Supporting Information

Efficient Near-Infrared-Excitable Quantum Dots-Based Triplet-Triplet Annihilation Upconversion with a Record Anti-Stokes Shift via Low Coverage of Mono-Styryl-BODIPY Ligands

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1. Materials and characterization

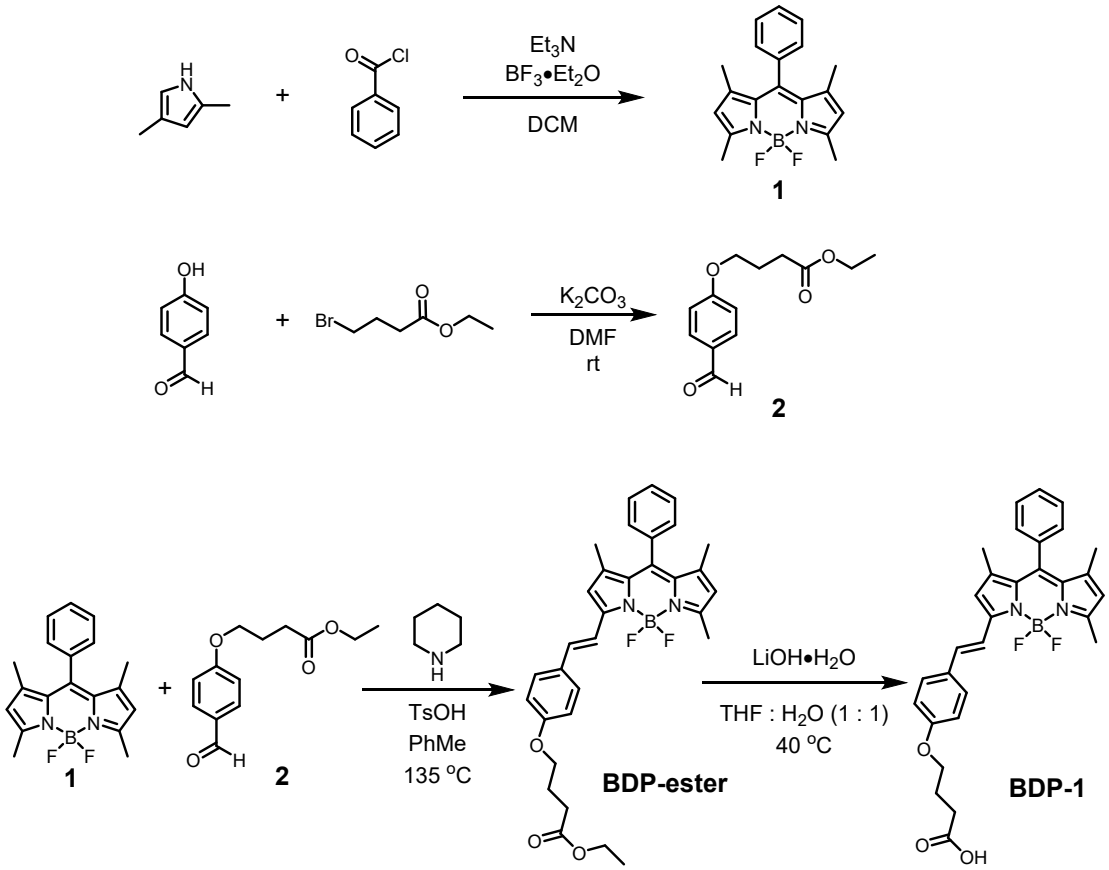
1.1 Chemicals

Yellow lead monoxide (PbO), oleic acid (OA), 1-octadecene (ODE), and bis(trimethylsilyl)sulfide ($(TMS)_2S$) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Toluene (PhMe), piperidine, chloroform ($CHCl_3$), 2,4-dimethylpyrrole, benzoyl chloride, triethylamine (Et_3N), and tetrahydrofuran (THF) were purchased from Tianjin Bohua Chemical Reagent. *P*-toluene sulfonic acid (TsOH), and lithium hydroxide monohydrate ($LiOH•H_2O$), 4-hydroxybenzaldehyde, 4-bromobutyric acid ethyl ester, deuterated Methanol (MeOH-*d*4) and deuterated chloroform ($CDCl_3$) were purchased from Heowns Biochem Technologies. Lc. Tianjin. Methanol (MeOH), ethyl acetate (EtOAc), ethanol (EtOH), acetone, dichloromethane (DCM), hexane, anhydrous Na_2SO_4 and silica gel (200 mesh) were purchased from the Tianjin Hedong District Guangda Service Department. All the mentioned chemicals were used as received without further purification unless otherwise noted.

1.2 Instrumentation and characterization

^1H NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer using MeOH-*d*4 as the deuterated solvent, approximately 3.31 ppm and $CDCl_3$ as the deuterated solvent, δ = 7.26 ppm. High-resolution mass spectrometry (HRMS) was performed on a Varian 7.0T FTMS. Absorption spectra were recorded by a Shimadzu UV-3600 plus spectrophotometer. A Hitachi HT7800 transmission electron microscope (TEM) was used for the acquisition of TEM images. Photoluminescence (PL) spectra, fluorescence quantum yields (Φ_f, measured with an integrating sphere) and transient PL spectra of BDP-1 were measured on an Edinburgh FLS1000 spectrometer under 405 nm excitation. Photoluminescence (PL) spectra, photoluminescence quantum yields (PLQY, measured with an integrating sphere) of PbS QDs were measured on an Edinburgh FLS1000 spectrometer under 808 nm excitation. Photoluminescence (PL) spectra and transient PL spectra of PbS/BDP-1 or PbS/5-CT complexs were measured on an Edinburgh FLS1000 spectrometer under 808 nm excitation. For the photon upconversion experiments, 808 nm solid-state laser was used as excitation source, and the final concentration of PbS/BDP-1 or PbS/5-CT was 10 μM, the final concentration of rubrene was 20 mM. PL spectra were obtained in argon-saturated toluene using a 1 mm × 1 cm quartz cuvette. The femtosecond transient absorption (fs-TA) spectra of BDP-1, PbS and PbS/BDP-1 were acquired in argon-saturated toluene using a 2 mm × 1 cm quartz cuvette, the pump wavelength of BDP-1 was set to 500 nm and the pump wavelength of PbS and PbS/BDP-1 were set to 750 nm. Please note that fs-TA spectra, PL spectra, and upconversion spectra measurements in this study were performed in an inert environment.

2. Supplementary Methods



Scheme S1. The synthesis route of compound **BDP-1**.

2.1 Synthetic procedure of compound 1

Compound **1** was synthesized following a reported method.[1] 2,4-dimethylpyrrole (951.4 mg, 10 mmol) and benzoyl chloride (702.9 mg, 5 mmol) were added to a 500 mL three-neck round-bottom flask containing 150 mL nitrogen-degassed dry DCM. The mixture was then stirred 6 h at 30 ℃. After complete consumption of the aldehyde (monitored via TLC), 3 mL dry triethylamine (Et_3N) was added to the mixture and after stirring for 30 min, BF_3•OEt_2 (8 mL) was added dropwise at 0 ℃. The mixture was stirred continuously for 4 h at 30 ℃. And then the reaction mixture was washed with saturate aqueous $NaHCO_3$ (50 mL) and extracted with DCM. The organic phase was dried over Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography over silica gel (PE/EA = 6:1 v/v) to obtain orange solid compound **1**, yield 324.1 mg, 20%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54 – 7.45 (m, 3H), 7.32 – 7.27 (m, 2H), 5.98 (s, 2H), 2.58 (s, 6H), 1.37 (s, 6H).

2.2 Synthetic procedure of compound 2

Compound **2** was synthesized following a reported method.[2] A mixture of 4-hydroxybenzaldehyde (1.22 g, 10 mmol), potassium carbonate (7.60 g, 55 mmol) and 4-bromobutyric acid ethyl ester (2.34 mL, 12 mmol) in *N, N*-dimethylformamide (40 mL) was stirred vigorously for 16 hours at room temperature. The mixture was filtered and concentrated *in vacuo* to to obtain light yellow oil compound **2**, yield 2.47 g, 100%. ^{1}H-NMR ($CDCl_3$) δ (ppm): 9.81 (s, 1H), 7.76 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 4.13 – 4.01 (m, 4H), 2.46 (t, J = 7.2 Hz, 2H), 2.20 – 1.99 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H).

2.3 Synthetic procedure of compound BDP-1

Knoevenagel condensation between compound **1** and compound **2**, yielding the **BDP-ester** intermediate,[3] followed by LiOH-mediated hydrolysis.[4] Dissolve **1** (32.4 mg, 0.1 mmol) and **2** (23.6 mg, 0.1 mmol) in 5 ml of dry PhMe in a 50 mL three-neck round-bottom flask. Add 10 mg TsOH and 300 μL piperidine to the reaction mixture. Stir the resulting mixture in the dark for 20 min under nitrogen atmosphere at 135 °C. Wash the reaction mixture with twice with water and brine solution. Extract the mixture with DCM. Dry the filtrate over anhydrous Na_2SO_4. Concentrate the filtrate under reduced pressure. Purify the crude product by column chromatography using hexane/EtOAc (4/1, v/v) to obtain purple oily compounds. Due to the nearly identical polarity between the product **BDP-ester** and the aldehyde **2**, the unreacted aldehyde **2** cannot be removed during the purification process, resulting in the isolation of a purple oily compounds by column chromatography. Since a noticeable polarity difference was anticipated for the hydrolysis step, the mixture of **BDP-ester** and **2** was hydrolyzed directly, with the aldehyde impurity being removed during the subsequent purification. **BDP-ester** (0.046 mmol, 25.0 mg) was dissolved in THF/H_2O (v/v, 1 mL/1 mL). Then added LiOH·H_2O (10.8 mg, 0.138 mmol) and stirred for 12 h at 40 °C. After cooling, the mixture was acidified to pH = 3–4 by adding a 10% (v/v) aqueous solution of hydrochloric acid. The crude mixture was extracted three times with DCM. The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was distilled off under reduced pressure. The crude product was purified by column chromatography (EtOAc/MeOH = 5/1, v/v) to afford pinkish purple soild **BDP-1**, yield 13.4 mg, 57%. ^{1}H NMR (400 MHz, Methanol-*d*4) δ (ppm): 7.53 – 7.43 (m, 6H), 7.32 – 7.28 (m, 3H), 6.93 (d, J = 8.8 Hz, 2H), 6.71 (s, 1H), 6.03 (s, 1H), 4.03 (t, J = 6.2 Hz, 2H), 2.49 (s, 3H), 2.47 (t, J = 7.2 Hz, 2H), 2.05 (m, 2H), 1.41 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ (ppm): 159.81, 154.71, 153.62, 142.78, 142.32, 140.11, 136.30, 135.32, 132.98, 131.77, 129.59, 129.18, 128.40, 121.20, 117.69, 117.13, 114.92, 66.93, 29.85, 22.84, 14.72, 14.46, 14.26. HRMS: calcd. for $C_{30}H_{29}BF_2N_2O_3$ ($[M]^{+}$•): 514.2239, found 514.2235.

2.4 Theoretical calculation of BDP-1

The ground state (S_0) optimization and excited state geometric structure calculation of BDP-1 were performed by using Orca at B3LYP/def2-TZVP level with CPCM model for solvation in toluene.[5-8] To ensure that the obtained configuration is stable, frequency calculation was further performed on the optimized structure. In addition, using unrestricted density functional theory (UDFT) revealed the T_1 excited state adiabatic energies of 1.37 eV for BDP-1.

2.5 Preparation of PbS QDs

PbS QDs was synthesized based on literature.[9]

A typical synthetic procedure for PbS QDs with a diameter of 2.65 nm is as follows: A mixture of yellow PbO (0.45 g), oleic acid (2 mL) and ODE (18 mL) were heated to 110 °C in a 50 mL three-neck flask for an hour in a vacuum. Meanwhile, the sulfur precursor was prepared by mixing $(TMS)_2S$ (0.21 mL) in anhydrous ODE (10 mL). Then the reaction temperature was set to 65 °C. The sulfur precursor was swiftly injected, and the heater was removed right after injection. 5 min after injection, the reaction flask was rapidly cooled down to room temperature, and the injection of cold hexane (10 mL) was performed. As-synthesized PbS QDs was washed three times by adding a 1:3 volume hexanes:ethanol mixture, followed by centrifuging at 8000 rpm for 10 min. The supernatant was discarded, and the final pellet was quickly transferred to a glovebox and redispersed in toluene for future use. The size of the PbS QDs was determined by measuring the position of the first exciton peak and verified by transmission electron microscopy. The bandgap of the PbS QDs was determined using the Tauc plot method, and the concentration of the PbS QDs was determined using the absorption of the first exciton peak.

2.6 Preparation of PbS/BDP-1[10]

Ligand exchange was conducted by mixing 10 μM PbS QDs with varying concentrations of BDP-1 (0, 100, 200, 400, and 1600 μM) in argon-saturated toluene (1 mL), followed by stirring for 1 h. The resulting PbS/BDP-1 complexes were then purified by washing with a 1:6 (v:v) toluene:acetone mixture and centrifuging at 8000 rpm for 10 minutes. After discarding the supernatant, the final pellet was promptly transferred to a glovebox and redispersed in toluene (400 μL) for subsequent use. The average number of BDP-1 ligands bound per PbS QD was estimated using the molar extinction coefficient of BDP-1 (Extinction coefficient of BDP-1 at 571 nm is 1.82×10^4 M^{-1} cm^{-1}). The absorption of BDP-1 is determined by subtracting the contribution of PbS QDs from the absorbance of PbS/BDP-1 at 573 nm. Then, the concentration of BDP-1 in solution can be calculated based on the molar extinction coefficient.

2.7 Preparation of PbS/5-CT[11]

5-CT (1 mM) were dissolved in a 10:1 volume toluene/THF mixture. An aliquot of this solution of 5-CT and 10 μM PbS QDs in argon-saturated toluene (1 mL) were mixed with varying concentrations of 5-CT (100, 200 μM), followed by stirring for 1 h. The resulting PbS/5-CT complexes were then purified by washing with a 1:6 (v:v) toluene:acetone mixture and centrifuging at 8000 rpm for 10 minutes. After discarding the supernatant, the final pellet was promptly transferred to a glovebox and redispersed in toluene (400 μL) for subsequent use. The average number of 5-CT ligands bound per PbS QD was estimated using the molar extinction coefficient of 5-CT (Extinction coefficient of 5-CT at 482 nm is 5.3×10^3 M^{-1} cm^{-1}). The absorption of 5-CT is determined by subtracting the contribution of PbS QDs from the absorbance of PbS/5-CT at 489 nm. Then, the concentration of 5-CT in solution can be calculated based on the molar extinction coefficient.

2.8 Air stability of the ligands BDP-1 and 5-CT

To assess the air stability of BDP-1 and 5-CT, steady-state absorption spectra of their dilute solutions (10 μM for BDP-1 and 5-CT) were recorded over 166 h in untreated (i.e., not degassed) solvent. During the testing period, the samples were kept in a dark and low-temperature environment to avoid light exposure and solvent evaporation. The absorbance at the absorption maximum was recorded at various time points, normalized to the initial absorbance measured at the first time point, and compared across different intervals. The absorption maximum of 5-CT decreased to 6% of its initial value after 103 h, while that of BDP-1 remained at 92% of its initial value after 166 h.

2.9 Photoluminescence quantum yields of PbS and fluorescence quantum yields of BDP-1

The absolute photoluminescence quantum yield (PLQY) of PbS QDs and absolute fluorescence quantum yields (Φ_f) of BDP-1 were measured measured on an Edinburgh FLS1000 spectrometer using the integrating sphere method.

For the PbS QDs, an 808 nm laser was used as the excitation source, and an InGaAs detector coupled with the integrating sphere was employed for detection across the wavelength range of 780–1400 nm. First, a reference scan was performed by placing a cuvette containing pure toluene solvent into the sample position of the integrating sphere. Under 808 nm excitation, the emission spectrum was scanned and saved. Subsequently, the prepared quantum dot sample (1 μM in deoxygenated toluene solution) was accurately positioned in the sample location of the integrating sphere, ensuring that the excitation light spot fully illuminated the sample. Under 808 nm excitation, the emission spectrum was again scanned and saved. Finally, the software was used for data processing to calculate the absolute quantum yield of the PbS QDs.

When the sample was BDP-1, a xenon lamp was used as the excitation source, and a PMT900 detector coupled with the integrating sphere was employed for detection across the wavelength range of 370–850 nm. First, a reference scan was performed by placing a cuvette containing pure chloroform solvent into the sample position of the integrating sphere. Under 405 nm excitation, the emission spectrum was scanned and saved. Subsequently, the prepared BDP-1 sample (10 μM in chloroform solution) was accurately positioned in the sample location of the integrating sphere, ensuring that the excitation light spot fully illuminated the sample. Under 405 nm excitation, the emission spectrum was again scanned and saved. Finally, the software was used for data processing to calculate the absolute quantum yield of BDP-1.

Multiple measurements were conducted on the same sample to assess repeatability.

2.10 Fluorescence lifetime measurement of BDP-1

The fluorescence lifetime of BDP-1 was measured using time-correlated single photon counting (TCSPC) on an Edinburgh FLS1000 spectrometer equipped with a HAMAATSU 405 nm pulsed laser and a PMT900 detector. The sample was dissolved in chloroform to prepare a 10 μM solution, which was then loaded into a 1 cm × 1 cm quartz cuvette. The excitation wavelength was set to 405 nm, and the emission wavelength was set to the emission peak wavelength of BDP-1 (583 nm). Both the excitation and emission slit widths were set to 1 nm. The time range was set to 100 ns, the number of channels was set to 4096, and the peak counts were set to 2000.

2.11 Photoluminescence lifetime measurement of PbS QDs

The photoluminescence lifetime of was measured using an Edinburgh FLS1000 spectrometer equipped with an 808 nm pulsed laser and a PMT-1700 detector. The sample was dissolved in deoxygenated toluene to prepare a 1 μM solution, which was then transferred under inert atmosphere into a sealed quartz cuvette (1 cm × 1 cm) equipped with a cap and a rubber septum inside a glovebox to isolate it from air. The emission wavelength was set to 960 nm (the emission peak wavelength of PbS QDs). The time range was set to a 100 μs, the number of channels was set to 2000, and the peak counts were set to 10,000.

2.12 The upconversion efficiencies (η_{UC}, normalized to 100%) measurements

The η_{UC} was calculated by comparison with the standard (IR780 in $CHCl_3$, Φ_{std} = 15.8%) via equation 1 and 2.[10]

$$\eta_{UC} = 2 \times \Phi_{std} \times \left(\frac{A_{std}}{A_{sam}}\right) \times \left(\frac{I_{sam}}{I_{std}}\right) \times \left(\frac{n_{sam}}{n_{std}}\right)^2 \quad (1)$$

$$A = \left(\frac{Laser\ Power}{hc/\lambda}\right) \times \left(1 - 10^{-Abs}\right) \quad (2)$$

Φ_{std} is the fluorescence quantum yield of standard. A_{sam}/A_{std} and I_{sam}/I_{std} represent the number of photons absorbed and the integrated luminescence intensity by the sample/standard, respectively. n_{sam}/n_{std} represent the refractive indices of the solvents for the sample/standard, which are PhMe and $CHCl_3$, respectively. The upconversion samples were excited at 808 nm, and the standard was excited at 830 nm.

2.13 The corrected upconversion quantum efficiency (η'_{UC}, normalized to 100%) measurements

The corrected upconversion quantum efficiency (η'_{UC}) was calculated from equation 3.

$$\eta'_{UC} = \eta'_{UC} \times \frac{I_t}{I_0} \quad (3)$$

The I_t was the integrated intensity of corrected upconversion spectra, and the I_0 was the integrated intensity of actually measured upconversion spectra.

2.14 Correction of TTA-UC spectra

Due to the high concentration of rubrene or BPEA and the strong absorption of PbS in the visible region, the upconversion spectra were corrected using the fluorescence spectra of rubrene or BPEA in diluted solution to exclude the influence of the inner-filtering effect.[12] Specifically, for PbS/BDP-1/rubrene system, at 700 nm the inner-filtering effect is negligible, the intensity ratio between the upconversion spectra and the diluted rubrene solution spectra was calculated. This ratio was then multiplied by the latter spectra to simulate the corrected upconversion spectra. The consistency of the spectra from 700 nm to 750 nm before and after correction confirmed the feasibility of this simulation, while the spectral differences below 700 nm were attributed to the inner-filtering effect. For PbS/BDP-1/BPEA system, at 625 nm the inner-filtering effect is negligible, the intensity ratio between the upconversion spectra and the diluted rubrene solution spectra was calculated. This ratio was then multiplied by the latter spectra to simulate the corrected upconversion spectra. The consistency of the spectra from 625 nm to 675 nm before and after correction confirmed the feasibility of this simulation, while the spectral differences below 625 nm were attributed to the inner-filtering effect.

2.15 Measurement of femtosecond transient absorption (fs-TA) spectra

The femtosecond transient absorption (fs-TA) spectra of PbS and PbS/BDP-1 were acquired using an ultrafast transient absorption fluorescence microscopic spectroscopy system (PH-Tuning + TA100). The samples were prepared in a glovebox, dissolved in degassed toluene at appropriate concentrations, and loaded into a 2 mm × 1 cm quartz cuvette for measurement. The pump wavelength was set to 750 nm. The detection time window ranged from -1 ps to 7000 ps, and the spectral acquisition range covered 450 – 950 nm. Spectra measurements were performed in an inert environment.

3. Supplementary Tables

Table S1. Photophysical parameters of PbS QDs. [a]

QDs	λ_{abs} [b]	Bandgap [c]	Diameter [d]	λ_{em} [e]	PLQY [f]
PbS QDs	831	1.38	2.65	960	79

[a] Measured in toluene, 1 μM. [b] The first exciton absorption peak (nm). [c] The bandgap (eV) was determined using the Tauc Plot method. [d] Particle size was calculated from bandgap energy (nm). [e] Maximum emission wavelength (nm). [f] The absolute photoluminescence quantum yield (%) was determined with an integrating sphere.

Table S2. Photophysical parameters of BDP-1. [a]

Ligand	λ_{abs} [b]	ε [c]	λ_{em} [d]	S_1 [e]	T_1 [f]	Φ_f [g]	τ_f [h]
BDP-1	571	1.82	583	2.15	1.37	96	3.88

[a] Measured in $CHCl_3$, 10 μM. [b] Maximum absorption wavelength (nm). [c] Molar absorption coefficient ($\times 10^4$ M^{-1} cm^{-1}). [d] Maximum fluorescence emission wavelength (nm). [e] The S_1 energy levels (eV) was determined by the intersection of absorption and emission. [f] The T_1 energy levels (eV) was determined by theoretical calculation used B3LYP/def2-TZVP level in Orca program.[6-9] [g] Absolute fluorescence quantum yield was determined with an integrating sphere (%). [h] Fluorescence lifetime (ns).

Table S3. The average number of BDP-1 ($<N_{BDP-1}>$) per PbS QD.

C_{BDP-1} [a]	0	100	200	400	1600
$<N_{BDP-1}>$	0	2	3	7	28

[a] Concentration of BDP-1 during ligand exchange (μM).

4. Supplementary Figures

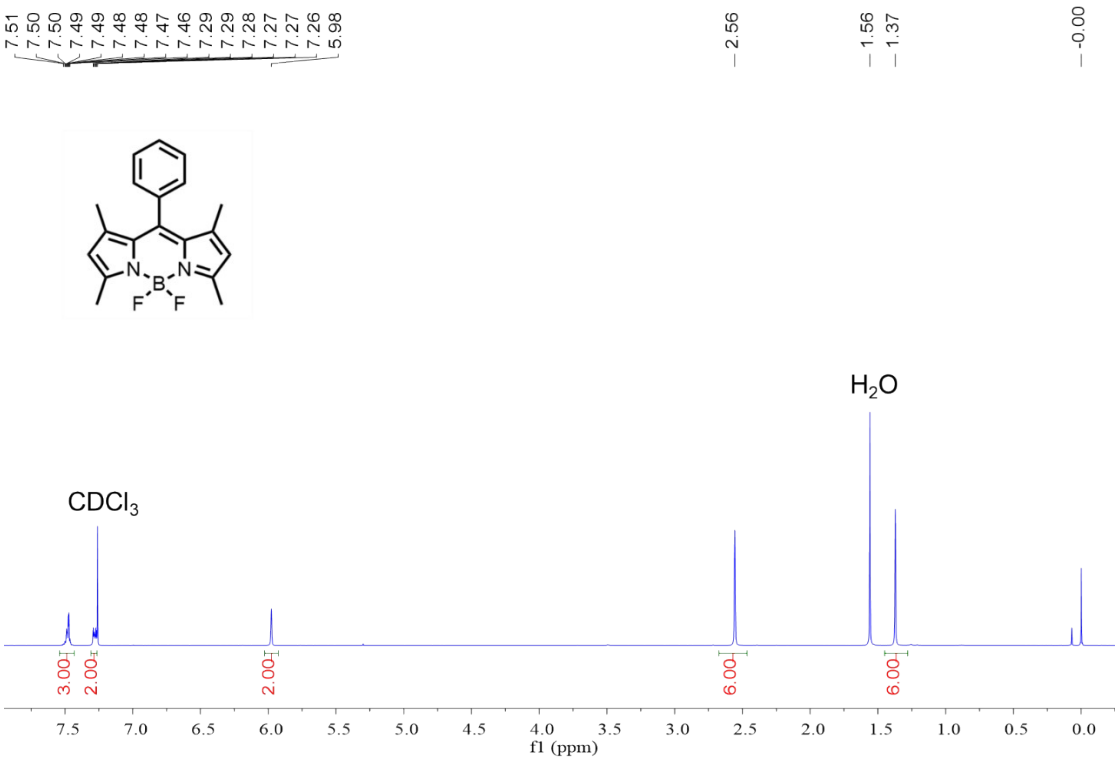


Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **1**.

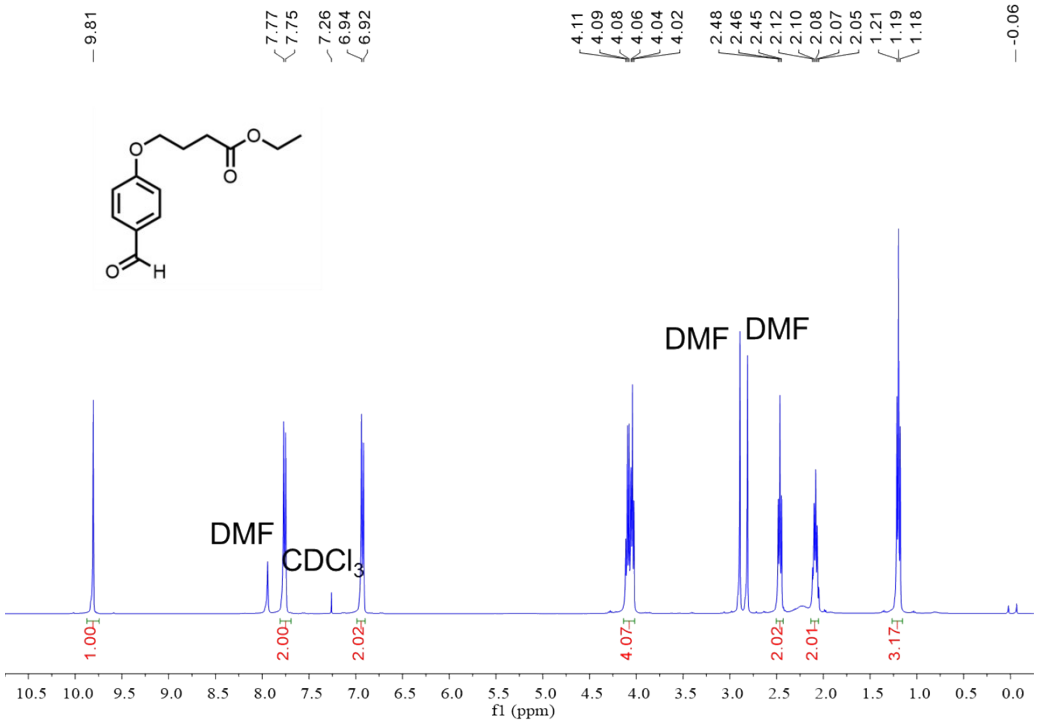


Fig. S2. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2**.

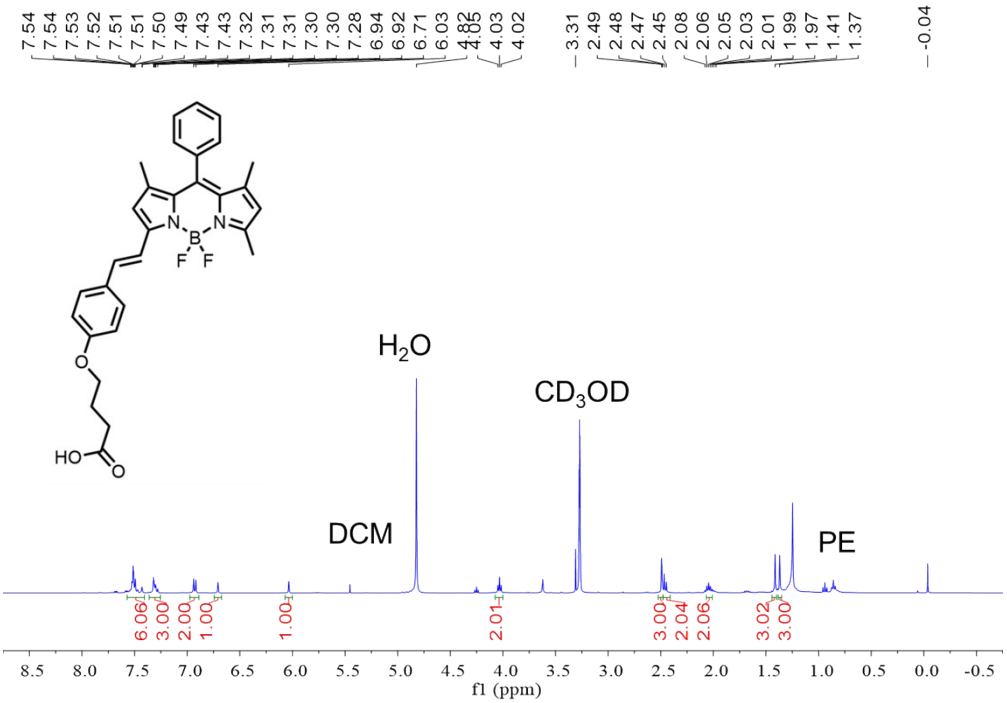


Fig. S3. ^{1}H NMR (400 MHz, MeOH-*d*4) of BDP-1.

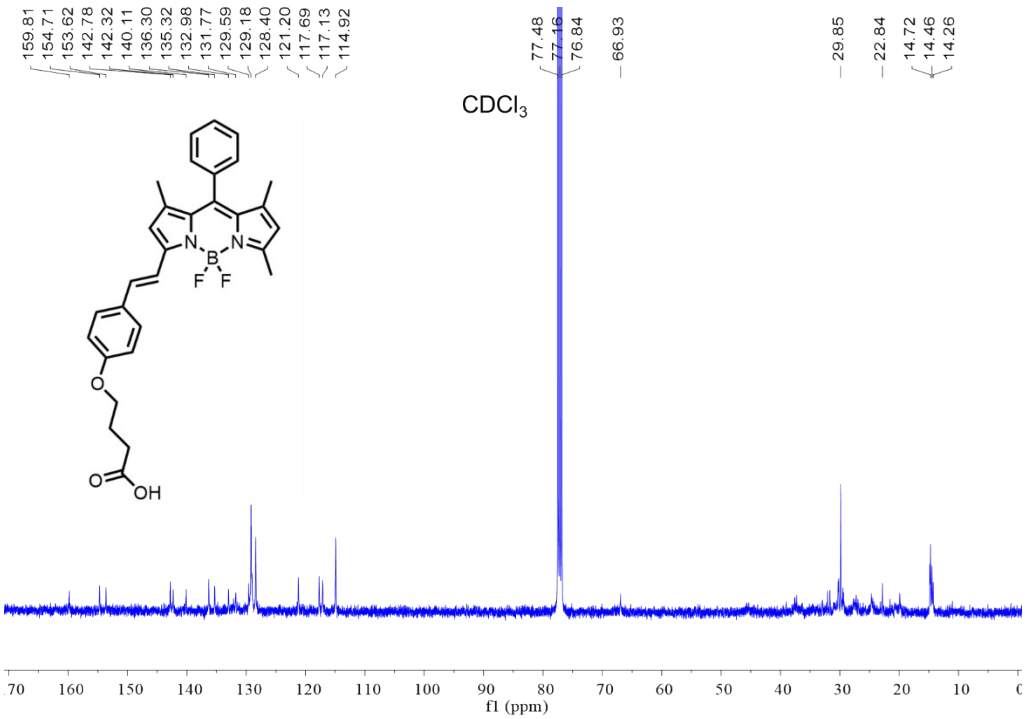


Fig. S4. ^{13}C NMR (100 MHz, $CDCl_3$) of BDP-1.

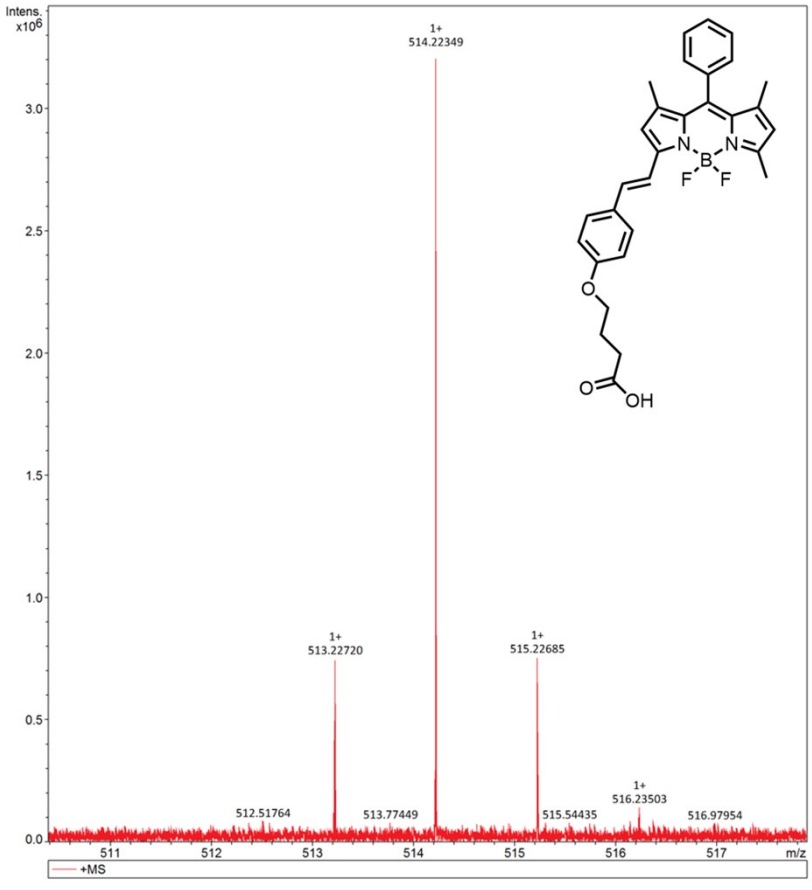


Fig. S5. High-resolution mass spectrum of BDP-1.

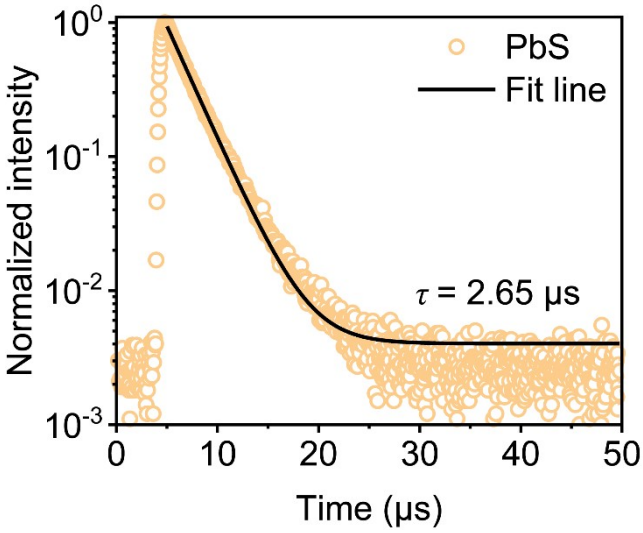


Fig. S6. Time-resolved photoluminescence spectra of PbS QDs.

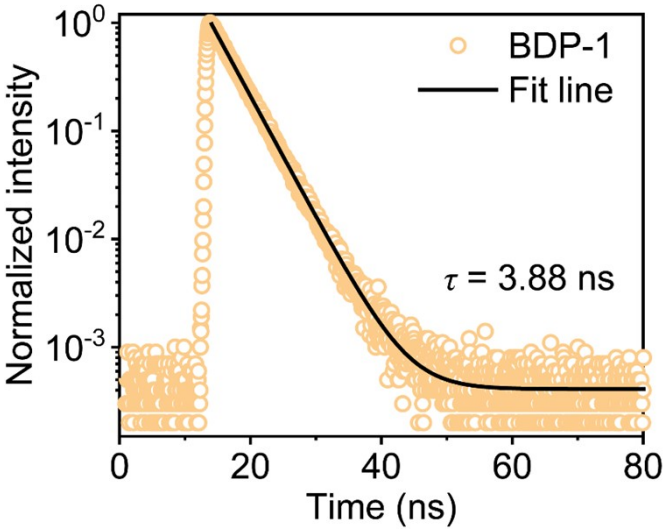


Fig. S7. Fluorescence decay traces of BDP-1 in $CHCl_3$, 10 μM, λ_{ex} = 405 nm.

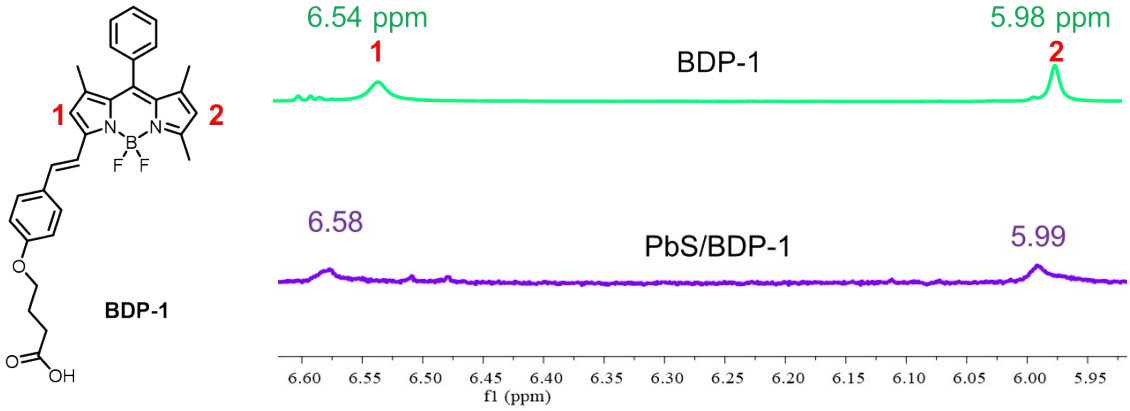


Fig. S8. Nuclear magnetic resonance (^{1}H NMR, 800 MHz) investigation of free BDP-1 (upper panel) and PbS/BDP-1 (lower panel). The ^{1}H NMR spectra of free BDP-1, PbS/BDP-1 in $CDCl_3$ and calibrated at 7.26 ppm.

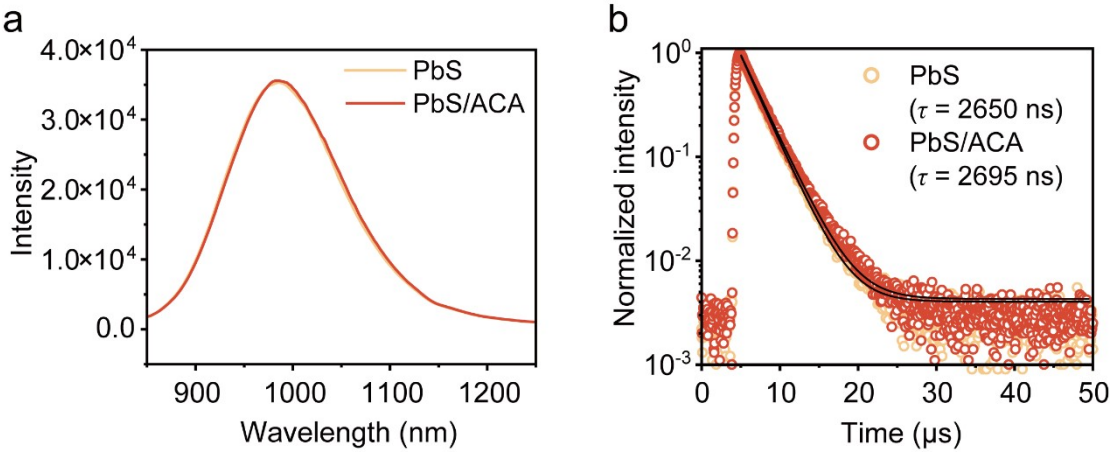


Fig. S9. (a) Photoluminescence spectra of PbS QDs before or after ligand exchange by 400 μM 9-anthracenecarboxylic acid (ACA) in argon-saturated toluene. (b)Time-resolved photoluminescence spectra of PbS QDs before or after ligand exchange by 400 μM 9-anthracenecarboxylic acid (ACA) in argon-saturated toluene.

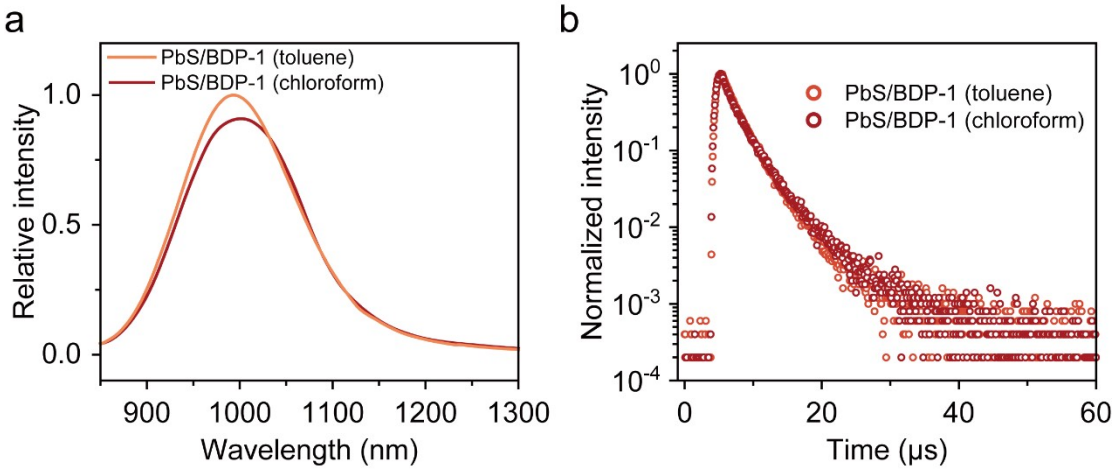


Fig. S10. (a) The photoluminescence intensity (a) and lifetime (b) of the PbS moiety in PbS/BDP-1 dispersed in nonpolar (toluene) and polar (chloroform) solvents.

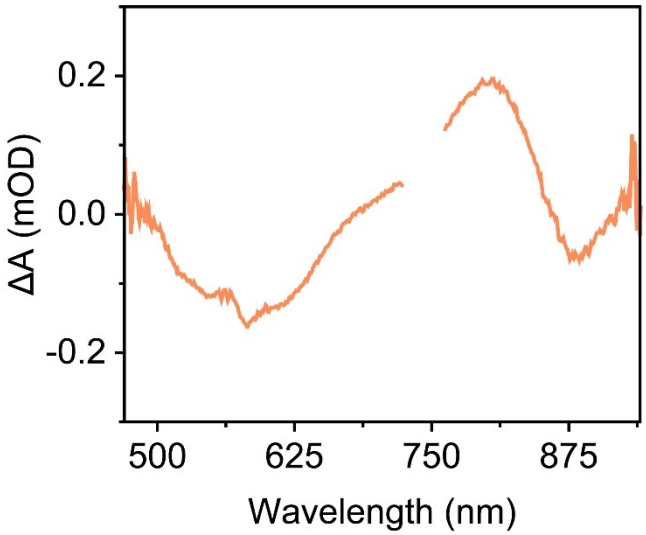


Fig. S11. The double-difference fs-TA spectra of PbS/BDP-1 after normalized to those of PbS/BDP-1 at the exciton peak at 859.5 nm. The negative features of double difference spectra at 580 nm match BDP-1 maximum absorption peak. The transient absorption spectrum of this triple excited state assigned to BDP-1.

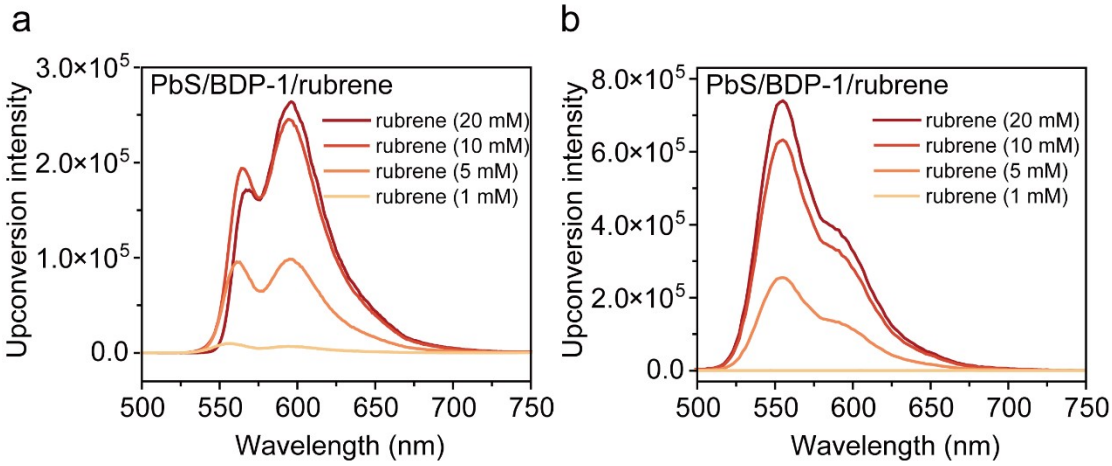


Fig. S12. (a) The upconverted emission intensity at various rubrene concentrations. (b) After spectral correction, the upconverted emission intensity at various rubrene concentrations.

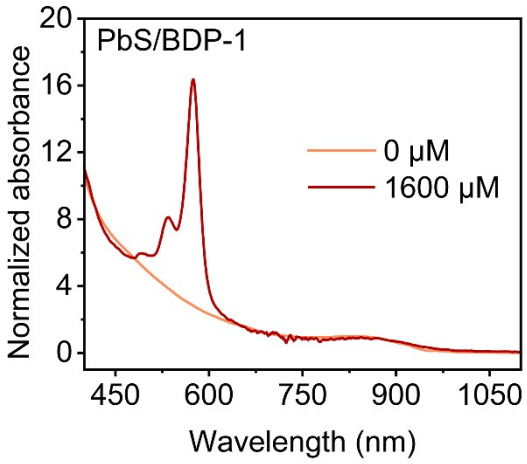


Fig. S13. Normalized absorption spectra of PbS QDs (normalize the first excitonic absorption peak of PbS QDs to 1) after ligand exchange with BDP-1 (1600 μM) in toluene, and the concentration of PbS is 10 μM.

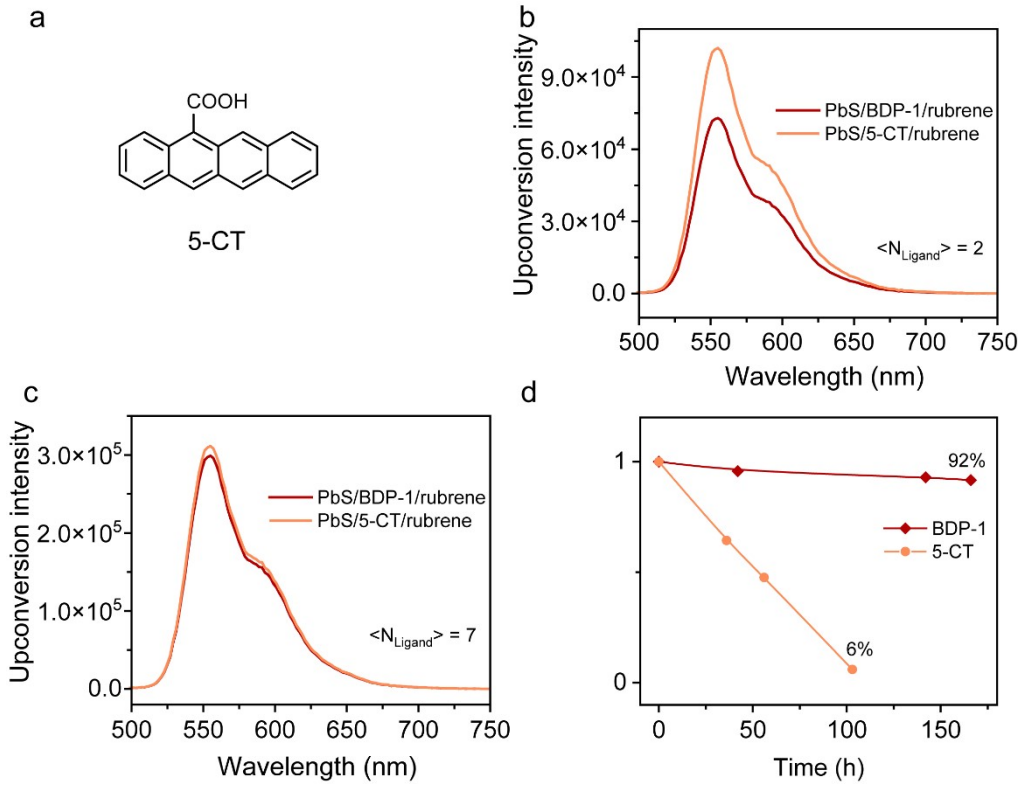


Fig. S14. (a) Molecular structure of 5-CT. Comparison of the upconversion intensity for PbS/BDP-1/rubrene and PbS/5-CT/rubrene with (b) 2 and (c) 7 surface ligands under 808 nm excitation. All samples were normalized to the same absorbance at 808 nm. (d) Stability comparison of BDP-1 and 5-CT. Both ligands were dissolved in organic solvent and exposed to ambient laboratory light; their stability was evaluated by monitoring the change in absorption spectra over time.

5. Cartesian coordinates obtained with DFT calculations

BDP-1 S_0

C	0.38378955135095	2.06768457723872	0.20115952806133
C	1.65439467676878	1.61050607635677	-0.17501457050402
C	2.78128920083599	2.40939494108323	0.03655821462887
C	2.64650513292835	3.67072871815816	0.62602627822978
C	1.38032230977845	4.13085165718122	1.00194877782613
C	0.25283482924846	3.33281983157860	0.79005168670402
H	1.75441886619308	0.62380920004180	-0.63334205003915
H	3.76833373348878	2.04493757283155	-0.25910282945879
H	3.52798156118385	4.29490386156468	0.79273921076082
H	1.26932096787320	5.11574388455282	1.46255460520412
H	-0.73815021237892	3.68774783894128	1.08276870162096
C	-0.81629270458326	1.21004557458691	-0.01466285314386
C	-1.53472214423321	1.30277136177446	-1.21572074591257
C	-1.21952479234585	0.32031830755300	0.99638662735801

N	-2.66535739015820	0.51741251492272	-1.43682812123456
N	-2.33295562472504	-0.50493575525845	0.81313029897623
B	-3.18175039241242	-0.59264856406321	-0.47959646449692
F	-3.02865780673552	-1.84939627849319	-1.07426264620255
F	-4.53451697721621	-0.38373987595290	-0.18135830949472
C	-1.34003624059623	2.13657571766139	-2.37530018745260
C	-2.36582073851913	1.82295953839650	-3.25521036336116
H	-2.52803192380364	2.27245918598953	-4.23282151649710
C	-3.18082988196781	0.81753498494700	-2.65759547772646
C	-0.26785889495003	3.15198801703525	-2.62441736103601
H	-0.28634441994989	3.95796719181766	-1.87515835202352
H	0.73647035038734	2.70513794285656	-2.57511774883177
H	-0.39884002893580	3.60148257295931	-3.61947439608522
C	-2.51272680073357	-1.25022522051366	1.92566884031917
C	-1.51191533528729	-0.91722459735778	2.86504018807393
C	-0.68856465748520	0.06252599030041	2.30375899064546
C	-3.60958605887195	-2.25055407978745	2.06134811633780
H	-3.53948696702782	-2.76924854822456	3.02669954668411
H	-4.59377804197474	-1.76262886417937	1.98196083668632
H	-3.55848207242808	-2.99135839803262	1.24758806617878
H	-1.40935154231956	-1.35854350571623	3.85534210639769
C	0.49309122146466	0.68853167611103	2.97805489712152
H	0.64284413685790	0.23786359423514	3.97005385568502
H	1.41735759058921	0.55708866651976	2.39541963119381
H	0.36182955050397	1.77373607545893	3.10921046704228
C	-4.36233578826658	0.17689212566404	-3.17579738710586
C	-4.85792664916797	0.38965855377848	-4.42202366368335
C	-6.04081973143307	-0.23216538491949	-5.00131485510589
C	-6.44729830493040	0.13146655102292	-6.30574553307751
C	-6.81560114818968	-1.19856919887701	-4.32770056823607
C	-7.56388452786885	-0.43495573522334	-6.90456987643950
H	-5.86485594768667	0.87641884453755	-6.85499794949998
C	-7.93694914218311	-1.77765000808627	-4.91626995384331
H	-6.53574725925130	-1.51465819317567	-3.32076539026927
C	-8.32268951757479	-1.39852447724866	-6.21583005018209
H	-7.87351388873670	-0.15183053415724	-7.91272692306823
H	-8.50373856147456	-2.52311256611877	-4.35913674998628
O	-9.39082535021252	-1.90428109330142	-6.87207768703653
C	-10.17851044813439	-2.91650383891527	-6.25909533780762
C	-11.26774730533790	-3.31538526581029	-7.23789860302146
H	-10.61809193967779	-2.53693883041154	-5.31783196434482
H	-9.54274342667619	-3.78431129235550	-6.00265054959117
C	-12.15175158013478	-4.42372271341477	-6.67963101627763
H	-11.87988725477660	-2.43247726706865	-7.48013350489995

H	-10.80365917610379	-3.64305906584828	-8.18178546822883
H	-11.57130016170200	-5.33518161457238	-6.45491309547574
H	-12.61359696440095	-4.12811212071116	-5.72063980533175
C	-13.27441312804676	-4.81406236835139	-7.61276644191639
O	-13.53011039497381	-4.28112694313382	-8.66677780747408
O	-13.98509750631986	-5.84810631834490	-7.12824297029718
H	-14.69385046518084	-6.04221139794192	-7.76775542939174
H	-4.87084202502987	-0.50549836660553	-2.49430285682433
H	-4.33430772634139	1.08934073451535	-5.08204442981829

BDP-1 T_1

C	0.39716332866630	2.05582661486879	0.20277224912036
C	1.67059802666610	1.59716990623710	-0.16860571159638
C	2.80356157739814	2.38805886275355	0.04275665609888
C	2.67682397646046	3.65090389421457	0.63079347352599
C	1.41254337303019	4.11765602407281	1.00526268653756
C	0.28172549378881	3.32446221185540	0.79188845223162
H	1.76673363078566	0.60947136414924	-0.62623613095424
H	3.78880737333523	2.01705138157454	-0.25150834864633
H	3.56197274950719	4.27003972465720	0.79788326401567
H	1.30669775531263	5.10342230215205	1.46570012373440
H	-0.70698847190499	3.68635083903706	1.08481565627583
C	-0.80816387331296	1.20490958114228	-0.01334561776533
C	-1.55153632738628	1.28171120861961	-1.22335556553965
C	-1.24522363385828	0.31300144019651	0.98828380629154
N	-2.65612691616491	0.51422497659755	-1.43826077125520
N	-2.35360001141131	-0.49660780392452	0.79973534977699
B	-3.18604582820222	-0.59020908400650	-0.49293645130187
F	-3.03780109321385	-1.85262684199383	-1.08709175199913
F	-4.54790370759629	-0.38206335671822	-0.21877733379466
C	-1.33848228024369	2.12785364602824	-2.40446409082398
C	-2.34684947715943	1.82009175769602	-3.28500275267136
H	-2.49536838216953	2.27079839448226	-4.26477475427252
C	-3.18928094401976	0.81481372287369	-2.69996136574804
C	-0.25156242393642	3.13143385430623	-2.62580835013565
H	-0.26644043204519	3.92688258776208	-1.86500171784355
H	0.74722399219908	2.67150220461552	-2.57170528044555
H	-0.36617956083610	3.59624107180247	-3.61612937114154
C	-2.55190341062097	-1.25409546165417	1.92558841706847
C	-1.55540732710888	-0.92722706031813	2.86794490368121
C	-0.72182661221579	0.04589337340832	2.31585033810066
C	-3.65931780220036	-2.24011812536441	2.04287113764018
H	-3.61533056871497	-2.75498220046809	3.01194946298504

H	-4.63777284895471	-1.74393492584538	1.93791959053607
H	-3.60076238366808	-2.98613318863961	1.23315862200277
H	-1.46336358221522	-1.36947541235339	3.85906050172974
C	0.46114731525784	0.66998759255771	2.98493371902993
H	0.60625986988837	0.22895125922106	3.98221107889942
H	1.38647824033421	0.52612621674762	2.40540792543700
H	0.34040603868831	1.75851072287526	3.10362861139599
C	-4.33961484236546	0.20449988951649	-3.20616838762226
C	-4.88201090407420	0.45670156235530	-4.46423135609412
C	-6.05248320297116	-0.16570354415765	-5.01595305989969
C	-6.49318129956466	0.20199155446601	-6.31759881234795
C	-6.81044442079450	-1.15215018808977	-4.33391328510043
C	-7.60747815643814	-0.37657769513246	-6.89786756220780
H	-5.93146180034621	0.95982147372631	-6.87036120117774
C	-7.93032129897961	-1.74099855160969	-4.90896595952973
H	-6.51347620107794	-1.46905565965935	-3.33262365435217
C	-8.34144423730822	-1.36023564910205	-6.20200978526651
H	-7.94020184785280	-0.09242989894598	-7.89835634923624
H	-8.48026833809595	-2.49618878403570	-4.34789556624268
O	-9.40799585593255	-1.87697582573692	-6.84620369445676
C	-10.17281224707468	-2.90884750756462	-6.23340222402800
C	-11.25640537999104	-3.32693449839035	-7.21038815030570
H	-10.61445498414895	-2.54025750822954	-5.28903209368748
H	-9.51695476667427	-3.76333388749144	-5.98429489416862
C	-12.11573004752772	-4.45473789305488	-6.65211770174778
H	-11.88746249894995	-2.45676624675317	-7.44992538811736
H	-10.78773284694806	-3.64366587392756	-8.15565247750932
H	-11.51471780400082	-5.35253575689514	-6.42626739932264
H	-12.58544969640220	-4.16914059556115	-5.69401802722610
C	-13.22679523811779	-4.87198253176491	-7.58759857115236
O	-13.48633731298917	-4.35180367402919	-8.64697775201560
O	-13.92190539252028	-5.91384367611020	-7.09766810700520
H	-14.62356962167843	-6.12656830697683	-7.73912561341926
H	-4.83618146332544	-0.50771269149673	-2.54630140535838
H	-4.38290642600754	1.18591428943272	-5.10947257158204

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