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Supplementary Information

PET-based BisBODIPY photosensitizers for Highly efficient excited triplet state and singlet oxygen generation: Tuning photosensitizing ability by the dihedral angles

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Table S1. Photophysical properties of dimer d1, d2, d3, and d4 in different solvents*

	Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ_f	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
d1	n-hexane	501,523	511,556	0.16	6.25		
	toluene	526	558s	0.013	2.20(84%)	3.59	
	DCM	507	514	0.077	0.70(3%)	6.08	
	CH_3CN	485	510	0.059	0.30(56%)	5.6	
d2	n-hexane	505	545	0.86	4.31		
	toluene	509	517	0.0017	2.79(64%)	3.87	
	DCM	506	526	0.0014	2.53(31%)	6.07	
	CH_3CN	503	517	0.0033	2.13(44%)	5.89	
d3	n-hexane	506	523	0.0010	1.12(21%)	5.14	
	toluene	510	520w	0.0010	1.32(68%)	4.90	
	DCM	508	524	1.24E-04	1.07(73%)	5.09	
	CH_3CN	505	516	4.75E-05	0.96(56%)	5.30	
d4	n-hexane	508	524	0.91	5.04		
	toluene	510	529	0.22	0.49(3%)	5.96	
	DCM	507	527	0.0052	0.35(8%)	2.77(70%)	5.38
	EtOH	506	516	0.010	0.44(39%)	3.37	
	CH_3CN	504	523	0.0018	0.28(8%)	3.57(46%)	6.65

*****: The fluorescence quantum yields in Table S1 is for LE (local excited state emission) band.**

Table S2. fluorescence properties of TICT band for dimer d1, d2, d3, and d4*

	Solvent	λ'_{em} (nm)	Φ_f'	τ_1' (ns)	τ_2' (ns)
d1	DCM	551	0.012	1.11(7%)	6.09
	toluene	642	0.097	2.39	n.a.
d2	DCM	740	0.0036	0.53(96%)	4.38
	toluene	610	0.076	1.95	n.a.
d3	c-hexane	627	0.013	1.01(97%)	4.81
	DCM	n.a.	n.a.	n.a.	n.a.
	toluene	727	0.0099	1.62(94%)	4.80
d4	DCM	650	0.0098	2.68(92%)	4.31
	toluene	n.a.	0.042	n.a.	n.a.

***: n.a.=not available. fluorescence lifetime τ was measured at emission maximum of TICT band (λ'_{em}).

Experimental Details

General Methods. All reagents were purchased from TCI chemicals, Alfa Aesar, or Sigma-Aldrich, and used without further purification unless otherwise noted. NMR spectra were recorded using a Bruker 600 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the TMS. Mass spectral analyses were provided by Thermal Fisher Micromass Q-Tof spectrometer. UV-Vis absorption spectra were recorded on a Agilent 8454 spectrophotometer. Fluorescence spectra were recorded on a FLS 920 instrument of Edinburgh Instruments Ltd.

Photophysics. The absorption and fluorescence spectra, fluorescence quantum yields and excited singlet-state lifetimes, as well as triplet properties were investigated at room temperature ca 22 ^{o}C. Steady-state fluorescence spectra were acquired on a FLS 920 instrument. All spectra were corrected for the sensitivity of the photo-multiplier tube. The fluorescence quantum yield (Φ_f) was measured by using Eq. (1),[1]

$$\Phi_f = \Phi_f^0 \cdot \frac{F_s}{F_0} \cdot \frac{A_0}{A_s} \frac{n_s^2}{n_0^2}, \qquad \text{Eq. (1)}$$

in which **F** is the integrated fluorescence intensity, **A** is the absorbance at excitation wavelength, n is the refractive index of the solvent used, the subscript 0 stands for a reference compound and s represents samples. Fluorescein was used as the reference (Φ_f^0 = 0.92 in 0.1 M NaOH aq. solution).[2-3] Excitation wavelengths of 485 nm corresponding to the vibronic band of S_0 to S_1 transitions were employed for both fluorescein and BODIPYs. The sample and reference solutions were prepared with the same absorbance (A_i) at the excitation wavelength (near 0.09 per cm). All solutions were air saturated for Φ_f measurements. Since LE and ICT bands are mostly separated or not overlapped significantly, we could integrate the area under LE and ICT band respectively to calculate Φ_f for LE and Φ_f' for ICT emission.

Fluorescence lifetime of S_1 was measured by time-correlated single photon counting method (Edinburgh Instruments Ltd. FLS920 spectrophotometer) with excitation at 509 nm diode laser (169 ps FWHM) and fluorescence was monitored at emission maximum. The lifetime values were fit by the software F900 supplied by Edinburgh Instruments Ltd. Fluorescein was used as the reference (τ_f= 4.16 ns in 0.1 M NaOH aq. solution).[2-3]

Transient Absorption spectra were recorded in degassed solution (prepared by bubbling with Argon for 20 min) with an Edinburgh LP920 laser flash photolysis system. A Nd:YAG laser (Brio, 355 nm and 4 ns FWHM) was used as excitation source. The analyzing light was from a pulsed xenon lamp. The laser and analyzing light beams perpendicularly passed through a quartz cell with an optical path length of 1 cm. The signal was displayed and recorded on a Tektronix TDS 3012B oscilloscope and an R928B detector. The laser energy incident at the sample was attenuated to ca. 20 mJ per pulse. Time profiles at a series of wavelengths from which point by-point spectra were assembled were recorded with the aid of a Pc controlled kinetic absorption spectrometer. The concentrations of the target compounds were typically 20 μM providing A_{355} = 0.25 in a 10 mm cuvette.

The triplet–triplet absorption coefficients ($\Delta\varepsilon_T$) of the samples were obtained using the singlet depletion method,[4] and the following equation was used to calculate the $\Delta\varepsilon_T$.[4]

$$\Delta\varepsilon_T = \varepsilon_S \frac{\Delta A_T}{\Delta A_S} \qquad \text{Eq. (2)}$$

Where ΔA_S and ΔA_T are the absorbance change of the triplet transient difference absorption spectrum at the minimum of the bleaching band and the maximum of the positive band, respectively, and ε_S is the ground-state molar absorption coefficient at the UV-vis absorption band maximum. Both ΔA_S and ΔA_T were obtained from the triplet transient difference absorption spectra.

The triplet quantum yield Φ_T was obtained by comparing the ΔA_T of the optically matched sample solution at 355 nm in a 1 cm cuvette to that of the reference using the equation (3):[4]

$$\Phi_T = \Phi_T^{ZnPc} \cdot \frac{\Delta A_T}{\Delta A_T^{ZnPc}} \cdot \frac{\Delta\varepsilon_T^{ZnPc}}{\Delta\varepsilon_T}, \qquad \text{Eq. (3)}$$

Where the superscript represents the reference, ΔA_T is the absorbance of the triplet transient difference absorption spectrum at the selected wavelength, and $\Delta\varepsilon_T$ is the triplet state molar absorption coefficient. Zinc phthalocyanine (ZnPc) was used as the reference compound (its Φ_T=0.58 in toluene with 1% pyridine).[5]

Singlet oxygen chemical trapping. Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the chemical trapping method.[6] Typically, a 3 ml portion of the respective PS solutions that contained diphenylisobenzofuran (DPBF) was irradiated at 505 nm in an air saturated solvent. Φ_Δ value was obtained by the relative method using (Eq. 4):[6]

$$\Phi_\Delta = \Phi_\Delta^{ref} \frac{k}{k^{ref}} \frac{I_a^{ref}}{I_a}, \qquad \text{Eq. (4)}$$

where Φ_Δ^{ref} is the singlet oxygen quantum yield for the standard (8-methylthio-2,6-diiodoBODIPY, Φ_Δ^R=0.85, practically independent of the solvent) for excitation at 505 nm),[7] k and k^{ref} are the DPBF photo-bleaching rate constants in the presence of the respective samples and the standard 8-methylthio-2,6-diiodoBODIPY, respectively; I_a and I_a^{ref} are the rates of light absorption at the irradiation wavelength of 505 nm by the samples and the standard 8-methylthio-2,6-diiodoBODIPY, respectively. Their ratio can be obtained by Eq. (5).

$$\frac{I_a^{ref}}{I_a} = \frac{1-10^{-A_{ref}}}{1-10^{-A}}, \qquad \text{Eq. (5)}$$

In which, A and A_{ref} is the absorbance of a BODIPY and the reference compound 8-methylthio-2,6-diiodoBODIPY at excitation wavelength 505 nm, respectively. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of DPBF was lowered to ~4×10^{-5} mol dm^{-3}. A solution of sensitizer (absorbance ~0.80 at the irradiation wavelength) that contained DPBF was prepared in the dark and irradiated in the visible region (505 nm). DPBF degradation was monitored by UV-vis absorption spectrum. The error in the determination of Φ_Δ was ~10% (determined from several Φ_Δ values).

Electrochemistry. Cyclic voltammetry (CV) was carried out with an CHI600 potentiostat. A three-electrode system was used, and it consisted of a platinum disk working electrode, a platinum wire counter electrode, and a Ag^+/AgCl reference electrode ($AgNO_3$ 0.01 M, TBAP 0.1 M). Tetra-n-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical Co. and was twice recrystallized from absolute ethanol and dried in a vacuum oven at 45 ^oC for a week prior to use. Dichloromethane (DCM) was used as th solvent which was dried and redistilled before use. All BODIPY samples were dried in vacuum at 45 ^oC for 24 hours and the concentration was adjusted

to ca. 1 mM for CV measurements. The solutions were all bubbled and saturated with argon for 20 minutes before measurements.

Triplet energy measurements for dimer d4. We measured the phosphorescence for 2,2',6-iodine substituted BODIPY dimer d4 at room temperature, the peak maximum is 782 nm and the triplet state energy is 1.59 eV. We estimate that this value is smaller than that of d4 by about 0.025 eV, since its S_1 energy based on absorption and emission is smaller than than that of d4 by about 0.025 eV. Therefore ET of d4 is about 1.62 eV.

Computational simulation. The calculations were carried out using density functional theory (DFT) method as implemented in the Gaussian 09 package. The B3LYP exchange-correlation functional was chosen together with a 6-31G(d) basis set for structural optimization. The solvent effect was modeled using the Polarizable Continuum Model (CPCM) method. In all the cases frequency analysis was made after geometry optimization to ensure the convergence to an energy minimum.

Synthesis of monomer m1

Meso-phenyldipyrromethane precursor preparation. A solution of benzaldehyde (0.1 mL, 1 mmol) and pyrrole (2.8 mL, 40 mmol) was degassed by bubbling with argon for 10 min, then trifluoroacetic acid (0.008 mL, 0.1 mmol) was added. The solution was stirred for 15 min at room temperature, at which point no starting aldehyde was shown by TLC analysis. The mixture was diluted with CH_2Cl_2 (50 mL) then washed with 0.1 M aq NaOH, washed with water and dried (Na_2SO_4). The solvent was removed under reduced pressure and then the unreacted pyrrole was removed by vacuum distillation at room temperature. The resulting yellow amorphous solid was dissolved in a minimal quantity of the eluant and was purified by Bash chromatography (silica, 4 cm dia x 20 cm long, 230-400 mesh, cyclohexane/ethyl acetate/triethylamine = 80/20/l). Any remaining pyrrole elutes first, followed slowly by the dipyrromethane, and followed later by tailing materials. Elution of the dipyrromethane required about 500-700 mL solvent. Yield 0.11 g (49%); mp 100-101°C; ^{1}H NMR ($CDC1_3$) δ 7.89 (bs, 2 H, NH), 7.35-17.19 (m, 5 H, ArH), 6.69 (q, 2 H), 6.15 (q, 2 H), 5.91 (m, 2 H), 5.47 (s, 1 H, meso-H); EI-MS calcd 222.1157, obsd 222.1165.

N,N'-difluoroboryl-5-phenyldipyrrin and m1. A sample of 500 mg (2.25 mmol) of 5-phenyldipyrromethane was dissolved in 20 mL toluene at room temperature in a 50 mL one-neck

round bottom flask. DDQ (510 mg, 2.25 mmol) was added and the reaction mixture was stirred at room temperature. After 5 min, TLC (silica, toluene) showed the dipyrromethene, several other components, and no unreacted dipyrromethane. Then triethylamine (2.20 mL, 15.75 mmol) was added to the black reaction mixture followed immediately by BF_3-etherate (1.94 mL of neat BF_3-etherate, 15.75 mmol). After 30 min TLC (silica, CH_2C1_2) showed that product formation had leveled off. The reaction mixture was decanted from the black sludge and washed twice with H_2O, dried (Na_2SO_4), and evaporated to a black viscous material. Column chromatography (silica, CH_2C1_2/hexanes 2: 1) gave the desired product, which eluted as the second component. Removal of the solvent gave a viscous orange oil. Trituration of the orange oil with hexanes followed by vacuum filtration gave 130 mg (22%) of the title compound as an orange solid. mp 99-100 ^oC; $C_{14}H_{11}BF_2N_2$ calcd mass 268.1, obsd 268.4; λ_{abs} (toluene) 502 nm. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.95 (s, 2H), 7.61 – 7.51 (m, 5H), 6.94 (d, *J* = 4.2 Hz, 2H), 6.57 – 6.53 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.40, 144.14, 134.95, 133.78, 131.68, 130.81, 130.51, 128.48, 118.61, 118.59, 118.57, 118.56 ppm.

m2 *(4,4'-Difluoro-4-bora-(3a,4a)-diaza-s-indacene) Synthesis*

BODIPY monomer **m2** was synthesized by modifying the procedure in literature.[8] In a round-bottom flask (250 ml), pyrrole (2 mmol) and a drop of trifluoroacetic acid was added and stirred in dichlormethane (50 ml) at room temperature. 2-formylpyrrole (2.3 mmol) in dichlormethane (25 ml) was then added dropwisely in 10 min. The mixture was stirred about 4 hours until thin layer chromatography showed that the aldehyde was completely consumpted. Under ice cooling condition, triethylamine (7 ml) in dichlormethane (20 ml) was added, and then borontrifluoride-etherate (10 ml) in dichlormethane (20 ml) was slowly added and stirred for 15 minutes. The mixture was concentrated to 5 ml using rotavapor under vacuum, then purified by several cycles column chromatography with silica gel (CH_2Cl_2-n-hexane 1:1 v/v). The overall yield was about 9%. HRMS (ESI) m/z calcd for $[M+Na]^+$ cald. 215.0563, found: 215.0554. ^1H NMR (600 MHz, Chloroform-d) δ 7.90 (s, 2H), 7.43 (s, 1H), 7.16 (d, J = 3.9 Hz, 2H), 6.56 (d, J = 3.6 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-d) δ 145.08, 141.42,135.17, 131.38, 118.81.

Synthesis of m3. 2,4-dimethylpyrrole (0.5 mL, 4.76 mmol) was added to dichloromethane (30 mL)

in a 100 mL three–necked round bottom flask, after which argon was bubbled during the whole reaction process. Benzoyl chloride (0.3 mL, 2.60 mmol in 10 mL DCM) was then added and stirred for four hrs at room temperature. Triethyl amine (4 mL, 28.46 mmol) was put in under ice bath. After white smoke was disappeared, boron trifluoride diethyl ether (4 mL, 31.08 mmol) was added and the reaction proceeded for three hrs at room temperature. The solution was then added to deionized water (100 mL) and stirred for 12 hrs. The organic layer was separated and washed by water three times (3×150 mL), then dried by Na_2SO_4 and filtered. The filtrate was evaporated to give the solid, which was then purified by column chromatography (eluent CH_2Cl_2: n-hexane = 2: 1). Yield: 154 mg, 20 %. mp 127-130℃; IR (KBr)/cm^{-1}: 723, 978, 1072, 1155, 1196, 1471, 1508, 1543 (ν BODIPY ring); 1508, 1543 (ν B-F); 1308, 2854, 2924 (ν CH_3); UV/vis (DCM) λ_{max}/nm: 501; ^{1}H NMR (600 MHz, Chloroform-d) δ 7.54 – 7.47 (m, 3H), 7.31 – 7.28 (m, 2H), 6.00 (s, 2H), 2.58 (s, 6H), 1.39 (s, 6H). HRMS (APCI): m/z calcd for $C_{19}H_{20}BF_2N_2$ $[M+H]^+$ 325.1682, found 325.1683; HRMS (APCI): m/z calcd for $C_{19}H_{19}BFN_2$ $[M-F]^+$, 305.1625, found 305.1623.

Synthesis of m4. m4 was synthesized by modifying a literature procedure.[9] 250 mL 1,2-dichloroethane was deaerated by bubbling N_2. 2,4-dimethyl pyrrole (1 mL, 11.37 mmol), triethylorthoformate (0.95 mL, 5.69 mmol) and $POCl_3$ (0.58 mL, 6.25 mmol) were added to the deaerated solvent. Reaction was allowed to stir for 2 hours at room temperature. Then 11.5 mL NEt3 and 11.5 mL BF_3-etherate were added. After 1 hour the reaction was washed with water (3x250 mL), the organic layer separated, dried on $NaSO_4$ and evaporated in vacuo. Column chromatography with $CHCl_3$ yielded the pure product as reddish solid (400 mg, 28 %). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.07 (s, 1H), 6.07 (s, 2H), 2.55 (s, 6H), 2.27 (s, 6H) ppm. ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.69, 133.35, 120.06, 118.99, 14.67, 11.29 ppm.

Synthesis of compound 2a. Under ice bath, DMF (7.5 mL) in 100 mL three-necked round bottom flask was saturated by N_2 with bubbling the gas for 20 min, $POCl_3$ (7.5 mL) was added drop wise with stirring in 5 min. Ice bath was then removed, and the resulted solution was stirred at room temperature for 20 min. which resulted in a white sticky mixture. Monomer m1 (161 mg, 0.6 mmol) in 1,2-$ClCH_2CH_2Cl$ (70 mL) was added drop wise into the white mixture, it was then stirred for 6 hrs. at 50 ^oC. After cooling down, the solution was added drop wise into saturated $NaHCO_3$ aq. solution (400 mL) with stirring for 30 min. The organic layer was extracted by dichloromethane, washed by water (2×200 mL), dried by $MgSO_4$ and filtered. Red solid was obtained after evaporating the filtrate under vacum. The crude compound 2b was purified by

column chromatography (eluent CH_2Cl_2: n-hexane = 2: 1). Yield, 141 mg，79%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.78 (s, 1 H, CHO), 8.23 (s, 1 H, py), 8.10 (s, 1 H, py), 7.55–7.51 (m, 5H, ph), 7.25 (s, 1 H, py), 7.09 (s, 1 H, py), 6.66 (s, 1 H, py) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.8, 149.4, 142.8, 137.0, 135.0,134.7, 132.9, 131.7, 131.6, 130.5, 128.8, 128.7, 121.5 ppm. HRMS (EI): calcd. for $C_{16}H_{11}BF_2N_2O$ $[M]^+$ 296.0932; found 296.0928.

Synthesis of compound 2b. The procedure is the same as that for **2a**, except that monomer **m3** (194 mg, 0.6 mmol) was used to replace **m1**. Yield, 180 mg，85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.52 (s, 3H), 7.27 (s, 2H), 6.15 (s, 1H), 2.83 (s, 3H), 2.62 (s, 3H), 1.65 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.2, 161.8, 156.5, 147.3, 143.6, 142.9, 134.1, 129.6, 129.5, 127.7, 126.3, 124.1, 15.1, 14.9, 13.0, 11.6; ESI-MS 351.2 $[M-H]^-$, 374.4 $[M+Na]^+$.

Derivation of equation (7) from the decay kinetics of ICT state emission. Emission from ICT state was observed for each dimer in some solvents, as shown in previous section. Their emission quantum yields (Φ_f') were easily calculated because ICT emission is not overlapped with LE emission band, which is in the range from 0.001 to 0.11. The decay of ICT state include three ways:

1) charge recombination (CR) with heat releasing, $[M_1]^{\bullet+}$-$[M_2]^{\bullet-} \rightarrow$ M_1-M_2+heat,

2) CR with photon releasing (fluorescence), $[M_1]^{\bullet+}$-$[M_2]^{\bullet-} \rightarrow$ M_1-M_2+hν,

3) CR with spin conversion (T_1 formation) $[M_1]^{\bullet+}$-$[M_2]^{\bullet-} \rightarrow$ $M_1(T_1)$-M_2 or M_1-$M_2(T_1)$.

The fluorescence lifetime and quantum yield of ICT state (τ_f' and Φ_f') are then given by:

$$\tau_f' = 1/(k_{CR,ic}+k_{CR,f}+k_{CR,isc}), \quad (1)$$

$$\Phi_f' = \Phi_{PET}\, k_{CR,f}/(k_{CR,ic}+k_{CR,f}+k_{CR,isc}) = \Phi_{PET}\, \tau_f'\, k_{CR,f}, \quad (2)$$

in which $k_{CR,ic}$ is the rate constant of internal conversion (heat releasing) for ICT state, $k_{CR,f}$ is the rate constant of fluorescence from ICT state, $k_{CR,isc}$ is the rate constant of ISC for ICT state. $k_{CR,f}$

is calculated by

$$k_{CR,f} = \Phi_f'/(\Phi_{PET}\ \tau_f'). \quad (3)$$

Since $\Phi_T = \Phi_{PET}k_{CR,isc}/(k_{CR,ic}+k_{CR,f}+k_{CR,isc}) = \Phi_{PET}k_{CR,isc}\tau_f'$

$$= k_{PET}k_{CR,isc}\tau_f\tau_f' = k_{PET}k_{CR,isc}/[(k_{ic}+k_f+k_{isc}+k_{PET})\ (k_{CR,\ ic}+k_{\ CR,f}+k_{\ CR,isc})]. \quad (4)$$

We have then

$$k_{CR,isc} = \Phi_T/(\Phi_{PET}\ \tau_f'), \quad (5)$$

$$k_{CR,ic} = (1-\Phi_T-\Phi_f')/(\ \Phi_{PET}\ \tau_f') \quad (6)$$

The formation of excited triplet state is made possible, because $k_{CR,isc}$ value is comparable to ($k_{CR,f}$+$k_{CR,ic}$). Since k_f, k_{isc}, k_{ic}, $k_{\ CR,isc}$ and $k_{\ CR,f}$ are much less affected by solvent polarity, we may simplify the expression of Φ_T in equation (4) to:

$$\Phi_T = C_1k_{PET}/[(C_2+k_{PET})\ (C_3+\ k_{CR,\ ic})] = C_1/[(C_2/k_{PET}+1)\ (C_3+\ k_{CR,\ ic})], \quad (7)$$

In which C_1, C_2, and C_3 are constants. We see that Φ_T is mainly dependent on k_{PET} and $k_{CR,ic}$. This expression explains the dihedral angle and solvent effect on Φ_T and Φ_Δ. Increase in the solvent polarity (or decrease in dihedral angle) leads to the increase of k_{PET} and $k_{CR,\ ic}$, but k_{PET} appears in both the denominator and the numerator in the expression, this is why there is an optimal solvent (and a dihedral angle) which makes Φ_T and Φ_Δ highest.

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HRMS and NMR Figures

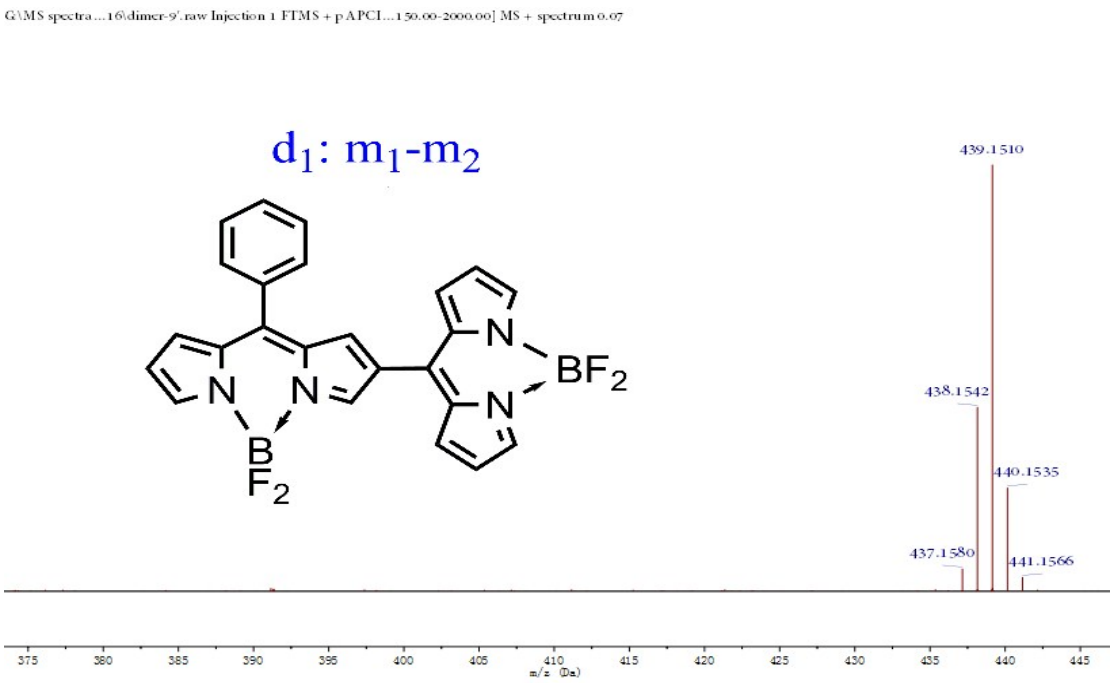

Figure s1. The HRMS of compound d1 in methanol.

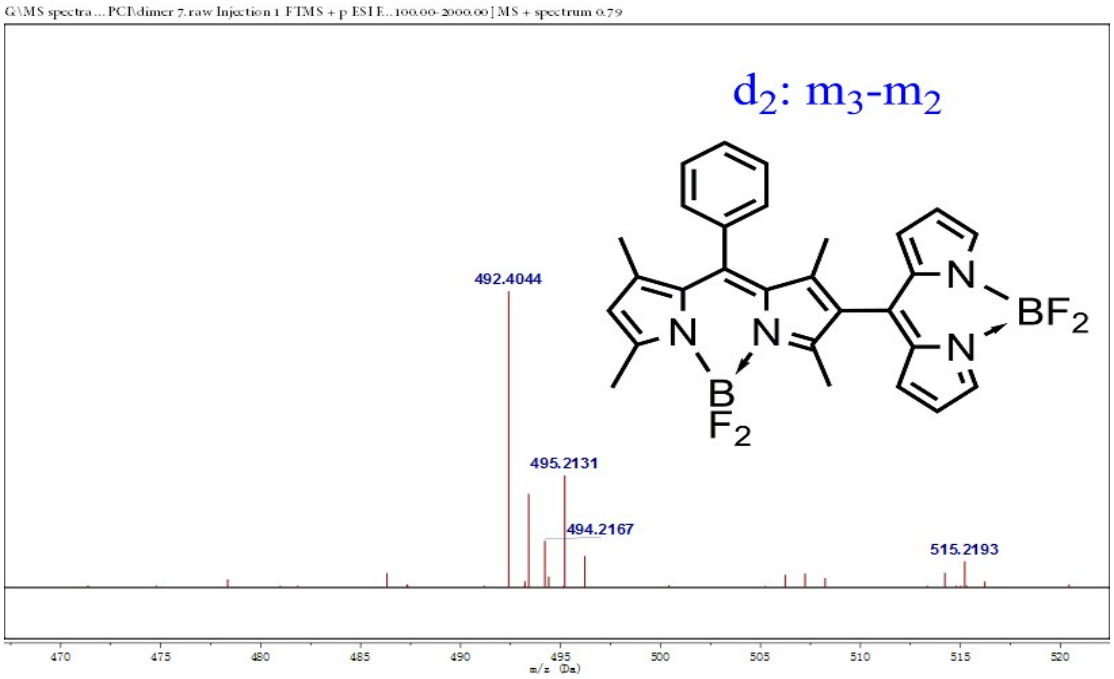

Figure s2. The HRMS of compound d2 in methanol.

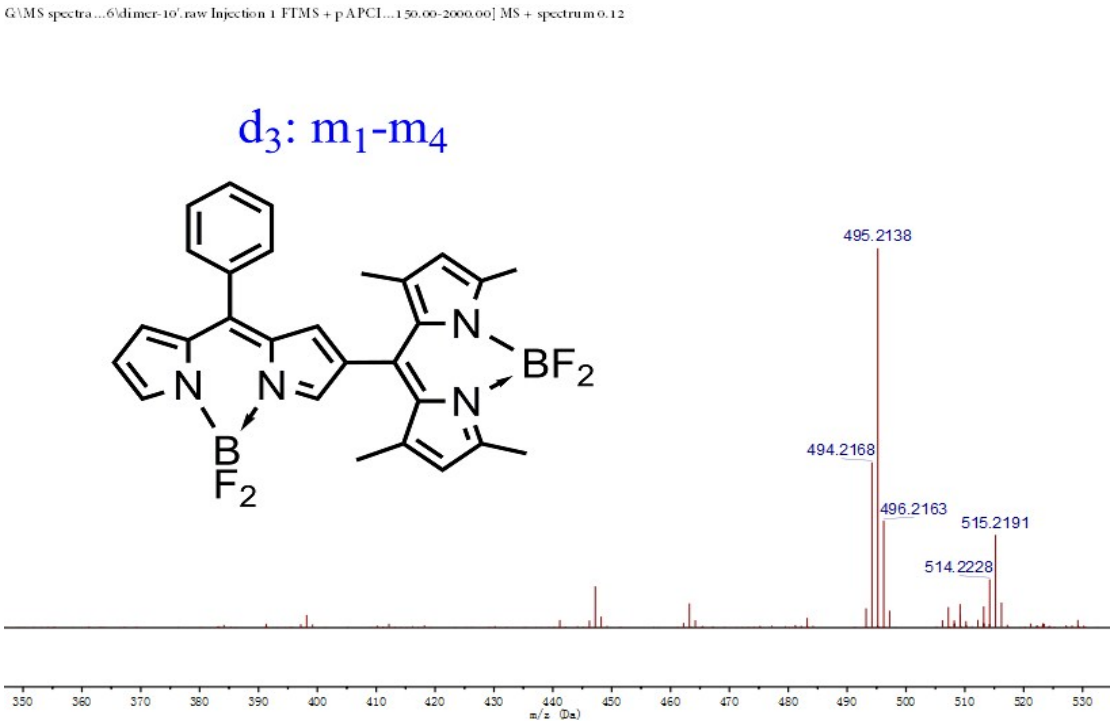

Figure s3. The HRMS of compound d3 in methanol.

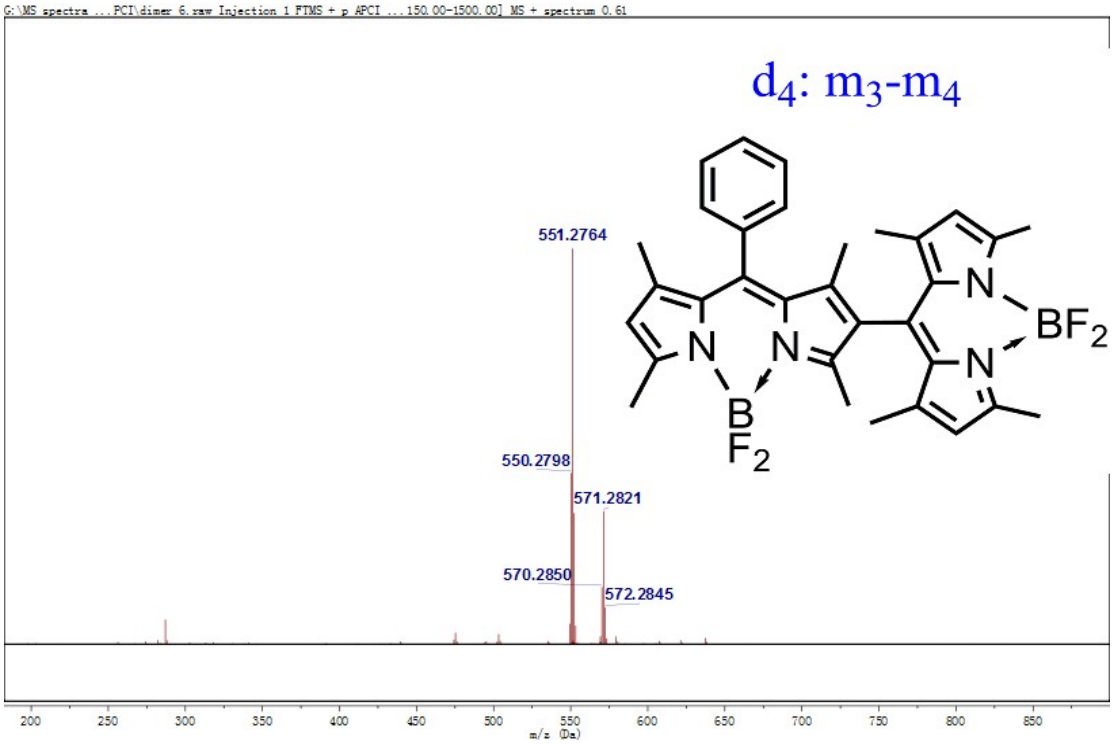

Figure s4. The HRMS of compound d4.

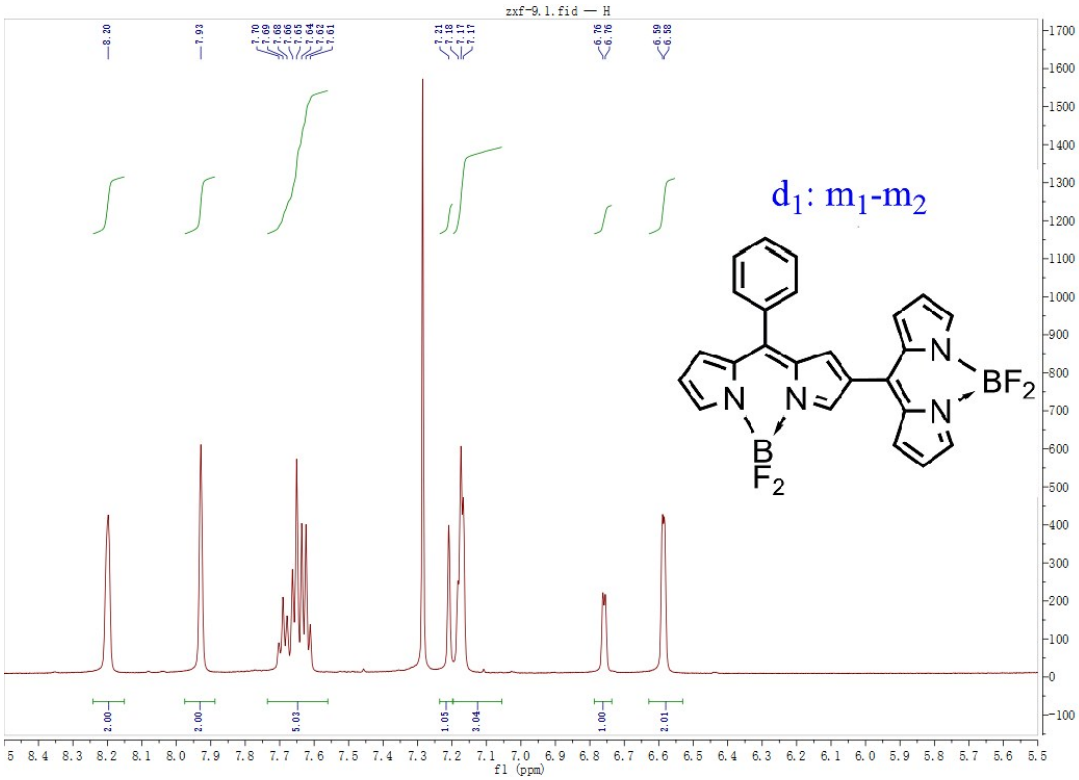

Figure s5. The ^{1}H NMR of compound d1 in $CDCl_3$.

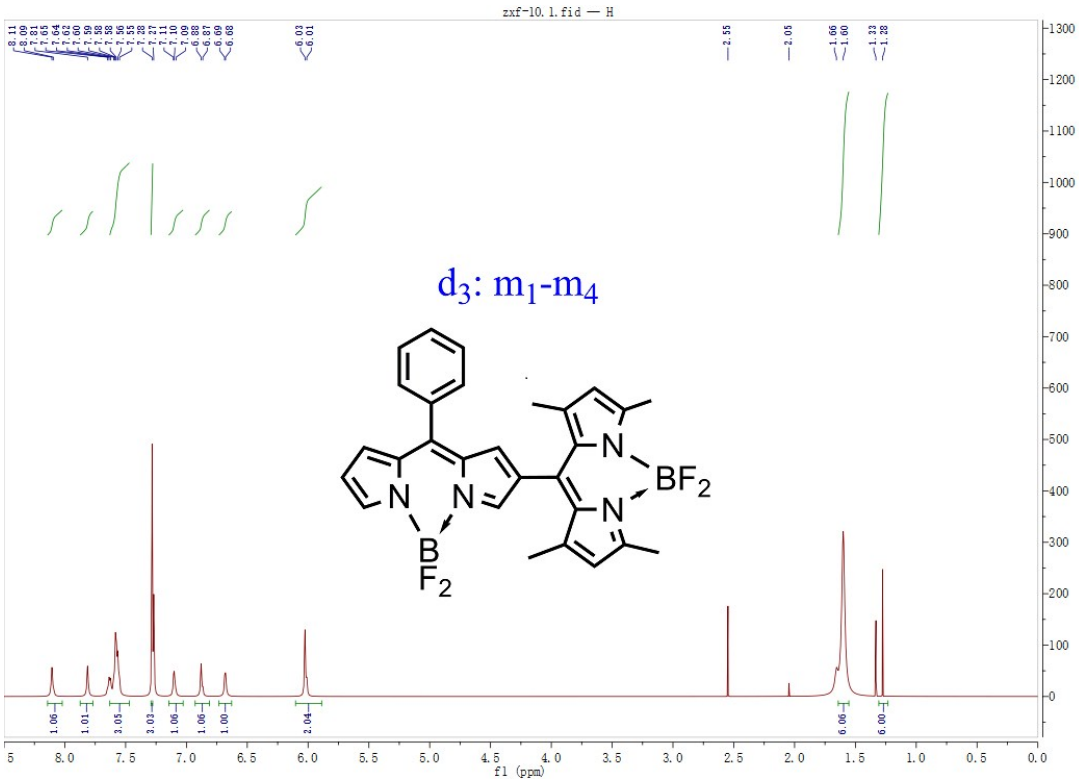

Figure s7. The ^{1}H NMR of compound d2 in $CDCl_3$.

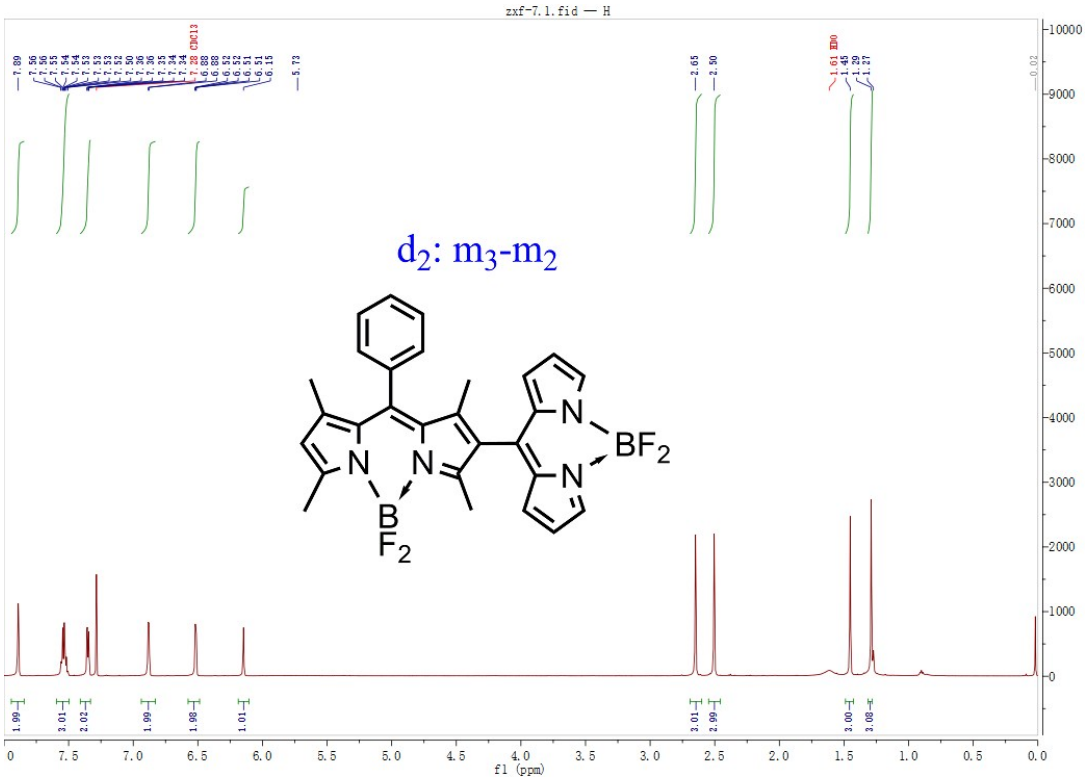

Figure s6. The ^{1}H NMR of compound d3 in $CDCl_3$.

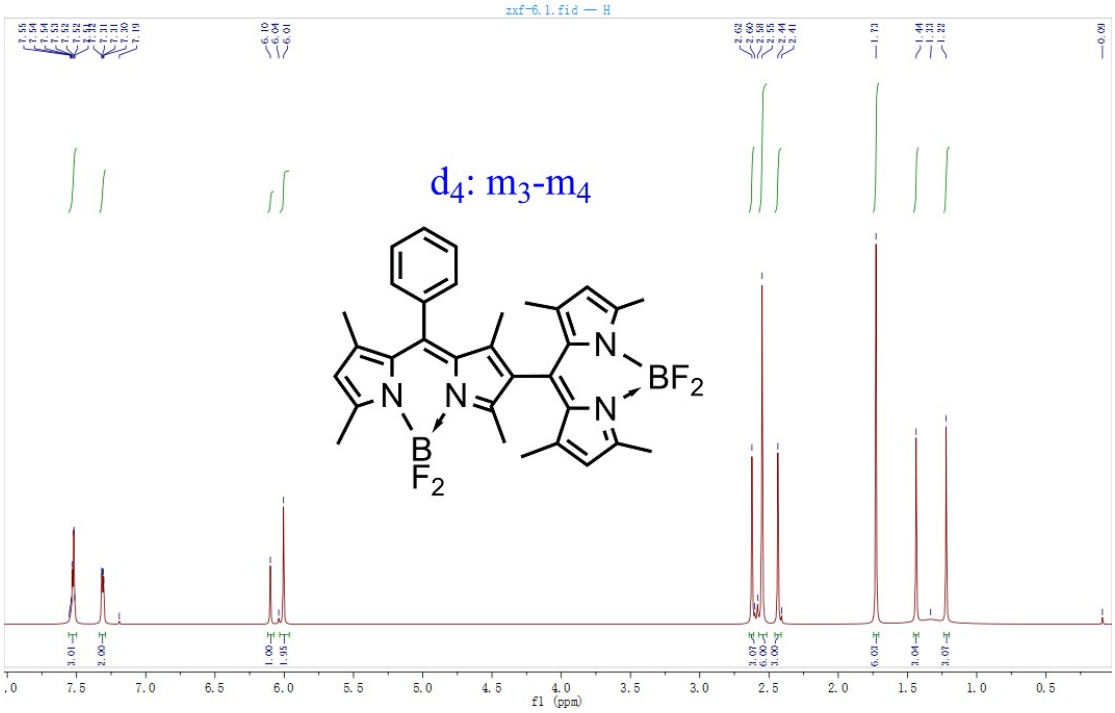

Figure s8. The ^{1}H NMR of compound d4 in $CDCl_3$.

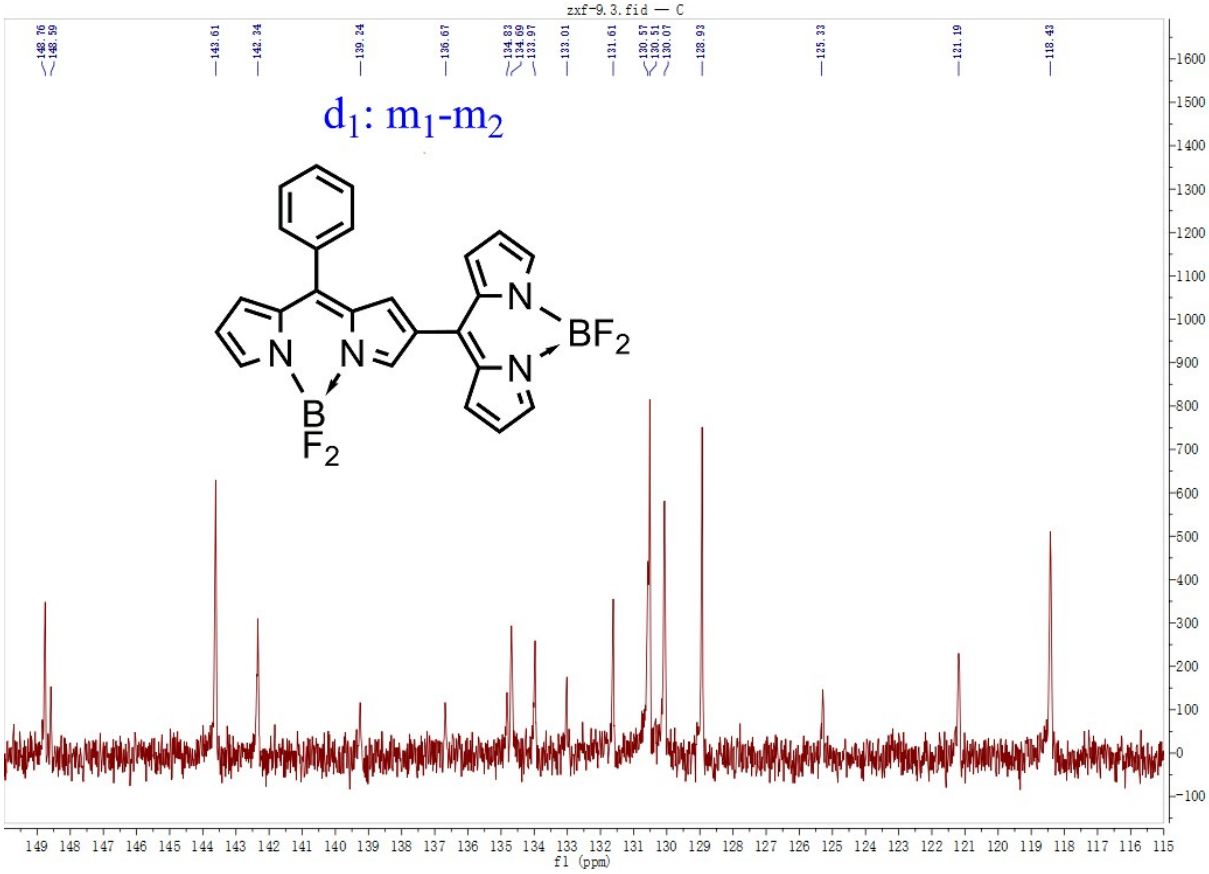

Figure s9. The ^{13}C NMR of compound d1 in $CDCl_3$.

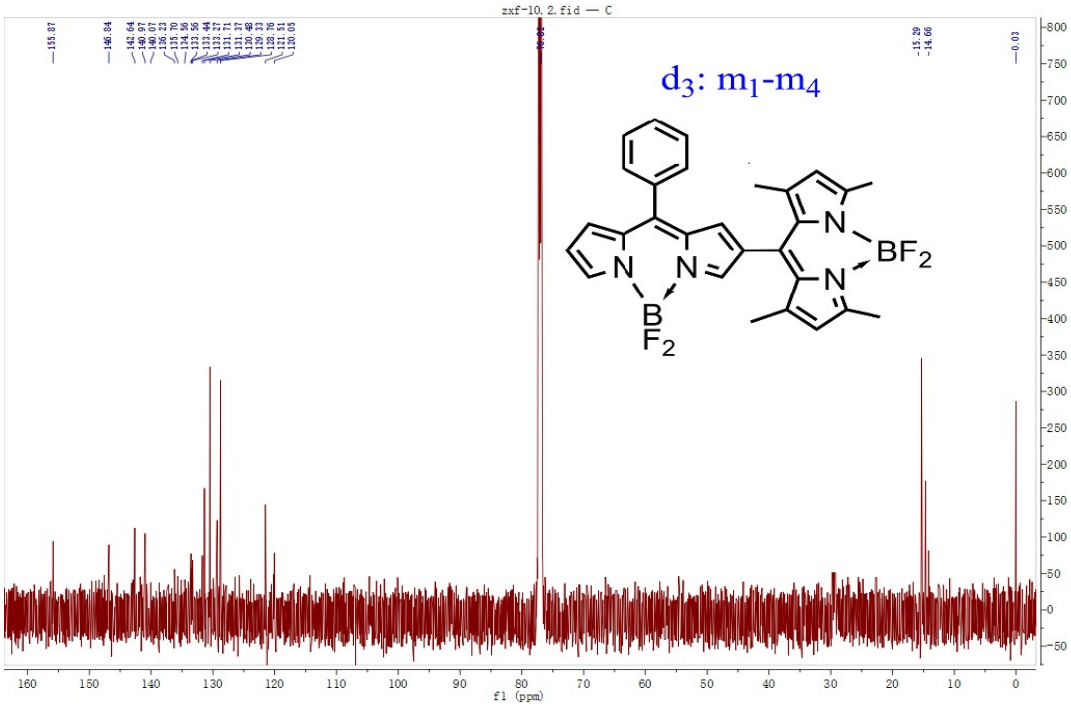

Figure s11. The ^{13}C NMR of compound d2 in $CDCl_3$.

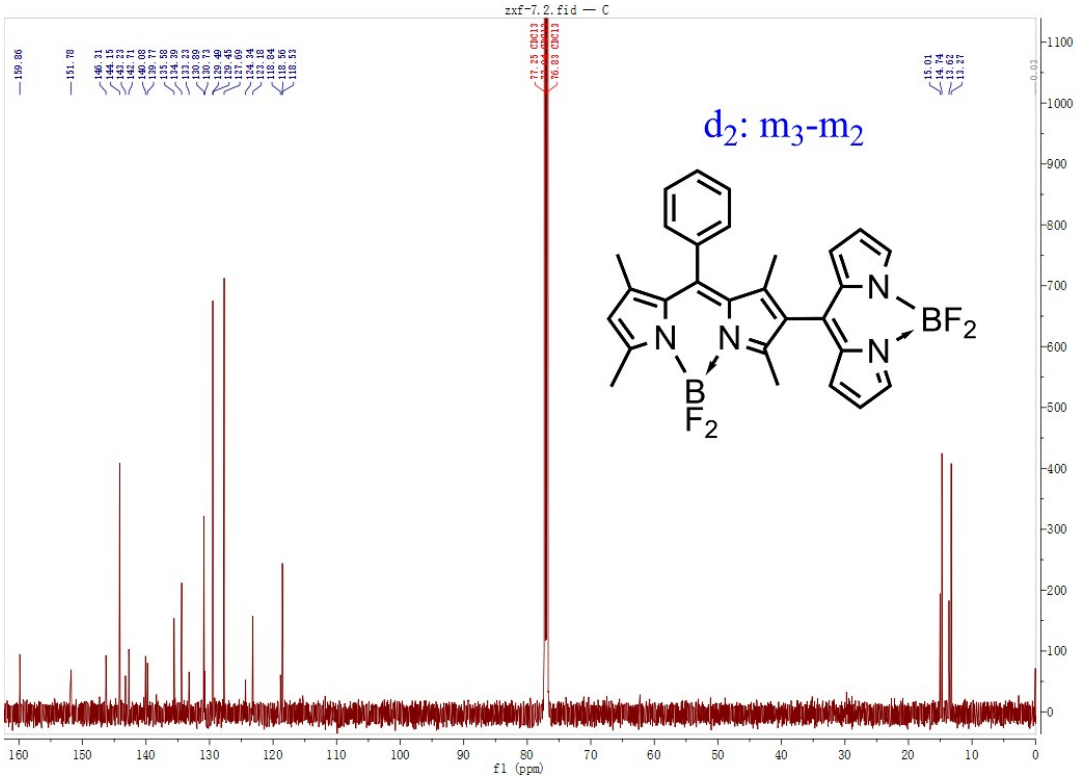

Figure s10. The ^{13}C NMR of compound d3 in $CDCl_3$.

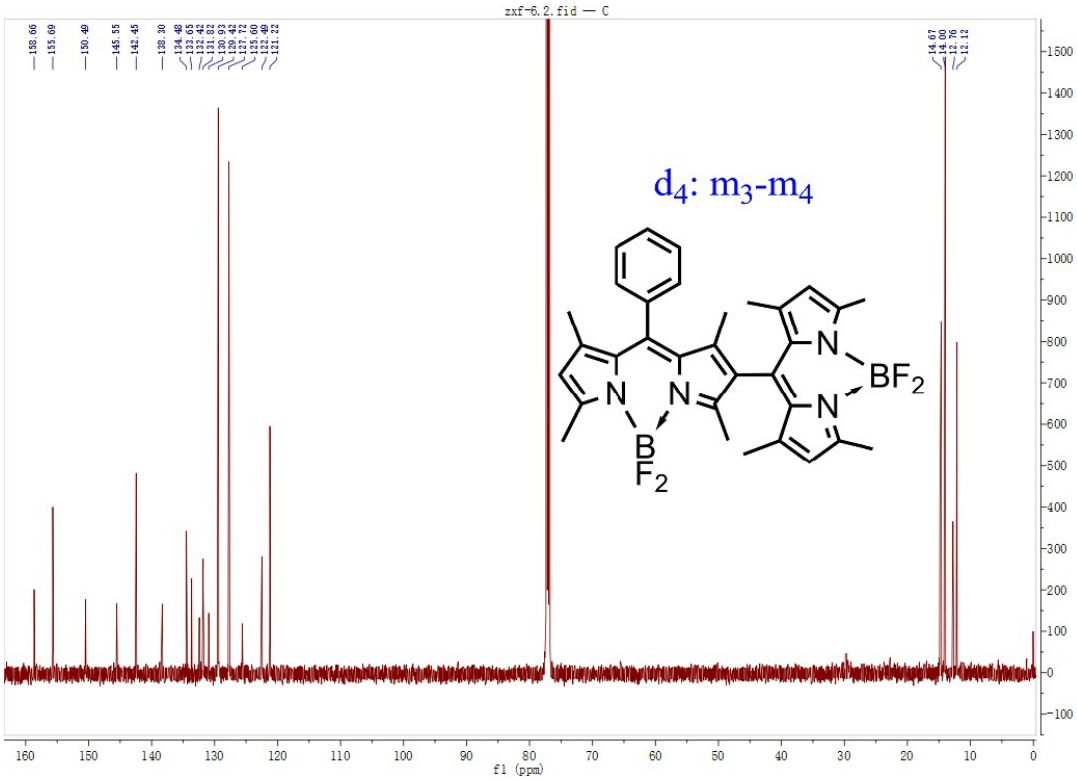

Figure s12. The ^{13}C NMR of compound d4 in $CDCl_3$.