Supporting Information

Ligand enhanced upconversion of near-infrared photons with nanocrystal light absorbers.

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1. Materials

Chemical reagents were purchased from Acros Organics, Aldrich Chemical Co, Strem, TCI America, or Alfa Aesar and used as received. Specifically, dry and degassed acetone and toluene were obtained from JC Meyer's solvent purification system, HPLC grade hexane was purchased from Fisher Scientific.

2. Instrumentation

Absorption spectra were recorded on a Jasco-V670 UV-Vis absorption spectrophotometer. Fluorescence spectra were recorded on a HORIBA FluoroMax-3 fluorometer. Lasers: A Coherent Sapphire 532 nm laser with an output power of 5.0 mW was used. A 943 W/cm^2 808 nm TO can cw elliptical laser diode (Thor Labs) with the largest and the smallest diameters of 0.12 and 0.06 mm respectively was used for excitation. NMR spectra were recorded on a Varian Inova-400MHz NMR spectrometer at room temperature. The ^{1}H and ^{13}C Chemical shifts (δ) are reported in parts per million with the residual solvent ($CHCl_3$) peak as an internal standard. Mass spectra were recorded on the Agilent 6210 MS TOF and Agilent LC TOF.

Upconversion fluorescence spectra were recorded from the front face at a 70 degree to the excitation with an Ocean Optics Inc. JAZ spectrometer as shown in Fig. S4. The 808 nm laser is focused by two focal lenses to a spot size of 565.2 μm^2. A slit is used to block the unfocused laser. In front of the detector, a 790 nm blocking edge BrightLine® multiphoton short-pass emission filter (part number FF01-790/SP-25) and 532 nm StopLine® single-notch filter (part number NF01-532U-25) are used to block the scattered laser light. The upconverted light was collected from the front of the cuvette and focused by a 30 mm focal lens to the A PAF-SMA-11-A (Thor Labs) fiberport through an Ocean Optics QP400-2-SR fiber connected to a JAZ spectrometer. The upconversion sample is in 100 μm or 200 μm thick capillary tubes (Friedrich & Dimmock, Inc. with part numbers of LRT-010-2-10 and LRT-020-4-15 respectively) in air tight Starna cuvettes with screw tops.

The photoluminescence (PL) of nanocrystals (NC) was collected from the front of the cuvette (at right angles from the excitation beam). An Edmund Optics-FC10650836 dichroic mirror was used to collect NC PL. The NC PL was focused on an Ocean Optics QP400-2-VIS-NIR fiber with a 25.4 mm focal length N-BK7 plano-convex lens on a NIRS-0900-1700 Bayspec fluorometer.

3. Synthesis of PbS and PbSe nanocrystals.

3.1 **Synthesis of 2.9 nm PbS NCs**

PbS quantum dots were synthesized by modifying a protocol reported by Hines et al.[1] 50 PbO (0.45 g), oleic acid (OA, 2 mL), and 1-octadecene (ODE, 18 mL) were mixed in a 50 ml three-neck flask and heated to 110 °C under vacuum for an hour. Pb oleate is formed, indicated by the discoloration of the reaction to a clear solution. Then the reaction atmosphere was switched to Ar, and reaction temperature was set to 78 °C. The sulfide precursor, containing 0.21 mL of bis(trimethylsilyl)sulfide in 10 mL of anhydrous ODE, was injected, and the temperature dropped to about 68°C. Immediately after injection, the heater was turned off. After 105 seconds the reaction solution were cooled with compressed air and the injection of 10 ml Hexane. The PbS NCs were transferred to a glovebox and washed 3 times by adding 1:1 hexanes/ethanol mixture; followed by centrifuging at 7000 rpm for 5 min. The supernatant was discarded. The final pellet was dissolved in hexane and stored in the dark inside the glovebox for future use. The PbS NC size (2.9 nm diameter) was determined by measuring the energy of the first exciton peak (907 nm). The concentration of the PbS NCs was determined from the absorption at 400 nm. The size and the concentration of PbS NCs were determined by measuring the energy of the first exciton peak and the absorption at 400 nm respectively.[2]

3.2 Synthesis of 2.5 nm PbSe NCs

PbSe quantum dots were synthesized via a modified protocol reported by Ma et al.[3] PbO (0.23 g), oleic acid (OA, 3.5 mL), and 1-octadecene (ODE, 10 g) were mixed in a 50 ml three-neck flask and heated to 100 °C under vacuum for an hour. The solution was then heated for an additional 1 h to 150 °C under argon, resulting in a clear, colorless solution. The temperature was reduced to 130 °C. The sulfide precursor, containing 62 µl of bis(trimethylsilyl)sulfide in 4 mL of anhydrous ODE, was injected, and the temperature dropped to about 120 °C. Immediately after injection, the heater was turned off. After 105 seconds the reaction solution were cooled with compressed air and the injection of 10 ml Hexane. The PbSe NCs were transferred to a glovebox and washed 3 times by adding 1:1 hexanes/ethanol mixture; followed by centrifuging at 7000 rpm for 5 min. The supernatant was discarded. The final pellet was dissolved in hexane and stored in the dark inside the glovebox for future use. The size of the PbSe NCs was determined by measuring the first exciton peak (845 nm) of the absorption spectrum,[4] and the concentration was determined from the calculated size of the PbSe NCs and the absorption at 400 nm.[5]

4. Synthesis of CPT transmitter ligand

4.1 synthesis of ethyl 4-(tetracen-5-yl)benzoate[6]

To a mixture of 5-Bromo-tetracene[7] (0.5g, 1.63mmol), 4-(ethoxycarbonyl)phenylboronic acid (380mg, 1.96mmol, 1.2 mol amt.), cesium carbonate (2.12g, 6.53mmol, 4 mol amt.), toluene (19.4ml) and H_2O (6.536ml) were added. The reaction was bubbled under argon for 20 min, followed by the addition of 1,1' –Bis diphenylphosphino-ferrocene-palladium(II)dichloride dichloromethane complex (133.4mg, 0.1634mmol, 0.1 mol amt.) the mixture was then stirred at 60°C overnight. The reaction was cooled then washed with H_2O, and extracted with ethyl acetate four times. The organic layer was washed with brine, dried with magnesium sulfate, filtered and then concentrated using the rotary evaporator. The crude product was purified by flash column chromatography using silica gel and dichloromethane as the eluent to give an orange powder with 61% yield. ^{1}H NMR (400MHz, $CDCl_3$): δ 1.49 (t, 3H), 4.52 (q, 2H), 7.42-7.31 (m, 4H), 7.62-7.57 (m, 3H), 7.80 (d, 1H), 7.99 (d, 1H), 8.06 (d, 1H), 8.20 (s, 1H), 8.34 (d, 2H), 8.72 (s, 1H), 8.76 (s, 1H) ppm. ^{13}C NMR (400MHz, $CDCl_3$): δ 14.61, 61.32, 125.05, 125.28, 125.43, 125.61, 125.66, 126.50, 126.72, 127.41, 128.10, 128.76, 128.79, 129.11, 129.53, 129.90, 129.91, 130.01, 130.05, 131.22, 131.36, 131.77, 135.72, 144.23, 166.84 ppm; HRMS (ESI) Calcd. for $C_{27}H_{20}O_2$ (MH^+) 377.1536, Found 377.1551.

4.2 synthesis of 4-(tetracen-5-yl)benzoic acid (CPT)[8]

To a suspension of ethyl 4-(tetracen-5-yl)benzoate (0.5g, 1.32mmol) in 154.4ml of tetrahydrofuran-methanol (1:1), 3.32ml of a 2M KOH aqueous solution was added. The mixture was then bubbled for 20min under argon, then allowed to reflux for 3 hours. THF was removed and the resulting suspension was acidified with 2M of HCl. The crude solid was filtered and washed with H_2O then hot chloroform to give the desired product (orange powder) at 64% yield. ^{1}H NMR (400MHz, DMSO): δ 7.29-7.42 (m, 4H), 7.61 (d, 1H), 7.68 (d, 2H), 7.82 (d, 1H), 8.08 (d, 2H), 8.21 (s, 1H), 8.42 (d, 2H), 8.73 (s, 1H), 8.79 (s, 1H) ppm. ^{13}C NMR (400MHz, DMSO): δ 125.05, 125.76, 126.34, 126.35, 126.72, 127.42, 127.94, 128.52, 128.94, 129.13, 129.31, 129.46, 129.97, 130.40, 130.97, 131.30, 131.43, 131.83, 132.11, 132.14, 135.80, 143.61, 167.96 ppm. HRMS (ESI) Calcd. for $C_{25}H_{16}O_2$ (M^{*+}) 348.1145, Found 348.1160.

5. Upconversion sample preparation for upconversion QY measurement (general sample preparation)

5.1 ligand exchange 2.9 nm PbS with CPT

51.3 μL of PbS/THF (194.8 μM), 150 μL **CPT**/toluene (1 mM), and 803.5 μL of toluene was mixed leading to a final concentration of [PbS] =10 μM, [**CPT**] = 150 μM. The mixture was stirred for 40 min. Then, 0.3 mL of this ligand exchange solution was transferred into 15 mL centrifuge tube followed by adding 2.4 mL acetone. The resulting solution was centrifuged for 5 min at 7830 rpm. The clear supernatant was removed and the pellet was redispersed into 0.3 mL of 20 mM rubrene/toluene solution. 150 uL of this upconversion solution was transferred to 1 cm by 1 cm path length Starna cuvettes containing 100 μm thick borosilicate capillary tube sticking on the wall. The solution will diffuse up through the space inside the capillary tube. Samples were prepared in an argon glovebox.

5.2 ligand exchange of 2.5 nm PbSe with CPT

Similar to the procedure in section 5.1. In the ligand exchange solution, [PbSe] =29 μM, and [**CPT**] =150 μM. The resulting solution was stirred for 5 min.

5.3 preparation of PbS+rubrene and PbSe+rubrene control sample

The desired volume of PbS/PbSe stock solution was measured out, and the solvent was evaporated in the glovebox before adding 0.3 mL of 20 mM rubrene/toluene solution.

6. Calculation of upconversion quantum yield.

The upconversion quantum yield is calculated by equation S1 and S2, with rubrene/toluene sample as the reference excited at 532 nm. Both 532 and 808 laser beams are aligned to hit the same position on the sample.

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

$$photons\ absorbed\,/\,s = \frac{Laser\ Power}{hc/\lambda}\left(1 - 10^{-Abs}\right) \qquad \text{(S2)}$$

Φ_{ref} is the quantum yield of rubrene and is 0.98, *h* is Planck's constant, *c* is the speed of light, and *Abs* is the sample absorption.

7.

Table S1. Optical properties of upconversion transmitter **CPT** and rubrene*

	λ_{max} (Abs.) (nm)	λ_{max} (Em.) (nm)	Ɛ@ λ_{max} ($M^{-1}cm^{-1}$)	Fluorescence QY(%)
CPT	484	494	9340	53.1
rubrene	526	556	12000	98.0

*All data was obtained in toluene at room temperature.

8. Evaluation of the average number of bound CPT per NC, *n*, and resultant surface density

After ligand exchange, the NCs were spun down by adding acetone as the bad solvent. Then the supernatant containing the free ligand was removed and the pellet was redispersed in toluene. The absorption of this solution was measured. The absorption at 484 nm provided the concentration of CPT, while the absorption at 400 nm gave the NC concentration. The molar extinction coefficient of CPT at 484 nm is given in Table S1, and that of the NCs at 400 nm is known.[1,5] This allows a quantitative ratio of the concentrations of CPT and NCs to be obtained, i.e. the number of CPT ligand per NC. Due to the fact that both CPT and PbX NCs absorb at 484 nm, the contribution of the NC must be subtracted. Since the absorption of the NC is not perturbed by ligand binding, its contribution at 484 nm can be calculated by the measurement of the optical density at its absorption maxima (e.g. 907 nm for PbS). The CPT ligand density is calculated given the surface area estimated from the diameter of the NCs.[2,4]

9. Figures in the Supporting Information

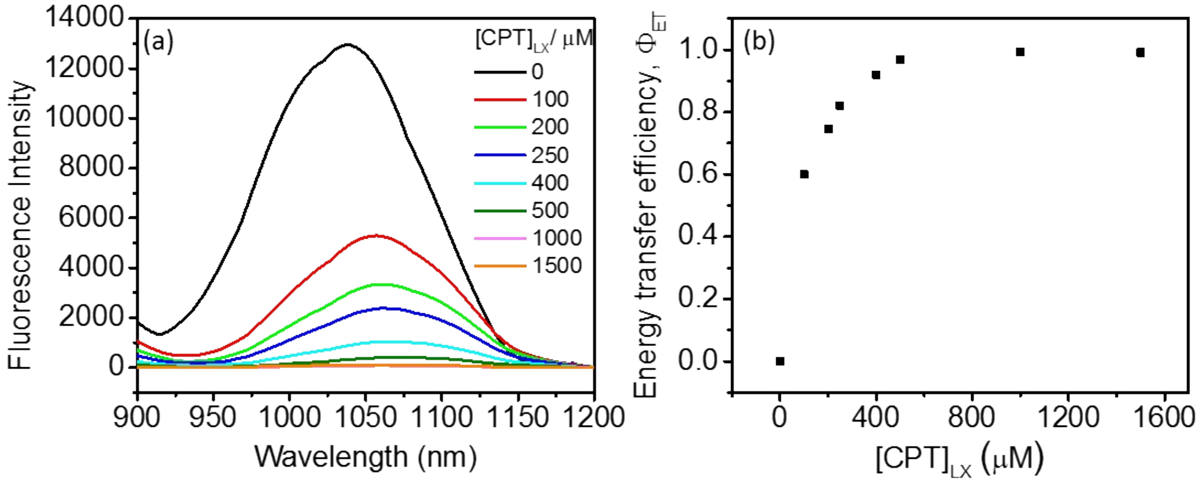

Figure S1. (a) PL quenching of 2.9 nm diameter PbS after undergoing ligand exchange with the **CPT** transmitter. Ligand exchange conditions: [PbS]= 10 µM, stirring in THF for 1h. The concentration of **CPT** during ligand exchange, [**CPT**]$_{LX}$ is indicated. After being spun down, the PbS/ **CPT** pellet was redispersed in toluene. Samples were measured in 1 cm by 1 cm air tight Starna cuvette. (b) The efficiency of triplet energy transfer, Φ_{ET}, from PbS NCs to **CPT** based on Φ_{ET}=1-F/F$_0$. F is the integrated fluorescence intensity of the PbS NCs in Fig S1(a) with the corresponding [**CPT**]$_{LX}$; F$_0$ corresponds to the same quantity when [**CPT**]$_{LX}$=0.

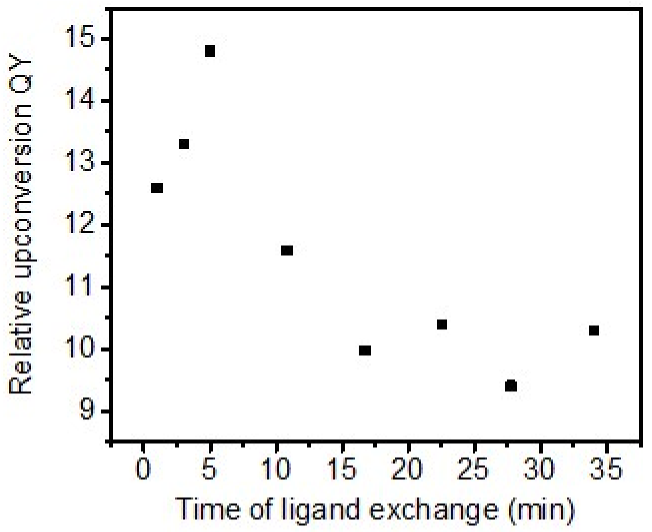

Figure S2. The relative upconversion quantum yield (upconversion fluorescence intensity at 560 nm normalized by the absorption at 808 nm) of PbSe/**CPT**/rubrene samples for different ligand exchange times. Ligand exchange conditions: 29 µM PbSe, 150 µM **CPT**, stirring in toluene at RT. Samples contain 1 mM rubrene, and were measured in 200 µm thick capillary tube sealed in air tight Starna cuvettes.

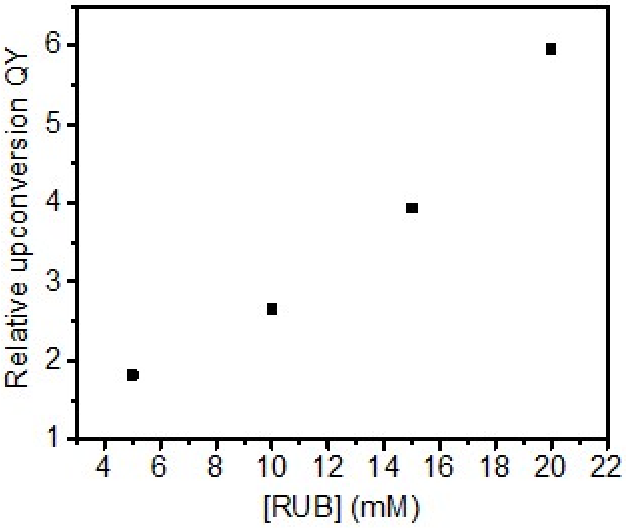

Figure S3. The relative upconversion quantum yield (upconversion fluorescence intensity at 560 nm normalized by the absorption at 808 nm) of PbS/**CPT**/rubrene samples containing different concentrations of rubrene. Ligand exchange condition: 10 µM PbS, 1 mM **CPT**, and stirring in THF for 1h. Samples were measured in 200 µm thick capillary tube sealed in air tight Starna cuvettes.

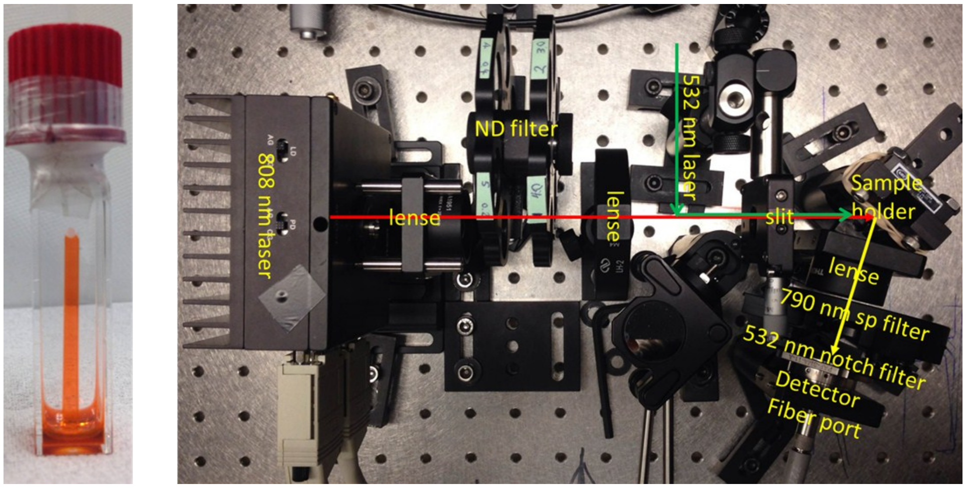

Figure S4. Photos of a cuvette containing the sample in a 100 µm thick capillary tube (left) and the upconversion measurement setup (right). Each part is described under the Instrumentation section.

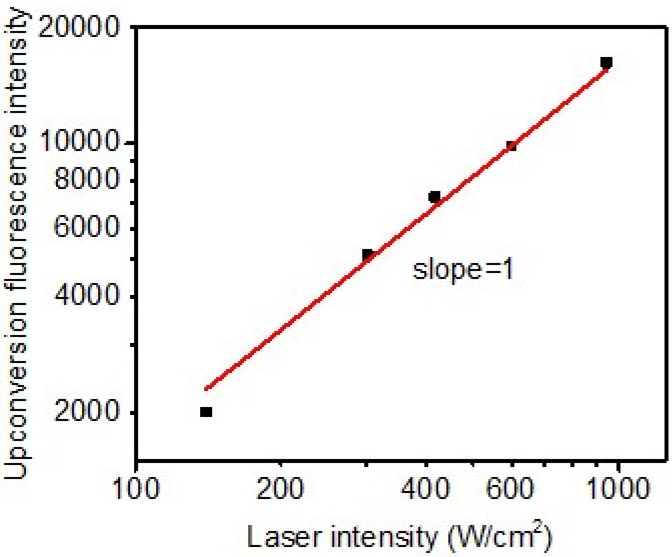

Figure S5. Log-log plot of the upconversion signal versus laser intensity for the 2.9 nm PbS/**CPT**/rubrene sensitizer/ligand/emitter system, showing the laser intensity in use is in linear (slope = 1) regime. Ligand exchange conditions: 10 µM PbS, 1mM **CPT**, stirring in THF for 40 min. The sample cotain 1 mM rubrene, and was measured in 100 µm thick capillary tube sealed in air tight Starna cuvettes.

10. References

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