Supporting Information

On the efficacy of anthracene isomers for triplet transmission from CdSe nanocrystals

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Experimental section

1. Materials

Chemical reagents were purchased from Sigma-Aldrich, TCI America, Alfa Aesar and were used without further purification. As for nanocrystal synthesis, cadmium oxide was purchased from Alfa Aesar, and trioctylphosphine oxide (90%) (TOPO), trioctylphosphine (97%) (TOP), octadecylphosphonic acid (97%) (**ODPA**) were purchased from Strem Chemicals. 9, 10-diphenylanthracene (>93%) (**DPA**) 9-anthracenecarboxylic acid (97%) (**9-ACA**), 2-anthracenecarboxylic acid (98%) (**2-ACA**) and 1-anthracenecarboxylic acid (99%) (**1-ACA**) were obtained from TCI America. 9-nitroanthrancene (97%); 2-aminoanthracene (98%); 1-aminoanthracene (90%); *N*-methyl-pyrrolidone (99%) (NMP); rhodamine 6G (99%), hexane (99%), methoxybenzene, poly(4-bromostyrene) (MW ~65,000) (4-BrPS) and carbon disulfide (99%) were purchased from Sigma-Aldrich. Triethylamine (99.7%) (NEt_3) and tetra-*n*-butylammonium hexafluorophosphate (98%) were from Acros. Glacial acetic acid (99.9985%) was from Alfa Aesar. Dry and degassed acetone, toluene, tetrahydrofuran (THF) and dichloromethane (DCM) were obtained from JC Meyer's solvent purification system.

2. Instrumentation

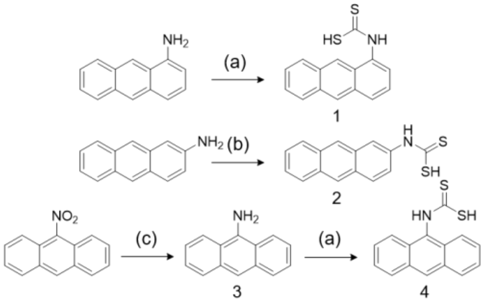
Proton NMR (^1H) spectra was recorded on Varian Inova-300 MHz or 400 MHz spectrometers; carbon NMR (^{13}C) spectra were recorded on a Varian Inova-600 MHz spectrometer at room temperature. The ^1H and ^{13}C chemical shifts (δ) are reported in parts per million and the residual solvent peak was used as an internal standard. Absorption spectra were recorded on a Jasco-V670 UV-Vis absorption spectrophotometer. Upconversion samples were prepared in the glove box with air-free cuvettes and measurements were performed as described earlier.[1] Infrared absorption spectra were obtained from ALPHA FTIR Spectrometer (Bruker Corporation). Samples for transient absorption measurements were prepared in toluene in a 2 mm air-tight quartz cuvettes, which the optical density of CdSe NCs around 0.4-0.5 at 465 nm. Ground state absorption was taken before and after the transient absorption experiment to show there is no decomposition.

Details of the setup are described in previous work.[1] Fluorescence spectra and phosphorescence were measured with the fluorimeter (Fluoromax-3 from Horiba Scientific).

3. 2.4 nm CdSe Nanocrystals were synthesized as previously reported.[2]

4. Synthesis of anthracene dithiocarbamate acid transmitters

All the anthracene dithiocarbamate acid **(ADTC)** ligands were obtained from the corresponding aminoanthracene precursors by reaction with carbon disulfide (CS_2) and triethylamine at 45°C in acetone or THF under nitrogen, as shown in Scheme S1.[3] **1-ADTC (1)** and **2-ADTC** (**2**), precipitated from acetone or THF after 24 hours, resulting in ~90% yield. For **9-ADTC** (**4**), we firstly synthesized its precursor, 9-aminoanthracene (**3**) from 9-nitroanthracene.[4]



Scheme S1. Synthesis of **ADTC** isomers. Reagents and conditions: (a) CS_2, NEt_3, acetone, 45°C, 24h. (b) CS_2, NEt_3, THF, 45°C, 24h. (c) 1. AcOH, 80°C; 2. $SnCl_2$, HCl, 80°C.

Compound **1**: 1-aminoanthracene was purified by silica gel based chromatography (1: 3 = hexane: DCM as eluent) before synthesis because the commercially available precursor contained 10% impurities. It is a yellow powder and forms brown solution in anhydrous acetone. A solution of purified 1-aminoanthracene (0.8 mmol, 154.5 mg) and NEt_3 (2.4 mmol, 0.69 ml) in 1 mL of acetone was stirred at ambient temperature for 10 min, after which 1.5 mL of CS_2 was added dropwise. The resulting solution was further stirred at 45°C for 24 hr. The yellow solid was collected by filtration, washed with ether, acetone and dried under vacuum at RT for 5 hr (90%, 200mg). The product was further purified by washing with hot THF twice. ^1H NMR (300 MHz, DMSO-d_6): δ_H = 10.00 (s, 1H), 8.65 (s, 1H), 8.60 (s, 1H), 8.12(d, J=9 Hz, 1H), 8.06-7.99 (m, 2H), 7.64 (d, J= 6.0 Hz, 1H), 7.57-7.52 (m, 3H) ppm. ^{13}C NMR (600 MHz, DMSO-d_6): δ_C =182.89, 131.58, 131.33, 130.82, 129.10, 128.12, 128.19, 127.82, 125.87, 125.73, 125.25, 125.29, 124.47, 124.43, 118.97 ppm. IR (ATR): 2937, 1628, 1535, 1487, 1384, 1316, 1269, 1243, 1171, 970, 897, 795, 743 cm^{-1}.

Compound **2** was obtained in the same way as compound **1** as a yellow solid (yield 90%, 200mg). ^1H NMR (400 MHz, DMSO-d_6): δ_H = 10.30 (s, 1H), 8.55 (s, 1H), 8.51 (s, 1H), 8.22 (s, 1H), 8.09-8.06 (m, 3H), 7.72 (dd**,** J=9 Hz, 3Hz, 1H), 7.51-7.49 (m, 2H) ppm. ^{13}C NMR (600 MHz, DMSO-d_6): δ_C = 182.72, 135.21, 132.21, 129.95, 128.73, 128.33, 121.12, 121.06, 127.29, 126.60, 125.94, 125.86, 125.29, 125.21, 121.73 ppm. IR (ATR): 2965, 1633, 1588, 1534, 1486, 1314, 1291, 1176, 1013, 954, 904, 824, 875, 744, 700, 685, 659 cm^{-1}.

Compound **3** is a known compound:[4] 9-nitroanthracene (0.362 g, 1.625 mmol) was added to acetic acid (0.363 mL) and stirred at 80 °C for 1.5 hr. This solution was allowed to cool down to room temperature and $SnCl_2$ (1.55 g, 8.16 mmol) in HCl (5.5 mL) was added slowly. The mixture was then heated for 30 min at 80 °C. After cooling down to room temperature, the reaction solution was filtered and washed by HCl three times to give a yellow solid. The yellow solid was basified with 150 mL 5% NaOH solution, stirred at room temperature for 15 min, filtered, and the filter cake was washed with DI water to pH=7, then dried to give a yellow solid which was recrystallized from benzene to obtain compound **3** (yield 72%, 500 mg**)**. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H =7.96(m, 4 H), 7.89 (s, 1 H), 7.43 (m, 4 H), 4.89 (broad, 2 H) ppm.

Compound **4** was synthesized from compound **3** in the same way as compound **1** and **2**. A yellow solid was obtained (yield 91%, 400 mg). Then it was purified with silica gel chromatography (1:1 = hexane: DCM as eluent, yield 85%, 400 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 8.40 (s, 1H), 8.30 (dd, J= 8, 1 Hz, 2H), 8.03 (d, J= 8 Hz, 2H), 7.63 (td, J= 8.6, 1.2 Hz, 2H), 7.54 (td**,** J=8.0 Hz, 0.8 Hz, 2H) ppm. ^{13}C NMR (600 MHz, DMSO-d_6): δ_C = 182.32, 130.95, 129.09, 128.23, 127.24, 127.21, 127.04, 126.49, 125.09 ppm. IR (ATR): 2965, 1775, 1730, 1621, 1531, 1442, 1479, 1409, 1347, 1262, 1163, 1108, 1016, 958, 891, 844, 781,733, 670 cm^{-1}.

5. The fluorescence quantum yield (Φ_F) of ACA and ADTC isomers

With DPA in cyclohexane at room temperature as standard (λ_{ex}= 350 nm), Φ_F of all isomers were measured at room temperature in anhydrous THF. Firstly, 4 or 5 samples with optical densities ranging from 0.02, 0.04, 0.06, 0.08 to 0.10 at 350 nm for each molecule were made in an air- and water- free manner (including DPA); Then, the fluorescence spectrum (λ_{ex}= 350 nm) of these solutions in 10 mm path length cuvettes were recorded. The integrated fluorescence intensity was calculated. Lastly, the integrated fluorescence intensity vs. absorbance was plotted and the slope of this line recorded. $\Phi_{F,sample} = \Phi_{F,standard} \cdot \left(\frac{Gradient\ of\ sample}{Gradient\ of standard}\right) \cdot (\frac{\eta_{standard\ solvent}}{\eta_{sample\ solvent}})^2$ was applied to calculate the Φ_F. Table S1 also lists the absorption and emission maxima (λ_{ex}=350 nm) in THF. As shown in Table S1, different isomers have different absorption maxima even though they share the same anthracene core.

Transmitter	**1-ACA**		**2-ACA**		**9-ACA**		**1-ADTC**		**2-ADTC**		**9-ADTC**		**DPA**
Φ_F (%)	21.2		48.7		43.2		0.03		1.2		0.05		86[5]
λ_{max}/ nm & ε_{max}×100/ L•mol^{-1}•cm^{-1}	346	40	338	42	329	31	330	162	336	448	353	19	-
	361	58	355	48	345	60	348	248	353	339	371	36	-
	377	64	373	52	362	89	366	361	379	313	391	38	-
	395	50	393	53	382	78	386	371	401	374	414	34	-
λ_{em}/ nm	423, 442		406, 428		451		425, 444		438, 481		423, 444		404, 425

Table S1. Fluorescence quantum yield of **ACA** and **ADTC** isomers in anhydrous tetrahydrofuran with DPA in cyclohexane as standard at room temperature. The absorption maxima, λ_{max}, and the corresponding extinction coefficients, ε_{max}, from experiment are listed, as well as the emission maxima, λ_{em}, of the six ligands in THF.

6. Phosphorescence spectra of ACA and ADTC isomers

Following Reineke's work,[6] phosphorescence spectra were measured at room temperature. All anthracene isomers were first dissolved in methoxybenzene (10 mg/L) and then mixed with the 10 mg/L 4-BrPS in methoxybenzene to make a final solution with 2 wt% of anthracene (**ACA** isomers or **ADTC** isomers) in 4-BrPS. A thick film was dropcast on a glass substrate, and heated to 80°C until the solvent evaporated. It is probable that such thick films will introduce significant re-absorption of the fluorescence, owing to the small Stokes-shift. Thus, the high-energy side of the fluorescence spectra is artificially reduced in our measurements. In Table S2, the T_1 to S_0 and the T_2 to T_1 transitions of different anthracene derivatives are shown. For T_1 to S_0, these peak positions are in agreement with Kasha's report of 0, 0 vibrational frequencies of the T_1 to S_0 transition in various anthracenes at 77 K in a rigid glass solution.[7] The T_2 to T_1 transition in solid state is consistent with Kellogg's transient absorption measurements at 298 K in poly (methyl methacrylate) rods for anthracene crystals.[8]

Molecule	**S_1 to S_0**		**T_1 to S_0**		**T_2 to T_1**	
	$\lambda_{em/}$nm	Energy/eV	$\lambda_{em/}$nm	Energy/eV	$\lambda_{em/}$nm	Energy/eV
Anthracene	410	3.019	674	1.840	877	1.442
9-ACA	468	2.645	685	1.810	885	1.414
2-ACA	449	2.757	680	1.823	877	1.400
1-ACA	456	2.714	687	1.805	856	1.414
9-ADTC	453	2.732	664	1.868	915	1.378
2-ADTC	429	2.885	664	1.868	900	1.355
1-ADTC	464	2.668	668	1.856	T1-T2	1.448

Table S2. The S_1 to S_0 transition, T_1 to S_0 transition and T_2 to T_1 transition of anthracene and its derivatives when measured as thin film and embedded in 4-BrPS at 23°C.

7. Measurement of upconversion quantum yield (%) ($\Phi_{upconversion}$)

7.1. Ligand exchange 2.4 nm CdSe with ACA and ADTC isomers

Ligand exchange in the mixture of THF: toluene =1:1 (v/v) for 12 hours was performed for the **ACA** ligands. 12 hours is enough for **ACA** isomers to achieve equilibrium between the number of ligands on the CdSe NCs surface and number of free ligands in the solution. Ligand exchange requires 120 mins for **1-ADTC** and **2-ADTC** and 40 mins for **9-ADTC** to get the highest $\Phi_{upconversion}$ in NMP. During ligand exchange, the concentration of CdSe NCs were kept at 57.5 µmol/L and the concentration of ligands varied to optimize the $\Phi_{upconversion}$. In Fig. S1, the maximum $\Phi_{upconversion}$ is 0.55% when the ratio of number of ligands to number of NCs is 1 during ligand exchange. The detail procedure is the same as previously work.[1]

7.2. *N*, the average number of ligands bound on a CdSe NCs.

The average numbers of bound anthracene ligands after ligand exchange was determined with UV-Vis absorption.[1] Fig. S1 shows that the **ADTC** isomers bind more strongly than the **ACA** isomers. **9-ADTC** has up to 16 ligands on the CdSe surface, yet 9-**ACA** has only no more than 4 ligands on the CdSe NC surface. Interestingly, both ligands at 9- positions (red) shows that the ligands loading¸ *N*, is proportional to the concentration of ligands, whereas *N* at 1- and 2- positions at first increase to the maximum number of ligands and then decrease with a continued increase in the concentration of ligands. Moreover, we also found that the solubility of these ligands in THF is 9- > 1- > 2-. We hypothesize that 9-, 1- and 2- isomers bind on different types of Cd^{2+} sites on the CdSe NCs.

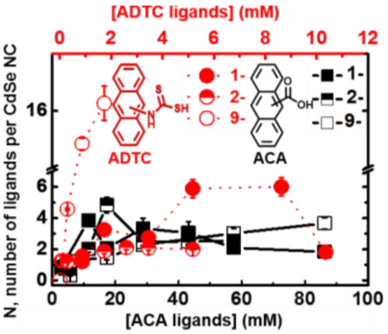


Fig. S1 The relationship between N, the average number of bound ligands per CdSe quantum dot against various concentrations of anthracene carboxylic acid (**ACA**) (black square, solid line) and anthracene dithiocarbamate acid (**ADTC**) (red circle, dotted line) isomers.

8. Femtosecond TA spectra were measured for all CdSe/ACA and ADTC complexes.

Femtosecond TA spectra were measured for all CdSe/**ACA** and CdSe/**ADTC** hybrid complexes as well as the native CdSe/**ODPA** NCs (**Fig. S1**Fig. S2 and Fig. 3a). Excitation was at 465 nm and the pump power was 300 nJ (>30 fs HWFM). In Fig. S5, comparing the ground state recovery of CdSe/**ODPA** NCs with CdSe/**ACA** or CdSe/**ADTC** hybrid complexes, there is much faster recovery for the ground state bleach for the CdSe NCs in the **ACA** or **ADTC** functionalized NCs. The measurements cover 2.4 ns after excitation and range from 430 nm to 800 nm, but the signal is noisy around 430 nm to 480 nm due to the scattering of the pump light. However, we can still see the growth of a new band at 433 nm, which corresponds to the triplet states of anthracene. Therefore, since no absorption associated with the radical cation or anion was observed, we can conclude that there is direct triplet transfer from excited CdSe NCs to the triplet state of surface bonded **ACA** or **ADTC** isomers.

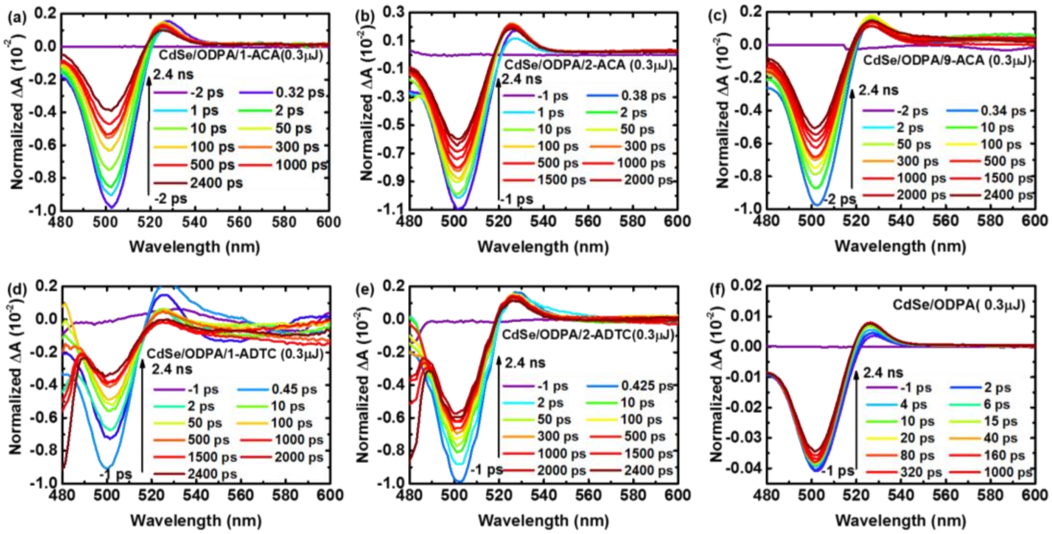


Fig. S2 Ultrafast transient absorption (TA) different spectra of (a) CdSe/**1-ACA** (a); (b) CdSe/**2-ACA**; (c) CdSe/**9-ACA**; (d) CdSe/**1-ADTC**; (e) CdSe/**2-ADTC** and (f) CdSe/**ODPA**, illustrating more rapid recovery of ground state of CdSe when binding with **ACA** or **ADTC** isomers. TA experiments were done by selectively exciting the CdSe NCs in toluene using 465 nm pulse laser (0.3 µJ per pulse, >30 fs fwhm).

9. Measurement of molecular HOMO and LUMO by cyclic voltammetry (CV)

Electrochemical measurements were conducted on a Gamry interface 1000 electrochemical analyzer with a three-electrode system under argon in an anhydrous dichloromethane (DCM) solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). A glassy carbon electrode was used as a working electrode, a platinum-wire was used as the counter electrode, and an Ag/Ag$^+$ (0.01 M $AgNO_3$ in DCM) electrode was used as the reference electrode. The sample was dissolved in DCM. The CV curves were calibrated with the ferrocene/ ferrocenium (Fc/Fc$^+$) redox couple as a standard measured together with the samples under the same conditions, after the samples were measured. The energy level of Fc/Fc$^+$ was assumed at to be – 4.8 eV with respect to vacuum.[9,10] The half-wave potential of the ferrocene/ ferrocenium (Fc/Fc$^+$) redox couple ($E_{1/2,\ Fc,\ Fc+}$) was estimated from $E_{1/2,\ Fc,\ Fc+} = (E_{ap} + E_{cp})/2$, where E_{ap} and E_{cp} are the anodic and cathodic peak potentials, respectively. The half-wave potential of Fc/Fc$^+$ was found to be 0.453V $\{E_{1/2,\ Fc,Fc+} = (E_{ap} + E_{cp})/2 = (0.630+0.275)/2 = 0.453\ V\}$ related to the Ag/Ag+ reference electrode. The HOMO energy levels of **9-ACA** and **9-ADTC** were calculated using the equation: $E_{HOMO} = -(4.8 - E_{1/2,\ Fc,Fc+} + E_{ox,\ onset}) = -(4.347 + E_{ox,\ onset})$ eV, where $E_{ox,\ onset}$ is the onset oxidation potential relative to the Ag/Ag+ reference electrode. The LUMO energy levels of molecules were calculated by adding the optical gap from the respective HOMO energy levels ($E_{LUMO} = E_{HOMO} + E_{g,\ opt}$).

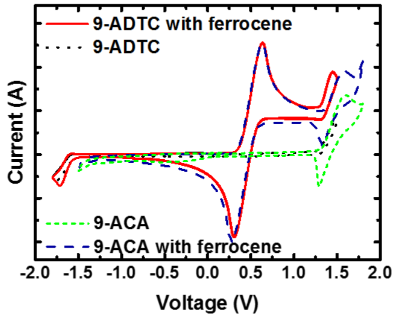


Fig. S3 Cyclic voltammogram of **9-ACA** and **9-ADTC** in dichloromethane (vs. Ag/Ag+) in dichloromethane solution with 0.1 M tetra-n-butylammonium hexafluorophosphate as supporting electrolyte, at a scan speed of 50 mV s^{-1}.

10. Power dependence of TA measurement

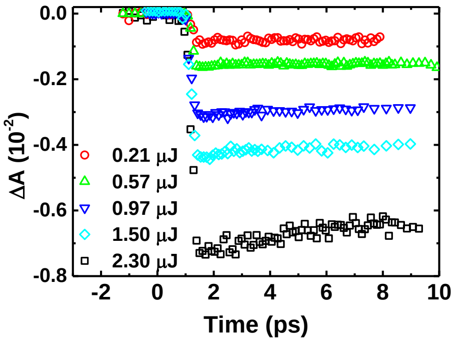


Fig. S4 The transient absorption kinetics (λ_{probe}= 505nm) of CdSe/**ODPA** dispersed in toluene at different excitation powers (λ_{ex}= 465nm): 0.21 µJ (red circle), 0.57 µJ (green triangle), 0.97 µJ (blue triangle), 1.5 µJ (cyan diamond) and 2.3 µJ (black square), verifying the power dependence in the amplitude of the sample. The TA spectra of the as-synthesized CdSe/**ODPA** (λ_{ex} = 465 nm) shows that there is a symmetrical decay at the first few picoseconds (Fig. S2) at high excitation densities. This observation can be explained by multi-exciton annihilation in the NCs. To avoid this, the pump power was kept as 0.3 µJ (> 30 fs full width at half maximum).

11. Ultrafast TA Spectroscopy Kinetic Analysis

11.1 Ultrafast TA Spectroscopy Kinetic Analysis at 490 nm

Kinetics were monitored at 505 nm and at 490 nm, which is close to the first excitonic peak of CdSe NC (Fig. S5). Other than triplet energy transfer to the anthracene transmitter, the initially populated CdSe excited states can be quenched by dark states or trap states. Thus a stretched exponential function was used to capture the rate of TTET[11]. The kinetic traces obtained from ultrafast TA experiments were fit using equation S1, S2 and S3; results from these fitting procedures are shown in Table 1 and Table S3, Fig. 3a and 3b for 505 nm, and in Fig. S5 for 490 nm.

$$\Delta A = A \bullet exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right) \tag{S1}$$

Where A and τ are the amplitude and the stretched lifetime respectively, corresponding to the TET between CdSe and the surface-bound acceptor. β is the stretching exponent. Using

$$\langle \tau \rangle = \frac{\tau}{\beta} \bullet \Gamma\left(\frac{1}{\beta}\right) \tag{S2}$$

The average weighted lifetime, $<\tau>$, was calculated using τ and β.

$$\langle k \rangle = \frac{1}{\langle \tau \rangle} - \frac{1}{\langle \tau_0 \rangle} \tag{S3}$$

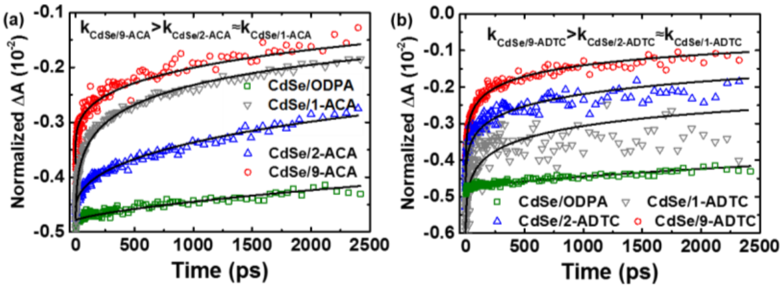


Fig. S5 Ground state recovery of CdSe NCs investigated by kinetics at 490 nm, illustrating much faster quenching in (a) anthracene carboxylic acid (ACA) functionalized CdSe NCs. Native octadecylphosphonic acid functionalized CdSe NCs (ODPA, green square), 1-ACA (grey triangle), 2-ACA (blue triangle) and 9-ACA (red circle) isomers; and (c) 9-anthracene dithiocarbamate (ADTC) functionalized NCs, 1-ADTC (grey triangle), 2-ADTC (blue triangle) and 9-ADTC (red circle). The black solid line is the fit.

11.2. Fitting parameters of TA at 490 and 505 nm

Transmitter	Probe wavelength						
	505 nm			490 nm			
	β	τ/ ns	<τ>/ns	β	τ/ ns	<τ>/ns	<k>x10^7/s^{-1}
ODPA	0.66	29.9	39.9	0.75	32.6	39.0	-
1-ADTC	0.24	1.30	39.7	0.21	0.515	38.8	0.13
2-ADTC	0.25	1.60	39.9	0.24	1. 41	38.8	0.13
9-ADTC	0.20	0.18	19.5	0.22	0.244	14.5	4.46
1-ACA	0.24	1.34	39.7	0.24	1.24	37.3	0.41
2-ACA	0.41	12.5	39.9	0.44	13.7	35.1	0.24
9-ACA	0.31	2.0	16.0	0.38	2.86	39.0	6.82

Table S3 Fitting parameters from transient absorption data of the ground state bleach at 490 nm and 505 nm with equation S1 and S3.

12. The upconversion emission spectra of various concentration of ligands in ligand exchange solution.

All upconversion experiments are conducted in hexane.[2] Fig. S6 shows the emission of DPA and CdSe NCs during photon upconversion as the concentration of ligands in the ligands exchange solution is increased.

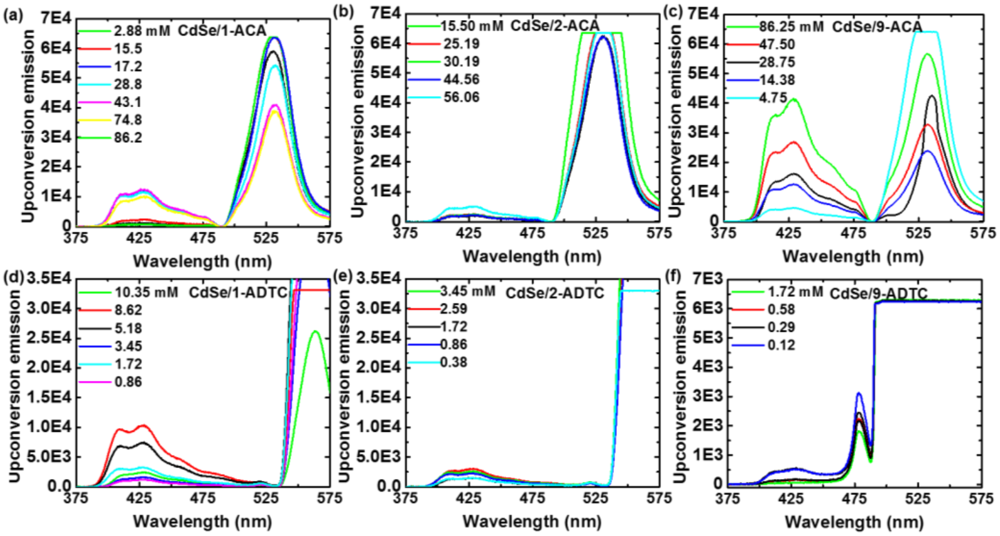


Fig. S6 The normalized emission of DPA and photoluminescence of CdSe nanocrystals (NCs) in this hybrid upconversion platform. CdSe NCs serve as sensitizers while DPA is the annihilator emitting the upconverted light. In general, the upconverted emission increases with the concentration of the ligand exchange solution (listed in mM). The different anthracene isomers are the (a) 1-anthracenecarboxylic acid (**1-ACA**); (b) **2-ACA**; (c) **9-ACA**; (d) 1-anthracene dithiocarbamate (**1-ADTC**); (e) **2-ADTC** and (f) **9-ADTC**. Upconversion sample was strictly air-free and excited with 12.7 W/cm^2 532 nm or 488 nm laser at room temperature. During ligand exchange, the concentration of CdSe was kept as 57.5 μmol/L while the concentration of ligands was varied as shown above to optimize the $\Phi_{\text{upconversion}}$.

13. $\Phi_{\text{upconversion}}$ of CdSe/9-ADTC in THF solution

Due to the low solubility of **1-ADTC** and **2-ADTC** in THF and improved solubility in NMP, NMP has been chosen as the solvent in ligand exchange for **ADTC** isomers. Fig. S7 shows the data obtained for **9-ADTC** using THF, while Fig. 3 in the main text gives the data with NMP. There is a 5 times higher $\Phi_{\text{upconversion}}$ when ligand exchange is performed in THF compared to NMP for **9-ADTC**. The upconversion QY (%) is defined as

$$\Phi_{UC} = 2 \cdot \Phi_{ref} \cdot \frac{photons\ absorbed\ by\ R}{photons\ absorbed\ by\ S} \cdot \frac{photons\ emitted\ by\ S}{photons\ emitted\ by\ R} \qquad \text{(S4)}$$

where R and S are reference and sample respectively. The upconverted emission of **DPA** and photoluminescence of CdSe NCs are shown in Fig. S6.

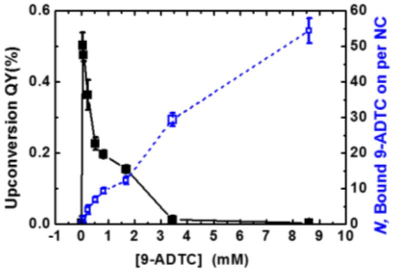


Fig. S7 $\Phi_{\text{upconversion}}$ and N, number of 9-ADTC bound per CdSe nanocrystal (NC), as the concentration of 9-ADTC is increased. Ligand exchange was performed in a solution of tetrahydrofuran: toluene =1:1 at room temperature for 40 mins with the concentration of CdSe constant at 57.5 µM.

13. References and Notes

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