Supporting Information

Triplet-Triplet Annihilation based Photon Up-conversion in Hybrid Molecule–Semiconductor Nanocrystal Systems

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1. Chemicals.

The CdSe nanocrystals used in this work were purchased from Sigma-Aldrich (*Lumidot* 560, CAS number 1306-24-7), as well as 9-anthracenecarboxylic acid (9-ACA) and 9,10-diphenylanthracene (DPA). All molecules were used as received. All samples were prepared and sealed in a glove box under nitrogen atmosphere, with oxygen concentration below 0.1 ppm.

1.1 *Ligand exchange protocol.*

The nanocrystals native capping ligand, i.e. oleic acid, was partially substituted with 9-ACA, according to the following ligand exchange procedure. First, 3 mg of 9-ACA were added to 1 ml of a 5 mg/ml CdSe nanocrystals solution in toluene and the sealed suspension was sonicated for 8 hours at 50 °C. After sonication, the suspension was filtered over glass wool to remove the suspended particles, and the resulting colloidal dispersion was diluted up to a final volume of 1 ml. Dry nitrogen was bubbled in the solution for 15 minutes, after which time the vial was sealed.

2. Photophysical studies.

The absorption measurements were performed with a Varian Cary 50 UV-Vis spectrophotometer, using quartz cuvettes with optical path of 1 mm, in normal incidence conditions. For the steady-state continuous wave (CW) photoluminescence (PL) measurements, a Coherent Verdi CW laser at 532 nm was used as excitation source, coupled with a portable spectrometer (USB2000+VIS-NIR, Ocean Optics) with bandpass of 1 nm for signal detection. The excitation laser beam is Gaussian shaped, with a spot diameter of 194 μm. Shape and spot size were measured following the *knife-edge* method. The time-resolved PL measurements were carried out using the 532 nm II harmonic of a Nd:YAG pulsed laser (Laser-Export Co. LSC-DTL-374QT, pulse width 5 ns), while the signal of up-converting sample was recorded modulating the 532 nm laser with a TTi TG5011 wavefunctions generator, with a time resolution better than 0.1 μs (5 ns pulse width). For signal detection, a Triax 190 from J-Horiba monochromator with 0.5 nm bandpass was used with a Hamamatsu R943-02 photomultiplier coupled with an Ortec 9353 multichannel scaler, with a temporal resolution of 0.1 ns. Fluorescence lifetimes were determined using a 355 nm pulsed laser (DTL-375QT, pulse width 5 ns). In both CW and time resolved PL measurements, the laser stray light was reduced using a 532 nm notch filter. To change the excitation intensity, a set of neutral filters with varying optical density was adopted (Thorlabs and Edmund Optics). All the measurements were performed at room temperature and corrected for the instrumental spectral response.

3. Colloidal Nanocrystals Properties.

The CdSe nanocrystals (NCs) diameter, molar extinction coefficient and concentration were calculated according to established empirical formulas from literature[1]:

NCs diameter: $D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57$

where λ is the first absorption peak wavelength.

NCs molar extinction coefficient at the absorption peak wavelength: $\varepsilon = 5857\ (D)^{2.65}$

NCs concentration: $C = \frac{A}{\varepsilon\, d}$ given absorbance *A* and optical path *d*.

4. Perrin model for short-range interactions.

The sensitizer-to-emitter energy transfer rate in the Perrin model is given by $k''_{ET} = 4\pi\, D\, R_0 C_e$, where R_0 is the effective ligand-emitter contact distance (7.65 Å), C_e is the emitter concentration and $D = 9.93\times10^{-6}$ cm^2 s^{-1} is the total diffusion coefficient, given by the sum of sensitizer and emitter diffusion coefficients’$D_s + D_e$. Each *D* coefficient can be calculated according to the Stokes-Einstein relation $D = \frac{k_b T}{6\pi z r}$, where *z* is the solvent viscosity (0.6 cP at room temperature for toluene) and *r* the sensitizer radius (2.03 nm for the nanocrystal+ligand sensitizer and 0.45 nm for the emitter). Using these values with an emitter concentration of 10^{-2} M, we calculate $k''_{ET} = 57$ MHz (Tab.1).Considering from literature the ligand spontaneous decay rate $k_{T_L} \sim 7.4$ kHz , we have therefore a transfer yield of $\Phi''_{ET} = \frac{k''_{ET}}{k''_{ET} + k_{T_L}} \sim 1.$

Tab.1 Energy transfer rate k''_{ET} calculated in the Perrin approximation for different emitter concentrations C_e.

C_e (M)	k''_{ET} (kHz)
10^{-2}	57×10^3
5×10^{-3}	27×10^3
2×10^{-3}	11×10^3
10^{-3}	6×10^3
10^{-4}	570
10^{-5}	57

5. Relative up-conversion quantum yield.

The up-conversion (UC) quantum yield of the hybrid system was measured with respect to the quantum yield of a rhodamine 6g reference sample and it was carried out using a UC solution in toluene (1.4×10^{-5} M CdSe/9-ACA and 10^{-2} M DPA) and a 10^{-5} M rhodamine 6g reference in ethanol. We measured the luminescence intensity for both the samples, under the same experimental conditions, that is under a CW 532 nm excitation in the UC linearity regime, in normal incidence conditions, using quartz cuvettes of 1 mm optical path.

We exploited the following relation to measure the relative UC quantum yield (QY_{UC}):

$$QY_{UC} = QY_{std}\left(\frac{A_{std}}{A_{UC}}\right)\left(\frac{I_{UC}}{I_{std}}\right)\left(\frac{n_{UC}}{n_{std}}\right)^2$$

where QY_{std} is the rhodamine quantum yield (0.95), *A* is the fraction of photons absorbed by a sample at the excitation wavelength, *I* is the PL intensity and *n* is the solvent refractive index. The UC sample absorbance at 532 nm was 0.0566, while the rhodamine absorbance was 0.1224. The measured QY_{UC} was 0.3%.

6. Additional Data.

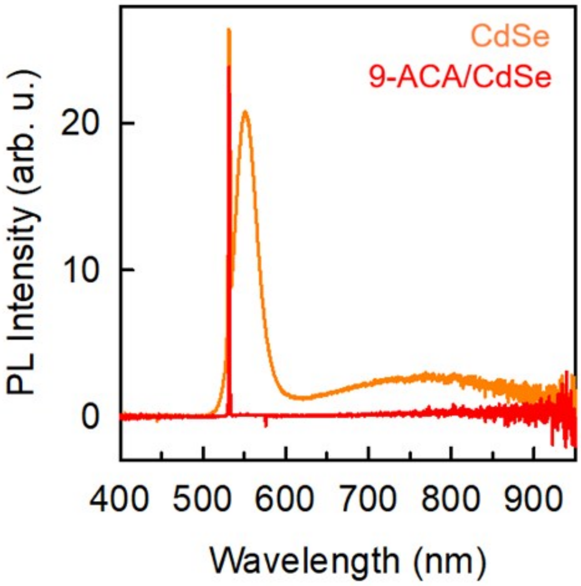

Figure S1. PL emission of a solution of CdSe NCs (orange, 3×10^{-5} M) and of a 9-ACA/CdSe NCs (red, 3×10^{-5} M) in toluene under a CW 532 nm excitation at the same power density (2.0 W cm^{-2}) at room temperature.

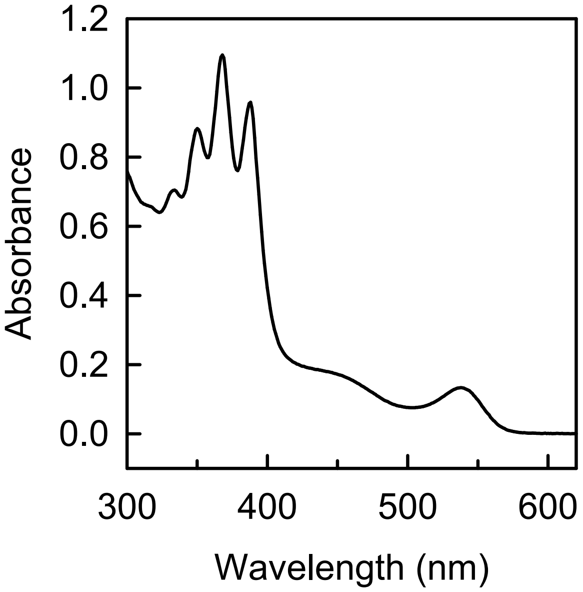

Figure S2. Absorption spectrum of a solution of 9-ACA/CdSe NCs (1.4×10^{-5} M) and DPA (10^{-4} M) in toluene.

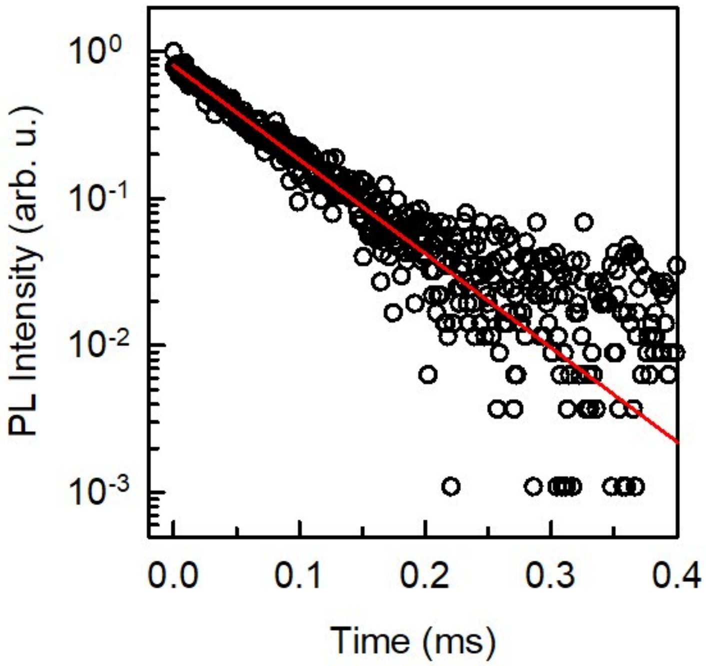

Figure S3. Decay of the 430 nm emission of a solution of CdSe/9-ACA in toluene (4.9×10^{-5} M) under a modulated 473 nm excitation in the low power regime ($I_{exc} = 0.67\ W\ cm^{-2}$). From the single exponential fit (red line) we obtain the ligand triplet state spontaneous decay rate, $k_{T_L} = 7.4\ kHz$.

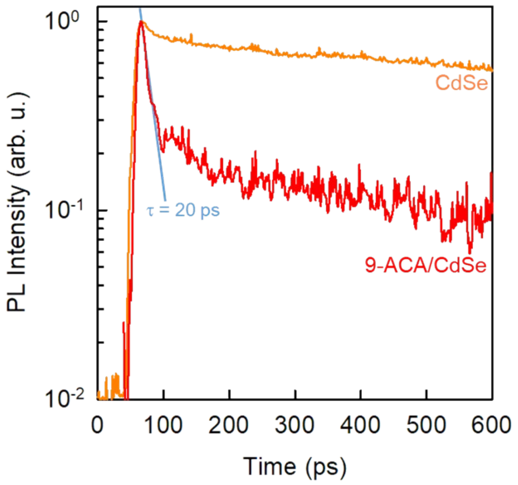

Figure S4. Normalized PL decay at 560 nm of a CdSe (orange) and 9-ACA/CdSe (red) nanocrystals solution in toluene (1.5×10^{-5} M) under pulsed excitation at 440 nm. The excitation source is the 2nd harmonic of a Ti:Sapphire Laser Coherent Mira 900 with a 150 fs pulse width. The data show that in 9-ACA capped nanocrystals there is a fast recombination in the first 100 ps after the excitation pulse, which accounts for a 5 times reduction of the integrated PL intensity with respect to the native nanocrystals. This phenomenon occurs on the typical timescale of charge transfer processes[2] and therefore it can be ascribed to hole withdrawal by the ligands. However, these results account only for a small fraction of the time-zero loss observed, thus demonstrating that ultrafast quenching occurs on the sub-picosecond timescale.

REFERENCES

1. Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chemistry of Materials* **2003,** 15, (14), 2854-2860.
2. Califano, M.; Gómez-Campos, F. M. *Nano Letters* **2013,** 13, (5), 2047-2052.