

Supplementary information:

Unusual Approach to *meso*-Alkoxy BODIPYs with Good Balance between Larger Stokes Shift and Higher Fluorescence Quantum Yields

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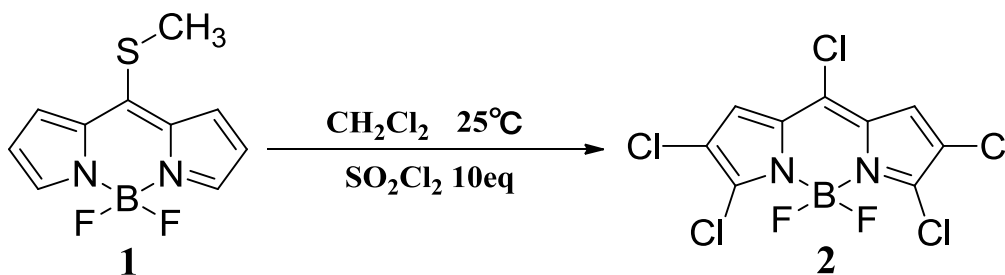
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1 General method

^1H NMR and ^{13}C NMR spectra were recorded using 400 MHz and 100 MHz. Melting points were measured, and were uncorrected. Chromatographic purification was conducted with silica gel (200 - 300 mesh). Absorption spectra were recorded on TU-1901 UV-Vis absorption spectrometer and fluorescence spectra were recorded on F-4500 spectrometer. Cyclic voltammetry (CV) was performed in 0.05M solution in CH_2Cl_2 with a standard commercial electrochemical analyzer in a three electrode single-component cell under argon with a scan rate of 100 mV/s. Working electrode: glassy carbon; reference electrode: Ag/AgCl; auxiliary electrode: Pt disk; internal standard: ferrocene (Fc). The energy of Fc/Fc^+ is 5.08 eV relative to vacuum.¹ Compound **1** was obtained as previously reported.² The films of BDP and Compound **3a** were prepared by spin coating method. The self-quenching experiment can be found in the literatures.³ The photostability measurement was evaluated by using Olympus FV1000 confocal microscope.^{1b} Unless otherwise noted, materials were commercially available and were used without further purification.

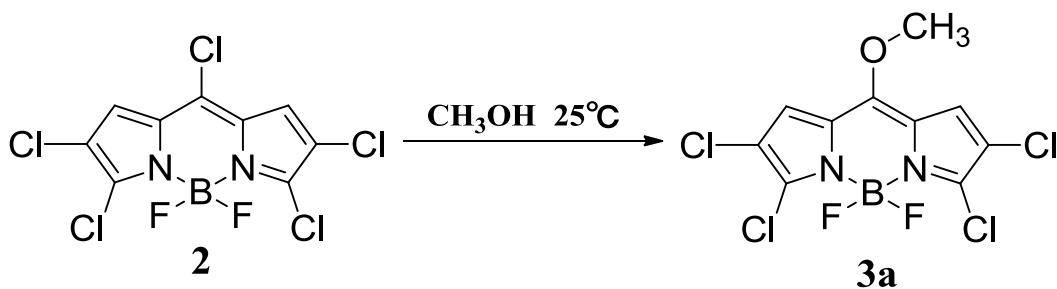
2. Synthesis and characterization of 2-3 (a, b, c)

Synthesis of Compound 2



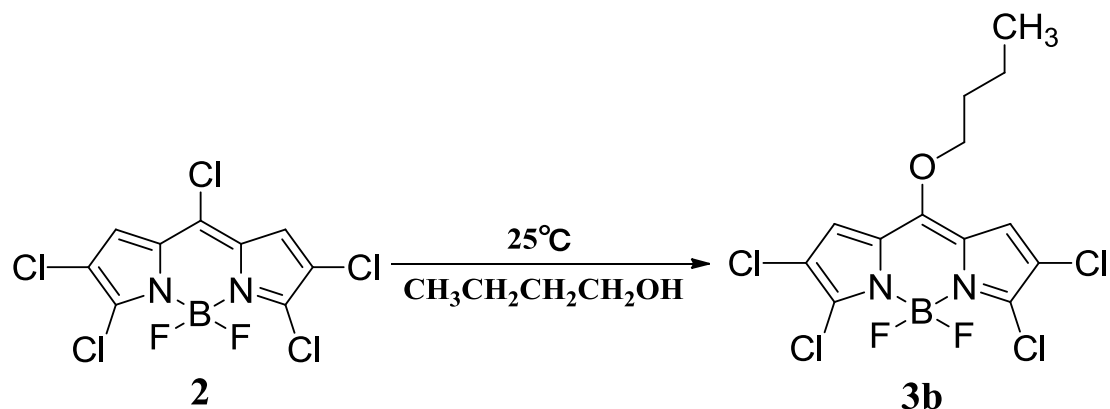
Compound **1** (131mg, 0.55mmol) was stirred in anhydrous dichloromethane (20ml) at room temperature. A solution of sulfonyl chloride (0.45ml, 5.5mmol) in dichloromethane (2ml) is added. The resulting solution is stirred at room temperature for 0.5h. After TLC showed that the reaction went to completion, the reaction mixture was allowed to be poured into ice-water and extracted with dichloromethane. The solution was dried over MgSO_4 , filtered and concentrated in vacuo. The product is purified chromatographically (Silica, CH_2Cl_2 /hexane; 1:6, v/v) to yield red solid (155 mg, 78%). Mp:119-122°C. ^1H -NMR (CDCl_3): 7.33 (s, 2H); ^{13}C -NMR (CDCl_3): 144.0, 136.7, 130.4, 125.8, 122.6; MALDI-TOF-MS: Calcd. for $\text{C}_9\text{H}_2\text{BCl}_5\text{F}_2\text{N}_2$ 361.8722, found 361.8747.

Synthesis of Compound 3a



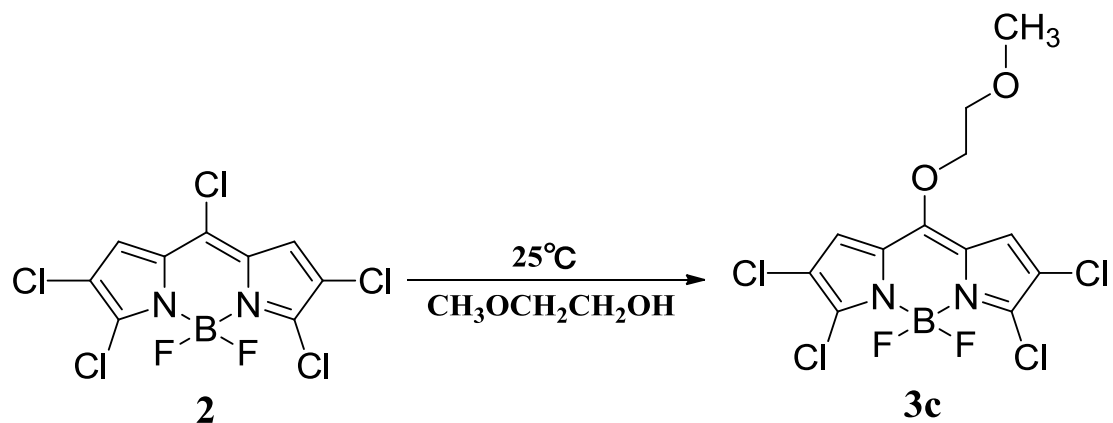
Compound **2** (102mg, 0.28mmol) was stirred in anhydrous methanol (20ml) at room temperature. The resulting solution is stirred for 2h. After TLC showed that the reaction went to completion, the reaction mixture was concentrated in vacuo. The product is purified chromatographically (Silica, CH_2Cl_2 /hexane; 1:2, v/v) to yield orange solid (96mg, 97%). Mp:155-157°C. $^1\text{H-NMR}$ (CDCl_3): 7.28 (s, 2H), 4.45 (s, 3H); $^{13}\text{C-NMR}$ (CDCl_3): 158.1, 137.4, 123.2, 123.0, 119.6, 62.7; MALDI-TOF-MS: Calcd. for $\text{C}_{10}\text{H}_5\text{BCl}_4\text{F}_2\text{N}_2\text{O}$ 357.9217, found 357.9224.

Synthesis of Compound 3b



Compound **2** (110mg, 0.3mmol) was stirred in anhydrous butyl alcohol (22ml) at room temperature. The resulting solution is stirred for 3h. After TLC showed that the reaction went to completion, the reaction mixture was concentrated in vacuo. The product is purified chromatographically (Silica, CH_2Cl_2 /hexane; 1:2, v/v) to yield orange solid (115mg, 96%). Mp:147-150°C. $^1\text{H-NMR}$ (DMSO): 7.87 (s, 2H), 4.83-4.80 (t, $J = 5.7$ Hz, 2H), 1.86-1.80 (m, 2H), 1.55-1.46 (m, 2H), 0.98-0.96 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C-NMR}$ (DMSO): 166.8, 129.6, 119.7, 112.1, 111.6, 60.3, 34.9, 18.6, 13.8; MALDI-TOF-MS: Calcd. for $\text{C}_{13}\text{H}_{11}\text{BCl}_4\text{F}_2\text{N}_2\text{O}$ 399.9687, found 399.9699.

Synthesis of Compound 3c



Compound **2** (127mg, 0.35mmol) was stirred in anhydrous 2-Methoxyethanol (26ml) at room temperature. The resulting solution is stirred for 2.5h. After TLC showed that the reaction went to completion, the reaction mixture was concentrated in vacuo. The product is purified chromatographically (Silica, CH₂Cl₂/hexane; 1:2, v/v) to yield orange solid (133mg, 95%). Mp:159-161 °C. ¹H-NMR (CDCl₃): 7.29 (s, 2H), 4.74-4.72 (t, 2H), 3.84-3.82 (t, *J* = 5.6 Hz, 2H), 3.46 (s, 3H); ¹³C-NMR (CDCl₃): 157.7, 137.8, 123.4, 123.3, 119.7, 75.5, 70.4, 59.6; MALDI-TOF-MS: Calcd. for C₁₂H₉BCl₄F₂N₂O₂ 401.9479, found 401.9489.

3. The absorption and fluorescence spectra in different solvents⁴ of **3**

a-3c

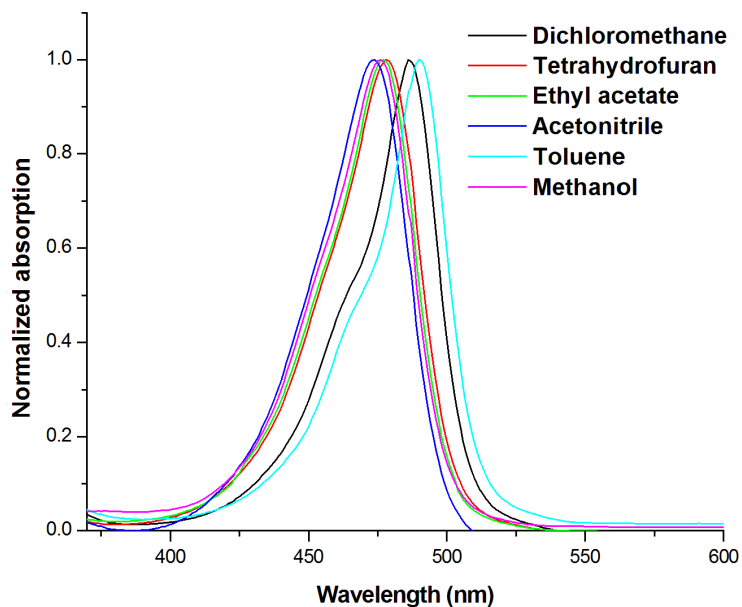


Fig. S1 Normalized absorption of **3a** in different solvents.

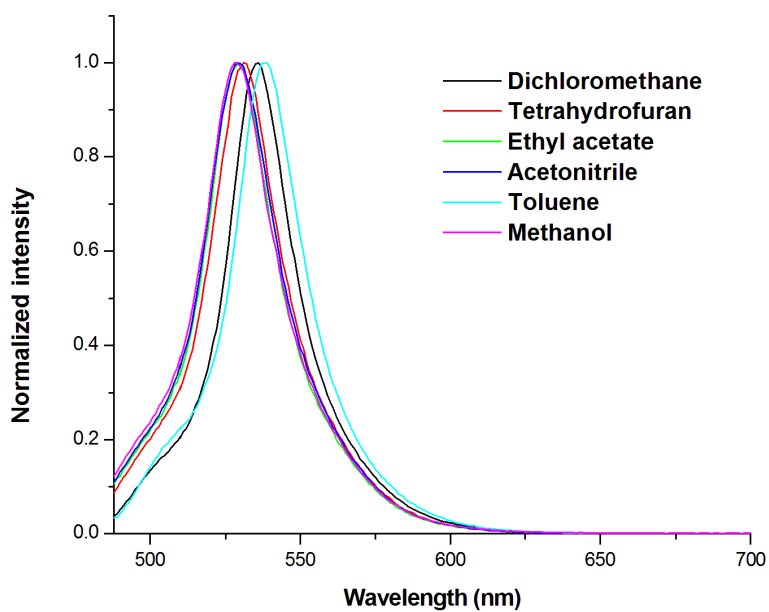


Fig. S2 Normalized fluorescence of **3a** in different solvents.

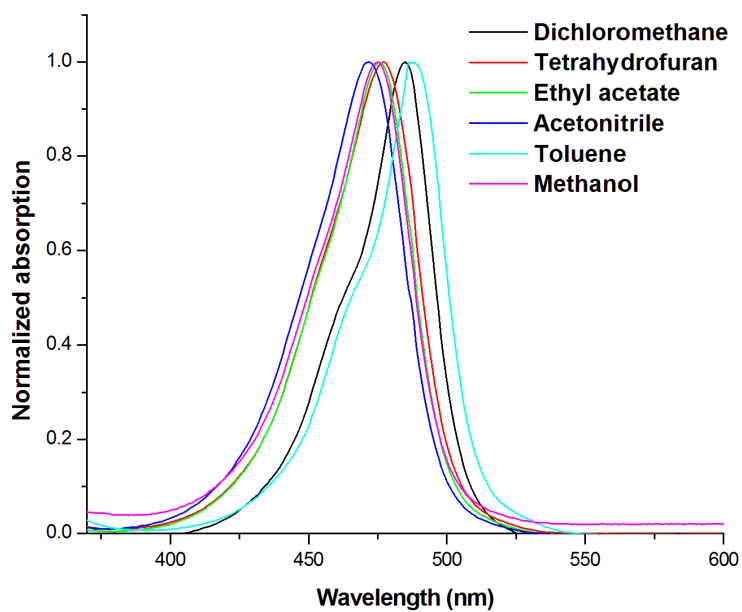


Fig. S3 Normalized absorption of **3b** in different solvents.

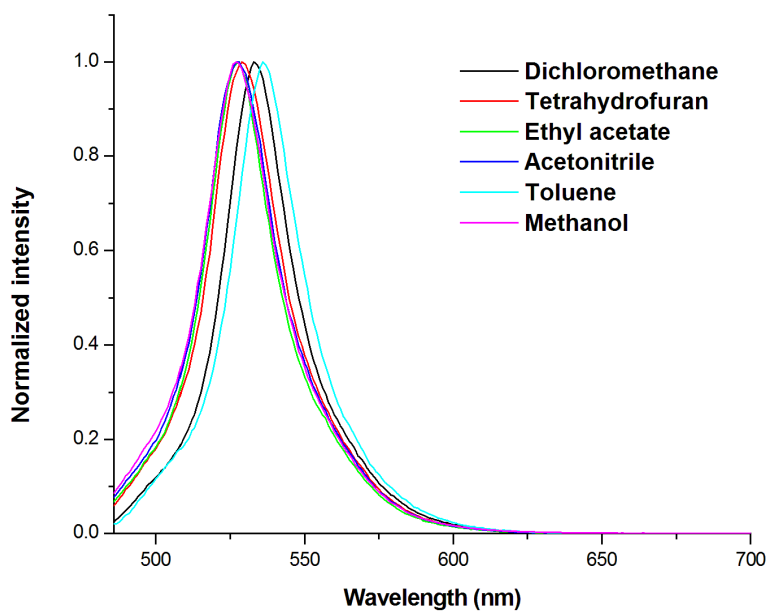


Fig. S4 Normalized fluorescence of **3b** in different solvents.

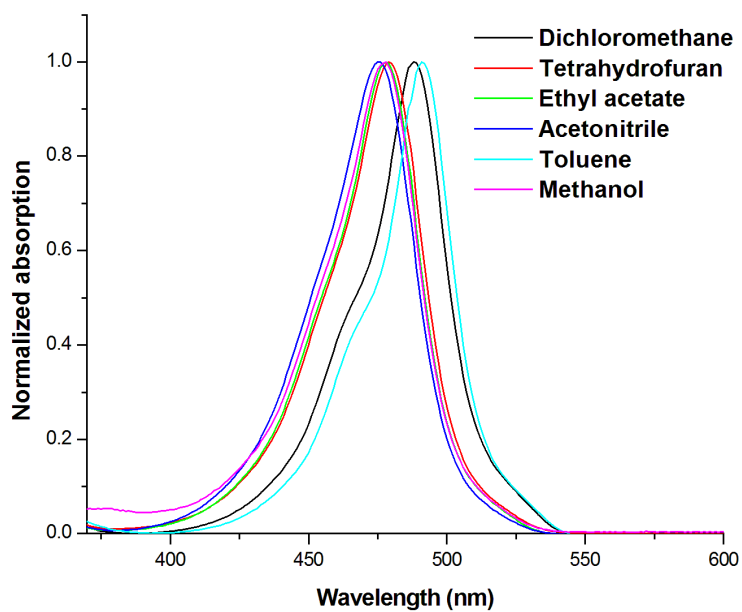


Fig. S5 Normalized absorption of **3c** in different solvents.

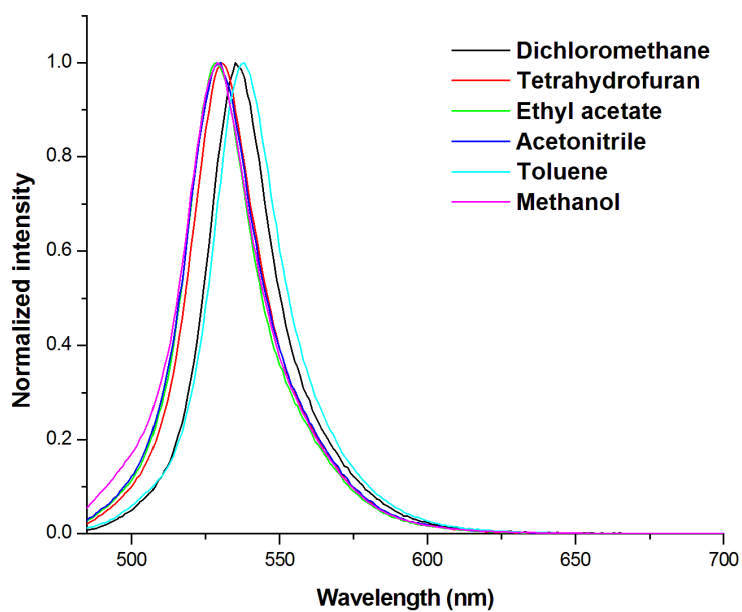


Fig. S6 Normalized fluorescence of **3c** in different solvents.

Table S1 Effects of the solvent polarity on photophysical properties of **3a-3c**

Solvent	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$	$\Delta S^{\text{a}}(\text{nm})$	$\Phi_{\text{F}}^{\text{b}}$
3a				
Toluene	488	538	50	0.63
Dichloromethane	486	536	50	0.80
Tetrahydrofuran	478	531	53	0.81
Ethyl acetate	478	529	51	0.58
Acetonitrile	476	530	54	0.84
Methanol	476	529	53	0.96
3b				
Toluene	487	536	49	0.74
Dichloromethane	485	533	48	0.92
Tetrahydrofuran	477	529	52	0.76
Ethyl acetate	476	528	52	0.98
Acetonitrile	474	527	53	0.98
Methanol	475	527	52	0.78
3c				
Toluene	489	537	48	0.74
Dichloromethane	488	535	47	0.86
Tetrahydrofuran	479	530	51	0.67
Ethyl acetate	477	530	53	0.73
Acetonitrile	476	529	53	0.88
Methanol	478	529	51	1.00

^a Stokes shift

^b The fluorescein quantum yields were calculated using NaOH aqueous solution ($\Phi_{\text{F}}=0.85$) for **3a-3c** as the standard.

4. Calculations details

Table S2 The vertical excitation (absorption) and the emission of **2** and **3a**. The oscillator strengths (f) and excitation energy (eV). The calculation of the $S_0 \rightarrow S_1$ energy gaps are based on the optimized ground state geometry (absorption) and the optimized S_1 excited state geometry (emission).

Compounds	Electronic Transitions ^a	TDDFT/B3LYP/6-31G (d)			
		Excitation energy ^a	f^b	Composition ^c	CI ^d
2	absorption^e $S_0 \rightarrow S_1$	2.84 eV	0.634	H-1 \rightarrow L	0.1341
				H \rightarrow L	0.6982
	emission^f $S_0 \rightarrow S_1$	2.77 eV	0.702	H \rightarrow L	0.7031
3a	absorption^e $S_0 \rightarrow S_1$	2.93 eV	0.600	H \rightarrow L	0.7013
				H \rightarrow L	0.7043
	emission^f $S_0 \rightarrow S_1$	2.69 eV	0.656	H \rightarrow L	0.7043

^a The numbers are the excitation energy. ^b Oscillator strength. ^c H stands for HOMO and L stands for LUMO. ^d Coefficient of the wave function for excitations. The CI coefficients are in absolute values. ^e The calculations on absorption are based on the optimized ground state geometry. ^f The calculations on the fluorescence are based on the optimized S_1 state geometry.

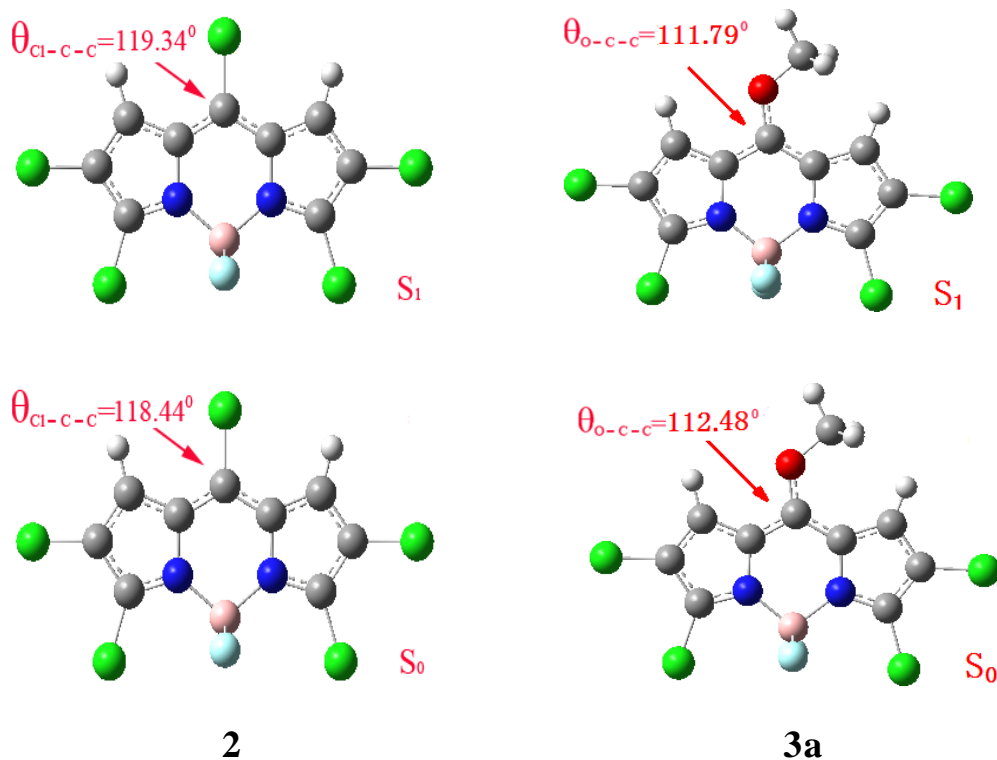


Fig. S7 The change of the bond angle in S_0 and S_1 states of **2** and **3a**.

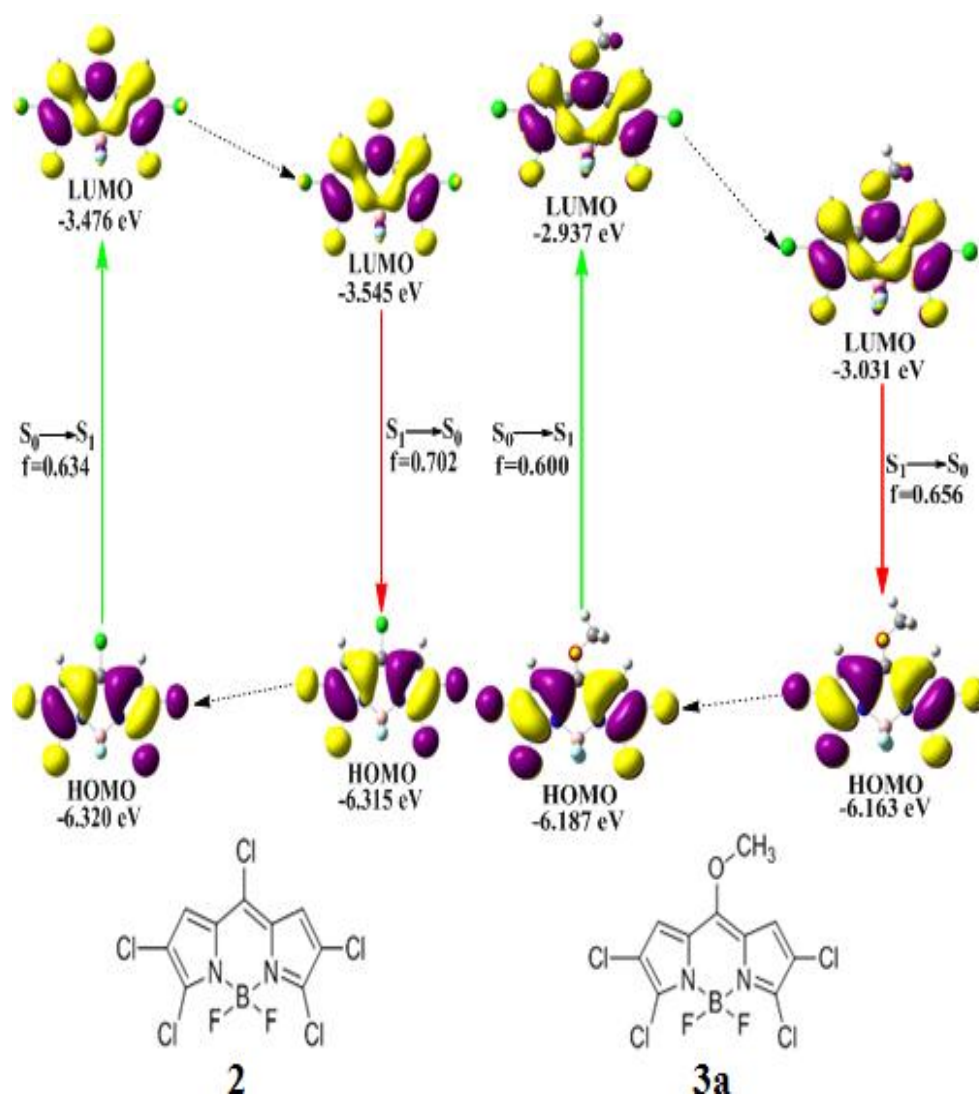


Fig. S8 The frontier molecular orbitals involved in the vertical excitation (absorption, left column) and emission (right column) of **2** and **3a**.

The coordinates of ground state of Compounds (optimized geometry)

The coordinates of **2** (DFT/B3LYP/6-31G)

Charge = 0 Multiplicity = 1

C	-5.36900000	0.76200000	0.00800000
N	-5.45500000	-0.50900000	0.00900000
B	-4.24000000	-1.38700000	-0.01700000
N	-3.00000000	-0.55000000	-0.00600000
C	-3.04200000	0.75500000	0.00300000
C	-4.20200000	1.43100000	0.00700000
C	-1.75700000	-0.94200000	-0.00800000
C	-0.97800000	0.15000000	-0.00100000
C	-1.78300000	1.22100000	0.00500000
C	-6.62400000	1.24500000	0.01000000
C	-7.44500000	0.18600000	0.01200000
C	-6.66400000	-0.90700000	0.01200000
C1	-4.19400000	3.15700000	0.01300000
F	-4.23800000	-2.30300000	1.22100000
F	-4.25300000	-2.24200000	-1.29900000
C1	-9.16400000	0.25800000	0.01500000
C1	-7.20400000	-2.54000000	0.01500000
C1	0.73700000	0.22000000	0.00000000
C1	-1.20100000	-2.57000000	-0.01900000
H	-1.45700000	2.26900000	0.01100000
H	-6.93600000	2.29700000	0.01000000

1 2 2.0 6 2.0 10 2.0
2 3 1.0 12 2.0
3 4 1.0 14 1.0 15 1.0
4 5 2.0 7 2.0
5 6 2.0 9 2.0
6 13 1.0
7 8 2.0 19 1.0
8 9 2.0 18 1.0
9 20 1.0
10 11 2.0 21 1.0
11 12 2.0 16 1.0
12 17 1.0
13
14
15
16
17
18

19
20
21

The coordinates of **3a** (DFT/B3LYP/6-31G)

Charge = 0 Multiplicity = 1

C	-2.83326198	0.29671860	-0.53470815
N	-2.93595693	-0.95025318	-0.78231096
B	-1.97340318	-1.95642436	-0.22834451
N	-0.95260224	-1.25296465	0.61102601
C	-0.96100894	0.04336763	0.75910012
C	-1.85600000	0.87600000	0.18800000
C	0.02494083	-1.76690313	1.30274690
C	0.65921612	-0.76273581	1.92592573
C	0.03851534	0.37636307	1.59143314
C	-3.89312110	0.90463266	-1.09615373
C	-4.61500783	-0.04983035	-1.69994914
C	-3.97232644	-1.20901335	-1.47632351
F	-2.73049251	-2.97206573	0.64812931
F	-1.26345318	-2.68700859	-1.38443951
Cl	2.01444606	-0.86264062	2.97493328
Cl	0.43033546	-3.43453726	1.41520403
Cl	-6.07498914	0.20337390	-2.57577057
Cl	-4.46243596	-2.76007596	-2.03601398
O	-1.88300000	2.20700000	0.52200000
C	-2.86803936	2.95456471	-0.15197215
H	0.30802782	1.38198646	1.93603527
H	-4.13094930	1.97608405	-1.07104042
H	-2.78259406	4.01289157	0.18138707
H	-3.88064173	2.57120877	0.10318204
H	-2.70244839	2.90243728	-1.25114109

1 2 2.0 6 2.0 10 2.0
2 3 1.0 12 2.0
3 4 1.0 13 1.0 14 1.0
4 5 2.0 7 2.0
5 6 2.0 9 2.0
6 19 1.0

7 8 2.0 16 1.0
8 9 2.0 15 1.0
9 21 1.0
10 11 2.0 22 1.0
11 12 2.0 17 1.0
12 18 1.0
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5. Cyclic voltammograms

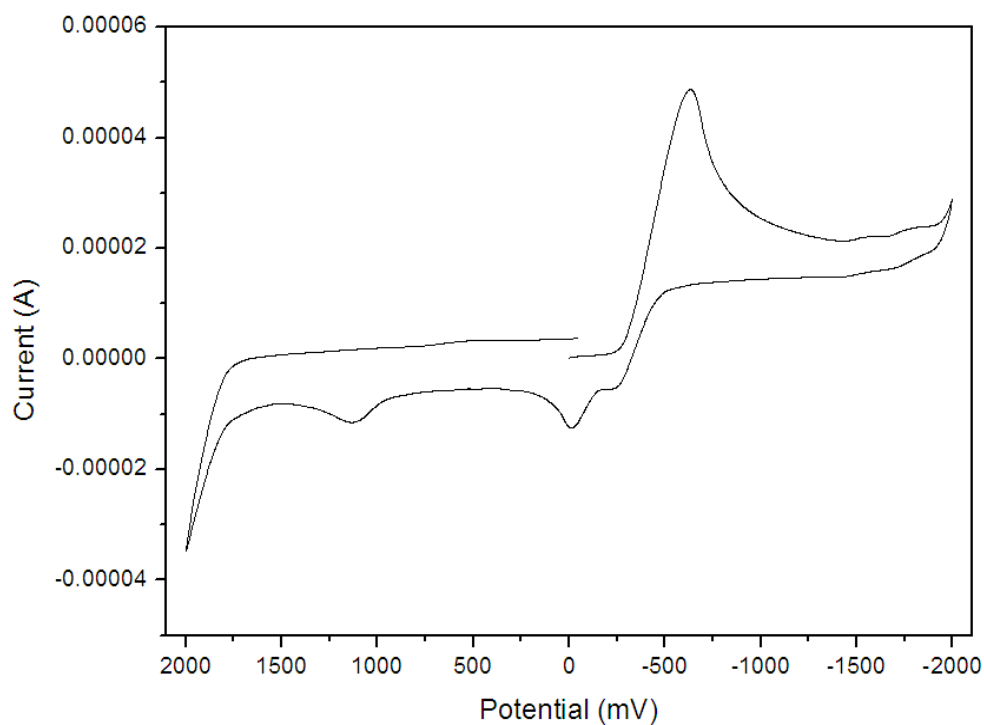


Fig. S9 Cyclic voltammogram of **2** in CH₂Cl₂ (at 100 mV s⁻¹)

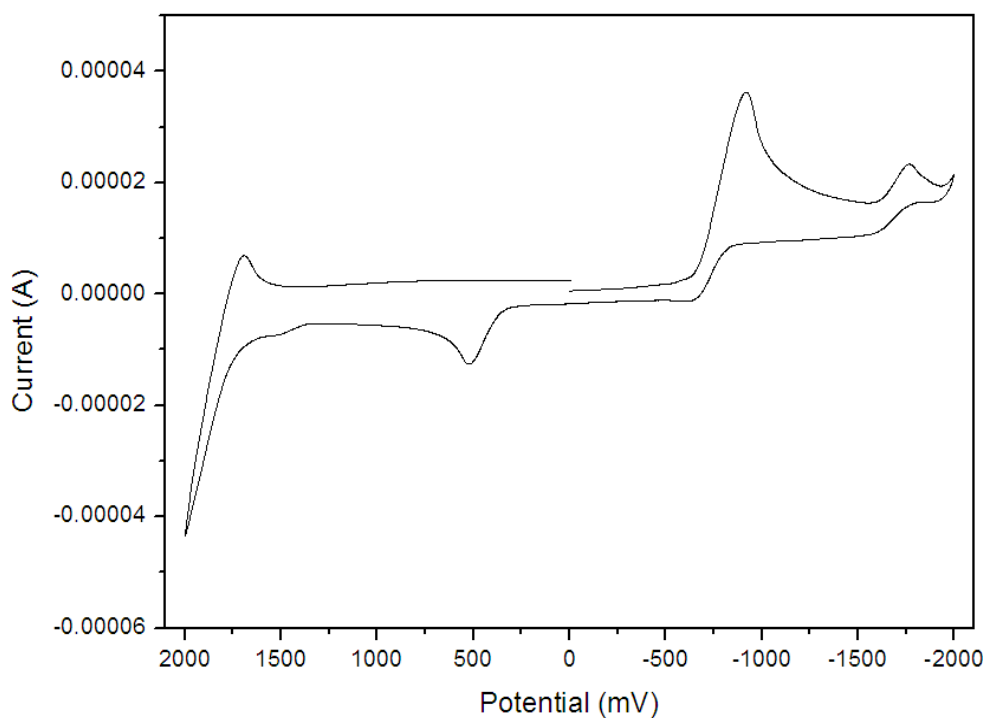


Fig. S10 Cyclic voltammogram of **3a** in CH₂Cl₂ (at 100 mVs⁻¹)

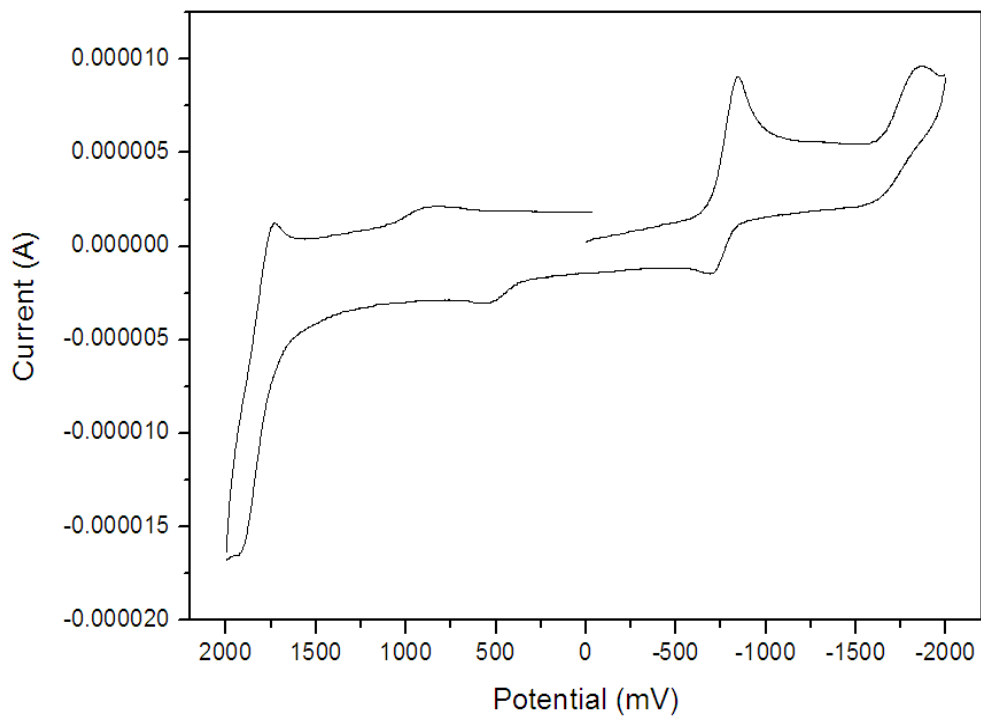


Fig. S11 Cyclic voltammogram of **3b** in CH₂Cl₂ (at 100 mVs⁻¹)

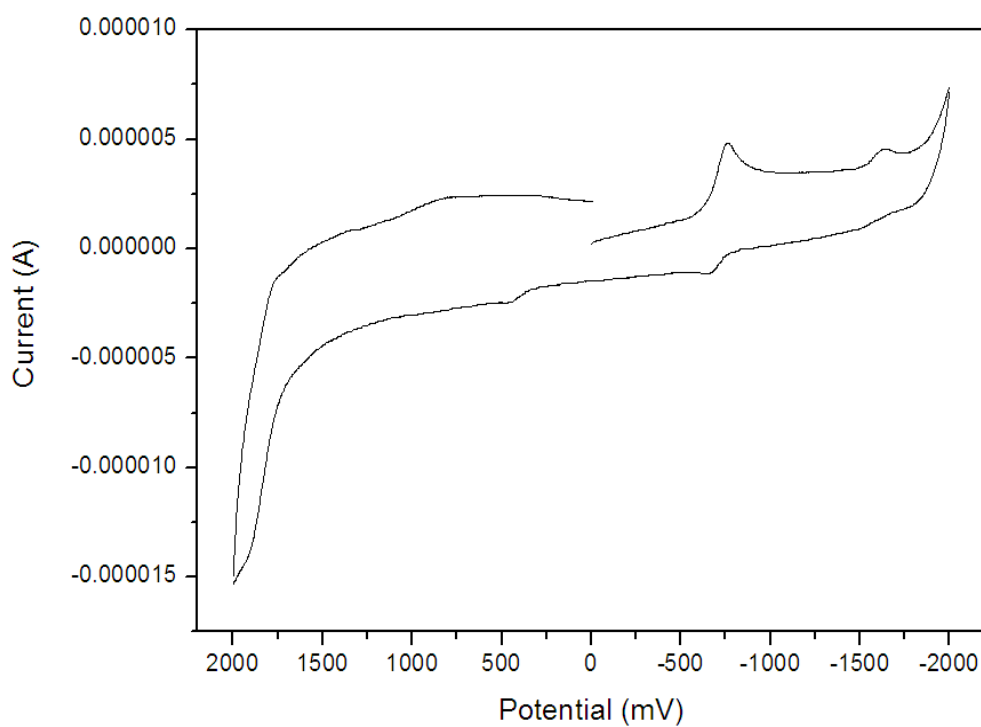


Fig. S12 Cyclic voltammogram of **3c** in CH₂Cl₂ (at 100 mVs⁻¹)

Table S3 Electrochemical data of **2-3(a, b, c)** in CH₂Cl₂ (Scan rate 100 mV/s)

Compound	E _g ^a (eV)	E _{red1/2} (V) vs ferrocene	HOMO ^b /LUMO ^c (eV)
2	2.21	-0.92	-6.37/-4.16
3a	2.45	-1.32	-6.21/-3.76
3b	2.46	-1.27	-6.27/-3.81
3c	2.41	-1.19	-6.30/-3.89

^a Optical band gap, E_g = hc/λ

^b HOMO = LUMO - E_g

^c Based on the assumption that the energy of F₂/F₂⁺ is 5.08 eV relative to vacuum.

6. X-ray crystallographic data of **3a**

Table S4. Crystal data and structure refinement for **3a**

Empirical formula	C10 H5 B Cl4 F2 N2 O
Formula weight	359.77
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group	P2(1)/c
Unit cell dimensions	a = 9.8376(14) Å $\alpha = 90^\circ$ b = 9.1284(12) Å $\beta = 95.922^\circ$ c = 15.0458(19) Å $\gamma = 90^\circ$
Volume	1343.9(3) Å ³
Z	4
Calculated density	1.778 Mg/m ³
Absorption coefficient	0.896 mm ⁻¹
F(000)	712
Crystal size	0.4 x 0.3 x 0.2 mm
Theta range for data collection	2.08 to 24.99°
Index ranges	-9 ≤ h ≤ 11, -10 ≤ k ≤ 9, -17 ≤ l ≤ 17
Reflections collected	7960
Independent reflections	2353 [R(int) = 0.0192]
Completeness to theta = 24.990	100 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2353 / 0 / 181
Goodness-of-fit on F ²	1.068
Final R indices [I > 2σ(I)]	R1 = 0.0384, wR2 = 0.1098
R indices (all data)	R1 = 0.0475, wR2 = 0.1159
Largest diff. peak and hole	0.54 and -0.31 e. Å ³

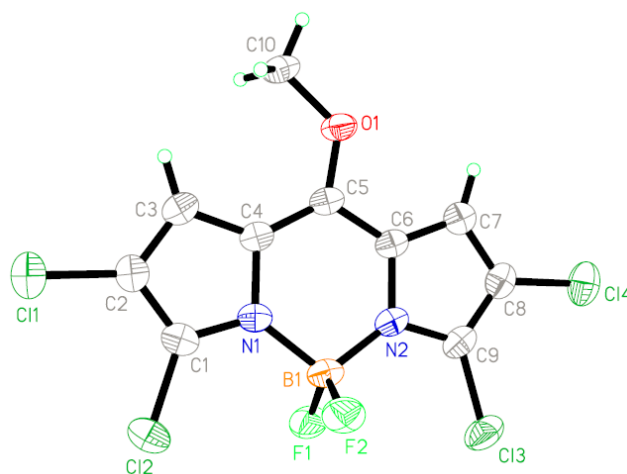


Fig. S13 X-Ray structure of **3a**

7. NMR spectra

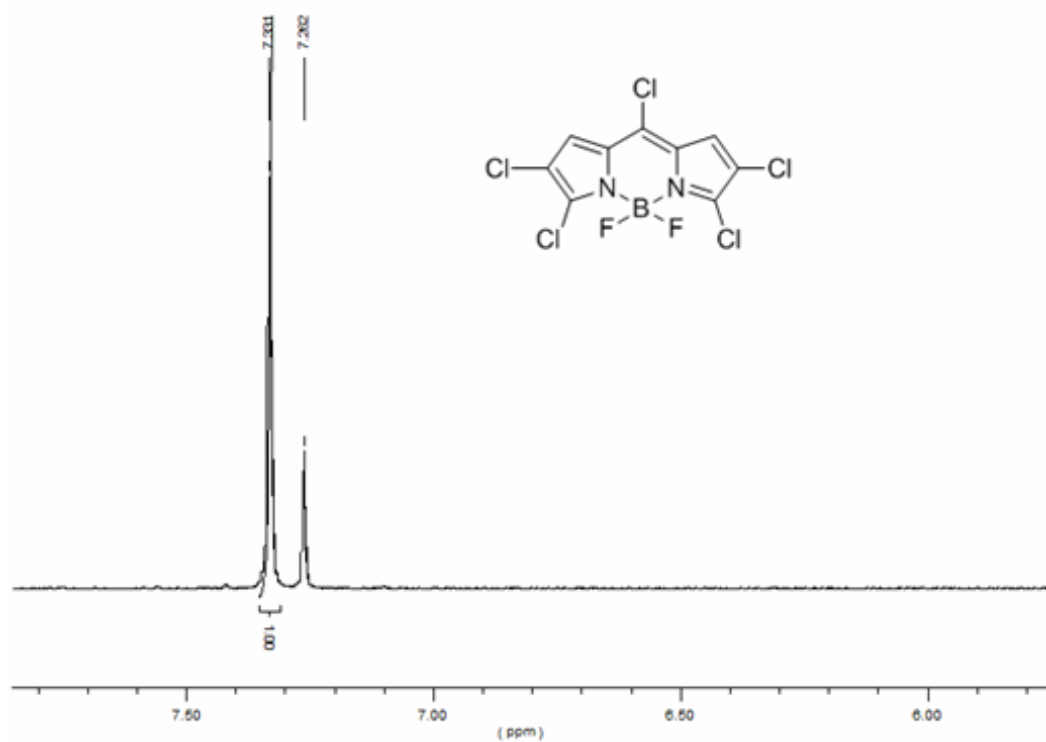


Fig. S14 ^1H NMR (CDCl₃) spectrum of **2**

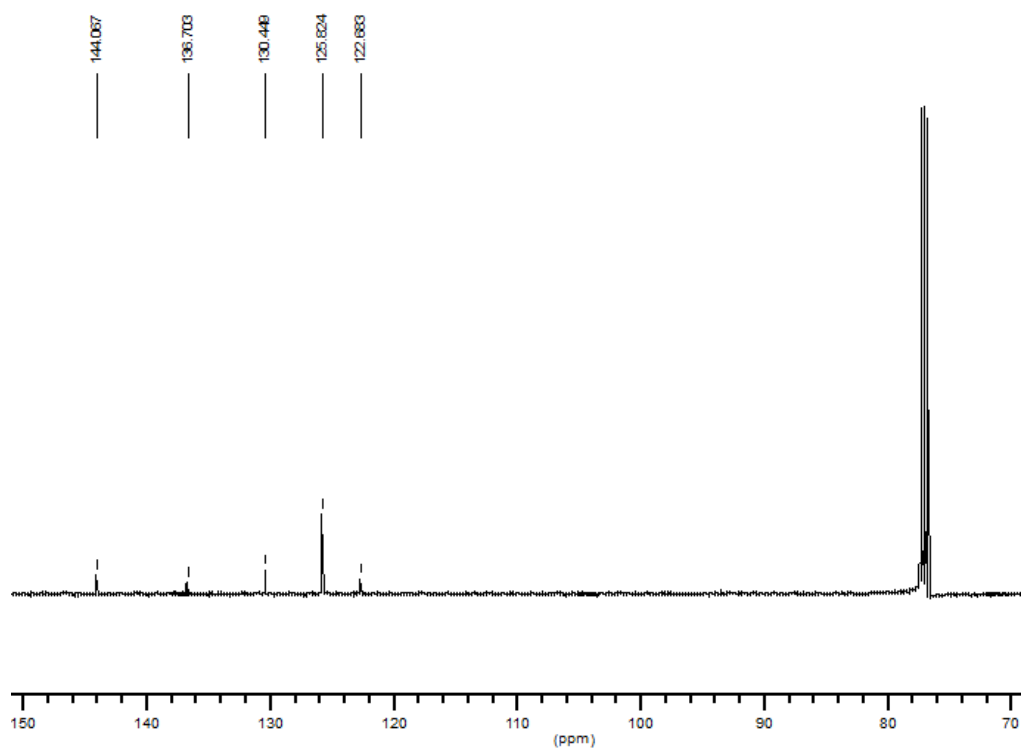


Fig. S15 ^{13}C NMR (CDCl₃) spectrum of **2**

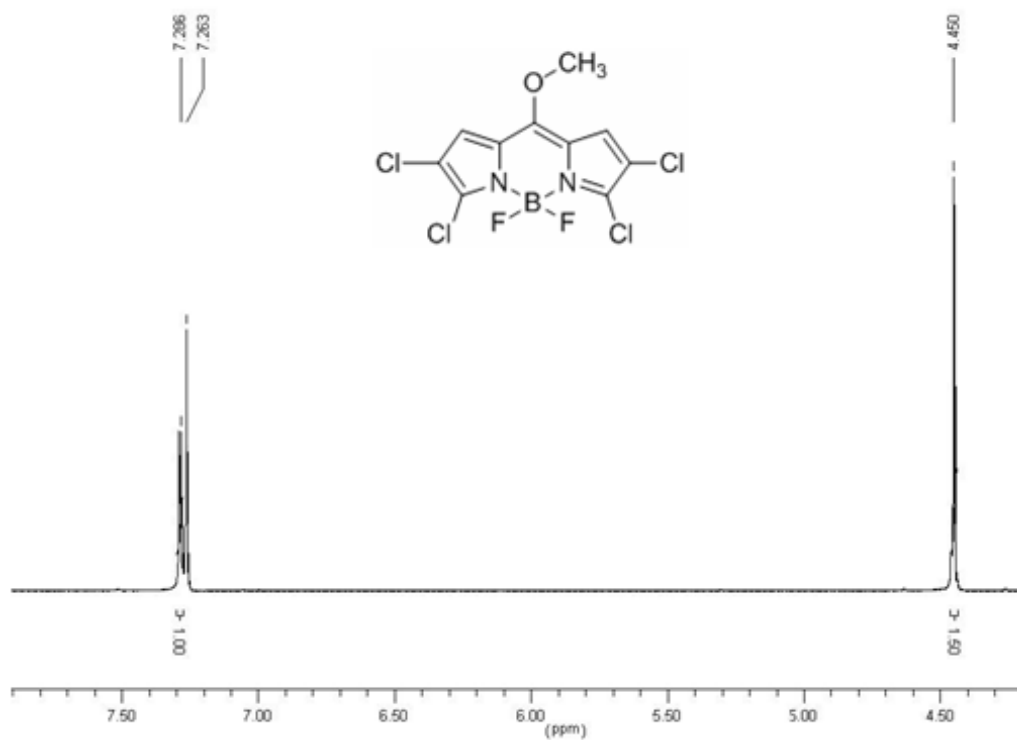


Fig. S16 ^1H NMR (CDCl_3) spectrum of **3a**

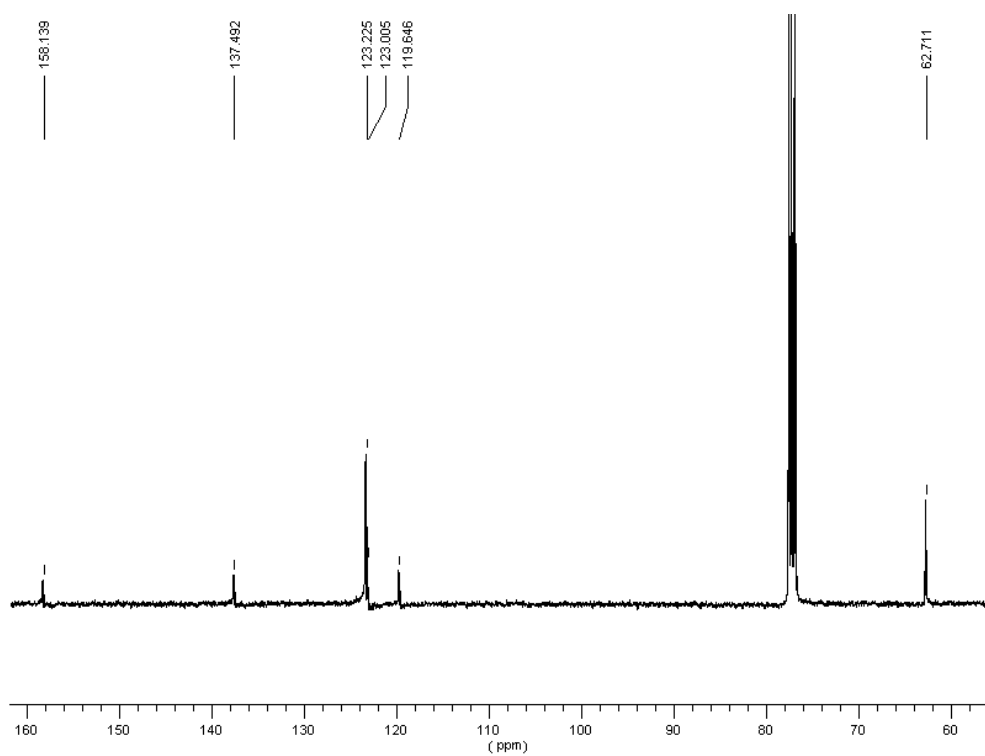


Fig. S17 ^{13}C NMR (CDCl_3) spectrum of **3a**

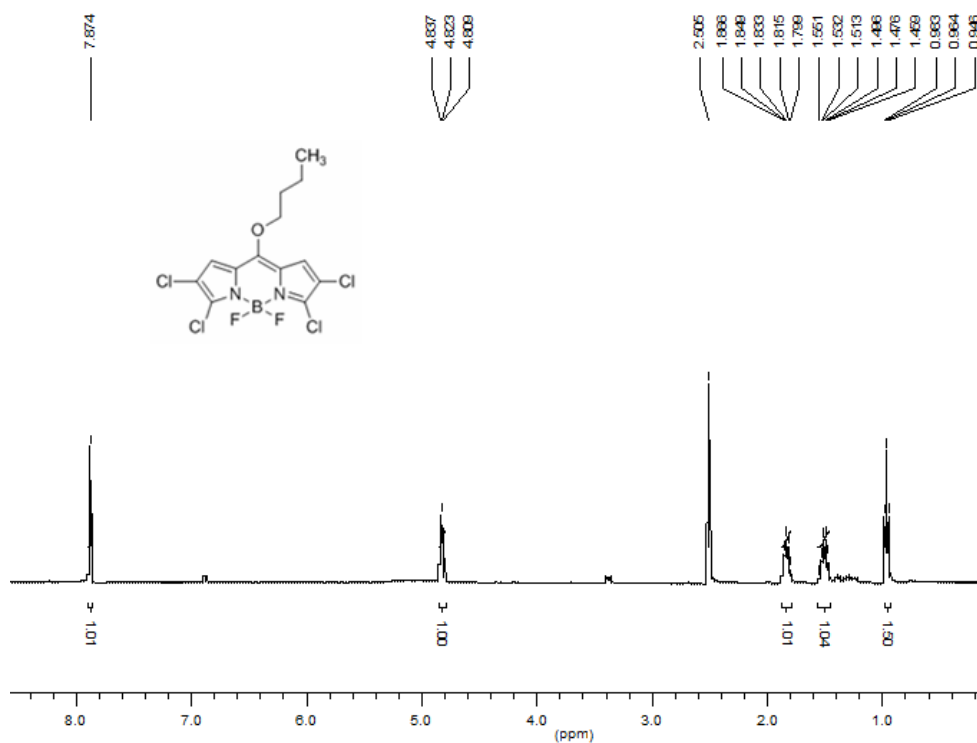


Fig. S18 ^1H NMR (DMSO) spectrum of **3b**

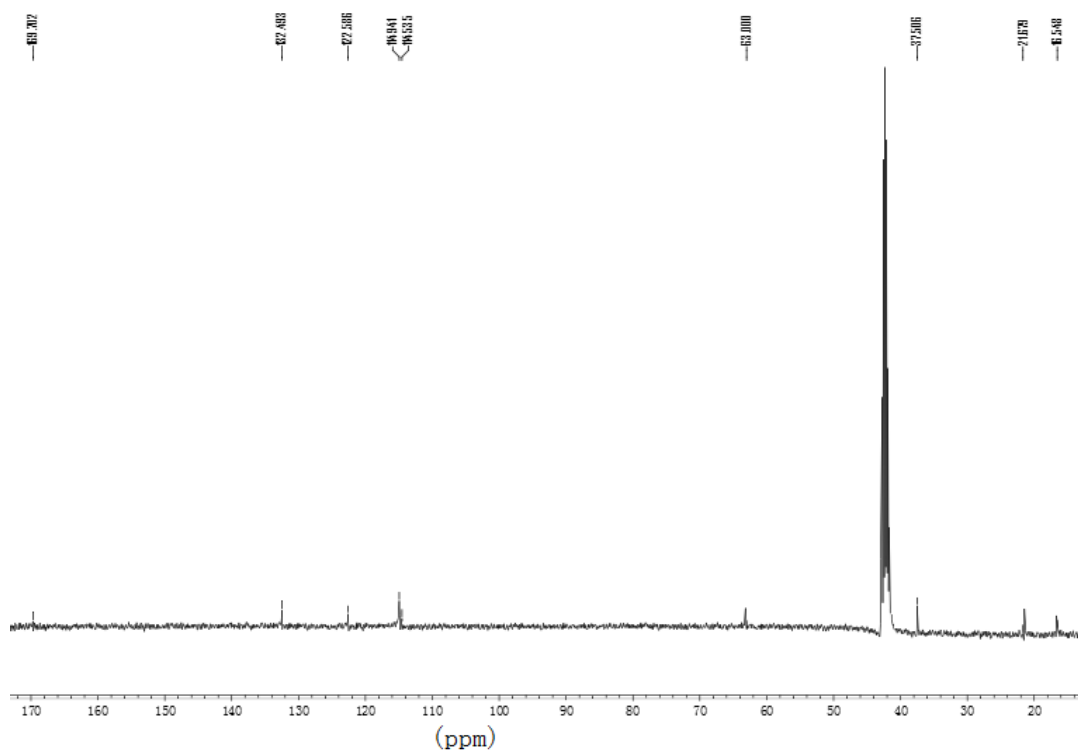


Fig. S19 ^{13}C NMR (DMSO) spectrum of **3b**

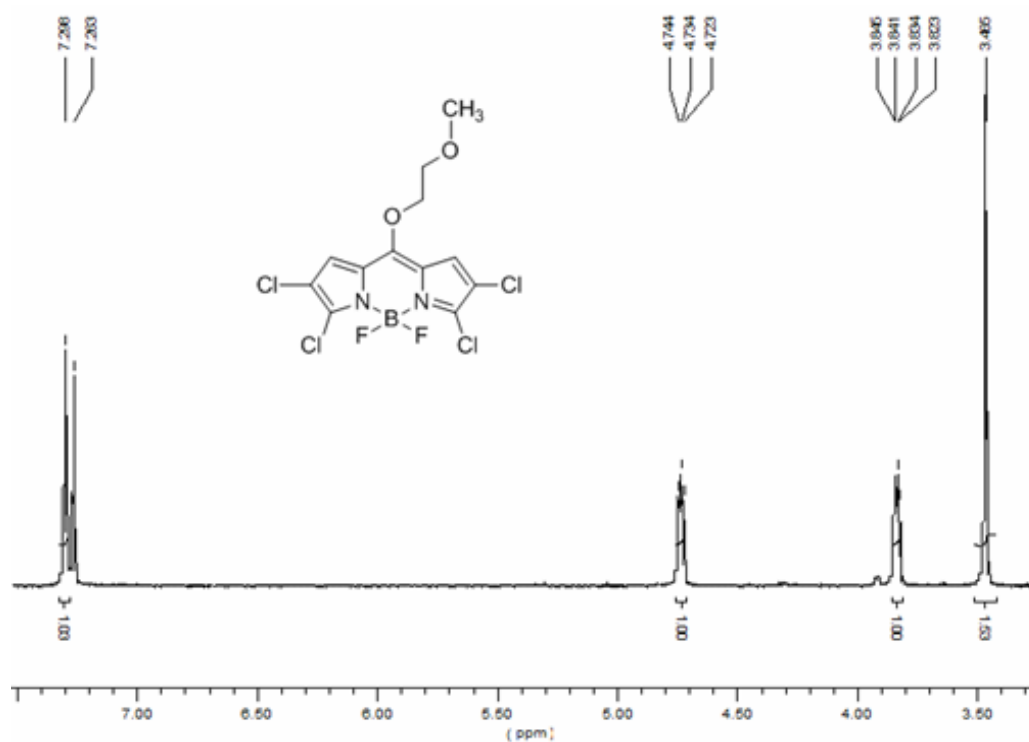


Fig. S20 $^1\text{H NMR}$ (CDCl₃) spectrum of **3c**

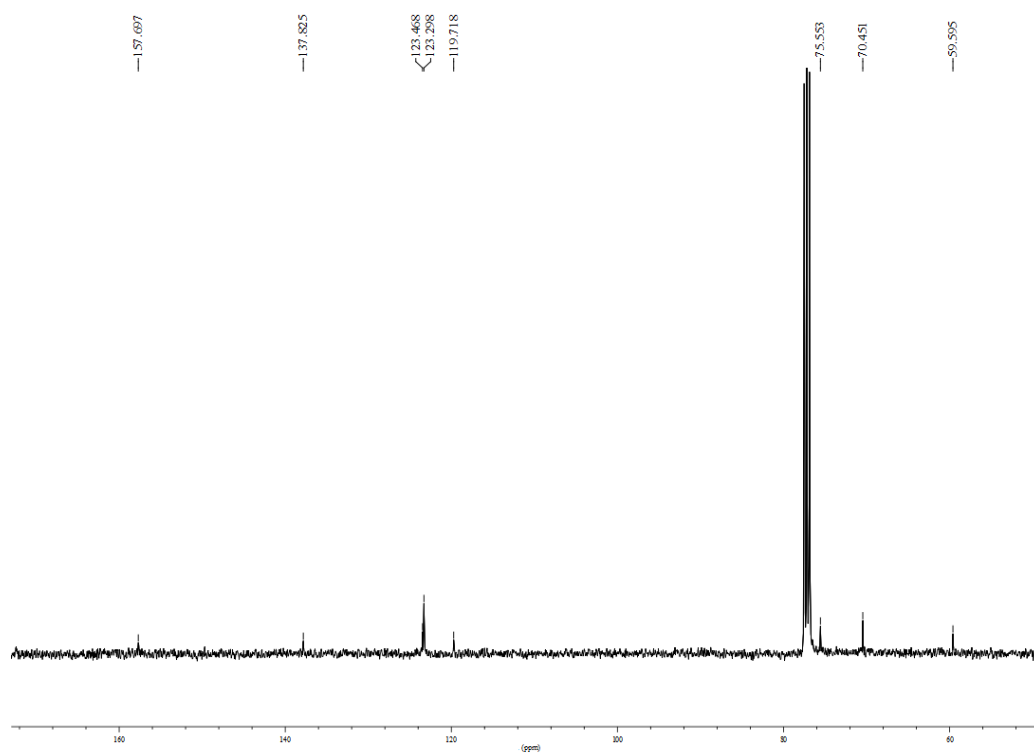


Fig. S21 $^{13}\text{C NMR}$ (CDCl₃) spectrum of **3c**

Reference

1. (a) B. C. Thompson, Y. G. Kim, T. D. Mccarley and J. R. Reynolds, *J. AM. CHEM. SOC.*, 2006, **128**, 12714 (b) Y. P. Xie, X. F. Zhang, Y. Xiao, Y. D. Zhang, F. Zhou, J. Qi and J. L. Qu, *Chem. Comm.*, 2012, **48**, 4338.
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