Supporting Information

A borane–bithiophene–BODIPY triad: intriguing tricolor emission and selective fluorescence response towards fluoride ions

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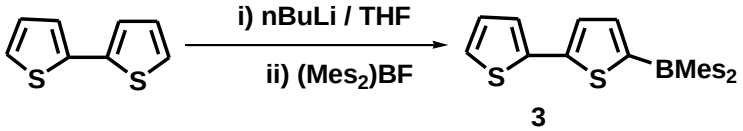
Experimental Section

Materials and general methods:

$BF_3.Et_2O$, DDQ, Magnesium, *n*-BuLi (1.6 M solutions in hexane), anhydrous calcium hydride (CaH_2) were purchased from Sigma-Aldrich (USA). Pyrrole, 2-Bromo-thiophene, triethylamine, TFA, DMF were purchased from SD Fine Chemicals (India). $CDCl_3$ was purchased from Merck (Germany). Standard Schlenk technique was used for reactions requiring inert nitrogen atmosphere. CH_2Cl_2 was dried over CaH_2 and distilled under N_2 atmosphere. DMF was dried over Na_2SO_4 for overnight and distilled out at reduced pressure and stored over 3Å molecular sieves. THF and Et_2O were dried over sodium. Triethylamine was refluxed over sodium for 24 hours and distilled out at N_2 atmosphere and stored in an air tight round bottom flask. Bithiophene, 5-formyl-2,2´-bithiophene were synthesized according literature procedure[1,2]. All 400 MHz ^{1}H NMR, 125.7 ^{13}C NMR Spectra were recorded on a Bruker Advance 400 MHz NMR Spectrometer. Solution ^{1}H NMR and ^{13}C NMR Spectra were referenced internally to the solvent signals. High resolution mass spectra were obtained from Q-TOF instrument by electrospray ionization (ESI). Electronic absorption spectra were recorded on a Perkin Elmer LAMBDA 750 UV/visible spectrophotometer. Solution were prepared using a microbalance (± 0.1mg) and volumetric glassware and then charged in quartz cuvettes with sealing screw caps. Fluorescence emission studies were carried out on a Horiba JOBIN YVON Fluoromax-4 spectrometer. Single-crystal X-ray diffraction studies were carried out with a Bruker SMART APEX diffractometer equipped with 3-axis goniometer. The crystals were kept under a steady flow of cold dinitrogen during the data collection. The data were integrated using SAINT, and an empirical absorption correction was applied with SADABS. The structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL software.[3]

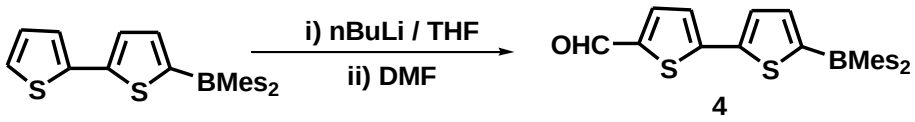
Synthesis of 3



3

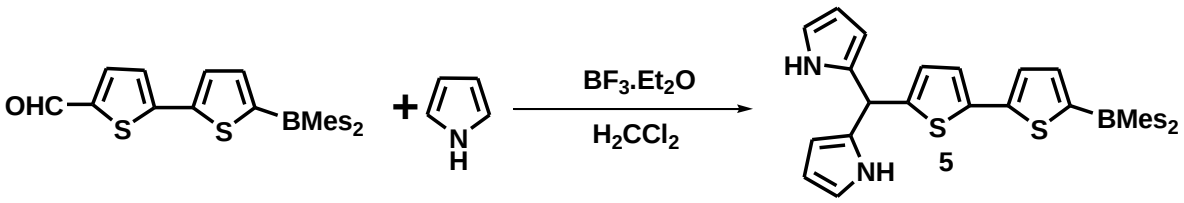
A solution of bithiophene (1.0 g, 6.01 mmol) in THF was degassed by purging N_2 for 30 min. *n*-BuLi (3.7 mL, 6.01 mmol) was added over 30 min at -78 ^{o}C (Acetone/liq-N_2). After 1h, a solution of dimesitylfluoroborane (1.6 g, 6.01 mmol) in 15 mL of THF was added over 10 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for 16 h. The organic layer was extracted with petroleum ether and thoroughly washed with brine solution and dried over anhydrous Na_2SO_4. Evaporation of the solvents under reduced pressure gave compound **3** as green solid. Compound **3** was purified by silica gel column using hexane as eluting solvent. Yield: 1.8 g, 72 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.35 (s, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.28 (m, 2H), 7.03 (m, 1H), 6.84 (s, 4H), 2.32 (s, 6H), 2.15 (s, 12H).^{13}C NMR (100.00 MHz, $CDCl_3$, δ in ppm) 150.3, 141.9, 141.3, 138.9, 137.8, 128.6, 126.2, 126.1, 125.4, 23.9, 21.7.

Synthesis of 4



A solution of **3** (1.50 g, 3.62 mmol) in THF was degassed by purging N_2 for 30 minutes followed by cooling to -78 ^{o}C (Acetone/liq-N_2). *n*-butyllithium (2.5 mL, 3.98 mmol) was added over 30 min. After 1 h, dimethylformamide (DMF) was added over 5 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for 12 h. The organic layer was extracted with ethylacetate and washed with brine solutions and dried over anhydrous Na_2SO_4. Evaporation of the solvents under reduced pressure gave compound **4** as gray solid. Compound **4** was purified by neutral alumina gel column chromatography using EtOAc and hexane (10:90) as eluting solvents. Yield: 1.1 g, 74 %. ^{1}H NMR (400 MHz, $CDCl_3$, in δ ppm) 9.86 (s, 1H): 7.66 (d, *J* = 3.6 Hz, 1H), 7.46 (d, *J* = 4 Hz, 1H), 7.39 (d, *J* = 3.6 Hz, 1H), 7.32 (d, *J* = 4 Hz, 1H), 6.84 (s, 4H), 2.32 (s, 6H), 2.13 (s, 12H).^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 183.0, 147.9, 147.1, 143.1, 141.5, 139.4, 137.6, 128.7, 125.8, 23.9, 21.7.

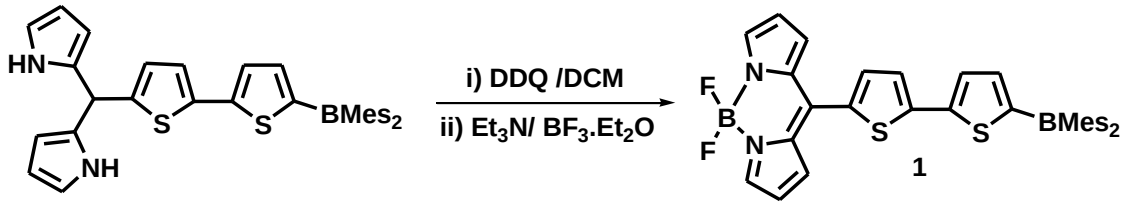
Synthesis of 5



Scheme S3: Synthesis of **5**

Pyrrole (3.5 mL, 50.44 mmol) and compound **4** (0.5 g, 1.13 mmol) were stirred at room temperature under nitrogen atmosphere for 30 min, then one drop $BF_3.OEt_2$ was added. The resultant mixture was stirred for another 6 h at room temperature and then quenched with 2N NaOH solution. The crude product was extracted with dichloromethane and dried over anhydrous Na_2SO_4. Column chromatography on neutral alumina gel (ethylacetate and petroleum ether (10:90)) afforded pure compound **5** as a gray color solid. Yield: 0.4 g, 63 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 8.01 (br, 2H), 7.34 (d, *J* = 3.6 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.15(d, *J* = 3.6 Hz, 1H) 6.87 (s, 4H), 6.81 (d, *J* = 3.6 Hz, 1H) , 6.71 (d, *J* = 0.8 Hz, 2H) , 6.21 (d, *J* = 2 Hz, 2H), 6.10 (s, 2H), 5.71 (s, 1H), 2.34 (s, 6H), 2.18 (s, 12 H).^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 151.1, 148.2, 141.2, 139.0, 137.8, 136.9, 132.0, 128.6, 127.0, 126.0, 125.1, 118.1, 109.0, 107.7, 39.8, 23.9, 21.7.

Synthesis of 1



Scheme S4: Synthesis of **1**

A solution of **5** (0.16 g, 0.36 mmol) in dichloromethane (DCM) (20 mL) was allowed to react with DDQ (80 mg, 0.43 mmol) and stirred for 6 h at room temperature. The resultant product was treated with triethylamine (0.4 mL, 3.58 mmol) and $BF_3.Et_2O$ (0.4 mL, 3.59 mmol). The reaction mixture was stirred for additional 5 h at RT and the solvent was removed in vaccuo to give crude product, which was further purified by alumina gel column chromatography (ethylacetate : petroleum ether (10:90)) to give compound **1** as a red color solid. Yield: 0.95 g, 65 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.93 (s, 2H), 7.52 (d, *J* = 4Hz, 1H), 7.46 (d, *J* = 4 Hz, 1H), 7.42 (m, 2H), 7.33 (d, *J* = 4.4 Hz, 2H), 6.86 (s, 4H), 6.60 (m, 2H), 2.33 (s, 6H), 2.15 (s, 12H).^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 149.1, 147.8, 144.2, 141.6, 139.3, 134.7, 131.4, 128.7, 127.7, 126.1, 118.9, 23.8, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$, δ in ppm) -145.2.

Synthesis of 6

Scheme S5: Synthesis of **6**

Compound **6** was prepared following a procedure similar to that used for compound **1**. The quantities involved and characterization data are as follows. 5-formyl-2,2′-bithiophene (0.4 g, 1.29 mmol), pyrrole (2 mL), DDQ (0.35 g, 1.55 mmol), Et_3N (2 mL, 12.89 mmol), $BF_3.Et_2O$ (2 mL, 12.89. mmol). Yield: 250 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm) 7.93 (s, 2H), 7.52 (d, *J* = 4Hz, 1H), 7.36 (m, 5H), 7.11 (m, 1H), 6.59 (d, *J* = 4.4 Hz, 2H), ^{13}CNMR (100 MHz, $CDCl_3$, δ in ppm) 144.7, 143.9, 139.4, 136.2, 134.8, 134.4, 133.4, 131.5, 128.8, 126.9, 118.9. ^{19}F NMR (376 MHz, $CDCl_3$, δ in ppm): -145.2.

Spectral Characterization

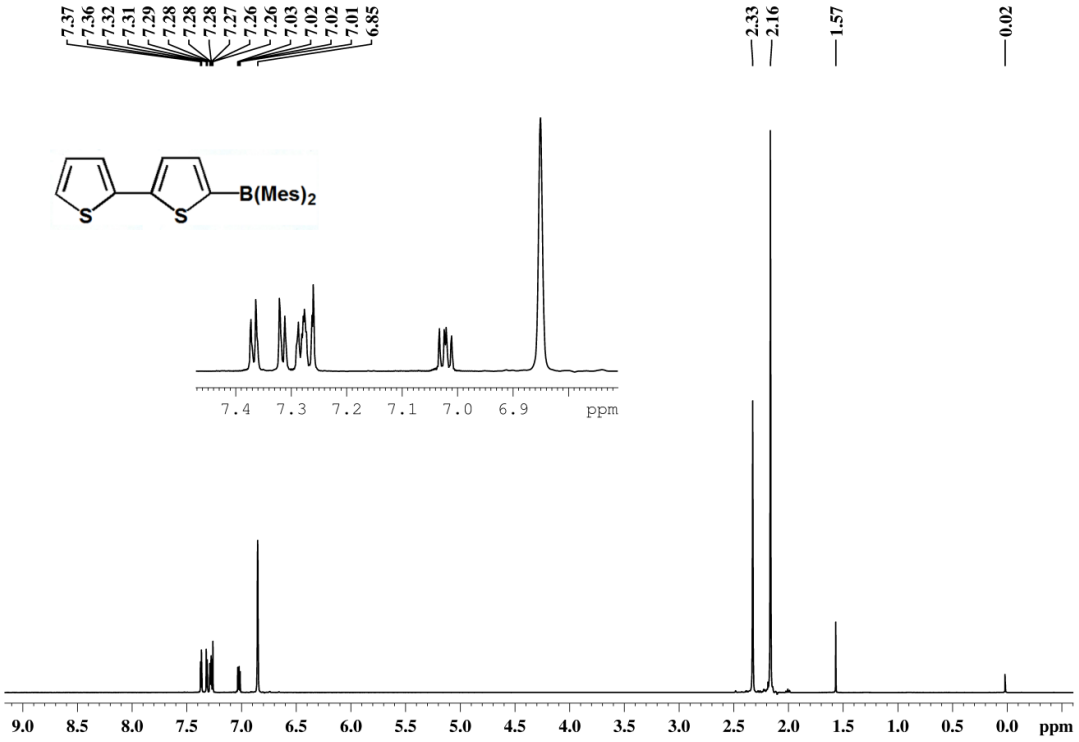


Figure S1: ^{1}H NMR spectrum of **3** in $CDCl_3$

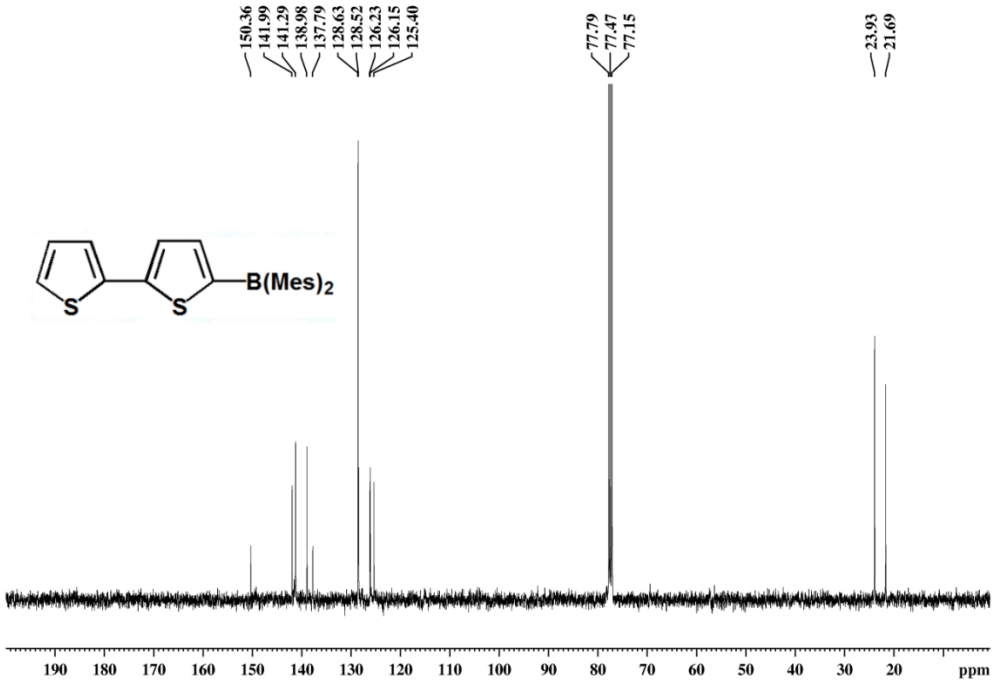


Figure S2: ^{13}C NMR spectrum of **3** in $CDCl_3$

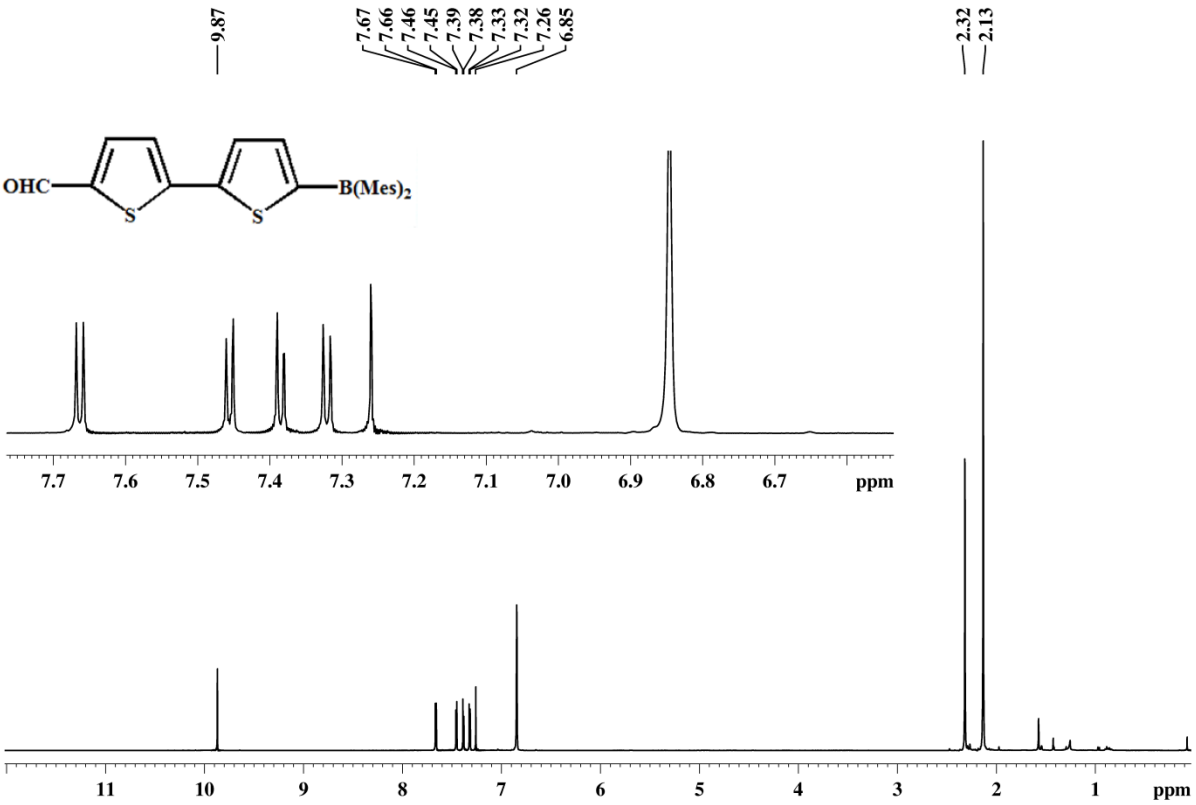


Figure S3: ^{1}H NMR spectrum of **4** in $CDCl_3$

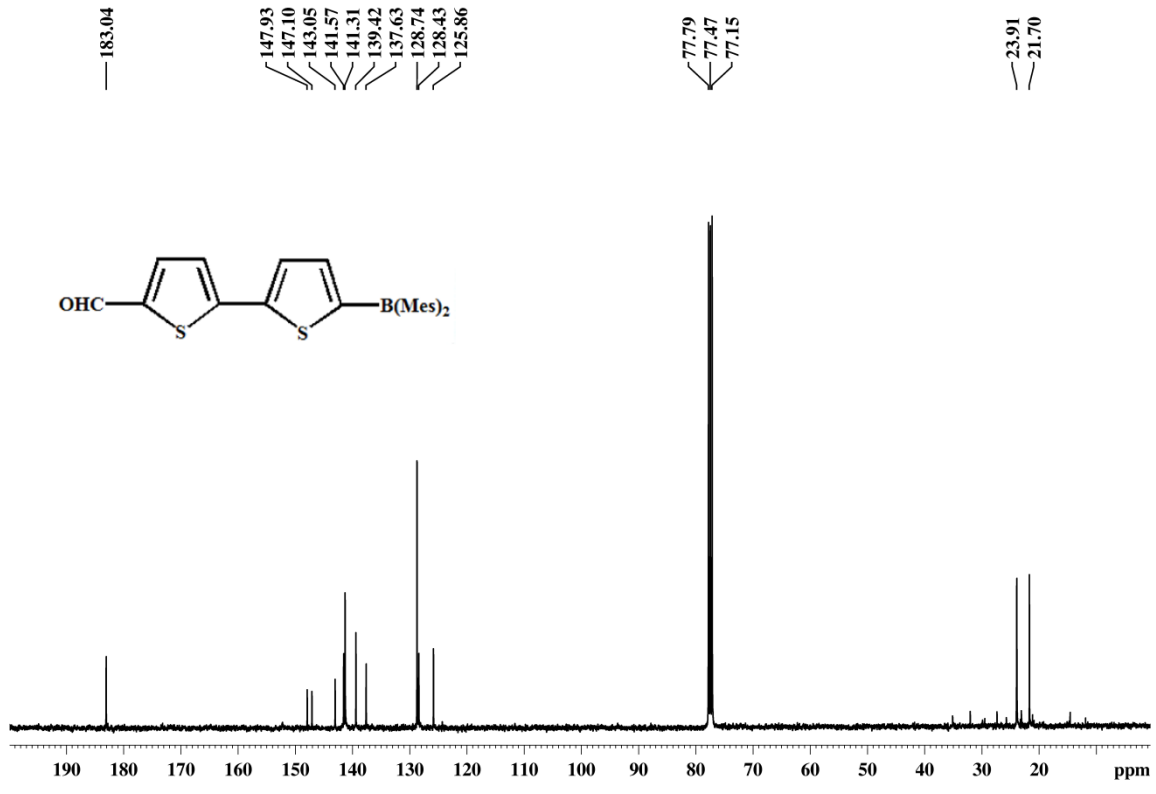


Figure S4: ^{13}C NMR spectrum of **4** in $CDCl_3$

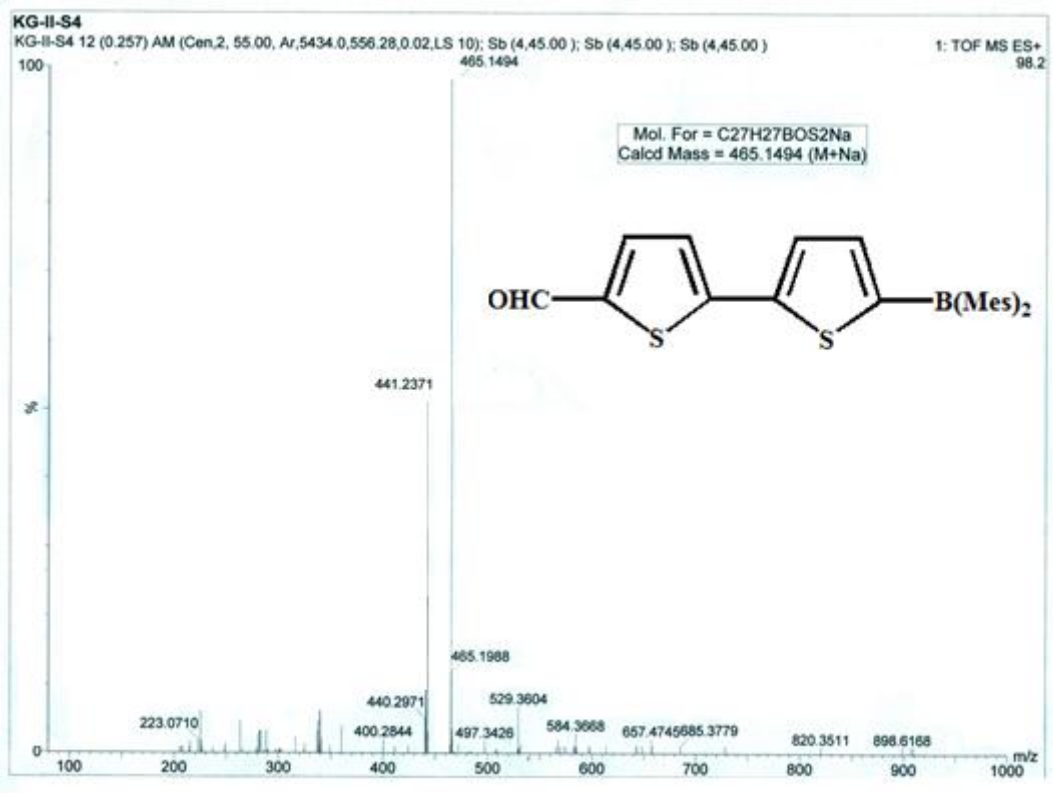


Figure S5: HRMS of **4** (dissolved in MeOH)

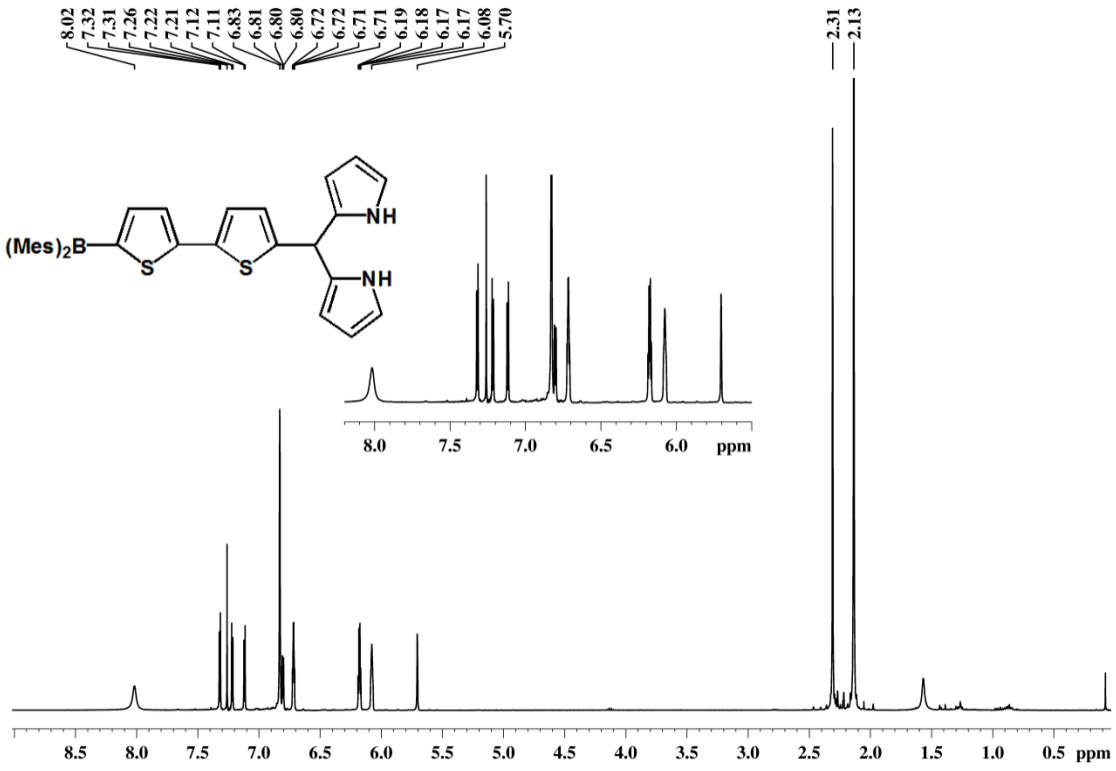


Figure S6: ^{1}H NMR spectrum of **5** in $CDCl_3$

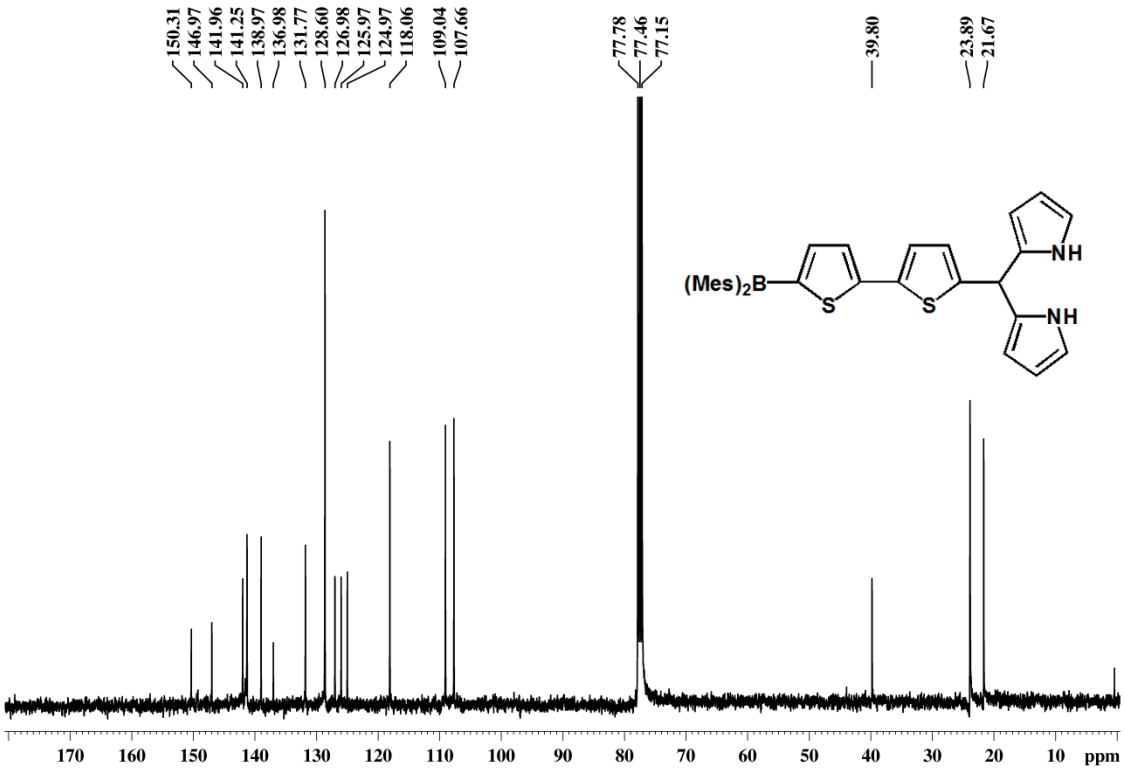


Figure S7: $S^{13}C$ NMR spectrum of **5** in $CDCl_3$

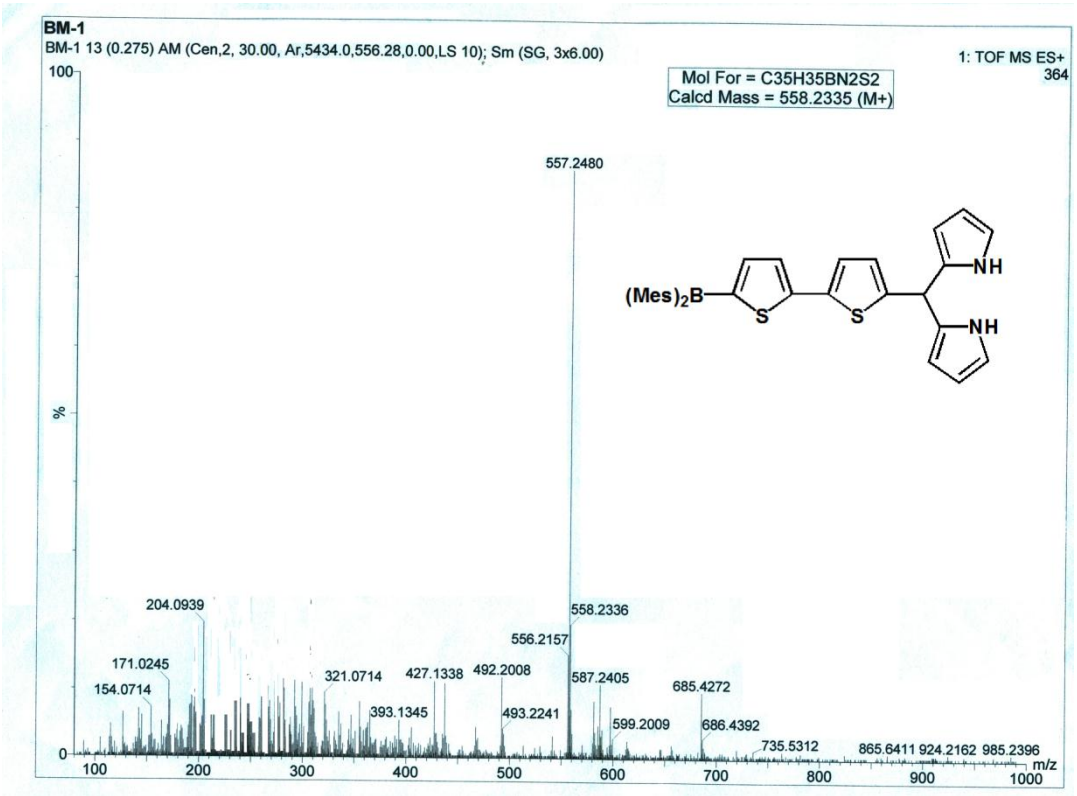


Figure S8: HRMS of **5** (dissolved in MeOH)

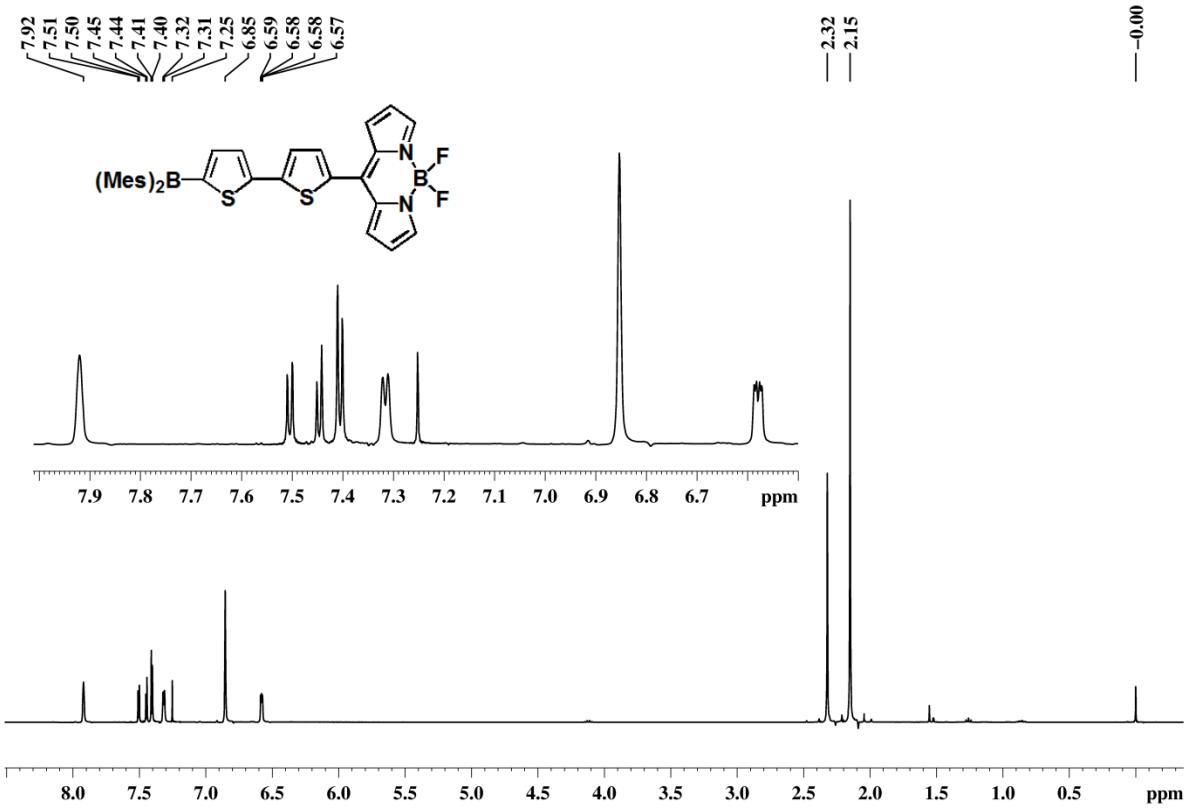


Figure S9: ^{1}H NMR spectrum of **1** in $CDCl_3$

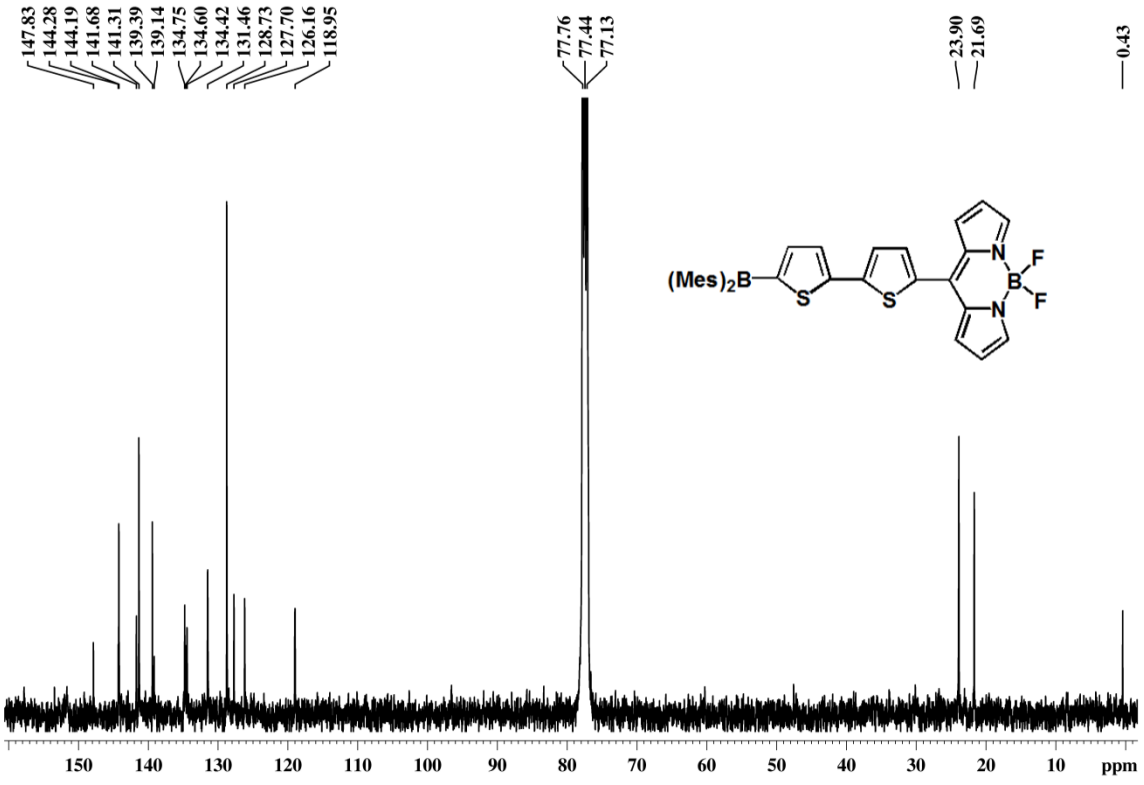


Figure S10: ^{13}C NMR spectrum of **1** in $CDCl_3$

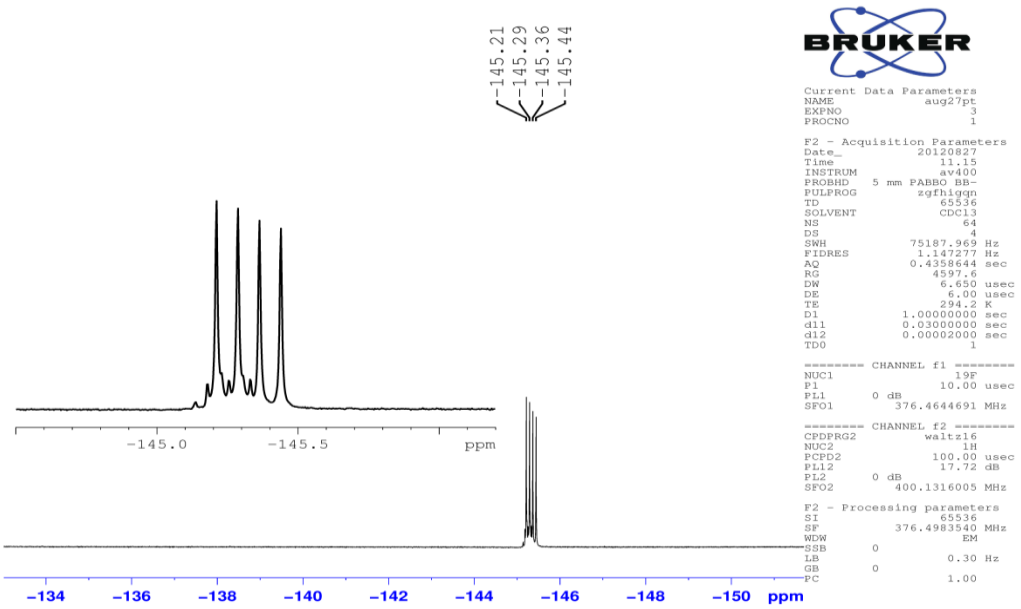


Figure S11: ^{11}F NMR spectrum of **1**

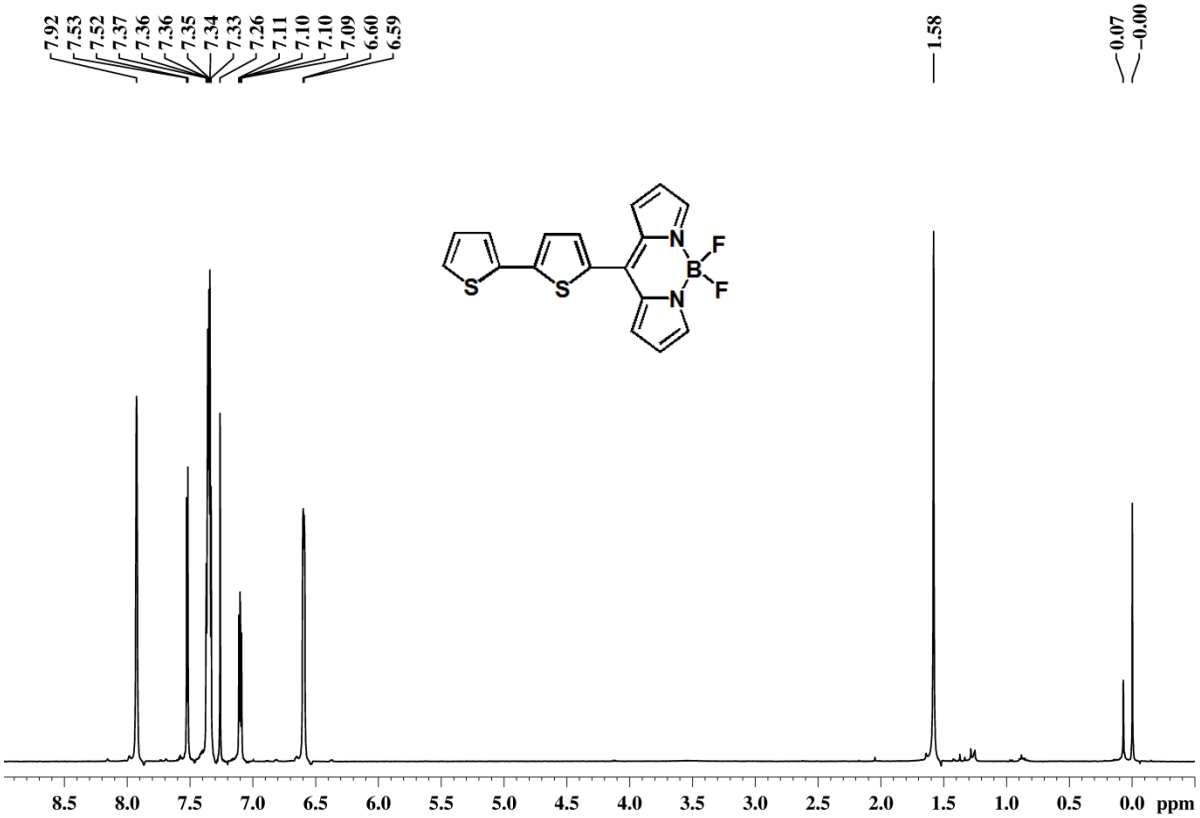


Figure S12: ^{1}H NMR spectrum of **6** in $CDCl_3$

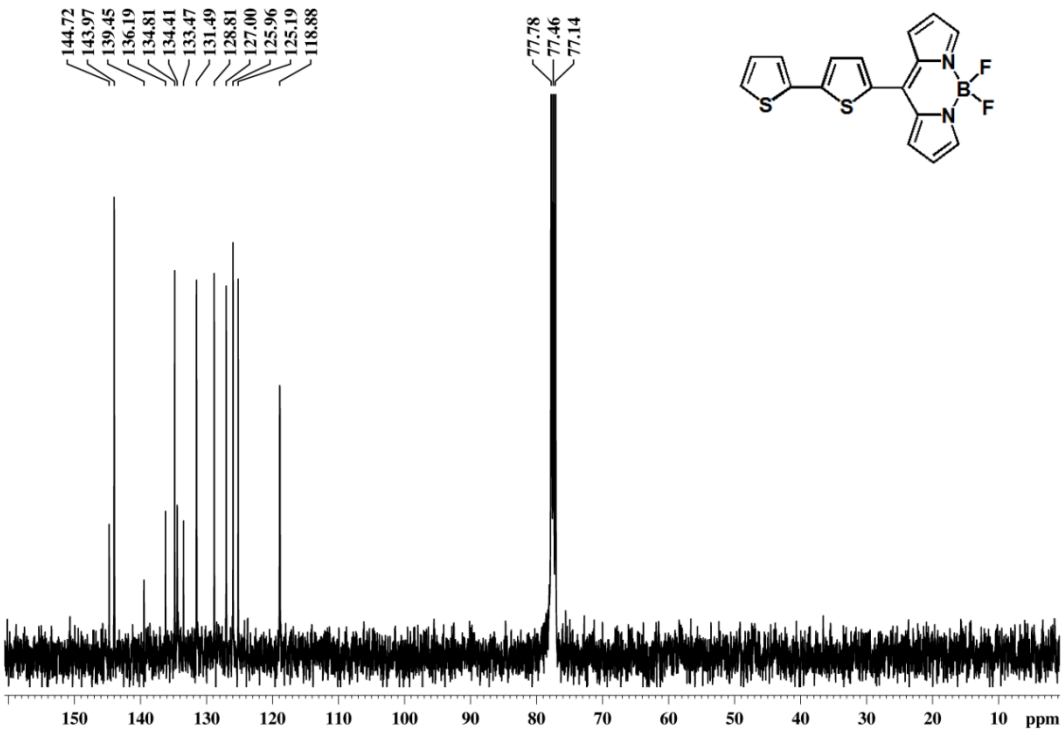


Figure S13: ^{13}C NMR spectrum of **6** in $CDCl_3$

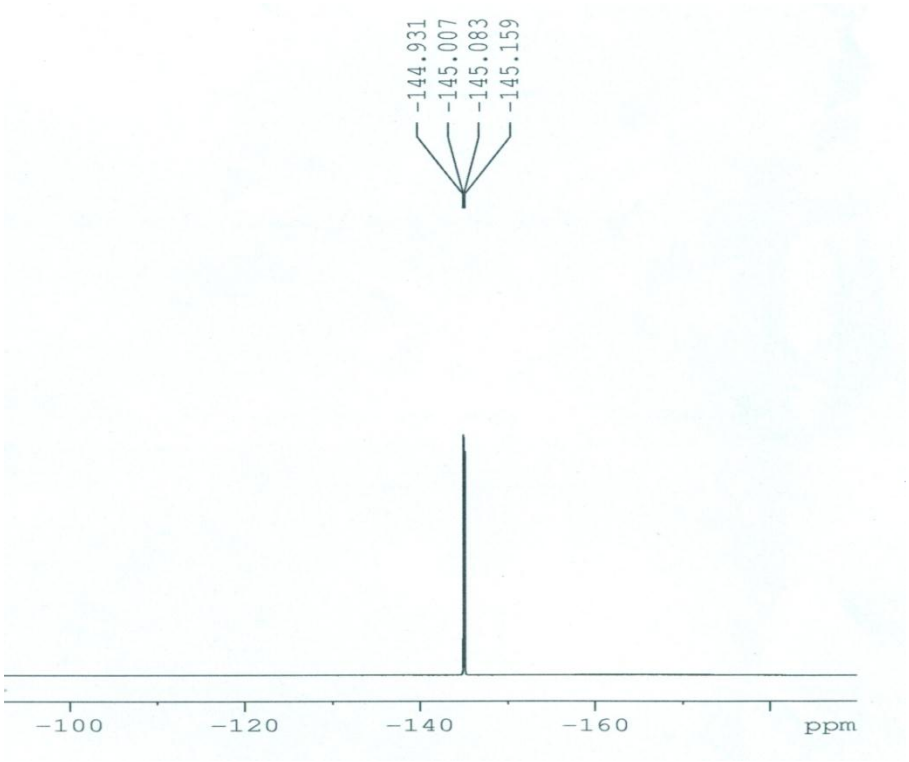


Figure S14: ^{19}F NMR spectrum of **6** in $CDCl_3$

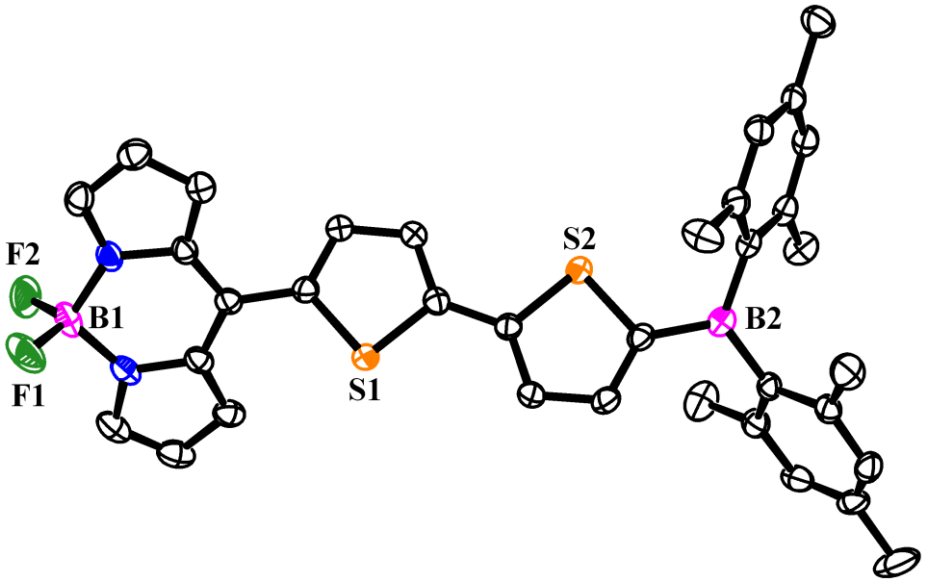


Figure S15: Molecular structure of **1** (50 % thermal ellipsoid)

Table S1. Crystallographic data collection and refinement parameters for **1**

Formula	$C_{35}\ H_{32}\ B_2\ F_2\ N_2\ S_2$
Formula weight	604.39
Crystal system	monoclinic
Space group	P 2_1/n
a(A^0)	17.249
b(A^0)	8.0755
c(A^0)	22.638
A	90.00
B	103.615
Γ	90.00
V(A^3)	3064.73
ρcalc (g cm^{-3})	1.130
μ (mm^{-1})	0.214
F(000)	1265.68
T (K)	150k
scan mode	multi
*Hkl*range	24 11 32
Meads reflns	9481
R1[a](I > 2σ(I))	0.0557
wR2[b]all data	0.1307
GOF on F^2	1.003
Correction method	Empirical
Data completeness	0.992
Theta(max)	30.650

[a]R1 = Σ||*Fo*| − |*Fc*||/Σ|*Fo*|. [b]wR2 = {[Σ*w*($Fo^2 - Fc^2$)^2]/[Σ*w*(Fo^2)^2]}$^{1/2}$.

Table S2. Selected bond lengths and angles of **1** obtained from single crystal X-ray diffraction studies.

	Bond Length (Å)
B (2)-C (18)	1.564
B (2)-C (27)	1.574
B (2)-C (17)	1.562
C (14)-C (13)	1.452
C (10)-C (5)	1.466
C (6)-C (5)	1.398
C (4)-C (5)	1.407
B (1)-F (1)	1.382
B (1)-F (2)	1.385
B (1)-N (1)	1.538
B (1)-N (2)	1.549
	Bond Angle (°)
C (19)-B (2)-C (27)	124.90
C (19)-B (2)-C (17)	118.89
C (17)-B (2)-C (27)	116.18
N (1)-B (1)-N (2)	106.32
F (1)-B (1)-F (2)	110.00

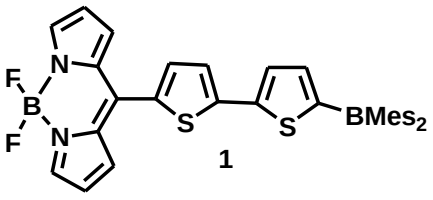
Table S3. The dihedral angels (°) involved in **1** and **1•F**

Atoms involve in the Plane	1		1•F
	Single crystal structure	Optimized structure	Optimized structure
C10-C11-C12-C13-S1 (thiophene unit) and C1-C2-C3-C7-C8-C9 (boradiazaindacene unit)	45.48°	48.62°	36.65°
C18- B2-C27 (dimesitylborane unit) and C16-C15-S2 (thiophene unit)	19.61°	19.58°	59.59°

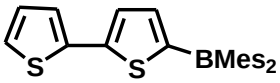
Table S4. Comparison among the bond distances (Å) of **1**, Optimized structures **1** and **1•F**

Bond	**1** (Bond Length (Å))	Optimized structure **1** (Bond Length (Å))	Optimized structure **1•F** (Bond Length (Å))
B1-F1	1.382	1.390	1.396
B1-F2	1.385	1.387	1.395
B1-N1	1.538	1.562	1.552
B1-N2	1.549	1.566	1.557
N2-C9	1.340	1.340	1.345
C9-C8	1.395	1.406	1.399
C8-C7	1.369	1.387	1.393
C7-C6	1.420	1.420	1.414
C6-C5	1.398	1.409	1.424
C5-C4	1.407	1.410	1.426
C4-C3	1.405	1.420	1.414
C3-C2	1.380	1.387	1.394
C2-C1	1.390	1.407	1.399
C1-N1	1.343	1.340	1.346
N1-C4	1.394	1.390	1.387
N2-C6	1.400	1.392	1.391
C10-C5	1.466	1.461	1.436
C10-C11	1.367	1.379	1.392
C11-C12	1.413	1.411	1.397
C12-C13	1.360	1.380	1.394
C13-C14	1.452	1.446	1.426
C14-C15	1.371	1.365	1.389
C15-C16	1.407	1.408	1.405
C16-C17	1.373	1.386	1.388
B2-C17	1.562	1.549	1.651
B2-C18	1.564	1.582	1.668
B2-C27	1.574	1.582	1.667

Chart S1. Compounds used for photophysical studies



1



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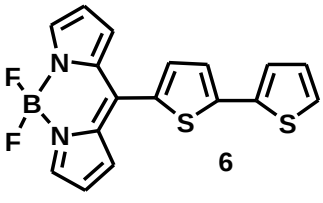

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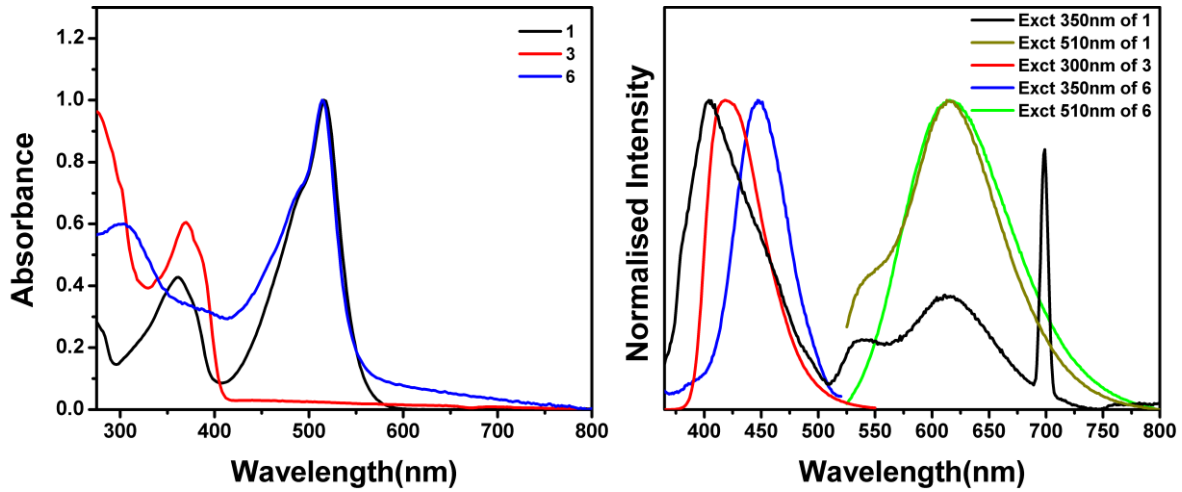

Figure S16: Absorption (left) and emission (right) spectra of **1, 3** and **6** in CH_2Cl_2 (10^{-5}M solution)

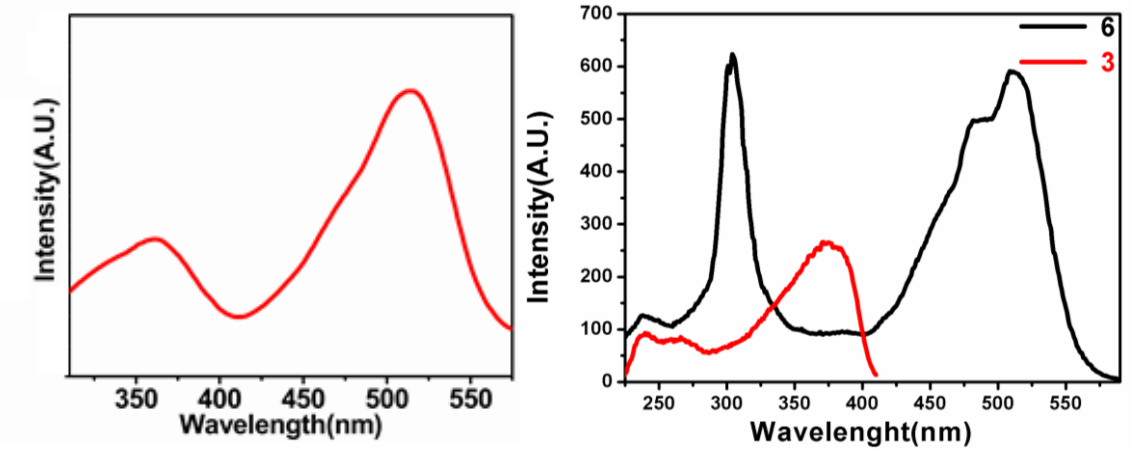

Figure S17: Excitation spectra of compound **1** (left) (λ_{em} 600 nm) and model compound **3** (right, red color) (λ_{em} 425 nm) and **6** (right, black color) (λ_{em} 600 nm).

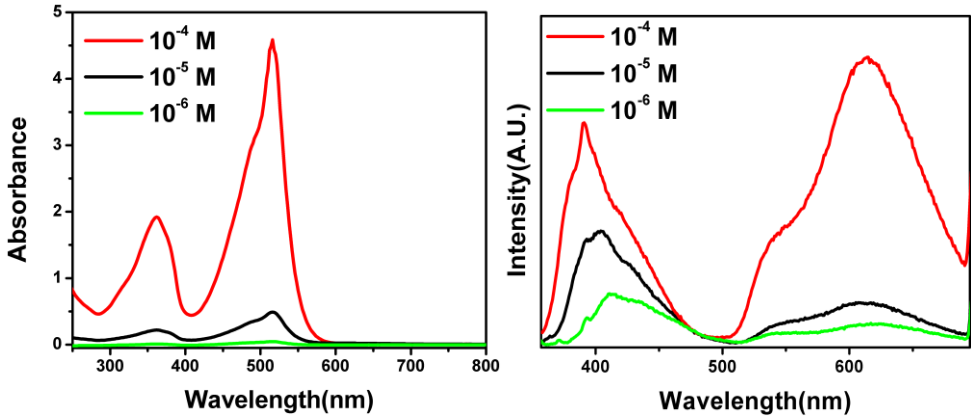

Figure S18: UV-Vis Spectra (left) and emission spectra (λ_{ex} 350 nm) (right) of **1** in variable concentration (CH_2Cl_2)

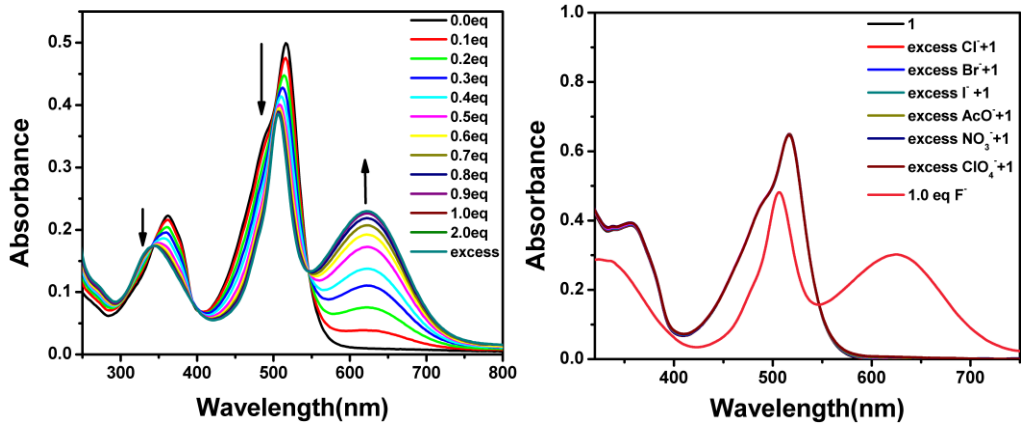

Figure S19: UV-Vis spectra of compound **1** (10^{-5}M in CH_2Cl_2**)** in presence of TBAF (left) and with different anions (right)

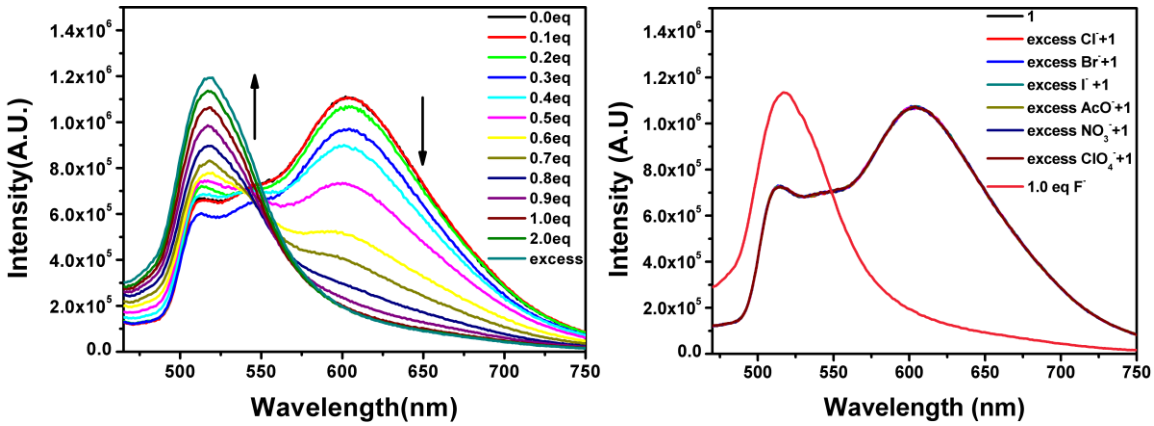

Figure S20: Fluorescence emission spectra (λ_{ex} 450 nm) of compound **1 (**10^{-5}M in CH_2Cl_2**)** in presence of TBAF (left) and with different anions (right)

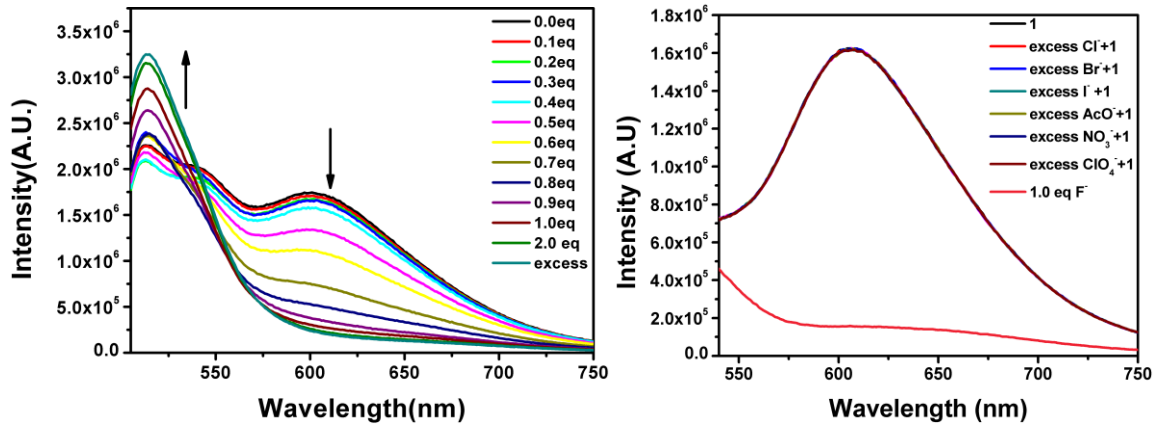

Figure S21: Fluorescence emission spectra (λ_{ex} 490 nm) of compound **1** (10^{-5}M in CH_2Cl_2) in presence of TBAF (left) and with different anions (right)

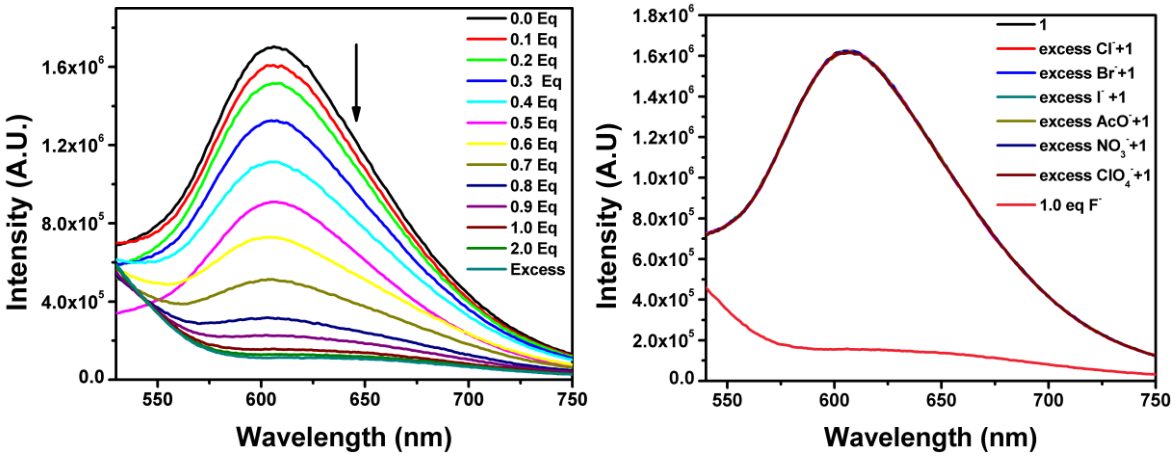

Figure S22: Fluorescence emission spectra (λ_{ex} 515 nm) of compound **1** (10^{-5}M in CH_2Cl_2) in presence of TBAF (left) and with different anions (right)

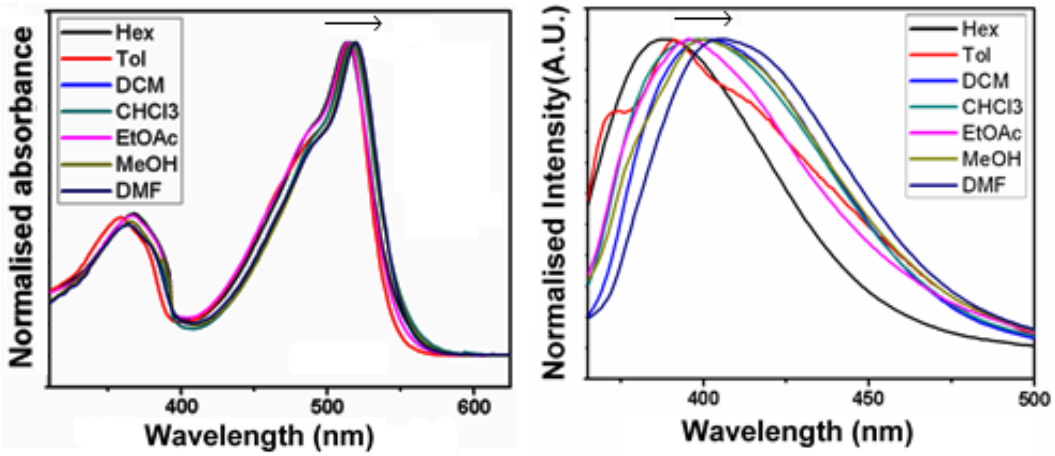

Figure S23: Absorption (left) and emission (right) spectra of **1** in different solvents (10^{-5}M in CH_2Cl_2)

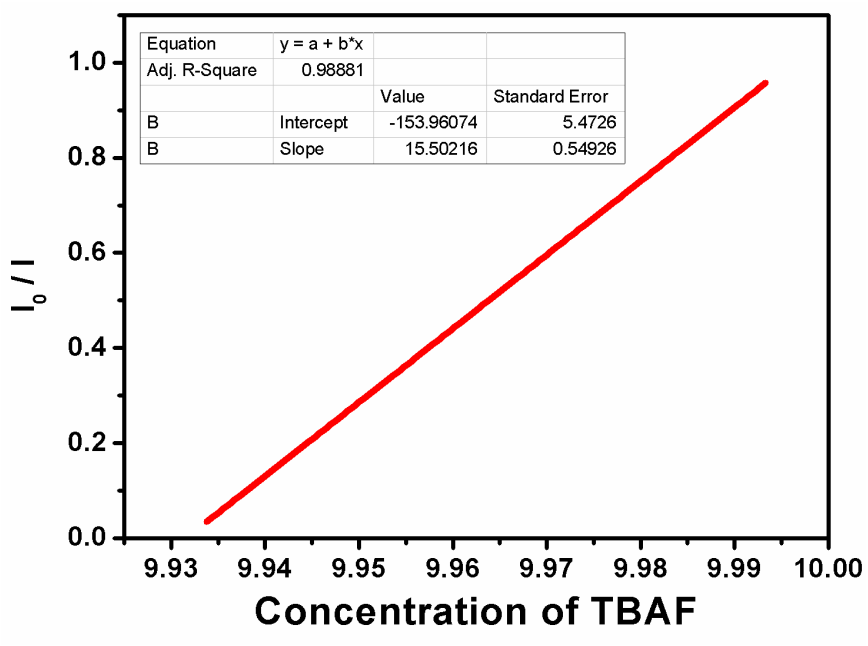

Figure S24: Stern-Volmer plot (binding constant K_{SV}= 1.55 x $10^{8}M^{-1}$) of compound **1**

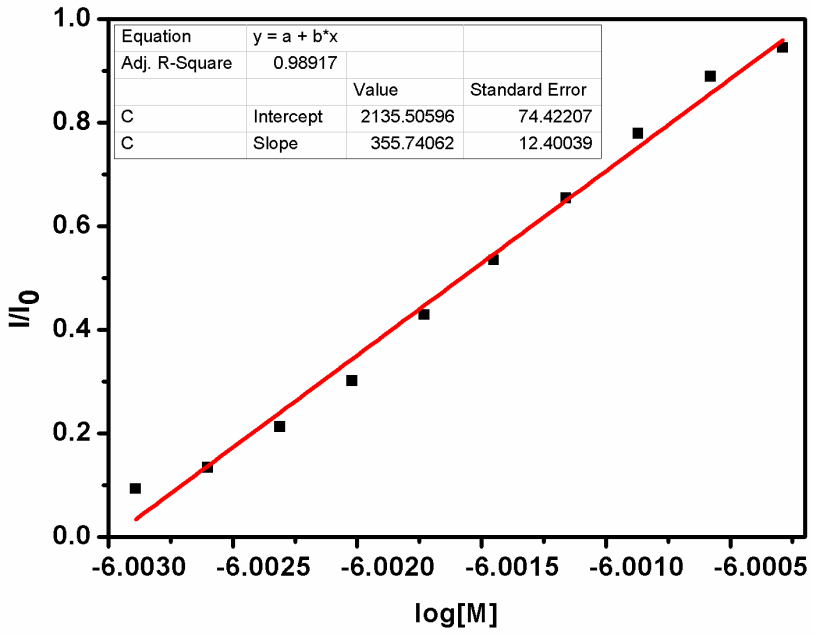

Figure S25: Determination of fluoride detection limit (limit = 9.9 x 10^{-7} M) of compound **1**

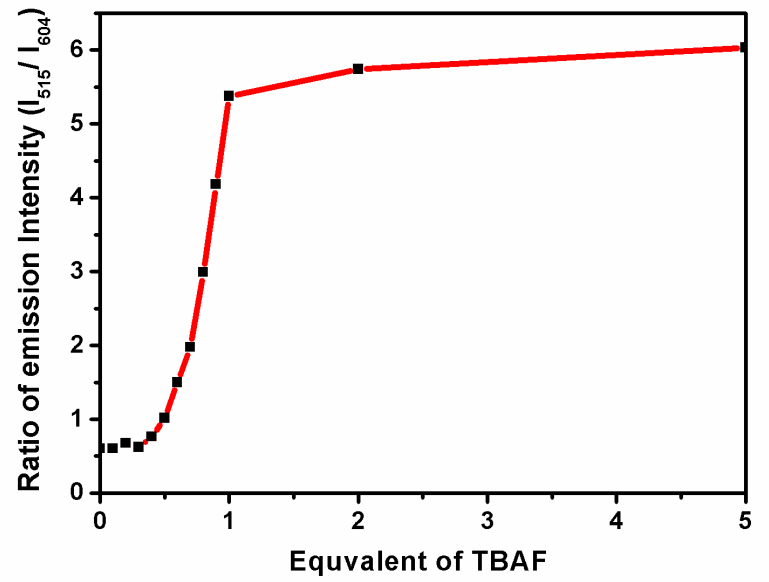

Figure S26: Fluorescence ratiometric response of **1** towards TBAF (fluorescence emission ratio at maxima 515 and 604 nm (I_{515}/I_{604}))

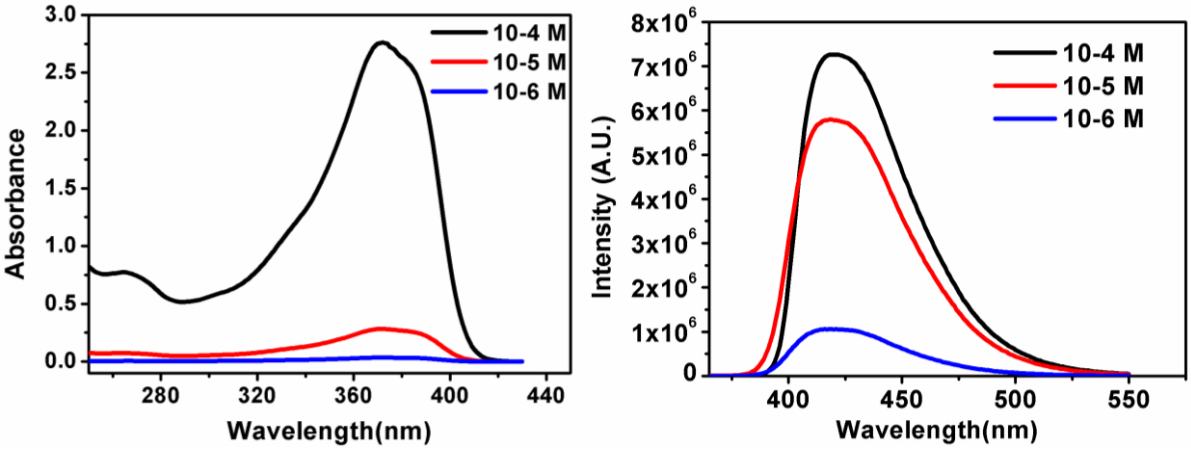

Figure S27: UV-Vis (left) and fluorescence spectra (right) of compound **3** in different concentrations in CH_2Cl_2 solution

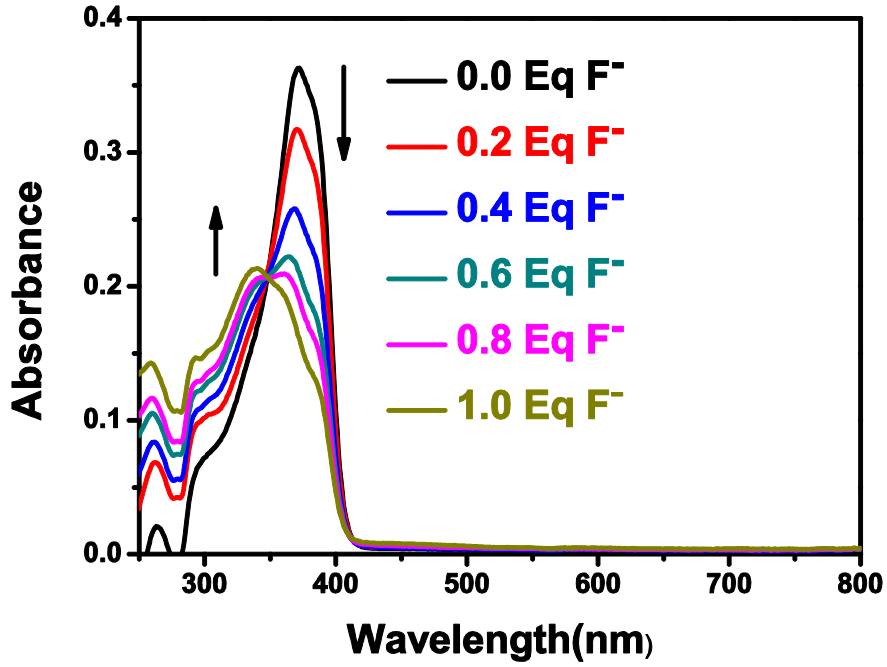

Figure S28: Absorbance spectral changes in **3** (10^{-5} M in CH_2Cl_2) upon addition of TBAF

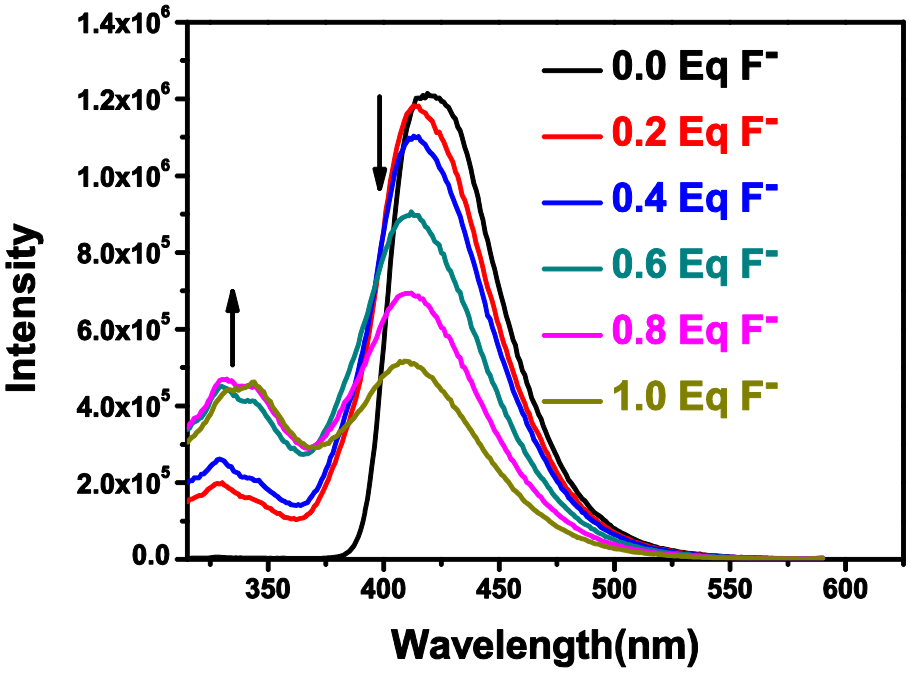

Figure S29: Fluorescence spectral changes in **3** (10^{-5} M in CH_2Cl_2, λ_{ex} = 300 nm) upon addition of TBAF

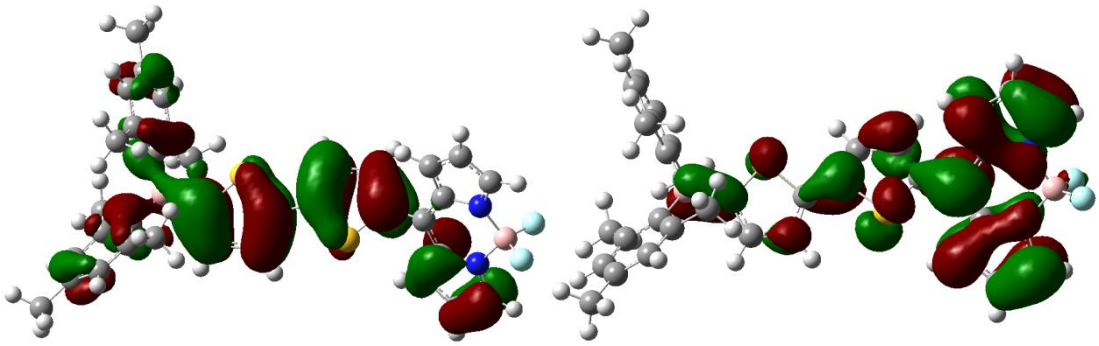

Figure S30: HOMO (left) and LUMO (right) of **1** (isovalue = 0.02)

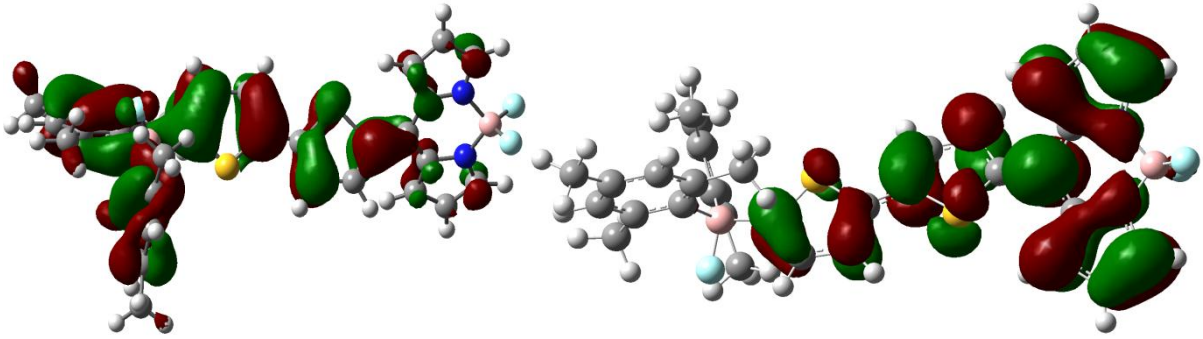

Figure S31: HOMO (left) and LUMO (right) of **1.F** (isovalue = 0.02)

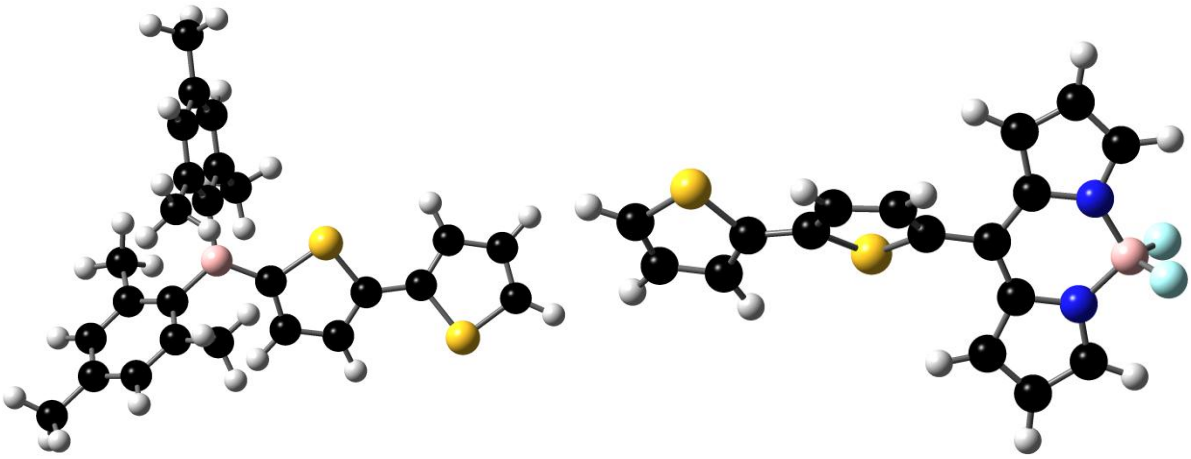

Figure S32: The energy optimized geometry of **3** (left) and **6** (right)

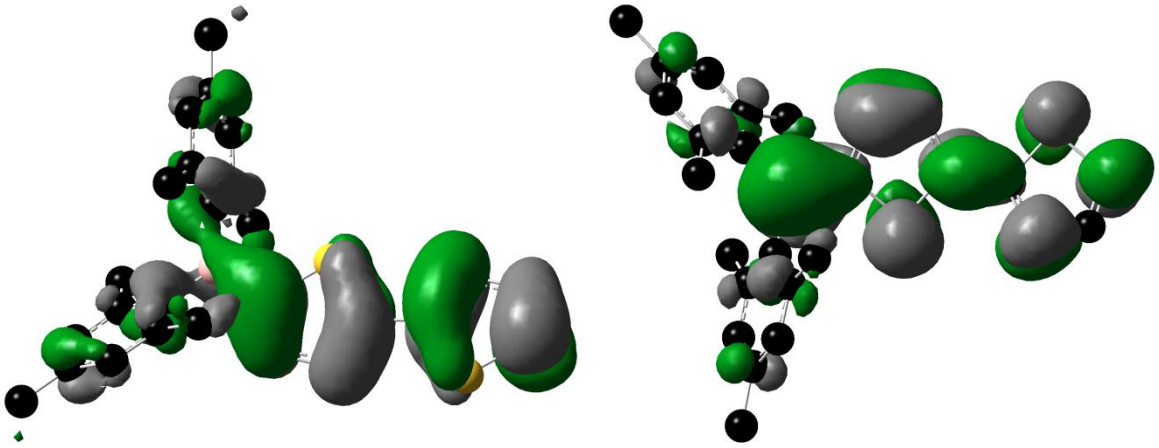

Figure S33: HOMO (left) and LUMO (right) of **3** (isovalue = 0.02)

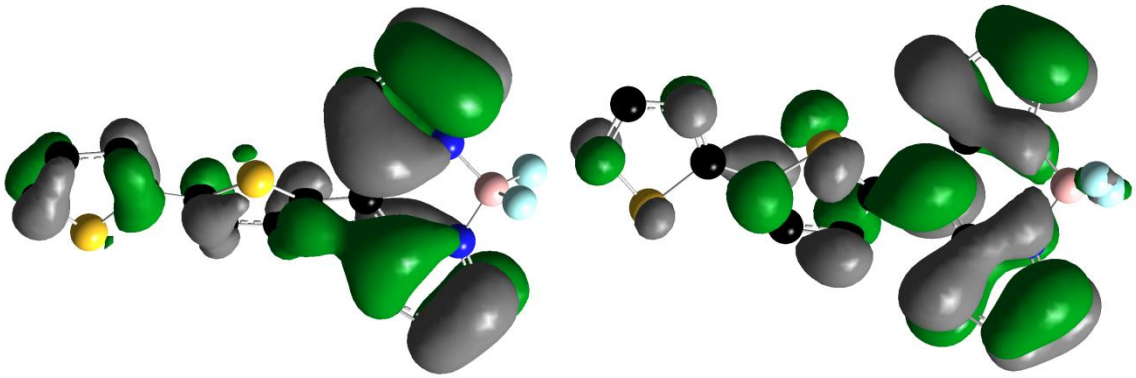

Figure S34: HOMO (left) and LUMO (right) of **6** (isovalue = 0.02)

Computational details[4]

Table S5: Coordinates of **1**

C	-2.59189	-0.39461	-0.24053
C	-1.95026	-1.58519	-0.54271
C	-0.5485	-1.49212	-0.63291
C	-0.07105	-0.21765	-0.37684
S	-1.392	0.8699	-0.04784
H	-2.50138	-2.50189	-0.70905
H	0.09741	-2.32292	-0.88727
B	-4.10695	-0.11651	-0.07578
C	-4.62723	1.37385	-0.1839
C	-5.30116	1.98701	0.90949
C	-4.41752	2.14993	-1.34855
C	-5.70531	3.31642	0.82418
C	-4.85504	3.47879	-1.39761
C	-5.49212	4.08614	-0.32283
H	-6.20333	3.76788	1.67772
H	-4.69384	4.04843	-2.30904
C	-5.04741	-1.35673	0.21016
C	-6.14998	-1.6447	-0.64096
C	-4.81595	-2.2225	1.30637
C	-6.94627	-2.76184	-0.40105
C	-5.65631	-3.3201	1.52494
C	-6.72058	-3.61594	0.68112
H	-7.77271	-2.97034	-1.07478
H	-5.47062	-3.9569	2.38571
C	-6.48106	-0.78503	-1.84277
H	-6.69128	0.2471	-1.55457
H	-5.65745	-0.75842	-2.56207
H	-7.35707	-1.17638	-2.36347
C	-3.70527	-2.0081	2.31852
H	-4.07091	-2.21322	3.3284
H	-2.86519	-2.68565	2.13508
H	-3.30459	-0.99616	2.30779
C	-7.61679	-4.80484	0.92657
H	-8.64048	-4.48802	1.15106
H	-7.66602	-5.45216	0.04568
H	-7.26148	-5.4056	1.76603
C	-5.56691	1.24628	2.20302
H	-6.12992	0.32613	2.03569
H	-4.63689	0.96852	2.70867
H	-6.13663	1.87128	2.89333
C	-3.80489	1.59127	-2.61812
H	-4.56302	1.52497	-3.40592
H	-3.01223	2.24678	-2.99004
H	-3.37876	0.59813	-2.488
C	-5.93394	5.52796	-0.37905
H	-6.97459	5.63804	-0.06033
H	-5.32576	6.15175	0.28462
H	-5.84523	5.93288	-1.38909
C	1.30271	0.23217	-0.33719

C	1.79352	1.52057	-0.39528
S	2.61565	-0.91116	-0.16864
C	3.19906	1.59441	-0.29675
H	1.15623	2.38512	-0.52476
C	3.81342	0.36562	-0.18291
H	3.75937	2.51752	-0.35113
C	5.24374	0.10067	-0.04935
C	5.98548	0.86264	0.87595
C	5.88511	-0.89769	-0.80956
C	7.78274	1.47163	2.01241
C	5.56585	1.7782	1.87671
C	6.69753	2.16401	2.5798
H	4.54731	2.07393	2.06703
H	6.74908	2.84201	3.41696
H	8.82565	1.48648	2.29052
N	7.36014	0.6991	1.00275
C	5.39266	-1.80354	-1.78537
C	7.59244	-2.12611	-1.49689
C	6.46415	-2.57897	-2.20351
H	8.6178	-2.45782	-1.55937
H	6.45134	-3.37362	-2.93255
H	4.37528	-1.86179	-2.13434
N	7.25042	-1.12931	-0.66974
B	8.25649	-0.22167	0.11458
F	8.98892	0.54497	-0.78357
F	9.08911	-0.99331	0.91162

Table S6: Coordinates of **1·F**

C	-2.49928	-0.34518	-0.86833
C	-1.783	-1.08033	-1.80298
C	-0.3856	-1.00528	-1.67544
C	0.03122	-0.1845	-0.63576
S	-1.38304	0.50304	0.15587
H	-2.29339	-1.64922	-2.56864
H	0.30928	-1.51748	-2.3315
B	-4.13903	-0.1634	-0.81384
C	-4.45793	1.38479	-0.28273
C	-4.76271	1.70963	1.06596
C	-4.38622	2.47604	-1.19085
C	-5.03256	3.02902	1.4488
C	-4.66819	3.78178	-0.77081
C	-5.00525	4.08516	0.54368
H	-5.26898	3.23211	2.49132
H	-4.61129	4.58744	-1.4996
C	-5.01614	-1.37126	-0.07136
C	-6.42224	-1.37078	-0.30647
C	-4.51689	-2.4395	0.71349
C	-7.2453	-2.36822	0.22279
C	-5.37505	-3.42575	1.22402
C	-6.74394	-3.41523	0.99243
H	-8.3143	-2.32213	0.02502
H	-4.94984	-4.22512	1.82692
C	-7.11178	-0.3016	-1.13283
H	-6.8802	0.70218	-0.77081
H	-6.78062	-0.34008	-2.17086
H	-8.19692	-0.43571	-1.10008
C	-3.05403	-2.60228	1.08233
H	-2.93177	-3.43913	1.77548
H	-2.42847	-2.79943	0.20966
H	-2.64273	-1.71442	1.56595
C	-7.64843	-4.49985	1.5296
H	-8.58416	-4.08579	1.91865
H	-7.91618	-5.22324	0.74984
H	-7.16564	-5.05511	2.33857
C	-4.8167	0.67554	2.17568
H	-5.69263	0.02884	2.0927
H	-3.94416	0.02073	2.17376
H	-4.85358	1.17281	3.14943
C	-3.98516	2.31811	-2.64638
H	-4.74433	1.7895	-3.22394
H	-3.81991	3.30158	-3.09688
H	-3.06799	1.7349	-2.75001
C	-5.28712	5.50365	0.98236
H	-6.17855	5.55853	1.61562
H	-4.45429	5.9191	1.5623
H	-5.44673	6.15962	0.12238
C	1.3586	0.1233	-0.21519
C	1.78455	1.0847	0.6998
S	2.74272	-0.75559	-0.83888
C	3.1674	1.10691	0.89538

H	1.09645	1.76361	1.18472
C	3.8778	0.18132	0.13612
H	3.66756	1.82367	1.53133
C	5.30037	-0.01657	0.12664
C	6.022	0.1466	1.34613
C	6.02185	-0.38255	-1.04481
C	7.81049	0.18232	2.65784
C	5.56981	0.22274	2.68375
C	6.69773	0.25964	3.50222
H	4.54081	0.19437	3.00072
H	6.72018	0.30365	4.58002
H	8.86138	0.15317	2.90101
N	7.40864	0.11058	1.37538
C	5.60074	-0.66606	-2.36475
C	7.82913	-0.869	-2.23809
C	6.73722	-0.98465	-3.10521
H	8.88223	-1.00126	-2.43334
H	6.77822	-1.26364	-4.1466
H	4.58744	-0.6344	-2.72683
N	7.40649	-0.51364	-1.01171
B	8.33699	-0.02908	0.13898
F	8.90333	1.20305	-0.19379
F	9.33793	-0.96778	0.38876
F	-4.50346	-0.29873	-2.22849

Table S7: Coordinates of **3**

C	0.44522	-0.5046	-0.19188
C	0.92871	-1.73147	-0.61941
C	2.33225	-1.84043	-0.63632
C	2.97246	-0.69408	-0.19739
S	1.80505	0.52804	0.22333
H	0.26279	-2.52645	-0.92977
H	2.86727	-2.71913	-0.97326
C	4.3945	-0.45745	-0.05835
C	5.0689	0.74094	0.00346
S	5.52421	-1.79319	0.06712
C	6.47452	0.59536	0.14163
H	4.5673	1.69701	-0.06849
C	6.87053	-0.71116	0.18331
H	7.1636	1.4273	0.19913
H	7.86922	-1.10858	0.27778
B	-1.01885	-0.02872	-0.07079
C	-1.32186	1.52282	0.0385
C	-1.99259	2.04864	1.1776
C	-0.91809	2.43279	-0.96682
C	-2.21075	3.41882	1.29091
C	-1.1724	3.80205	-0.82085
C	-1.80821	4.31928	0.30061
H	-2.71117	3.79813	2.17767
H	-0.86413	4.47784	-1.61433
C	-2.14967	-1.14032	-0.06111
C	-3.17141	-1.13771	-1.05206
C	-2.16936	-2.17816	0.90046
C	-4.13229	-2.14479	-1.07074
C	-3.16459	-3.16303	0.85464
C	-4.15059	-3.17225	-0.12335
H	-4.89259	-2.1293	-1.84682
H	-3.16382	-3.94078	1.61394
C	-1.19577	-2.26049	2.06089
H	-1.72897	-2.14431	3.01039
H	-0.70356	-3.23754	2.08786
H	-0.41624	-1.50351	2.0205
C	-3.23464	-0.07985	-2.1335
H	-3.30124	0.92519	-1.71205
H	-2.34855	-0.10317	-2.77497
H	-4.10488	-0.23752	-2.77363
C	-5.20895	-4.24699	-0.17147
H	-6.21407	-3.81499	-0.14159
H	-5.13711	-4.83111	-1.09472
H	-5.11503	-4.93773	0.66889
C	-2.4592	1.1581	2.30963
H	-3.16639	0.40189	1.96195
H	-1.6251	0.62853	2.77952
H	-2.94955	1.74865	3.08603
C	-0.27536	1.99859	-2.26971
H	-0.95029	2.19714	-3.1092
H	0.64448	2.56033	-2.45652
H	-0.02462	0.93976	-2.29051

C	-2.0503	5.80043	0.45939
H	-1.84984	6.33933	-0.46887
H	-3.08387	6.00512	0.75341
H	-1.40403	6.22356	1.23592

Table S8: Coordinates of **6**

C	-2.0176	1.63455	-0.05533
C	-0.67123	1.78624	0.1917
C	-0.34012	3.14962	0.47893
C	-1.45293	3.95982	0.43537
S	-2.83148	3.09068	0.06051
H	0.06824	0.98358	0.1758
H	0.67517	3.4825	0.70194
C	-1.46941	5.47805	0.69289
C	-2.58235	6.28812	0.64929
S	-0.09102	6.34725	1.06794
C	-2.25159	7.65129	0.93795
H	-3.59749	5.95529	0.42555
C	-0.90518	7.80324	1.18445
H	-2.99131	8.45371	0.95494
H	-0.40587	8.73929	1.42672
C	-1.60336	-0.9396	-0.35039
C	-2.35743	0.23519	-0.35063
C	-3.76063	0.13238	-0.35077
B	-3.67692	-2.1662	-0.35039
F	-4.08809	-2.93093	0.82338
F	-4.08809	-2.93135	-1.52389
N	-4.42016	-1.04257	-0.35059
N	-2.27005	-2.1662	-0.35039
C	-0.11434	-0.88538	-0.35014
C	-1.20822	-3.24354	-0.30695
C	0.06912	-2.47772	-0.12825
C	-4.84363	1.26442	-0.3579
C	-5.88918	-1.09613	-0.3506
C	-6.09951	0.44486	-0.39083
H	-6.57799	-1.91468	-0.32999
H	-7.07184	0.88892	-0.43864
H	-4.72135	2.32731	-0.34331
H	0.59601	-0.09229	-0.45647
H	0.99499	-2.94999	0.12597
H	-1.33809	-4.30273	-0.3853

TD-DFT results Table S9

For 1:

Excitation energies and oscillator strengths:

```
 Excited State   1:   Singlet-A      2.4714 eV  501.67 nm  f=0.5980
     157 -> 159       -0.17627
     158 -> 159        0.64468
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:   Singlet-A      2.7768 eV  446.50 nm  f=0.0109
     156 -> 159        0.69038
     156 -> 160        0.13270

 Excited State   3:   Singlet-A      2.8392 eV  436.69 nm  f=0.2403
     152 -> 159       -0.18548
     157 -> 159        0.56046
     157 -> 160        0.12615
     158 -> 159        0.14518

 Excited State   4:   Singlet-A      2.8576 eV  433.87 nm  f=0.0069
     155 -> 159        0.69099
     155 -> 160        0.11085

 Excited State   5:   Singlet-A      2.9419 eV  421.44 nm  f=0.0094
     153 -> 159       -0.15135
     154 -> 159        0.67659
     154 -> 160        0.10324

 Excited State   6:   Singlet-A      2.9752 eV  416.72 nm  f=0.0116
     153 -> 159        0.66991
     154 -> 159        0.15768
```

For 1·F:

Excitation energies and oscillator strengths:

```
 Excited State   1:   Singlet-A      1.7482 eV  709.20 nm  f=0.0445
     162 -> 164       -0.44655
     163 -> 164        0.53567
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:   Singlet-A      1.8268 eV  678.70 nm  f=0.0227
     161 -> 164        0.63826
     162 -> 164        0.24711
     163 -> 164        0.16320

 Excited State   3:   Singlet-A      1.9593 eV  632.81 nm  f=0.6618
     160 -> 164        0.11370
     161 -> 164       -0.28256
     162 -> 164        0.44517
     163 -> 164        0.32456
```

```
 Excited State   4:   Singlet-A      2.0785 eV  596.49 nm  f=0.0324
     159 -> 164         0.35200
     160 -> 164         0.60386

 Excited State   5:   Singlet-A      2.1007 eV  590.20 nm  f=0.0255
     159 -> 164         0.61166
     160 -> 164        -0.34286

 Excited State   6:   Singlet-A      2.7444 eV  451.78 nm  f=0.0479
     156 -> 164         0.13094
     157 -> 164         0.67616
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