Electronic Supplementary Material (ESI) for Chemical Communications

Dual emissive Borane-BODIPY dyads: Molecular conformation control over electronic properties and fluorescence response towards fluoride ion

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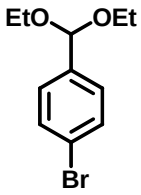
Experimental Section

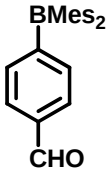
n-Butyllithium (1.6 M in hexanes), 4-bromobenzaldehyde, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were purchased from Aldrich and pyrroles were purchased from SRL (India). All reactions were carried under an atmosphere of purified Nitrogen using schlenck techniques. THF, and Diethylether were distilled over sodium. Chlorinated solvents were distilled over CaH_2 and subsequently stored over 3Å molecular sieves. The (400 MHz) ^{1}H NMR, (376 MHz) ^{19}F NMR, (100 MHz) ^{13}C NMR and (160 MHz) ^{11}B NMR were recorded on a Bruker Advance 400 MHz NMR spectrometer. All solution ^{1}H and ^{13}C spectra were referenced internally to the solvent signal. ^{11}B and ^{19}F NMR spectra were referenced externally to $BF_3.Et_2O$ ($\delta = 0$) in C_6D_6. . Elemental analyses of C, H, and N were performed using a Perkin-Elmer 240C elemental analyzer. 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 F2 using SHELXTL software[5]. All the non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were refined isotropically on the positions calculated using a riding model.

Synthesis of **1-bromo-4-(diethoxymethyl)benzene:**



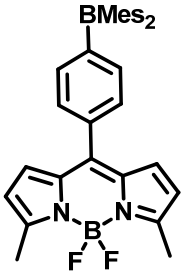
4-Bromobenzaldehyde (9.5 g, 51.41 mmol) and triethylorthoformate (113.24 mmol) (catalytical amount of conc. HCl) were dissolved in ethanol and the resultant solution was refluxed for 4h. After all the 4-Bromobenzaldehyde was consumed, reaction temperature was brought to room temperature and extracted with mixture of cold water/ethyl acetate. The combined organic layer was washed with brine and dried over anhydrous sodium sulphate. The volatiles were removed under reduced pressure afforded product as a colorless liquid. Yield: 13.98 g, 98%. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.49 (d, J = 6.8 Hz, 2H), 7.35 (d, J = 8 Hz, 2H), 5.46 (s, 1H), 3.63-3.49 (m, 4H), 1.24 (t, 6H).

Synthesis of **1** (4-dimesitylborylbenzaldehyde)**:**



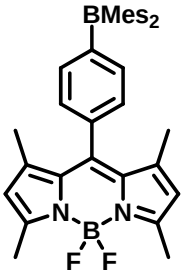
A solution of 1-bromo-4-(diethoxymethyl)benzene (2.5 g, 9.64 mmol) in dry THF was degassed by purging N_2 for 30 minutes followed by cooling to -78^{o}C (Acetone/liq-N_2). *n*-Butyllithium (6.6 mL, 10.61 mmol (1.6 M solution in hexane)) was added over 30 min. After 1 h, a solution of dimesitylfluoroborane (2.9 g, 10.08 mmol) in 15 mL of dry THF was added over 10 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for 12 h. Then, 30 mL of 1N HCl was added and stirring was continued for another 4 h and extracted with ether. The combined organic layers were washed with brine solutions and dried over anhydrous Na_2SO_4. Evaporation of the solvents under reduced pressure affords crude product. Recrystallization of the crude product in EtOAc gave pure **1** as a colorless solid. Yield: 2.05 g, 59%. ^{1}H NMR (400 MHz, $CDCl_3$ δ ppm) 10.07 (s, 1H), 7.85 (d, J = 8 Hz, 2H), 7.66 (d, J = 8Hz, 2H), 6.83 (s, 4H), 2.32 (s, 6H), 1.98 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 193.3, 152.8, 141.3, 140.8, 139.9, 138.4, 136.4, 129.5, 128.9, 23.9, 21.8. ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm) 76.7.

Synthesis of **2:**



2-methylpyrrole (0.21 g, 1.47 mmol) and **1** (0.20 g, 0.56 mmol) were stirred at room temperature under nitrogen atmosphere for 30 min then BF_3•Et_2O (13μL, 0.19 mmol) was added. The resultant mixture was stirred for another 6 h at room temperature and a solution of DDQ (0.28 g, 1.12 mmol) in benzene (10 mL) was added and stirring was continued for another 6 h. The resultant solution was allowed to react with triethylamine (1.63 mL, 11.20 mmol) and subsequently with BF_3•Et_2O (1.5 mL, 11.20 mmol). After stirring for 5 h at RT, the solvents were removed under reduced pressure affords crude product. Which was further purified by silica gel column chromatography (1:99 EtOAc:petroleum ether) to give compound **2** as a red colour solid. Yield 50 mg, 16.67%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 7.67 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 6.89 (s, 4H), 6.75 (d, *J* = 4.0 Hz 2H), 6.32 (d, *J* = 4.4 Hz 2H) 2.70 (s, 6H), 2.37 (s, 6H), 2.08 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm) 155.6, 143.0, 141.7, 140.8, 139.2, 136.7, 131.2, 129.2, 128.4, 127.8, 127.0, 122.9, 121.4, 23.5, 21.3, 14.5. ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm) 1.2 (t, *J* = 36 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm) -147.4 (q, *J* = 34 Hz). ES-MS m/z $C_{35}H_{36}BN_2H$ (M-BF_2)+ calcd 495.3086, found 495.3028. Elemental analysis: calcd (%) for $C_{35}H_{36}B_2F_2N_2$: C 77.23, H 6.67, N 5.15; found: C 77.33, H 6.80, N 5.20.

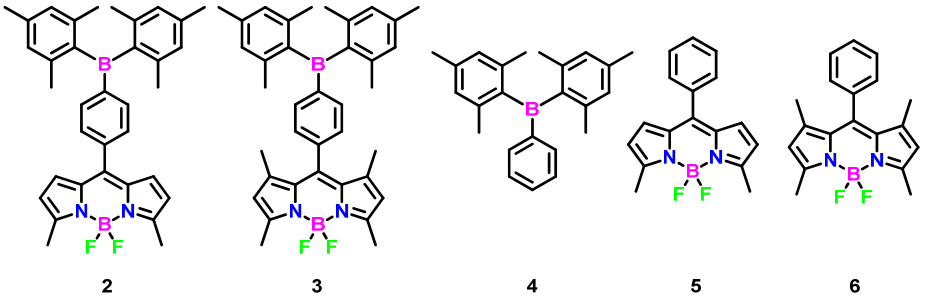
Synthesis of **3:**



Compound **3** was prepared following a procedure similar to that used for compound **2**. The quantities involved and characterization data are as follows. 2,4-Dimethylpyrrole (0.14 g,

1.47 mmol), **1** (200 mg 0.56 mmol), BF_3•Et_2O (13μL, 0.11 mmol), DDQ (0.14 mg , 0.62 mmol), triethylamine (0.80 mL, 5.64 mmol), BF_3•Et_2O (0.75 mL, 5.64 mmol). Yield: 57 mg, 17%, color: red color solid. ^{1}H NMR (400 MHz, $CDCl_3$ δ ppm) 7.67 (d, *J* = 8 Hz, 2H), 7.36 (d, *J* = 8 Hz, 2H), 6.88(s, 4H), 6.04 (s, 2H), 2.60 (s, 6H), 2.36 (s, 6H), 2.25, (s, 12H) 1.46 (s, 6H). ^{13}CNMR (100 MHz, $CDCl_3$, δ ppm) 155.9, 143.3, 142.0, 141.9, 141.2, 139.5, 138.8, 137.0, 131.5, 128.8, 128.7, 128.2, 121.7, 23.9, 21.7, 15.0, 14.9. ^{11}B NMR (160 MHz, $CDCl_3$, δ ppm) 1.03 (t, J = 36 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm) -146.11 (q, *J* = 34 Hz). ES-MS m/z $C_{37}H_{42}BN_2H$ (M-BF_2+H)+ calcd 525.3556, found 525.3555. Elemental analysis: calcd (%) for $C_{37}H_{40}B_2F_2N_2$: C 77.64, H 7.04, N 4.89; found: C 77.72, H 7.12, N 4.78.

Chart S1: Compounds used for Photophysical Studies:



Photophysical Data

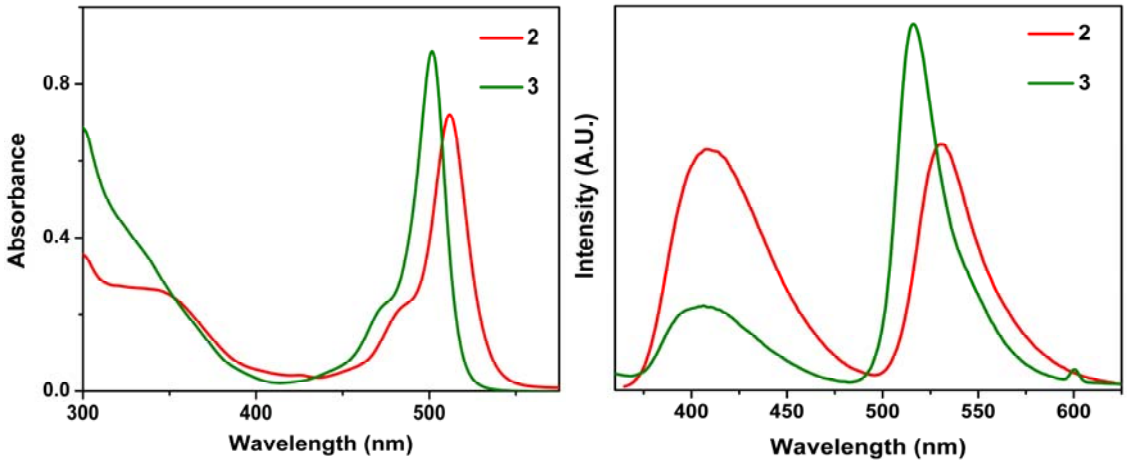


Figure S1: Comparison of UV-Vis (left) and emission spectra (right) of **2** and **3** (10μM in DCM, λ_{ex}=350nm)

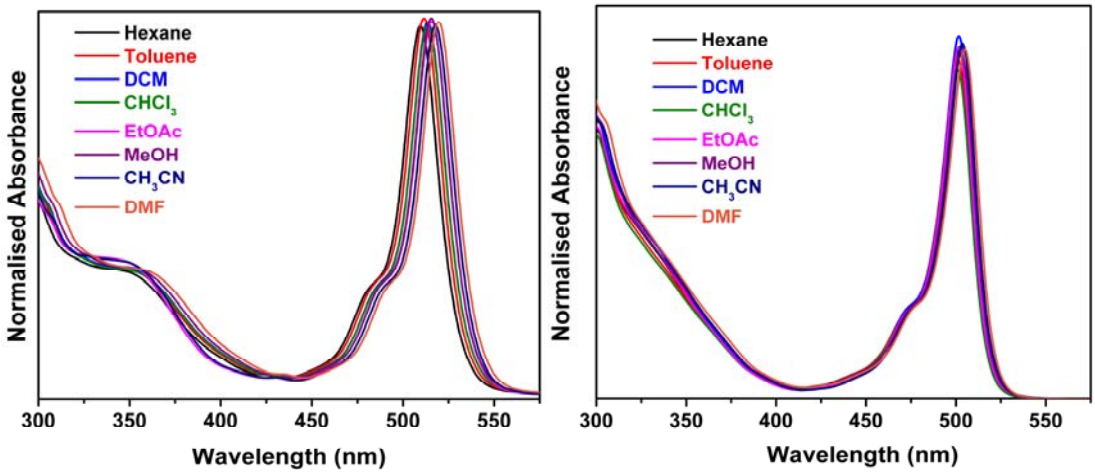


Figure S2: Normalized UV-Vis spectra of **2** (left) and **3** (right) in different solvents (10 μM)

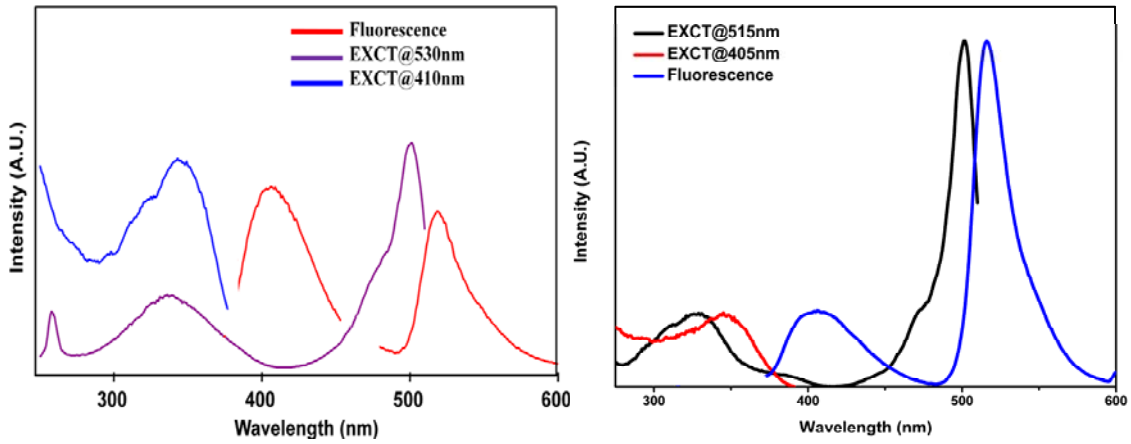


Figure S3: Fluorescence emission and excitation spectra for **2** (left) and **3** (right) (1μM in DCM)

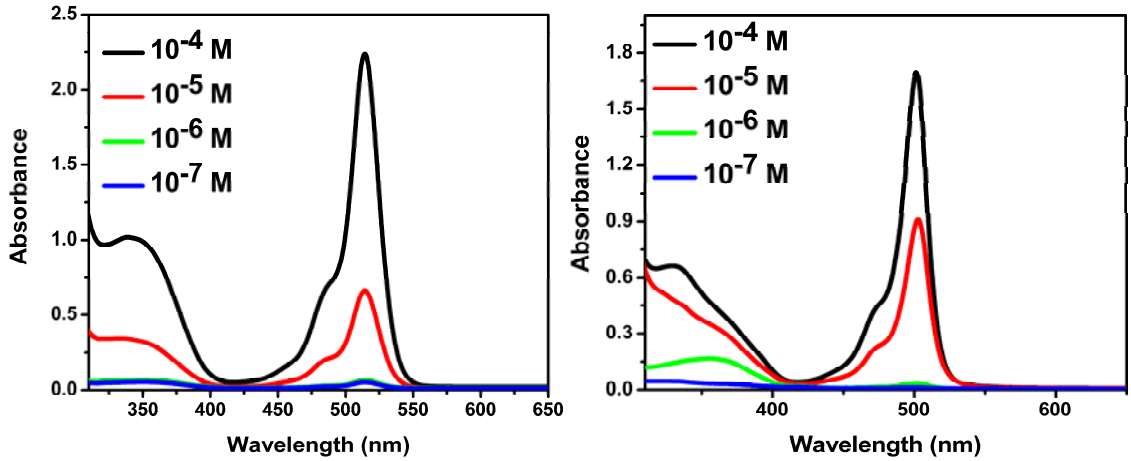


Figure S4: UV-Vis spectra of **2** (left) and **3** (right) in different concentrations (in DCM)

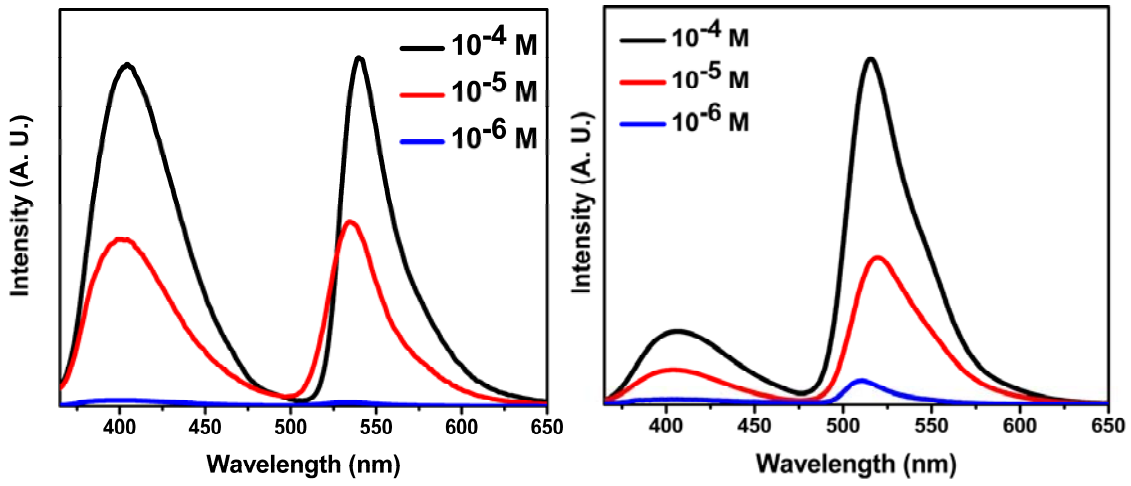


Figure S5: Emission spectra of **2** (left) and **3** (right) in different concentrations (in DCM); λ_{ex}=350nm

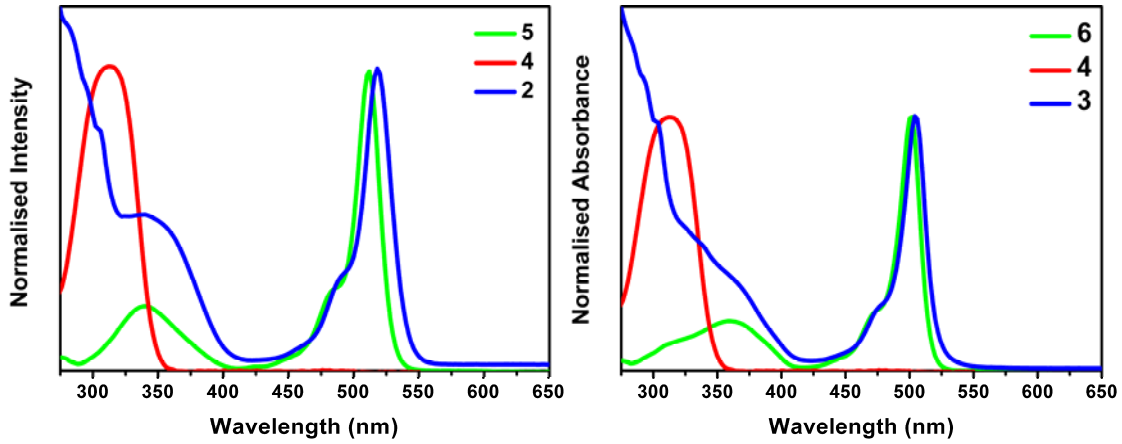


Figure S6: UV-Vis spectra (Normalized) of **2** (left) and **3** (right) compared to the model compounds (10μM in DCM)

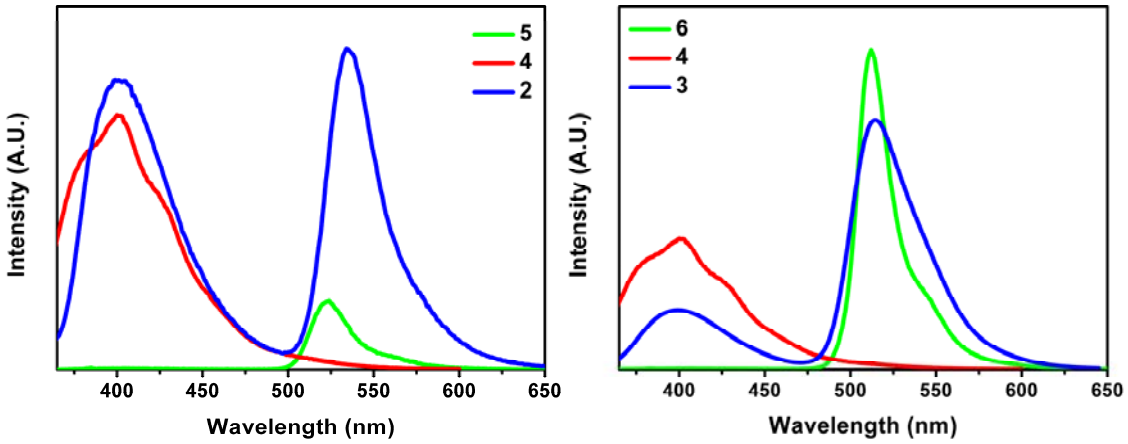


Figure S7: Emission spectra of **2** (left) and **3** (right) with model compounds (10 μM in DCM); λ_{ex}=350nm

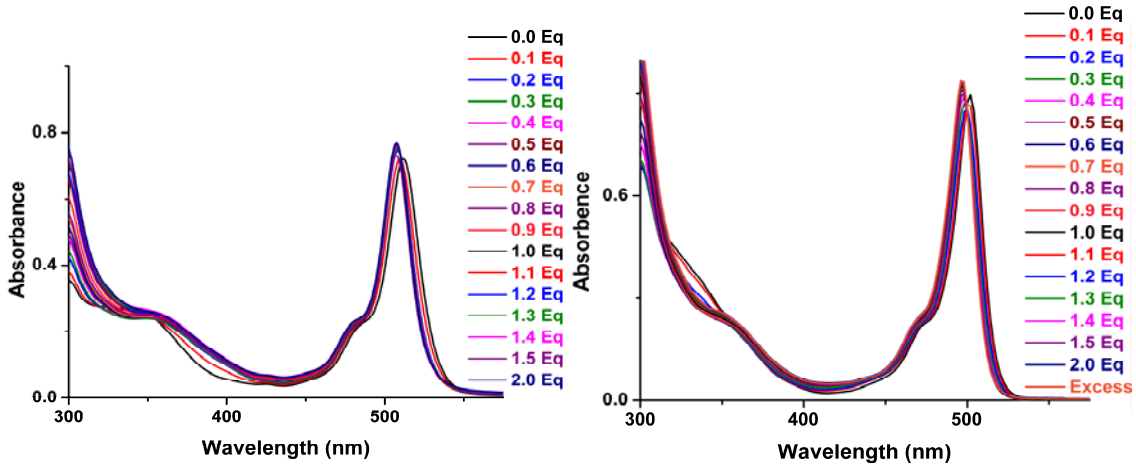


Figure S8: UV-Vis spectra of **2** (left) and **3** (right) (in 10μM DCM solutions) in presence of TBAF

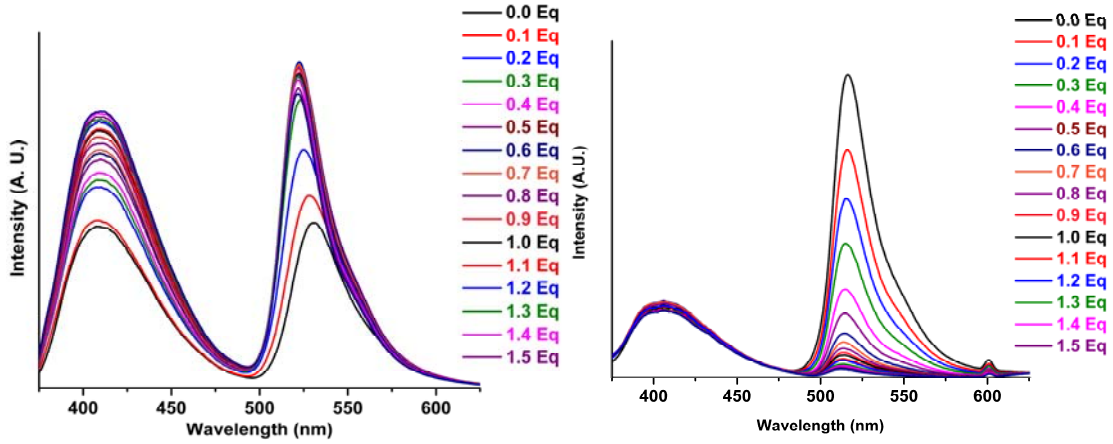


Figure S9: Fluorescence spectra of **2** (left) and **3** (right) (in 10μM DCM solution; λ_{ex}=350nm) in presence of TBAF

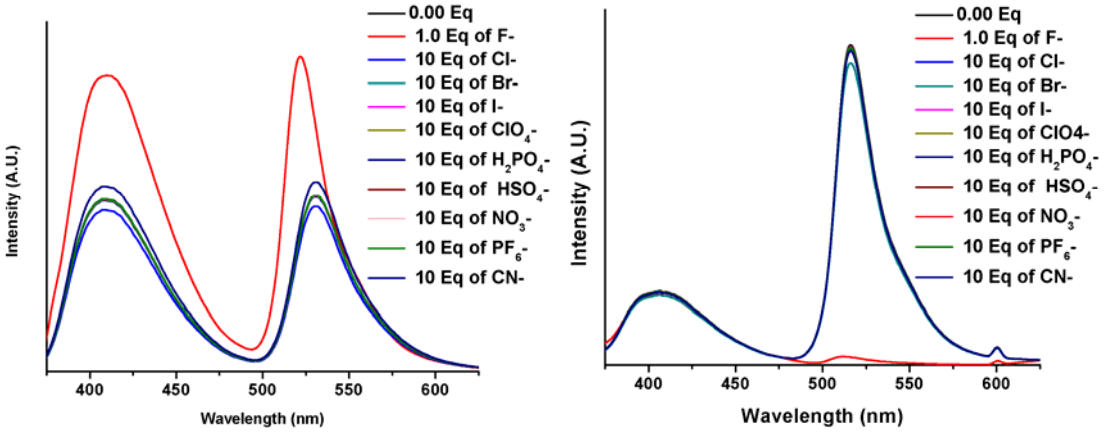


Figure S10: Fluorescence spectra of **2** (left) and **3** (right) in (10μM in DCM, λ_{ex}= 350nm) presence of different Anions;

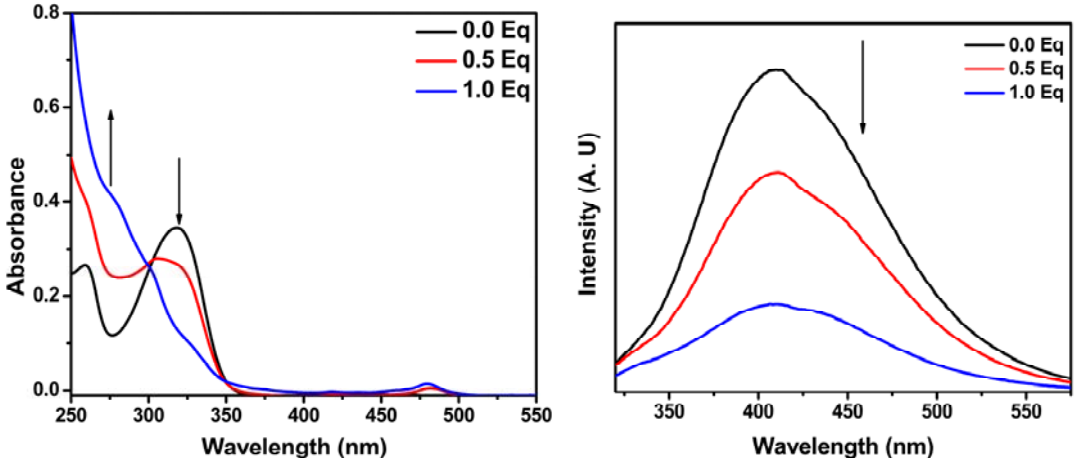


Figure S11: UV-Vis (left) and fluorescence spectra (right) of **4** (in 10μM DCM solutions) in presence of TBAF

Table S1:

Compound	λ_{max}(nm)	λ_{max} (nm)	λ_{max}(nm)
2	**340**	**486**	**512**
2+F	**343**	**479**	**507**
3	**334**	**474**	**501**
3+F	**331**	**470**	**497**
5	**339**	**484**	**511**
6	**360**	**473**	**501**

From a comparison of the absorption spectra of **2** and **3** with the model compounds **4**, **5** and **6**, one can conclude that there is very little electronic communication between borane and BODIPY units in **2** and **3**. Since the electronic communication between the two chromophores is little, the F^- binding induced minimum changes on the absorption bands of **2** and **3.** For example the lower energy absorption bands of **2** (512 nm) and **3** (501nm) decreased slightly and was blue-shifted to 507 and 497 nm respectively ($\Delta\lambda$ = ~5 nm). This hypsochromic shift is may be due to the interruption in electronic communication between the borane and BODIPY units in **2•F** and **3•F.**

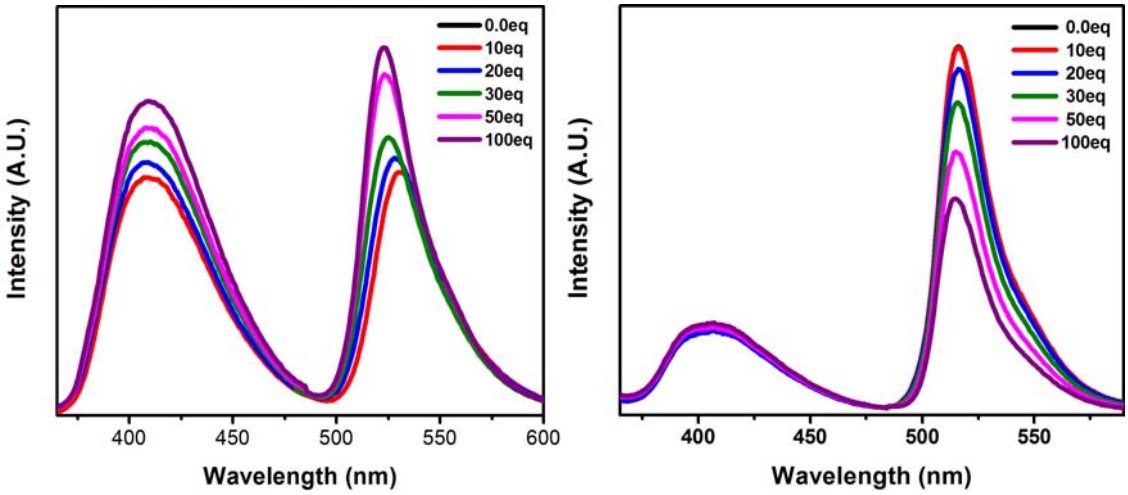


Figure S12: Fluorescence spectra of **2** (left) and **3** (right) in (10μM in DCM, λ_{ex}=350nm) presence of different amount of cyanide (as TBA-CN)

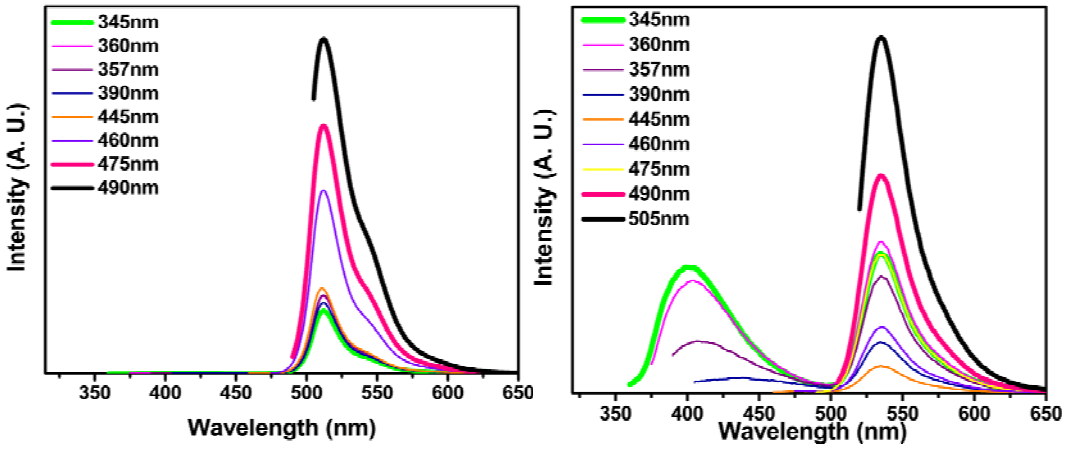


Figure S13: Emission spectra of compound **5** (left) and **2** (right) at different excitation wavelengths (10μM in DCM)

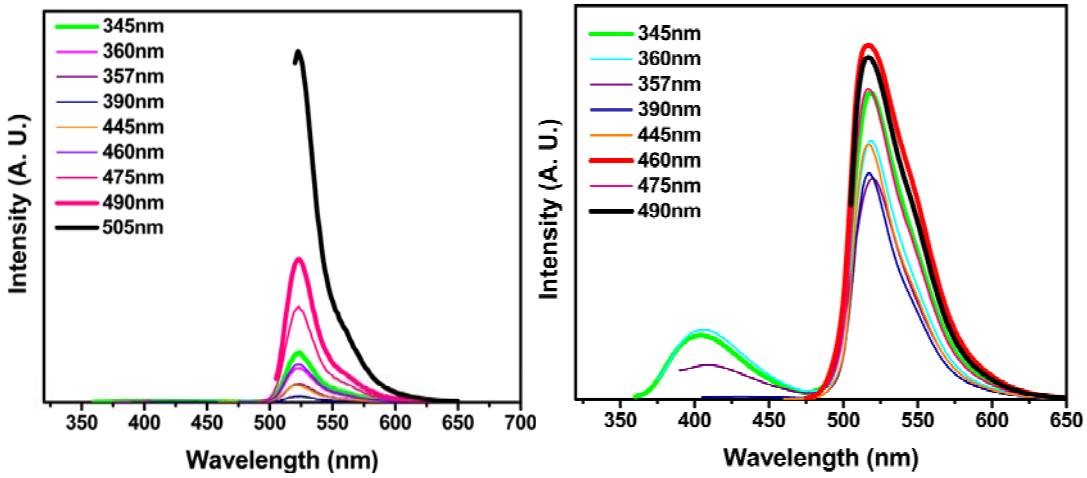


Figure S14: Emission spectra of compound **6** (left) and **3** (right) at different excitation wavelengths (10μM in DCM)

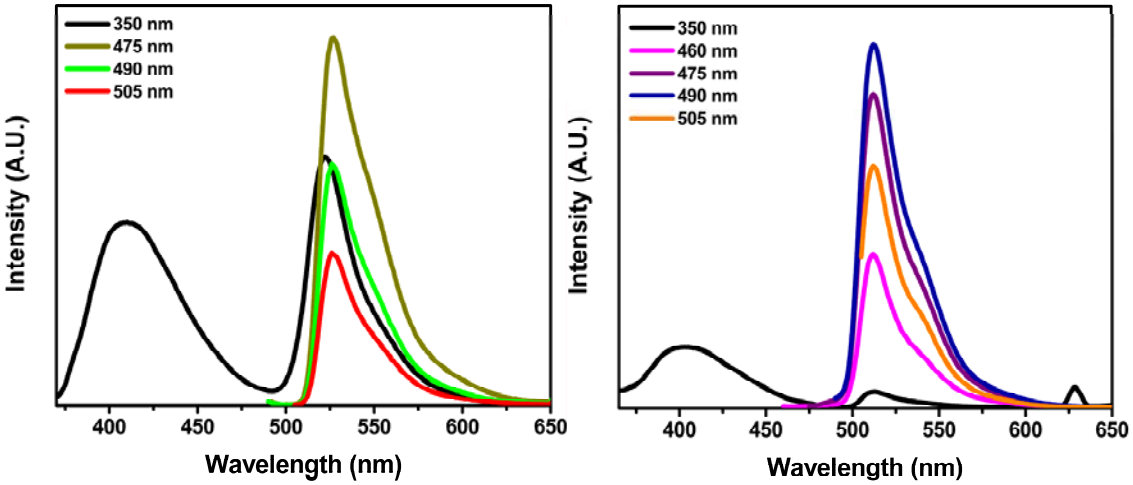


Figure S15: Emission spectra of **2+F-** (left) and **3+F-** (right) at different excitation wavelengths (1.5eq of TBAF in 10 μM DCM solution)

DFT Computational Results:

The hybrid B3LYP functional[1] has been used in all calculations as incorporated in *Gaussian 09* package, [2] mixing the exact Hartree-Fock-type exchange with Becke's exchange functional[3] and that proposed by Lee-Yang-Parr for the correlation contribution.[4] We used 6-31G(d) basis set for all the atoms which provides reasonably high quality results in moderate timescales. Visualizations of the optimized structures and the MOs were performed using *Gaussview5.0*.

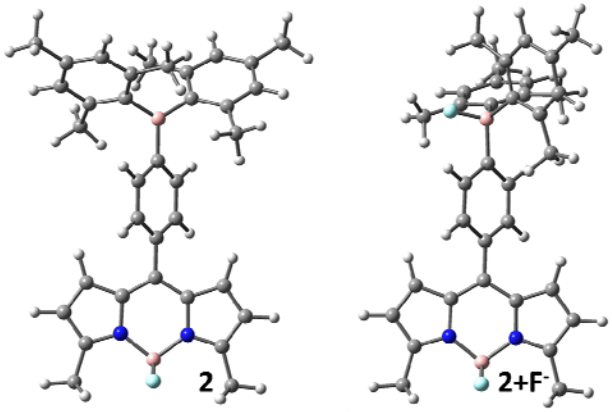


Figure S16: optimized structures of **2** and **2+F-**

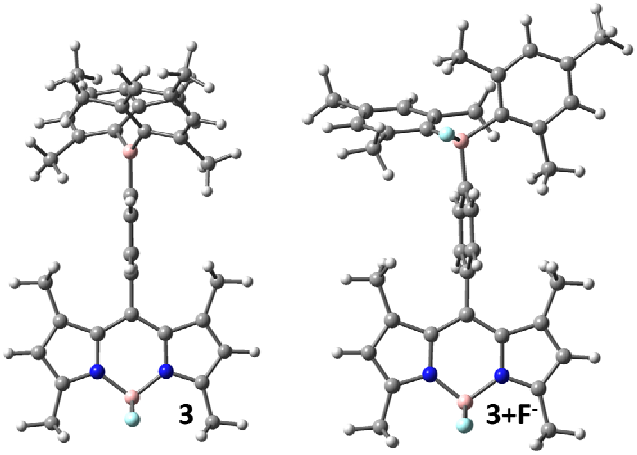


Figure S17: optimized structures of **3** and **3+F-**

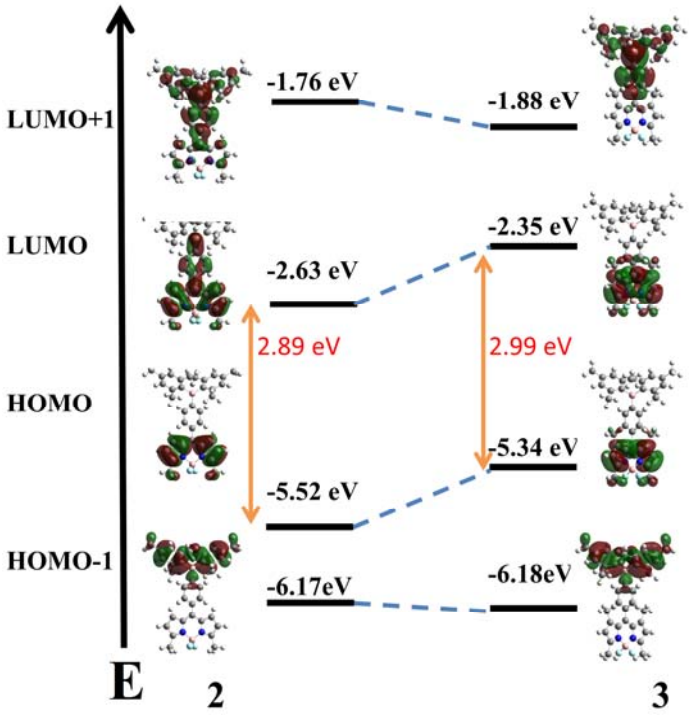


Figure S18: Comparison of electronically important MOs (Isovalue 0.02) of **2** and **3***(Schematic: Not to scale)*

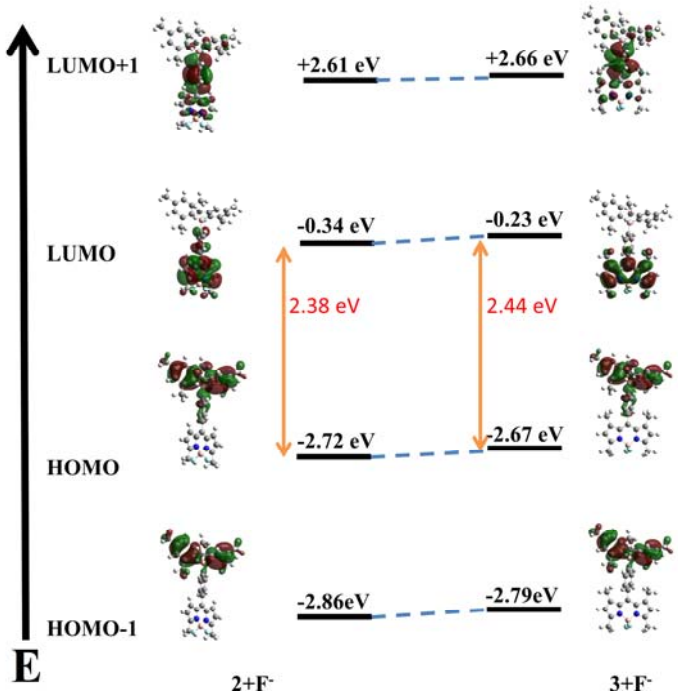


Figure S19: Comparison of electronically important MOs (Isovalue 0.02) of **2**+F^- and **3**+F^-*(Schematic: Not to scale)*

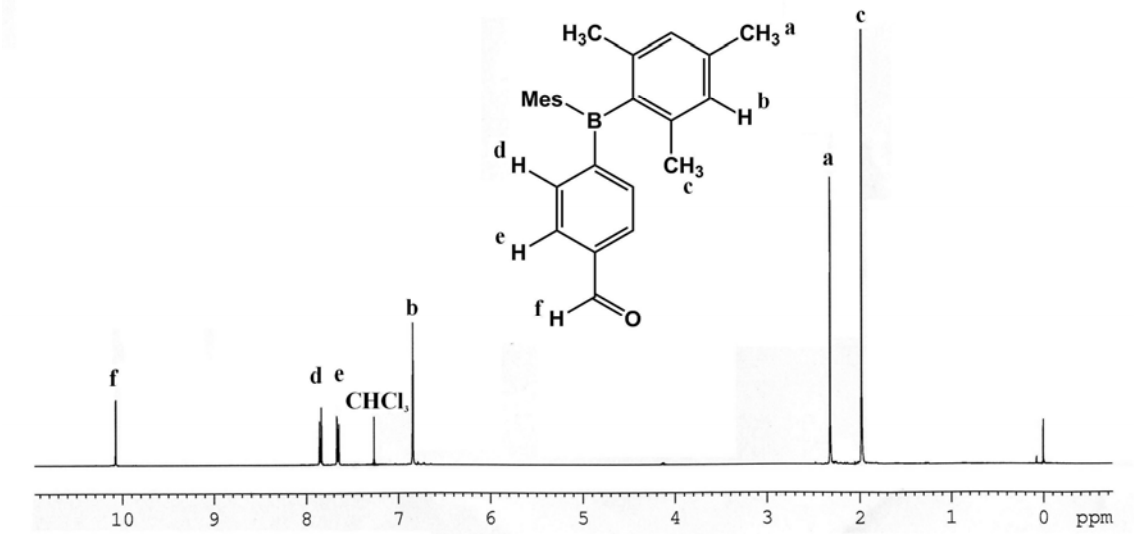


Figure S20: ^{1}H NMR spectra of **1**

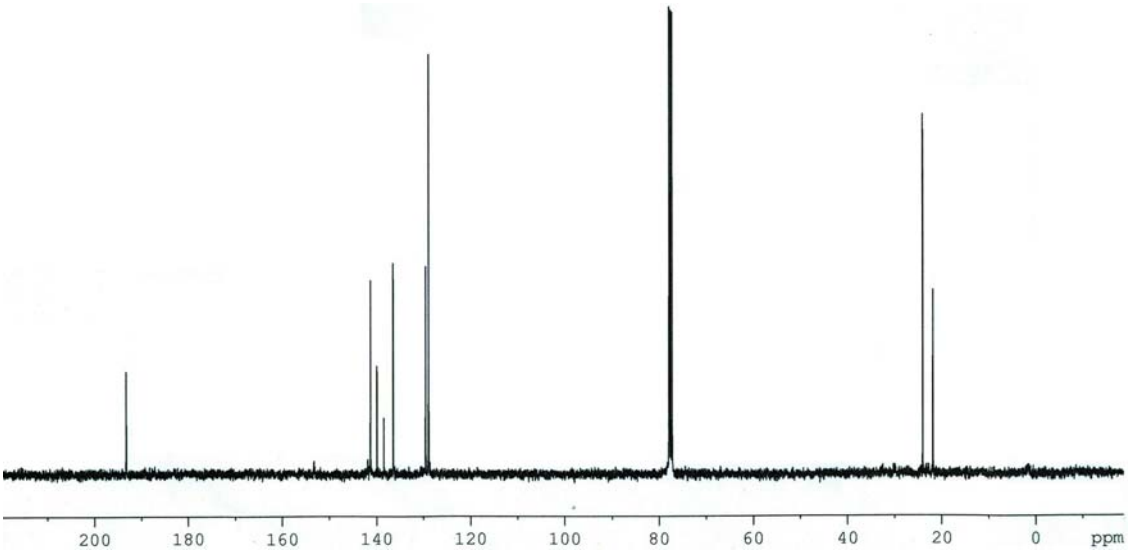


Figure S21: ^{13}C NMR spectra of **1**

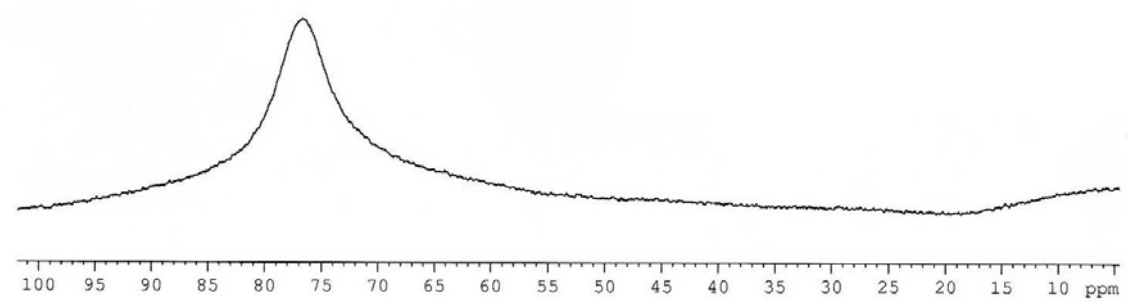


Figure S22: ^{11}B NMR spectra of **1**

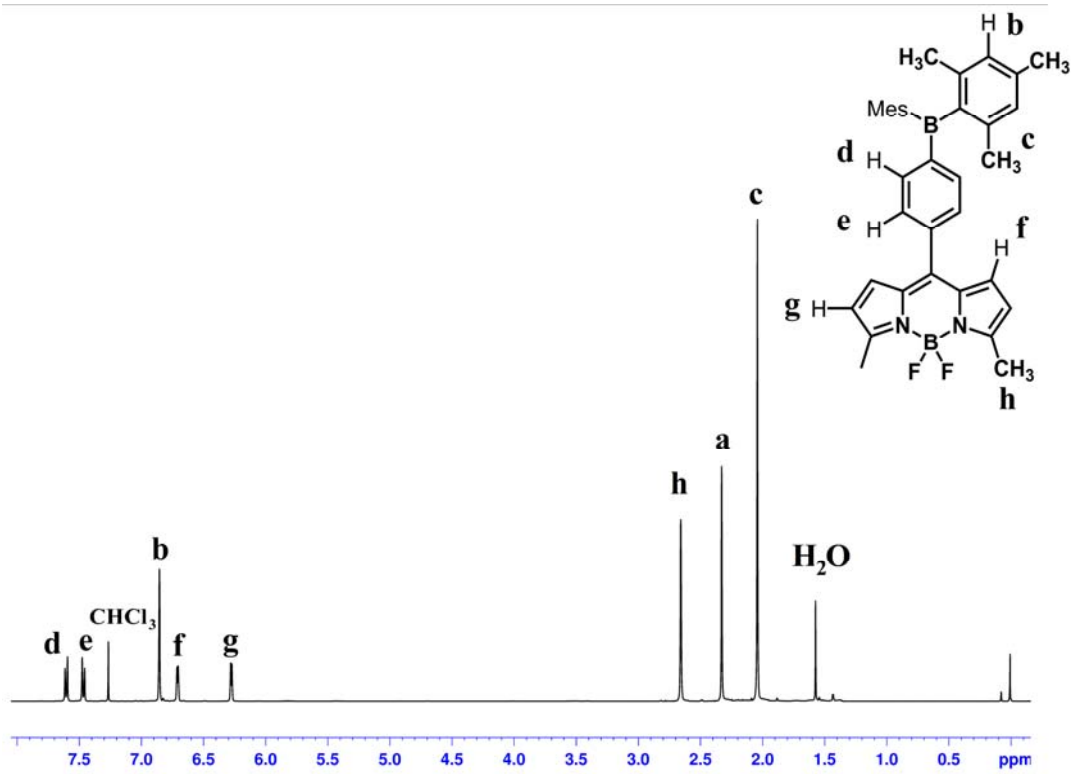


Figure S23: ^{1}H NMR spectra of **2**

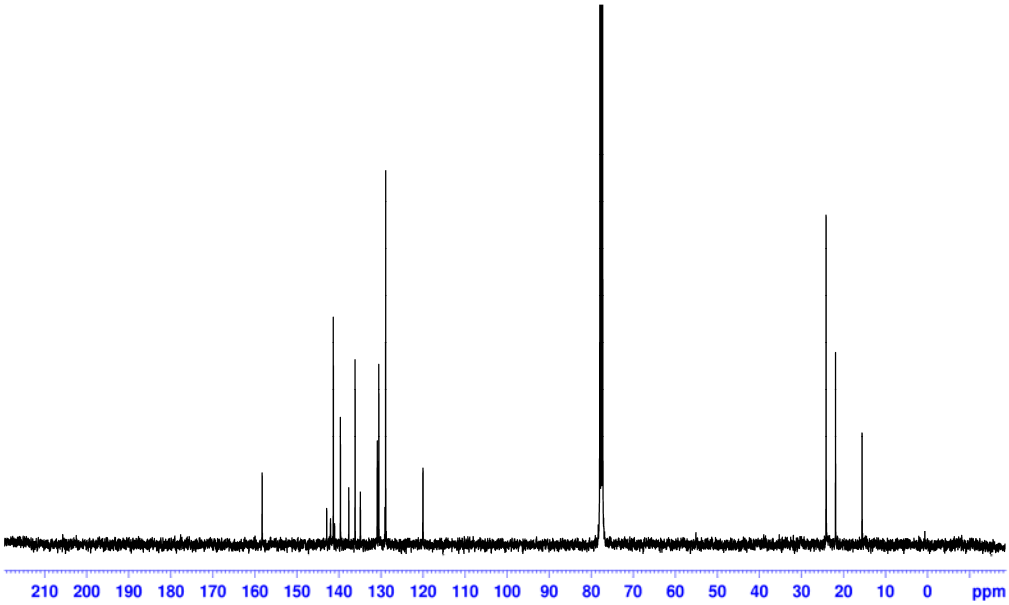


Figure S24: ^{13}C NMR spectra of **2**

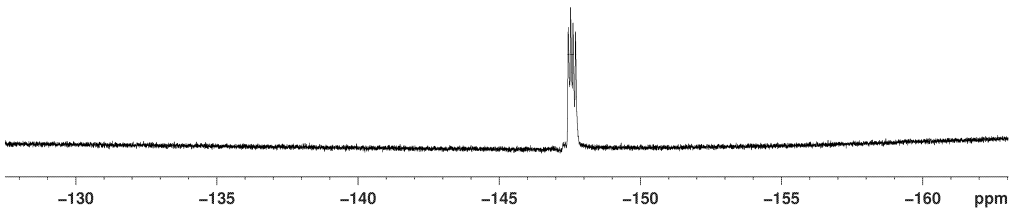


Figure S25: ^{19}F NMR spectra of **2**

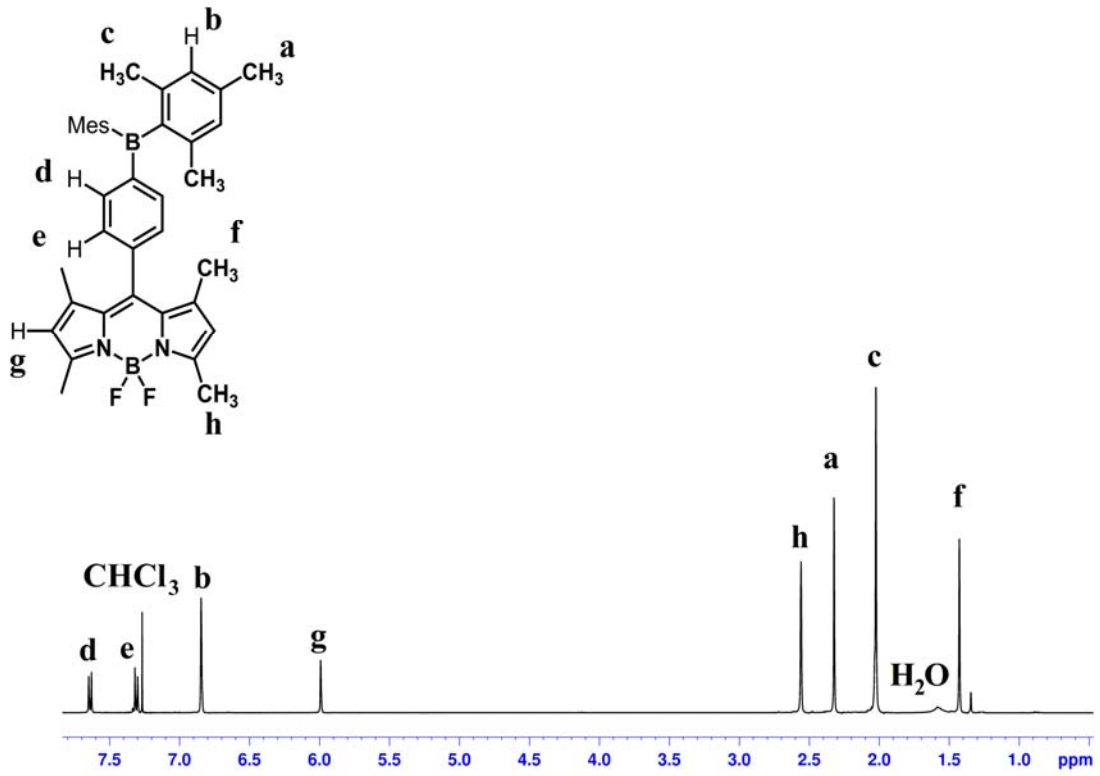


Figure S26: ^{1}H NMR spectra of **3**

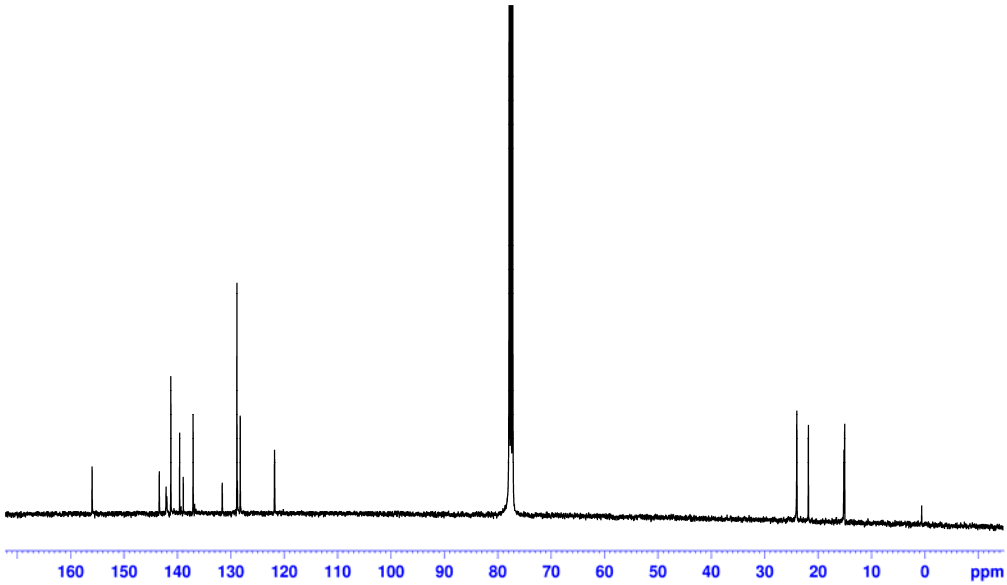


Figure S27: ^{13}C NMR spectra of **3**

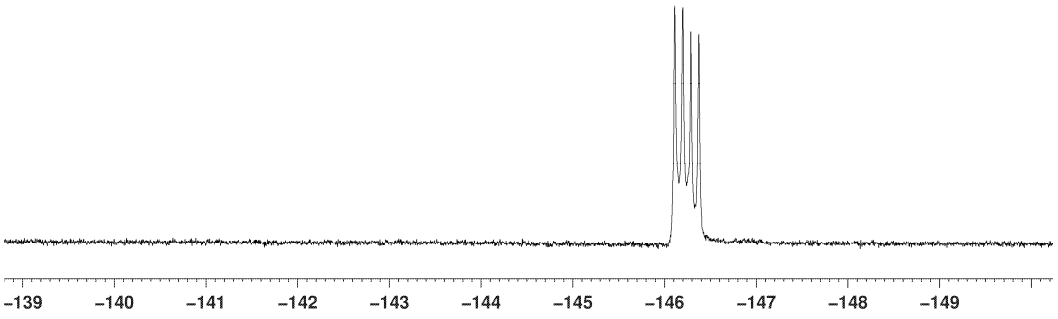


Figure S28: ^{19}F NMR spectra of **3**

Figure S29: HRMS for **2**

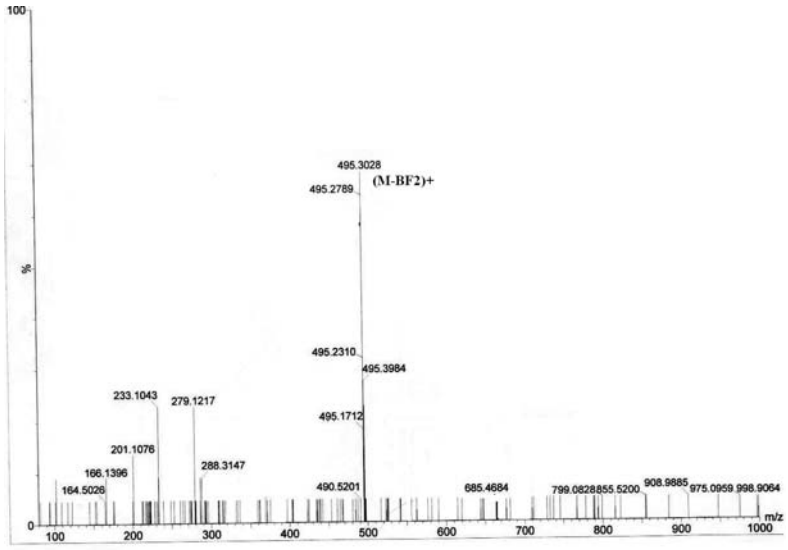
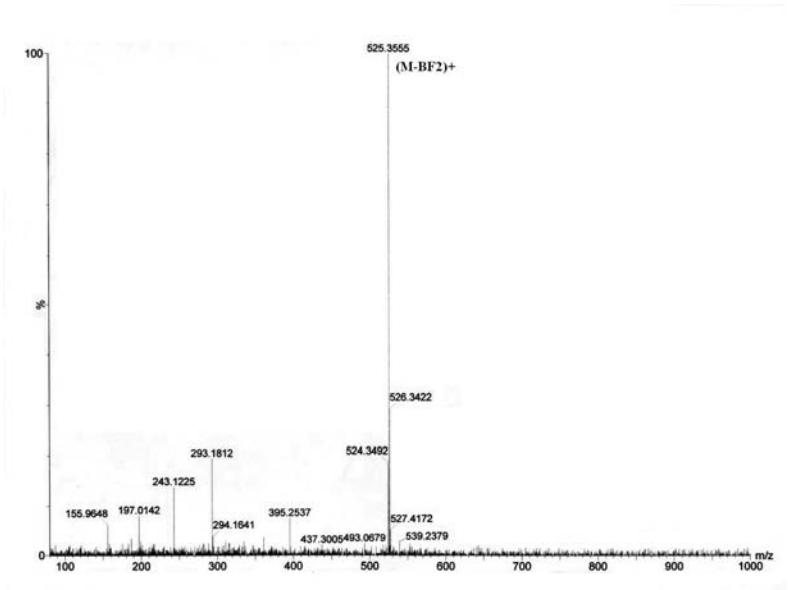


Figure S30: HRMS for **3**



Compound **2** and **3** not stable in mass spectrometry experimental conditions, we are getting mass for only $(M\text{-}BF_2)^+$ ion for both the dyads.

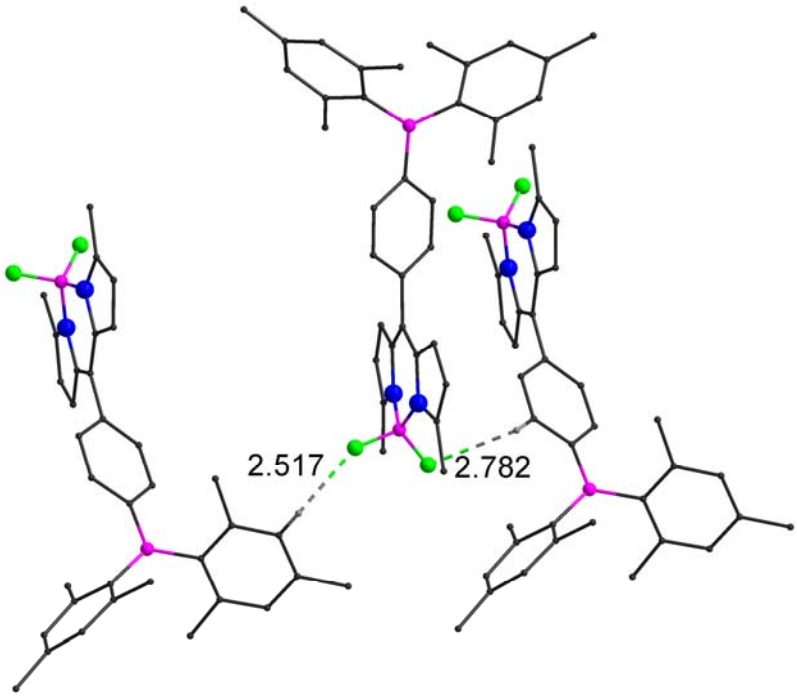


Figure S31: Intermolecular interactions in solid state structure of **2** (distances shown in Å) Color codes: C = Black, H = Grey, B = Magenta, N = Blue, F = Green

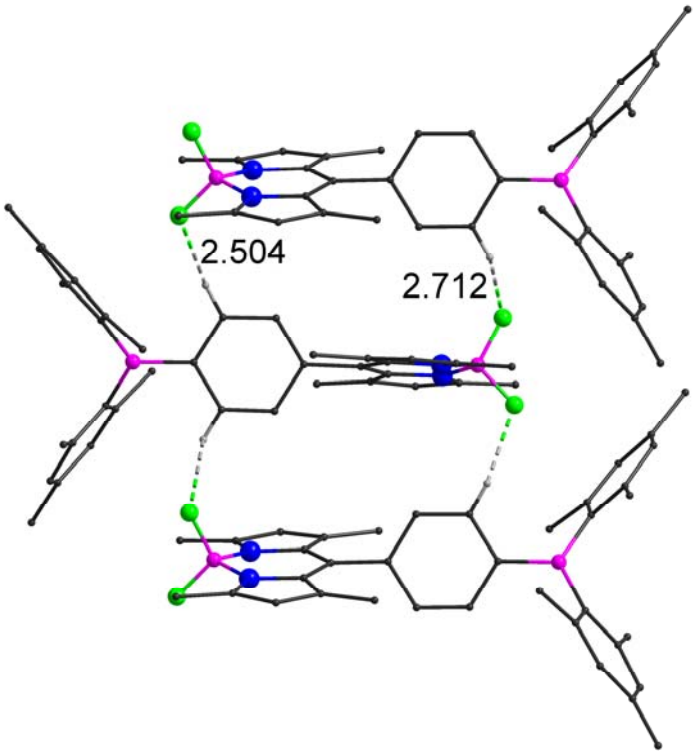


Figure S32: Intermolecular interactions in solid state structure of **3** (distances shown in Å) Color codes: C = Black, H = Grey, B = Magenta, N = Blue, F = Green

Table S2: Crystallographic data for **1**, **2** and **3**

Crystals of **1**, **2** and **3** suitable for single crystal X-ray diffraction studies were obtained from mixture of chloroform and petroleum-ether. The crystal quality were very poor. After several attempts, we got the reasonable diffraction data and solved the structure. In spite of the poor diffraction of **1**, **2** and **3**, the molecular structure refined well without any disorder and we don't find any residual electron density higher than 0.6 $Å^3$ asymmetric unit. The high R1 and wR2 values may be due to the poor quality of the crystal.

	1	**2**	**3**
Empirical formula	C25 H27 B O	C35 H36 B2 F2 N2	C37 H40 B2 F2 N2
Formula weight	354.28	544.28	572.33
Temperature	293(2) K	273(2) K	273(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, P -1	Orthorhombic, $Pca2_1$	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 8.506(19) Å α = 83.27(4) °. b = 11.56(3) Å β = 88.36(4) °. c = 11.58(3) Å γ = 76.94(4) °.	a = 36.823(8) Å α = 90 ° b = 8.3144(17) Å β = 90 ° c = 9.7870(17) Å γ = 90 °	a = 18.770(2) Å α = 90 °. b = 9.8560(13) Å β = 90.167(8) °. c = 16.662(2) Å γ = 90 °.
Volume	1102(4) $Å^3$	2996.4(10) $Å^3$	3082.4(7) $Å^3$
Z, Calculated density	2, 1.068 mg/m^3	4, 1.207 Mg/m^3	4, 1.233 Mg/m^3
Absorption coefficient	0.062 mm^{-1}	0.077 mm^{-1}	0.079 mm^{-1}
F(000)	380	1152	1216
Crystal size	0.10 x 0.09 x 0.08 mm	0.12 x 0.10 x 0.10 mm	0.09 x 0.07 x 0.07 mm
Theta range for data collection	1.77 to 27.74 °.	2.21 to 30.66 °	2.17 to 28.00 °.
Limiting indices	-10<=h<=10, -14<=k<=14, -15<=l<=15	-52<=h<=51, -11<=k<=11, -14<=l<=13	-24<=h<=24, -13<=k<=11, -22<=l<=14
Reflections collected / unique	11674 / 4855 [R(int) = 0.0623]	62836 / 8945 [R(int) = 0.1748]	49266 / 7401 [R(int) = 0.1077]
Completeness to theta = 28.00	93.6 %	99.3 %	99.70%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9950 and 0.9938	0.9923 and 0.9908	0.9945 and 0.9930
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4855/0/250	8945 / 1 / 378	7401 / 0 / 388
Goodness-of-fit on F^2	0.953	0.960	1.103
Final R indices [I>2sigma(I)]	R1 = 0.0839, wR2 = 0.2055	R1 = 0.0695, wR2 = 0.1138	R1 = 0.1390, wR2 = 0.3285
R indices (all data)	R1 = 0.1717, wR2 = 0.2562	R1 = 0.2095, wR2 = 0.1538	R1 = 0.1890, wR2 = 0.3567
Largest diff. peak and hole	0.403 and -0.228 $e.A^{-3}$	0.241 and -0.248 $e.A^{-3}$	0.653 and -0.715 $e.A^{-3}$

Table S3. Computed Structure of **2.**
2 -1714.54527021a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	5.081614	-1.203704	-0.341846
2	7	0	5.073755	1.195429	0.345697
3	5	0	6.019007	-0.002323	0.006337
4	9	0	6.804818	-0.313879	1.111520
5	9	0	6.814312	0.312242	-1.091151
6	6	0	-1.353418	-0.011052	-0.001713
7	6	0	-0.613066	-0.976393	0.712269
8	1	0	-1.145068	-1.734389	1.281379
9	6	0	0.778781	-0.976029	0.721664
10	1	0	1.321489	-1.711131	1.308334
11	6	0	1.496211	-0.011931	-0.008533
12	6	0	0.775738	0.951096	-0.736508
13	6	0	-0.616125	0.953191	-0.719986
14	6	0	2.980286	-0.008683	-0.006116
15	6	0	3.686910	-1.172086	-0.354396
16	6	0	3.227622	-2.440249	-0.797705
17	1	0	2.192177	-2.718523	-0.932082
18	6	0	4.349277	-3.220999	-1.030497
19	1	0	4.378658	-4.245944	-1.375608
20	6	0	5.485035	-2.427999	-0.743199
21	6	0	3.679097	1.157839	0.347378
22	6	0	3.210913	2.423700	0.788406
23	1	0	2.173331	2.697632	0.914979
24	6	0	4.327401	3.208909	1.030513
25	1	0	4.349752	4.233655	1.376757
26	6	0	5.468767	2.420956	0.751511
27	1	0	1.316043	1.687575	-1.323670
28	1	0	-1.149582	1.715482	-1.281274
29	5	0	-2.930030	-0.003470	0.012862
30	6	0	-3.694078	-1.364247	0.273763
31	6	0	-4.649126	-1.476778	1.321819
32	6	0	-3.440272	-2.517585	-0.515905
33	6	0	-5.289965	-2.695068	1.561680
34	6	0	-4.126746	-3.710325	-0.261421
35	6	0	-5.051867	-3.826127	0.776286
36	1	0	-6.001665	-2.761180	2.382833
37	1	0	-3.930359	-4.574464	-0.894285
38	6	0	-3.680663	1.365759	-0.249321
39	6	0	-3.443460	2.512654	0.551691
40	6	0	-4.594243	1.496369	-1.335944
41	6	0	-4.085009	3.724607	0.259865
42	6	0	-5.200759	2.724850	-1.599699
43	6	0	-4.962713	3.857600	-0.812509
44	1	0	-3.891565	4.586164	0.897273
45	1	0	-5.880071	2.803096	-2.447039
46	6	0	-4.985136	-0.312277	2.232850
47	1	0	-5.427335	0.521855	1.678646
48	1	0	-5.698474	-0.619897	3.003979
49	1	0	-4.098444	0.078404	2.746080
50	6	0	-2.453558	-2.525438	-1.670476
51	1	0	-1.443524	-2.789766	-1.334157
52	1	0	-2.751012	-3.265055	-2.421593
53	1	0	-2.374187	-1.557468	-2.171916
54	6	0	-5.795095	-5.117345	1.023598
55	1	0	-6.775770	-5.112077	0.528821
56	1	0	-5.240858	-5.979526	0.637977
57	1	0	-5.974641	-5.278528	2.092293
58	6	0	-2.583462	2.484055	1.800799
59	1	0	-3.213185	2.429348	2.699252
60	1	0	-1.898763	1.635247	1.830770
61	1	0	-1.986618	3.399352	1.887476
62	6	0	-4.913046	0.340264	-2.263419
63	1	0	-4.026882	-0.002471	-2.812390
64	1	0	-5.306113	-0.523812	-1.719371
65	1	0	-5.657774	0.638200	-3.008173
66	6	0	-5.643144	5.170443	-1.119702
67	1	0	-6.734487	5.081008	-1.046635

68	1	0	-5.326049	5.957313	-0.428083
69	1	0	-5.418399	5.508845	-2.138888
70	6	0	6.927468	-2.800796	-0.848819
71	1	0	7.437134	-2.160547	-1.577012
72	1	0	7.434183	-2.650805	0.110465
73	1	0	7.033344	-3.845238	-1.152827
74	6	0	6.908699	2.799489	0.869886
75	1	0	7.414185	2.161675	1.603136
76	1	0	7.424676	2.650840	-0.084634
77	1	0	7.007694	3.844500	1.174250

Table S4. Computed Structure of **3.**

3 -1793.17666675a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	4.989297	0.881677	-0.877389
2	7	0	4.988219	-0.890212	0.872990
3	5	0	5.924511	-0.004721	-0.002075
4	9	0	6.718276	-0.810001	-0.816393
5	9	0	6.718753	0.799758	0.812488
6	6	0	-1.441304	-0.001120	-0.013191
7	6	0	-0.701091	-0.832881	-0.879871
8	1	0	-1.232691	-1.488974	-1.564354
9	6	0	0.692364	-0.829344	-0.890358
10	1	0	1.236644	-1.470315	-1.579170
11	6	0	1.404474	-0.005605	-0.007001
12	6	0	0.691012	0.820661	0.872768
13	6	0	-0.702241	0.829292	0.855912
14	6	0	2.899281	-0.005698	-0.005067
15	6	0	3.589463	0.866823	-0.862898
16	6	0	3.130951	1.840315	-1.813534
17	6	0	4.275616	2.403313	-2.364979
18	1	0	4.308598	3.177589	-3.121062
19	6	0	5.403265	1.797766	-1.773387
20	6	0	3.588465	-0.877072	0.854821
21	6	0	3.128770	-1.849511	1.805765
22	6	0	4.272585	-2.410337	2.361195
23	1	0	4.304475	-3.183225	3.118745
24	6	0	5.401007	-1.804405	1.771525
25	1	0	1.234288	1.461863	1.562150
26	1	0	-1.234274	1.491953	1.533189
27	5	0	-3.017012	0.003823	-0.017924
28	6	0	-3.772837	1.280092	0.540165
29	6	0	-3.567268	2.570800	-0.010854
30	6	0	-4.653975	1.171353	1.655393
31	6	0	-4.209958	3.687592	0.541609
32	6	0	-5.262224	2.310465	2.183859
33	6	0	-5.058091	3.584156	1.640813
34	1	0	-4.039852	4.665017	0.092349
35	1	0	-5.915563	2.202858	3.048239
36	6	0	-3.782072	-1.271880	-0.563659
37	6	0	-4.715724	-1.161711	-1.632232
38	6	0	-3.548096	-2.562997	-0.022740
39	6	0	-5.355365	-2.300018	-2.127476
40	6	0	-4.233653	-3.674687	-0.528109
41	6	0	-5.137211	-3.569972	-1.584622
42	1	0	-6.050939	-2.191778	-2.958046
43	1	0	-4.052696	-4.650856	-0.080562
44	6	0	-2.734479	2.813697	-1.255178
45	1	0	-3.383109	2.968180	-2.128020
46	1	0	-2.124858	3.718620	-1.148988
47	1	0	-2.063701	1.985682	-1.490027
48	6	0	-4.929018	-0.154842	2.335516
49	1	0	-4.026979	-0.569269	2.803496
50	1	0	-5.675864	-0.035906	3.126852
51	1	0	-5.298449	-0.906146	1.631463
52	6	0	-5.746713	4.794984	2.224536
53	1	0	-6.831652	4.753815	2.061998

54	1	0	-5.588555	4.862467	3.307693
55	1	0	-5.379100	5.721572	1.772258
56	6	0	-5.022125	0.166457	-2.294996
57	1	0	-5.421959	0.893353	-1.581080
58	1	0	-4.127973	0.615621	-2.744209
59	1	0	-5.758005	0.038907	-3.095257
60	6	0	-2.583281	-2.815610	1.122529
61	1	0	-2.437777	-1.941379	1.760737
62	1	0	-2.945657	-3.633202	1.755515
63	1	0	-1.591937	-3.106881	0.752950
64	6	0	-5.877821	-4.777205	-2.109075
65	1	0	-6.912287	-4.800138	-1.740928
66	1	0	-5.927488	-4.772624	-3.203975
67	1	0	-5.397559	-5.709757	-1.795413
68	6	0	6.847640	2.071572	-2.039169
69	1	0	7.350587	2.404669	-1.125002
70	1	0	7.358592	1.158899	-2.363552
71	1	0	6.956674	2.839036	-2.809700
72	6	0	6.845012	-2.075842	2.041716
73	1	0	7.351890	-2.405165	1.128368
74	1	0	7.352900	-1.163069	2.370635
75	1	0	6.952920	-2.845296	2.810425
76	6	0	1.726844	-2.237300	2.174519
77	1	0	1.158166	-1.396232	2.585345
78	1	0	1.160709	-2.606823	1.312715
79	1	0	1.749834	-3.029898	2.928971
80	6	0	1.729645	2.226324	-2.187135
81	1	0	1.169471	1.387766	-2.615003
82	1	0	1.154111	2.580871	-1.325522
83	1	0	1.754618	3.028861	-2.930969

Table S5. Computed Structure of **2**+F^-.

2+F^-.-1814.49391729.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	-3.024128	0.556349	-2.128128
2	6	0	-3.463738	1.429609	0.238210
3	6	0	-3.354262	2.781076	-0.203781
4	6	0	-3.997936	1.244241	1.542365
5	6	0	-3.801953	3.842682	0.593957
6	6	0	-2.732874	3.166670	-1.535669
7	6	0	-4.429567	2.332993	2.316782
8	6	0	-4.137357	-0.122472	2.191376
9	6	0	-4.357684	3.645497	1.857970
10	1	0	-3.700251	4.860688	0.215848
11	1	0	-2.606070	4.255399	-1.590924
12	1	0	-1.752417	2.701747	-1.675444
13	1	0	-3.343644	2.843350	-2.382159
14	1	0	-4.831272	2.141684	3.312600
15	1	0	-4.945509	-0.710499	1.744719
16	1	0	-3.229627	-0.724014	2.094769
17	1	0	-4.352266	-0.013866	3.261914
18	6	0	-4.864583	4.803765	2.686867
19	1	0	-4.257005	5.704657	2.535113
20	1	0	-5.900281	5.070261	2.429053
21	1	0	-4.851489	4.567048	3.757677
22	6	0	-3.776006	-1.237474	-0.625035
23	6	0	-3.315360	-2.505420	-0.182973
24	6	0	-5.118513	-1.200343	-1.110538
25	6	0	-4.147944	-3.637318	-0.217844
26	6	0	-1.919298	-2.747767	0.364283
27	6	0	-5.921719	-2.346852	-1.125195
28	6	0	-5.757811	0.070382	-1.641672
29	6	0	-5.457125	-3.586883	-0.685419
30	1	0	-3.752236	-4.589315	0.137381
31	1	0	-1.820408	-3.785511	0.705336
32	1	0	-1.143227	-2.568700	-0.386074
33	1	0	-1.680716	-2.098167	1.212582

34	1	0	-6.944696	-2.265757	-1.494974
35	1	0	-5.672119	0.896667	-0.929555
36	1	0	-5.261942	0.402215	-2.556959
37	1	0	-6.822017	-0.092345	-1.852483
38	6	0	-6.331076	-4.819574	-0.735545
39	1	0	-6.418676	-5.219047	-1.756526
40	1	0	-5.926237	-5.622124	-0.107679
41	1	0	-7.351309	-4.607310	-0.390337
42	5	0	-2.897341	0.184106	-0.724121
43	6	0	-1.262986	0.090327	-0.484631
44	6	0	-0.422216	-0.186774	-1.583733
45	6	0	-0.605470	0.362316	0.731832
46	1	0	-0.886900	-0.373862	-2.547753
47	6	0	0.963880	-0.226318	-1.477927
48	6	0	0.778066	0.305244	0.867537
49	1	0	-1.198033	0.647719	1.598115
50	1	0	1.570297	-0.481608	-2.343293
51	6	0	1.598826	0.006669	-0.239748
52	1	0	1.242176	0.546020	1.820574
53	6	0	3.062063	-0.050346	-0.111419
54	6	0	3.892461	0.618927	-1.038687
55	6	0	3.662653	-0.779083	0.940424
56	7	0	5.284193	0.547936	-0.959961
57	6	0	3.563851	1.477266	-2.114864
58	7	0	5.048437	-0.826731	1.101939
59	6	0	3.083130	-1.598521	1.937848
60	5	0	6.096742	-0.179748	0.150741
61	6	0	5.808253	1.309843	-1.947696
62	1	0	2.560930	1.753408	-2.405674
63	6	0	4.761129	1.895210	-2.686490
64	6	0	5.328965	-1.623591	2.159078
65	1	0	2.025488	-1.786756	2.049644
66	6	0	4.124849	-2.112161	2.703338
67	9	0	6.909195	-1.167685	-0.412548
68	9	0	6.882877	0.740355	0.849473
69	6	0	7.283075	1.464513	-2.140547
70	1	0	4.889953	2.557424	-3.532867
71	6	0	6.730036	-1.906004	2.598928
72	1	0	4.050180	-2.776709	3.554402
73	1	0	7.739594	1.944520	-1.267893
74	1	0	7.763151	0.485931	-2.247428
75	1	0	7.491159	2.066674	-3.029597
76	1	0	7.284056	-2.431557	1.813227
77	1	0	7.270659	-0.973766	2.794684
78	1	0	6.729251	-2.517859	3.505568

Table S6. Computed Structure of **3**+F^-.

3+F^-.-1893.12358318.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	9	0	-3.101799	0.275389	-2.136379
2	6	0	-3.481713	1.468008	0.096612
3	6	0	-3.270581	2.742112	-0.509136
4	6	0	-4.033962	1.488548	1.406430
5	6	0	-3.635027	3.926489	0.144991
6	6	0	-2.625743	2.908857	-1.874887
7	6	0	-4.381754	2.695695	2.033980
8	6	0	-4.284406	0.228793	2.218751
9	6	0	-4.206052	3.931641	1.417440
10	1	0	-3.455122	4.878490	-0.356277
11	1	0	-2.408148	3.968178	-2.062347
12	1	0	-1.690772	2.346567	-1.952823
13	1	0	-3.267428	2.537217	-2.677737
14	1	0	-4.800345	2.662455	3.040546
15	1	0	-5.121671	-0.355977	1.824622
16	1	0	-3.420045	-0.441348	2.230502
17	1	0	-4.516462	0.488580	3.259315
18	6	0	-4.622932	5.219090	2.091529

19	1	0	-3.946000	6.044834	1.838848
20	1	0	-5.633633	5.531707	1.789880
21	1	0	-4.632075	5.115427	3.183371
22	6	0	-3.955508	-1.263327	-0.421794
23	6	0	-3.569978	-2.488950	0.180764
24	6	0	-5.294658	-1.211504	-0.915978
25	6	0	-4.464546	-3.568284	0.281912
26	6	0	-2.190524	-2.734293	0.765836
27	6	0	-6.161646	-2.303859	-0.793209
28	6	0	-5.862744	0.020132	-1.598249
29	6	0	-5.768204	-3.503715	-0.199131
30	1	0	-4.123355	-4.488693	0.756987
31	1	0	-2.149725	-3.720787	1.243887
32	1	0	-1.408041	-2.699514	0.001747
33	1	0	-1.914305	-1.989484	1.519117
34	1	0	-7.178654	-2.211907	-1.176815
35	1	0	-5.750961	0.914434	-0.977212
36	1	0	-5.334255	0.227575	-2.531555
37	1	0	-6.929616	-0.115948	-1.814596
38	6	0	-6.710163	-4.682299	-0.102264
39	1	0	-6.820902	-5.199597	-1.066593
40	1	0	-6.350562	-5.422380	0.622466
41	1	0	-7.716722	-4.372593	0.207747
42	5	0	-2.992834	0.077943	-0.694579
43	6	0	-1.360259	-0.067398	-0.439267
44	6	0	-0.536083	-0.515523	-1.491310
45	6	0	-0.687944	0.340024	0.728295
46	1	0	-1.010030	-0.802723	-2.426114
47	6	0	0.854633	-0.577172	-1.386232
48	6	0	0.702212	0.297404	0.851528
49	1	0	-1.267401	0.729817	1.562654
50	1	0	1.454083	-0.923001	-2.227005
51	6	0	1.495322	-0.163341	-0.209180
52	1	0	1.181509	0.636157	1.768402
53	6	0	2.983006	-0.163755	-0.103122
54	6	0	3.691084	1.036458	-0.302449
55	6	0	3.672536	-1.354102	0.197177
56	7	0	5.087374	1.072459	-0.181160
57	6	0	3.248831	2.350454	-0.667410
58	7	0	5.070585	-1.365379	0.296579
59	6	0	3.203848	-2.678946	0.472357
60	5	0	6.006108	-0.135667	0.143781
61	6	0	5.510710	2.325781	-0.440977
62	6	0	4.399222	3.133086	-0.742071
63	6	0	5.471272	-2.614446	0.608654
64	6	0	4.341655	-3.444374	0.720812
65	9	0	6.914426	-0.344942	-0.900156
66	9	0	6.703257	0.090918	1.335534
67	6	0	6.955128	2.710933	-0.403153
68	1	0	4.441000	4.185068	-0.996320
69	6	0	6.910494	-2.972605	0.798863
70	1	0	4.362347	-4.499307	0.965383
71	1	0	7.393155	2.468618	0.570898
72	1	0	7.524449	2.148801	-1.151509
73	1	0	7.070427	3.781581	-0.594334
74	1	0	7.493718	-2.709166	-0.089673
75	1	0	7.341000	-2.409830	1.634562
76	1	0	7.015674	-4.043281	0.995868
77	6	0	1.862854	2.848418	-0.951469
78	1	0	1.348612	2.229998	-1.693663
79	1	0	1.227651	2.841323	-0.059944
80	1	0	1.909505	3.875613	-1.328651
81	6	0	1.799248	-3.202396	0.511929
82	1	0	1.148815	-2.589318	1.142590
83	1	0	1.337257	-3.214059	-0.480901
84	1	0	1.796212	-4.226554	0.900306

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