Supporting Information for:

Thienyl-substituted BODIPYs with strong visible light absorption and long-lived triplet excited states as organic triplet sensitizers for triplet-triplet annihilation upconversion

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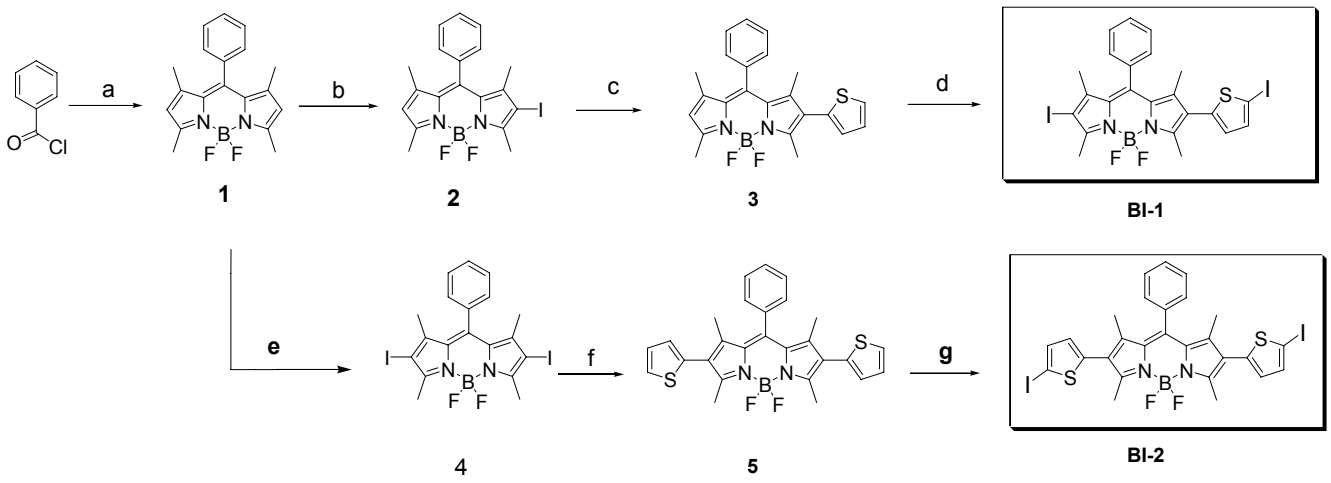
1.0 Synthesis and molecular structure characterization data.



Scheme S1: (a) 2,4-dimethylpyrrole, under Ar, overnight; TEA, $BF_3{\cdot}OEt_2$, overnight; yield: 55.0 %; (b) *N*-Iodosuccinimide (NIS), CH_2Cl_2; yield: 45.0 %; (c) thiophene-2-boronic acid, $K_3PO_4{\cdot}3H_2O$, $Pd(COO)_2$, toluene, ethanol, under Ar, 80 °C, 8 h; yield: 63.4 %; (d) $CHCl_3$, glacial acetic acid, NIS, overnight; yield: 70.0 %; (e) NIS, CH_2Cl_2; yield: 77.0 %; (f) thiophene-2-boronic acid, $K_3PO_4{\cdot}3H_2O$, $Pd(COO)_2$, toluene, ethanol, under Ar, 80 °C, 8 h; yield: 54.4 %; (g) $CHCl_3$, glacial acetic acid, NIS, overnight; yield: 50.0 %.

2.0 NMR and HR-MS spectra.

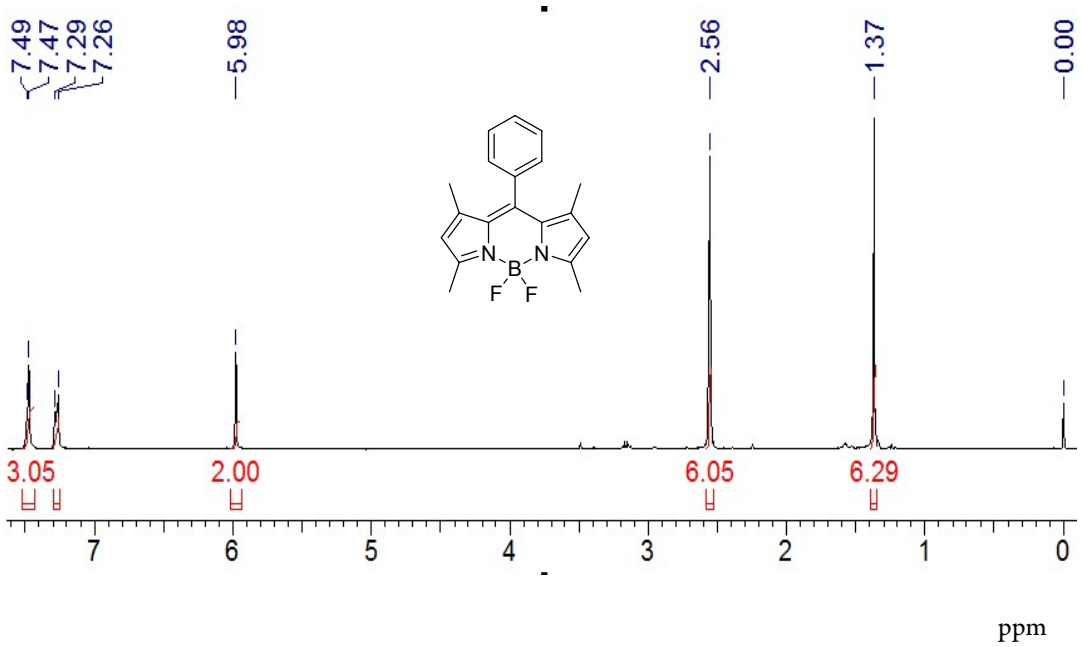


Fig. S1 ^{1}H NMR of compound **1** (400 MHz. $CDCl_3$).

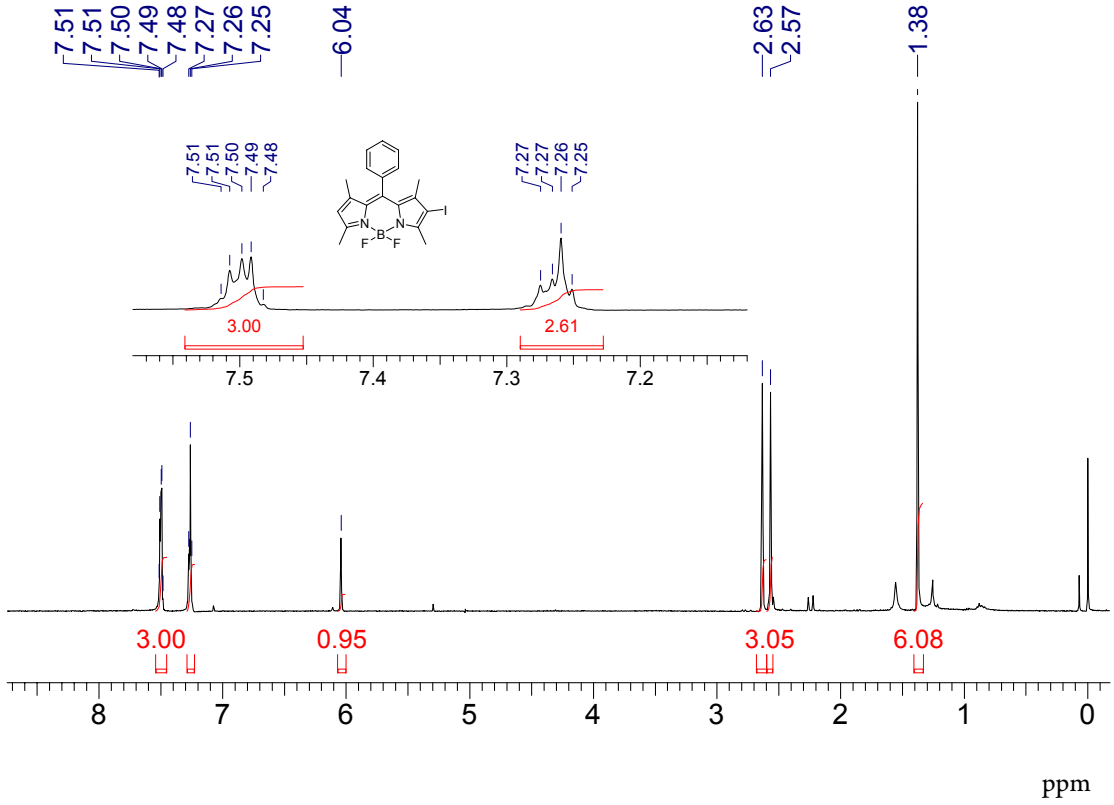


Fig. S2 ^{1}H NMR of compound **2** (400 MHz. $CDCl_3$).

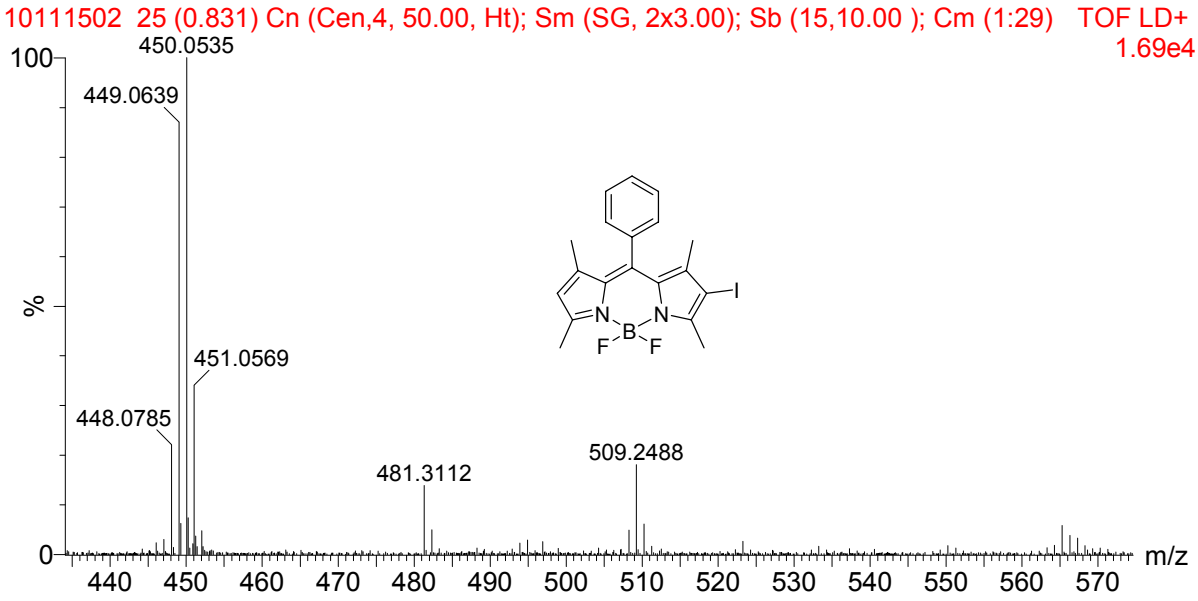


Fig. S3 TOF LD^+ of **2.**

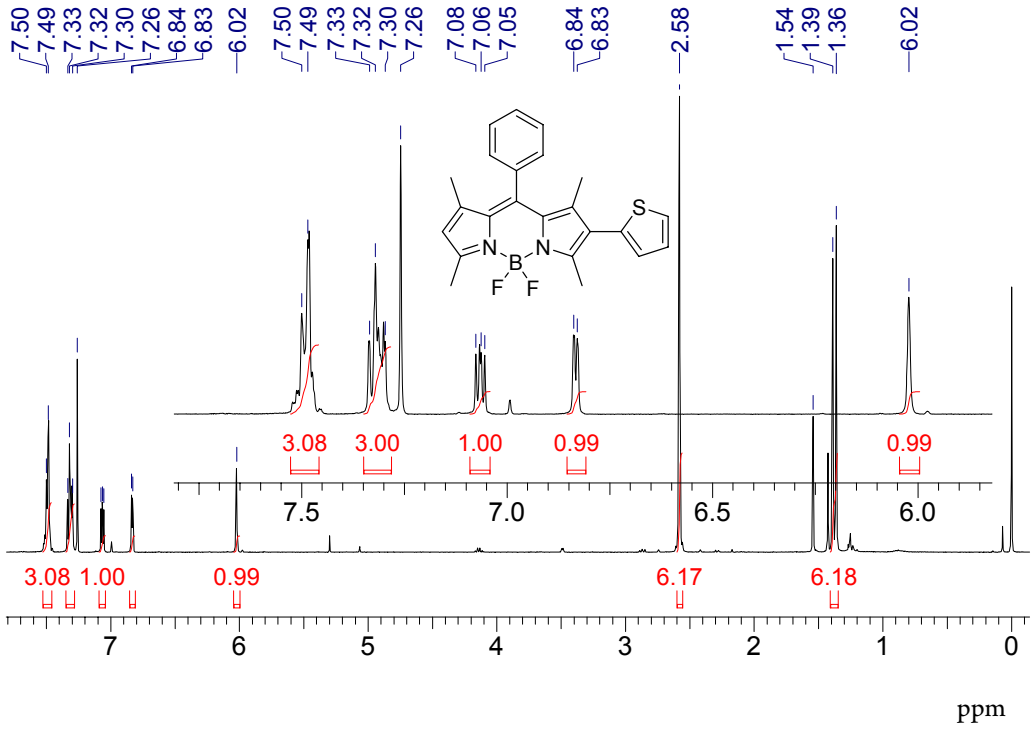


Fig. S4 ^{1}H NMR of compound **3** (400 MHz. $CDCl_3$).

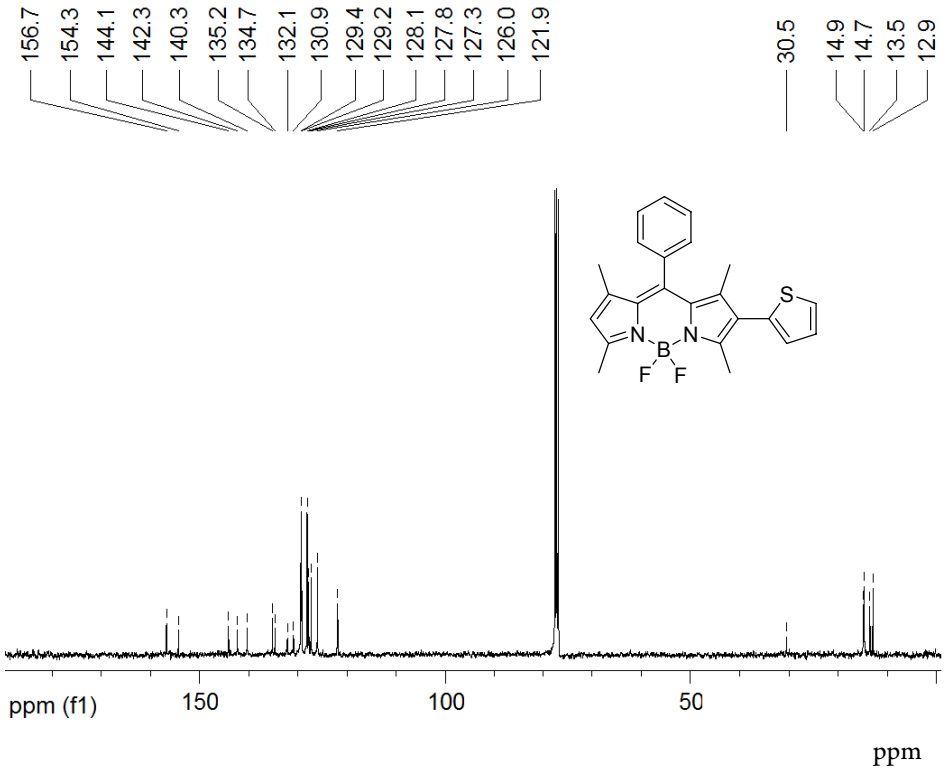


Fig. S5 ^{13}C NMR of compound **3** (400 MHz. $CDCl_3$).

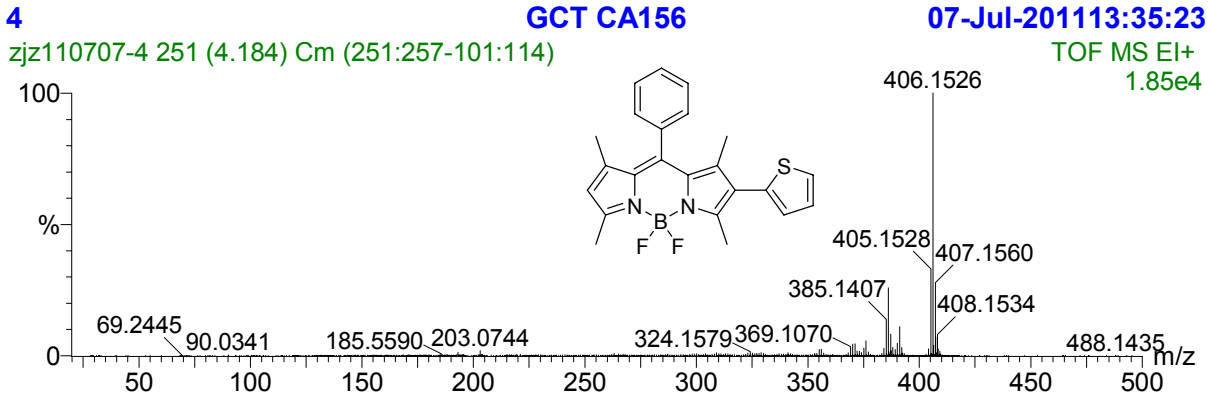


Fig. S6 TOF MS EI^+ of **3.**

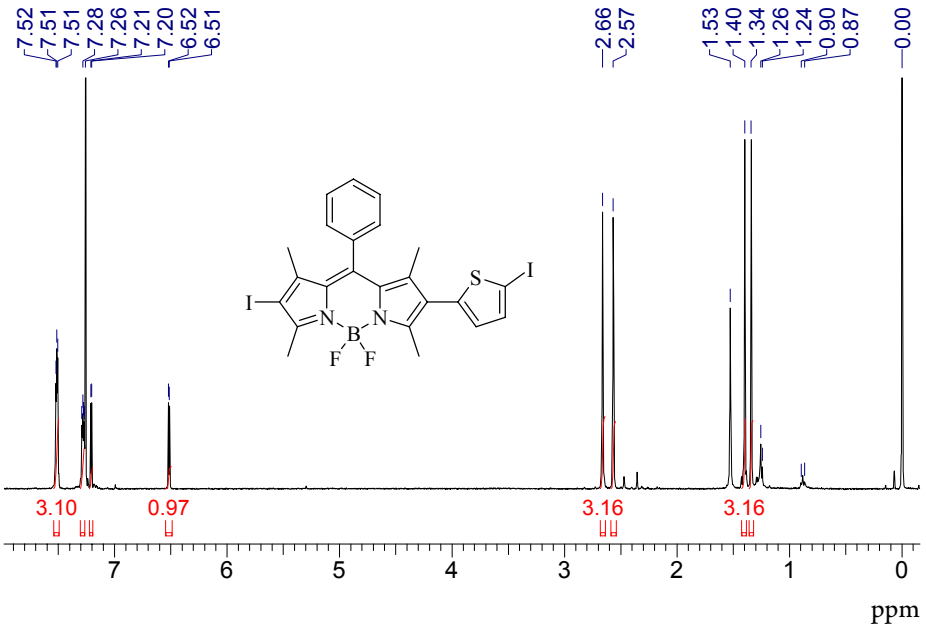


Fig. S7 ^{1}H NMR of compound **BI-1** (400 MHz. $CDCl_3$). (δ 1.53 is due to H_2O, peaks at 1.25 and 0.88 ppm are due to *n*-hexane).

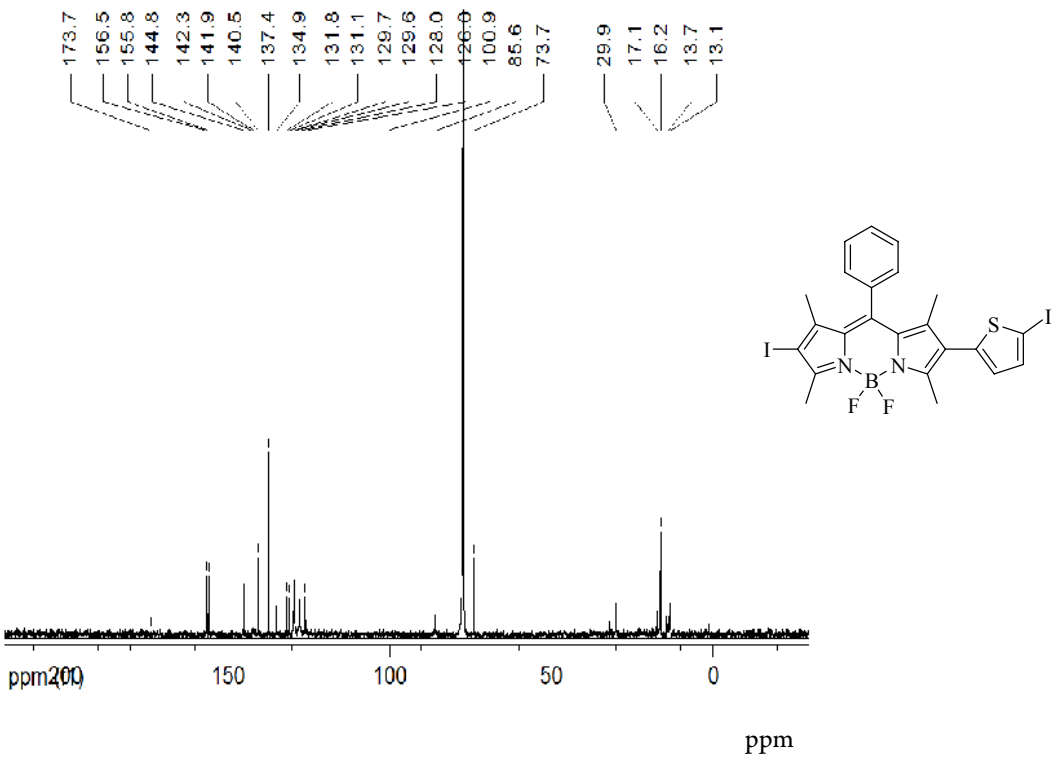


Fig. S8 ^{13}C NMR of compound **BI-1** (100 MHz. $CDCl_3$).

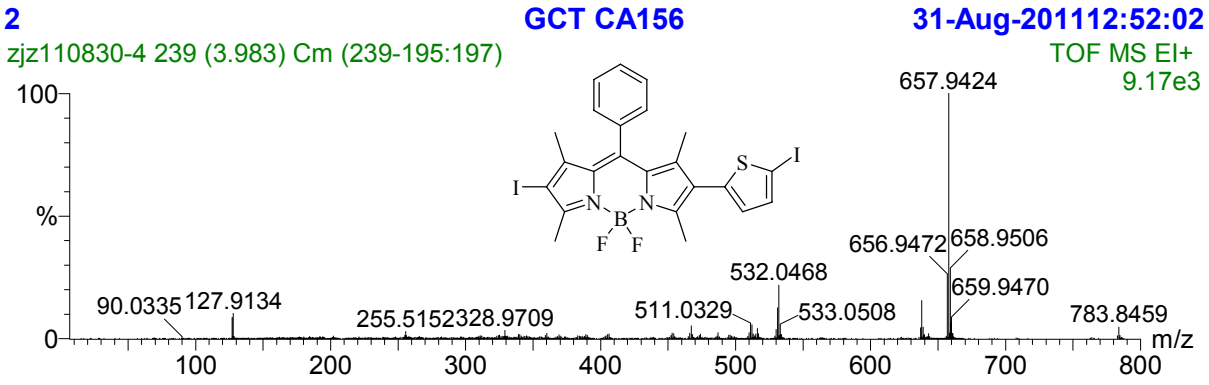


Fig. S9 TOF MS EI⁺ of **BI-1.**

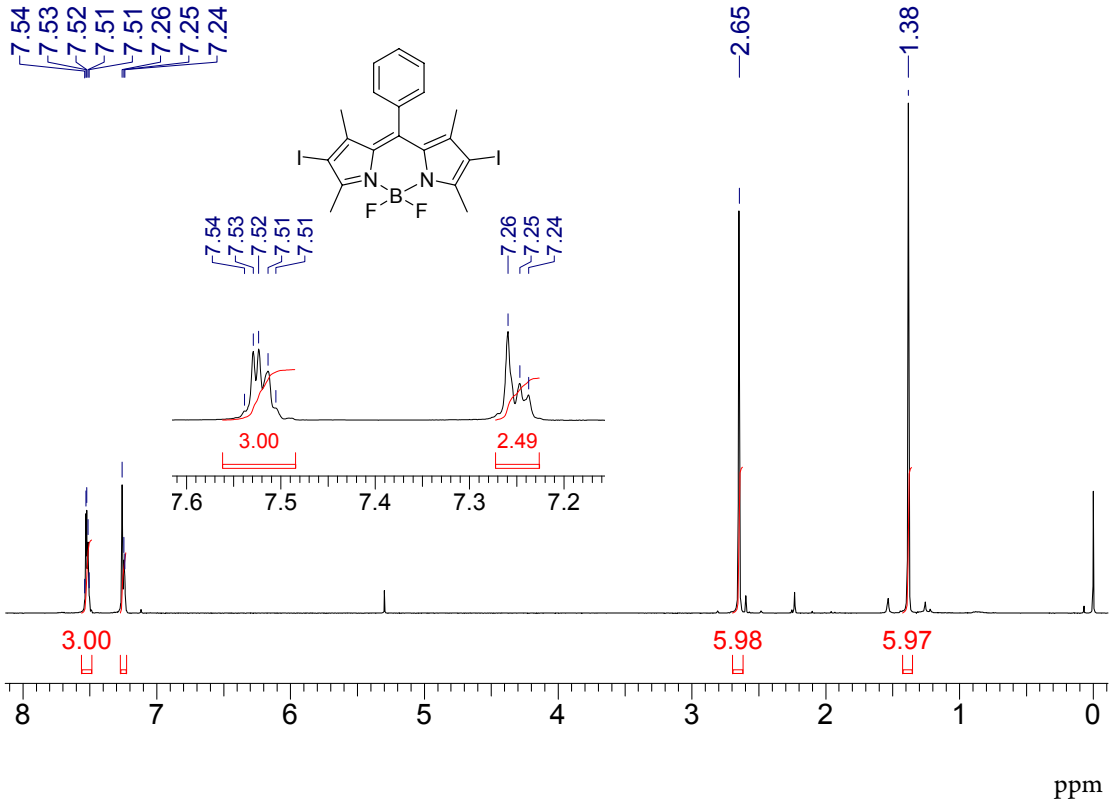


Fig. S10 ^{1}H NMR of **B-2** (400 MHz, $CDCl_3$).

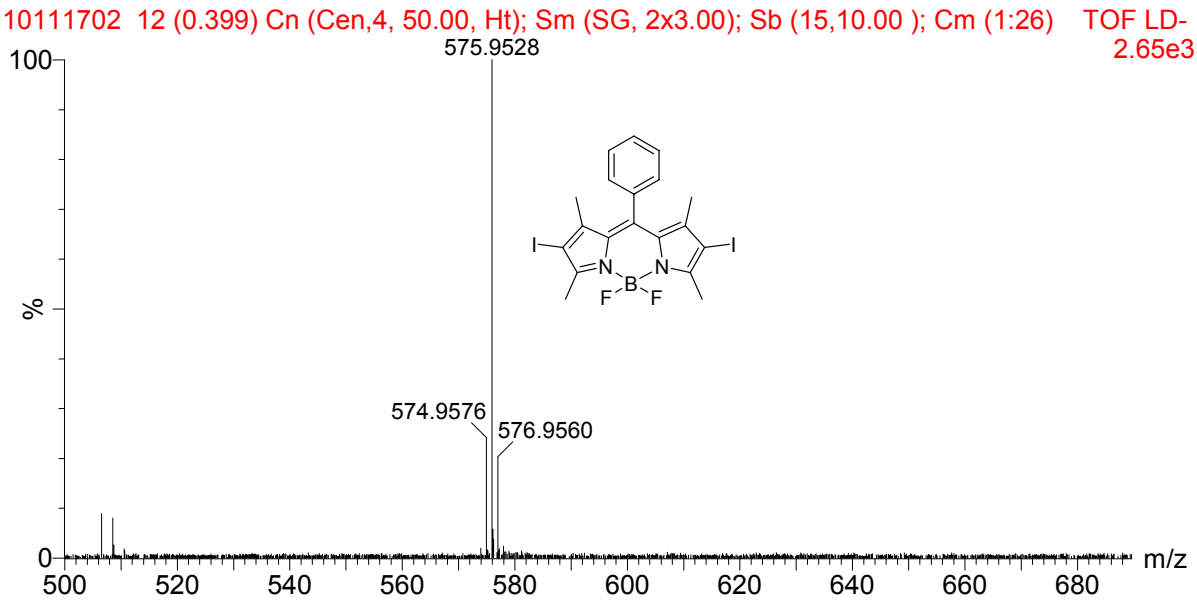


Fig. S11 TOF LD$^-$ of **B-2.**

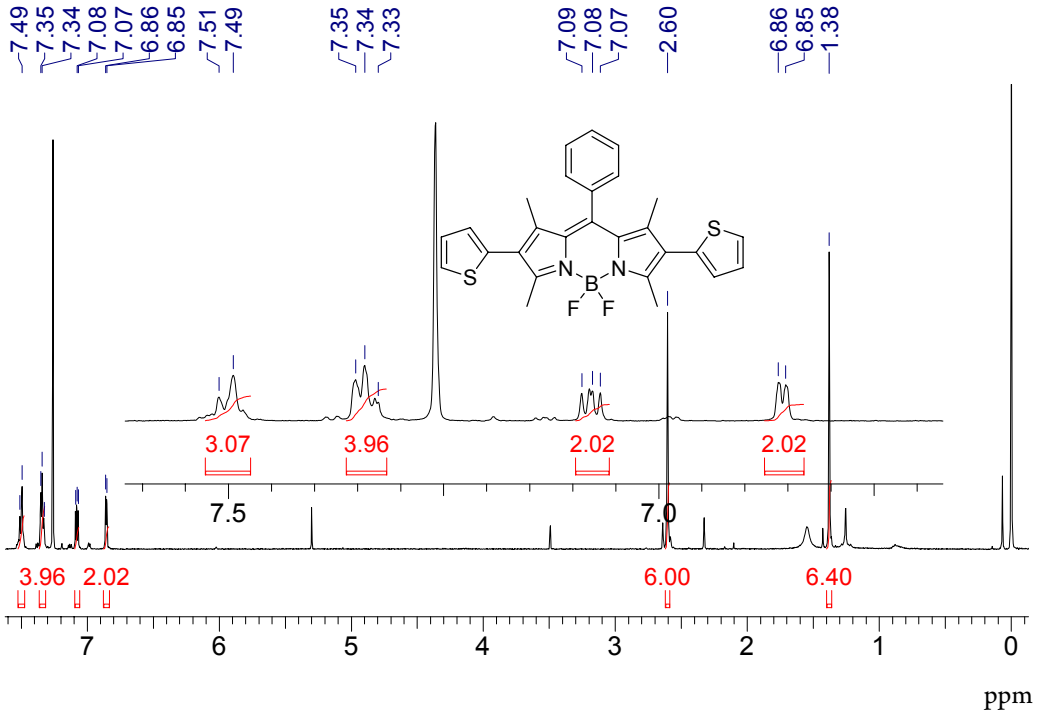


Fig. S12 ^{1}H NMR of **4** (400 MHz, $CDCl_3$).

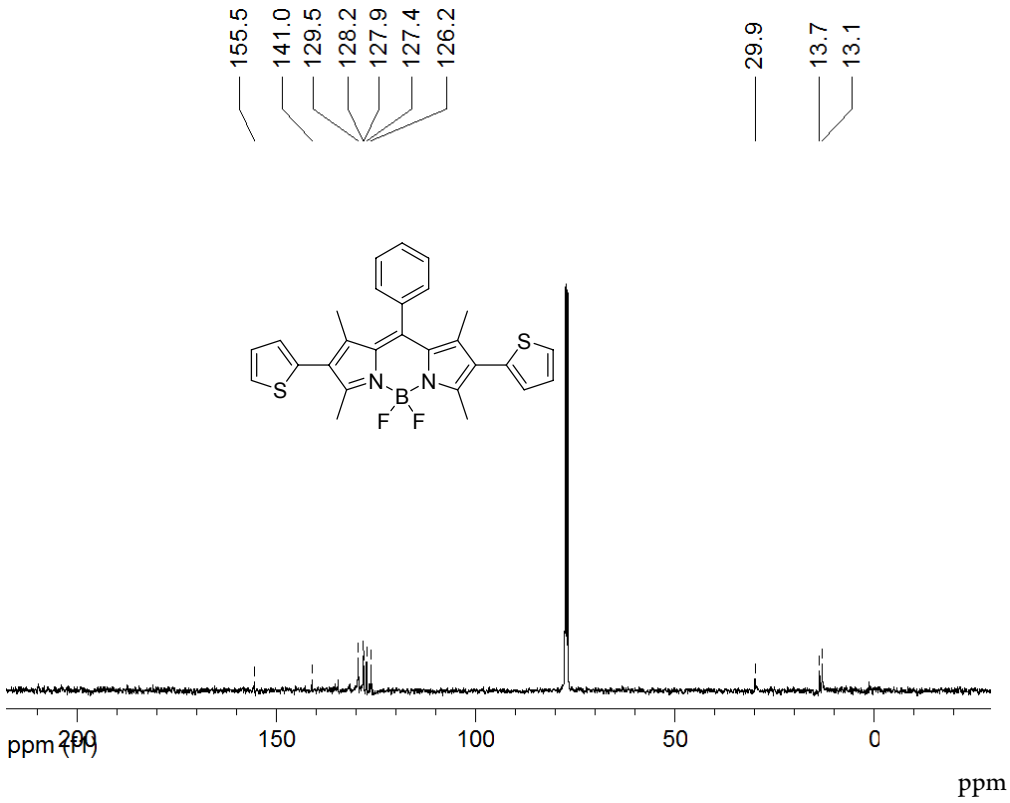


Fig. S13 ^{13}CNMR of compound **4** ($CDCl_3$).

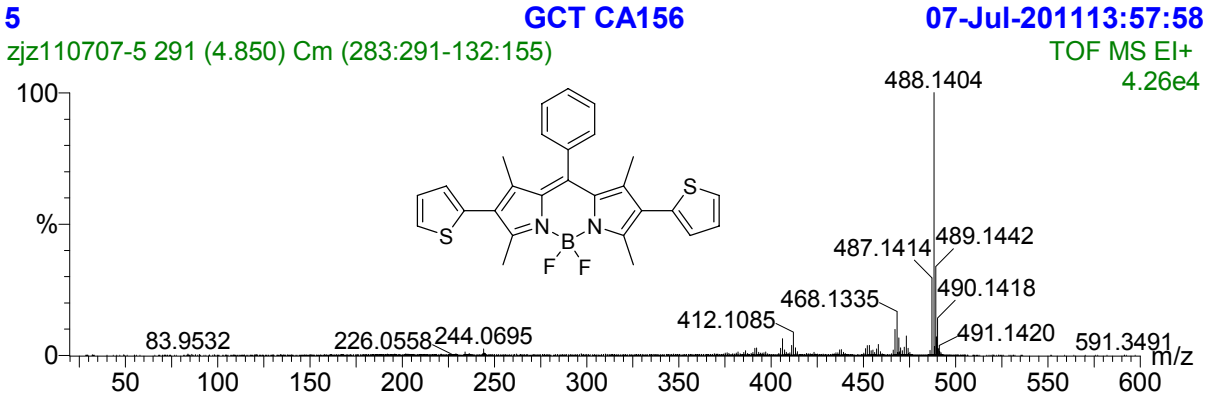


Fig. S14 TOF MS EI$^+$ of **4.**

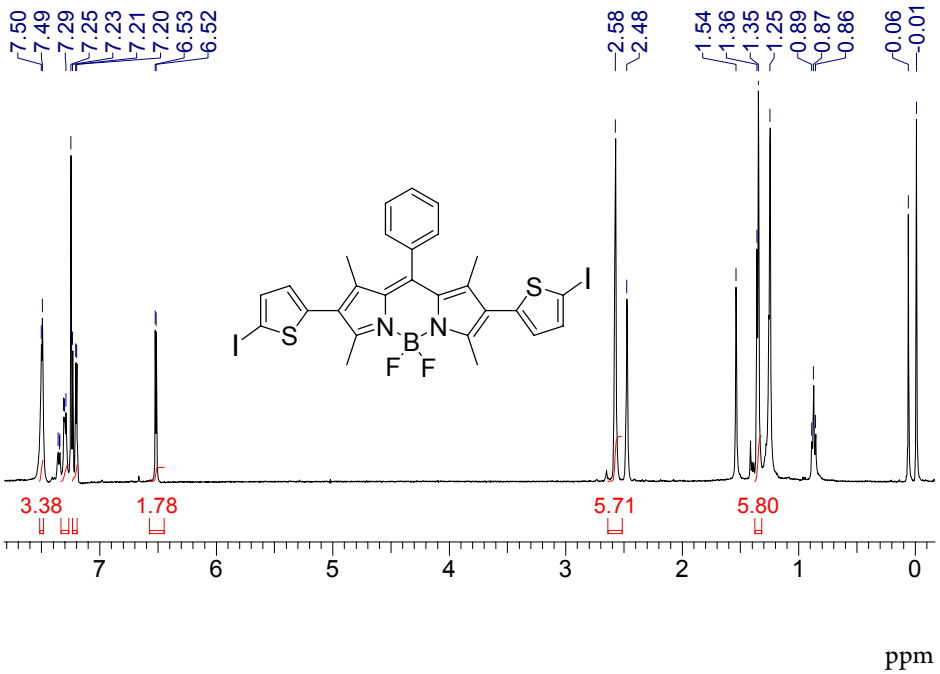


Fig. S15 ^{1}H NMR of compound **BI-2** (400 MHz. $CDCl_3$).

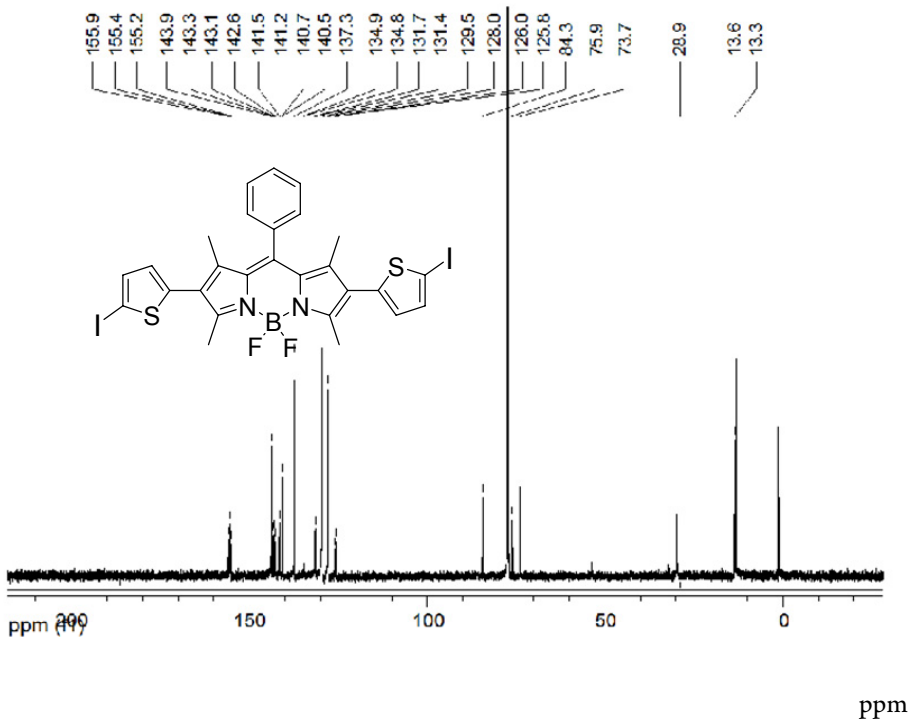


Fig. S16 ^{13}C NMR of compound **BI-2** (100 MHz. $CDCl_3$).

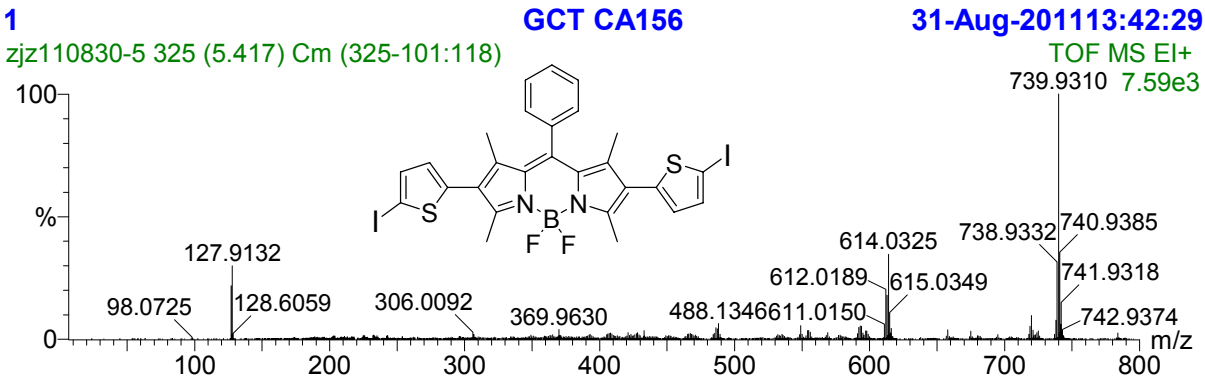


Fig. S17 TOF MS EI⁺ of **BI-2.**

3.0 Transient absorption details

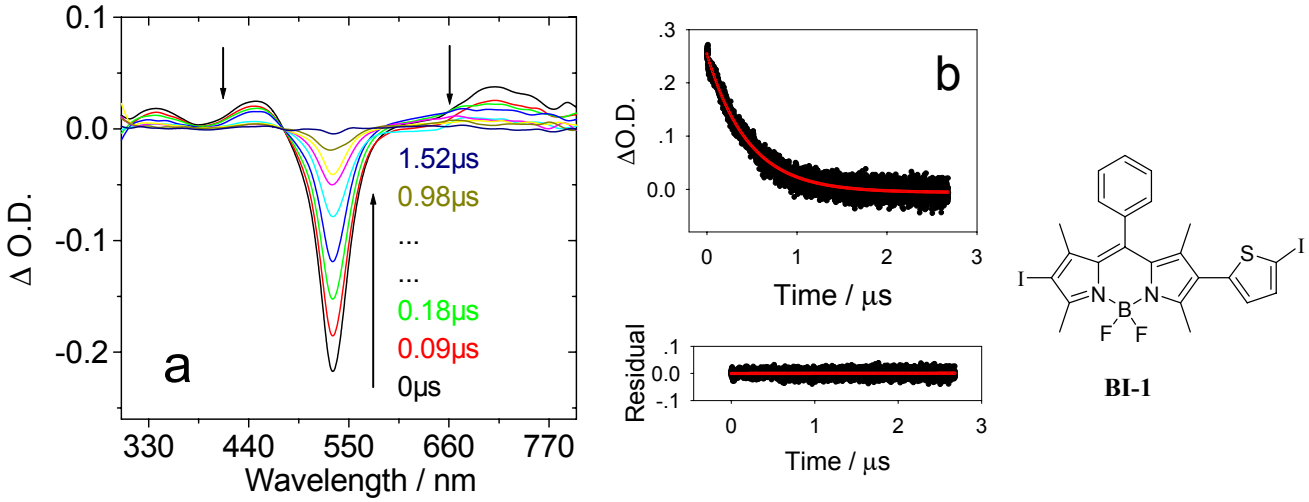


Fig. S18 (a) Transient absorption difference spectra of **BI-1** after pulsed laser excitation (λ_{ex} = 532 nm). (b) Decay trace of the transient at 532 nm. 1.0×10^{-5} M. In aerated toluene . 20 °C.

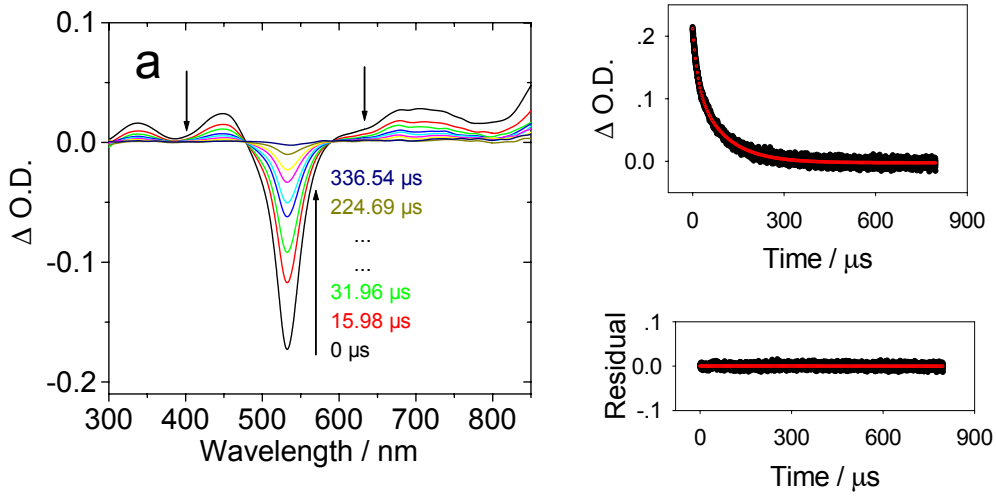


Fig. S19 (a) Transient absorption difference spectra of **BI-1** after pulsed laser excitation (λex = 532 nm). (b) Decay trace of the transient at 532 nm. 1.0×10^{-5} M. in deaerated toluene. 20 °C.

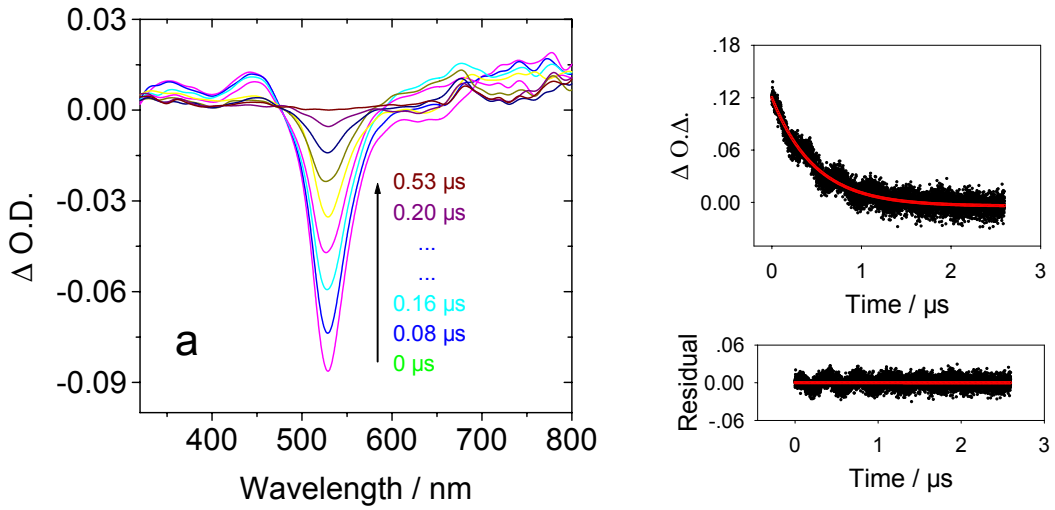


Fig. S20 Transient absorption difference spectra of **BI-2** (b) Decay trace of the transient at 530 nm after pulsed laser excitation (λ_{ex} = 532 nm). 1.0 × 10^{-5} M. In aerated toluene. 20 °C.

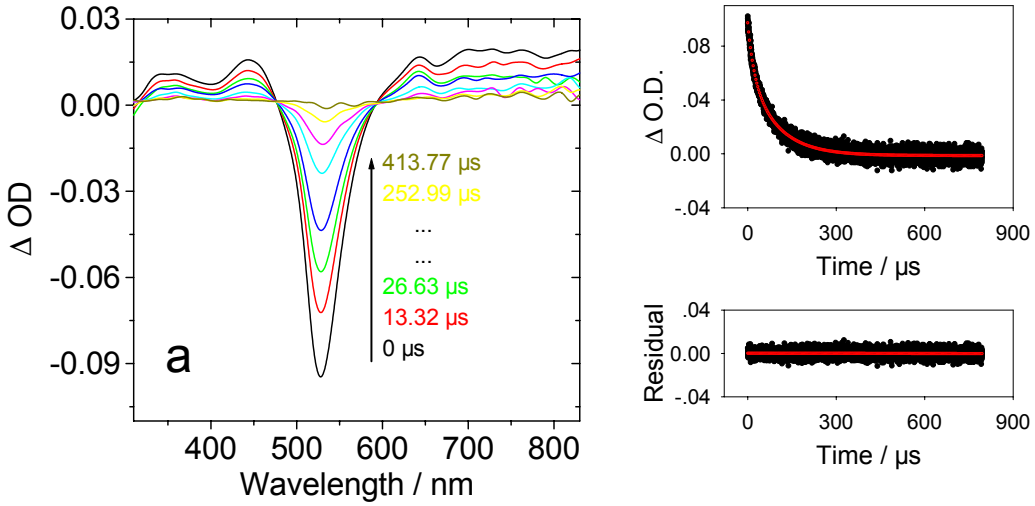


Fig. S21 Transient absorption difference spectra of **BI-2**. (b) Decay trace of the transient at 527 nm after pulsed laser excitation (λ_{ex} = 532 nm). 1.0 × 10^{-5} M. In deaerated toluene. 20 °C.

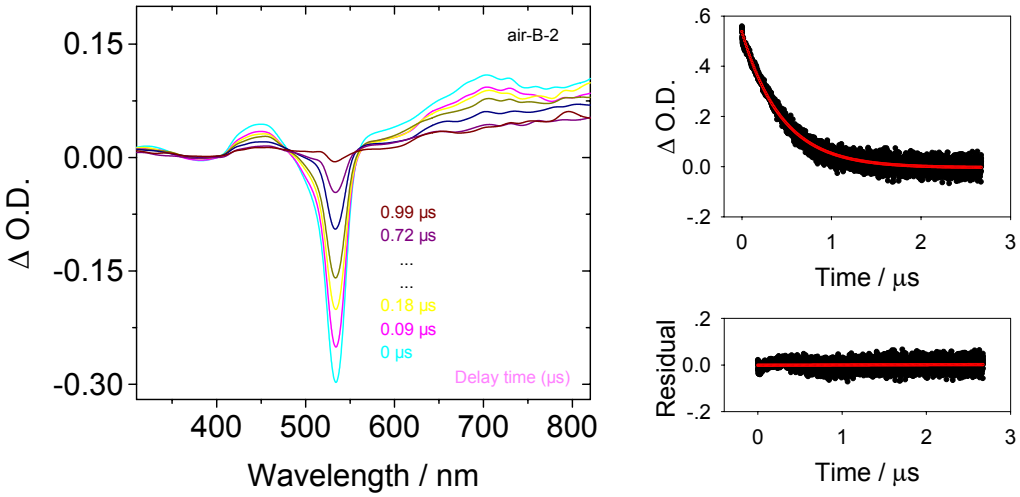


Fig. S22 Transient absorption difference spectra of **B-2**. (b) Decay trace of the transient at 531 nm after pulsed laser excitation (λ_{ex} = 532 nm). 1.0 × 10^{-5} M. In toluene. 20 °C.

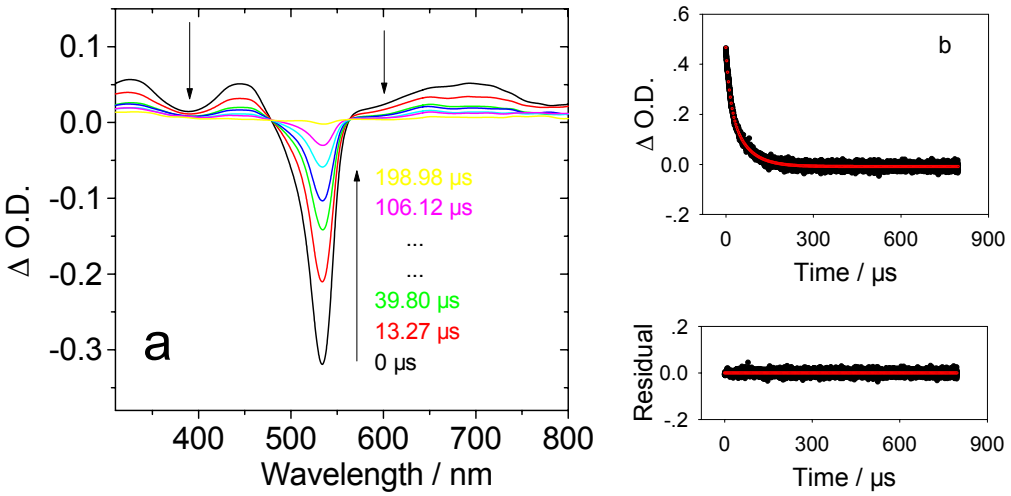


Fig. S23 Transient absorption difference spectra of **B-2**. (b) Decay trace of the transient at 531 nm after pulsed laser excitation (λ_{ex} = 532 nm). 1.0 × 10^{-5} M. In deaerated toluene. 20 °C.

4.0 Calculation details

Table 1. Selected parameters for the vertical excitation (UV-vis absorptions) and the emission of **1**. Electronic excitation energies (eV) and oscillator strengths (*f*), configurations of the low-lying excited states of the compounds. The calculation of the S_0–S_1 energy gaps are based on the optimized ground state geometries (UV-vis absorption) and the optimized S_1 excited state geometries (fluorescence emission). Methanol was used as solvent in all the calculations. Calculated by DFT/TDDFT//B3LYP/6-31G(d) with Gaussian 09W.

Compounds		Electronic Transitions [a]	TDDFT//B3LYP/6-31G(d)			
			Excitation Energy	*f* [b]	Composition [c]	CI [d]
1	Absorption [e]	$S_0 \rightarrow S_1$	2.92 eV(425 nm)	0.5874	H-1→L	0.1272
					H→L	0.6990
	Emission [f]	$S_1 \rightarrow S_0$	2.63 eV (472 nm)	0.7741	H→ L	0.7066

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] oscillator strength. [c] H stands for HOMO and L stands for LUMO. Only the main configurations are presented. [d] Coefficient of the wavefunction for each excitations. The CI coefficients are in absolute values. [e] The calculations on UV-vis absorption were based on the optimized ground state geometry. [f] The calculations on fluorescence are based on the optimized S_1 state geometry.

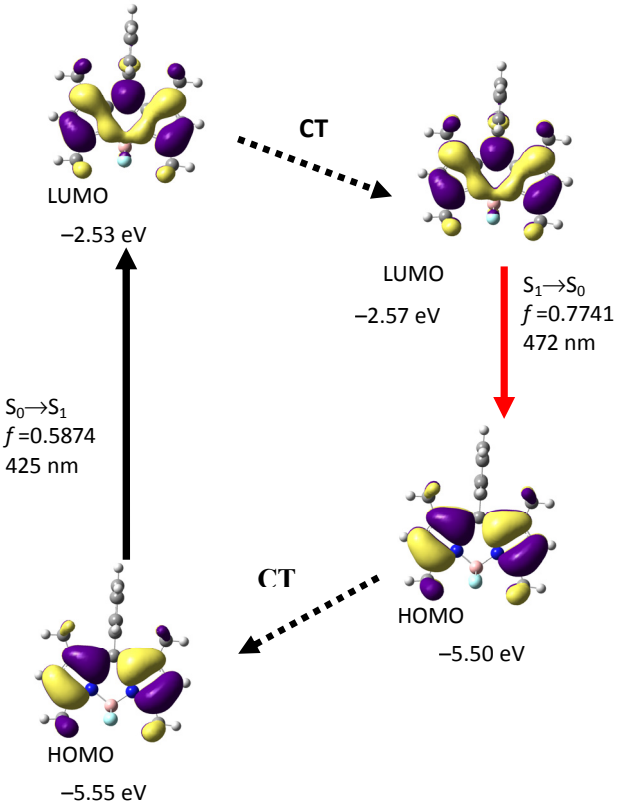


Fig. S24 The frontier molecular orbitals (MOs) involved in the vertical excitation (i.e. UV-vis absorption, the left column) and emission of **1** (the right column). Methanol was used as the solvent.

5.0 Absorption and emission spectra of the acceptor.

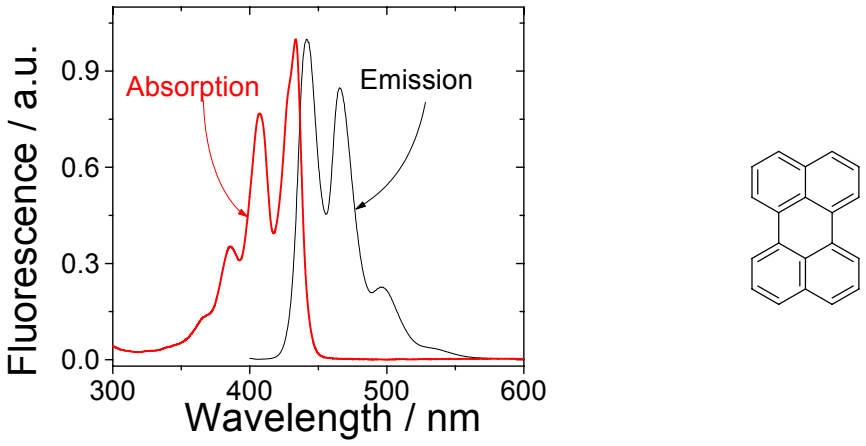


Fig. S25 UV-vis absorption and emission spectra of perylene. λ_{ex} = 390 nm. c = 1.0 ×10^{-5} M, in toluene. 20 °C.

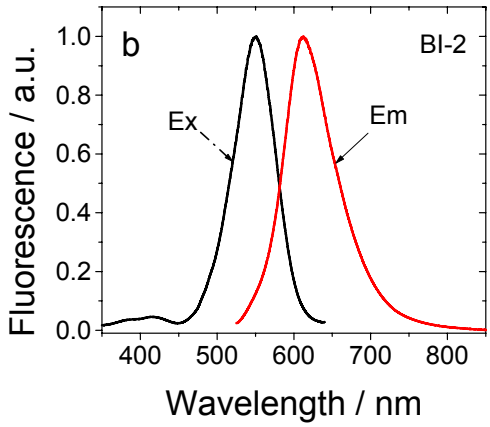


Fig. S26 Emission spectra and excitation spectra of compounds **BI-2**. λ_{ex} = 520 nm. c = 1.0 × 10^{-5} mol/L. In toluene. 25 °C.

The coordinates of the organic triplet sensitizers

The coordinates of **BI-1**（DFT//B3LYP/6-31G(d)/ LanL2DZ）
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

C	1.05041200	-1.65139800	0.31953000
C	1.13219300	0.62618500	0.41163800
C	1.92343700	-0.53306300	0.43838800
C	-0.22237600	0.18537700	0.26580600
C	-1.43392800	0.89420100	0.18032300
C	-2.66416300	0.21704700	0.07352200
C	-4.00642000	0.70363000	-0.07090400
C	-4.79866800	-0.44199000	-0.13229500
C	-3.98142600	-1.59127100	-0.03972300
N	-0.21674300	-1.21472300	0.22200800
N	-2.70368800	-1.18149500	0.08121500
B	-1.47031900	-2.13120600	0.13770000
F	-1.42706100	-2.91179200	-1.01801500
F	-1.53555100	-2.94499600	1.26924300
C	1.65237900	2.02517500	0.56380500
H	1.64456900	2.57265200	-0.38577800
H	1.05217500	2.60603300	1.26876800
H	2.68328000	2.00356400	0.92647500
C	-4.36041300	-3.03426800	-0.08298600
H	-5.43759600	-3.15646600	0.04230300
H	-4.06661000	-3.47708800	-1.04189200
H	-3.83702500	-3.58712800	0.70150800
C	-4.49102600	2.11924600	-0.15295200
H	-3.88832300	2.71723900	-0.84100400
H	-5.52827900	2.14051700	-0.49633000
H	-4.45265600	2.61727300	0.82258400
C	1.40219500	-3.10269700	0.29482400
H	0.86635300	-3.60923400	-0.51250100
H	2.47766000	-3.23400000	0.16171800
H	1.10325300	-3.58803900	1.23156800
C	-1.41448700	2.38820300	0.19906100
C	-1.69065500	3.08443000	1.38420900
C	-1.11917900	3.10697500	-0.96779900
C	-1.66572500	4.48024300	1.40214600
H	-1.91907000	2.53072700	2.29064900
C	-1.10574300	4.50302500	-0.94937300
H	-0.90535000	2.57082000	-1.88819200
C	-1.37608400	5.19218200	0.23544100
H	-1.87519600	5.01014400	2.32712700
H	-0.88144000	5.05079300	-1.86036000
C	3.37981200	-0.62904600	0.55961500
C	4.12291200	-1.34775100	1.46668200
S	4.44864400	0.16805200	-0.59039400
C	5.53402000	-1.26197600	1.26839200
H	3.67039700	-1.91560800	2.27265500
C	5.85689700	-0.47508100	0.19767200

H	6.26405400	-1.75579200	1.89853000
H	-1.36119400	6.27829800	0.24948700
I	7.79933400	-0.01187000	-0.49070500
I	-6.90637100	-0.49883100	-0.33916800

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6 7 1.5 11 1.0
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50

SCF Done: E(RB+HF-LYP) = -1643.05342192 a.u.
Number of Imaginary frequencies: 0

The coordinates of **BI-2**（DFT//B3LYP/6-31G(d)/ LanL2DZ）
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

C	2.39806900	-1.54732300	0.58365400
C	2.62639400	0.71835800	0.45101100
C	3.34484900	-0.48632700	0.52341900
C	1.24063300	0.36106900	0.45786000
C	0.07064500	1.14144600	0.40500800
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C	-3.40917000	0.01585900	0.49411400
C	-2.63105400	-1.16689600	0.63551600
N	1.15625500	-1.03415000	0.54842200
N	-1.32678400	-0.84274500	0.61511500
B	-0.15391400	-1.86313100	0.67543300
F	-0.26500300	-2.76665400	-0.38227000
F	-0.16080300	-2.54375600	1.89461700
C	3.24344700	2.08600700	0.43311100
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H	2.74273700	2.76520500	1.12797000
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H	0.02486300	5.46097000	2.16253800
H	0.72209400	5.04323400	-2.06384400
C	-4.87155400	0.08832400	0.47753900
C	-5.70419300	0.85444200	1.25946000
S	-5.82202900	-0.82370200	-0.69112400
C	-7.09112000	0.71618600	0.95109000
H	-5.33343200	1.49226100	2.05470800
C	-7.30528900	-0.15931100	-0.07723100
H	-7.88223200	1.23681700	1.47740300
C	4.79742800	-0.67144000	0.53726500
C	5.56856000	-1.36169900	1.44311800
S	5.81381300	-0.04579600	-0.75760000
C	6.96102700	-1.38786200	1.12946100
H	5.15127700	-1.82851700	2.32899000
C	7.24097300	-0.71532100	-0.02773100
H	7.70952000	-1.87535100	1.74267600
H	0.46312600	6.49215300	-0.05845500
I	9.14486600	-0.43628600	-0.90024400
I	-9.17133500	-0.72577100	-0.88876800

1 3 1.5 10 1.5 27 1.0
2 3 1.5 4 1.5 15 1.0
3 48 1.0
4 5 1.5 10 1.0
5 6 1.5 31 1.0
6 7 1.5 11 1.0
7 8 1.5 23 1.0
8 9 1.5 41 1.0
9 11 1.5 19 1.0
10 12 1.0
11 12 1.0
12 13 1.0 14 1.0
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15 16 1.0 17 1.0 18 1.0
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19 20 1.0 21 1.0 22 1.0
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23 24 1.0 25 1.0 26 1.0
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27 28 1.0 29 1.0 30 1.0

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31 32 1.5 33 1.5
32 34 1.5 35 1.0
33 36 1.5 37 1.0
34 38 1.5 39 1.0
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36 38 1.5 40 1.0
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38 55 1.0
39
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41 42 2.0 43 1.0
42 44 1.5 45 1.0
43 46 1.0
44 46 2.0 47 1.0
45
46 57 1.0
47
48 49 2.0 50 1.0
49 51 1.5 52 1.0
50 53 1.0
51 53 2.0 54 1.0
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53 56 1.0
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SCF Done: E(RB+HF-LYP) = -2194.85790484 a.u.
Number of Imaginary frequencies: 0

The coordinates of compound **1**（DFT//B3LYP/6-31G(d)/ LanL2DZ）
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

C	-1.90287300	-2.53098100	-0.00016500
C	0.37009600	-2.58183900	-0.00018600
C	-0.77480800	-3.37316700	-0.00027300
C	-0.08889300	-1.22269800	-0.00000200
C	0.60321600	-0.00001000	0.00007000
C	-0.08882700	1.22268700	0.00006600
C	0.37020600	2.58182800	-0.00005700
C	-0.77465700	3.37318000	-0.00015100
C	-1.90275800	2.53102500	-0.00001000

N	-1.49153800	-1.24428800	-0.00001100
N	-1.49148000	1.24432700	0.00006700
B	-2.41645100	0.00001200	0.00019900
F	-3.22686400	0.00009900	-1.14359900
F	-3.22647200	0.00000900	1.14427200
C	1.77142100	-3.11796200	-0.00038600
H	2.33681400	-2.79020400	-0.87906500
H	2.33718200	-2.79003500	0.87797700
H	1.74703600	-4.21180200	-0.00028700
C	-3.34394700	2.92574000	-0.00006400
H	-3.43964100	4.01391700	0.00077600
H	-3.85720700	2.52398300	-0.88039600
H	-3.85767800	2.52253400	0.87931600
C	1.77156900	3.11784100	-0.00027300
H	2.33654000	2.79089100	-0.87953600
H	1.74727200	4.21168600	0.00086200
H	2.33769100	2.78901700	0.87751100
C	-3.34408600	-2.92561100	-0.00012100
H	-3.85764600	-2.52295400	-0.87985900
H	-3.43985100	-4.01378200	-0.00028800
H	-3.85748000	-2.52323900	0.87984800
C	2.09869100	-0.00003600	0.00009800
C	2.80653700	-0.00031200	1.20994700
C	2.80660600	0.00025500	-1.20971100
C	4.20295800	-0.00031400	1.20858900
H	2.26290700	-0.00051600	2.15065500
C	4.20302400	0.00023300	-1.20827300
H	2.26302800	0.00048500	-2.15044800
C	4.90369600	-0.00005100	0.00017700
H	4.74156300	-0.00052500	2.15208300
H	4.74168500	0.00044800	-2.15173600
H	5.99002400	-0.00005700	0.00020700
H	-0.80583300	4.45528100	-0.00020500
H	-0.80601100	-4.45526700	-0.00051100

1 3 1.5 10 1.5 27 1.0
2 3 1.5 4 1.5 15 1.0
3 43 1.0
4 5 1.5 10 1.0
5 6 1.5 31 1.0
6 7 1.5 11 1.0
7 8 1.5 23 1.0
8 9 1.5 42 1.0
9 11 1.5 19 1.0
10 12 1.0
11 12 1.0
12 13 1.0 14 1.0
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27 28 1.0 29 1.0 30 1.0
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31 32 1.5 33 1.5
32 34 1.5 35 1.0
33 36 1.5 37 1.0
34 38 1.5 39 1.0
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36 38 1.5 40 1.0
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38 41 1.0
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SCF Done: E(RB+HF-LYP) = -1069.72116028 a.u.
Number of Imaginary frequencies: 0