Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Electronic Supplementary Information for:

The Unquenched Triplet Excited State of the Fluorescent OFF/ON Bodipy-derived Molecular Probe Based on Photo-induced Electron Transfer

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1. Experimental Section

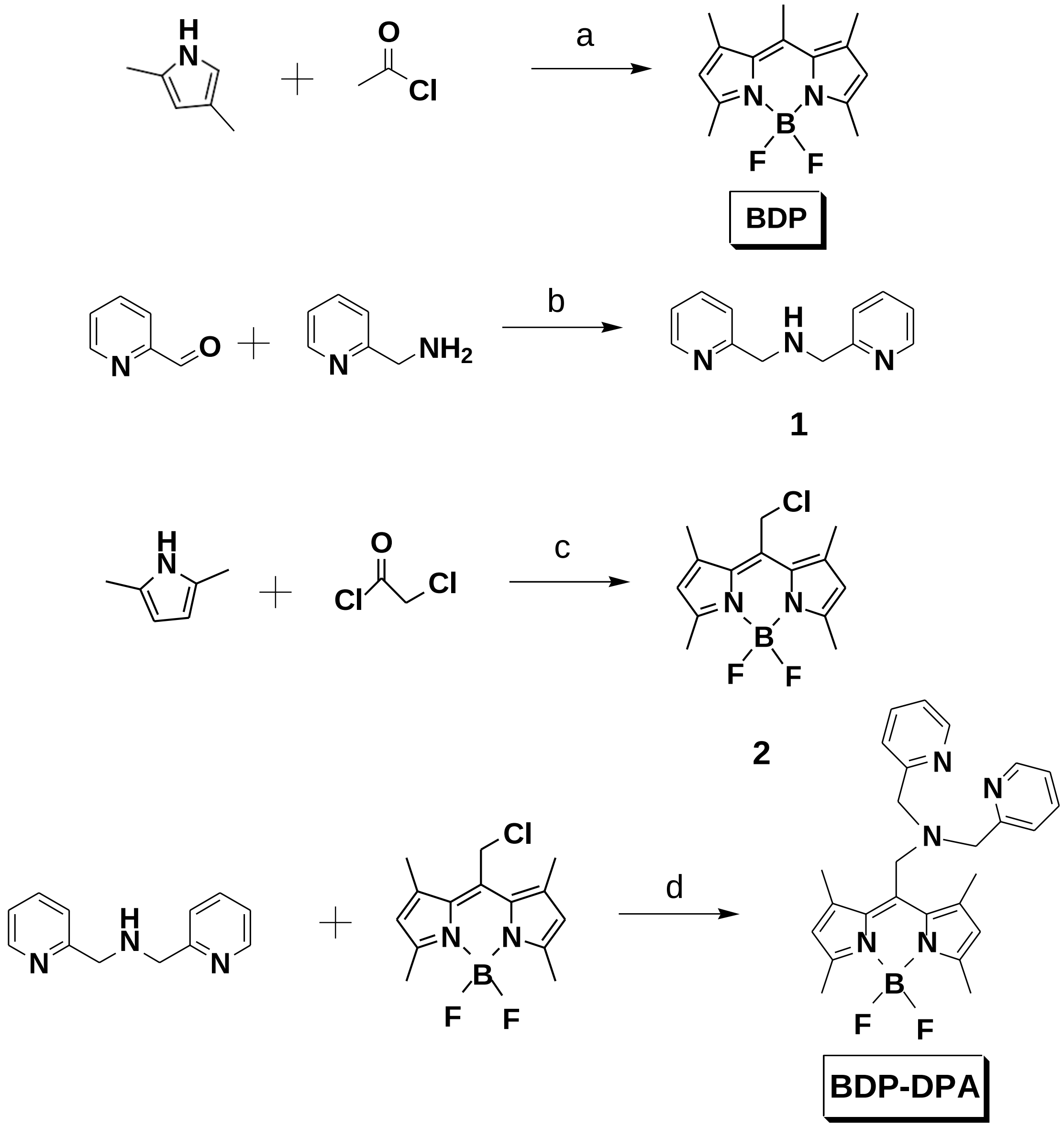
General information

All the chemicals used in synthesis are analytical pure and were used as received. Solvents were dried and distilled before used for synthesis. ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. ^{1}H NMR spectra were recorded on a 400 MHz and 500 MHz Varian Unity Inova spectrometer (TMS as the standard of the chemical shifts). The mass spectra were measured by TOF MS MALDI and ESI spectrometer. UV−vis absorption spectra were taken on a Agilent 8453 UV-visible spectrophotometer (Agilent, USA). The fluorescence was recorded with a RF 5301PC spectrofluorometer (Shimadzu, Japan).

Nanosecond transient absorption spectroscopy

Triplet absorption lifetimes were measured on LP920 laser flash photolysis spectrometer (Edinburgh Instruments, UK) and recorded on a Tektronix TDS 3012B oscilloscope and with a nanosecond pulsed laser (OpoletteTM 355II+UV nanosecond pulsed laser, typical pulse length: 7 ns. Pulse repetition: 20 Hz. Peak OPO energy: 4 mJ. The wavelength is tunable in the range of 410−2200 nm. OPOTEK, USA). The lifetime values (by monitoring the decay trace of the transients) were obtained with the LP900 software. All samples in flash photolysis experiments were deaerated with N2 for ca. 15 min before measurement and the gas flow is kept during the measurement.

Scheme S1. Synthesis of the compounds [a]



[a] Key: (a) **1.** CH_2Cl_2, rt, overnight; **2**. NEt_3, $BF_3.EtO_2$, 2 h (b) **1.** CH_3OH, rt, 10 h **2.** $NaBH_4$, rt, 2 h (c) **1.** CH_2Cl_2, rt, 2h; **2**. NEt_3, $BF_3.EtO_2$, 2 h (d) THF, reflux, 8 h

Synthesis of 8-(methyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacene (BDP). Under N_2 atmosphere, acetyl chloride (0.7 mL, 0.01 mol) and 2, 4-dimethylpyrrole (2.0 mL, 0.02 mol) were added to anhydrous CH_2Cl_2 (250 mL) via syringe, the mixture was stirred at room temperature overnight. Then Et_3N (20 mL) and $BF_3{\cdot}Et_2O$ (20 mL) were added under ice-cold condition, and reaction mixture was stirred for additional 1 h. After the reaction, the mixture was poured into water (200 mL), the organic layer was extracted with dichloromethane (DCM) and dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The crude product was further purified using column chromatography (silica gel, CH_2Cl_2: hexane = 1:1, v/v) to give compound 1 as red power (1.0 g, 46 %). ^1H NMR ($CDCl_3$, 500 MHz): δ 6.05 (s, 2H), 2.57 (s, 3H), 2.52 (s, 6H), 2.41 (s, 6H). TOF HRMS EI^+: Calcd ($[C_{14}H_{17}BF_2N_2]^+$), m/z = 262.1453; found, m/z = 262.1458.

Synthesis of *N,N*-Bis(2-Pyridylmethyl)amine (1). 2-pyridinecarboxaldehyde (2.67g, 25 mmol) was added dropwise to a stirred solution of 2-aminomethylpyridine in 50ml MeOH. A dark brown mixture developed immediately. The mixture was continuously stirred for 10 h. After stirring, sodium borohydride (1.89g, 50 mmol) was added in small fractions. The brown mixture turned to pale yellow solution during the addition and stirring was continued for 2 h. All the volatiles were removed under reduced pressure. 50 ml water was added in it and resulting solution was neutralized with 32% hydrochloric acid, followed by extraction with $CH2Cl_2$ (3 × 100 ml). The combined organic extract was dried over anhydrous $MgSO_4$ and rotary evaporated to give a yellow liquid which was used directly for the next reaction without further purification. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.53 (d, 2H, J = 5.0 Hz), 7.60 – 7.57 (m, 2H), 7.33 (d, 2H, J = 5.0 Hz), 7.11−7.09 (m, 2H), 3.97 (s, 4H), 2.89 (s, 1H). TOF HRMS ESI^+: Calcd ($[C_{12}H_{13}N_3+H]^+$), m/z = 200.1188; found, m/z = 200.1191.

Synthesis of 8-(Chloromethyl)-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza -s-indacene (2). Under N_2 atmosphere, chloroacetyl chloride (0.8 mL, 0.01 mol) and 2, 4-dimethylpyrrole (2.0 mL, 0.02 mol) were added to anhydrous CH_2Cl_2 (250 mL) via syringe, the mixture was stirred at room temperature for 2 h. Then Et_3N (20 mL) and $BF_3{\cdot}Et_2O$ (20 mL) were added under ice-cold condition, and reaction mixture was stirred for additional 1 h.

After the reaction, the solvent was removed under reduced pressure. The crude product was purified using column chromatography (silica gel, CH_2Cl_2: hexane = 1:1, v/v) to give compound 2 as red power (1.0 g, 34 %). Mp: 176−178 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.09 (s, 2H), 4.78 (s, 2H), 2.53 (s, 12H). TOF HRMS EI$^+$: Calcd ($[C_{14}H_{16}BF_2N_2Cl]^+$), *m/z* = 296.1063; found, *m/z* = 296.1072.

Synthesis of BDP−DPA. A suspension of 2 (100 mg, 0.34 mmol), di(2-picolyl)amine (67 mg, 0.34 mmol), potassium iodide (60 mg, 0.36 mmol) and potassium carbonate (55 mg, 0.34 mmol) in 50 ml THF was refluxed for 8 hours under an Ar atmosphere. The mixture was cooled to room temperature. THF was removed by evaporation, and the residue was diluted with 20 ml 2 N sodium carbonate and extracted with dichloromethane. The organic phase was washed with brine, dried over K_2CO_3, filtered, and evaporated to dryness. The crude compound was purified by flash column chromatography on neutral aluminium oxide (100 : 1 CH_2Cl_2–MeOH) to afford a brown solid (82 mg, 52%). Mp: 62−63 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, 2H, *J* = 4.0 Hz), 7.68−7.61 (m, 4H), 7.15 (t, 2H, *J* = 6.0 Hz), 6.60 (s, 1H), 6.07 (s, 1H), 4.11 (s, 2H), 3.99 (s, 4H), 2.58 (s, 3H), 2.50 (s, 3H), 2.42 (d, 6H, *J* = 8.0 Hz). TOF HRMS EI$^+$: Calcd ($[C_{26}H_{28}BF_2N_5+Na]^+$), *m/z* = 482.2304; found, *m/z* = 482.2315.

2. NMR and HRMS Spectra.

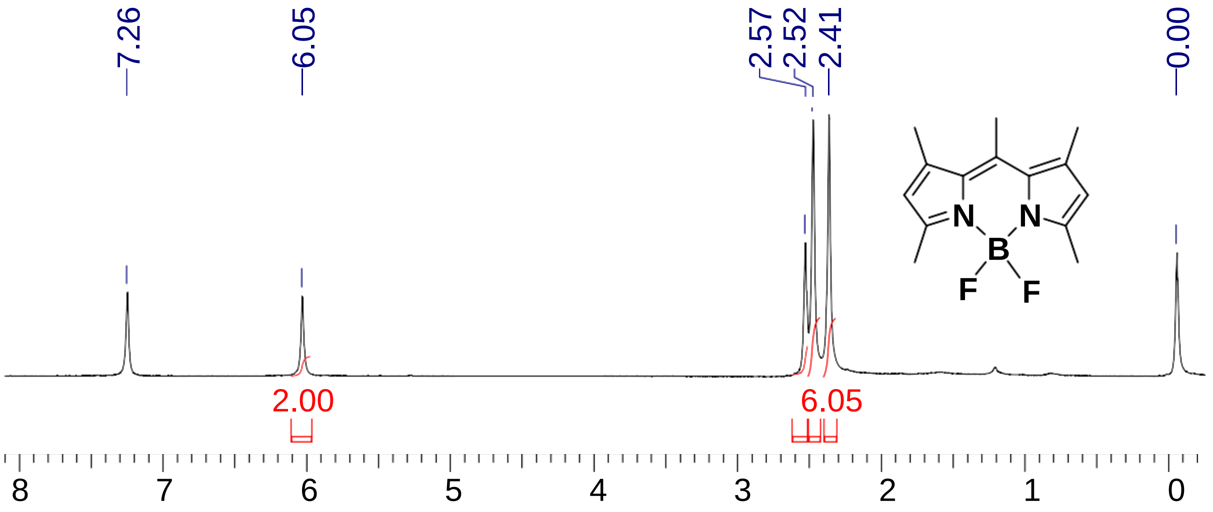


Fig. S1. ^{1}H NMR spectra of compound **BDP** (500 MHz, CDCl$_3$).

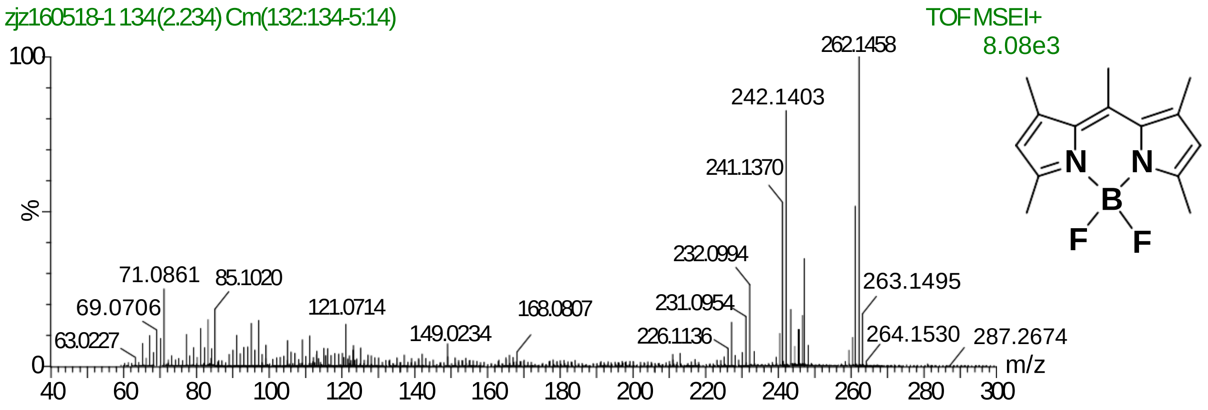


Fig. S2. TOF MS EI$^+$ of compound **BDP.**

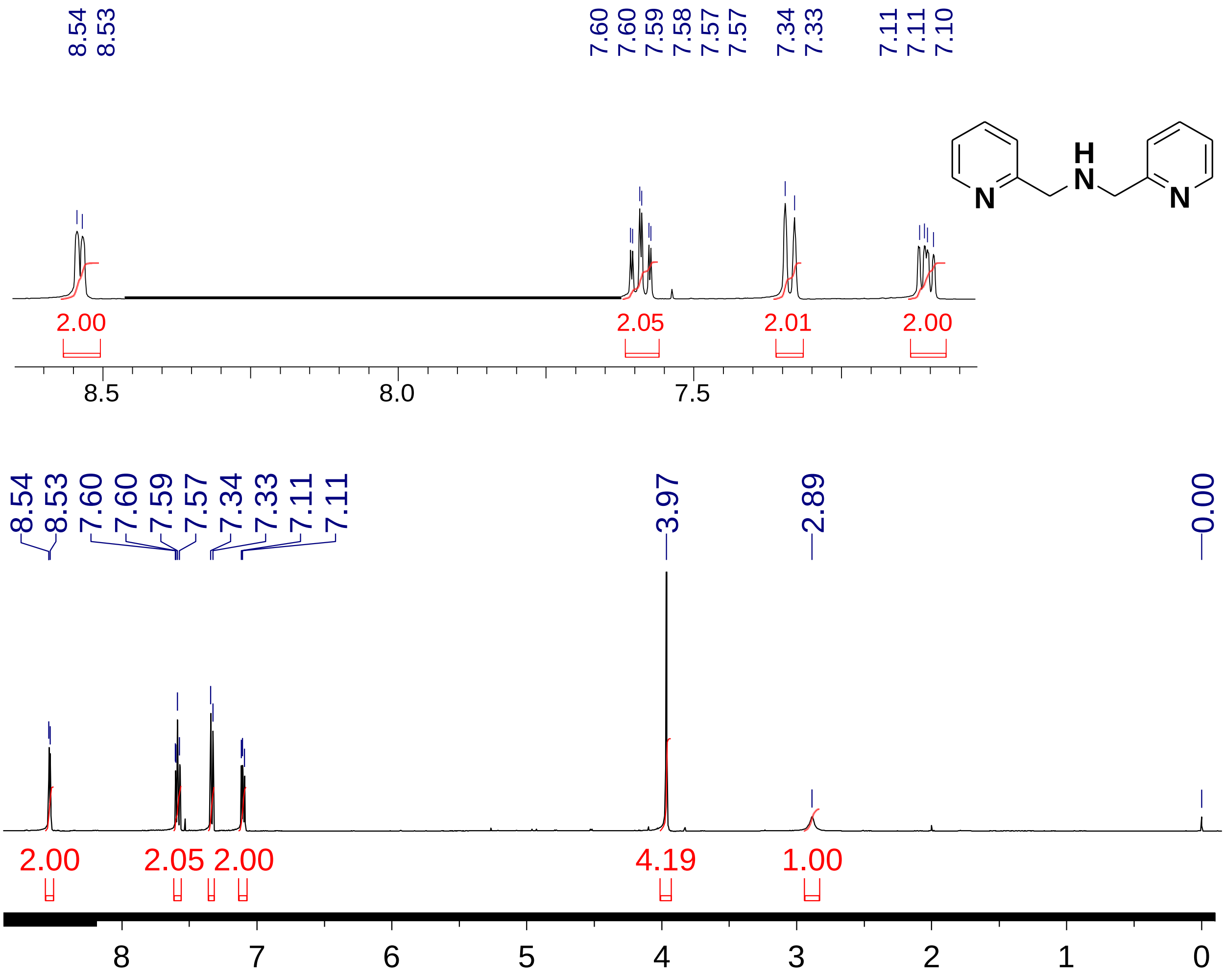


Fig. S3. ^{1}H NMR spectra of compound **1** (500 MHz, $CDCl_3$).

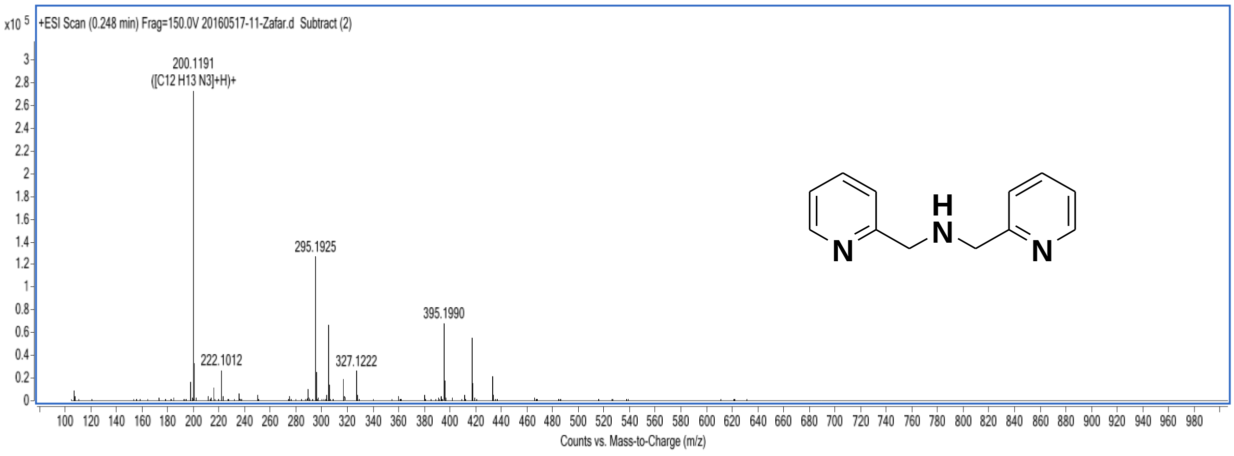


Fig. S4. TOF HRMS ESI of compound **1.**

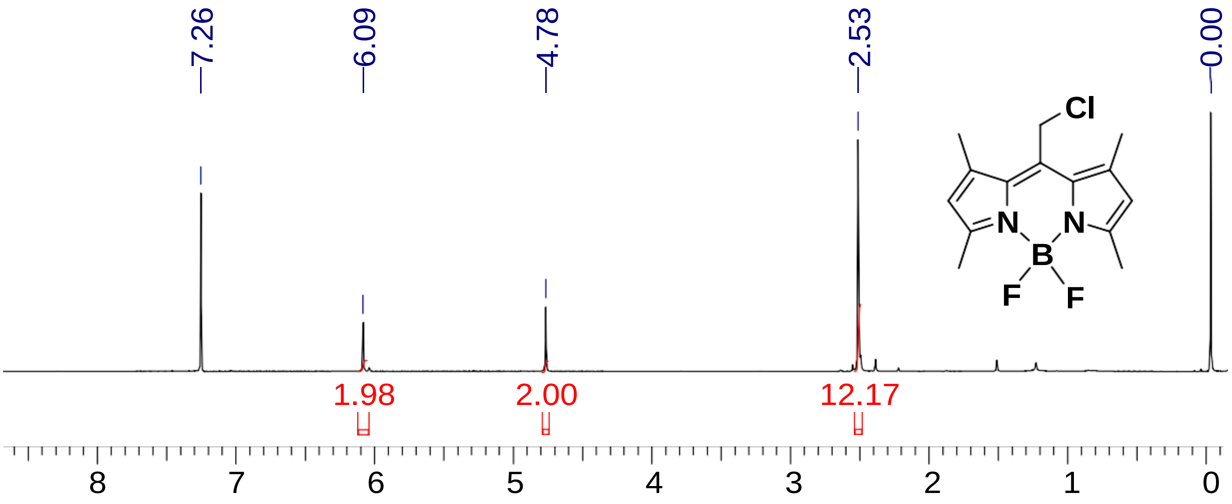


Fig. S5. ^{1}H NMR spectra of compound **2** (500 MHz, $CDCl_3$)

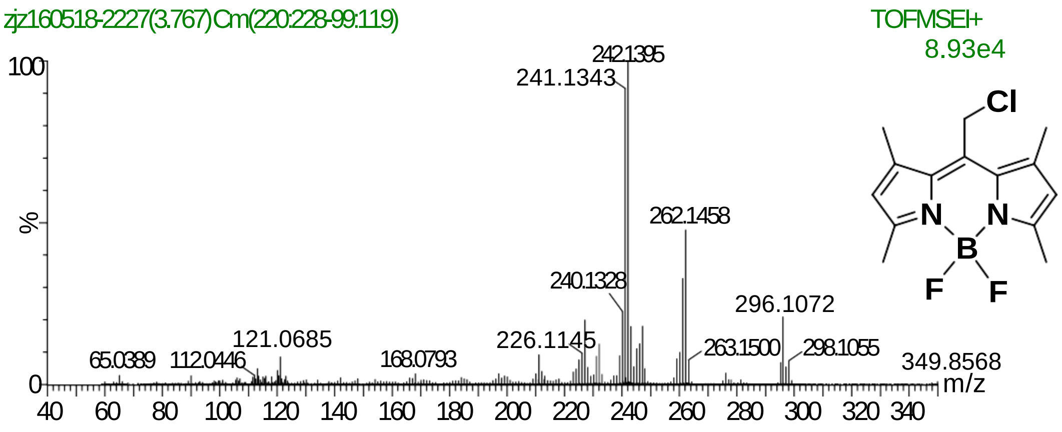


Fig. S6. TOF HRMS EI$^+$ of compound **2.**

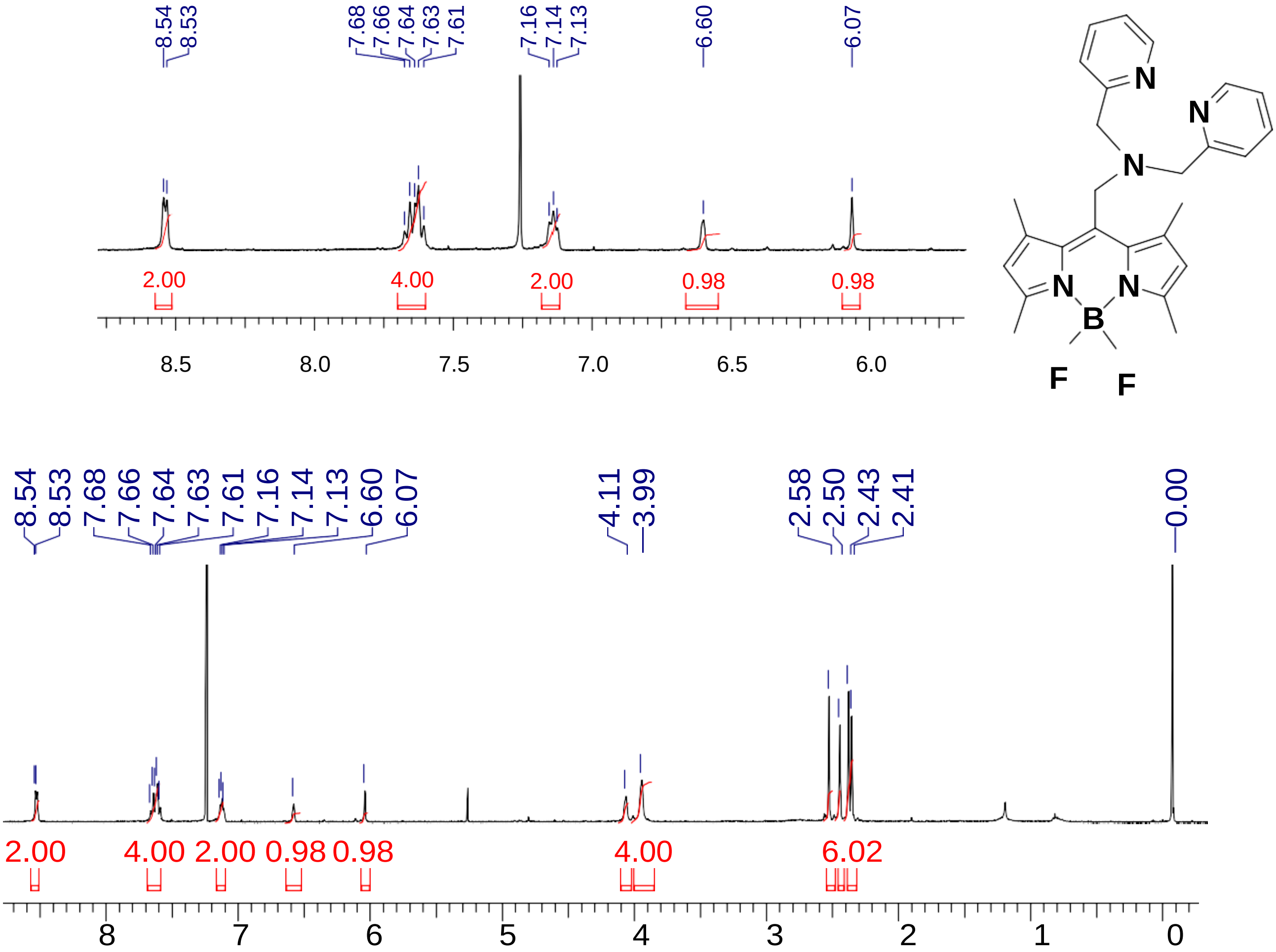


Fig. S7. ^{1}H NMR spectra of compound **BDP-DPA** (400 MHz, $CDCl_3$).

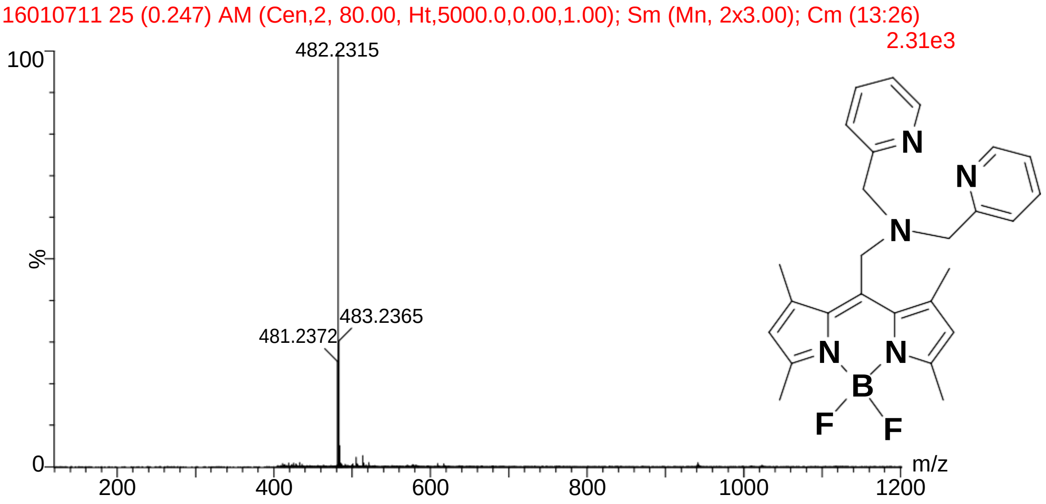


Fig. S8. TOF MS ESI of compound **BDP-DPA**

3. Changes in UV-visible absorption spectra with Zn^{2+}.

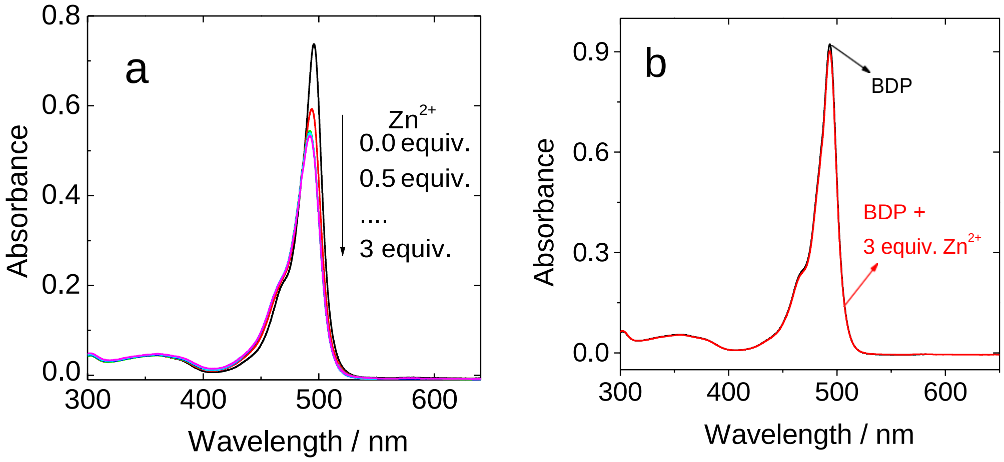


Fig. S9. UV-visible absorption spectra of (a) **BDP-DPA** and **BDP-DPA** with addition of $Zn(ClO_4)_2$ salt, (b) BDP in the absence and with addition of $Zn(ClO_4)_2$ salt, $c = 1.0 \times 10^{-5}$ M, in Methanol, 20 °C.

4. Changes in Fluorescence emission spectra with Zn^{2+}.

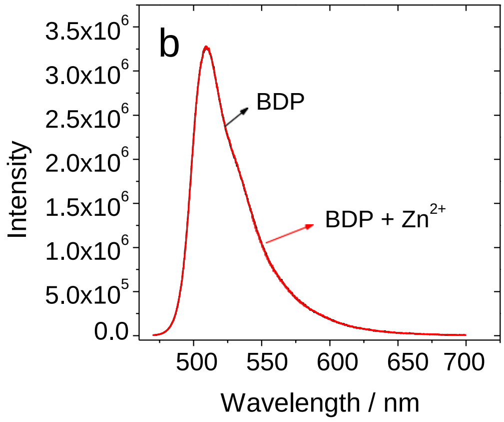


Fig. S10. Changes in Emission of **BDP** with different concentration of $Zn(ClO_4)_2$ salt, *c* = 1.0×10^{-5} M in methanol, 20 °C.

5. Calculation of charge transfer quantum yield (Φ_{CT}).

The Charge transfer Quantum yield (Φ_{CT}) was calculated by using equation 2. It is based on Fluorescence life time data.

$$\phi_{CS} = \left[\left(1/\tau_f \right)_{dyad} - \left(1/\tau_f \right)_{ref} \right] / \left(1/\tau_f \right)_{dyad} \tag{Eq. 2}$$

Where

ϕ_{CS} = Charge transfer Quantum yield

$(\tau_f)_{dyad}$ = short life time in biexponential decay curve of fluorescence life time

$(\tau_f)_{ref}$ = long life time in biexponential decay curve of fluorescence life time

For BDP-DPA in methanol, $(\tau_f)_{dyad}$ = 1.0 ns

$(\tau_f)_{ref}$ = 5.8 ns

ϕ_{CS} = [(1 / 1.0) – (1 / 5.8)] / (1 / 5.8)

=0.83
=83 %

6. TTET between PtOEP and triplet acceptor BDP-DPA.

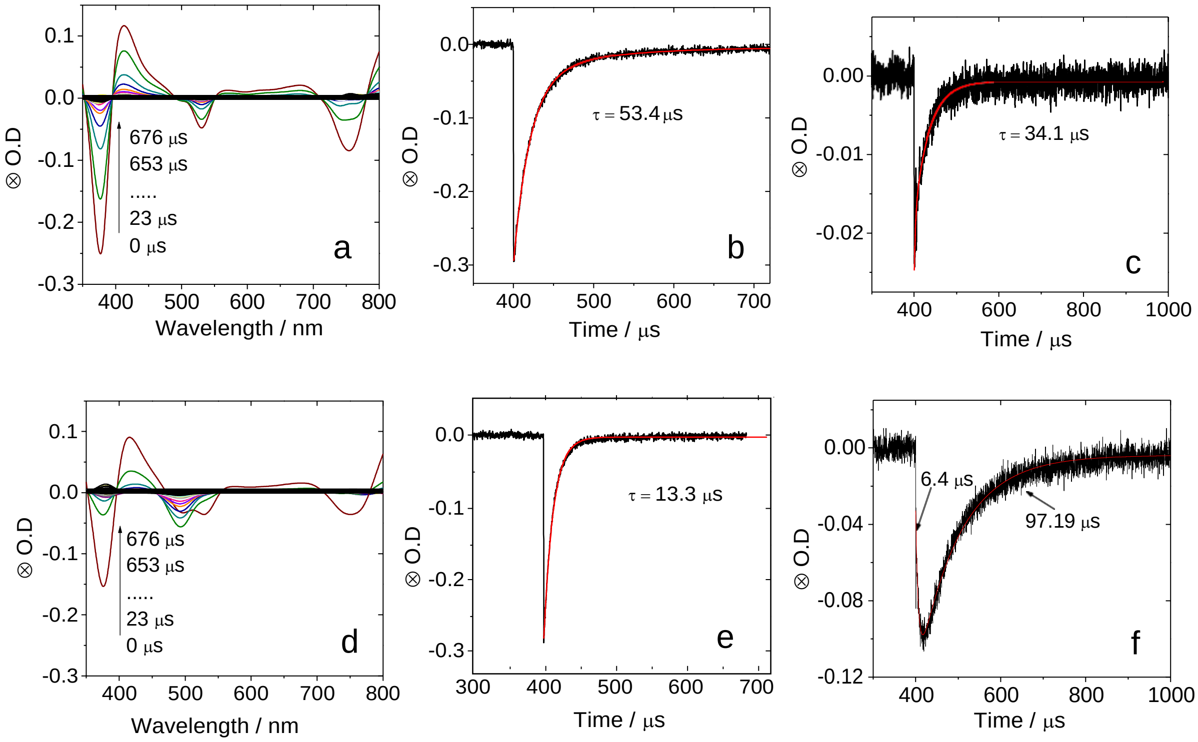


Figure S11. Nanosecond transient absorption spectra of (a) **PtOEP** (d) **PtOEP + BDP-DPA** (1:1), (b) and (e) are their respective decay curves at 535 nm while (e) and (f) are their respective decay curves at 500 nm. Excited with 532 nm pulsed laser. c = 1.0 × 10^{-5} M, in deaerated MeOH, 20 °C. In order to demonstrate that the triplet state of PtOEP was quenched by the **BDP-DPA** and new triplet state formed, the decay traces at 535 and 500 nm was monitored and the time windows for monitoring of the decay are the same. The Δ O. D. axial in the figures are also the same.

7. TTET between PtOEP and triplet acceptor BDP-DPA + Zn^{2+}.

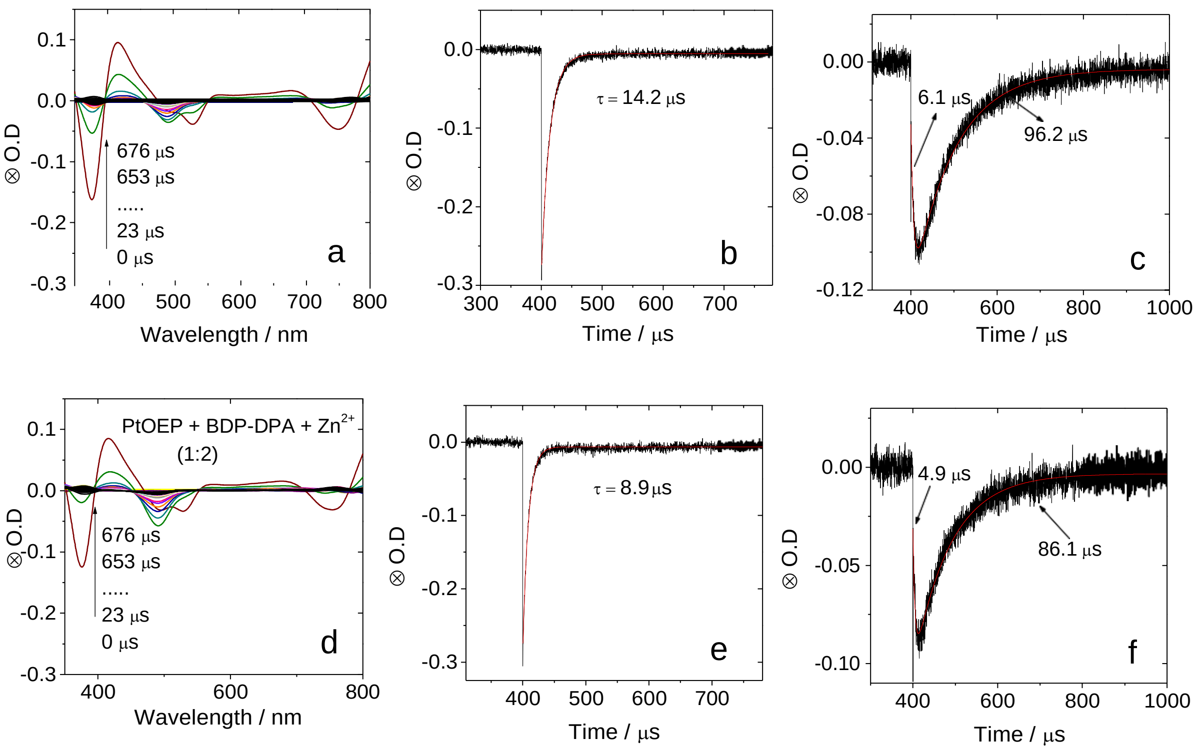


Fig. S12. Nanosecond transient absorption spectra of (a) **PtOEP + BDP-DPA (1:1) + 3 equiv Zn^{2+} salt**, (d) **PtOEP + BDP-DPA (1:2) + 3 equiv Zn^{2+} salt**. (b) and (e), are their respective decay curves at 535 nm while (c) and (f) are their respective decay curves at 500 nm. Excited with 532 nm pulsed laser. c = 1.0 × 10^{-5} M, in deaerated MeOH, 20 °C. In order to demonstrate that the triplet state of PtOEP was quenched by the Zn-complex of **BDP-DPA** and new triplet state formed, the decay traces at 535 and 500 nm was monitored and the time windows for monitoring of the decay are the same. The Δ O. D. axial in the figures are also the same

8. Changes in phosphorescence of PtOEP with addition of triplet acceptor.

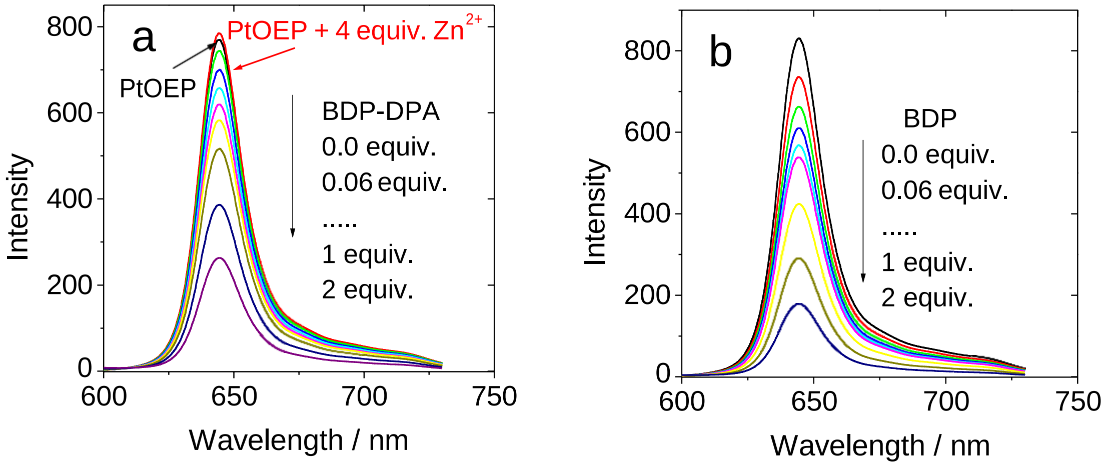


Fig. S13. Changes in the phosphorescence of **PtOEP** by addition of triplet acceptor (a) **BDP-DPA + Zn^{2+}** and (b) reference **BDP**

9. Emission titration of BDP-DPA with Zn^{2+}.

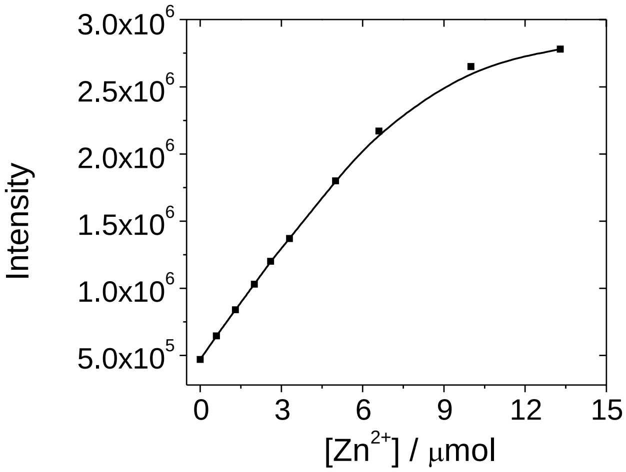
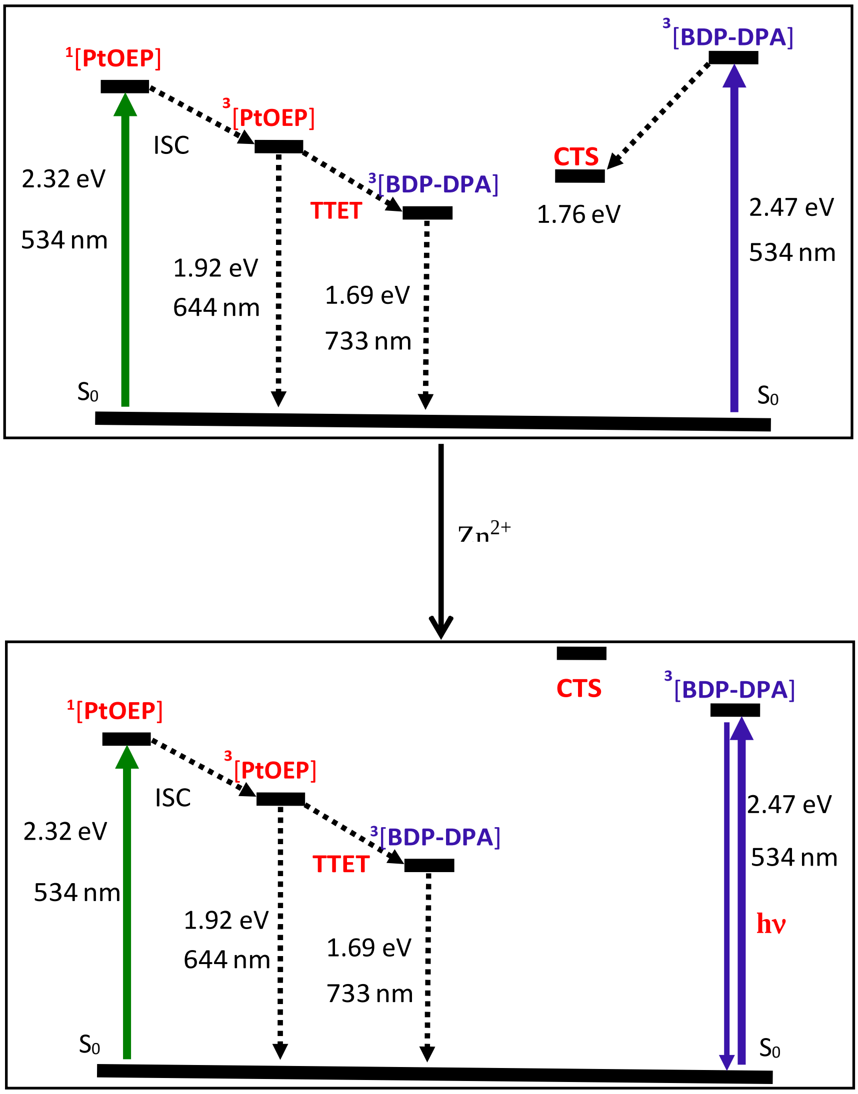


Fig. S14. Increasing the emission intensity of **BDP-DPA** with increasing concentration of Zn^{2+} ($\lambda_{ex} = 460$ nm). $c = 1.0 \times 10^{-5}$ M in MeOH. 20 °C.

10. Photophysical mechanism involve in BDP-DPA

The mechanism involved in the generation of triplet state of **BDP-DPA** by using **PtOEP** as triplet photosensitizer is given below:

Scheme S2. Simplified Jablonski Diagram Illustrating the Photophysical Processes in BDP-DPA



In this study, **PtOEP** was used as triplet photosensitizer and its triplet state was populated by excitation with 532 nm laser. The triplet state of **BDP-DPA** was generated by TTET process (with triplet photosensitizer as the energy donor and the **BDP-DPA** as the energy acceptor). It is evident from the Jablonski diagram that the **BDP-DPA** CTS is lower than its S_1 state. So its singlet state is quenched by PET, thus the fluorescence of the BDP moiety was quenched by PET. While after adding $Zn(ClO_4)_2$, its CTS is promoted to be above the S_1 state, and the PET stops. Thus the fluorescence of the Bodipy moiety recovered (or intensified). But in both cases the **BDP-DPA** triplet state generated through TTET process. It means the PET has no effect on the generation of triplet state. It can only quench its singlet state.