Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information for:

Preparation of Bodipy-Ferrocene Dyads and Modulation of the Singlet/Triplet Excited State of Bodipy via Electron Transfer and Triplet Energy Transfer

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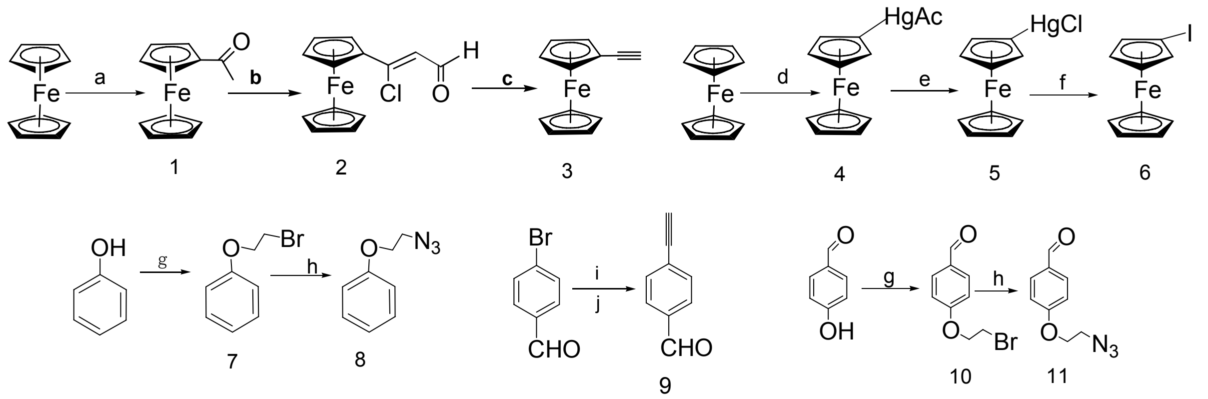
[¶] *These authors contributed equally to this work.*

1. Molecular synthesis data



Scheme S1 (a) Acetyl chloride and AlCl3, DCM, 25 °C, Ar, 30-60 min; yield 75.3%; (b) POCl3/DMF, 0 °C, Ar, 1.5 h. NaOAc, 25°C, Ar, 1 h; yield 76.3%; (c) 1,4-dioxane, NaOH, reflux,0.5 h; yield 90.7%; (d) HgOAc, MeOH / benzene, 25 °C, Ar,12 h; (e) LiCl, EtOH-H2O mixture, 25 °C, Ar, 1 h; yield 60.8 %; (f) NIS, dry DCM, 0 °C, Ar, 12 h; NaHSO3; yield 74.7%; (g) 1,2-dibromoethane K_2CO_3 and EtOH, reflux, 8 h. (h) NaN_3, DMF, 100 °C, 2 h. (i) Trimethylsilylacetylene, $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, NEt_3, Ar, 90 °C, 8 h. (j) K_2CO_3, DCM/MeOH (2/1, v/v), 25°C, Ar.

Synthesis of the Compound 1. A solution of ferrocene (930 mg, 5 mmol) in CH_2Cl_2 (5.0 mL) was prepared. Then solution of acyl chloride (5 mmol) and $AlCl_3$ (5 mmol) in CH_2Cl_2 (5 mL) was transferred to the ferrocene solution, while stirring at Ar atmosphere. The mixing of the two liquids generated an intense purple to blue mixture. After 30 – 60 min of stirring at room temperature (RT), water (10 mL) was added to the reaction mixture. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2, and the organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product (orange solid) was purified by column chromatography (silica gel, petroleum ether/ethyl ether = 2:1, v/v) to give **1** as orange-yellow powder. Yield: 873.5 mg (75.3%). ^1H NMR (500 MHz, $CDCl_3$) : δ 4.77 (s, 2H), 4.50 (s, 2H,), 4.20 (s, 5H), 2.40 (s, 3H). TOF HRMS EI^+: calcd ([$C_{12}H_{12}OFe$]) *m/z* = 228.0238, found, *m/z* = 228.0242.

Synthesis of the Compound 2. A stirred solution of acetylferrocene **1** (1.14g, 2.01 mmol) in dry *N,N*-dimethylformamide (DMF, 7.5 mL) was purged with Ar for 15 min and then cooled to 0 °C with an ice bath. The solution was stirred for 15 min under an Ar atmosphere. In a separate flask, dry DMF (5.0 mL) was cooled on ice with stirring, to which phosphorus oxychloride (1.5 mL) was added under Ar. The prepared mixture was transferred to the vigorously stirred solution of the acetylferrocene **1**. The addition was completed within 10 min and the stirring was continued at 0 °C under Ar for 1.5 h. Aqueous sodium acetate (20%, 37.5 mL) is cautiously added to the reaction mixture in one portion through a addition funnel, and stirring is continued for 1 h at RT. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2, and the combined organic phase was dried over anhydrous sodium sulfate. The solvent was removed and the crude material was purified by column chromatography (silica gel, petroleum ether/ethyl ether = 3:1, v/v) to give **2** as dark purple powder. Yield: 1.14g (76.3%). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 10.09 (d, J = 5.0 Hz, 1H), 6.41 (d, J = 5.0 Hz, 1H), 4.75 (s, 2H), 4.57 (s, 2H), 4.25 (s, 5H). TOF HRMS EI$^+$: calcd ([$C_{13}H_{11}OClFe$]) m/z = 273.9848, found, m/z =273.9844.

Synthesis of the Compound 3. A stirred solution of (2-formyl-1-chlorovinyl)-ferrocene **2** (466 mg, 1.73 mmol) in dry 1,4-dioxane (15 mL) was refluxed for 3 min under Ar. A 0.5 M sodium hydroxide solution (10 mL, 5 mmol) was added in one portion to the reaction mixture. The mixture was refluxed with stirring for 30 min. The solution was allowed to cool to RT, and the mixture was poured onto ice (ca. 50 g) and then the mixture was neutralized to pH ca. 7 by 2 M hydrochloric acid. The crude mixture was transferred into a separatory funnel. Water (20 mL) and petroleum ether (100mL) was added. The organic phase was separated and washed with saturated $NaHCO_3$ solution (2 × 20 mL), water (2 × 20 mL), the organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude residue was purified using column chromatography (silica gel, petroleum ether) to give the compound **3** as a dark orange oil. Yield: 298 mg (90.7%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.45 (t, J = 4.0 Hz, 2H), 4.21 (s, 5H), 4.18 (t, J = 4.0 Hz, 2H), 2.71 (s, 1H). TOF HRMS EI$^+$: calcd ([$C_{12}H_{10}Fe$]) m/z = 210.0132, found, m/z = 210.0135.

Synthesis of the Compound 5. A solution of mercuric acetate (7.87 g, 25 mmol) in absolute methanol (75 mL) was added dropwise to a stirred solution of ferrocene (9.3 g, 50 mmol) in dry benzene (50 mL). The reaction was continued in a Ar atmosphere at RT for 12 h, and then lithium chloride (2.2 g, 52 mmol) in ethanol-water mixed solvent (20 mL, 1: 1, v/v) was added dropwise. The resulting orange suspension was stirred at RT for 1 h, then refluxed for 1 h, and the mixture was extracted with dichloromethane. The dichloromethane extract was washed thoroughly with water and dried over magnesium sulfate. After removal of solvent, the solid residue was purified by chromatography (silica gel, petroleum ether). Two bands developed on the column upon elution, the second band gave chloromercuriferrocene as golden platelets. Yield: 4.98 g (60.8%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.41 (t, J = 4.0 Hz, 2H), 4.23 (s, 5H) and 4.16 (t, J = 4.0 Hz, 2H). TOF HRMS EI$^+$: calcd ([$C_{10}H_9ClFeHg$]) m/z = 421.9448, found, m/z = 421.9444.

Synthesis of the Compound 6. Under Ar atmosphere, a solution of *N*-iodosuccinimide (1.2 g., 6.0 mmol) in dry dichloromethane (100 mL) was added dropwise to a stirred suspension of chloromercuriferrocene (2.10 g, 5 mmol) in dichloromethane (75 mL) while the mixture was cooled with an ice bath. After allowing the reaction to continue for 12 h, aqueous sodium bisulfite solution (10%, 50 mL) was added, followed by an equal volume of a 10% sodium carbonate solution. The organic layer was separated and the aqueous solution was extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed successively with 10% sodium carbonate solution and water. Then the organic layer was dried over magnesium sulfate. The solvent was evaporated under reduced pressure, an oil was obtained. The crude product was purified by chromatography (alumina; petroleum ether). The first band gave an orange oil, The orange oil was cooled in refrigerator to get the iodoferrocene as deep yellow powder. Yield: 1.16 g (74.7%). ^{1}HNMR (400 Mz, $CDCl_3$): δ 4.41 (t, *J* = 4.0 Hz, 2H), 4.19 (s, 5H) and 4.15 (t, *J* = 4.0 Hz, 2H). TOF HRMS EI$^+$: calcd ([$C_{10}H_9FeI$]) *m/z* =311.9098, found, *m/z* = 311.9096.

Synthesis of the Compound 7. Under Ar atmosphere, phenol (3.76 g, 40 mmol) and anhydrous potassium carbonate (11.06 g, 80 mmol) were mixed in dry ethanol (150 mL), the mixture was stirred at 70 °C for 0.5 h. The mixture was then cooled to RT and 1,2-dibromoethane (14.9 g, 80 mmol) was added using syringe. The mixture was stirred at 79 °C for 8 h. The mixture was then cooled to RT. Potassium carbonate was removed by filtration and the filtrate was evaporated to dryness. The product was purified by column chromatography (silica gel, CH_2Cl_2 : petroleum ether = 5:1, v/v) to afford 3.78 g colourless oil. Yield: 47.3%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31–7.28 (m, 2H), 7.00 (t, *J* = 15.0 Hz, 1H), 6.92 (d, *J* = 5.0 Hz, 2H), 4.31 (t, *J* = 12.0 Hz, 2H), 3.65 (t, *J* = 10.0 Hz, 2H). TOF HRMS EI$^+$: calcd ([C_8H_9OBr]) *m/z* = 199.9837, found, *m/z* = 199.9839.

Synthesis of the Compound 8. A mixture of compound 7 (400 mg, 2.0 mmol) and NaN_3 (130 mg, 2.0 mmol) in DMF (15 mL) was heated at 100 °C. After 2 h, the mixture was poured to water, and the mixture was extracted with CH_2Cl_2. The solvent was evaporated under reduced pressure and the azide compound was obtained as colorless oil. Yield: 321mg (99 %). The compound was used without any further purification.

Synthesis of the Compound 9.Under Ar, 4-bromobenzaldehyde (7) (2.0 g, 10.80 mmol), [Pd-(PPh_3)$_2Cl_2$] (75.8 mg, 0.10 mmol), PPh_3 (56.6 mg, 0.21 mmol), CuI (42 mg, 0.20 mmol) were dissolved in Et_3N (30 mL). The mixture was stirred at RT for 10 min. Ethynyltrimethylsilane (1.65 mg, 17.2 mmol, 2.4

mL) was added through a syringe and the mixture was heated at reflux at 90℃ for 8 h. After completely consumption of the starting material, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether=3:1, v/v) to give a yellow solid (1.37 g, 71.6 %). K_2CO_3 (3.2 g, 23.0 mmol) was added to a solution of the above trimethylsilane-protected intermediate (1.37 mg, 7.5 mmol) in methanol (50 mL), the mixture was stirred at RT for 2 h. After completely consumption of the starting material, deionized water was added. The mixture was extracted with CH_2Cl_2 (4×50 mL). The organic phase was dried over Na_2SO_4. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether=2:1, v/v) to give **9** as a light yellow solid (653mg, 66.0 %).;^{1}H NMR (400 MHz, $CDCl_3$): d=10.04 (s, 1 H), 7.85 (d, 2H, J=8.0 Hz), 7.65 (d, 2H, J=8.0 Hz), 3.31 ppm (s, 1H); TOF ESI-HRMS: m/z calcd for $[C_9H_6O]^+$: 130.0419; found: 130.0414.

Synthesis of the Compound 10. A mixture of *p*-hydroxybenzaldehyde (2.44 g, 20.0 mmol) and K_2CO_3 (5.53 g, 40 mmol) were dissolved in EtOH (30 mL). The mixture was at 70 °C for 30 min, then 1,2-dibromoethane (7.43 g, 40.0 mmol) was added. The mixture was stirred and refluxed for 6 h. The reaction mixture was concentrated under reduced pressure to give yellow solid. Then the solid was dissolved in CH_2Cl_2, dried over anhydrous Na_2SO_4, then filtrated. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, CH_2Cl_2 : petroleum ether = 1:2, v/v) to give **10** as white solid. Yield: 2.50 g (60.0 %). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 9.90 (s, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.39 (t, *J* = 12.0 Hz, 2H), 3.69 (t, *J* = 12.0 Hz, 2H). TOF HRMS EI$^+$ calcd ($[C_{21}H_{19}BF_2N_2]$) *m/z* = 348.1609, found *m/z* = 348.1617.

Synthesis of the Compound 11. Compound **10** (2.50 g, 11.0 mmol) and NaN_3 (0.90 g, 12.0 mmol) were dissolved in DMF (5 mL), then the reaction mixture was stirred and refluxed for 2 h. The solution was cooled to RT and diluted with CH_2Cl_2, washed with water and the organic layer was dried over anhydrous Na_2SO_4. The mixture was filtrated and the solvent was removed under reduced pressure to give a yellow oil. Yield: 1.67 g (79.8%). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 9.89 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.24 (t, *J* = 8.0 Hz, 2H), 3.67 (t, *J* = 12.0 Hz ,2H). TOF HRMS EI$^+$: calcd ($[C_8H_9N_3O_2]$) *m/z* = 191.0695, found, *m/z* = 191.0698.

2. Molecular structure characterization data

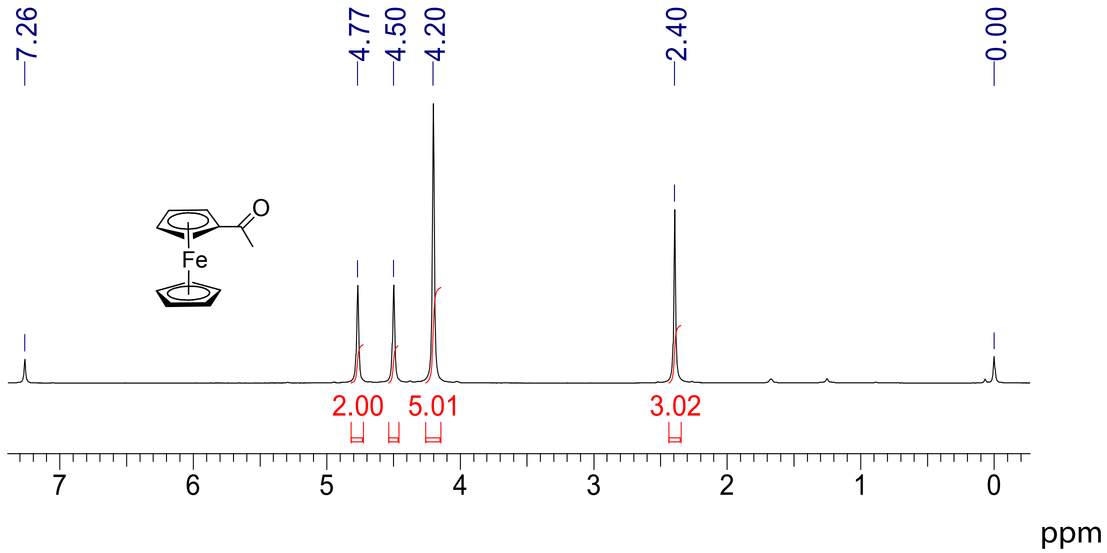
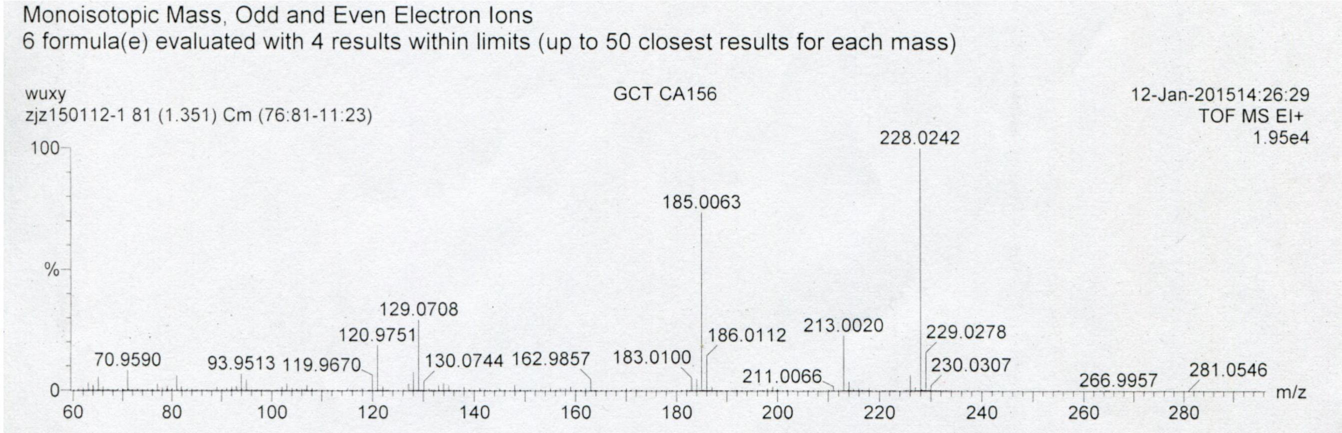


Figure S1. ^{1}H NMR of **1** (500 MHz, $CDCl_3$).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GCT CA156

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Figure S2. TOF ESI-HRMS of **1**.

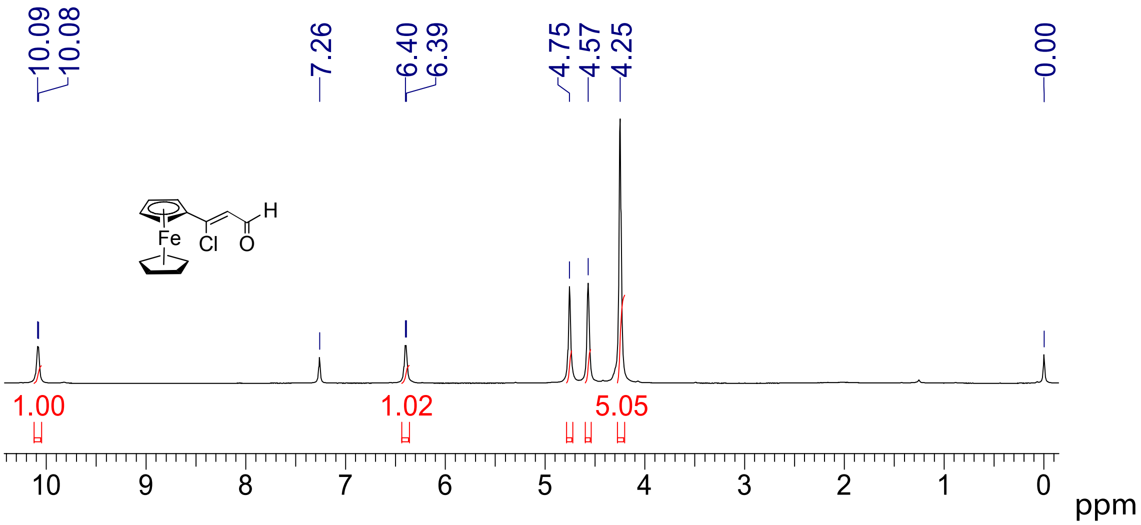


Figure S3. ^{1}H NMR of **2** (500 MHz, $CDCl_3$).

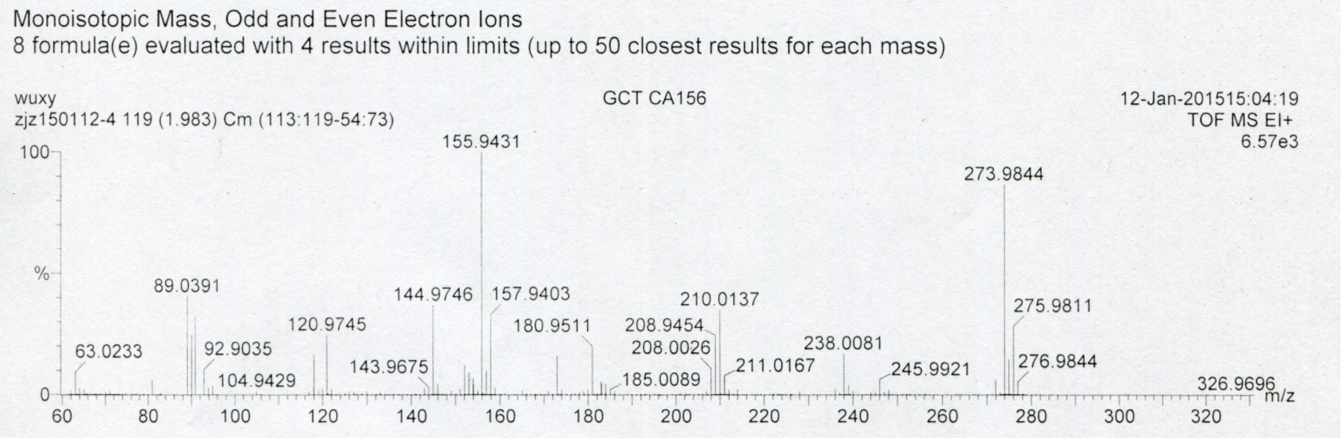


Figure S4. TOF ESI-HRMS of **2**.

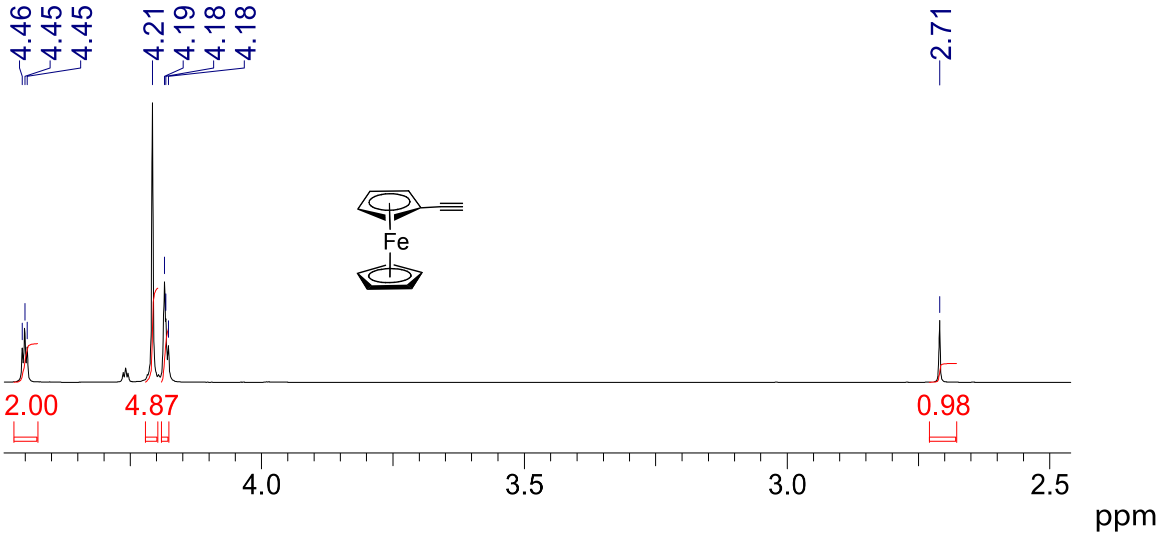
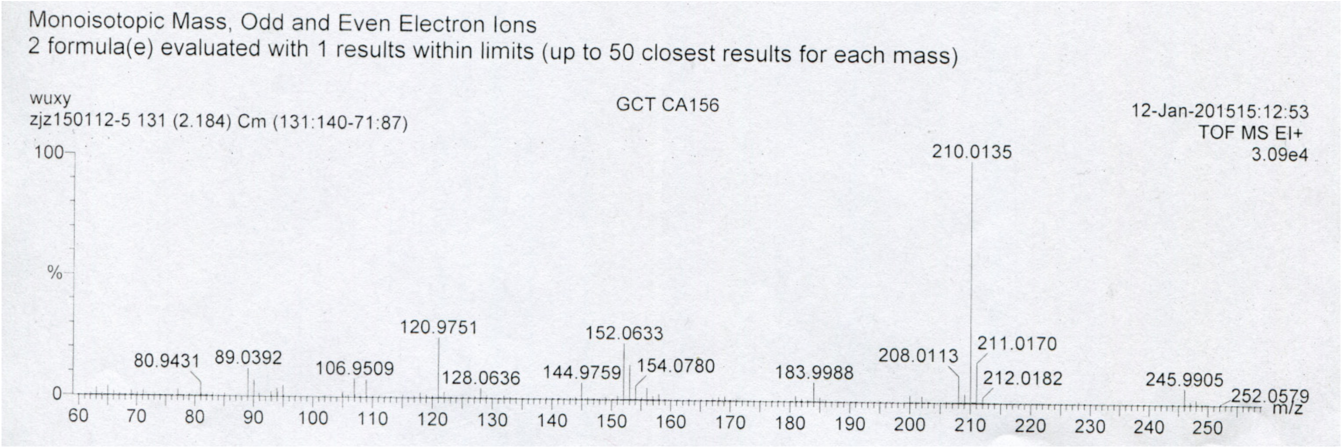


Figure S5. ^{1}H NMR of **3**(400 MHz, $CDCl_3$).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2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

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Figure S6. TOF ESI-HRMS of **3**.

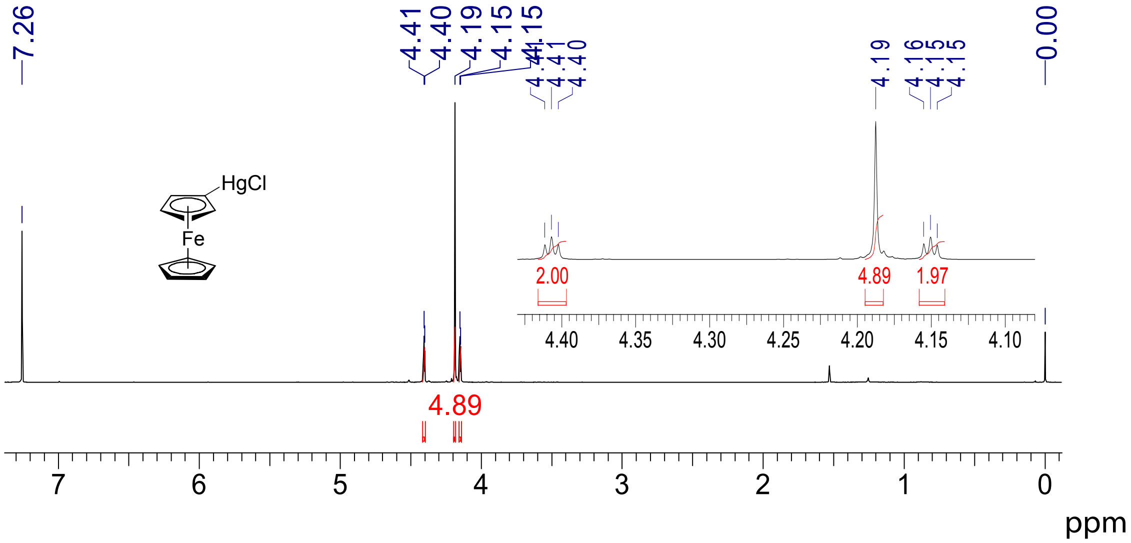


Figure S7. ^{1}H NMR of **5** (400 MHz, $CDCl_3$).

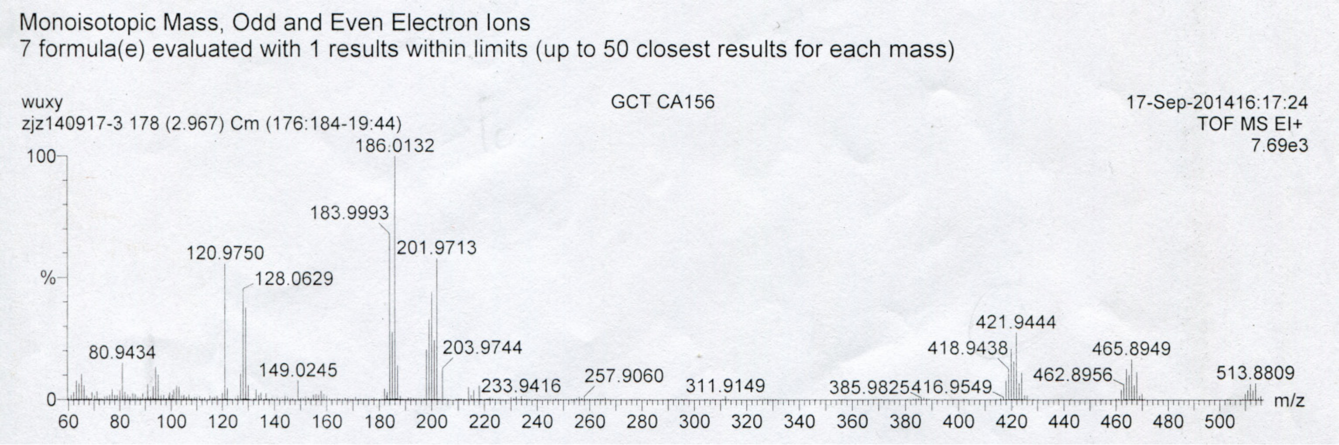


Figure S8. TOF ESI-HRMS of **5**.

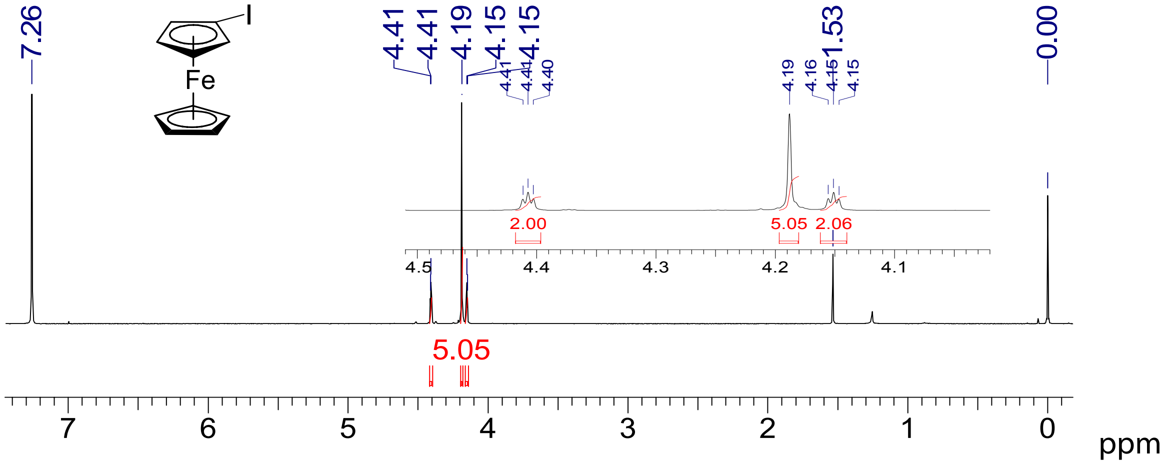


Figure S9. ^{1}H NMR of **7** (400 MHz, $CDCl_3$).

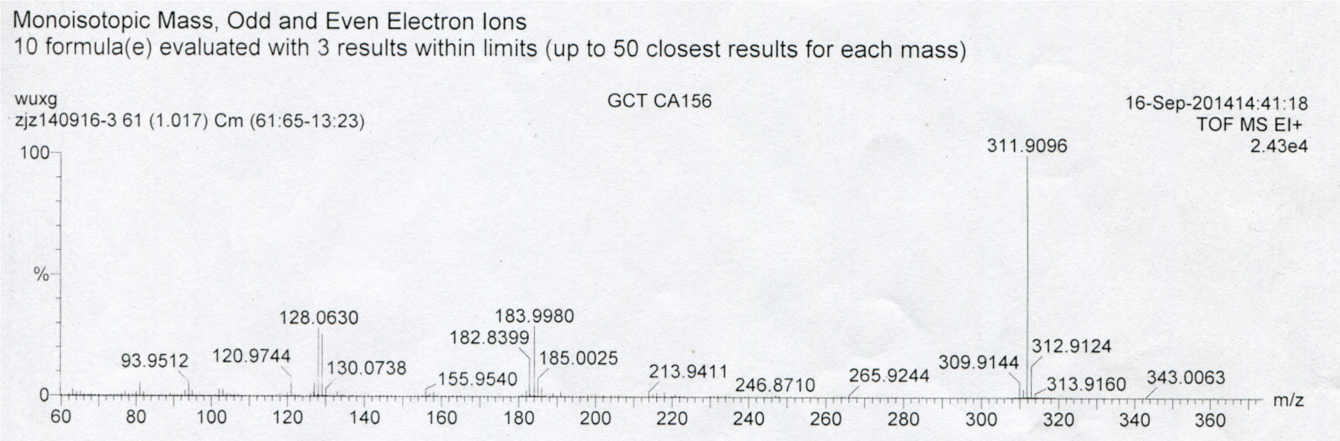


Figure S10. TOF ESI-HRMS of **7**.

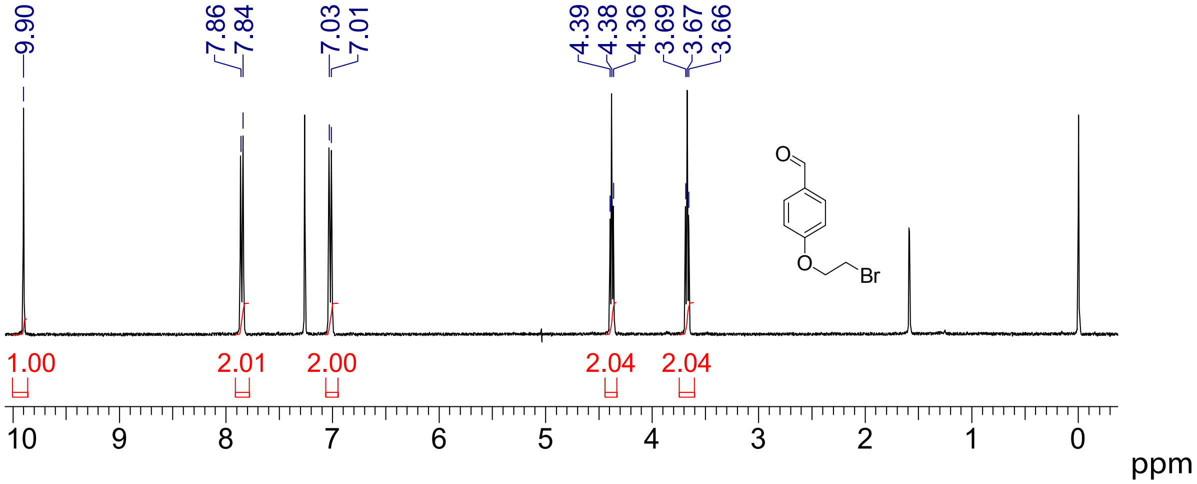


Figure S11. ^{1}H NMR of **8** (400 MHz, $CDCl_3$).

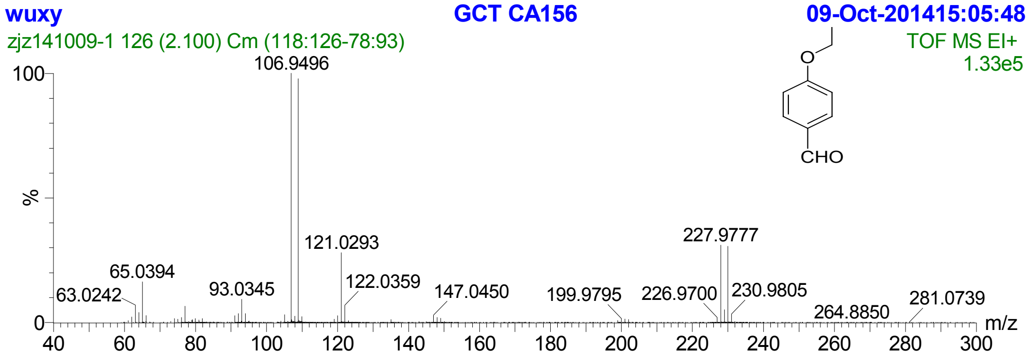


Figure S12. TOF ESI-HRMS of **8**.

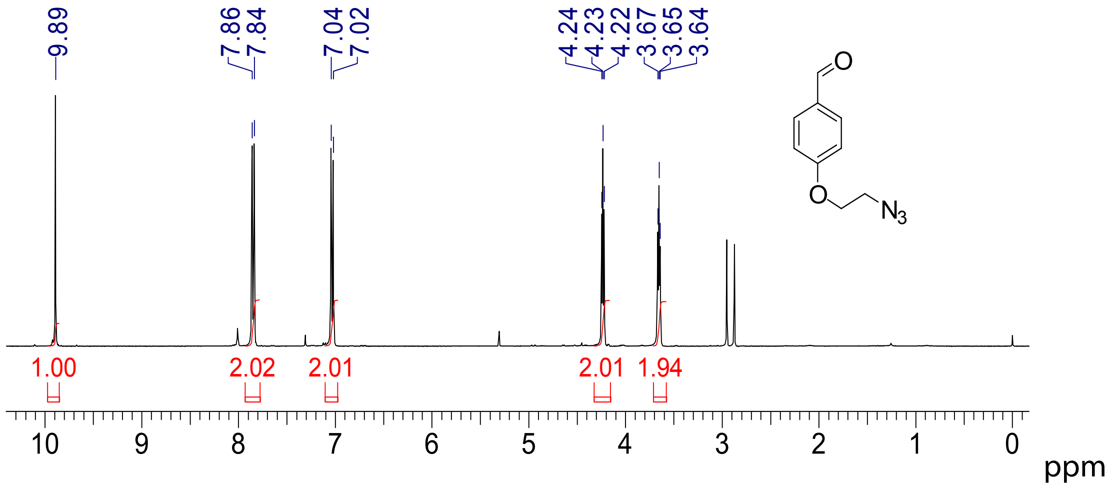


Figure S13. ^{1}H NMR of **9** (400 MHz, $CDCl_3$).

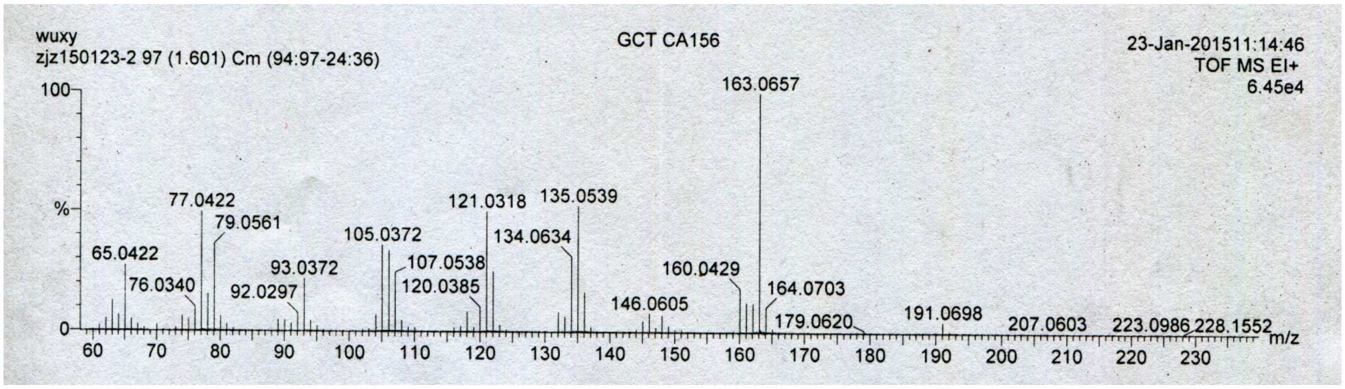


Figure S14. TOF ESI-HRMS of **9**.

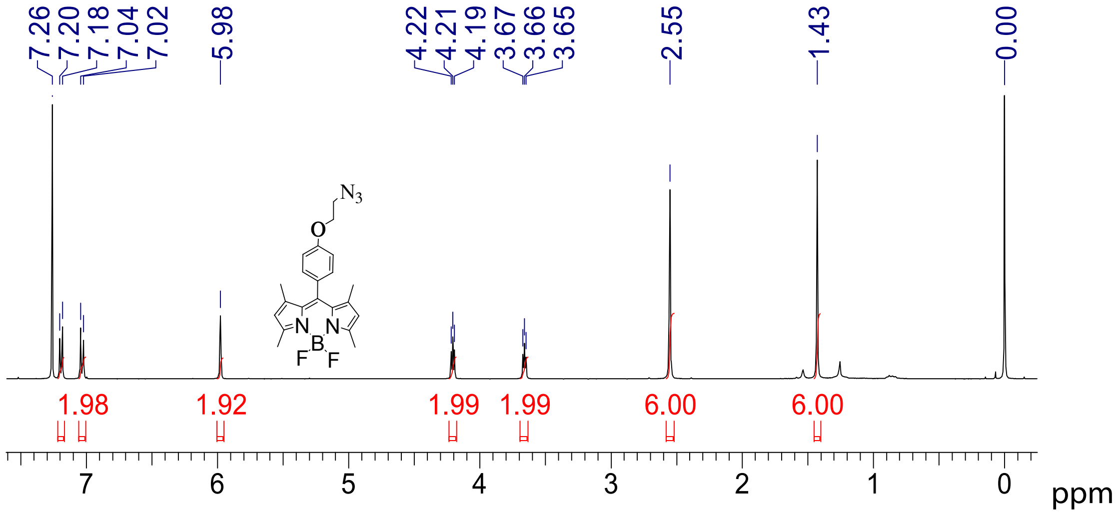


Figure S15. ^{1}H NMR of **B–1** (400 MHz, $CDCl_3$).

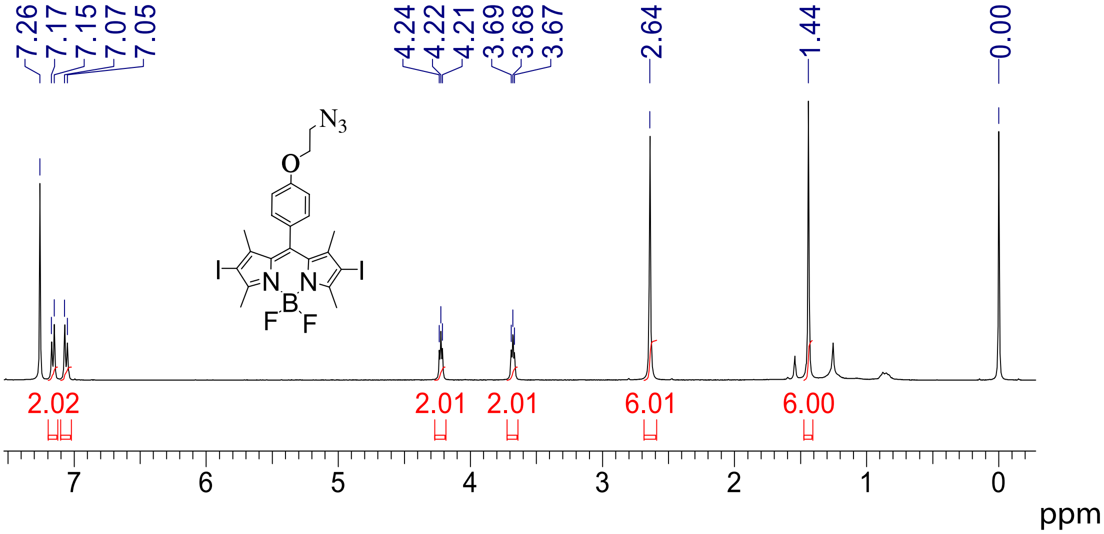


Figure S16. ^{1}H NMR of **B–2** (400 MHz, CDCl$_3$).

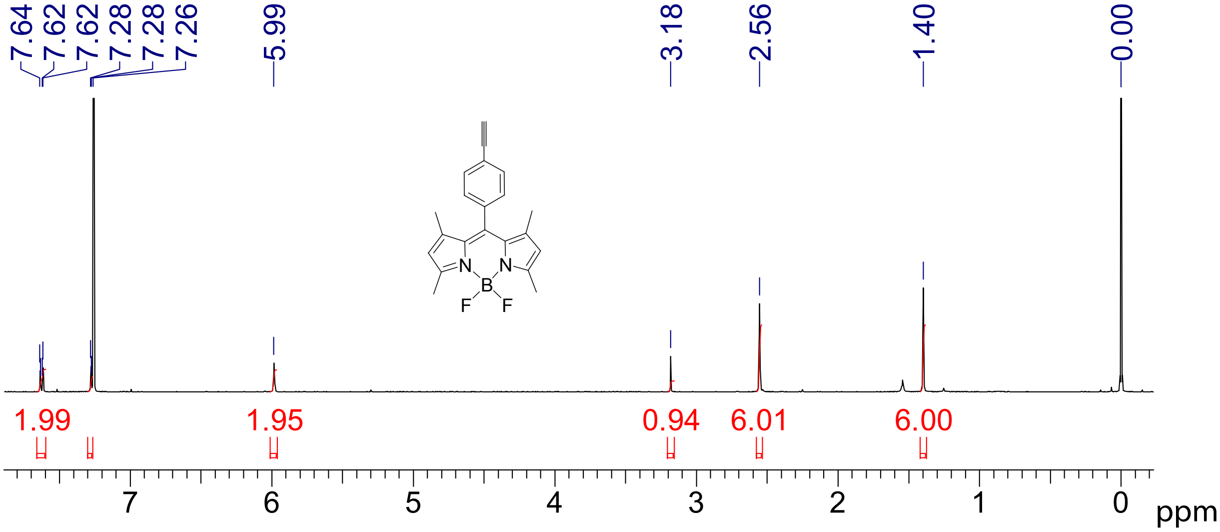


Figure S17. ^{1}H NMR of **B–3** (400 MHz, CDCl$_3$).

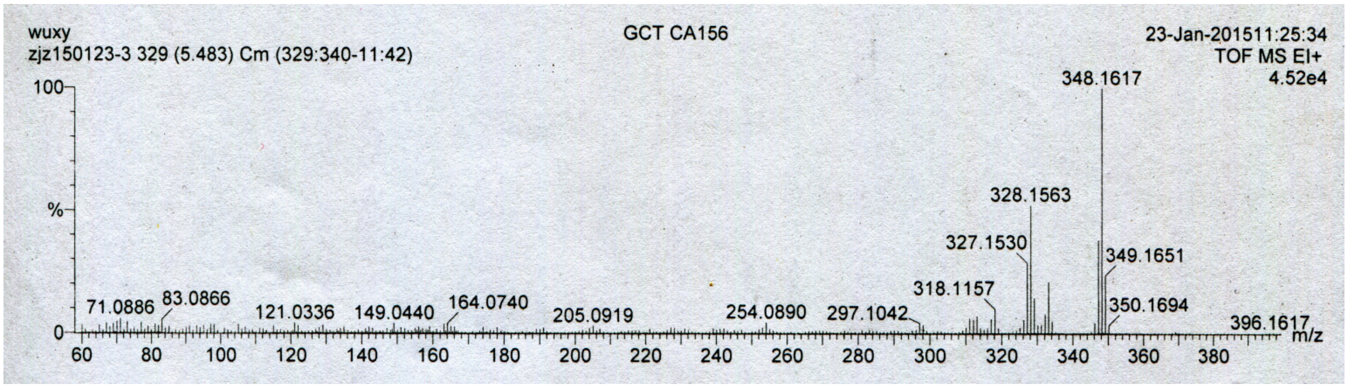


Figure S18. TOF ESI-HRMS of **B-3**.

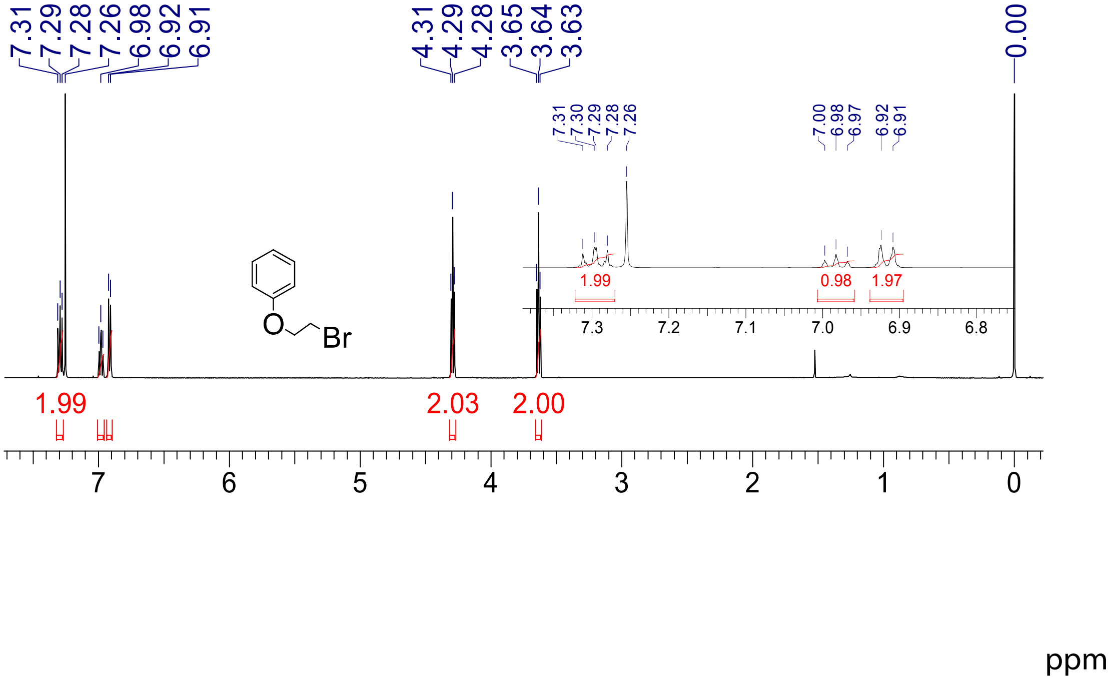


Figure S19. ^{1}H NMR of **12** (400 MHz, $CDCl_3$).

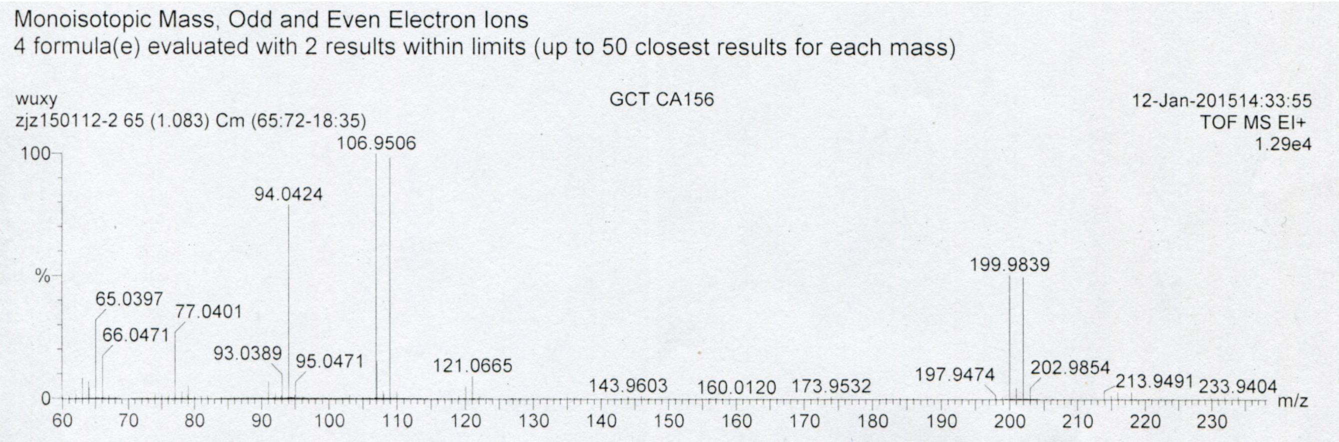


Figure S20. TOF ESI-HRMS of **12**.

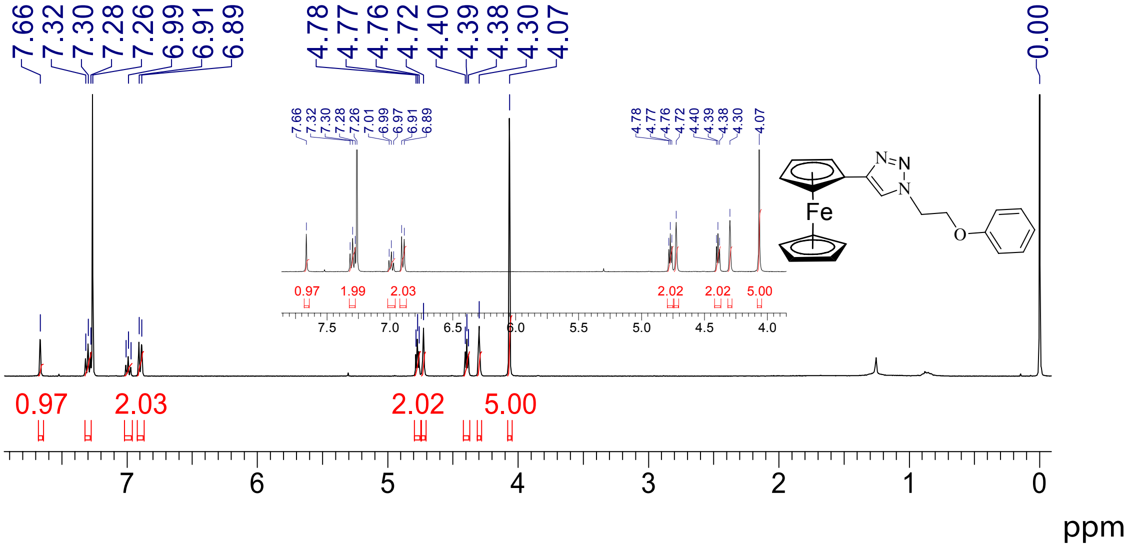


Figure S21. ^{1}H NMR of **FcB–0** (400 MHz, CDCl$_3$).

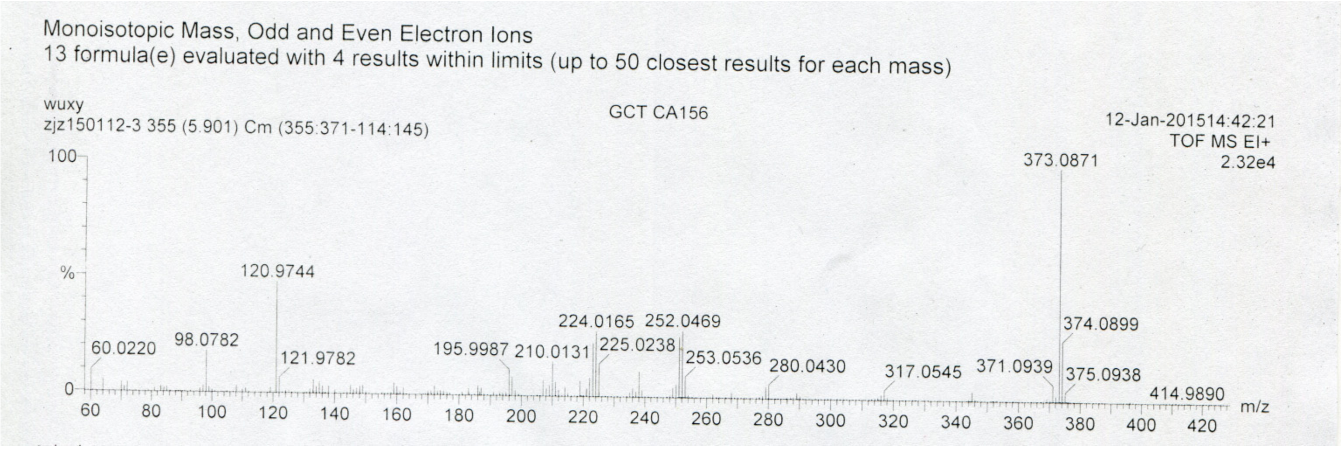


Figure S22. TOF ESI-HRMS of **FcB–0**.

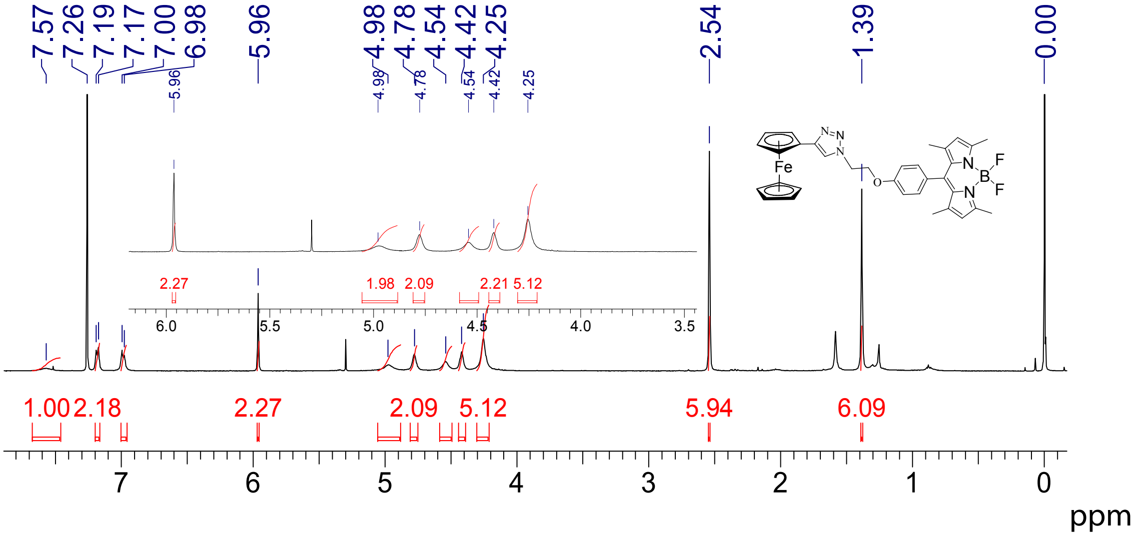


Figure S23. ^{1}H NMR of **FcB–1** (400 MHz, CDCl$_3$).

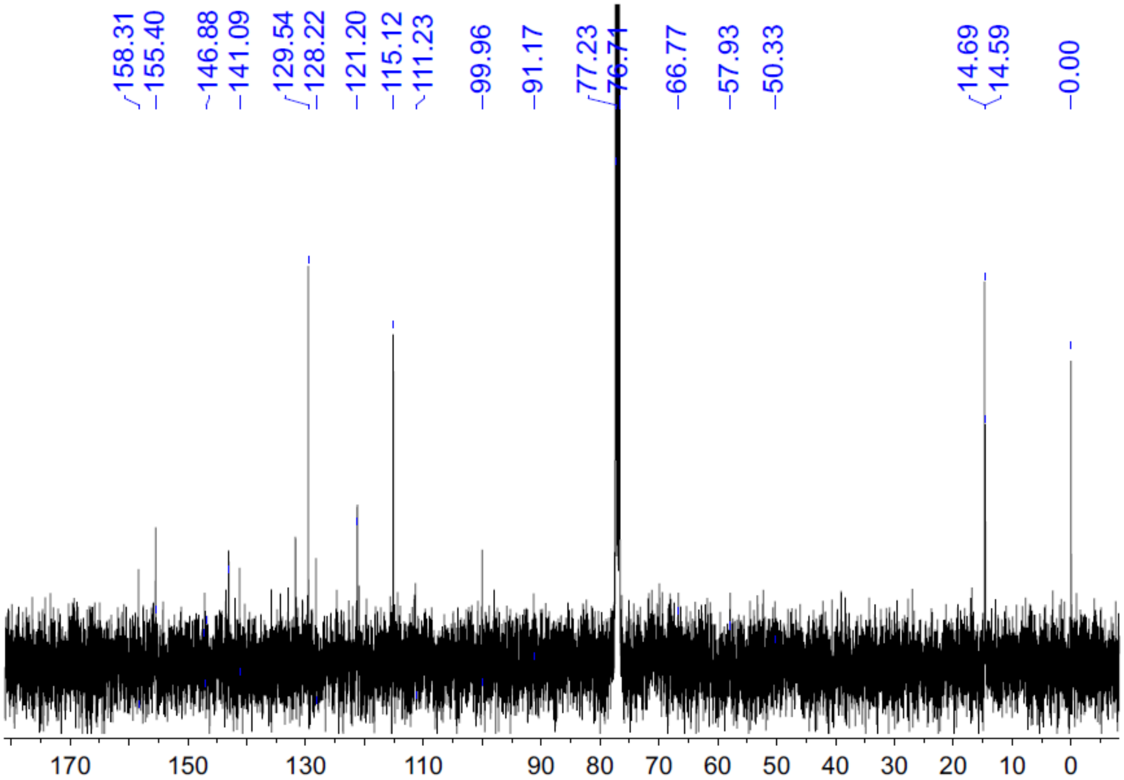


Figure S24. ^{13}C NMR of **FcB–1** (100 MHz, $CDCl_3$).

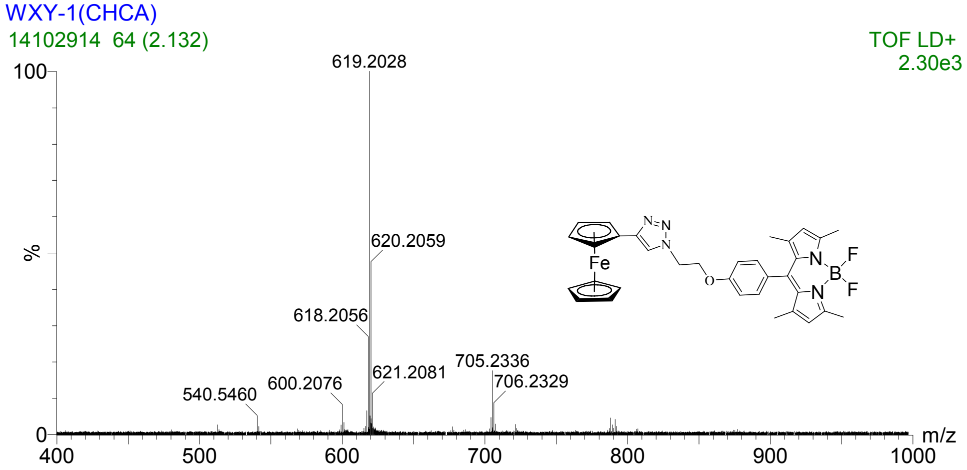


Figure S25. MALDI-HRMS of **FcB–1**.

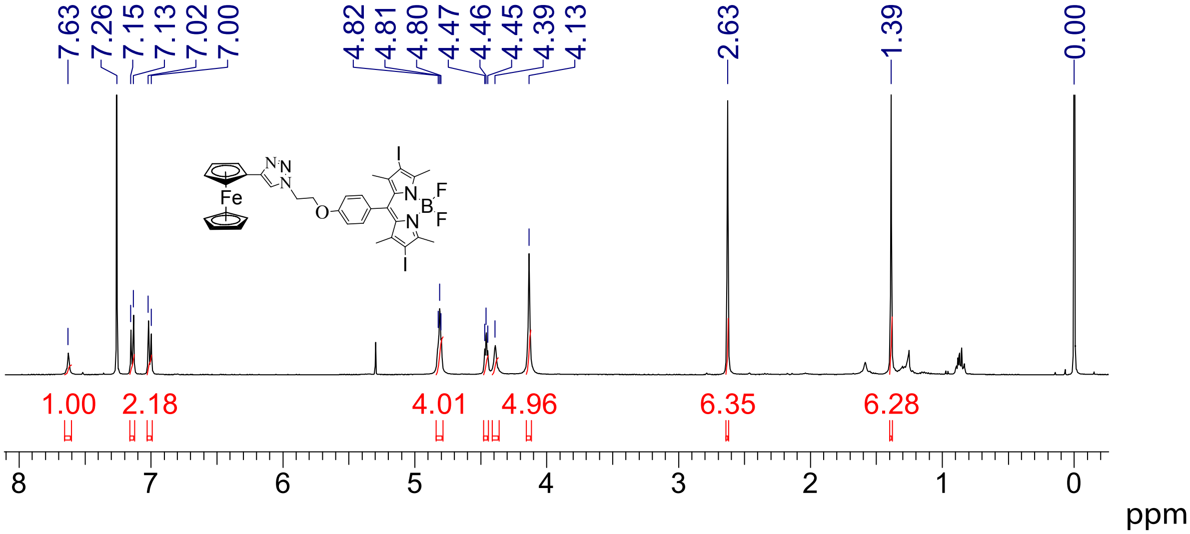


Figure S26. ^{1}H NMR of **FcB–2** (400 MHz, CDCl$_3$).

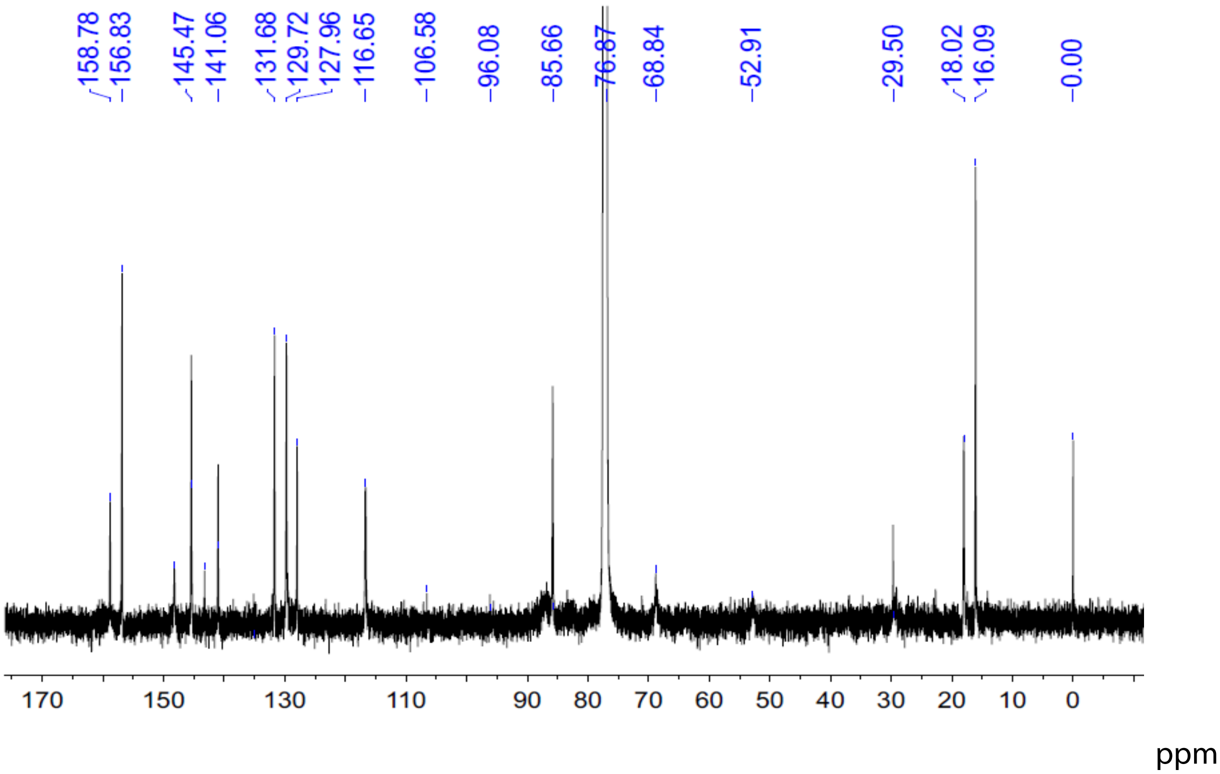


Figure S27. ^{13}C NMR of **FcB–2** (100 MHz, CDCl$_3$).

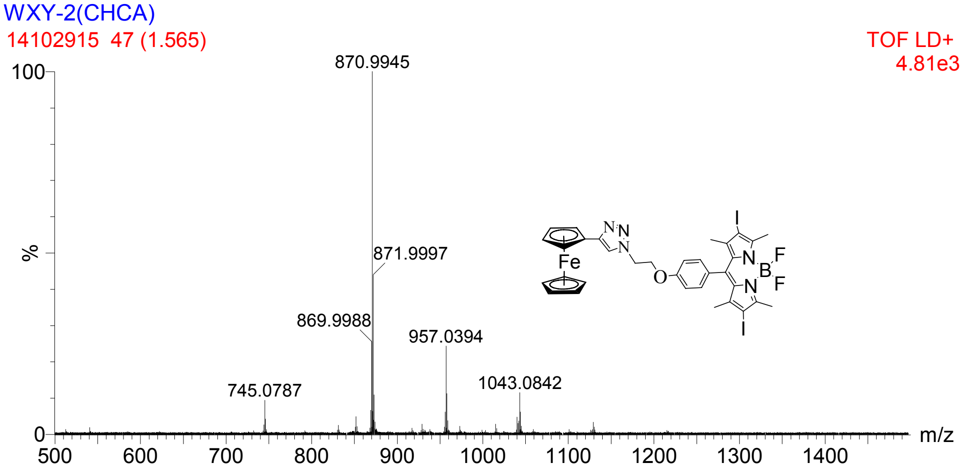


Figure S28. MALDI-HRMS of **FcB–2**.

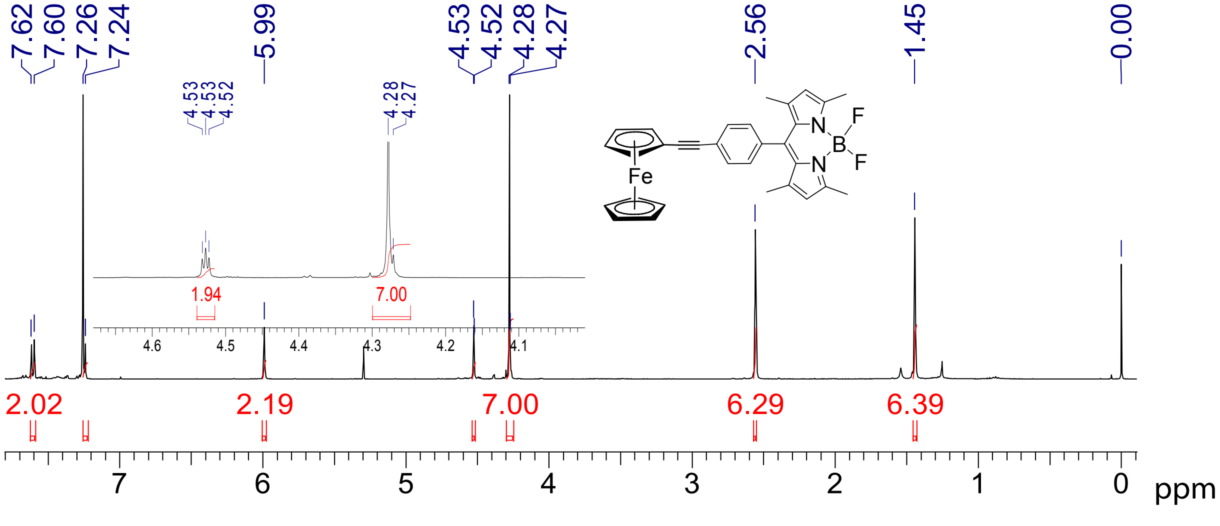


Figure S29. ^{1}H NMR of **FcB–3** (400 MHz, $CDCl_3$).

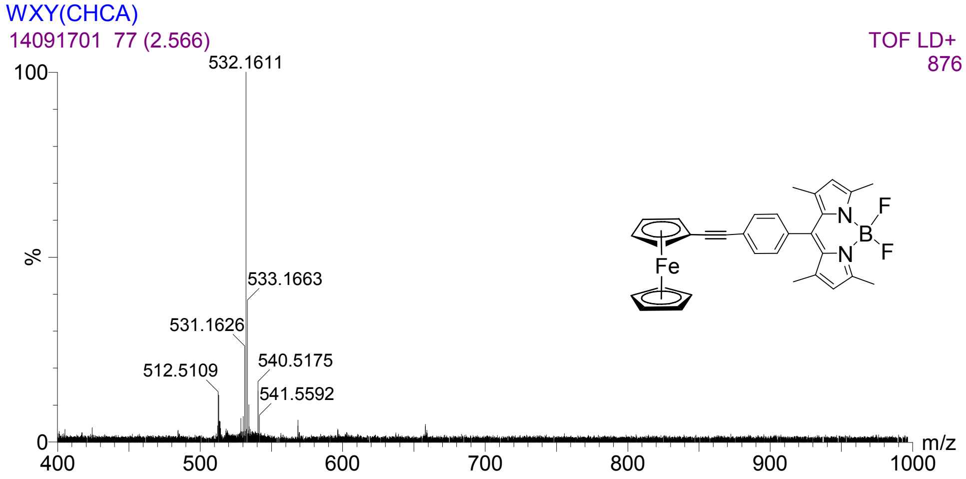


Figure S30. MALDI-HRMS of **FcB–3**.

3.UV–vis absorption and fluorescence emission spectra of the dyads

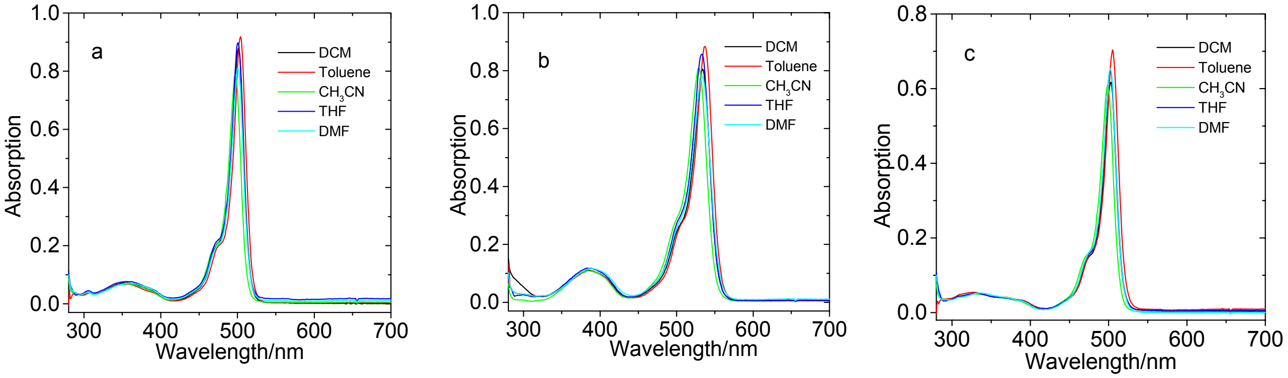


Figure S31. UV-Vis absorption of (a) **B–1**,(b) **B–2**,(c) **B–3** in DCM, Toluene, CH_3CN, THF and DMF. c = 1.0×10^{-5} M, 20 °C.

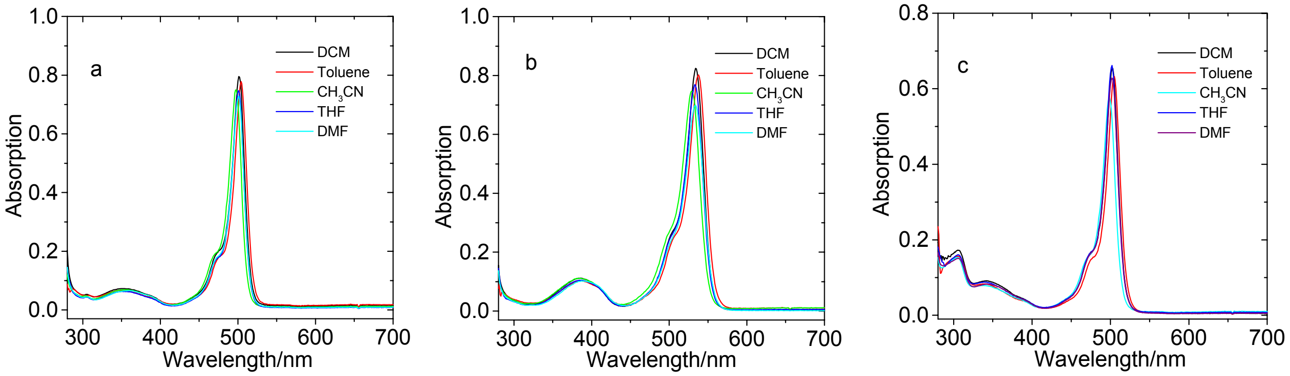


Figure S32. UV-Vis absorption of (a) **FcB–1**,(b) **FcB–2**,(c) **FcB–3** in DCM, Toluene, CH_3CN, THF and DMF. c = 1.0×10^{-5} M, 20 °C.

4. Electrochemical studies of the dyads

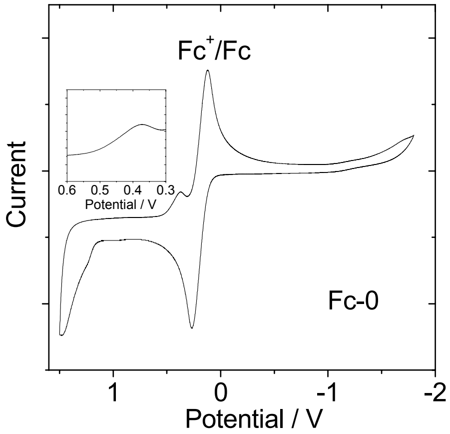


Figure S33. Cyclic voltammogram of **FcB–0** ($c = 5.0 \times 10^{-4}$ M). In deaerated CH_2Cl_2 solutions containing the compounds, 0.10 M Bu_4NPF_6 as supporting electrode, $Ag/AgNO_3$ as reference electrode, Scan rates: 100 mV/s. For all compound Ferrocene (Fc) ($c = 1.0 \times 10^{-5}$ M) was used as internal reference. 20 °C.

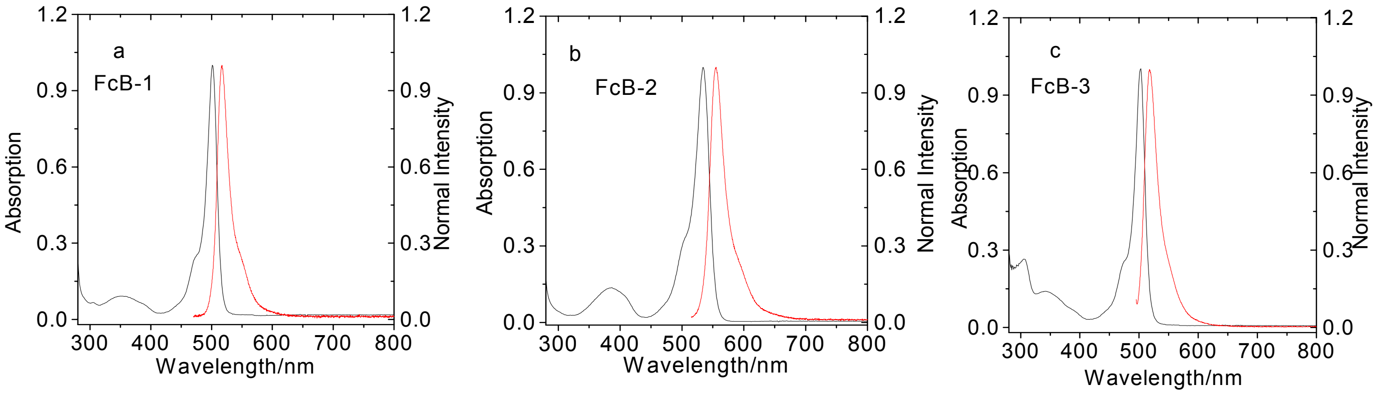


Figure S34. The intersection point of normalized absorption and emission spectra of (a) **FcB–1**, (b) **FcB–2** and (c) **FcB–3** in CH_2Cl_2. 20 °C. $E_{0,0}$ = energy level was estimated from intersection of normalized absorption and emission spectra.

In order to study the PET of the dyads, the Gibbs free energy changes of the PET processes of the dyads were calculated according to the Weller equation (Eq. 1 and Eq. 2).

$$\Delta G^{0}{}_{\mathrm{CS}} = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_{\mathrm{S}} \qquad \text{(Eq. 1)}$$

$$\Delta G_{\mathrm{S}} = -\frac{e^2}{4\pi\varepsilon_{\mathrm{S}}\varepsilon_0 R_{\mathrm{CC}}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{R_D}+\frac{1}{R_{\mathrm{A}}}\right)\left(\frac{1}{\varepsilon_{REF}}-\frac{1}{\varepsilon_S}\right) \qquad \text{(Eq. 2)}$$

Where ΔG_S is the static Coulombic energy, which is described by eq. 2. e= electronic charge, E_{OX} = half-wave potential for one-electron oxidation of the electron-donor unit, E_{RED} = half-wave potential for one-electron reduction of the electron-acceptor unit; note herein the anodic and cathodic peak potentials were used because in some cases the oxidation is irreversible therefore the formal $E_{0,0}$ = energy level was estimated from intersection of normalized absorption and emission spectra in CH_2Cl_2 (for the singlet excited state). Potential $E_{1/2}$ cannot be derived; ε_S = static dielectric constant of the solvent, R_{CC} = center-to-center separation distance between the electron donor (Fc unit) and electron acceptor (Bodipy unit), determined by DFT optimization of the geometry R_{CC} (**FcB–1**) = 16.6 and R_{CC} (**FcB–3**) = 12.8. R_D is the radius of the **3** based donor, R_A is the radius of the electron acceptor, ε_{REF} is the static dielectric constant of the solvent used for the electrochemical studies, ε_0 permittivity of free space($8.85\times10^{-12}m^{-3}\ kg^{-1}s^{4}\ A^{2}$). The solvents used in the calculation of free energy of the electron transfer are toluene (ε_S = 2.4), CH_2Cl_2 (ε_S = 9.1), CH_3CN (ε_S = 37.5). 20 °C.

Based on these parameters, for **FcB–1** in CH_2Cl_2, ΔG_S is calculated as –0.09 eV.

If the electron transfer from the energy donor to the acceptor occurs at the singlet excited state of energy donor (reference unit B–1), then $E_{0,0}$ of compound B–1 is approximate as 2.44 eV. (1240/509 = 2.44 eV)
With reference B–1 as electron acceptor, the $\Delta G^{o}{}_{CS}$ = 0.19– (–1.53) – 2.44– 0.09= –0.81 eV.

Based on these analysis, the intramolecular electron transfer in **FcB–1** is much significant from energy donor (**3**)to energy acceptor (**B–1**) at the singlet excited state.

Based on these parameters, for **FcB–3**in CH_2Cl_2, ΔG_S is calculated as–0.288 eV.

If the electron transfer from the energy donor to the acceptor occurs at the singlet excited state of energy donor (reference unit B–3), then $E_{0,0}$ of compound B–3 is approximate as 2.43 eV. (1240/509 = 2.43 eV)
With reference B–3 as electron acceptor, the $\Delta G^{o}{}_{CS}$ = 0.32– (–1.50) – 2.43– 0.288 = –0.90 eV.

Based on these analysis, the intramolecular electron transfer in **FcB–3** is much significant from energy donor (**7**) to energy acceptor (**B–3**) at the singlet excited state.

5. Switching of the Fluorescence of the Dyads

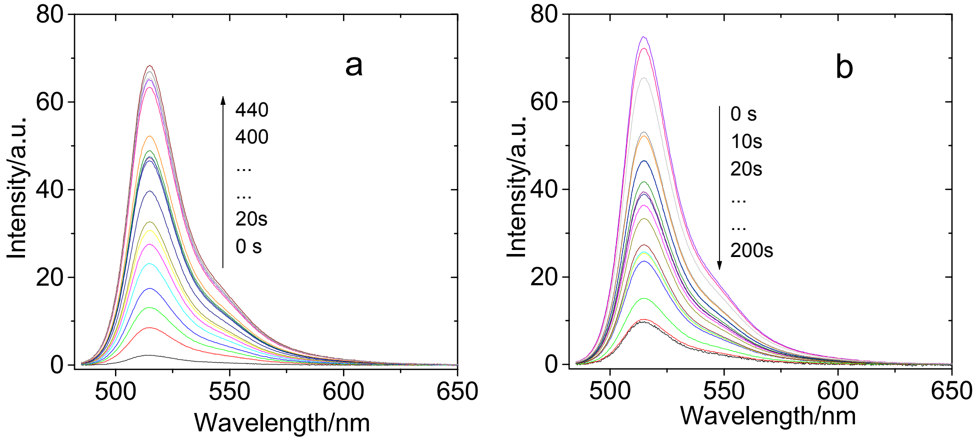


Figure S35. The fluorescence intensity changes of **FcB–3** (λ_{ex} =480nm).(a) upon oxidation under 0.9 V versus Ag/AgNO$_3$ (from neutral state to oxidative state). (b) upon reduction under -0.2 V versus Ag/AgNO$_3$ (from oxidative state to neutral state).Potentials were applied with a CHI610d electrochemical workstation. The sample solutions contained the compound **FcB–3** (5.0×10^{-4} M) and 0.1 M [Bu$_4$N][PF$_6$] as the supporting electrolyte in CH$_3$CN,20 °C.

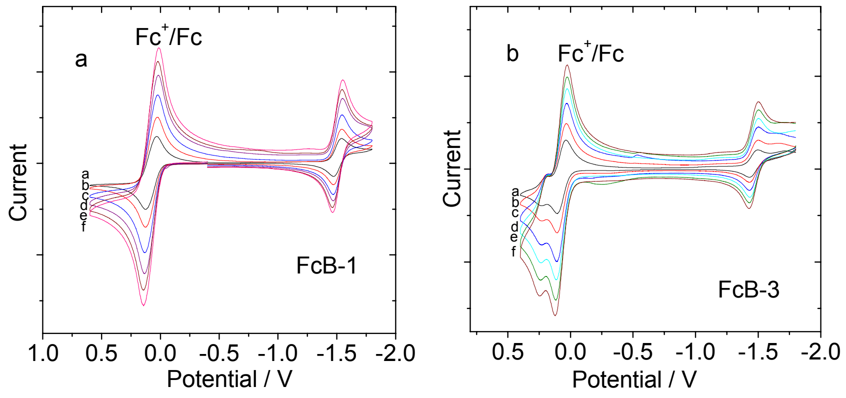


Figure S36. Cyclic voltammogram of (a) **FcB–1**, (b) **FcB–3**. c = 2.0×10^{-3} M. In deaerated CH$_3$CN solutions containing the compound, 0.10 M Bu$_4$NPF$_6$ as supporting electrode, Ag/AgNO$_3$ reference electrode. Ferrocene (Fc) was used as internal reference. Different scanning rates were used to check the reversibility of the system: (a) 0.05 V s$^{\square 1}$ (b) 0.10 V s$^{\square 1}$; (c) 0.20 V s$^{\square 1}$; (d) 0.30 V s$^{\square 1}$; (e) 0.40 V s$^{\square 1}$; (f) 0.50 V s$^{\square 1}$. 20 °C.

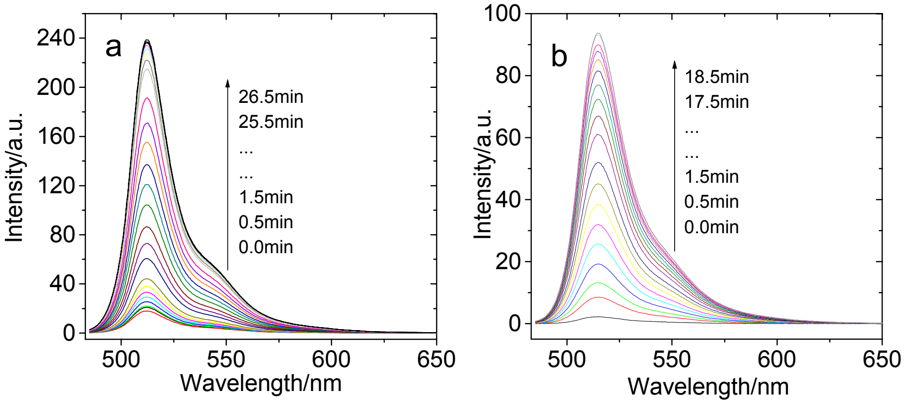


Figure S37. Fluorescence emission spectra of (a)**FcB–1** and(b)**FcB–3** recorded after the addition of one equivalent of $Fe(ClO_4)_3$ .Spectra were recorded at the beginning every minute until the fluorescence intensity not change.

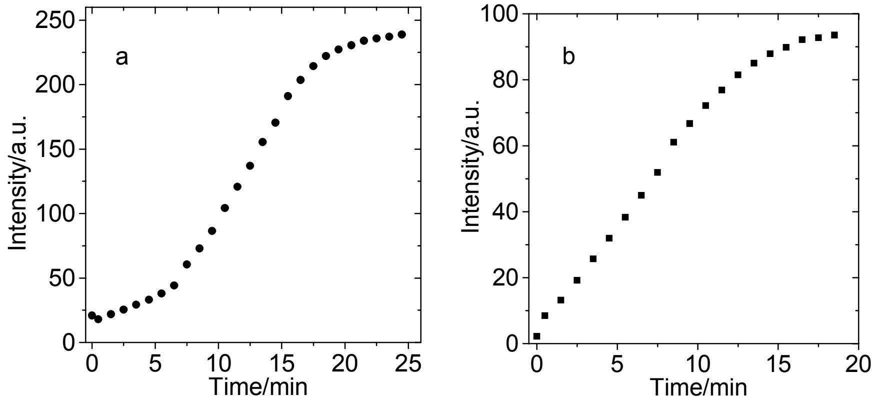


Figure S38. (a) Evolution of the fluorescence intensity of **FcB–1** versus time monitored at 512nm (c = 1.0×10^{-5} M in THF, λ_{ex} =480 nm).(b). Evolution of the fluorescence intensity of **FcB–3** versus time monitored at 514nm (c = 1.0×10^{-5} M in THF, λ_{ex} =489 nm). 20℃.

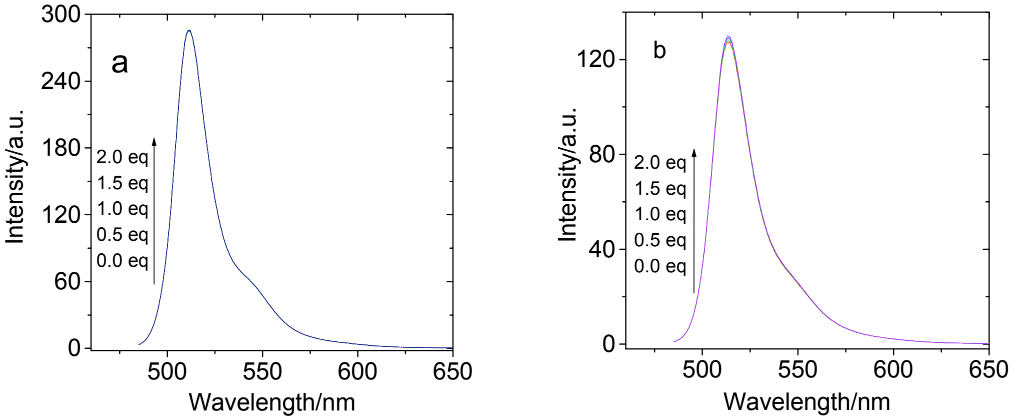
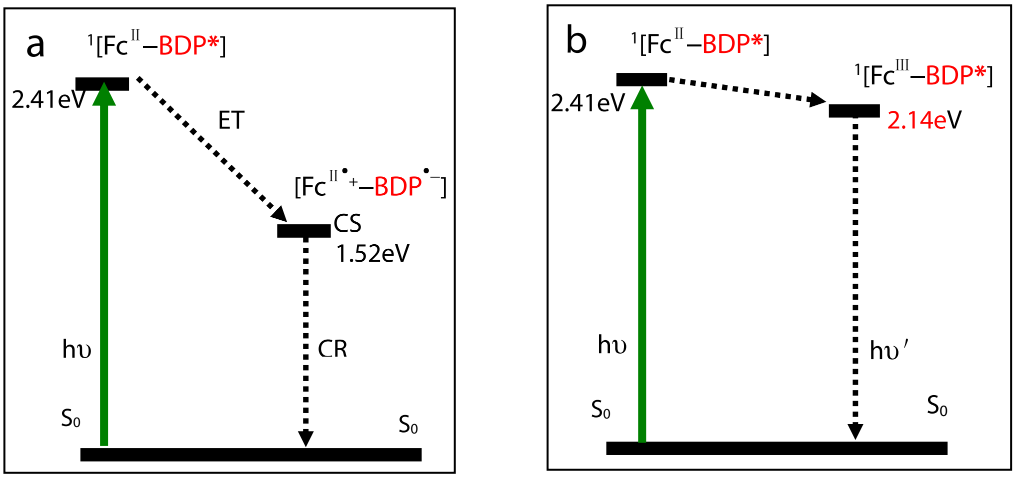


Figure S39. Fluorescence spectra of (a) **B–1** (c = 1.0×10^{-5} M), (b) **B–3** (c = 1.0×10^{-5} M) in THF in the presence of different amounts of $Fe(ClO_4)_3$,(λ_{ex} = 480nm). 20 °C.

Scheme S1. Simplified Jablonski Diagram Illustrating the Photophysical Processes Involved in (a) Fc–BDP and (b) Fc–BDP after oxidation [a]



[a] Keys: [Fc^{II}–BDP] stands for Fc–BDP in the natural state. [Fc^{III}–BDP] stands for Fc–BDP in the oxidative state. CS stands for charge-transfer state. CR stands for charge recombination. ET stands for electron transfer. The localization of the excited state in dyads is designated in red. The number of the superscript designates the spin multiplicity.

6. Nanosecond transient difference absorption spectra

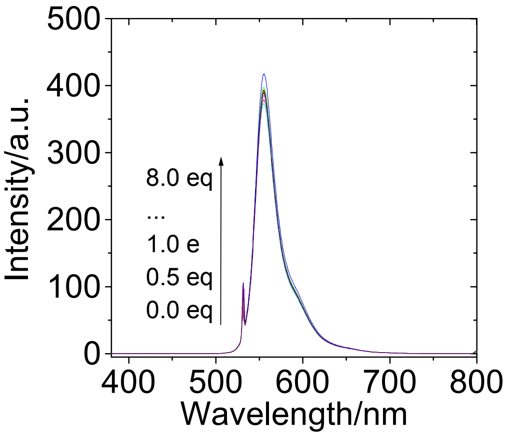


Figure S40. Triplet-triplet annihilation upconversion with **FcB-2** as the triplet photosensitizer and perylene as the triplet energy acceptor. Excited with 532 nm continuous laser (5.2 mW). *c* **[FcB–2]** = 1.0 × 10^{-5} M in deaerated toluene, 20 °C.

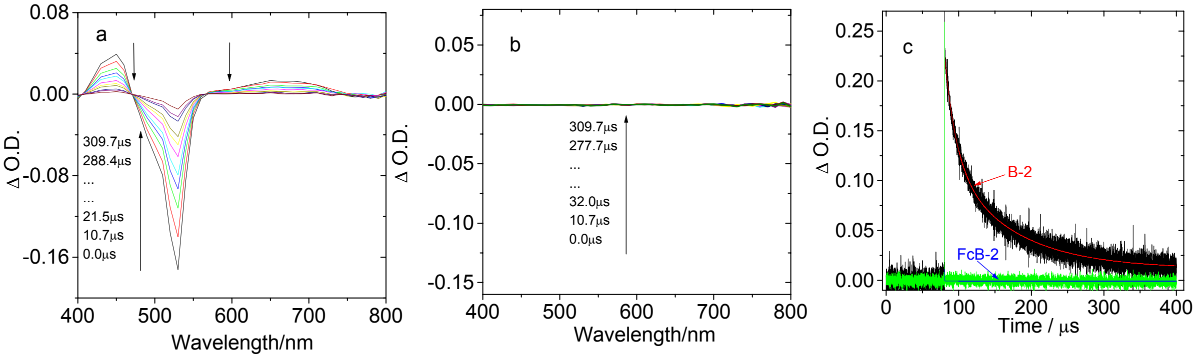


Figure S41. Comparison of the nanosecond transient absorption spectroscopy of (a) **B–2** and (b) **FcB–2** (c) Decay trace of the transient of **B–2** and **FcB–2** at 525 nm. Excited with 532 nm nanosecond pulsed laser. *c* = 1.0 × 10^{-5}M in deaerated CH_3CN, 20 °C.

Table S1. Quenching of the Lifetime of B–2 with Ferrocene.

$c_{[\text{ferrocene}]}$ [a]	0	0.1	0.2	0.5	0.75	1.0	1.5	2.0	2.5	3.0	4.0	5.0
$\tau_{\text{B-2}}$/μs [b]	83.96	47.74	38.41	22.49	19.69	14.18	9.71	7.36	6.07	5.15	3.94	3.15
$\tau_{\text{B-2}}$/μs [c]	76.23	42.57	26.51	16.87	12.75	7.01	4.75	3.98	3.19	2.51	1.91	1.53

[a] *c* [ferrocene] : 10^{-5} M. Pulsed excitation (λ_{ex} = 515 nm), The lifetime of the triplet excited states of **B-2**, [b] In deaerated toluene, [C] In deaerated CH_3CN, 25 °C.

Table S2. Triplet excited state lifetimes (τ_T), Stern-Volmer quenching constant (K_{SV}) and bimolecular quenching constants (k_q) of the B–2 sensitizers. In deaerated toluene and CH_3CN solution,Excited with 515 nm, 25 °C.

	τ_T / μs [a]	K_{sv} / 10^3 M^{-1}	k_q / 10^9 M^{-1} s^{-1}
Toluene	83.96	509.17± 14	6.06 ± 0.17
CH_3CN	76.23	984.54± 19	12.92 ± 0.22