Supporting Information for:

Near-Infrared-to-Deep-Blue Photon Upconversion Engineered from PbS Quantum Dots and Perylene Derivatives

Hongyu Li,[a, †] Qingxin Luan,[a, †] Shuai Zhang,[a] Lin Xi,[a] Yanan Feng,[a] Lili Hou*[a, b]

a. Hongyu Li, Qingxin Luan, Shuai Zhang, Lin Xi, Yanan Feng, Prof Lili Hou
State Key Laboratory of Precision Measurement Technology and Instruments, Key Laboratory of Optoelectronics Information Technology, School of Precision Instruments and Optoe-lectronics Engineering, Tianjin University, 92 Weijin Road Tianjin, 300072, China
E-mail: lilihou@tju.edu.cn

b. Prof Lili Hou
Department of Chemistry and Chemical Engineering
Chalmers University of Technology
Gothenburg 412 96, Sweden

Content

1 Sample preparation 3
1.1 Chemicals. 3
1.2 Synthesis of PbS QDs 3
1.3 Preparation of PbS QDs/3-PYCA complexes. 3
1.4 Preparation of PbS QDs/3-PYCA and perylene/rubrene mixture for TTA-UC measurements. 4
1.5 Measurement of the number of 3-PYCA anchored on PbS QDs. 4
Table S1. Summary of NIR-to-visible TTA-UC using QDs as sensitizers. 5
2 Instrumentation and optical measurements 6
2.1 Steady state spectroscopy measurements 6
2.2 Time-resolved spectroscopy measurements 6
2.3 TTA-UC measurements 7
2.4 Concentration-dependent absorption, photoluminescence (PL), and photoluminescence quantum yeild (PLQY) measurements 8
Table S2. The PLQY of perylene varies with its concentration. 8
2.5 Theoretical calculation 8
Table S3. Summary of 3-PYCA and perylene energy level calculations 9
2.6 Kinetics fitting 9
Table S4. Parameters of energy transfer from QDs to 3-PYCA 11
Fig. S1 12

Fig. S2.....12
Fig. S3.....13
Fig. S4.....14
Fig. S5.....14
Fig. S6.....15
Fig. S7.....16
Fig. S8.....16
Fig. S9.....17
Fig. S10.....18
Fig. S11.....18
Fig. S12.....19
Reference 20

1 Sample preparation

1.1 Chemicals.

Lead oxide (PbO, 99.999%), 1-octadecene (ODE, 90%), oleic acid (OA, 85%) and 1,2-dichlorobenzene (99%) were purchased from Aladdin. Perylene-3-carboxylic acid (3-PYCA, 95%) and hexamethyldisilathiane (TMS, 95%) were purchased from Macklin. Perylene (98%) was purchased from Meryer. Rubrene (98%) were purchased from Heowns. Anthracene was purchased from Meryer (Shanghai) Chemical Technology.[1] 9,10-diphenylanthracene (DPA) was purchased from Zancheng (Tianjin) Technology.[2] Azo (98%) were purchased from Sigma. Toluene was purchased from Damao Chemical Reagent Factory.

1.2 Synthesis of PbS QDs

The mixture of 4.0 mmol PbO, 3 mL OA and 6 mL ODE was heated for 20 min at 90 ^{o}C under the vacuum to remove water and oxygen. Subsequently, 420 μL TMS diluted in 20 mL ODE was swiftly

injected into Pb-OA solution. After 30 s nucleation process, the flask was quickly moved to the ice water bath for cooling. The PbS QDs was precipitated by adding acetone and centrifuged at 8000 rpm for 3 min. Finally, the precipitate was dispersed in toluene for subsequent tests.

1.3 Preparation of PbS QDs/3-PYCA complexes.

Ligand exchange was performed by mixing PbS QDs with various concentrations (10-500 μM) of 3-PYCA in nitrogen saturated toluene and sonicated at 50 ^{o}C for 10 minutes, and then stirred for 1 hour at 25 ^{o}C. The synthesized PbS/3-PYCA were washed by adding 1:5 volume toluene/acetone mixture, followed by centrifuging at 10000 rpm for 8 min. The supernatant was discarded and the final pellet was quickly transferred to a glove box and redispersed in toluene for further use. The concentration of the PbS QDs was determined using the absorption of the first exciton peak.[3]

1.4 Preparation of PbS QDs/3-PYCA and perylene/rubrene mixture for TTA-UC measurements.

PbS QDs/3-PYCA toluene solution (10 μM) was mixed with 600 μL of perylene toluene solution (10 mM) or 600 μL of rubrene toluene solution (20 mM) in a N_2-filled glove box. The TTA-UC solution was injected into a cuvette of 1 mm pathlength and sealed in inert gas environment for TTA-UC measurements. The perylene sample was prepared in a 1,2-dichlorobenzene solution for UCQY measurements.

1.5 Measurement of the number of 3-PYCA anchored on PbS QDs.

The number of 3-PYCA was quantified by absorption spectra. Specifically, the absorbance of 3-PYCA at 460 nm was determined by subtracting the absorbance contribution of PbS QDs. The concentration of 3-PYCA in solution was then calculated based on the molar extinction coefficient

at this wavelength, and finally divided by the concentration of PbS QDs.

Table S1. Summary of NIR-to-visible TTA-UC using QDs as sensitizers.

QDs	mediators	Annihilators	Excitation Wavelength (nm)	TTA-UC Emission (nm)	Anti-Stokes Shift (eV)[a]	UCQY (%)[b]	Ref
PbSe	\	Rubrene	800	568	0.66	0.005	[4]
PbS/CdS	5-CT	Rubrene	785	560	0.64	2.5	[5]
PbS	CPT	Rubrene	808	560	0.68	0.85	[6]
PbSe	CPT	Rubrene	808	560	0.68	1.05	
PbS/CdS	5-CT	Rubrene	808	560	0.68	4.2	[7]
PbS	5-CT	Rubrene	808	560	0.68	5.9	[8]
			808	580	0.68	6.75	
PbS	Th-DPP	Rubrene	980	580	0.95	0.225	[9]
			1064	580	1.07	0.185	
Zn-doped $CuInSe_2$/ZnS	5-CT	Rubrene	808	560	0.68	8.35	[10]
InAs	5-CT	Rubrene	808	570	0.68	10.55	[11]
PbS	\	Rubrene:DBP	808	610	0.50	0.6	[12]
PbS	\	TES-ADT	1064	610	1.00	0.047	[13]
PbS	TTCA	V_{79}	808	700	0.29	0.031	[14]
PbS		Perylene	808	470	1.30	2.1	\
PbS (This work)	3-PYCA	Rubrene	808	570	0.68	6.35	\

a. The anti-Stokes Shift is calculated from the energy level difference between the excitation light energy and the first singlet excited state (S_1) of the annihilator.

b. The maximum UCQY is 50%.

2 Instrumentation and optical measurements

2.1 Steady state spectroscopy measurements

Steady state absorption spectra were recorded on an Agilent-Cary 60 UV−Vis spectrophotometer. Steady state fluorescence was carried out on an Agilent Cary Eclipse Fluorescence spectrofluorometer.

2.2 Time-resolved spectroscopy measurements

Nanosecond transient spectrum measurements were performed on a Transient Absorption Spectrometer (LP980, Edinburgh Instruments) using an Nd: YAG laser (Agilite, Amplitude Continuum) equipped with an OPO (Horizon, Amplitude Continuum) generating a 600 nm excitation (10 ns pump beam, 7 mJ/pulse). A 150 W ozone-free, xenon arc lamp was used as the probe light. The time resolved decays for Fig. 2c and Fig. 3b were measured on a 5-stage PMT (R13456P, Hamamatsu) coupled with a monochromator (TMS302, Edinburgh Instruments) and recorded on an oscilloscope (RTM3002, Rohde and Schwarz). The transient spectra for Fig. 2f were recorded on a gated ICCD camera from Andor (DH320T-25F-03, Oxford Instruments). The data were collected at room temperature, and all samples were placed in 2 mm N_2-filled quartz cuvettes.

The femtosecond (fs) pump-probe TA experiment (TA-100, Time-Tech Spectra, Co., Ltd.) used a Pharos2 fs-laser (Light Conversion; full width at half-maximum, ~222 fs, 100 kHz, 1030 nm), which was split into the pump and probe beams. The pump beam was directed into an optical parametric amplifier (OPA, Orpheus-HP, Light Conversion) to generate a 700 nm excitation (240 nJ per pulse).

A broadband white light (10 nJ per pulse, 500 nm to 800 nm) was generated through a YAG crystal, and then passed through a 900 nm low-pass filter. A 7 ns optical delay stage was used and the two beams were focused and overlapped on the sample in a 1 mm quartz cuvette. The transient spectra and kinetics were acquired by averaging 2000 times at every given time delay.

The fluorescence lifetime of perylene and 3-PYCA (shown in Fig. S2) were determined using time-correlated single photon counting (TCSPC) on a setup using a 375 nm laser diode (PicoQuant) and recorded by an MCP-PMT detector (10 000 counts, 2048 channels).

2.3 TTA-UC measurements

Steady state upconversion fluorescence (UCPL) spectral measurements were performed on a home-built system,[15] consisting of a continuous-wave 808 nm laser (MDL-III-808-2W, Changchun New Industries Optoelectronics Technology Co., Ltd.) as the excitation source, a monochromator (Omni-λ3007i, Zolix), and a photomultiplier tube (PMT) detector. The laser beam was focused to the front surface with a spot radius of 0.58 mm. UCPL signals were collected at 90 degrees to the excitation.

The upconversion quantum yield (UCQY, Φ_{uc}) was calculated using diiodized BODIPY as a reference with quantum yield of 2.7% in acetonitrile under 532 nm excitation.

The Φ_{uc} (out of a 50% maximum) was calculated based on the equation as followed:

$$\Phi_{uc} = \Phi_r \frac{I_{uc} A_r n_{uc}^2}{I_r A_{uc} n_r^2} \#(S1)$$

$$A = \frac{Laser\ power}{hc/\lambda}\left(1 - 10^{-Abs}\right) \#(S2)$$

Where, uc, r represents as TTA-UC sample and reference sample, respectively, Φ is photoluminescence quantum yield, A is absorbance at the excitation wavelength, I is the integral emission intensity, n represents solvent refractive index.[9] The TTA-UC quantum efficiency Φ_{uc} was measured in 1,2-dichlorobenzene with a perylene concentration of 20 mM.

2.4 Concentration-dependent absorption, photoluminescence (PL), and photoluminescence quantum yeild (PLQY) measurements

Concentration-dependent absorption, PL, and PLQY measurements were performed under the same conditions as the UCQY experiments: dissolved in 1,2-dichlorobenzene in a 1 mm cuvette. The annihilator concentration was varied from 10 μM to 20 mM. Absorption spectra were collected with an Agilent-Cary 60 UV−Vis spectrophotometer. PL signals were acquired with TTA-UC measurement setup, employing a white lamp coupled with a grating for excitation. The PLQY was determined via a relative method, with a dilute anthracene solution in ethanol as the reference for high concentrated perylene (1 mM, 10 mM, 20 mM, excited at 320 nm), and a DPA solution in ethanol for low concentrated perylene (10 μM, 20 μM, excited 395 nm; 50 μM, 100 μM excited 375 nm). The results are summarized in Table S2.

Table S2. The PLQY of perylene varies with its concentration.

Concentration	20 mM	10 mM	1 mM	100 μM	50 μM	20 μM	10 μM
PLQY (%)	45	75	84	85	99	99	99

2.5 Theoretical calculation

All computational input files were prepared in GaussView 09 on a local Windows 10 terminal. DFT or TD-DFT calculations were carried out using the Gaussian 16W (g16) suite of programs. All calculations were performed on Orca at B3LYP/6-311g (d,p) level. The anti-Stokes shift of 1.3 eV was determined based on the energy difference between the first excited state of the annihilator perylene and the exciton energy of PbS QDs (corresponding to the triplet state of the QDs).

Table S3. Summary of 3-PYCA and perylene energy level calculations

	Theoretical calculation		Literature report	
	S_1 [a]	T_1	S_1	T_1
Perylene	2.73 eV	1.53 eV	2.83 eV[16]	1.53 eV[16]
3-PYCA	2.55 eV	1.47 eV	/	

[a] As calculated from the crossing point of the normalized absorption and emission spectra in Fig. 2a

2.6 Kinetics fitting

The spectra of upconverted emission are presented in the main text, see Fig. 3b. The traces were fitted to Equation S3.

$$y = \begin{cases} y0 + Ad + Ag * \left(\exp\left(-\frac{t_0}{tg}\right) - \exp\left(-\frac{t}{tg}\right)\right), & t < t_0 \\ y0 + Ad * \exp\left(-\frac{t - t_0}{td}\right), & t \geq t_0 \end{cases} \quad \#(S3)$$

where, A is the amplitude, t is time, $g,\ d$ represent the growth and decay component.

3-PYCA triplet-state lifetime (Fig. 2f) was fitted by a growth component (triplet energy transfer rate constant k_{TET}), and a decay component (3-PYCA triplet decay rate constant k_T)

$$\left[3-PYCA^{*}\right](t) = a_{TET}e^{-k_{TET}t} + a_{T}e^{-k_{T}t} \#(S4)$$

where, a_{TET} and a_T are the amplitudes, $\tau_g = 1/k_{TET}$, $\tau_d = 1/k_T$.

The PL decay curves (Fig. 2c) and exciton bleach kinetics (Fig. S4) at 720 nm for PbS QDs and PbS QDs/3-PYCA complexes were fitted by multiple exponential functions. The average lifetime τ_{ave} was calculated according to eq. S5,

$$\tau_{ave} = \frac{\sum_i A_i\tau_i}{\sum_i A_i} \#(S5)$$

Where A_i, τ_i are the amplitude and lifetime, respectively, of the i-th component. The decay rate K can be calculated as $K = \frac{1}{\tau_{ave}}$,

Rate of TET from PbS to 3-PYCA could be calculated as $K_{TET} = \frac{1}{\tau_{ave\ PbS}} - \frac{1}{\tau_{ave\ PbS@3-PCA}}$ and its efficiency $\emptyset_{TET} = 1 - \frac{\tau_{ave\ PbS\&3-PCA}}{\tau_{ave\ PbS}}$ = 97.1%, and the fitting parameters and calculation results were listed in Table S4.

Name	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	A_3 (%)	τ_3 (ns)	τ_{ave} (ns)	$\emptyset_{quenching}$ (%)	$K_{ave}(\mu s^{-1})$	$K_{TET}(\mu s^{-1})$	$\emptyset_{TET}$ (%)
PbS	70.1	1395.1	29.9	2908.1			1847.5		0.541		
PbS@3-PYCA	99.9	53.1	0.002	938.8	0.003	3035.6	53.2	97.1	18.8	18.3	97.1

Table S4. Parameters of energy transfer from QDs to 3-PYCA

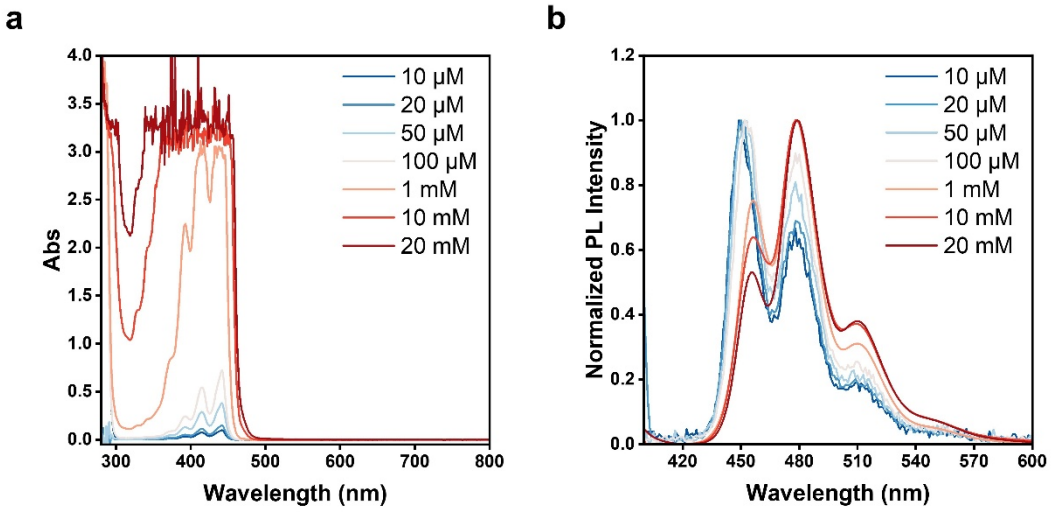


Fig. S1 Concentration-dependent (a) absorption and (b) PL spectra of perylene at varied concentrations.

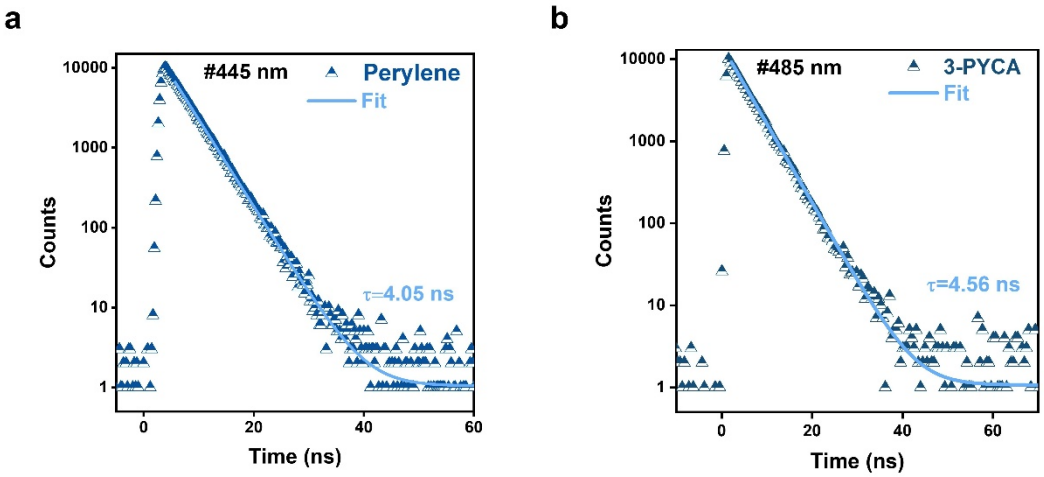


Fig. S2 The PL decay of dilute perylene (a) and 3-PYCA (b) (excitation: 377 nm). The single exponential fitting indicates a fluorescence lifetime of 4.05 ns for perylene and 4.56 ns for 3-PYCA.

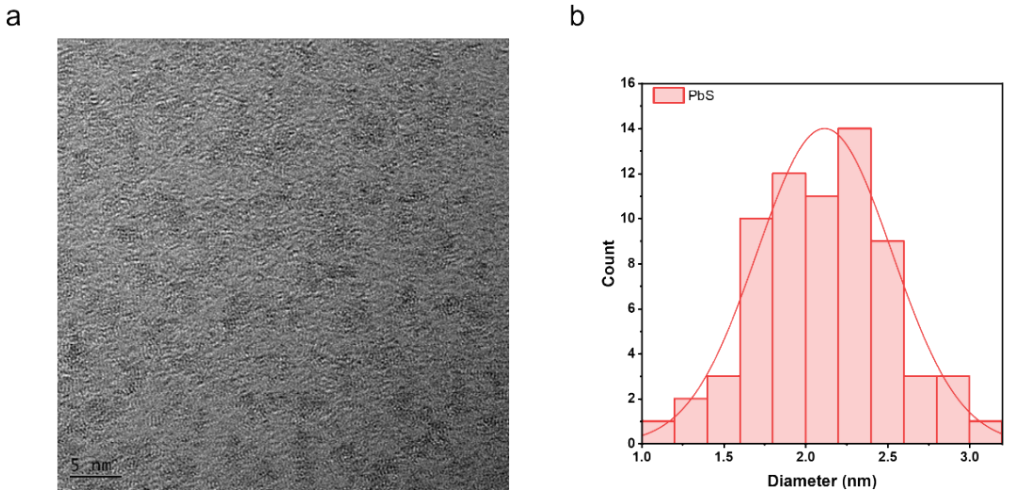


Fig. S3 (a) A transmission electron microscope (TEM) image of PbS QDs. (b) Size distribution of PbS QDs with an average diameter at 2.1±0.1 nm.

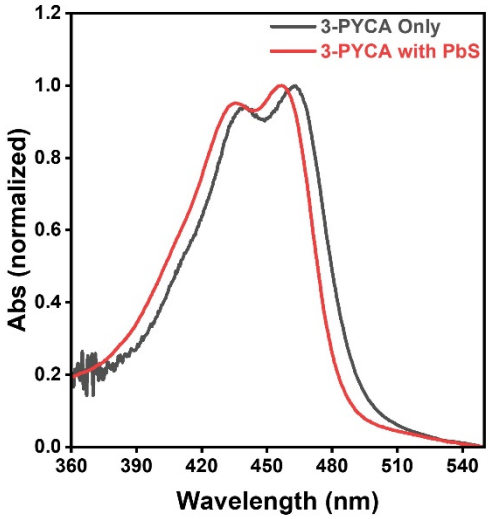


Fig. S4 The comparison of absorption spectra of 3-PYCA and 3-PYCA anchored to PbS QDs (the absorption spectrum of PbS QDs was subtracted).

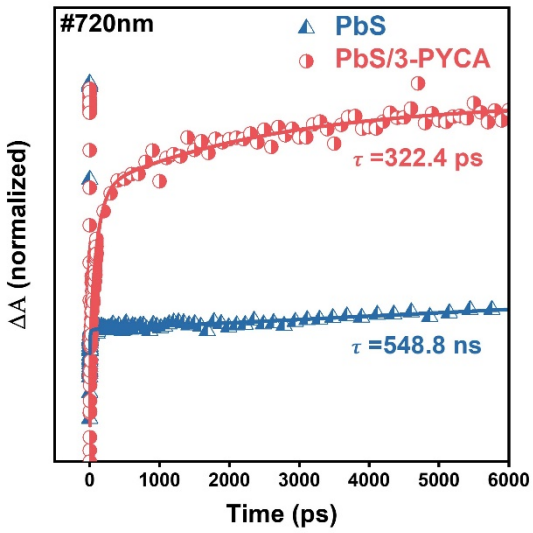


Fig. S5 Time-resolved XB decay and fitting of PbS QDs & PbS QDs/3-PYCA at 720 nm.

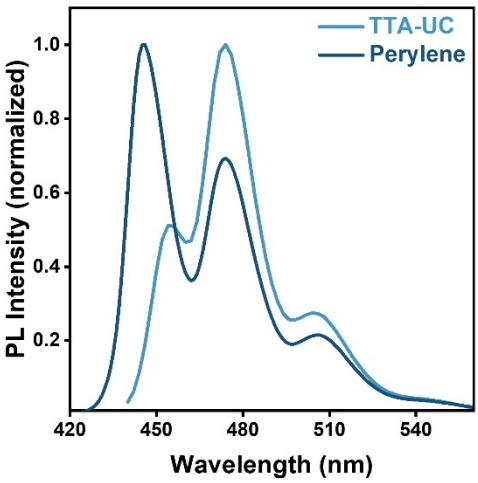


Fig. S6 Comparing the TTA-UC spectrum of perylene (Fig. 3a) with its intrinsic fluorescence spectrum. In the TTA-UC system, the decrease of the first PL peak is due to the reabsorption effect caused by the high concentration of perylene (10 mM in toluene).

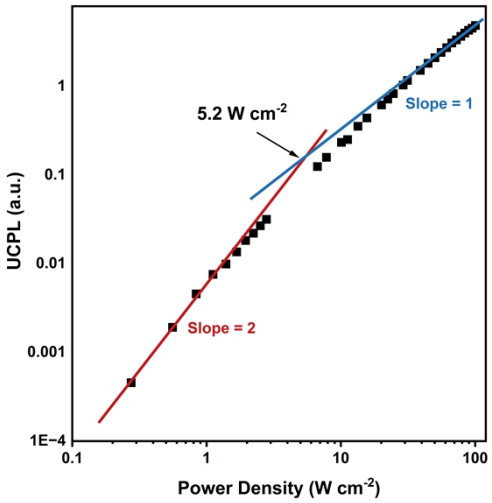


Fig. S7 Log-log plot of the UCPL intensity versus the excitation power density for the PbS QDs/3-PYCA/perylene TTA-UC system. The intersection between the quadratic fitting (slope = 2) at the low-power regime and the linear fitting (slope = 1) at the high-power regime is the threshold of TTA-UC. In the TTA-UC system of PbS QDs/3-PYCA/perylene, the TTA-UC threshold was determined to be ~5.2 W cm^{-2}.

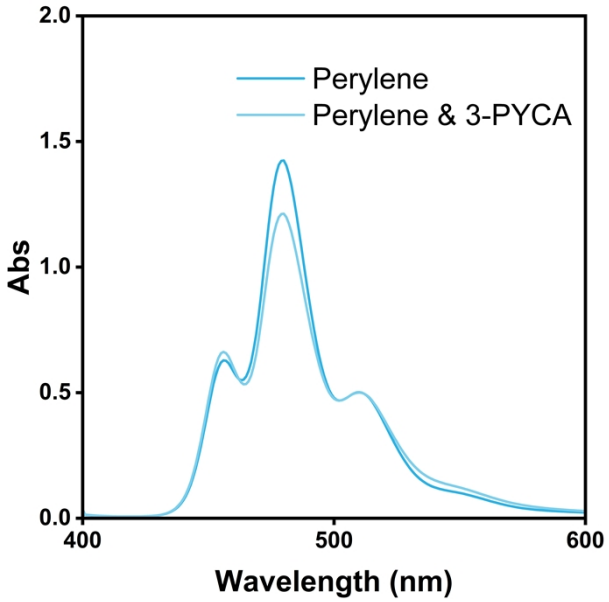


Fig. S8 PL spectra of perylene (20 mM), the perylene/3-PYCA blend (20 mM and 100 μM) under 365 nm excitation.

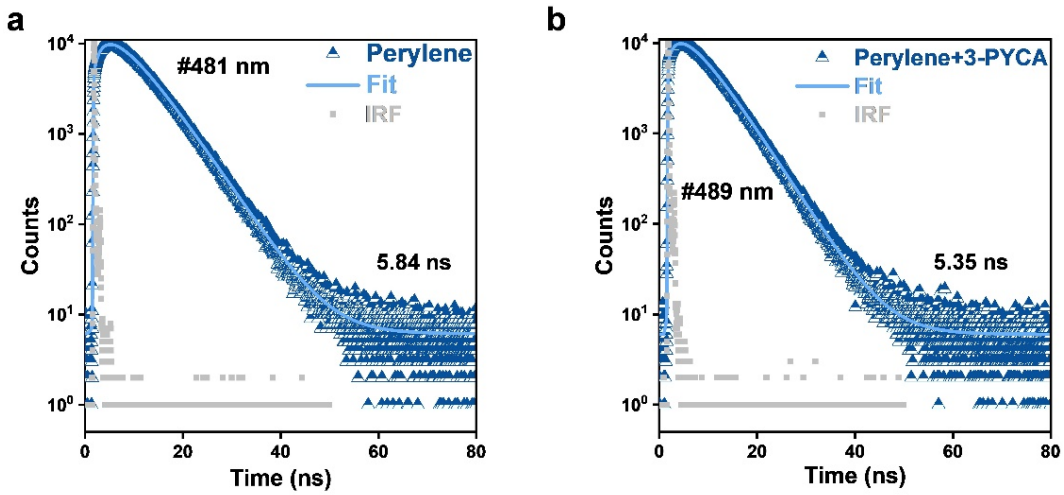


Fig. S9 The PL decay of perylene (a) and perylene/3-PYCA (b) (excitation: 375 nm). The fitting results yield a PL lifetime of 5.84 ns for perylene (20 mM), and 5.35 ns for perylene (20 mM) mixed with 3-PYCA (100 μM). *The rising in PL lifetimes is due to the reabsorption at such high concentration.

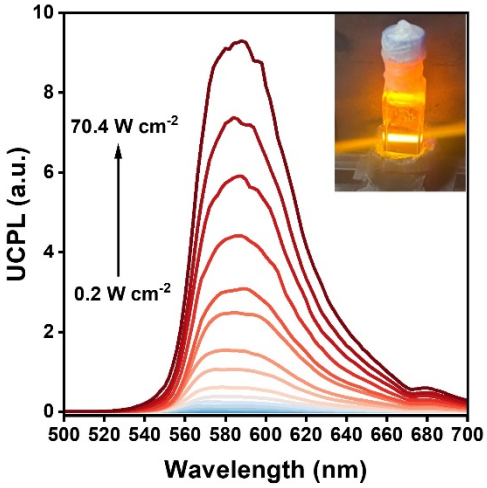
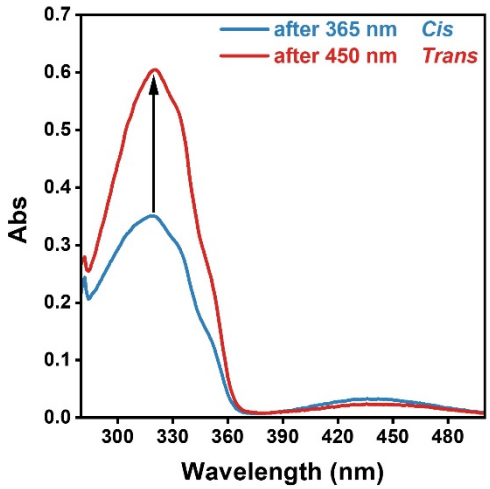


Fig. S10 The TTA-UC spectral of PbS QDs/3-PYCA and PbS QDs mixed rubrene as annihilator under 808 nm laser irradiation. Clear yellow emission was observed (insert photo) and the UCQY was



determined to be 6.35%.

Fig. S11 The absorption spectra of Azo after 365 nm and 450 nm light irradiation. Under irradiation with a 365 nm LED, Azo undergoes a transition from the *trans* to *cis* photoisomerization (blue). Under irradiation with a 450 nm LED, Azo transitions from the *cis* to *trans* isomers (red).

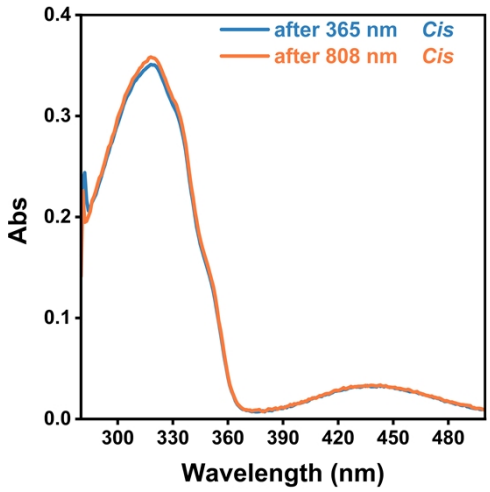


Fig. S12 *cis*-Azo (after irradiation under 365 nm to the photostationary state) under 808 nm light irradiation, in absence of TTA-UC solution.

Reference

1. W. R. Dawson and M. W. Windsor, Fluorescence yields of aromatic compounds, *J. Phys. Chem.*, 1968, **72**, 3251-3260.
2. M. Mardelli and J. Olmsted, Calorimetric determination of the 9,10-diphenyl-anthracene fluorescence quantum yield, *J. Photochem.*, 1977, **7**, 277-285.
3. I. Moreels, K. Lambert, D. Smeets, D. De Muynck, T. Nollet, J. C. Martins, F. Vanhaecke, A. Vantomme, C. Delerue, G. Allan and Z. Hens, Size-Dependent Optical Properties of Colloidal PbS Quantum Dots, *ACS Nano*, 2009, **3**, 3023-3030.
4. Z. Huang, X. Li, M. Mahboub, K. M. Hanson, V. M. Nichols, H. Le, M. L. Tang and C. J. Bardeen, Hybrid Molecule–Nanocrystal Photon Upconversion Across the Visible and Near-Infrared, *Nano Lett.*, 2015, **15**, 5552-5557.
5. Z. Huang, Z. Xu, M. Mahboub, X. Li, J. W. Taylor, W. H. Harman, T. Lian and M. L. Tang, PbS/CdS Core–Shell Quantum Dots Suppress Charge Transfer and Enhance Triplet Transfer, *Angew. Chem. Int. Ed.*, 2017, **56**, 16583-16587.
6. Z. Huang, D. E. Simpson, M. Mahboub, X. Li and M. L. Tang, Ligand enhanced upconversion of near-infrared photons with nanocrystal light absorbers, *Chem. Sci.*, 2016, **7**, 4101-4104.
7. M. Mahboub, Z. Huang and M. L. Tang, Efficient Infrared-to-Visible Upconversion with Subsolar Irradiance, *Nano Lett.*, 2016, **16**, 7169-7175.
8. Z. Huang, Z. Xu, M. Mahboub, Z. Liang, P. Jaimes, P. Xia, K. R. Graham, M. L. Tang and T. Lian, Enhanced Near-Infrared-to-Visible Upconversion by Synthetic Control of PbS Nanocrystal Triplet Photosensitizers, *J. Am. Chem. Soc.*, 2019, **141**, 9769-9772.
9. L.-H. Jiang, X. Miao, M.-Y. Zhang, J.-Y. Li, L. Zeng, W. Hu, L. Huang and D.-W. Pang, Near

Infrared-II Excited Triplet Fusion Upconversion with Anti-Stokes Shift Approaching the Theoretical Limit, *J. Am. Chem. Soc.*, 2024, **146**, 10785-10797.

10. W. Liang, C. Nie, J. Du, Y. Han, G. Zhao, F. Yang, G. Liang and K. Wu, Near-infrared photon upconversion and solar synthesis using lead-free nanocrystals, *Nat. Photonics*, 2023, **17**, 346-353.
11. R. Sun, J. Zang, R. Lai, W. Yang and B. Ji, Near-Infrared-to-Visible Photon Upconversion with Efficiency Exceeding 21% Sensitized by InAs Quantum Dots, *J. Am. Chem. Soc.*, 2024, **146**, 17618-17623.
12. M. Wu, D. N. Congreve, M. W. B. Wilson, J. Jean, N. Geva, M. Welborn, T. Van Voorhis, V. Bulović, M. G. Bawendi and M. A. Baldo, Solid-state infrared-to-visible upconversion sensitized by colloidal nanocrystals, *Nat. Photonics*, 2015, **10**, 31-34.
13. N. Nishimura, J. R. Allardice, J. Xiao, Q. Gu, V. Gray and A. Rao, Photon upconversion utilizing energy beyond the band gap of crystalline silicon with a hybrid TES-ADT/PbS quantum dots system, *Chem. Sci.*, 2019, **10**, 4750-4760.
14. E. M. Gholizadeh, S. K. K. Prasad, Z. L. Teh, T. Ishwara, S. Norman, A. J. Petty, J. H. Cole, S. Cheong, R. D. Tilley, J. E. Anthony, S. Huang and T. W. Schmidt, Photochemical upconversion of near-infrared light from below the silicon bandgap, *Nat. Photonics*, 2020, **14**, 585-590.
15. Q. Luan, L. Hou, H. Li, T. Wang, T. Xu, Z. Ding, J. Jiang and T. Liu, Measurement methods for triplet-triplet annihilation photon upconversion, *Opt. Continuum*, 2024, **3**, 2078-2087.
16. T. N. Singh-Rachford and F. N. Castellano, Triplet Sensitized Red-to-Blue Photon Upconversion, *J. Phys. Chem. Lett.*, 2009, **1**, 195-200.