COOH)_2$ and $C_{61}(COOH)_2$ respectively. ΔOD_{sample} and $\Delta OD_{reference}$ are triplet absorbance of NCs-$C_{61}(COOH)_2$ and $C_{61}(COOH)_2$ at 740 nm obtained under 355 nm and 635 nm irradiation respectively.

$\Delta\varepsilon_{T-T, sample} \approx \Delta\varepsilon_{T-T, reference}$

Therefore,

$$\frac{\Phi_{T, sample}}{\Phi_{T, reference}} \times \frac{\text{photons absorbed by sample}}{\text{photons absorbed by reference}} = \frac{\Delta OD_{sample}}{\Delta OD_{reference}}$$

eq 2

Photon absorbed is obtained by eq3[10], where Abs is the absorbance at the excitation wavelength,

$$\text{photons absorbed/s} = \frac{\text{Laser power}}{hc/\lambda}(1 - 10^{-Abs})$$

eq 3

The triplet quantum yield of $C_{61}(COOH)_2$ in our UC system was calculated to be 46.3 %.

Reference

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