

Electronic Supplementary Information for:

Hetero Bodipy-dimers as heavy atom-free triplet photosensitizer showing long-lived triplet excited state for triplet-triplet annihilation upconversion

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1. 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. All samples in flash photolysis and upconversion experiments were deaerated with Ar for ca. 15 min before measurement and the gas flow is kept during the measurement.

TTA Upconversion: Diode pumped solid state (DPSS) laser (532 nm) were used for the upconversions and the diameter of the laser spot is ca. 3 mm. In order to repress the scattered laser, a black box was put behind the fluorescent cuvette as beam dump to trap the laser after it passing through the cuvette. The upconversion quantum yields (Φ_{UC}) were determined with the prompt fluorescence of **I-BDP** (the molecular structure is shown in Chart 1 in the main text) ($\Phi_F = 2.7\%$ in MeCN) as the standards. The upconversion quantum yields were calculated with eq. 1, where Φ_{UC} stands the upconversion quantum yields, A , I and η represents the absorbance, integrated photoluminescence intensity and the refractive index of the solvent, sam represents the sample, and std represents standard (Eq. 1). The equation is multiplied by factor 2 in order to make the maximum quantum yield to be unity.¹

$$\Phi_{UC} = 2\Phi_{std} \left(\frac{1 - 10^{-A_{std}}}{1 - 10^{-A_{sam}}} \right) \left(\frac{I_{sam}}{I_{std}} \right) \left(\frac{\eta_{sam}}{\eta_{std}} \right)^2 \quad (1)$$

The TTET efficiency was evaluated by the Stern-Volmer quenching constants, the concentration of the sensitizer was fixed at 1.0×10^{-5} M, the lifetime of the sensitizer was measured by LP920 with increasing perylene concentration in the solution.

DFT Calculations: The density functional theory (DFT) calculations were used for optimization of the ground state geometries at B3LYP/6-31G level, The energy level of the T_1 state (energy gap between S_0 state and T_1 state) were calculated based on the optimized ground state geometries, The spin density surface of the organic sensitizer were optimized at the triplet state geometry. All the calculations were performed with Gaussian 09.²

Singlet oxygen (1O_2) quantum yields (Φ_Δ): Φ_Δ values of the triplet photosensitizers were calculated according to a modified literature method.³ The light source of a spectrofluorometer was used for irradiation light source to get the constant monochromatic light. The irradiation wavelength for the samples and the reference was the same. Quantum yields for singlet oxygen generation in CH_2Cl_2 were determined by monitoring the photooxidation of 1,3-diphenylisobenzofuran (DPBF) sensitized by the Ir complexes. The absorbance of DPBF was adjusted around 1.0 at 414 nm in air saturated CH_2Cl_2 , and absorbance of the photosensitizers were adjusted to 0.2–0.3 at the irradiation wavelength. The photooxidation of DPBF was monitored at the interval of 10 s. The quantum yields of singlet oxygen generation (Φ_Δ) were calculated with Eq. 2, using Rose Bengal ($\Phi_\Delta = 0.80$ in MeOH) as the reference,

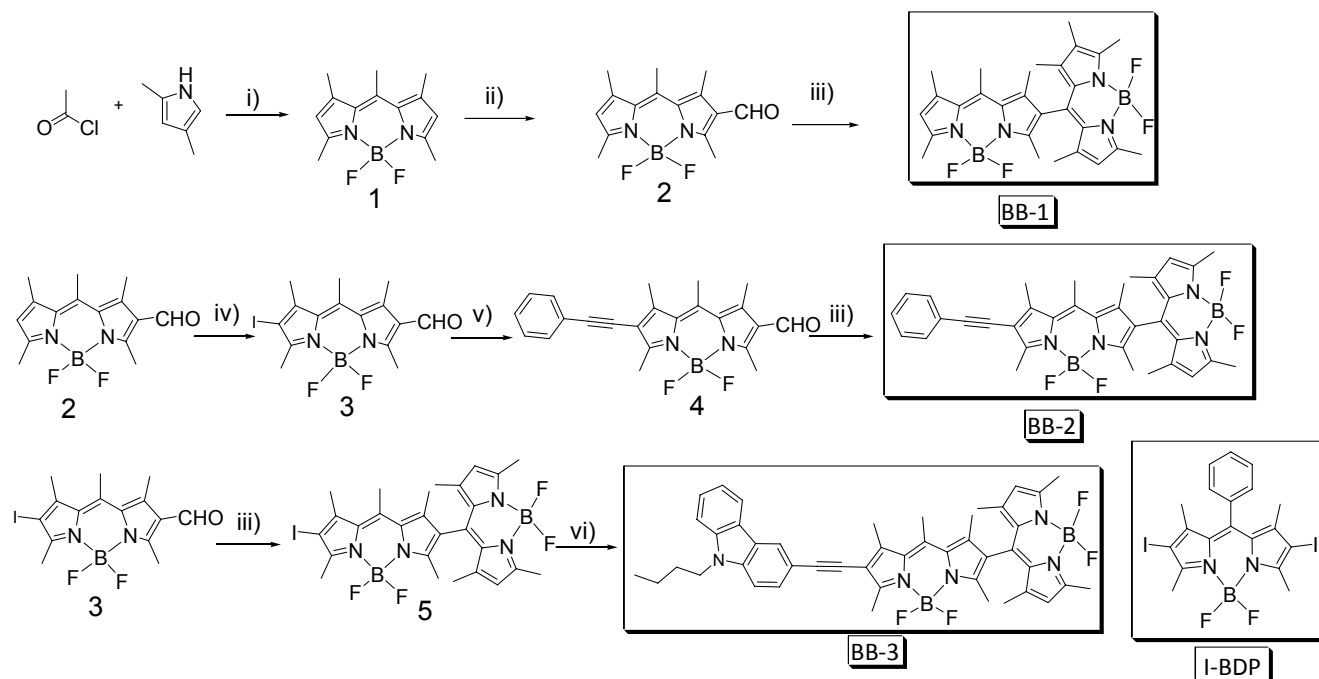
$$\Phi_{\Delta}^{sam} = \Phi_{\Delta}^{std} \frac{m^{sam} F^{std}}{m^{std} F^{sam}} \quad (2)$$

where superscripts 'sam' and 'std' designate Ru complexes and the standards, respectively, Φ_Δ is the quantum yield of singlet oxygen, m is the slope of a plot of difference in change in absorbance of DPBF (at 420 nm) with the irradiation time and F is the absorption correction factor, which is given by $F = 1 - 10^{-A}$ (A is the absorbance at the irradiation wavelength).

Reference:

- [1] T. N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.*, 2010, **254**, 2560–2573.
- [2] M. J. Frisch, et al. *Gaussian 09*, Revision 01; Gaussian Inc., Wallingford, CT, **2009**.
- [3] N. Adarsh, R. R. Avirah, D. Ramaiah, *Org. Lett.* 2010, **12**, 5720–5723.

2. Synthesis and Molecular Structure Characterization Data



Scheme S1. Synthesis of the Bodipy dimers as triplet photosensitizers **BB-1**, **BB-2** and **BB-3**. The molecular structure of the reference compound **I-BDP** was also shown. Reagents and conditions: i) dry CH_2Cl_2 , $\text{BF}_3\cdot\text{OEt}_2$, NEt_3 ; ii) DMF, POCl_3 ; iii) 2,4-Dimethyl-1H-pyrrole, DDQ, dry CH_2Cl_2 , $\text{BF}_3\cdot\text{OEt}_2$, NEt_3 iv) NIS, r.t.; v) phenylacetylene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, PPh_3 , CuI , NEt_3 , reflux, 8 h, vi) 9-butyl-3-ethynylcarbazole, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, PPh_3 , CuI , NEt_3 , reflux, 8 h.

Synthesis of compound 1: Under N_2 atmosphere, acetyl chloride (0.7 mL, 0.78 g, 0.01 mol) and 2, 4-dimethylpyrrole (2.0 mL, 1.8 g, 0.02 mol) were added to anhydrous CH_2Cl_2 (300 mL) via syringe, the mixture was stirred at room temperature over night. Then Et_3N (20 mL) and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (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. Yield: 1.2 g (45.8 %). ^1H NMR (400 MHz, CDCl_3): 6.05 (s, 2H), 2.56 (s, 3H), 2.51 (s, 6H), 2.40 (s, 6H).

Synthesis of compound 2: Under Ar atmosphere, DMF (0.5 mL, 0.48 g, 6.6 mmol) was added dropwise to a round bottom flask (50 mL) containing POCl_3 (0.5 mL, 0.82 g, 5.4 mmol), while the temperature of the mixture was kept at 0–5 °C. With the addition of DMF, white solid appeared. The solution of compound **1** (360 mg, 1.37 mmol) dissolved in 1,2-dichloroethane (60 mL) was added to the above solution, the mixture were heated at 50 °C and was stirred for 3 h. After the reaction, the mixture was poured into cold water, and the pH was brought to 7–8 using NaHCO_3 aqueous solution. The mixture was extracted with DCM, after evaporation of the solvent, the crude product was purified using column chromatography (silica gel, DCM was the eluent), red solid was obtained. Yield: 300.0 mg (75.5%). ^1H NMR (400 MHz, CDCl_3): 10.10 (s, 1H), 6.24 (s, 1H), 2.78 (s, 3H), 2.73 (s, 3H), 2.68 (s, 1H), 2.58 (s, 3H), 2.47 (s, 3H). EI-HRMS: calcd $[(\text{C}_{15}\text{H}_{17}\text{BF}_2\text{N}_2\text{O})^+]$, m/z = 290.1402, found, m/z = 290.1407.

Synthesis of compound 3: To a solution of **2** (310 mg, 1.07 mmol) in anhydrous CH_2Cl_2 (15 mL) was added excessive *N*-iodosuccinimide (NIS, 481.5 mg, 2.14 mmol). The mixture was stirred at 40 °C for 4 h (monitored by TLC until complete consumption of the starting material). The reaction mixture was then concentrated under vacuum, and the crude product was purified by column chromatography (silica gel, CH_2Cl_2). The red band was collected and the

solvent was removed under reduced pressure to give the product as red solid. Yield: 410.0 mg (92.1 %). ^1H NMR (400 MHz, CDCl_3): 10.11 (s, 1H), 2.78 (s, 3H), 2.74 (s, 3H), 2.71 (s, 3H), 2.67 (s, 3H), 2.52 (s, 3H). EI-HRMS: calcd $[\text{C}_{15}\text{H}_{16}\text{BF}_2\text{N}_2\text{OI}]^+$, $m/z = 416.0369$, found, $m/z = 416.0368$.

Synthesis of compound 4: Under Ar atmosphere, compound **3** (150.0 mg, 0.36 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (12.6 mg, 0.018 mmol), PPh_3 (9.4 mg, 0.036 mmol), CuI (7.2 mg, 0.036 mmol) were dissolved in triethylamine (15 mL), the flask was vacuumed and back-filled with Ar for several times, and then phenylacetylene (74.0 mg, 0.72 mmol) was added via syringe. The solution was stirred at 60 °C for 8 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, with CH_2Cl_2 as the eluent), dark red solid was obtained. Yield: 105.5 mg (75.1 %). ^1H NMR (400 MHz, CDCl_3): 10.12 (s, 1H), 7.54–7.52 (m, 2H), 7.38–7.36 (m, 3H), 2.80 (s, 3H), 2.76 (s, 3H), 2.74 (s, 3H), 2.72 (s, 3H), 2.61 (s, 3H).

Synthesis of compound 5: Under Ar atmosphere, compound **3** (430 mg, 1.03 mmol) and 2,4-dimethylpyrrole (196.4 mg, 2.06 mmol) were dissolved in dry CH_2Cl_2 (200 mL). A few drops of trifluoroacetic acid (TFA) was added to the solution and reaction mixture was stirred overnight at RT. After disappearance of the compound **3** (monitored via TLC), a solution of DDQ (230 mg, 1.03 mmol) in newly distilled THF was added and the stirring was continued for 2 h. Absolute triethylamine (3 mL) was then added to the mixture. After stirring for 15 min, $\text{BF}_3\cdot\text{OEt}_2$ (3 mL) was added dropwise with ice bath cooling. After stirring for another 2 h, the reaction mixture was washed with water several times 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 (silica gel, DCM) to obtain red solid. Yield: 225.2 mg (34.4 %). ^1H NMR (400 MHz, CDCl_3): δ 6.02 (s, 2H), 2.70 (s, 3H), 2.65 (s, 3H), 2.56 (s, 6H), 2.50 (s, 3H), 2.39 (s, 3H), 2.30 (s, 3H), 1.68 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 156.2, 151.2, 143.6, 142.6, 142.3, 138.2, 133.2, 133.0, 132.0, 126.7, 121.6, 86.3, 20.0, 17.7, 16.2, 15.4, 14.9, 14.2, 13.0. EI-HRMS: calcd $[\text{C}_{27}\text{H}_{29}\text{B}_2\text{F}_4\text{N}_4\text{I}]^+$, $m/z = 634.1559$, found, $m/z = 634.1567$.

Synthesis of compound BB-1: BB-1 was prepared by a similar procedure to compound **5**, compound **2** (40.0 mg, 0.14 mmol) was used as starting material, instead of compound **3**. BB-1 was obtained as red solid. Yield: 25.5 mg (34.9 %). ^1H NMR (400 MHz, CDCl_3): δ = 6.16 (s, 1H), 6.01 (s, 2H), 2.67 (s, 3H), 2.56 (s, 9H), 2.46 (s, 3H), 2.38 (s, 3H), 2.27 (s, 3H), 1.69 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ = 157.0, 155.9, 148.9, 143.6, 142.8, 142.3, 136.1, 134.0, 133.3, 132.2, 131.8, 125.5, 122.8, 121.4, 17.8, 16.9, 15.1, 14.8, 14.1, 12.8. MALDI-HRMS: calcd $[\text{C}_{27}\text{H}_{30}\text{B}_2\text{F}_4\text{N}_4]^+$, $m/z = 508.2593$, found, $m/z = 508.2579$.

Synthesis of compound BB-2: BB-2 was prepared by a similar procedure to compound **5**, compound **4** (84.0 mg, 0.22 mmol) was used as starting material, instead of compound **3**. BB-2 was obtained as red solid. Yield: 32.0 mg (23.9 %). ^1H NMR (400 MHz, CDCl_3): 7.54–7.52 (m, 2H), 7.37–7.35 (m, 3H), 6.03 (s, 2H), 2.72 (s, 3H), 2.71 (s, 3H), 2.61 (s, 3H), 2.57 (s, 6H), 2.41 (s, 3H), 2.31 (s, 3H), 1.70 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ = 158.0, 156.2, 151.0, 142.9, 142.7, 137.7, 133.4, 132.6, 132.3, 132.1, 131.5, 128.6, 128.5, 126.4, 123.5, 121.6, 116.8, 96.8, 81.7, 17.3, 16.5, 15.3, 14.9, 14.2, 13.9, 13.0. MALDI-HRMS: calcd $[\text{C}_{35}\text{H}_{34}\text{B}_2\text{F}_4\text{N}_4]^+$, $m/z = 608.2906$, found, $m/z = 608.2886$.

Synthesis of compound BB-3: Under Ar atmosphere, compound **5** (60.0 mg, 0.096 mmol) and 9-butyl-3-ethynylcarbazole (49.5 mg, 0.2 mmol) were dissolved in mixed solvent THF/Triethylamine (10 mL/ 5 mL), the flask was vacuumed and back-filled with Ar for several times, then $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (7.0 mg, 0.01 mmol), PPh_3 (5.2 mg, 0.02 mmol), CuI (4.0 mg, 0.02 mmol) was added. The mixture was stirred at 60 °C for 8 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, ethyl acetate : hexane = 1 : 4, v/v). Purple solid was obtained. Yield: 38.9 mg (53.8 %). ^1H NMR (400 MHz, CDCl_3): δ = 8.28 (s, 1H), 8.12 (d, 1H, $J = 7.5$ Hz), 7.64 (d, 1H, $J = 8.4$ Hz), 7.50 (t, 1H, $J = 7.5$ Hz), 7.44–7.37 (m, 2H), 7.28–7.25 (m, 2H), 6.03 (s, 2H), 4.32 (t, 2H, $J = 7.1$ Hz), 2.76 (s, 3H), 2.72 (s, 3H), 2.64 (s, 3H), 2.57 (s, 6H), 2.41 (s, 3H), 2.31 (s, 3H), 1.91–1.81 (m, 2H), 1.71 (s, 6H), 1.43–1.38 (m, 2H), 0.96 (t, 3H, $J = 7.5$ Hz). ^{13}C NMR (101 MHz, CDCl_3): δ = 158.4, 156.0, 150.2, 142.7, 142.5, 140.9, 140.2, 137.0, 133.5, 132.4, 132.1, 129.2, 126.3, 126.1, 123.9, 123.0, 122.5, 121.5, 120.7, 119.5, 117.6, 117.6, 113.2, 113.2, 109.1, 108.9, 98.3, 79.5, 43.1, 29.8, 20.7, 17.2, 16.5, 15.2, 14.8, 14.2, 14.0, 13.9, 12.9. MALDI-HRMS: calcd $[\text{C}_{45}\text{H}_{45}\text{B}_2\text{F}_4\text{N}_5]^+$, $m/z = 357.3797$, found, $m/z = 357.3843$.

3. NMR and HRMS spectra

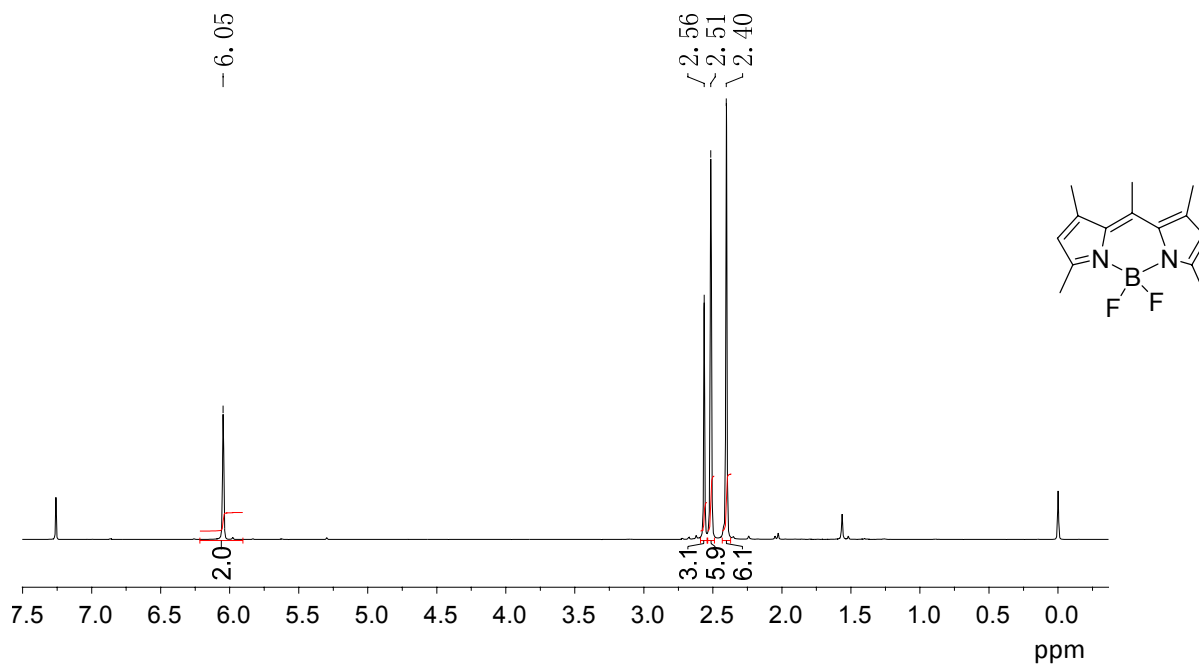


Fig. S1 ¹H NMR of **1** (400 MHz, CDCl₃).

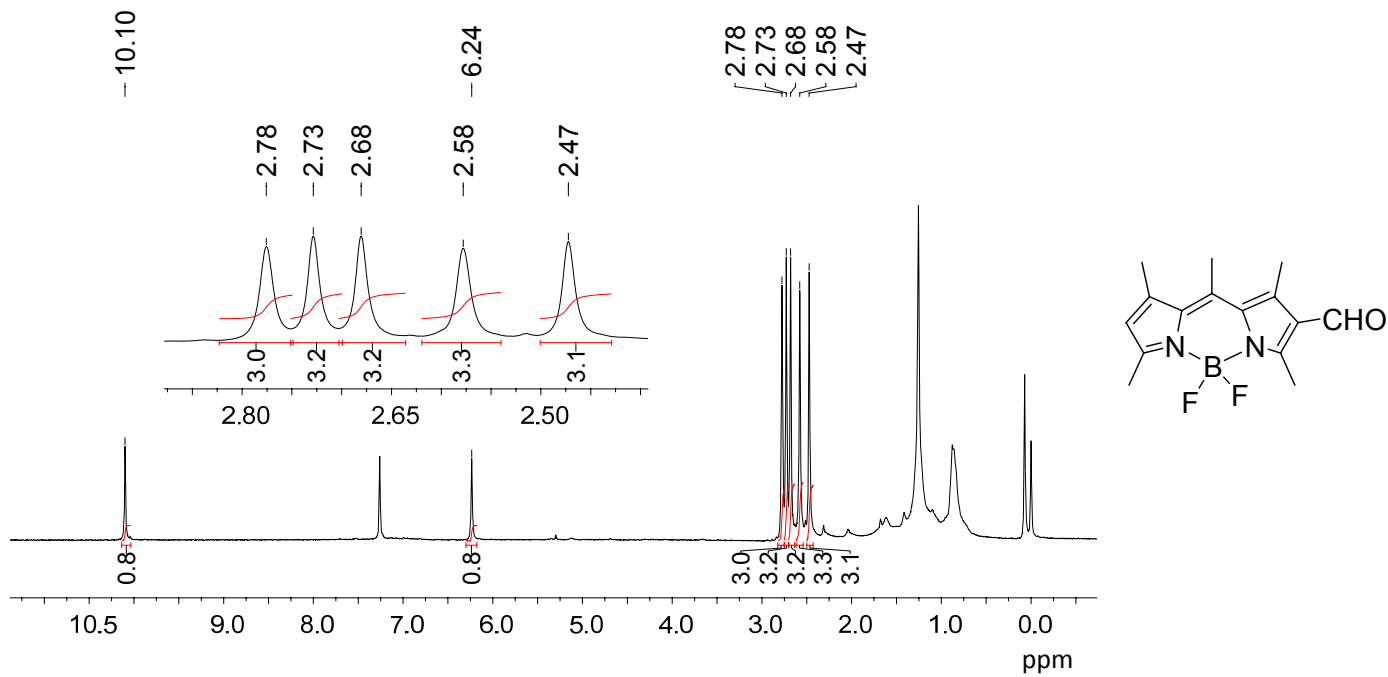


Fig. S2 ¹H NMR of **2** (400 MHz, CDCl₃).

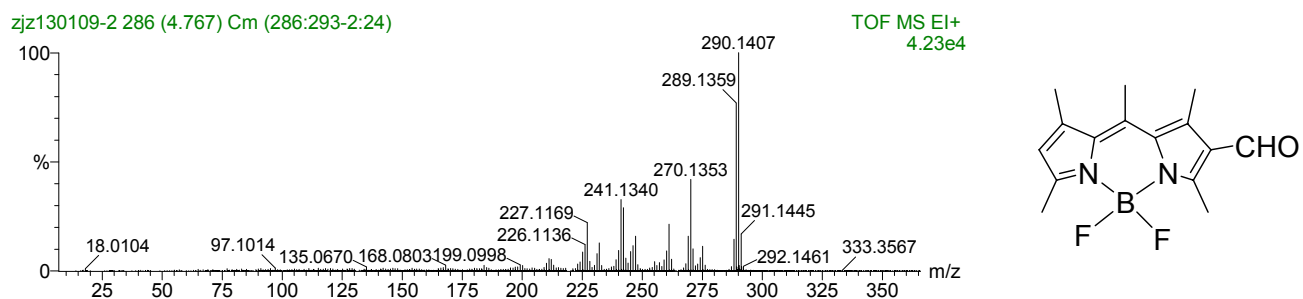


Fig. S3 EI-HRMS of compound **2**.

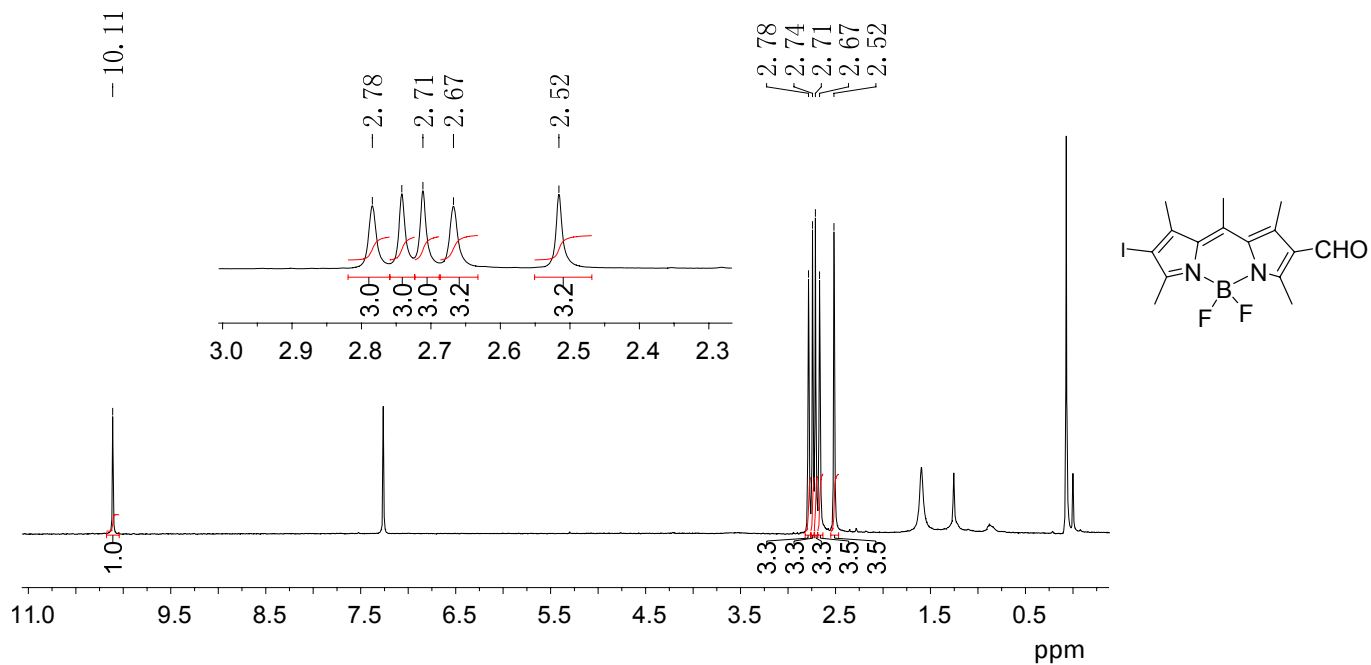


Fig. S4 ^1H NMR of **3** (400 MHz, CDCl_3).

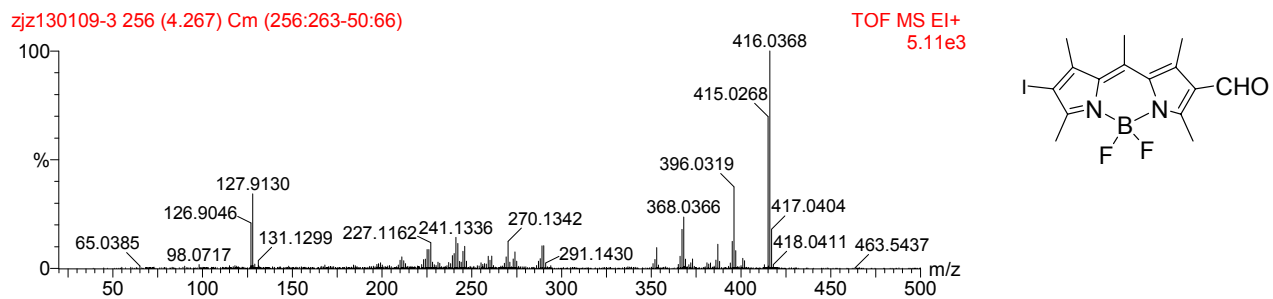


Fig. S5 EI-HRMS of compound 3.

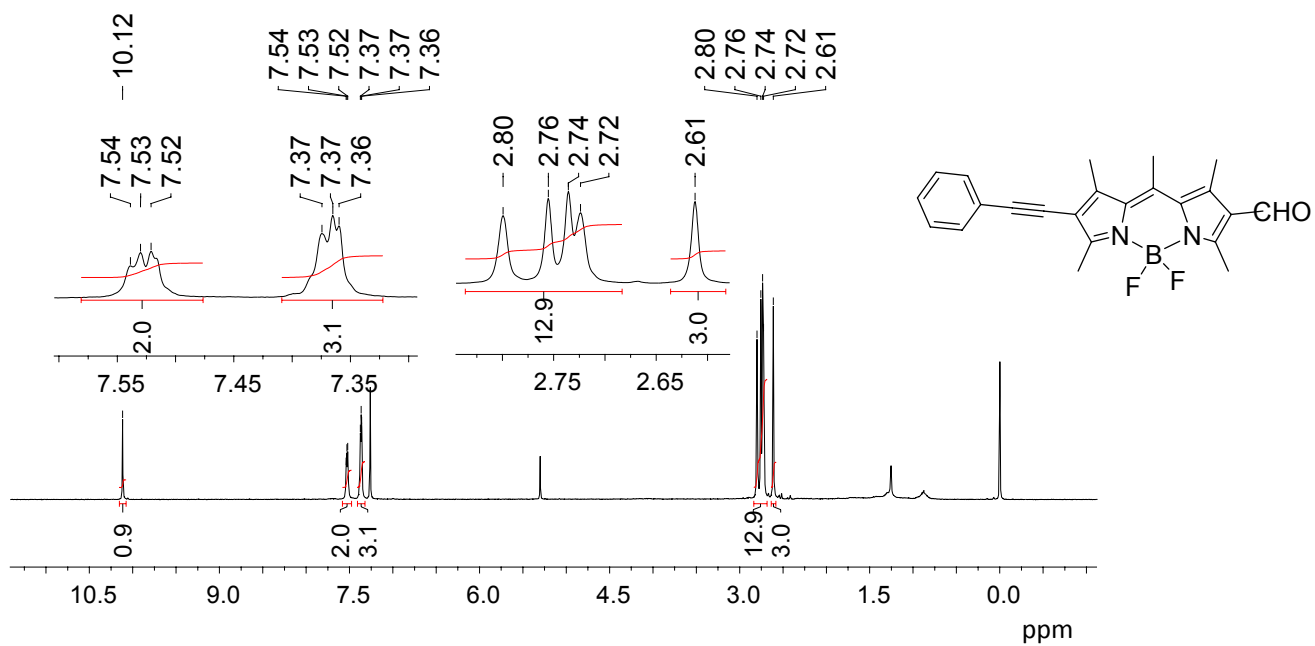


Fig. S6 ^1H NMR of 4 (400 MHz, CDCl_3).

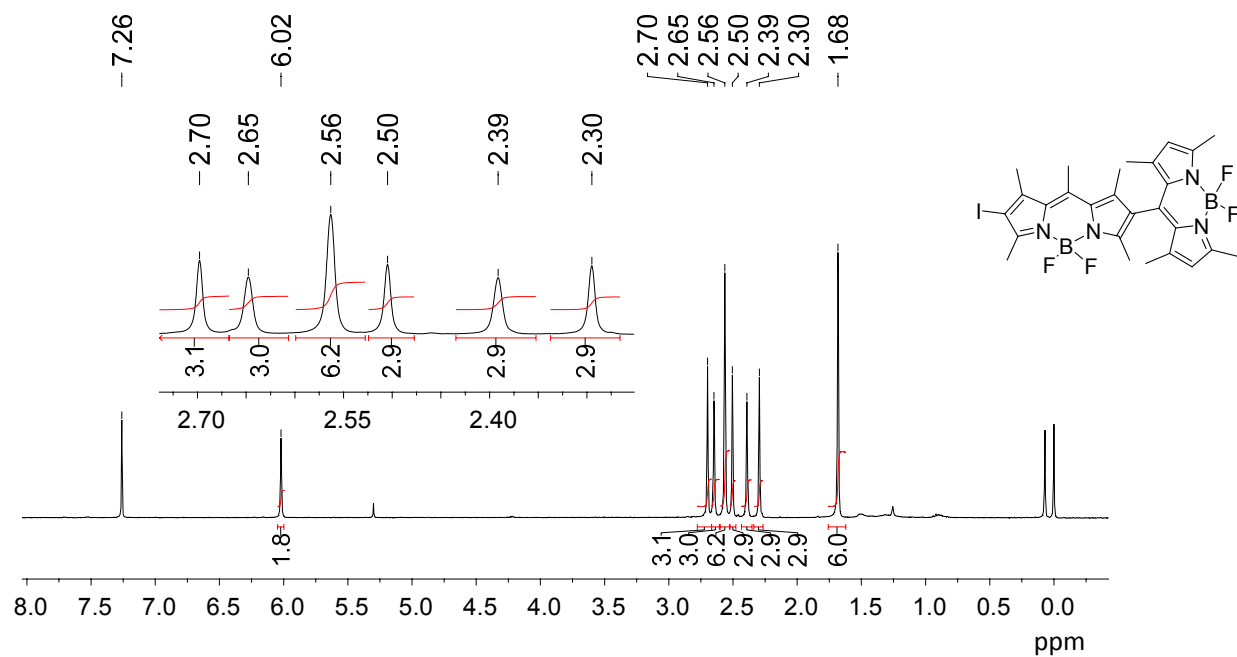


Fig. S7 ¹H NMR of **5** (400 MHz, CDCl₃).

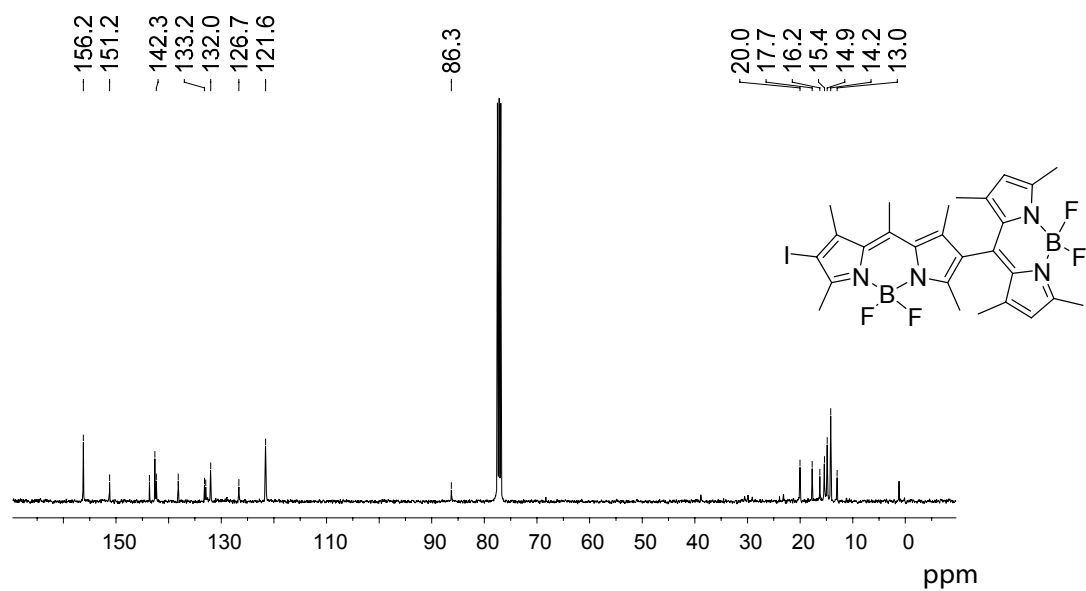


Fig. S8 ¹³C NMR of **5** (100 MHz, CDCl₃).

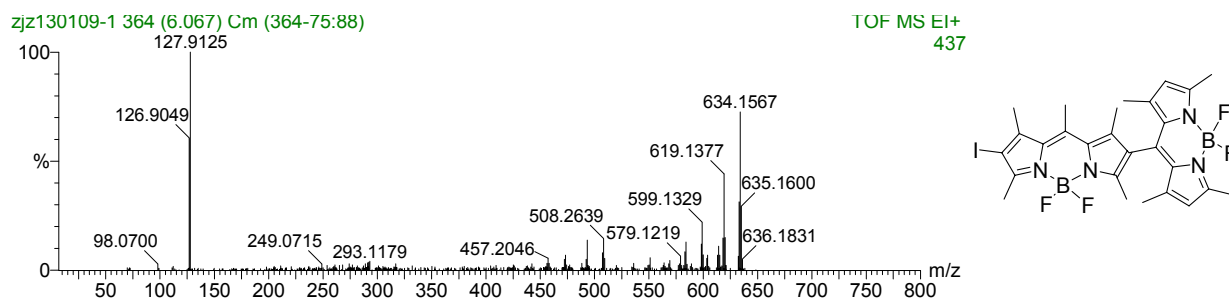


Fig. S9 EI-HRMS of compound 5.

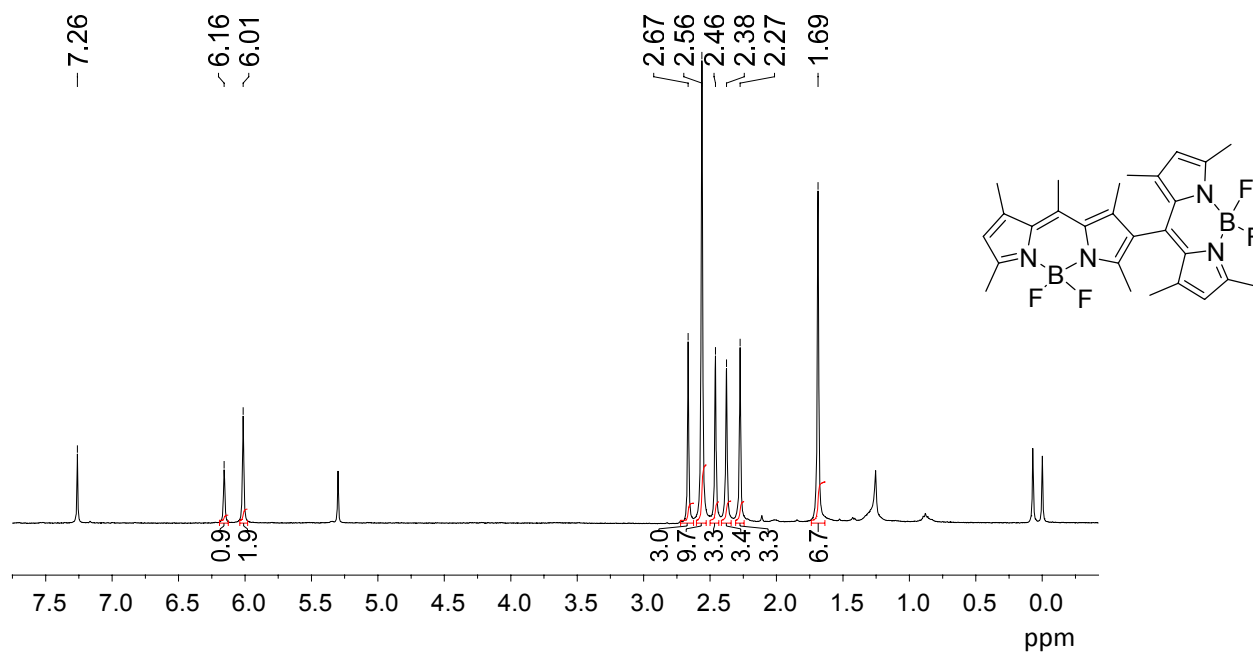


Fig. S10 ^1H NMR of BB-1 (400 MHz, CDCl_3).

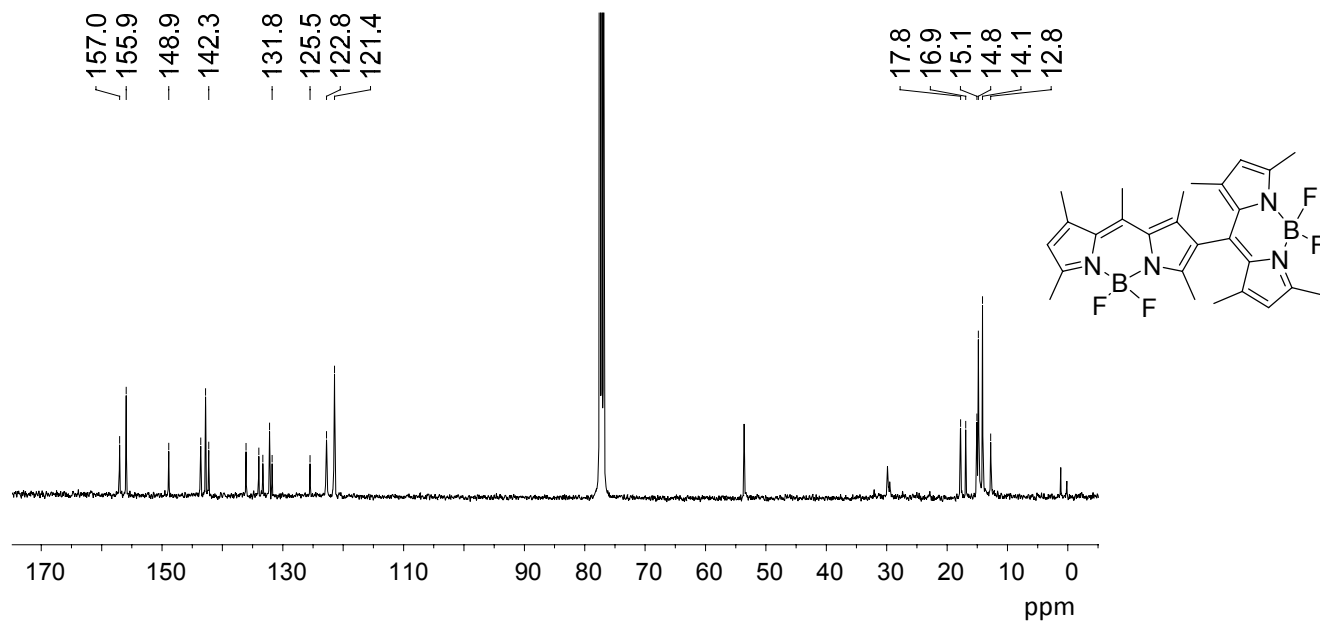


Fig. S11 ^{13}C NMR of BB-1 (100 MHz, CDCl_3).

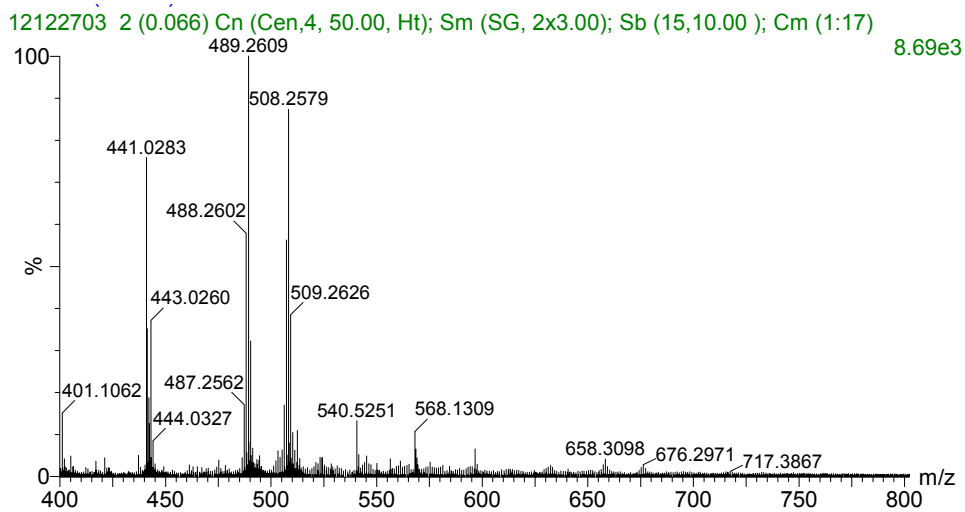


Fig. S12 MALDI-HRMS of BB-1.

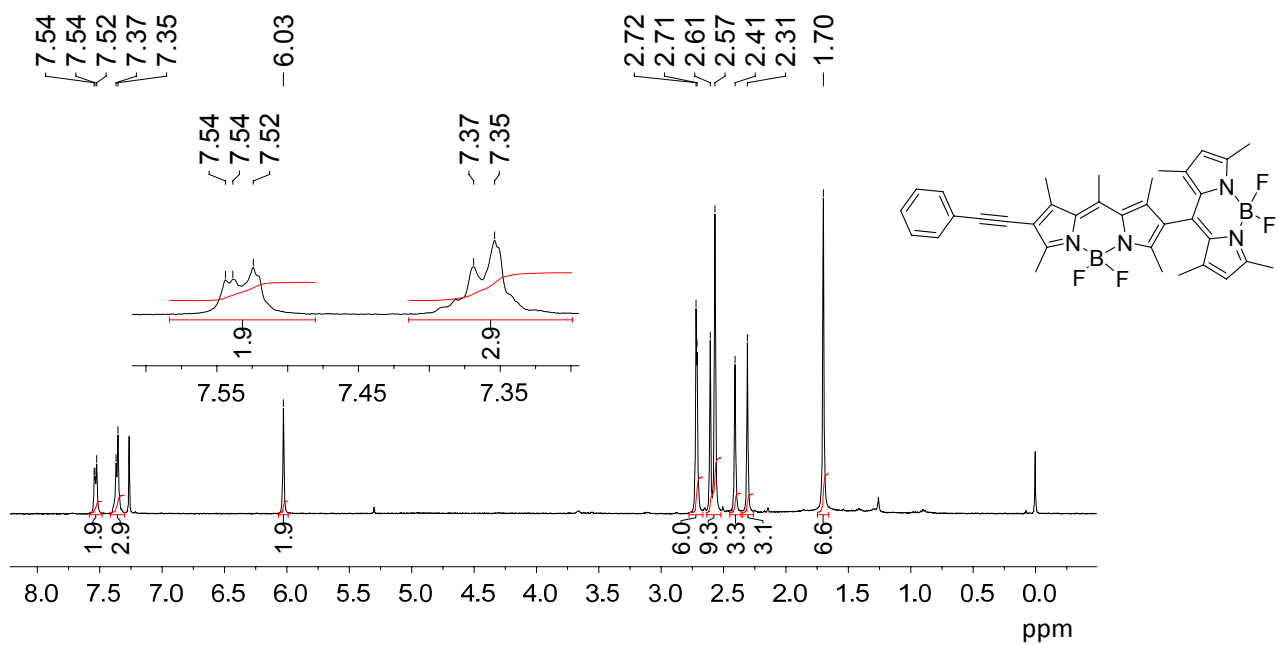


Fig. S13 ¹H NMR of **BB-2** (400 MHz, CDCl₃).

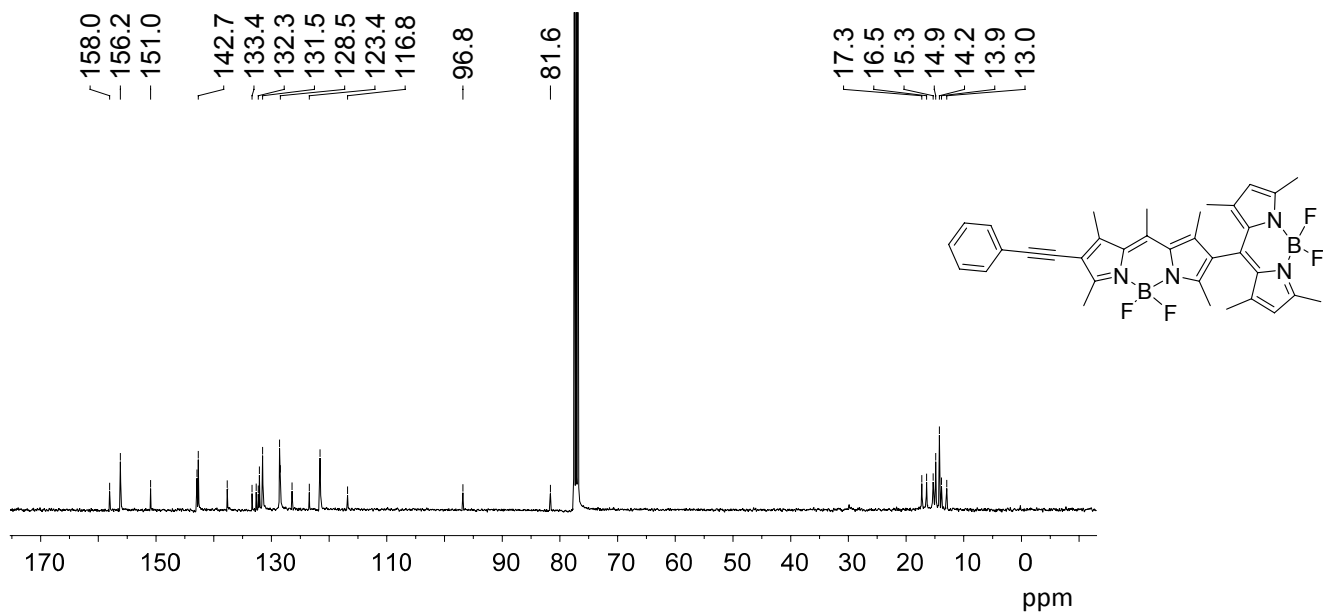


Fig. S14 ¹³C NMR of **BB-2** (100 MHz, CDCl₃).

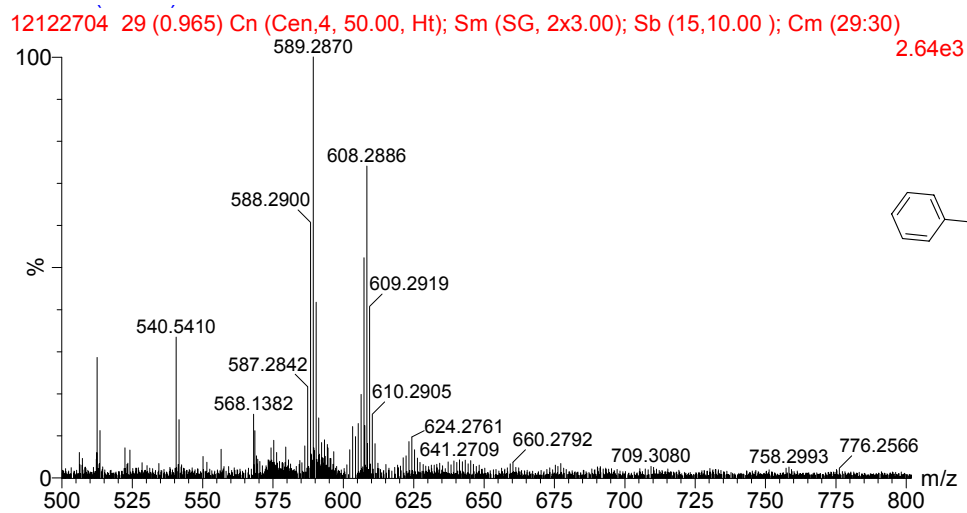


Fig. S15 MALDI-HRMS of BB-2.

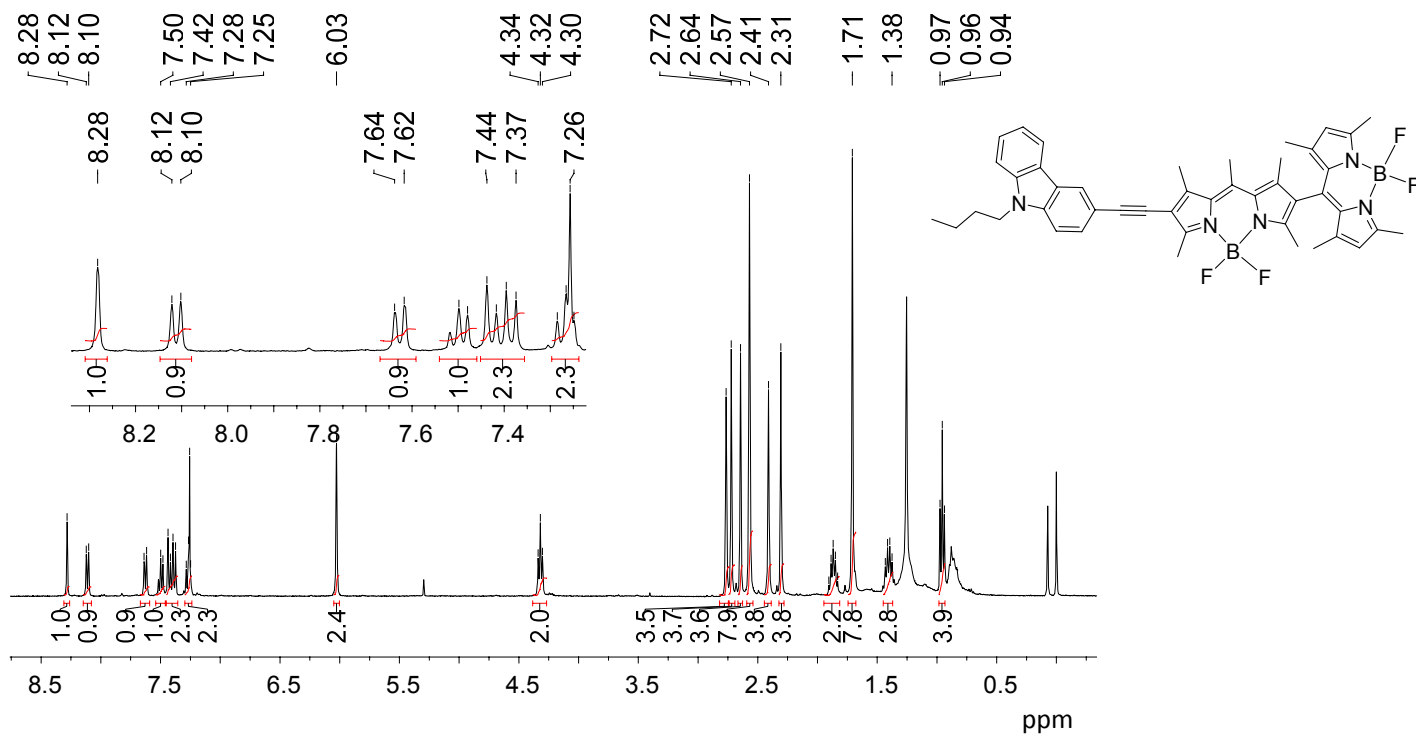


Fig. S16 ^1H NMR of BB-3 (400 MHz, CDCl_3).

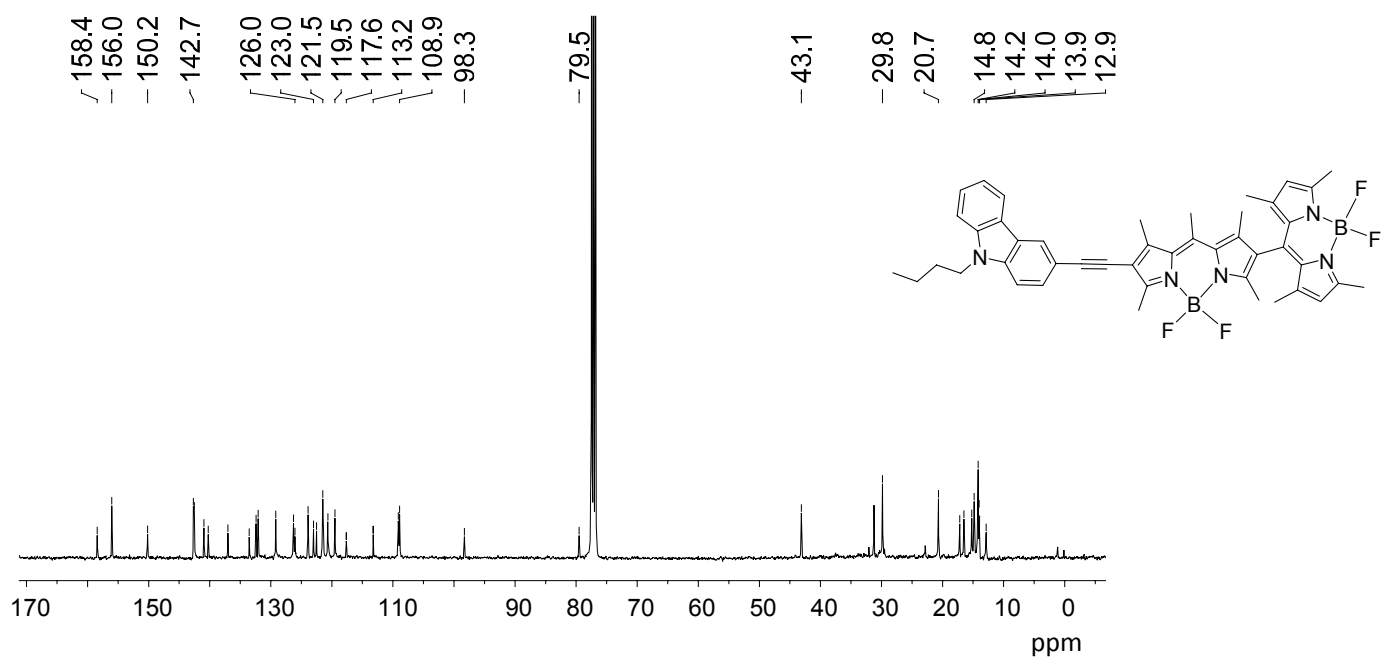


Fig. S17 ¹³C NMR of BB-3 (100 MHz, CDCl₃).

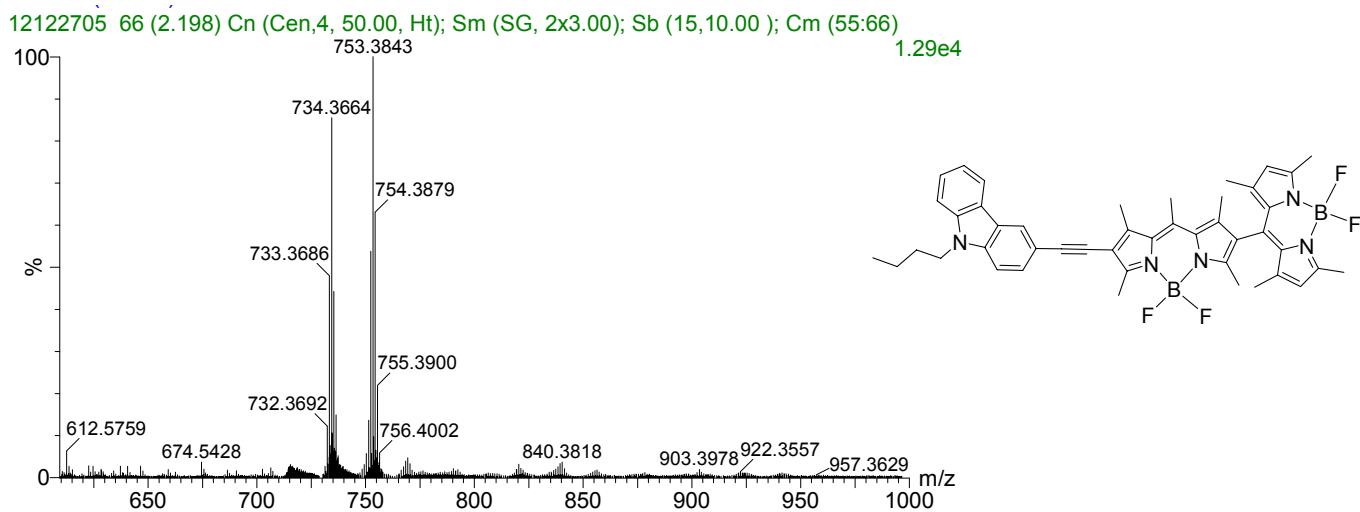


Fig. S18 MALDI-HRMS of BB-3.

4. Details of photophysical properties

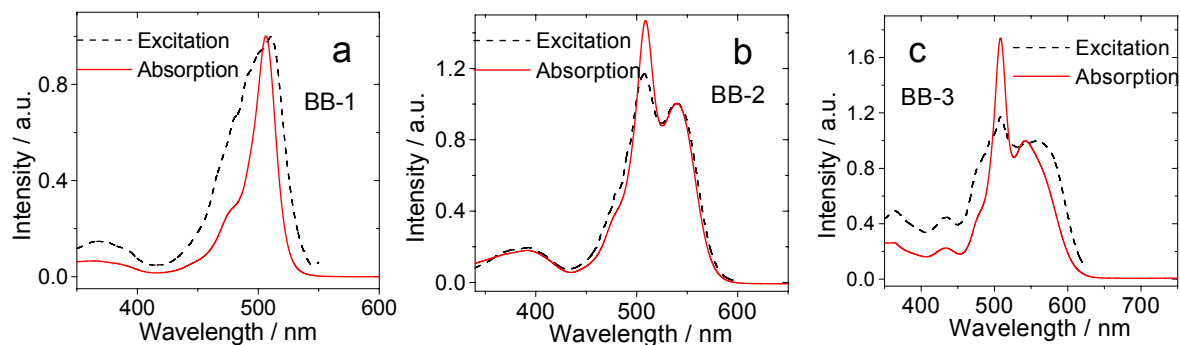


Fig. S19 Comparison of the normalized UV-vis absorption and the excitation spectra of the photosensitizers. The excitation spectra of (a) **BB-1**, (b) **BB-2** and (c) **BB-3** were recorded with $\lambda_{\text{em}} = 550$ nm, $\lambda_{\text{em}} = 600$ nm and $\lambda_{\text{em}} = 650$ nm respectively. $c = 1.0 \times 10^{-5}$ mol dm $^{-3}$ in DCM. 20 °C.

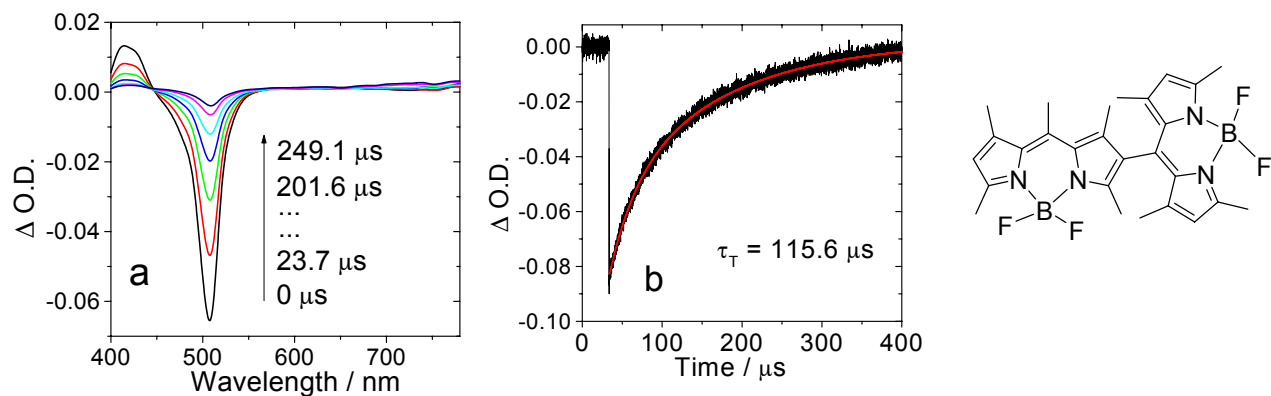


Fig. S20 (a): Nanosecond time-resolved transient absorption difference spectra of **BB-1**. After pulsed excitation ($\lambda_{\text{ex}} = 532$ nm). (b) Decay traces of **BB-1** at 510 nm. $c = 1.0 \times 10^{-5}$ M in deaerated CH $_2$ Cl $_2$. 20 °C.

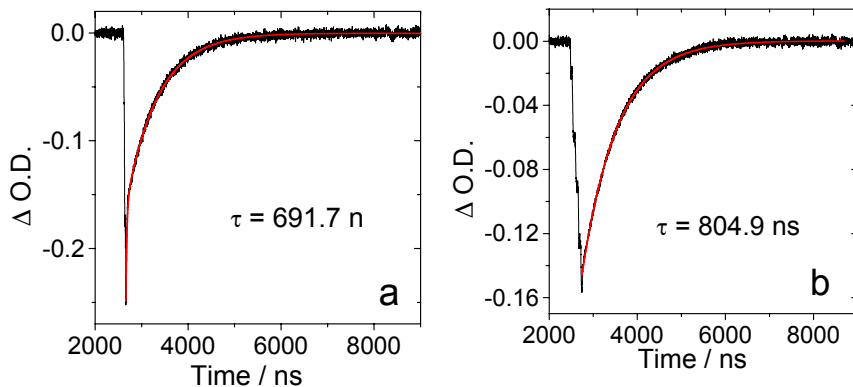


Fig. S21 Decay traces of (a) **BB-1** and (b) **BB-2** monitored at 510 nm. $c = 1.0 \times 10^{-5}$ M in air saturated DCM. 20 °C.

5. Upconversion details

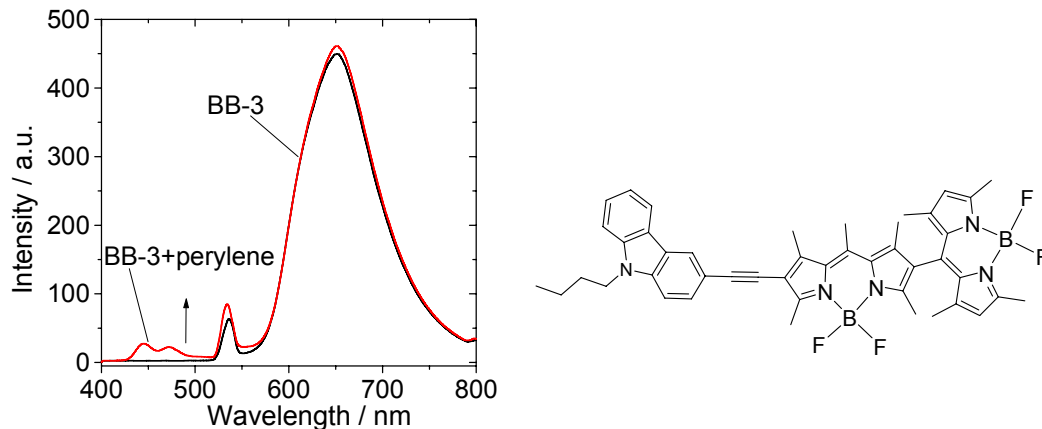


Fig. S22 Upconversion with **BB-3** as triplet photosensitizers (1.0×10^{-5} M) and perylene as acceptor (3.3×10^{-5} M) in DCM. $\lambda_{ex} = 532$ nm, laser power is 8.8 mW (124.6 mW cm^{-2}), 20 °C.

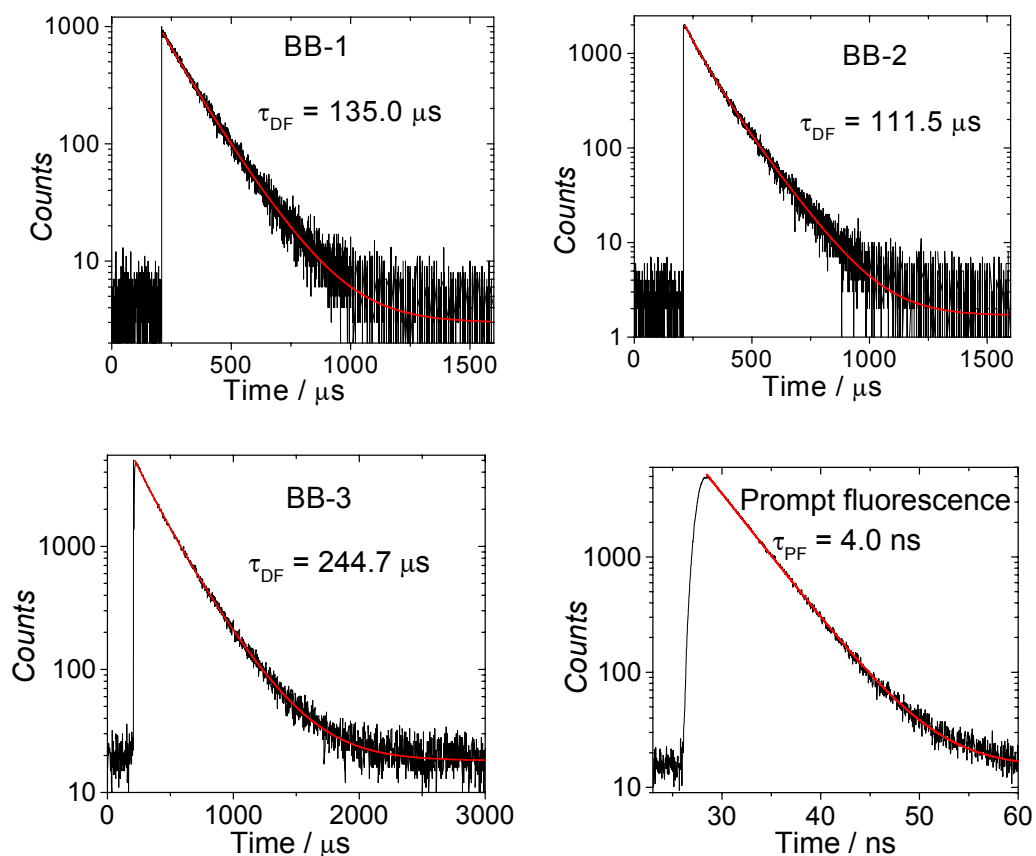


Fig. S23 Delayed fluorescence observed in the TTA upconversion with compound **BB-1**, **BB-2** and **BB-3** as triplet photosensitizers and perylene as the triplet acceptor. Excited at 532 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and monitored at 470 nm. Under this circumstance the compounds **BB-1**, **BB-2** and **BB-3** are selectively excited and the emission is due to the upconverted emission of perylene. In deaerated DCM. $c[\text{photosensitizers}] = 1.0 \times 10^{-5} \text{ M}$; $c[\text{perylene}] = 3.3 \times 10^{-5} \text{ M}$; 20 °C.

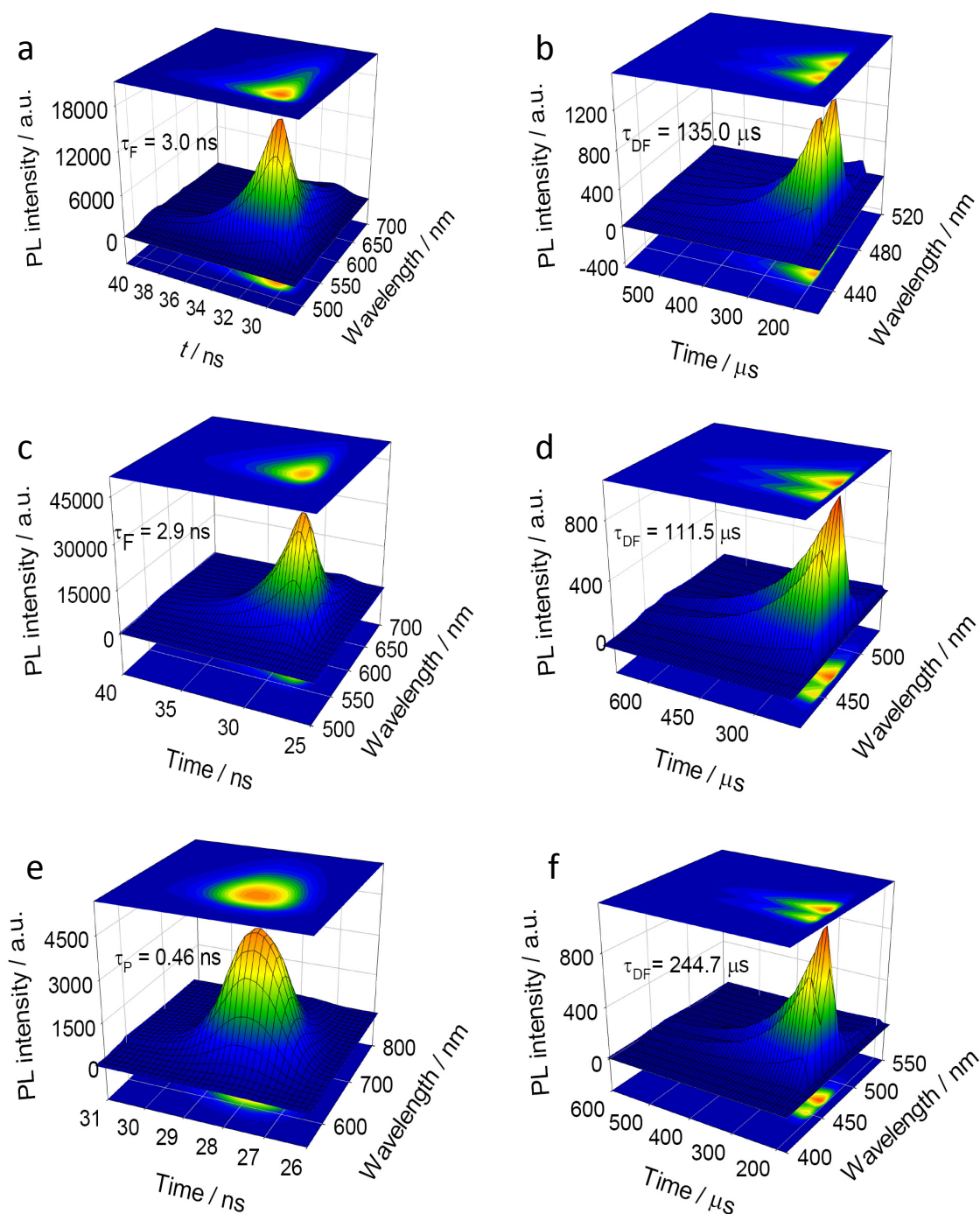


Fig. S24 Time-resolved emission spectra (TRES) of the sensitizers **BB-1** (a), **BB-2** (c), **BB-3** (e) and the upconverted fluorescence of perylene using **BB-1** (b) **BB-2** (d) **BB-3** (f) as the sensitizers. TRES of the prompt fluorescence of the triplet photosensitizers were recorded with excitation with EPL picosecond pulsed laser. The TRES of the delayed fluorescence (the TTA upconversion) of perylene were recorded with excitation with the nanosecond pulsed OPO laser. c [Photosensitizers] = 1.0×10^{-5} M. c [perylene] = 3.3×10^{-5} M. In deaerated CH_2Cl_2 . 20 °C.

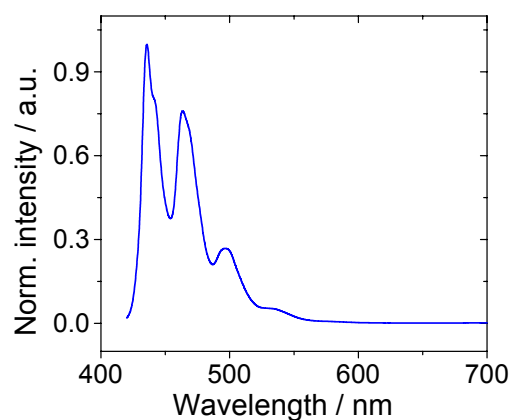


Fig. S25 Prompt fluorescence of perylene. Recorded with steady-state spectrofluorometer. $\lambda_{\text{ex}} = 400$ nm. In CH_2Cl_2 (1.0×10^{-5} M). 20 °C.

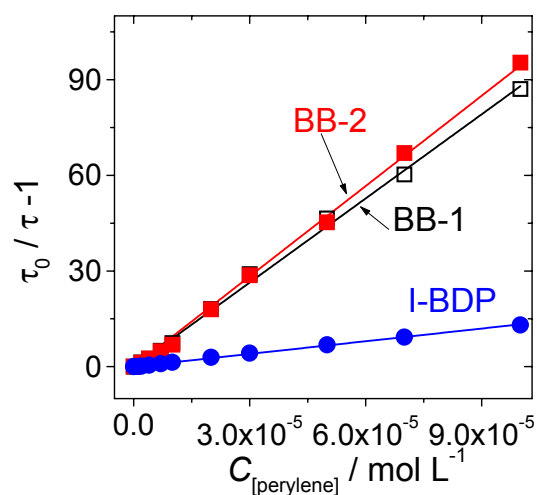


Fig. S26 Stern-Volmer plots generated from triplet excited state lifetime (τ_T) quenching of **BB-1**, **BB-2** and **I-BDP** measured as a function of perylene concentration in DCM. The lifetimes were measured with the nanosecond time-resolved transient absorption. The concentration of the sensitizers were fixed at 1.0×10^{-5} M. 20 °C.

6. Calculation details

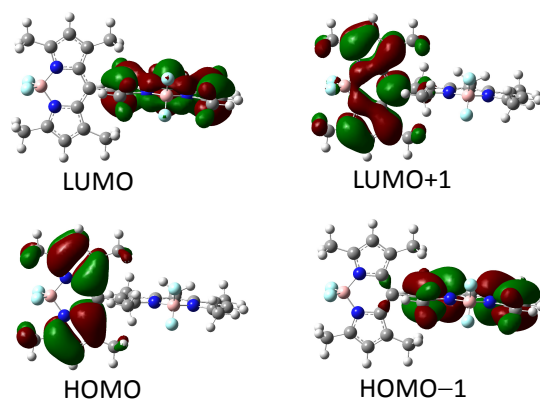


Fig. S27 Frontier molecular orbitals of **BB-1**. Calculated by DFT at the B3LYP/6-31G(d) using Gaussian 09W.²

Table S1. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (f), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **BB-1**, Calculated by TDDFT//B3LYP/6-31G(d), based on the DFT//B3LYP/6-31G(d) Optimized Ground State Geometries.

Electronic transition		TDDFT//B3LYP/6-31G(d)			
		Energy /eV ^[a]	f ^[b]	Composition ^[c]	CI ^[d]
Triplet	$S_0 \rightarrow T_1$	1.49 eV / 834 nm	0.0000 ^[e]	HOMO $\rightarrow$ LUMO +1	0.7108
				HOMO $\leftarrow$ LUMO +1	0.1211
	$S_0 \rightarrow T_2$	1.60 eV / 776 nm	0.0000 ^[e]	HOMO-1 $\rightarrow$ LUMO	0.7058
				HOMO-1 $\leftarrow$ LUMO	0.1056

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e] No spin-orbital coupling effect was considered, thus the f values are zero.

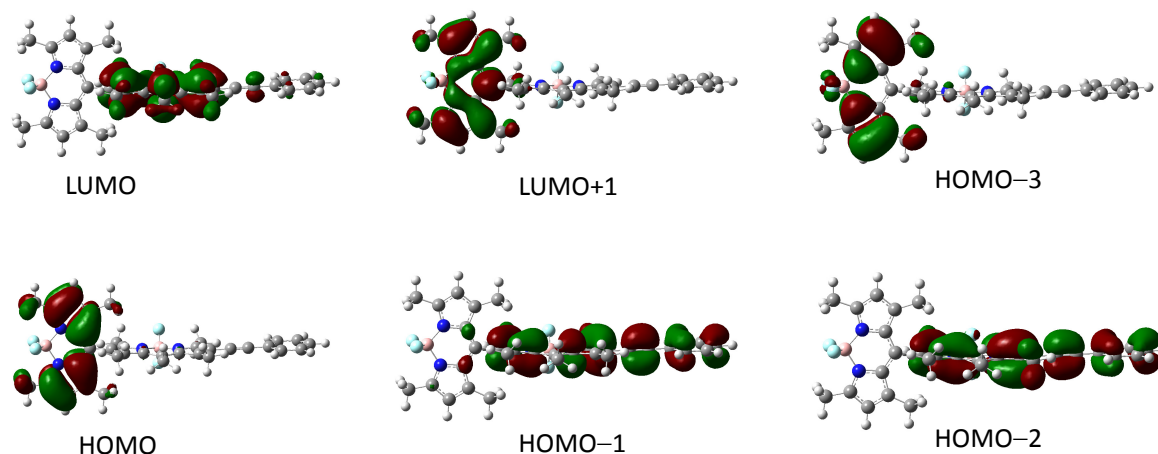


Fig. S28 Frontier molecular orbitals of **BB-2**. Calculated by DFT at the B3LYP/6-31G(d) using Gaussian 09W.

Table S2. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (f), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **BB-2**, Calculated by TDDFT//B3LYP/6-31G(d), based on the DFT//B3LYP/6-31G(d) Optimized Ground State Geometries.

Electronic transition		TDDFT//B3LYP/6-31G(d)			
		Energy / eV ^[a]	f ^[b]	Composition ^[c]	CI ^[d]
Triplet	$S_0 \rightarrow T_1$	1.48 eV / 836 nm	0.0000 ^e	HOMO-1 $\rightarrow$ LUMO +1	0.1033
				HOMO $\rightarrow$ LUMO +1	0.7038
				HOMO $\leftarrow$ LUMO +1	0.1202
	$S_0 \rightarrow T_2$	1.53 eV / 808 nm	0.0000 ^e	HOMO-2 $\rightarrow$ LUMO	0.2717
				HOMO-1 $\rightarrow$ LUMO	0.6444
				HOMO $\rightarrow$ LUMO	0.1132

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e] No spin-orbital coupling effect was considered, thus the f values are zero.

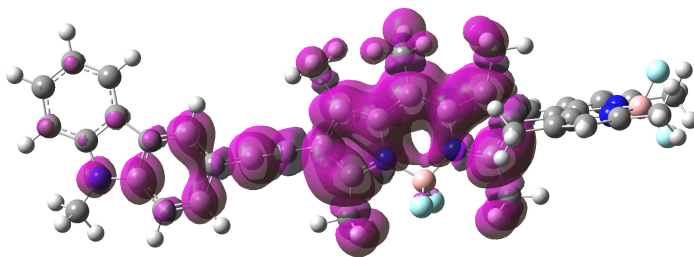


Fig. S29 Isosurfaces of spin density of **BB-3** at the optimized triplet state geometries. Calculation was performed at B3LYP/6-31G(d) level with Gaussian 09W.

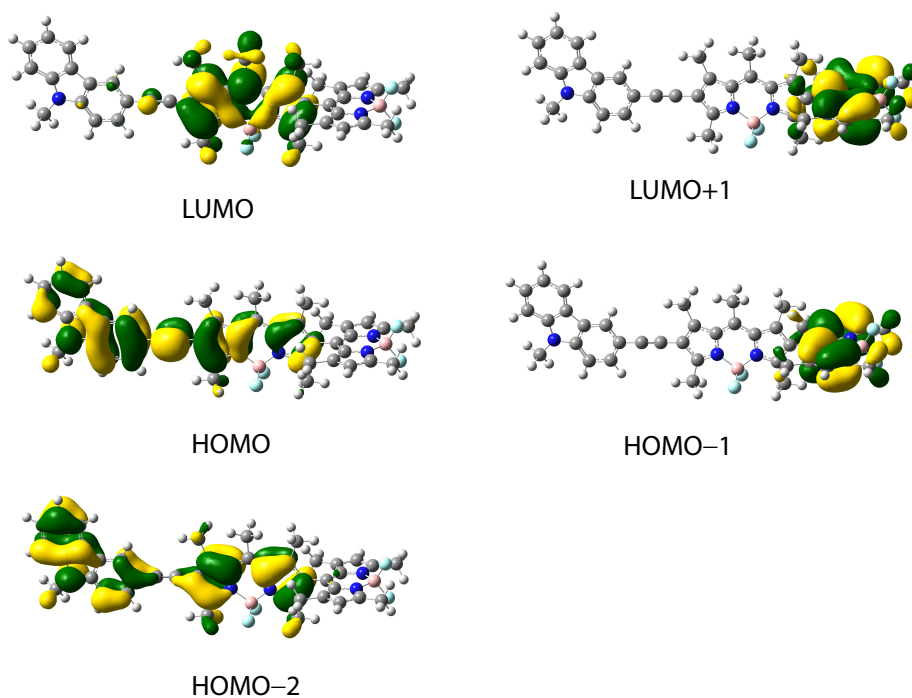


Fig. S30 Frontier molecular orbitals of **BB-3**. Calculated by DFT at the B3LYP/6-31G(d) using Gaussian 09W.

Table S3. Electronic Excitation Energies (eV) and corresponding Oscillator Strengths (f), main configurations and CI coefficients of the Low-lying Electronically Excited States of complex **BB-3**, Calculated by TDDFT//B3LYP/6-31G(d), based on the DFT//B3LYP/6-31G(d) Optimized Ground State Geometries.

Electronic transition		TDDFT//B3LYP/6-31G(d)			
		Energy / eV ^[a]	f ^[b]	Composition ^[c]	CI ^[d]
Triplet	$S_0 \rightarrow T_1$	1.48 eV / 840 nm	0.0000 ^e	HOMO-2 $\rightarrow$ LUMO +1	0.3546
				HOMO $\rightarrow$ LUMO	0.5965
	$S_0 \rightarrow T_2$	1.49 eV / 835 nm	0.0000 ^e	HOMO-1 $\rightarrow$ LUMO+1	0.7091

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values. [e] No spin-orbital coupling effect was considered, thus the f values are zero.

7. The coordinates of the optimized ground state geometries of compounds

Compound BB-1 (DFT//B3LYP/6-31G(d))

Charge = 0 Multiplicity = 1

C	5.69978953	-0.03456503	-1.00033061
C	5.76810382	0.20067721	1.25831562
C	4.40371265	0.07381425	0.81950029
C	1.95740650	0.02713840	0.81765715
C	0.59957595	0.10037886	1.26413514
C	-0.19730846	-0.01355210	0.11851749
C	0.66190689	-0.15169824	-0.99592997
N	4.42389979	-0.06069080	-0.57515994
N	1.93874613	-0.11735269	-0.57110075
B	3.18398618	-0.24797467	-1.49688095
F	3.15756439	0.75060994	-2.46662342
F	3.21079776	-1.50823478	-2.08931053
C	6.33182333	0.40096235	2.63604982
H	5.88411980	1.25628353	3.15424474
H	6.19413570	-0.47893903	3.27772877
H	7.40861150	0.58348686	2.56806966
C	0.29321893	-0.30474874	-2.43649378
H	-0.78730052	-0.41842987	-2.54758898
H	0.62365787	0.56533627	-3.01425945
H	0.79627572	-1.17588890	-2.86812871
C	0.05153483	0.28593883	2.65076856
H	0.51601773	1.12802332	3.17463526
H	-1.02358748	0.47813105	2.60350954
H	0.19318801	-0.60429685	3.27774435

C	6.07739290	-0.16833545	-2.43935707
H	5.64340395	0.64537232	-3.02953610
H	7.16432974	-0.15585445	-2.55227010
H	5.68300974	-1.10244907	-2.85344402
C	3.18388966	0.08939110	1.51529277
C	3.17594986	0.18191513	3.02090488
H	3.06449417	1.22253230	3.35420449
H	2.34969053	-0.38687203	3.44645055
H	4.09643496	-0.20514022	3.45202529
C	-4.15234974	2.54981967	-0.21162035
C	-1.87984307	2.57913145	-0.17019111
C	-3.01275094	3.37861385	-0.26587751
C	-2.35802884	1.23049143	-0.05342219
C	-2.38938466	-1.20835544	0.13044683
C	-1.94653077	-2.57007702	0.23756374
C	-3.09971055	-3.34553117	0.25691299
C	-4.21719341	-2.49004262	0.16651102
H	-3.14541162	-4.42495762	0.32748674
N	-3.75689117	1.26825729	-0.08704379
N	-3.78862837	-1.21543891	0.09035443
B	-4.70894633	0.03864703	0.00631178
F	-5.49746840	0.12983549	1.15240998
F	-5.50954576	-0.03178946	-1.13171841
C	-0.47074320	3.09381598	-0.20444815
H	0.07535245	2.87590018	0.71988337
H	0.11158129	2.65709314	-1.02294362
H	-0.47829675	4.17984806	-0.34119015
C	-5.66537591	-2.85614770	0.15208554
H	-5.78811852	-3.93837639	0.24302273
H	-6.19411680	-2.36219968	0.97428039
H	-6.13894261	-2.51585034	-0.77495277
C	-0.55193523	-3.11897332	0.31311903
H	0.00955111	-2.71073979	1.16013090
H	-0.58995121	-4.20707347	0.42616249
H	0.03358427	-2.89814600	-0.58633448
C	-5.59087993	2.94725424	-0.27610926
H	-6.12659331	2.59414870	0.61145384
H	-5.68574490	4.03386408	-0.34600326
H	-6.07912474	2.48625357	-1.14131552
H	-3.03031509	4.45623394	-0.36910678
C	-1.68078451	0.00378409	0.06297422
C	6.54920125	0.13235126	0.11272849
H	7.62872770	0.20142186	0.06849712

Compound BB-2 (DFT//B3LYP/6-31G(d))

Charge = 0 Multiplicity = 1

C	3.83929709	-0.24186958	-0.94789837
C	3.89479933	0.04328607	1.31824713
C	4.70216534	-0.06486967	0.17287255
C	2.54293728	-0.06869326	0.86833742
C	0.09520140	-0.05925690	0.84869764
C	-1.26476563	0.06665190	1.28146773
C	-2.05483268	-0.04801814	0.13258060

C	-1.19108468	-0.23919018	-0.97164871
N	2.56922268	-0.23348189	-0.52540242
N	0.08238591	-0.23342592	-0.53754060
B	1.32825076	-0.42439781	-1.45080324
F	1.33226743	0.54177962	-2.45081304
F	1.33299190	-1.70407928	-1.99729877
C	4.44840704	0.26953048	2.69318411
H	3.98707726	1.12686400	3.19507782
H	4.31573440	-0.60369216	3.34537425
H	5.52293256	0.45963892	2.62217192
C	-1.55459984	-0.41453574	-2.41070444
H	-2.63445558	-0.53345291	-2.52273008
H	-1.22683486	0.44863150	-3.00057579
H	-1.04741682	-1.29016867	-2.82765297
C	-1.81767268	0.30664891	2.65765213
H	-1.32362131	1.14106371	3.16633322
H	-2.88345720	0.54176233	2.59473550
H	-1.71871521	-0.57396371	3.30602567
C	4.22754276	-0.41438267	-2.37728333
H	3.82932161	0.40509985	-2.98452041
H	5.31520340	-0.44152359	-2.47015799
H	3.80247098	-1.34062956	-2.77795204
C	1.31552547	-0.01599740	1.55449140
C	1.30413391	0.09456055	3.05881222
H	1.27343792	1.14431036	3.38088487
H	0.43570368	-0.40485329	3.48583177
H	2.19147756	-0.35764584	3.49736953
C	-5.91071508	2.64769983	-0.29380722
C	-3.63937876	2.59758904	-0.21999044
C	-4.74156762	3.43461452	-0.34659924
C	-4.16690469	1.26889612	-0.08602486
C	-4.28859068	-1.16371137	0.14074171
C	-3.89615025	-2.53843584	0.27657093
C	-5.07649161	-3.27164761	0.29566384
C	-6.16145736	-2.37838425	0.17684220
H	-5.16181974	-4.34731231	0.38450864
N	-5.56284068	1.35560192	-0.13994759
N	-5.68650702	-1.12146722	0.08366639
B	-6.56012690	0.16342847	-0.03096483
F	-7.35198848	0.30496690	1.10766287
F	-7.35457790	0.10096855	-1.17322334
C	-2.21258203	3.06206179	-0.24021168
H	-1.69143728	2.84761013	0.69930269
H	-1.63082065	2.58670084	-1.03728644
H	-2.17942047	4.14418012	-0.40160864
C	-7.62153248	-2.69274186	0.15145957
H	-7.78424501	-3.76764634	0.26368670
H	-8.14203413	-2.16254939	0.95612748
H	-8.07129901	-2.35586553	-0.78861716
C	-2.52283479	-3.13504231	0.37602040
H	-1.95028240	-2.72272869	1.21347967
H	-2.60066182	-4.21728749	0.52006043
H	-1.92668470	-2.96216972	-0.52714728
C	-7.33309786	3.09365565	-0.38919777
H	-7.90275611	2.74507624	0.47848230
H	-7.39042368	4.18368575	-0.44537138

H	-7.81356000	2.66251807	-1.27420048
H	-4.71935362	4.51008762	-0.46937040
C	-3.53611301	0.02089128	0.06069379
C	6.11234998	-0.00201500	0.11108817
C	7.32787816	0.05298289	0.05601334
C	8.74911088	0.11787620	-0.01221598
C	9.52069099	0.22071524	1.16330235
C	9.41026255	0.08101641	-1.25701328
C	10.90922437	0.28501949	1.09132031
H	9.01796917	0.24894575	2.12525108
C	10.79930372	0.14528177	-1.31861987
H	8.82229895	0.00241588	-2.16631972
C	11.55431461	0.24757971	-0.14744805
H	11.49082482	0.36425404	2.00586242
H	11.29517037	0.11581095	-2.28511651
H	12.63835558	0.29777293	-0.19985576

Compound BB-3 (DFT//B3LYP/6-31G(d))

Charge = 0 Multiplicity = 1

0 1			
C	6.78008890	-0.71563662	-0.03243949
C	7.35468617	-2.01305002	-0.06253011
C	7.62091477	0.40981268	0.03154352
C	8.72907226	-2.20537015	-0.02826861
H	6.69410400	-2.87252781	-0.11721072
C	9.00309458	0.23628162	0.06755501
H	7.18425501	1.40378852	0.04964725
C	9.55172729	-1.07552244	0.04389498
H	9.14079364	-3.20932547	-0.06303835
C	10.12455103	1.15162457	0.12772256
C	11.29835523	0.35274796	0.13794780
C	10.23825704	2.54509012	0.17211911
C	12.57277354	0.92532749	0.17859864
C	11.50533137	3.12052132	0.22011374
H	9.34903632	3.17012553	0.16650480
C	12.65742332	2.31576517	0.22218956
H	13.47169116	0.31627688	0.17034590
H	11.60671300	4.20143535	0.25317559
H	13.63692877	2.78509223	0.25430778
C	4.15429669	-0.42971683	-0.10111861
C	5.36517890	-0.56126624	-0.06984622
N	10.93445665	-0.99084571	0.10459462
C	11.85281011	-2.10851928	0.05947639
H	12.14771821	-2.36076401	-0.96774612
H	12.75099228	-1.86804120	0.63459926
H	11.38650653	-2.98464499	0.51723533
C	1.81345207	-1.34142942	-0.29982554
C	2.01854865	0.91473930	-0.01277872
C	0.63739598	0.55212767	-0.10263348
C	-1.80703159	0.68446130	-0.06224964

C	-3.13366889	1.20541474	0.06791714
C	-3.99821600	0.10860147	-0.03474017
C	-3.21010112	-1.04985049	-0.22057321
N	0.57286241	-0.84058815	-0.26938019
N	-1.91017296	-0.69841719	-0.22700093
B	-0.72697702	-1.68908792	-0.42392958
F	-0.78163859	-2.25525770	-1.69376618
F	-0.76260266	-2.67346832	0.55904619
C	2.66286999	2.25078442	0.20722522
H	2.55926979	2.91325652	-0.66229172
H	2.24858493	2.77816180	1.07332091
H	3.73347136	2.10964303	0.37993138
C	-3.66746130	-2.46268452	-0.39007021
H	-4.75778345	-2.51965584	-0.36404821
H	-3.30745655	-2.87033557	-1.34098464
H	-3.25259744	-3.09877768	0.39849672
C	-3.59550998	2.61632220	0.29962927
H	-3.45568206	3.25200055	-0.58478263
H	-4.66299817	2.62408561	0.53526676
H	-3.06845445	3.09761756	1.13009965
C	2.10870019	-2.79242802	-0.47680902
H	1.61870363	-3.17348972	-1.37858696
H	3.18684938	-2.94910480	-0.55075994
H	1.71371837	-3.36959074	0.36603482
C	-0.54250378	1.31248711	-0.03295368
C	-0.46377214	2.81462635	0.07947927
H	0.46359511	3.20002299	-0.33825296
H	-1.28681840	3.29272530	-0.45090027
H	-0.51624017	3.13803095	1.12787724
C	-8.09422493	0.52458940	-2.34624133
C	-5.82841373	0.45081011	-2.51266652
C	-7.00522921	0.58138782	-3.24040986
C	-6.22736660	0.31081050	-1.14046029
C	-6.11898983	0.00202405	1.28334392
C	-5.60074813	-0.20615711	2.60601676
C	-6.70807502	-0.27364585	3.44325641
C	-7.87122334	-0.11225083	2.66247187
H	-6.69330436	-0.42685632	4.51494999
N	-7.62547564	0.36176172	-1.09409403
N	-7.51507228	0.05037486	1.37371501
B	-8.50279665	0.27501619	0.19006673
F	-9.20277485	1.46706502	0.37168019
F	-9.38502048	-0.79872550	0.09462502
C	-4.45330324	0.45566082	-3.11345554
H	-3.82138970	1.24892471	-2.70025615
H	-3.92138283	-0.48759018	-2.94591353
H	-4.52431680	0.60978648	-4.19482551
C	-9.29601350	-0.11105457	3.11126892
H	-9.35596923	-0.20866718	4.19824351
H	-9.79396887	0.81421037	2.80298117
H	-9.84738233	-0.93462593	2.64496208
C	-4.17862180	-0.34367911	3.06493682
H	-3.58039456	0.54586834	2.84003942
H	-4.15443441	-0.49974750	4.14810783
H	-3.66903903	-1.19150872	2.59407597
C	-9.55263451	0.62014125	-2.65558109

H	-10.01060647	1.44258681	-2.09585427
H	-9.70782648	0.78163395	-3.72536106
H	-10.07170681	-0.29461262	-2.35009031
H	-7.08544396	0.70385102	-4.31316528
C	-5.48061394	0.13930105	0.03811855
C	2.74974042	-0.27776899	-0.13682895