Supporting Information

Dual Binding-sites Assisted Chromogenic & Fluorogenic Recognition and Discrimination of Fluoride and Cyanide by a Peripherally Borylated Metalloporphyrin: Overcoming Anion-interference in Organoboron Based Sensors

Chinna Ayya Swamy P, Sanjoy Mukherjee and Pakkirisamy Thilagar *

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India. Fax: 91-80-2360-1552; Tel; 91-80-2293-3353

E-mail: thilagar@ipc.iisc.ernet.in

TABLE OF CONTENTS

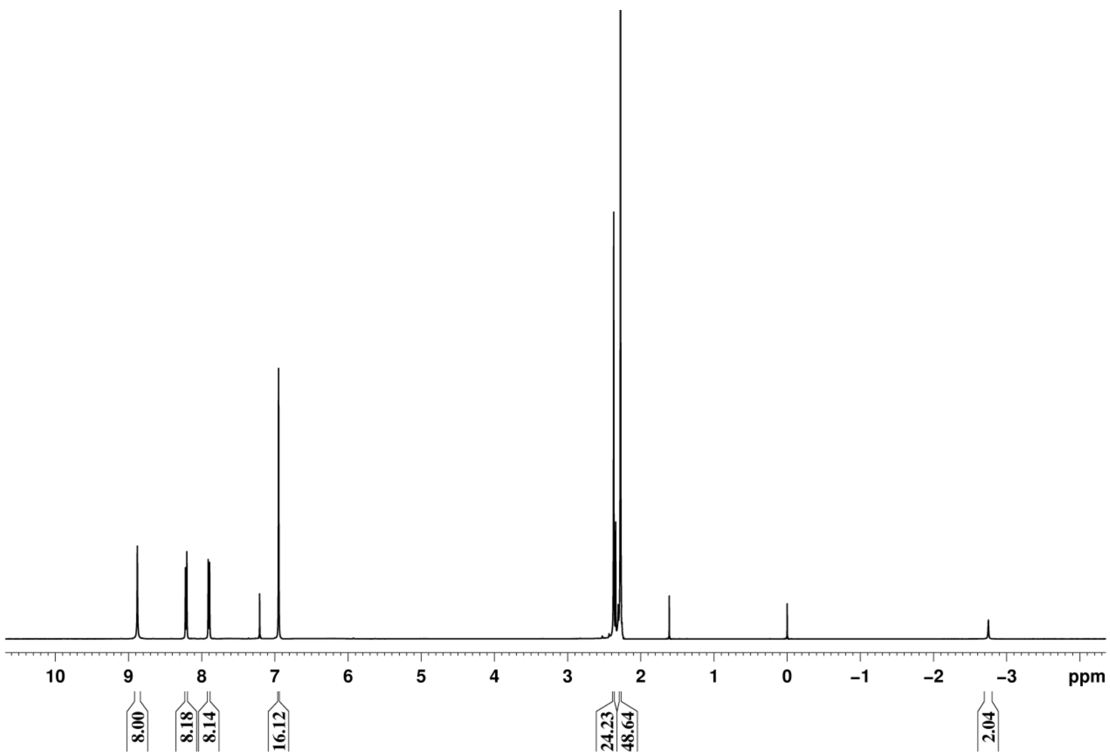


Figure S1: ^{1}H NMR of **2**

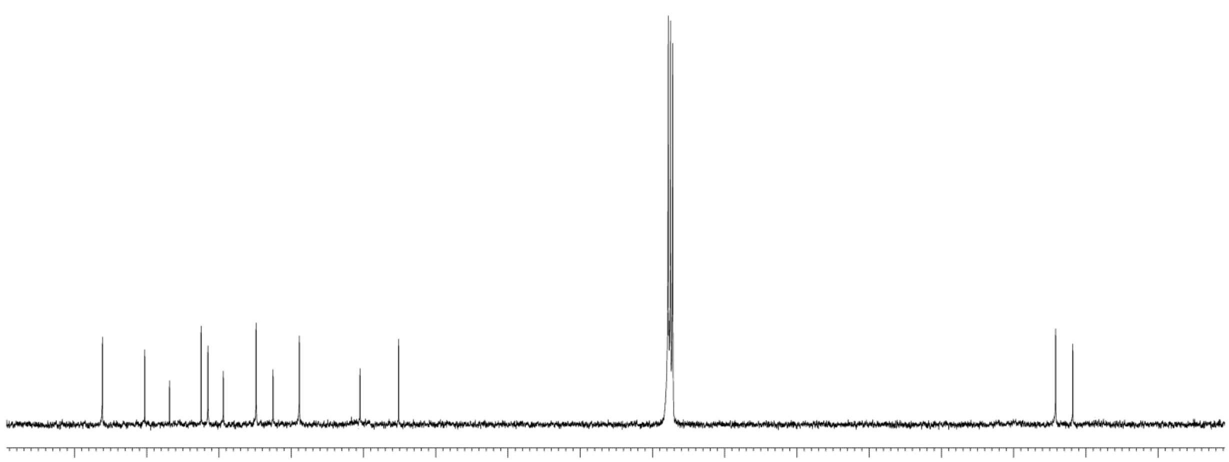


Figure S2: ^{13}C NMR of **2**

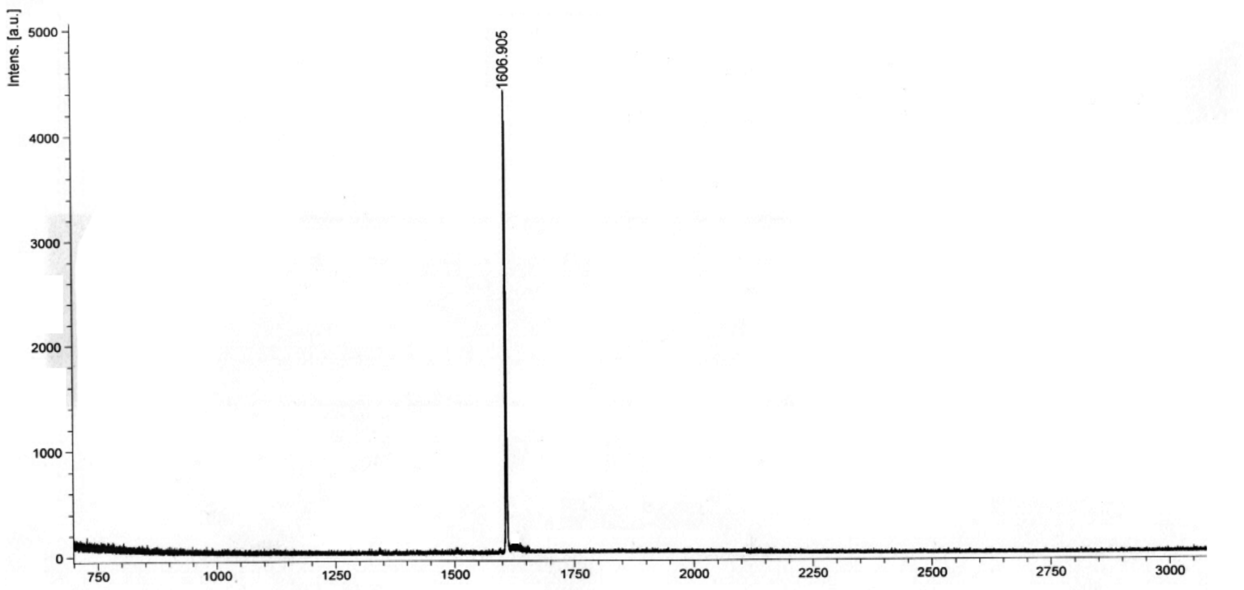


Figure S3: MALDI-TOF for **2**

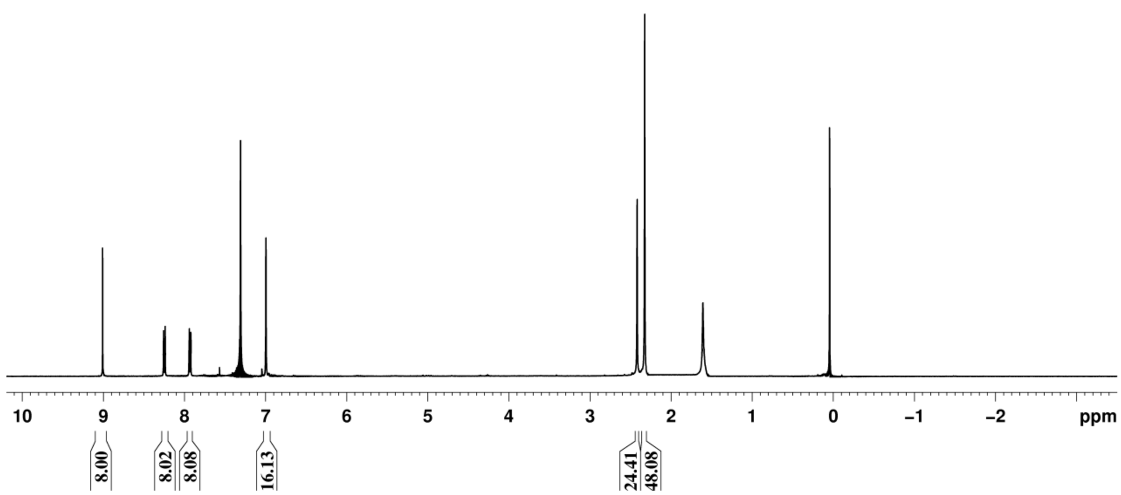


Figure S4: ^{1}H NMR of **3**

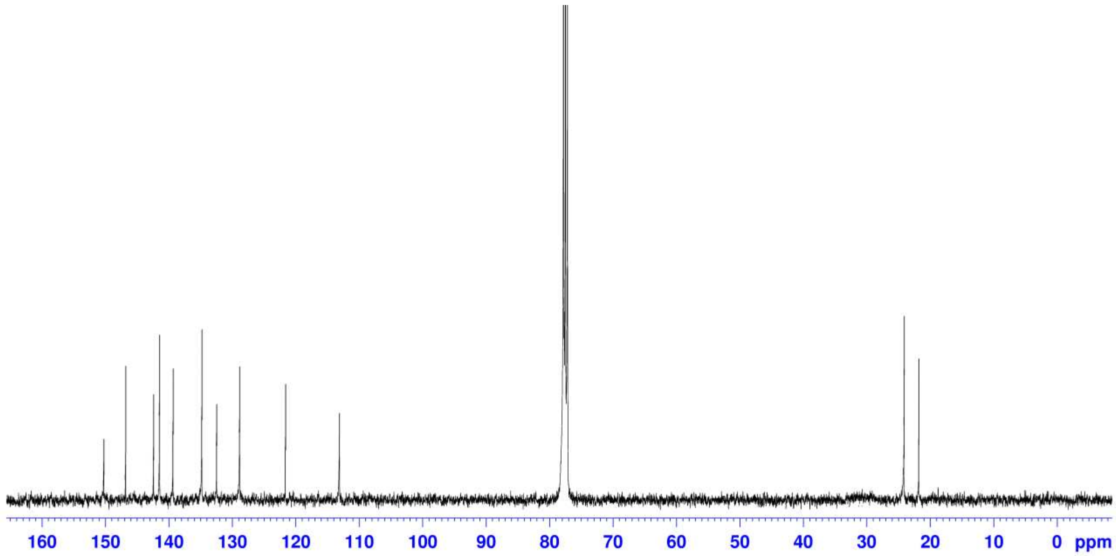


Figure S5: ^{13}C NMR of **3**

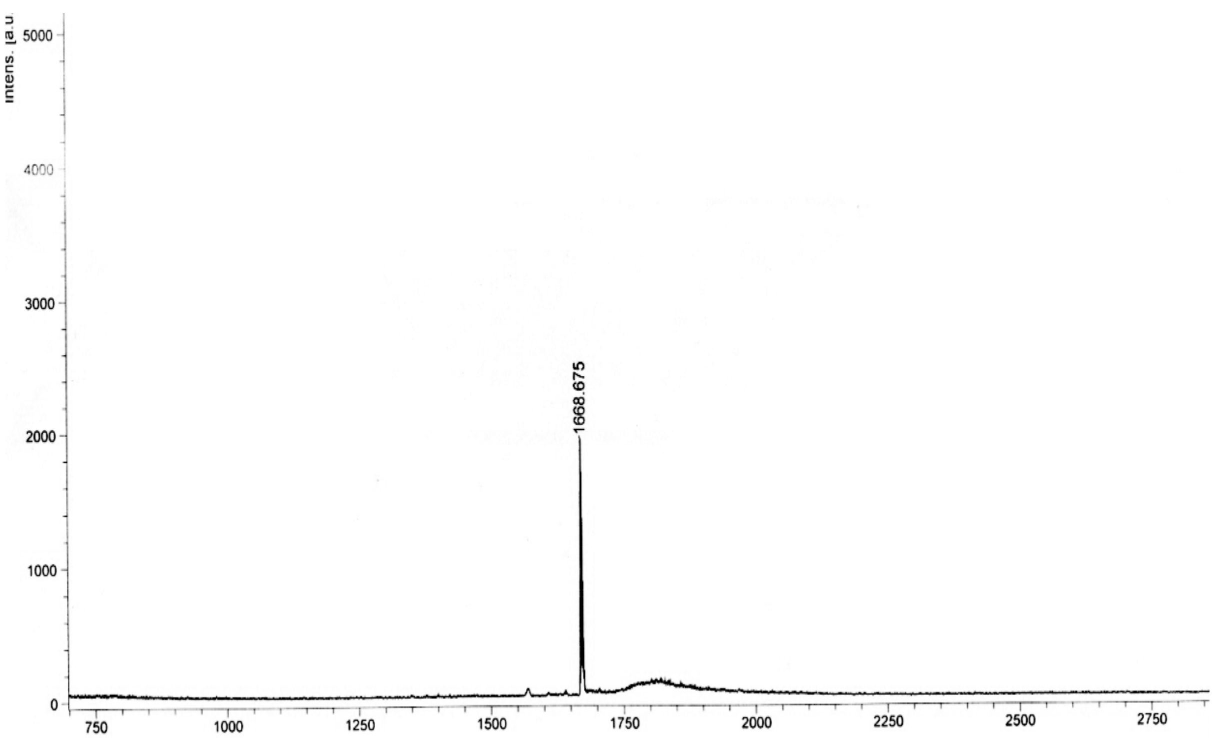


Figure S6: MALDI-TOF for **3**

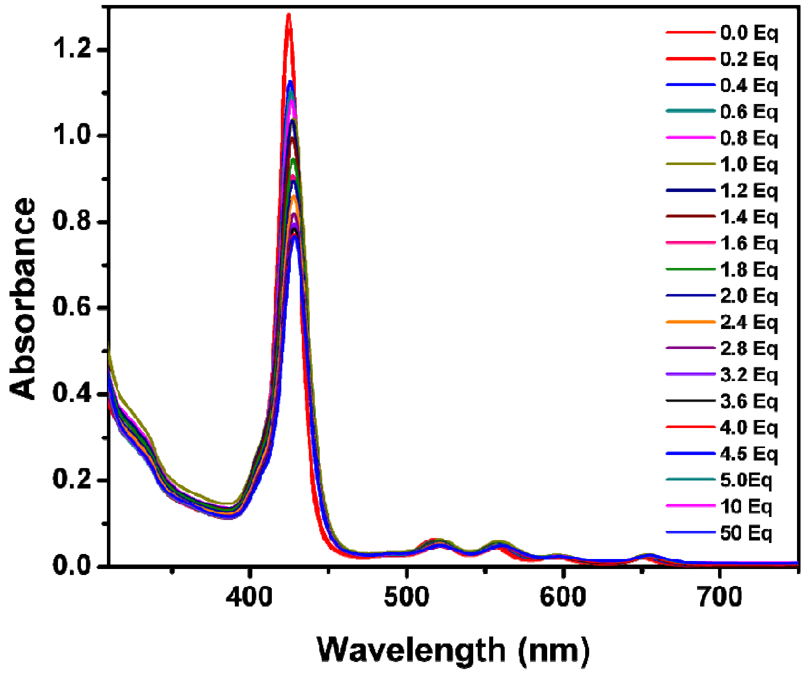


Figure S7: UV-Vis titration of **2** (1μM) in DCM upon addition of fluoride (as TBAF)

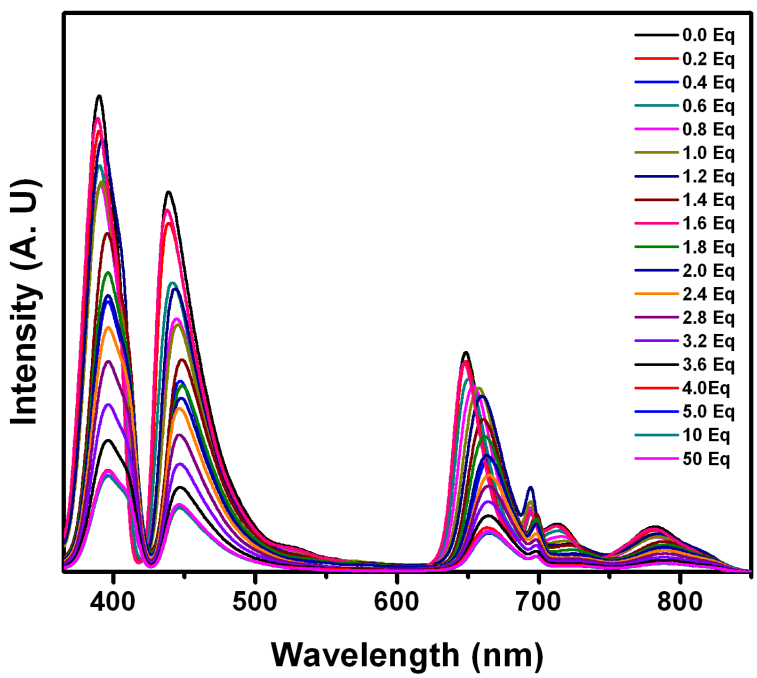


Figure S8: Fluorescence titration of **2** (λ_{ex} = 350 nm, 10μM solution) in DCM upon addition of fluoride (as TBAF)

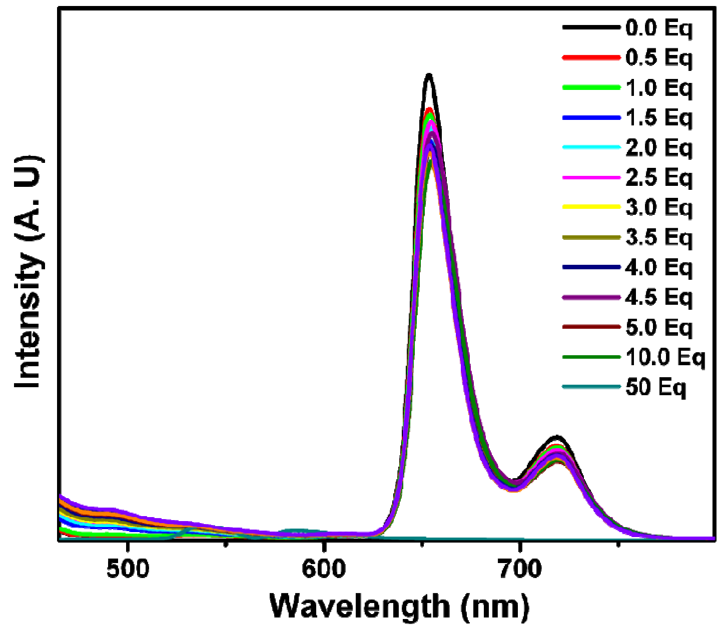


Figure S9: Fluorescence titration of **2** (λ_{ex} = 425 nm, 10μM solution) in DCM upon addition of fluoride (as TBAF)

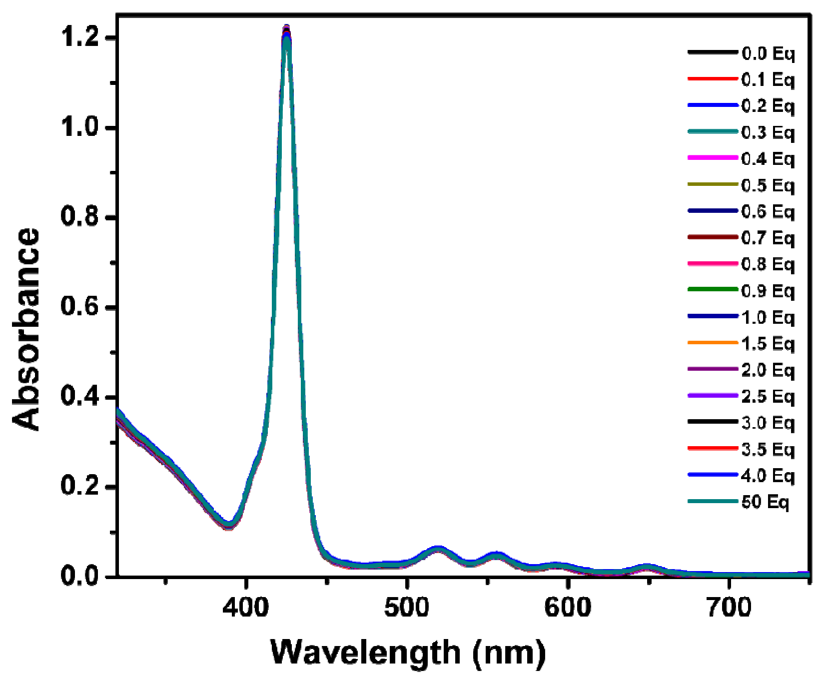


Figure S10: UV-Vis titration of **2** (1μM solution) in DCM upon addition of cyanide (as TBA-CN)

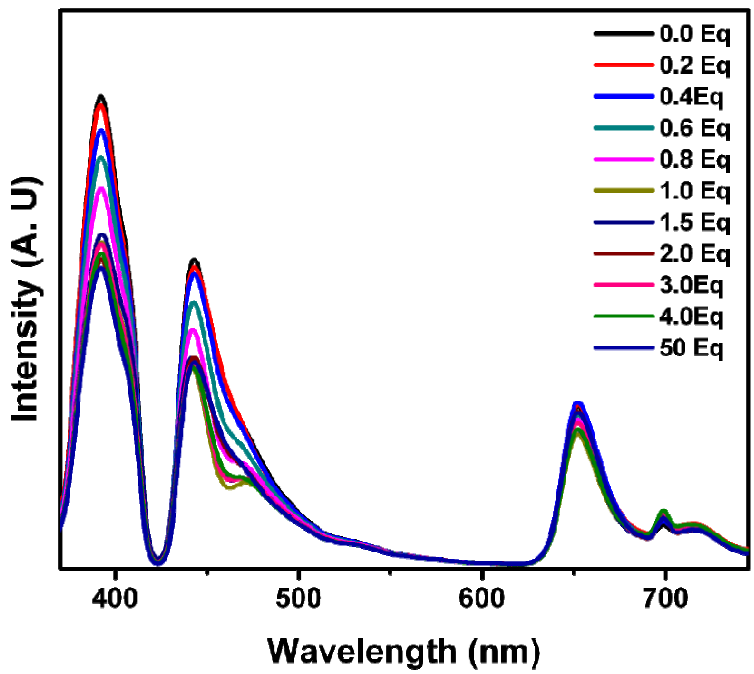


Figure S11: Fluorescence titration of **2** (λ_{ex} = 350 nm, 10μM solution) in DCM upon addition of cyanide (as TBA-CN)

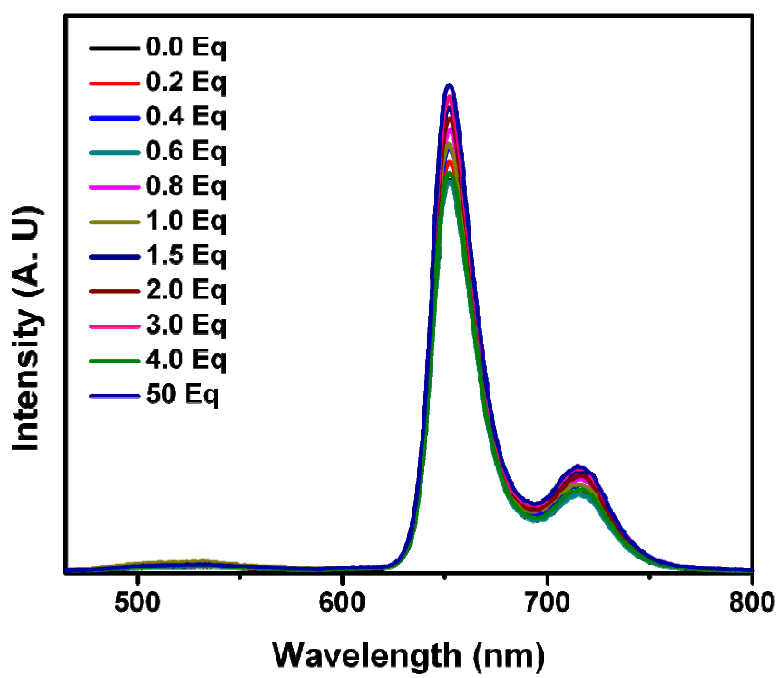


Figure S12: Fluorescence titration of **2** (λ_{ex} = 425 nm, 10μM solution) in DCM upon addition of cyanide (as TBA-CN)

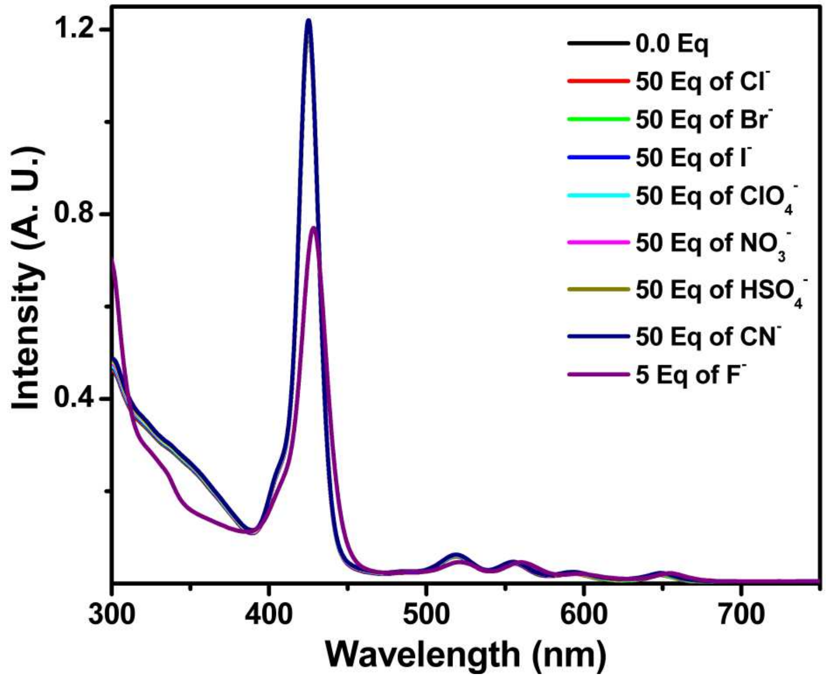


Figure S13: UV-Vis titration of **2** in presence of different anions (in DCM, 10μM solution)

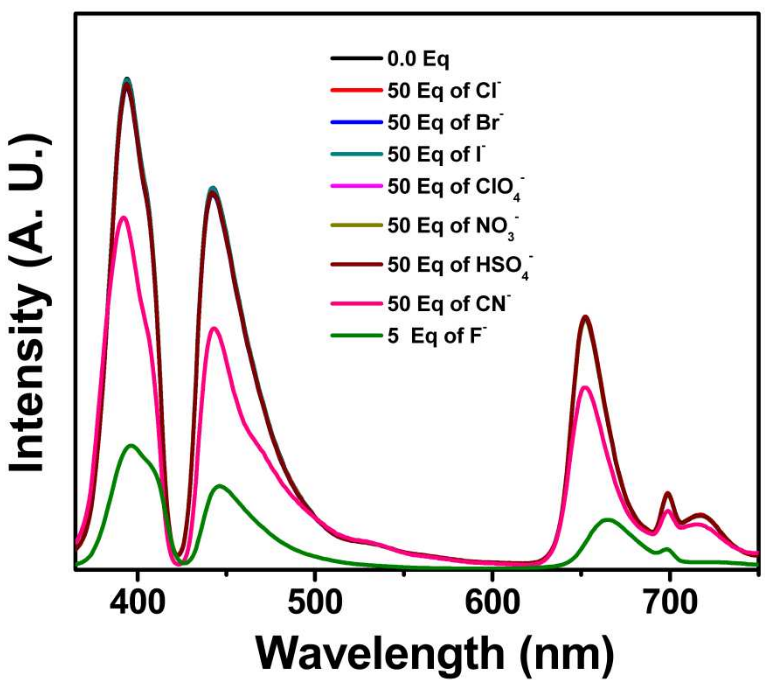


Figure S14: Fluorescence response of **2** in presence of different anions (in DCM, 10μM solution, $\lambda_{ex} = 350$ nm)

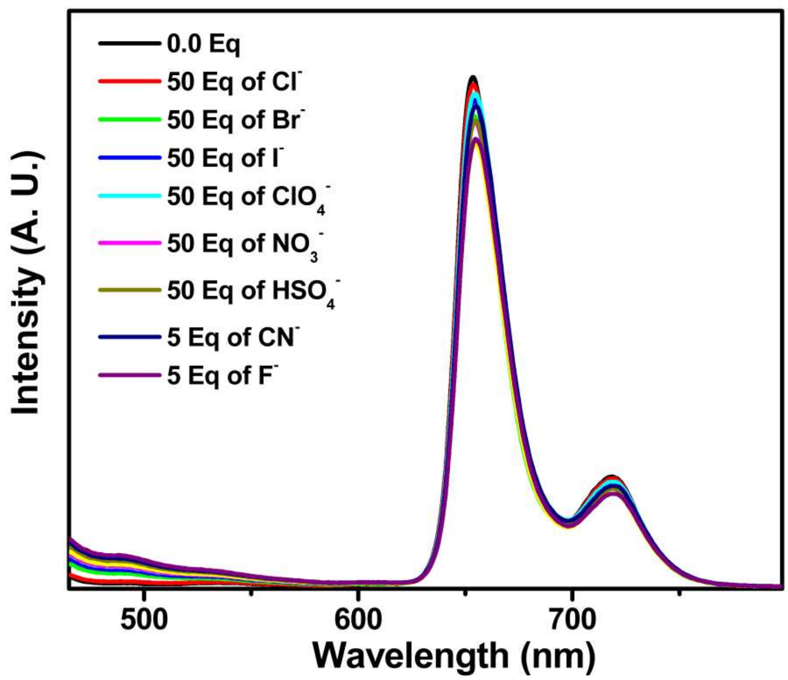


Figure S15: Fluorescence response of **2** in presence of different anions (in DCM, 10μM solution, $\lambda_{ex} = 425$ nm)

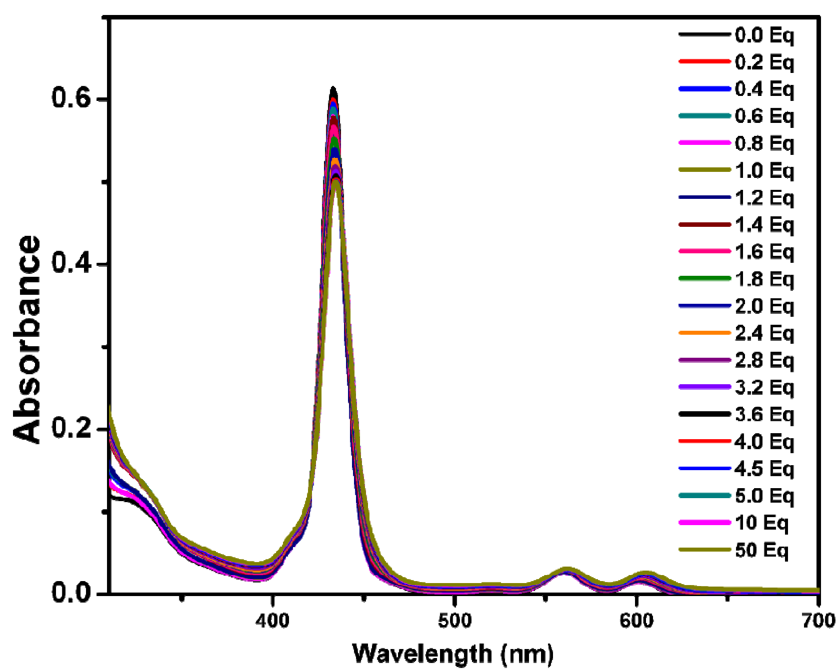


Figure S16: UV-Vis titration of **3** (1μM solution) in DCM upon addition of fluoride (as TBAF)

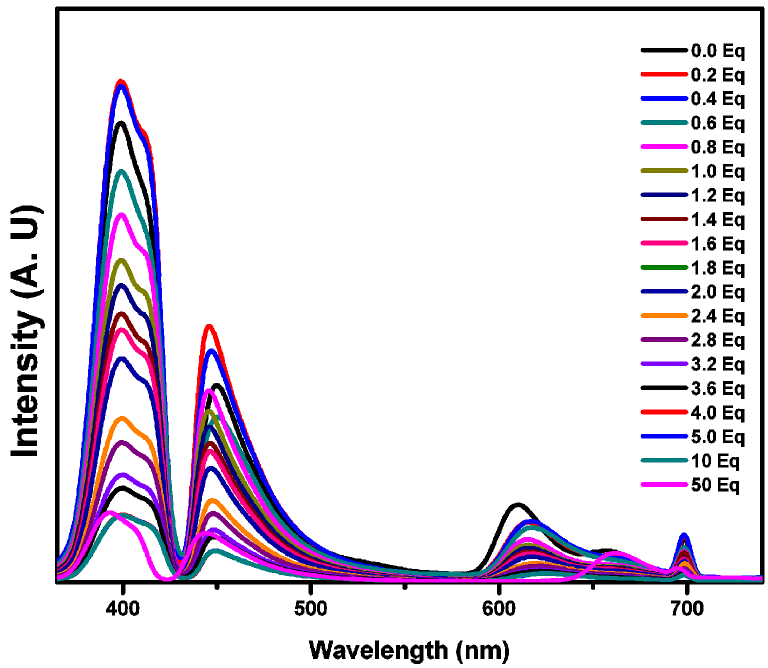


Figure S17: Fluorescence titration of **3** (λ_{ex} = 350 nm, 10μM solution) in DCM upon addition of fluoride (as TBAF)

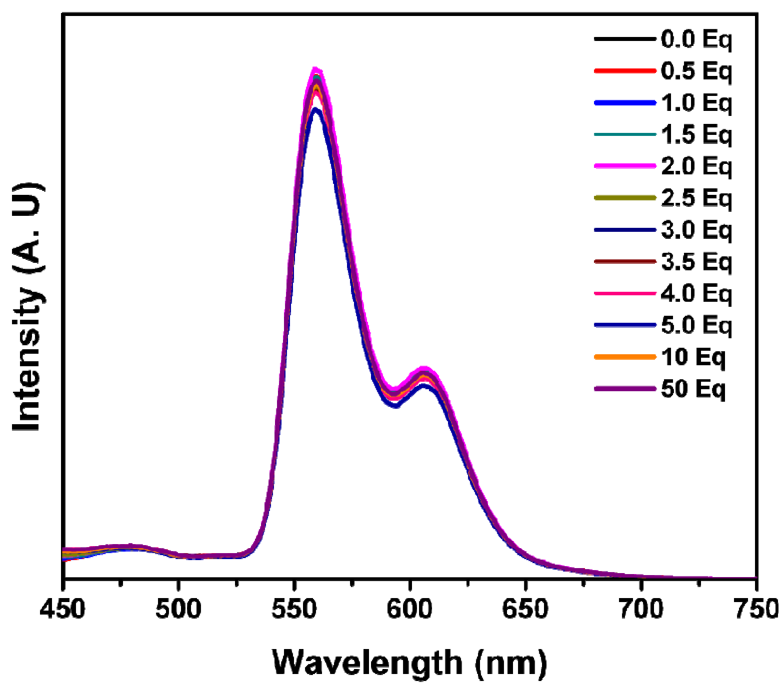


Figure S18: Fluorescence titration of **3** (λ_{ex} = 425 nm, 10μM solution) in DCM upon addition of fluoride (as TBAF)

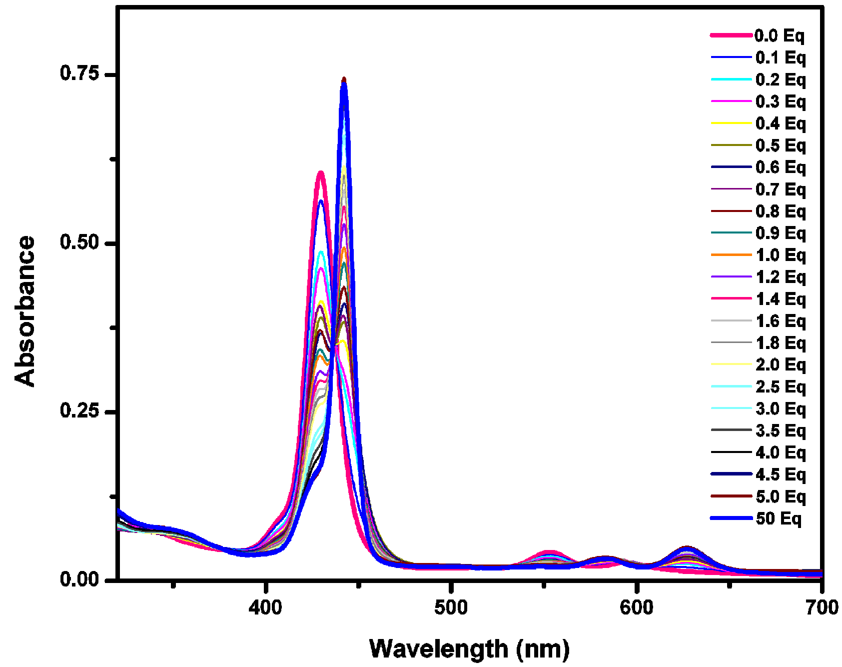


Figure S19: UV-Vis titration of **3**(1µM solution) in DCM upon addition of cyanide (as TBA-CN)

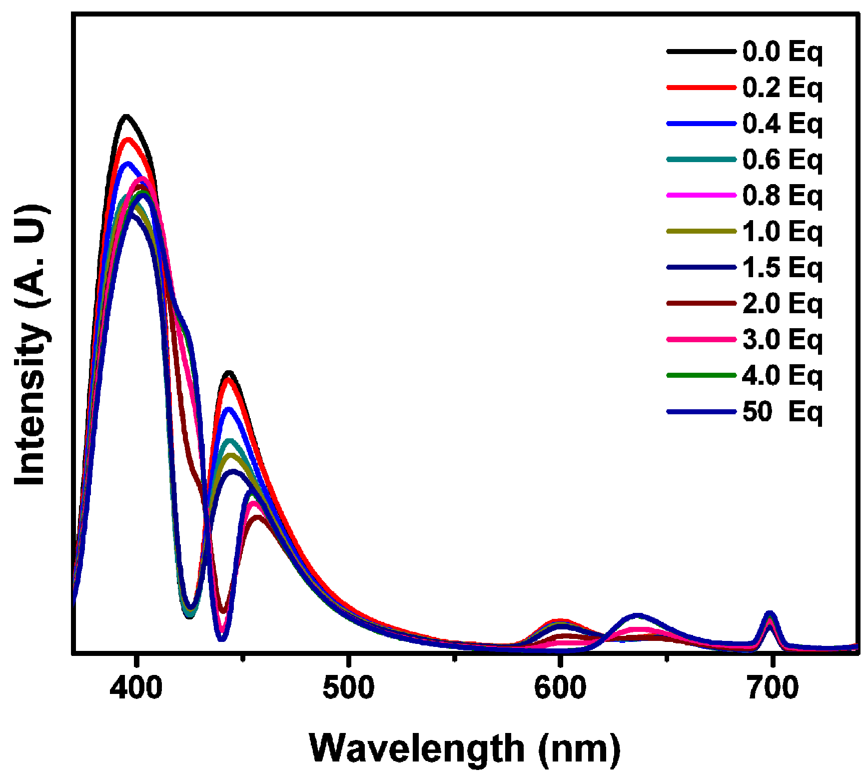


Figure S20: Fluorescence titration of **3** (λ_{ex} = 350 nm, 10µM solution) in DCM upon addition of cyanide (as TBA-CN)

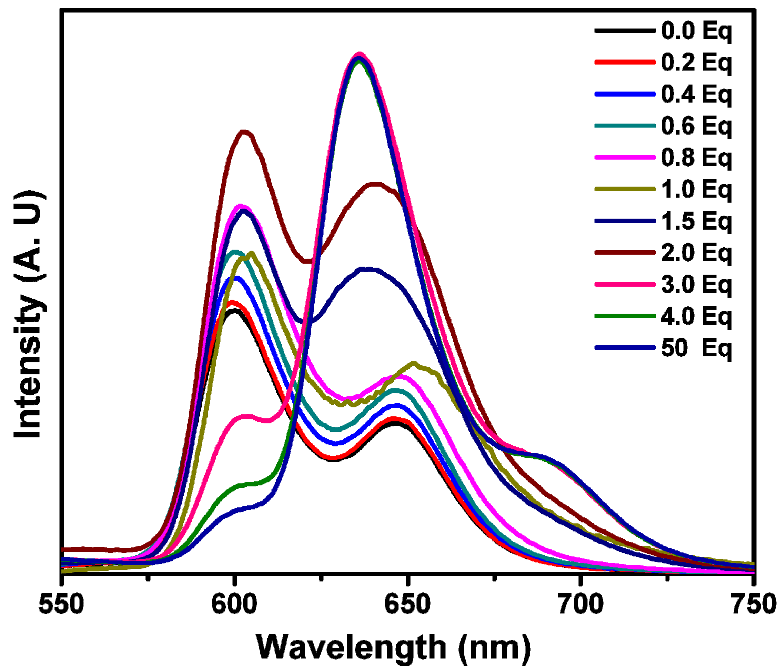


Figure S21: Fluorescence titration of **3** (λ_{ex} = 425 nm, 10μM solution) in DCM upon addition of cyanide (as TBA-CN)

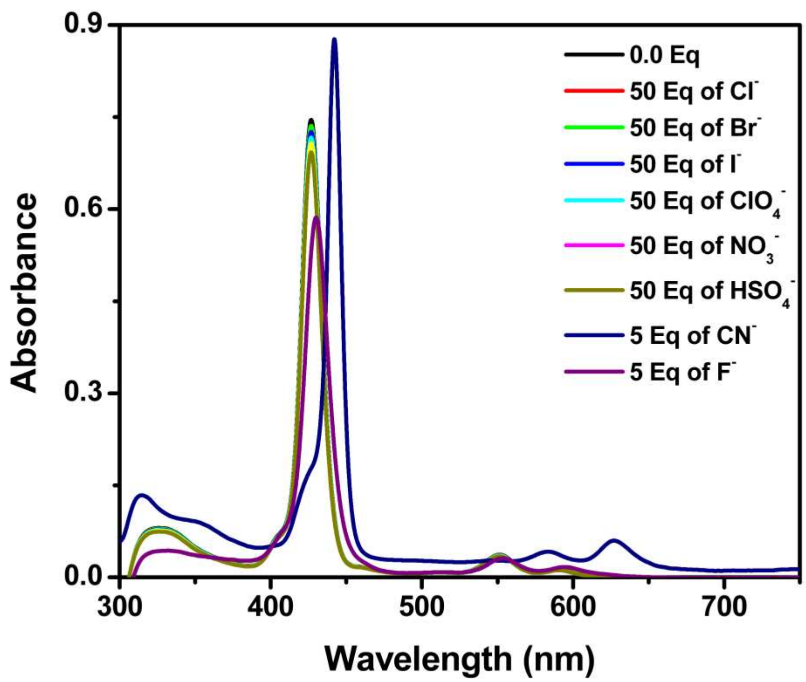


Figure S22: UV-Visible titration of **3** in presence of different anions (in DCM, 10μM solution)

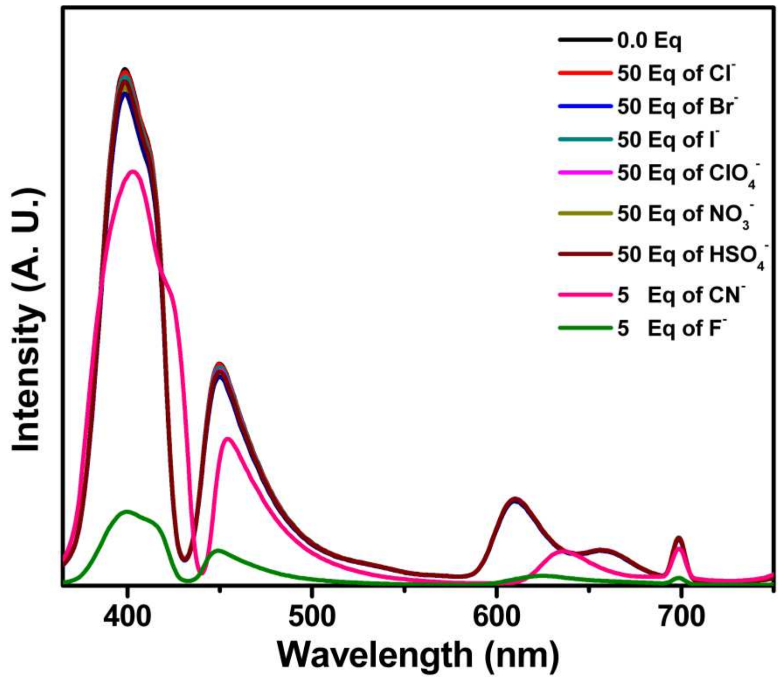


Figure S23: Fluorescence response of **3** in presence of different anions (in DCM, 10μM solution, $\lambda_{ex} = 350$ nm)

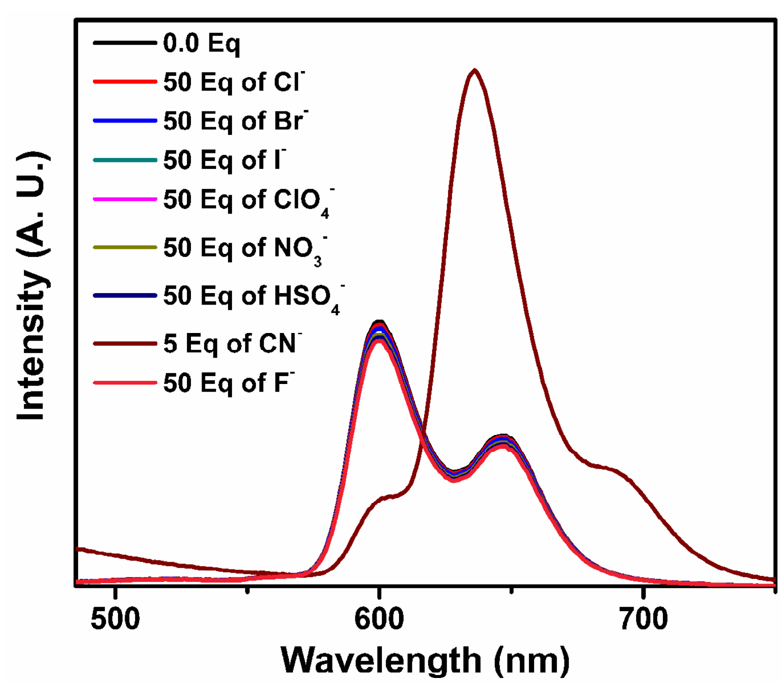


Figure S24: Fluorescence response of **3** in presence of different anions (in DCM, 10μM solution, $\lambda_{ex} = 425$ nm)

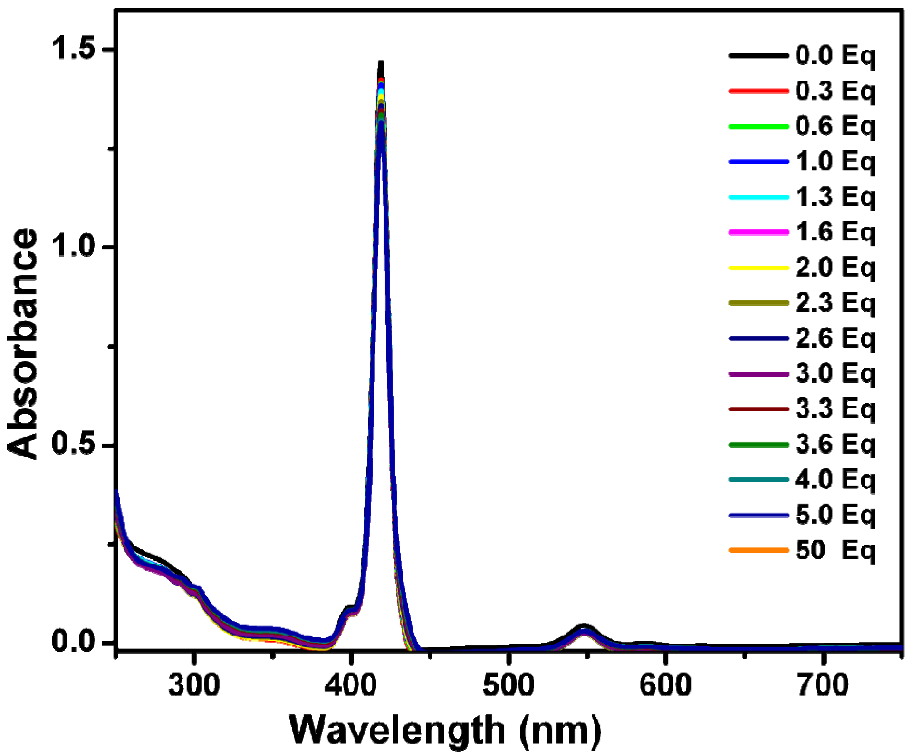


Figure S25: UV-Vis titration of **Zn-TPP** (1μM solution) in DCM upon addition of cyanide (as TBA-CN)

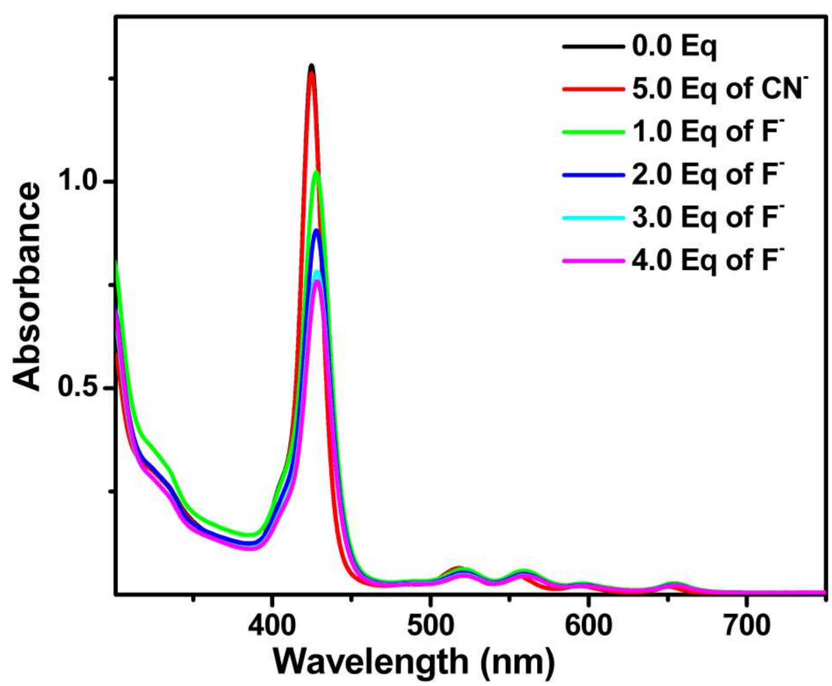


Figure S26: UV-Visible spectra of **2** (1 μM) with 5.0 Eq of CN^- (as TBACN) followed by 1.0, 2.0, 3.0 and 4.0 Eq of F^- (as TBAF)

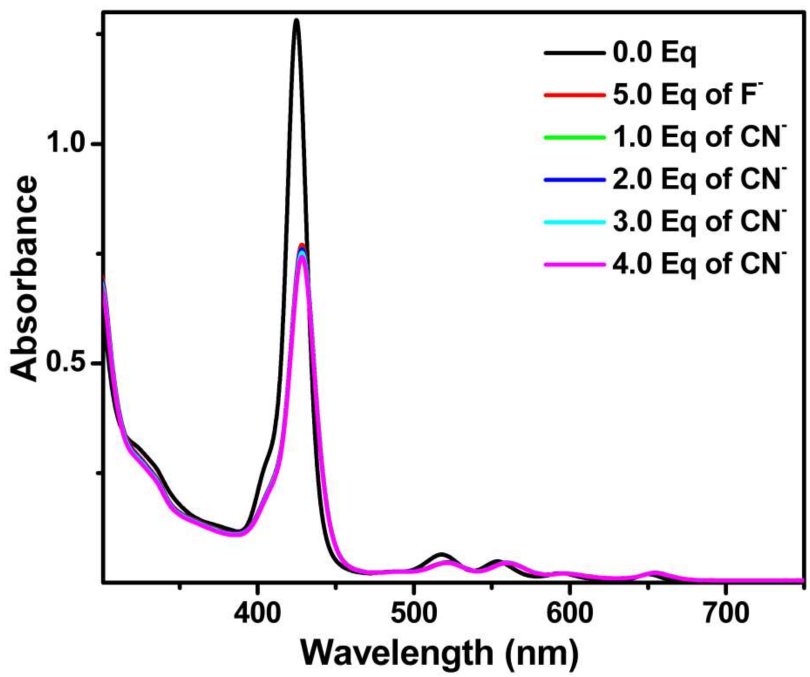


Figure S27: UV-Visible spectra of **2** (1μM) with 5.0 Eq of F^- (as TBAF) followed by 1.0, 2.0, 3.0 and 4.0 Eq of CN^- (as TBACN)

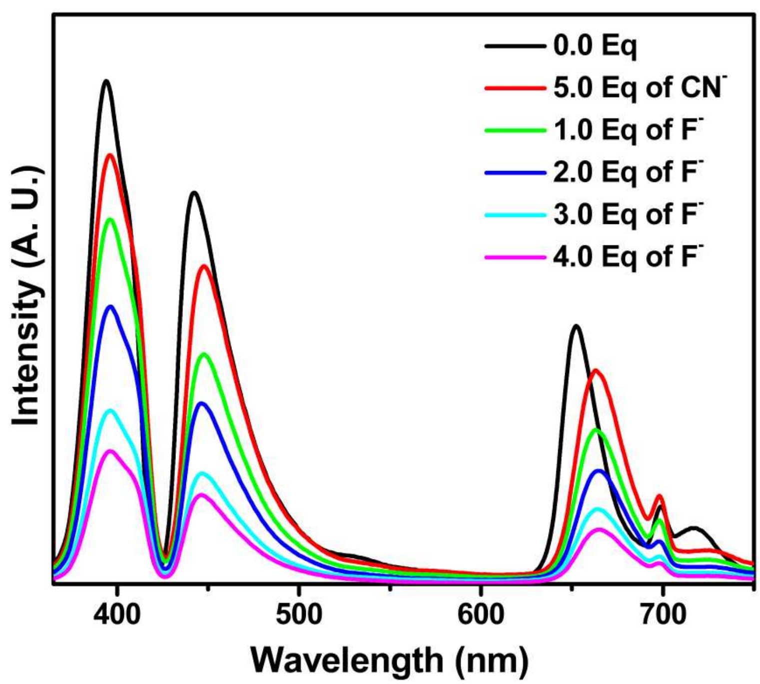


Figure S28: Fluorescence spectra of **2** (in DCM, 10 μM solution, λ_{Ex}= 350 nm) with 5.0 Eq of CN^- (as TBACN) followed by 1.0, 2.0, 3.0 and 4.0 Eq of F^- (as TBAF)

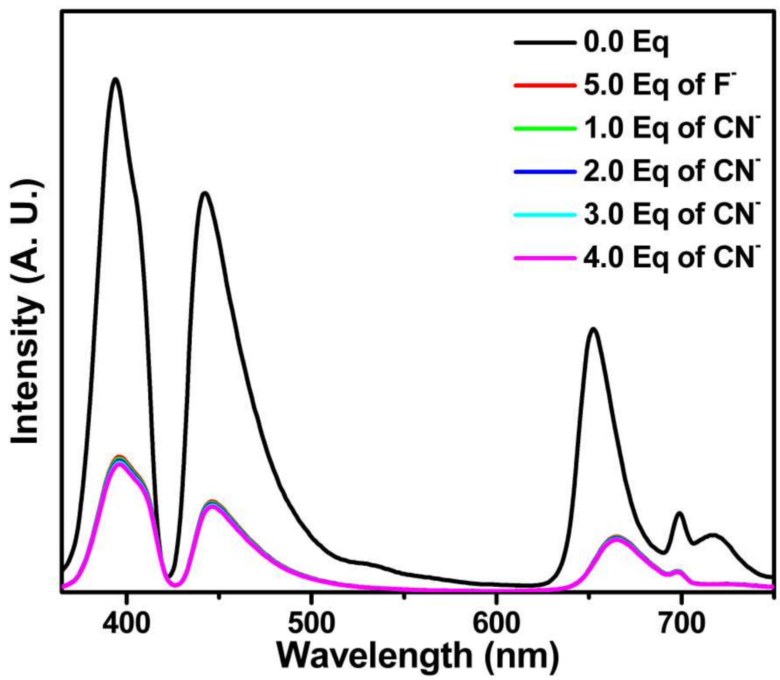


Figure S29: Fluorescence spectra of **2** (in DCM, 10 μM solution, λ_{Ex}= 350 nm) with 5.0 Eq of F^- (as TBAF) followed by 1.0, 2.0, 3.0 and 4.0 Eq of CN^- (as TBACN)

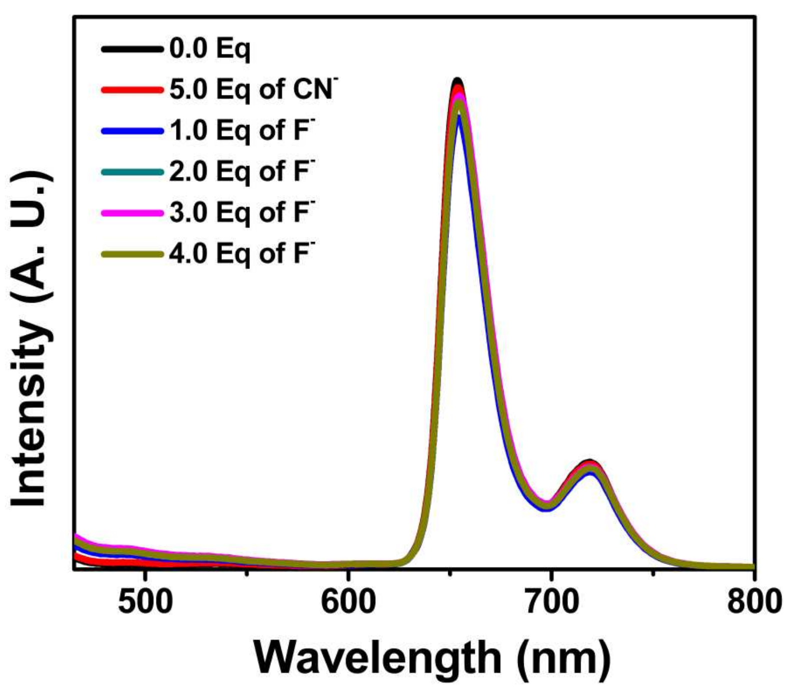


Figure S30: Fluorescence spectra of **2** (in DCM, 10 μM solution, λ_{Ex}= 425 nm) with 5.0 Eq of CN^- (as TBACN) followed by 1.0, 2.0, 3.0 and 4.0 Eq of F^- (as TBAF)

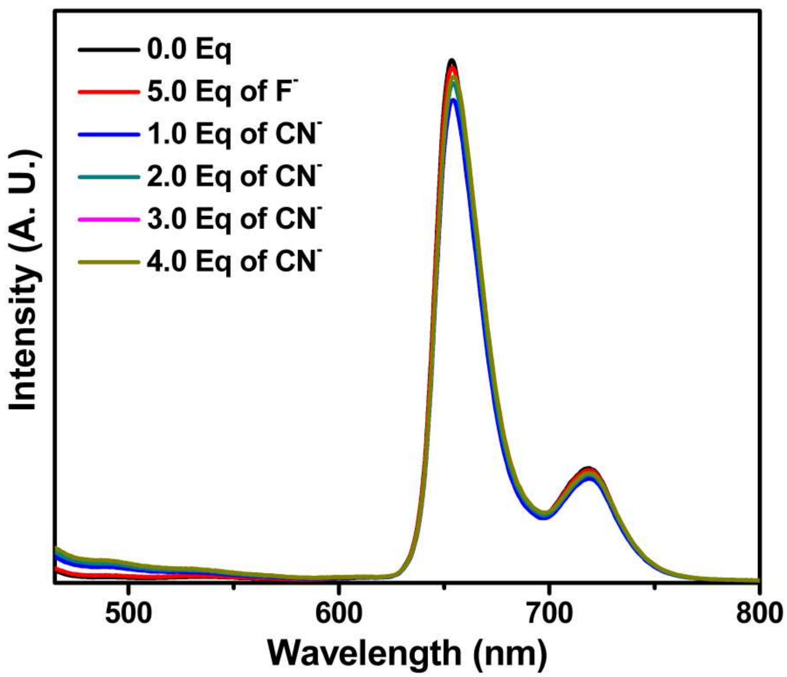


Figure S31: Fluorescence spectra of **2** (in DCM, 10 μM solution, λ_{Ex}= 425 nm) with 5.0 Eq of F^- (as TBAF) followed by 1.0, 2.0, 3.0 and 4.0 Eq of CN^- (as TBACN)

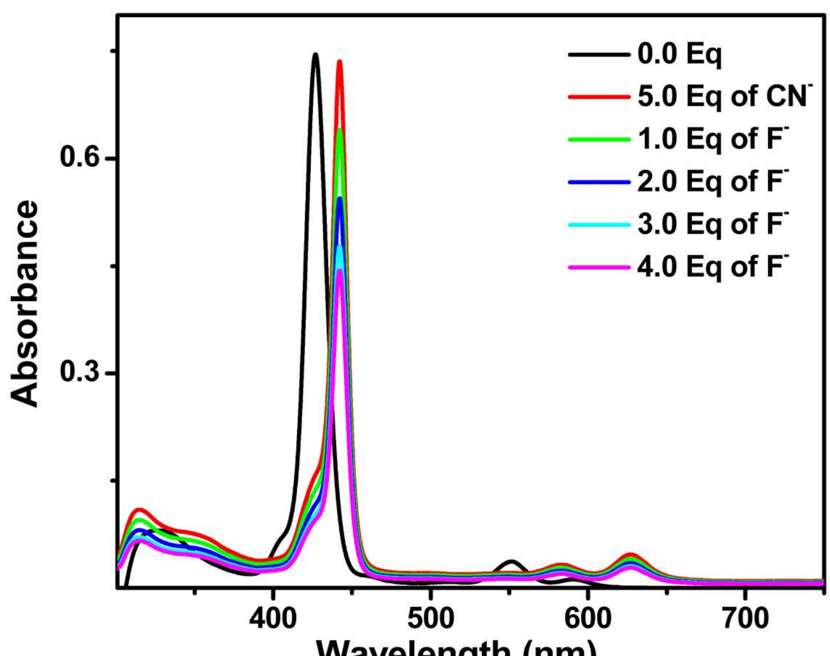


Figure S32: UV-Visible spectra of **3** (1 μM) with 5.0 Eq of CN^- (as TBACN) followed by 1.0, 2.0, 3.0 and 4.0 Eq of F^- (as TBAF)

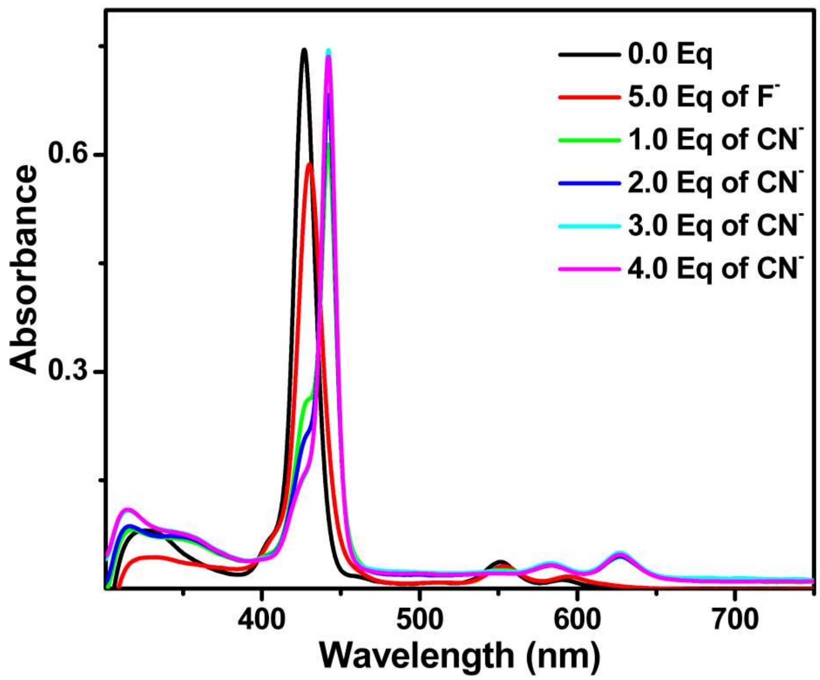


Figure S33: UV-Visible spectra of **3** (1 μM) with 5.0 Eq of F^- (as TBAF) followed by 1.0, 2.0, 3.0 and 4.0 Eq of CN^- (as TBACN)

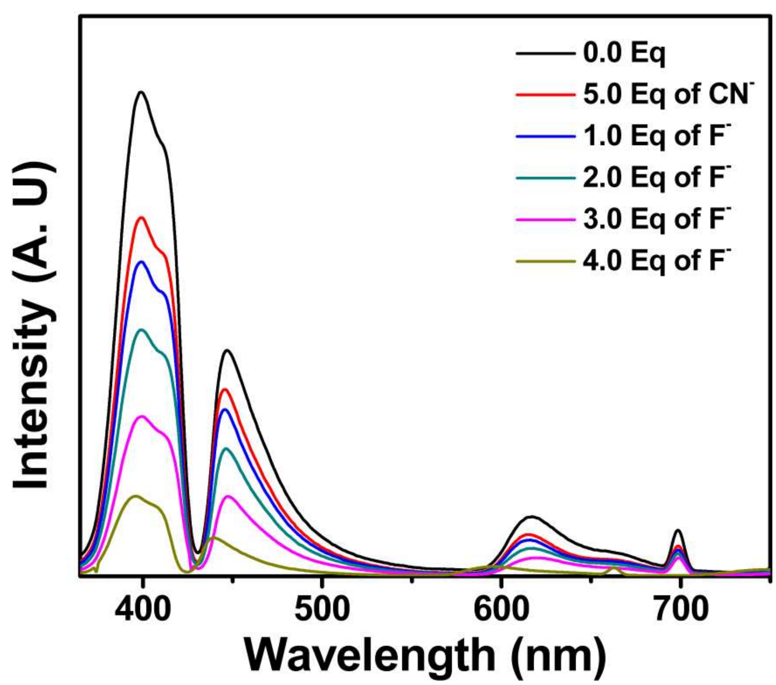


Figure S34: Fluorescence spectra of **3** (in DCM, 10 μM solution, λ_{Ex}= 350 nm) with 5.0 Eq of CN^- (as TBACN) followed by 1.0, 2.0, 3.0 and 4.0 Eq of F^- (as TBAF)

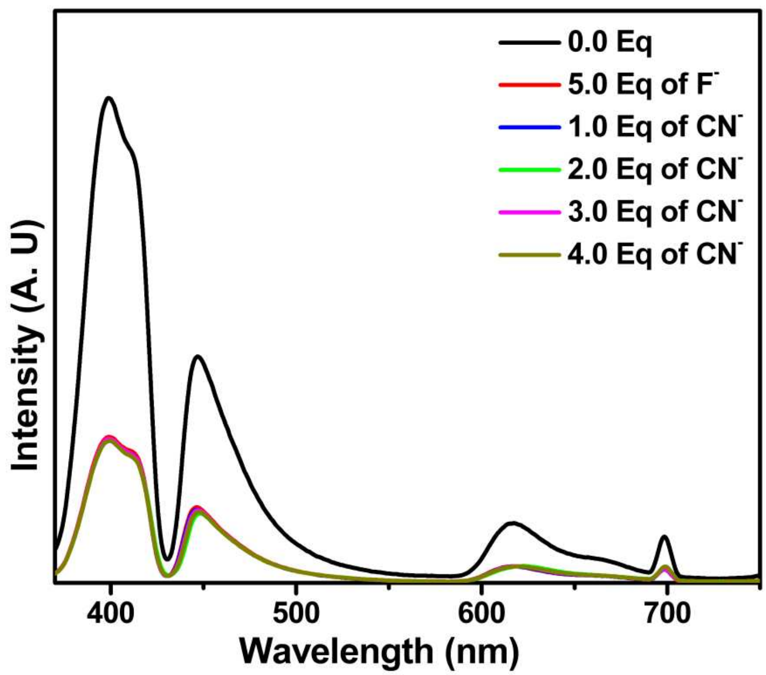


Figure S35: Fluorescence spectra of **3** (in DCM, 10 μM solution, λ_{Ex}= 350 nm) with 5.0 Eq of F^- (as TBAF) followed by 1.0, 2.0, 3.0 and 4.0 Eq of CN^- (as TBACN)

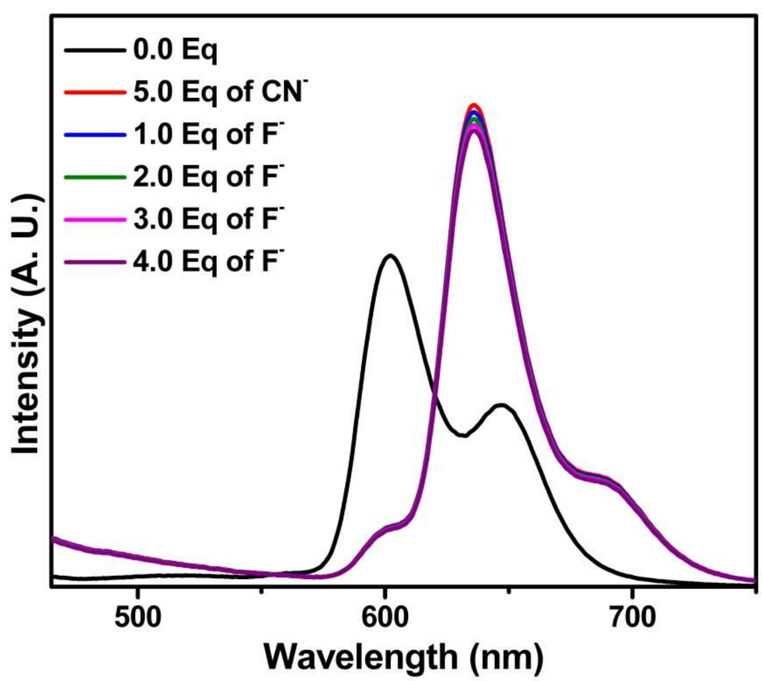


Figure S36: Fluorescence spectra of **3** (in DCM, 10 μM solution, λ_{Ex}= 425 nm) with 5.0 Eq of CN^- (as TBACN) followed by 1.0, 2.0, 3.0 and 4.0 Eq of F^- (as TBAF)

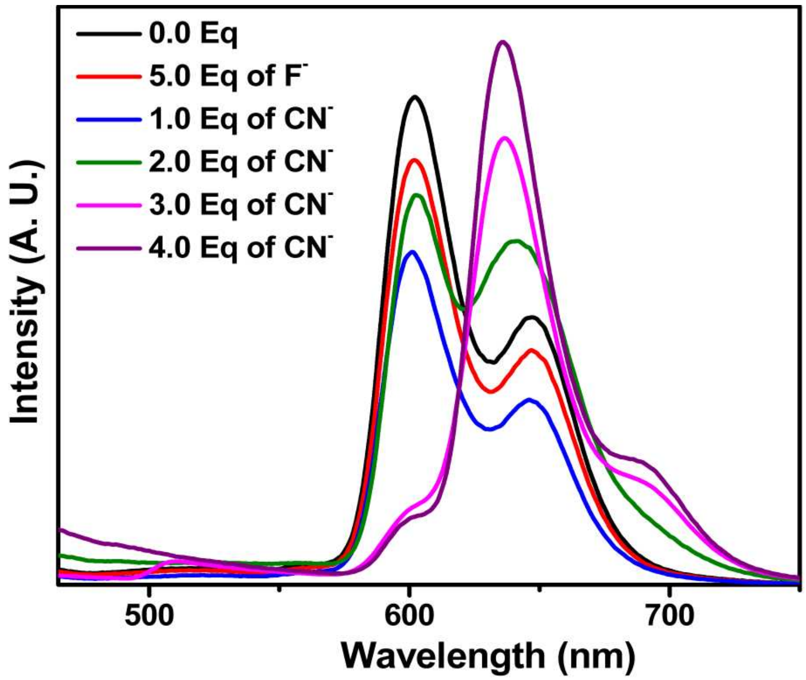


Figure S37: Fluorescence spectra of **3** (in DCM, 10 μM solution, λ_{Ex}= 425 nm) with 5.0 Eq of F^- (as TBAF) followed by 1.0, 2.0, 3.0 and 4.0 Eq of CN^- (as TBACN)

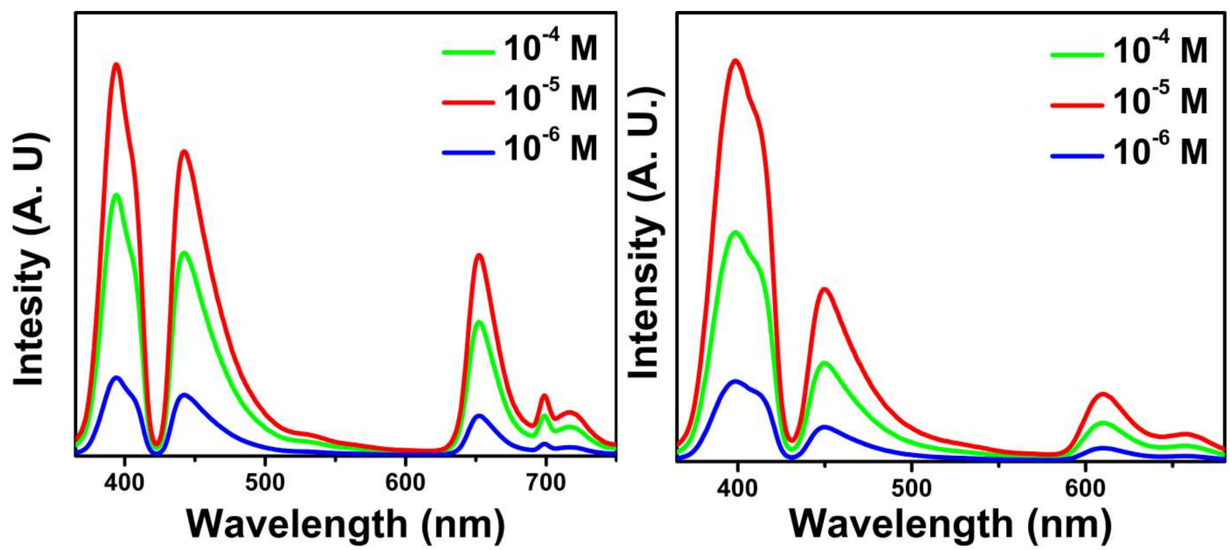


Figure S38: Emission spectra of **2** (left) and **3** (right) at different concentrations. (DCM solution, λ_{ex} = 350 nm)

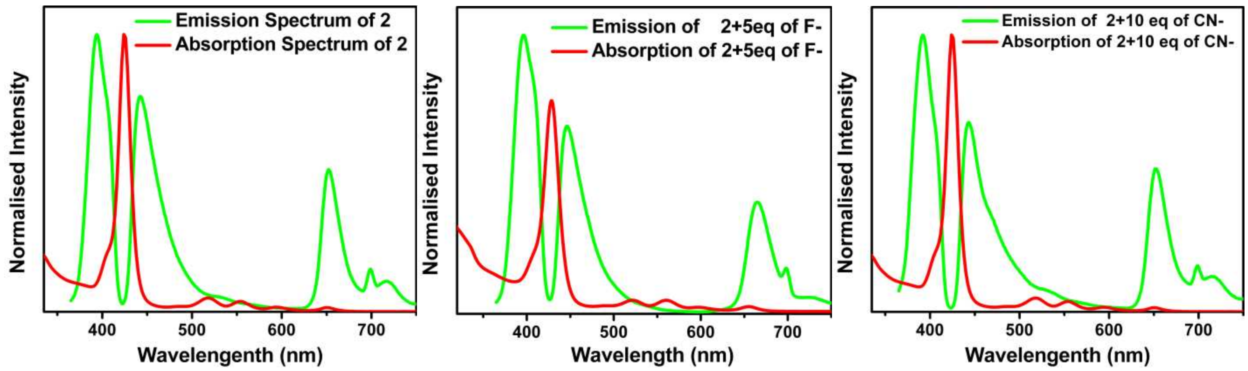


Figure S39: Comparison of UV-Vis absorption spectra and fluorescence emission spectra of **2** in free form (left) and upon addition of fluoride (middle) and cyanide (right) ions. (10 μM DCM solution, λ_{ex} = 350 nm)

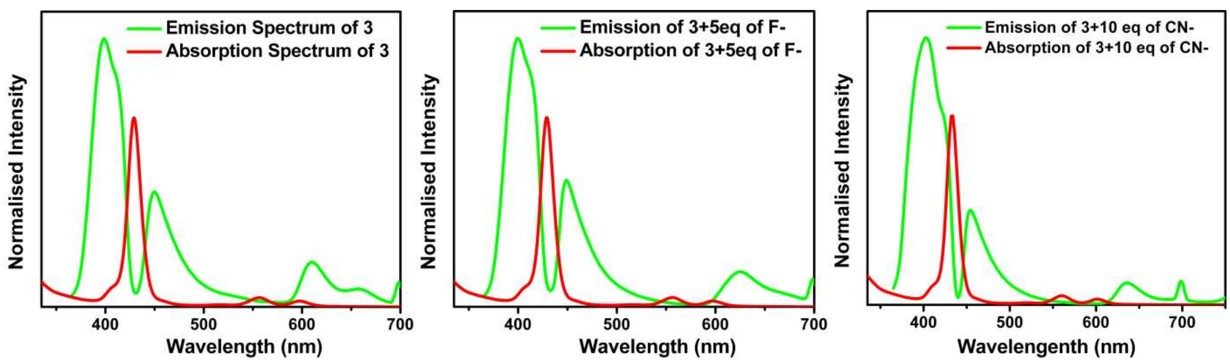


Figure S40: Comparison of UV-Vis absorption spectra and fluorescence emission spectra of **3** in free form (left) and upon addition of fluoride (middle) and cyanide (right) ions. (10 μM DCM solution, λ_{ex} = 350 nm)

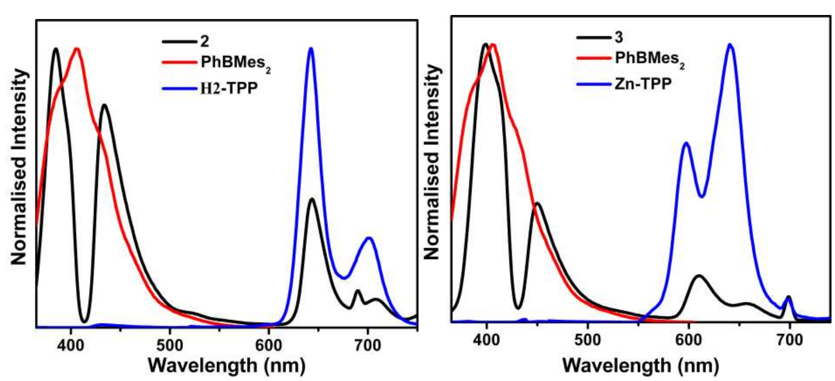


Figure S41: Comparison of emission spectra of **2** and **3** (10 μM DCM solution, λ_{ex} = 350 nm) compared to the model building units (i.e. **PhBMes$_2$**, **H2-TPP** and **Zn-TPP**)

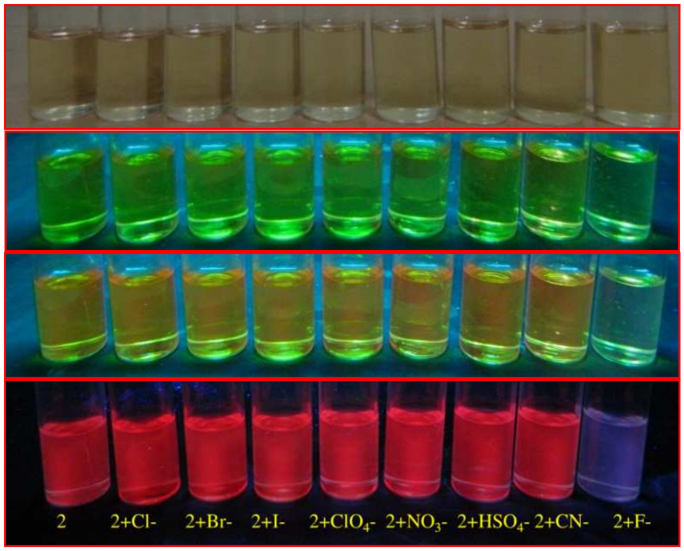


Figure S42: Photograph of **2** with different anions. From top to bottom: samples illuminated under Visible, Long wavelength UV, Both Long & Short wavelength UV and Short wavelength UV. Concentration: 10µM in DCM; Fluoride and Cyanide were added in 5eq amount. Other anions were used in greater than 10eq amount.

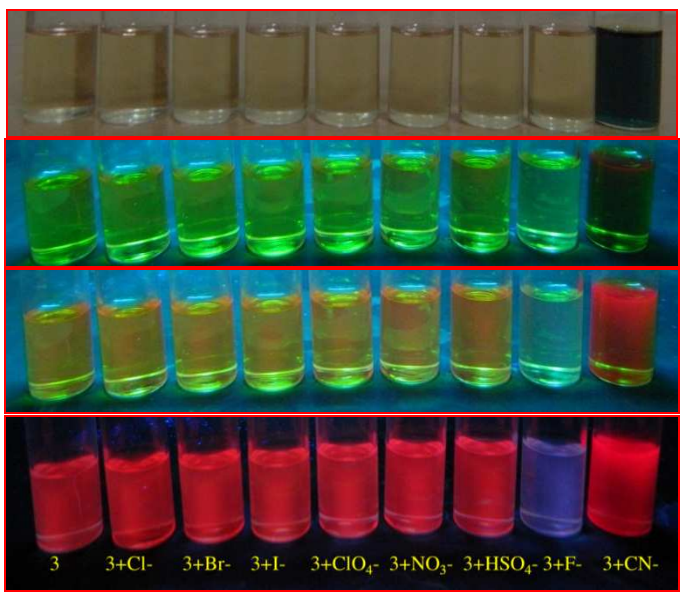
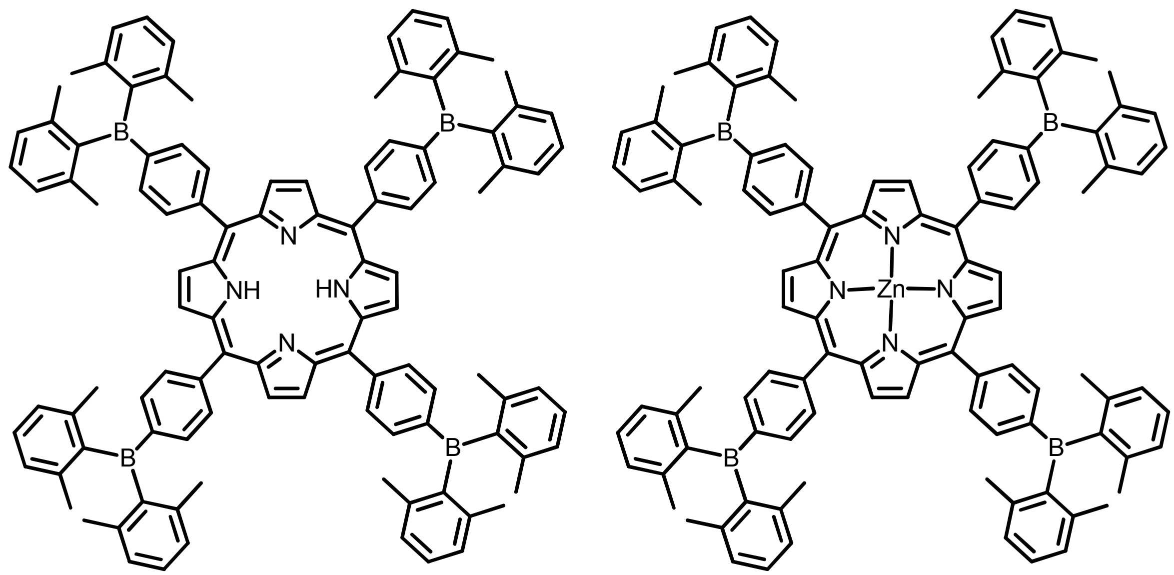


Figure S43: Photograph of **3** with different anions. From top to bottom: samples illuminated under Visible, Long wavelength UV, Both Long & Short wavelength UV and Short wavelength UV. Concentration: 10µM in DCM; Fluoride and Cyanide were added in 5eq amount. Other anions were used in greater than 10eq amount.



2m **3m**

Figure S44: Model compounds used for DFT computation

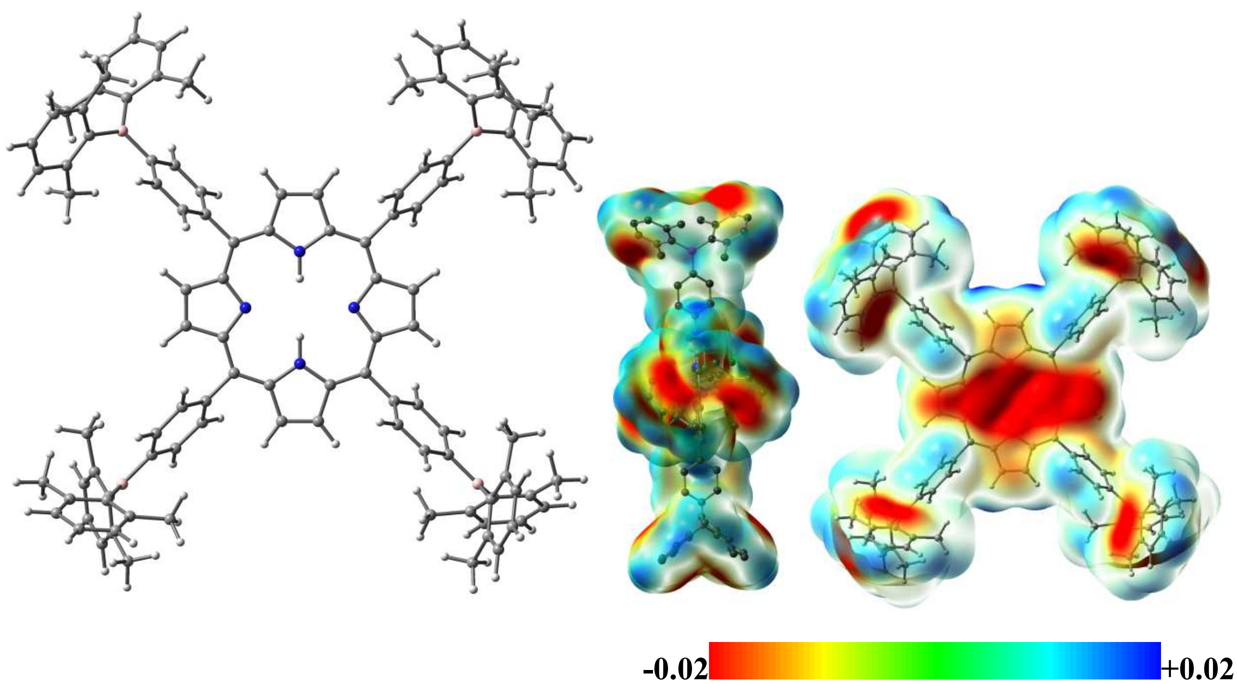


Figure S45: DFT B3LYP/lanl2dz optimised structure of **2m** and its ESP surface

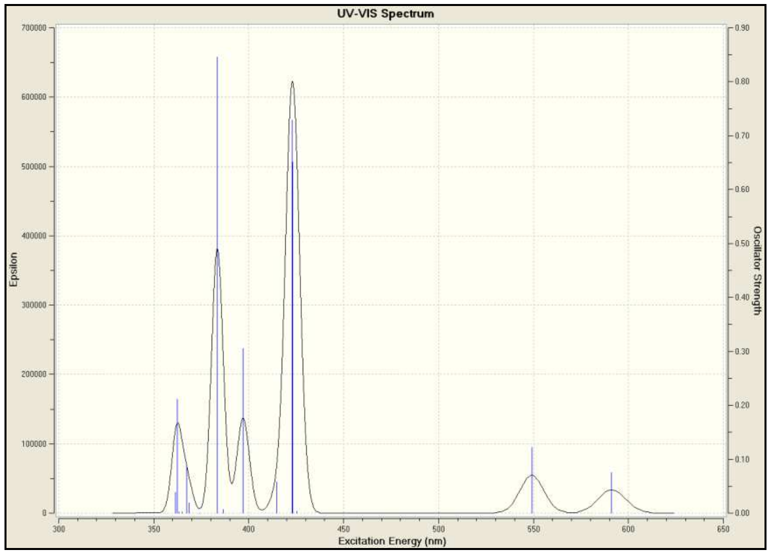
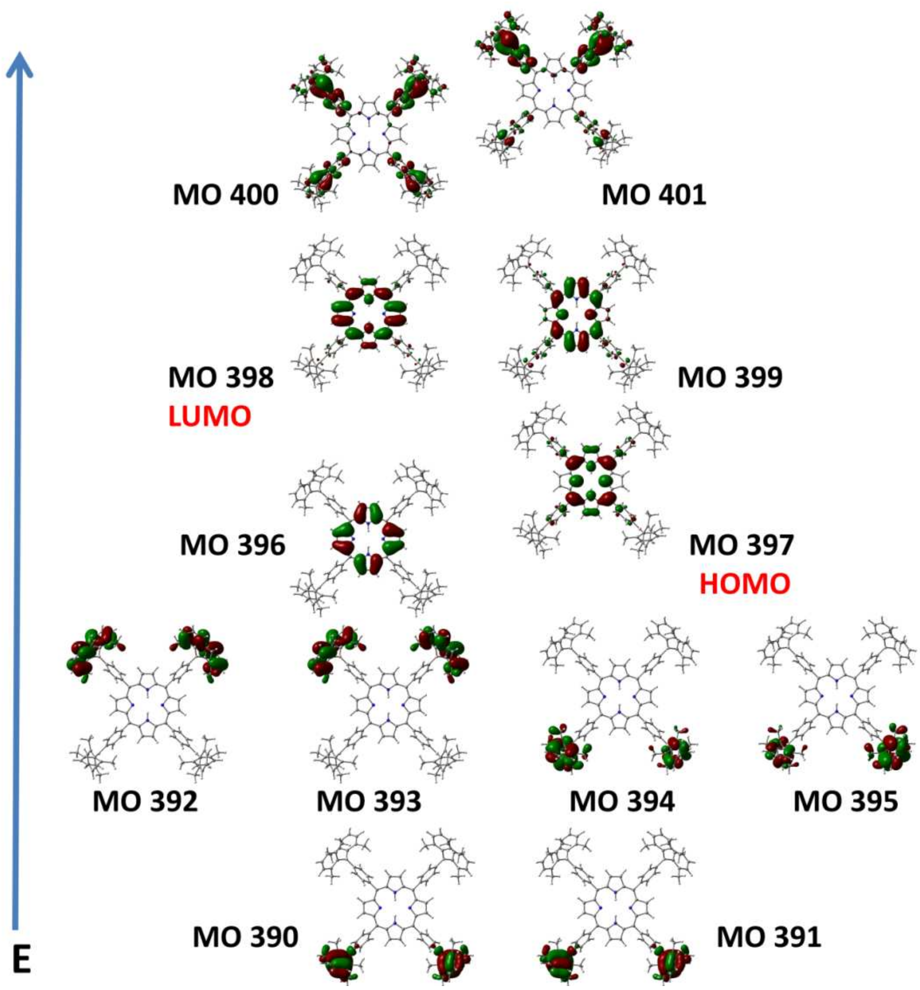


Figure S46: TD-SCF DFT Simulated UV-Vis Spectra of **2m**



(n=20)

Figure S47: Selected MOs of **2m** (schematic, not to scale)

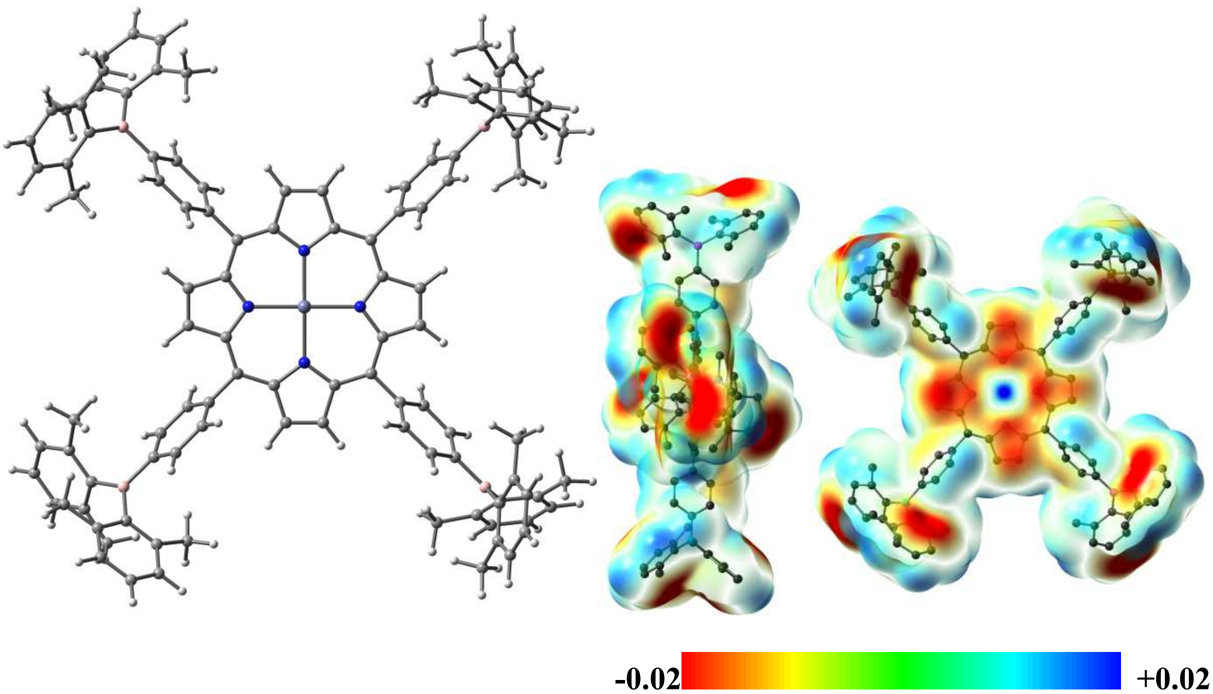


Figure S48: DFT B3LYP/lanl2dz optimised structure of **3m** and its ESP surface

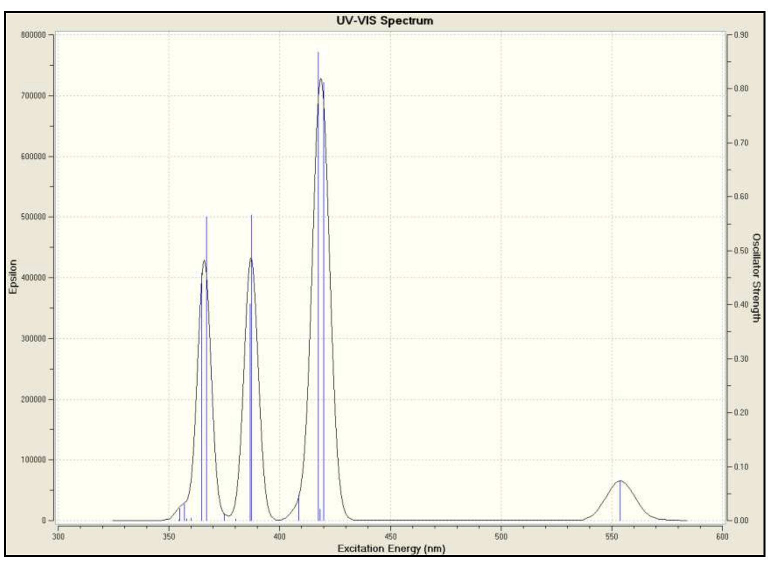


Figure S49: TD-SCF DFT Simulated UV-Vis Spectra of **3m** (n=20)

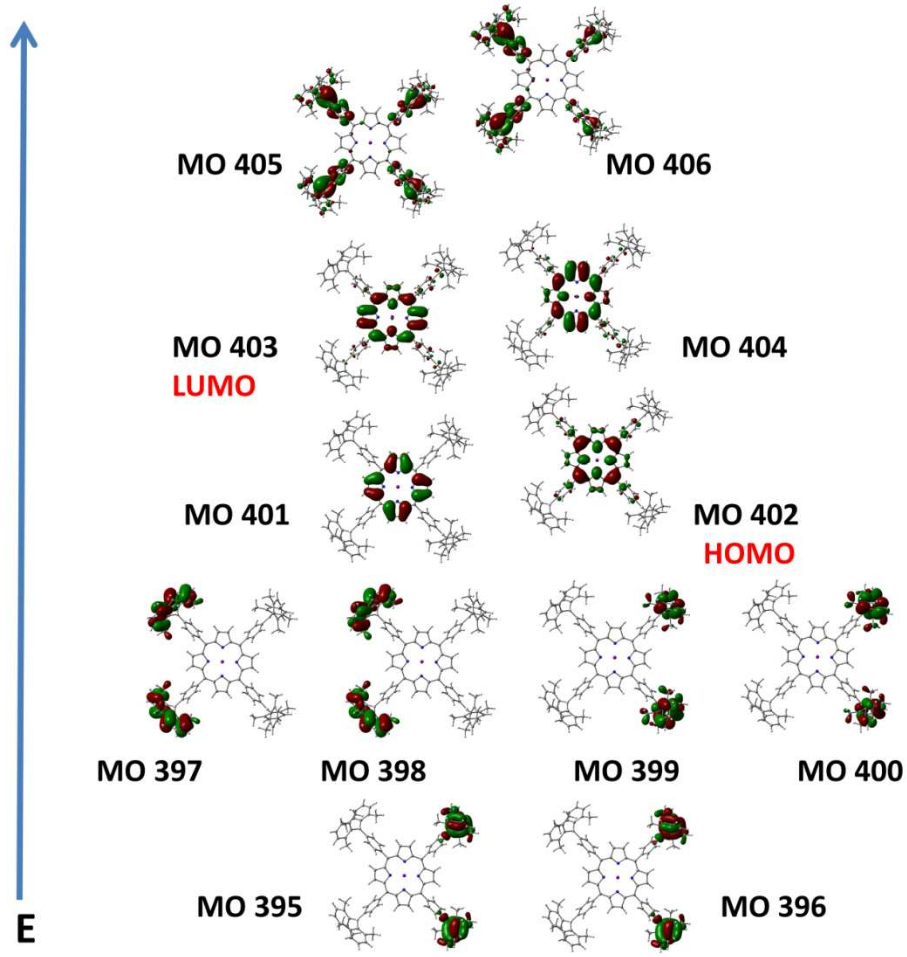


Figure S50: Selected MOs of **3m** (schematic, not to scale)

Table S1. Crystallographic data and refinement parameters for **2** and **3:** The crystal quality was 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.

Compound	**2**	**3**
empirical formula	C132 H114 B4 Cl12 N4	C129 H112 B4 Cl12 N4 Zn
fw	2224.91	2252.26
T (K)	100 K	100 K
crystal system	Monoclinic	Monoclinic
space group	C 2/c	C 2/c
a/Å	24.3381(17)	24.53000
b/Å	20.7253(16)	20.53900
c/Å	24.5830(19)	24.56800
α/deg	90	90
β/deg	103.632(4)	103.9300
γ/deg	90	90
V/Å^3	12050.7(16)	12013.864
Z	4	4
ρ_{calcd} (g cm^{-3})	1.226	1.245
μ (Mo Kα) (mm^{-1})	0.326	0.521
λ/Å	0.71073	0.71073
F (000)	4632.0	4672.0
collected reflns	13176	13022
unique reflns	8788	5118
GOF (F^2)	1.102	1.073
R_1 [I>2σ(I)][a]	0.1353	0.1035
wR_2 [I>2σ(I)][b]	0.3640	0.3570

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$

Table S2a. Photophysical properties of **2** and **3**

Compound	**Absorption (λ_{max}/nm, ε/M^{-1} cm^{-1})**	**Emission (λ_{em}/nm) λ_{ex}=350nm**	**Emission (λ_{em}/nm) λ_{ex}=425nm**	Φ_f (DCM), λ_{ex}
2	334, 4.3×10^3 425 3.0×10^5 518 1.7×10^4 554 1.3×10^4 591 7.6×10^3 648 6.3×10^3	395 445 650 715	655 720	27.0, 350 12.3, 515
3	338, 4.3×10^3 428, 2.8×10^5 514, 1.0×10^4 590, 1.1×10^3	400 450 610 660	615 660	19.7, 350 10.0, 515

Table S2b. Time resolved fluorescence measurements of **2** and **3**

	10 µM (DCM) τ_f/ns (λ_{em}/nm)
2	1.5 (410) 1.6 (450) 8.4 (660) 8.1 (710)
3	1.5 (410) 1.8 (450) 1.8 (560) 1.7 (610)

All given data are for single exponential fitting of "Time-Resolved Fluorescence" decay profiles. Incorporation of more than one exponential function was not required in any case. (λ_{ex} = 342 nm nano-LED) [$y = A\times\exp(-t/\tau_f) + y_0$] where y is the fluorescence intensity at any given time t. $y_0 = 0$; and A = Pre-exponential constant. τ_f indicates the average fluorescence lifetime of the observed events.]

COMPUTED GEOMETRY OF MODEL COMPOUND 2m

E=-4492.36281329a.u.

Table S3. Coordinates of **2m**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-2.046132	-0.008770	0.042241
2	6	0	2.482569	-2.473873	0.010400
3	6	0	1.142821	-2.920459	0.008363
4	6	0	0.690742	-4.293367	0.000220
5	1	0	1.343242	-5.152632	-0.006321
6	6	0	-0.690614	-4.293397	-0.000576
7	1	0	-1.343080	-5.152687	0.005970
8	6	0	-1.142753	-2.920509	-0.008712
9	6	0	-2.482523	-2.473981	-0.010720
10	6	0	-2.885465	-1.115187	-0.002527
11	6	0	-4.290874	-0.690279	-0.087990
12	1	0	-5.141913	-1.350487	-0.163381
13	6	0	-4.289868	0.676990	-0.086374
14	1	0	-5.139384	1.339767	-0.158711
15	6	0	2.885456	-1.115060	0.002239
16	6	0	3.550212	-3.531014	0.029264
17	6	0	4.419113	-3.701785	-1.074094
18	1	0	4.304900	-3.060176	-1.944383
19	6	0	5.402396	-4.703169	-1.062791
20	1	0	6.042671	-4.825772	-1.933813
21	6	0	5.590150	-5.555375	0.059443
22	6	0	4.722464	-5.355603	1.167480
23	1	0	4.842806	-5.975259	2.053256
24	6	0	3.713182	-4.380192	1.148700
25	1	0	3.062884	-4.254305	2.011014
26	6	0	-3.550118	-3.531171	-0.029533
27	6	0	-3.713123	-4.380368	-1.148949
28	1	0	-3.062898	-4.254449	-2.011312
29	6	0	-4.722344	-5.355845	-1.167640
30	1	0	-4.842714	-5.975523	-2.053397
31	6	0	-5.589922	-5.555670	-0.059529
32	6	0	-5.402146	-4.703429	1.062676
33	1	0	-6.042340	-4.826066	1.933753
34	6	0	-4.418932	-3.701978	1.073890
35	1	0	-4.304693	-3.060354	1.944164
36	7	0	2.046074	-0.008679	-0.042481
37	6	0	-2.481092	2.456838	-0.009847
38	6	0	-1.142324	2.903782	-0.008022
39	6	0	-0.690883	4.276808	-0.000922
40	1	0	-1.344976	5.135010	0.005294
41	6	0	0.690645	4.276836	0.000630
42	1	0	1.344706	5.135063	-0.005595
43	6	0	1.142144	2.903830	0.007740
44	6	0	2.480932	2.456945	0.009586
45	6	0	2.884142	1.099251	0.001565
46	6	0	4.289781	0.677174	0.086120
47	1	0	5.139274	1.339983	0.158453
48	6	0	4.290845	-0.690095	0.087719
49	1	0	5.141911	-1.350270	0.163098
50	6	0	-2.884244	1.099125	-0.001829
51	6	0	-3.548212	3.515645	-0.027939
52	6	0	-4.378723	3.724518	1.097201
53	1	0	-4.235710	3.112179	1.984146
54	6	0	-5.374787	4.713707	1.078038
55	1	0	-6.005130	4.846919	1.954230
56	6	0	-5.577582	5.549599	-0.053803
57	6	0	-4.732044	5.326697	-1.174558
58	1	0	-4.859252	5.940396	-2.063761
59	6	0	-3.744538	4.329086	-1.168300
60	1	0	-3.125797	4.169692	-2.048181

61	6	0	3.548003	3.515799	0.027736
62	6	0	3.744237	4.329222	1.168125
63	1	0	3.125458	4.169782	2.047971
64	6	0	4.731694	5.326880	1.174456
65	1	0	4.858824	5.940563	2.063682
66	6	0	5.577277	5.549846	0.053748
67	6	0	5.374582	4.713966	-1.078119
68	1	0	6.004969	4.847222	-1.954272
69	6	0	4.378563	3.724732	-1.097355
70	1	0	4.235626	3.112404	-1.984320
71	5	0	6.684878	6.666611	0.064585
72	6	0	6.540570	7.878956	1.076316
73	6	0	7.900071	6.545128	-0.947400
74	6	0	7.578300	8.166118	2.021272
75	6	0	5.374950	8.708645	1.079276
76	6	0	8.763888	5.405245	-0.942676
77	6	0	8.139471	7.569589	-1.922931
78	6	0	7.434450	9.233344	2.932403
79	6	0	8.845294	7.325178	2.103082
80	6	0	5.273259	9.786686	1.985788
81	6	0	4.207937	8.499889	0.118669
82	6	0	9.810248	5.300208	-1.886957
83	6	0	8.674759	4.299438	0.102860
84	6	0	9.184971	7.429114	-2.858081
85	6	0	7.265633	8.812948	-2.017988
86	6	0	6.290695	10.048241	2.915747
87	1	0	8.226970	9.428446	3.652034
88	1	0	9.424824	7.379794	1.174273
89	1	0	9.486720	7.668078	2.922785
90	1	0	8.619919	6.265964	2.282701
91	1	0	4.388792	10.420829	1.958914
92	1	0	3.464191	7.813427	0.545411
93	1	0	3.701152	9.451949	-0.081571
94	1	0	4.513907	8.075181	-0.841977
95	6	0	10.022252	6.300242	-2.845290
96	1	0	10.460529	4.427098	-1.861204
97	1	0	9.496370	4.393007	0.828274
98	1	0	7.737779	4.313509	0.663205
99	1	0	8.770167	3.310725	-0.364477
100	1	0	9.342204	8.209792	-3.599626
101	1	0	6.224724	8.561183	-2.263341
102	1	0	7.250011	9.371061	-1.075527
103	1	0	7.630871	9.484037	-2.803457
104	5	0	6.707330	-6.661903	0.076873
105	6	0	7.253359	-7.219693	-1.302451
106	6	0	7.239030	-7.185535	1.475971
107	6	0	8.650381	-7.159089	-1.612492
108	6	0	6.368752	-7.788695	-2.272910
109	6	0	7.809044	-6.292640	2.436956
110	6	0	7.126794	-8.572295	1.826194
111	6	0	9.124361	-7.639104	-2.851538
112	6	0	9.663451	-6.555798	-0.648272
113	6	0	6.878202	-8.285889	-3.492363
114	6	0	4.864360	-7.909307	-2.048485
115	6	0	8.230618	-6.775503	3.696565
116	6	0	8.074221	-4.819681	2.147134
117	6	0	7.546356	-9.019843	3.095537
118	6	0	6.524234	-9.599124	0.876698
119	6	0	8.247184	-8.206957	-3.789910
120	1	0	10.187091	-7.573080	-3.075853
121	1	0	9.717598	-7.125250	0.286955
122	1	0	10.664008	-6.543936	-1.095172
123	1	0	9.409264	-5.521319	-0.383168
124	1	0	6.193573	-8.735154	-4.209595
125	1	0	4.340359	-7.004267	-2.383517
126	1	0	4.458268	-8.755164	-2.616578
127	1	0	4.600259	-8.055235	-0.996666
128	6	0	8.097622	-8.129244	4.032913
129	1	0	8.668396	-6.079365	4.410417
130	1	0	9.151818	-4.646507	2.010044
131	1	0	7.565641	-4.461666	1.249924

132	1	0	7.751379	-4.190575	2.986803
133	1	0	7.440238	-10.072742	3.348940
134	1	0	5.470437	-9.381023	0.655008
135	1	0	7.056492	-9.628291	-0.080249
136	1	0	6.562454	-10.601944	1.316710
137	5	0	-6.707001	-6.662306	-0.076832
138	6	0	-7.252774	-7.220165	1.302566
139	6	0	-7.238818	-7.185993	-1.475861
140	6	0	-8.649758	-7.159703	1.612804
141	6	0	-6.367969	-7.789069	2.272901
142	6	0	-7.809021	-6.293153	-2.436789
143	6	0	-7.126517	-8.572747	-1.826085
144	6	0	-9.123511	-7.639759	2.851922
145	6	0	-9.663023	-6.556518	0.648723
146	6	0	-6.877193	-8.286303	3.492432
147	6	0	-4.863598	-7.909528	2.048259
148	6	0	-8.230703	-6.776060	-3.696344
149	6	0	-8.074300	-4.820218	-2.146939
150	6	0	-7.546193	-9.020339	-3.095375
151	6	0	-6.523772	-9.599530	-0.876656
152	6	0	-8.246141	-8.207509	3.790175
153	1	0	-10.186217	-7.573844	3.076389
154	1	0	-9.717219	-7.125956	-0.286509
155	1	0	-10.663525	-6.544788	1.095750
156	1	0	-9.408995	-5.522002	0.383608
157	1	0	-6.192413	-8.735486	4.209572
158	1	0	-4.339646	-7.004412	2.383159
159	1	0	-4.457331	-8.755309	2.616340
160	1	0	-4.599638	-8.055492	0.996410
161	6	0	-8.097638	-8.129793	-4.032696
162	1	0	-8.668622	-6.079963	-4.410149
163	1	0	-9.151886	-4.647156	-2.009624
164	1	0	-7.565568	-4.462133	-1.249844
165	1	0	-7.751708	-4.191095	-2.986691
166	1	0	-7.440024	-10.073232	-3.348781
167	1	0	-5.469957	-9.381372	-0.655113
168	1	0	-7.055897	-9.628715	0.080364
169	1	0	-6.561999	-10.602358	-1.316651
170	5	0	-6.685228	6.666319	-0.064547
171	6	0	-6.540982	7.878748	-1.076182
172	6	0	-7.900381	6.544738	0.947475
173	6	0	-7.578766	8.166000	-2.021052
174	6	0	-5.375356	8.708429	-1.079138
175	6	0	-8.764187	5.404850	0.942701
176	6	0	-8.139751	7.569129	1.923086
177	6	0	-7.434959	9.233301	-2.932102
178	6	0	-8.845779	7.325087	-2.102850
179	6	0	-5.273706	9.786542	-1.985569
180	6	0	-4.208289	8.499594	-0.118613
181	6	0	-9.810515	5.299740	1.887010
182	6	0	-8.675075	4.299109	-0.102908
183	6	0	-9.185215	7.428582	2.858265
184	6	0	-7.265921	8.812491	2.018183
185	6	0	-6.291192	10.048183	-2.915447
186	1	0	-8.227522	9.428470	-3.651667
187	1	0	-9.425259	7.379649	-1.174007
188	1	0	-9.487241	7.668055	-2.922497
189	1	0	-8.620432	6.265882	-2.282553
190	1	0	-4.389231	10.420673	-1.958697
191	1	0	-3.464450	7.813359	-0.545562
192	1	0	-3.701640	9.451678	0.081869
193	1	0	-4.514163	8.074580	0.841926
194	6	0	-10.022491	6.299704	2.845422
195	1	0	-10.460791	4.426628	1.861219
196	1	0	-9.496744	4.392675	-0.828256
197	1	0	-7.738135	4.313266	-0.663320
198	1	0	-8.770390	3.310362	0.364378
199	1	0	-9.342426	8.209201	3.599875
200	1	0	-6.224973	8.560717	2.263356
201	1	0	-7.250444	9.370723	1.075790
202	1	0	-7.631063	9.483477	2.803786

203	1	0	-0.000054	1.091405	-0.000154
204	1	0	-0.000005	-1.108195	-0.000187
205	7	0	-0.000073	2.109961	-0.000149
206	7	0	0.000016	-2.126762	-0.000185
207	1	0	8.420164	-8.488980	5.007593
208	1	0	8.626581	-8.586667	-4.736146
209	1	0	10.827382	6.206099	-3.570779
210	1	0	6.197247	10.877427	3.613730
211	1	0	-10.827594	6.205505	3.570932
212	1	0	-6.197778	10.877427	-3.613366
213	1	0	-8.625362	-8.587248	4.736470
214	1	0	-8.420265	-8.489564	-5.007334

Excitation energies and oscillator strengths:

*Excited State 1: Singlet-A 2.0976 eV 591.07 nm f=0.0755 <S**2>=0.000*
396 -> 399 0.37776
397 -> 398 0.59231
Total Energy, E(TD-HF/TD-KS) = -4492.28572768

*Excited State 2: Singlet-A 2.2581 eV 549.05 nm f=0.1217 <S**2>=0.000*
396 -> 398 -0.39303
397 -> 399 0.58546

*Excited State 3: Singlet-A 2.9141 eV 425.46 nm f=0.0035 <S**2>=0.000*
397 -> 400 0.70117

*Excited State 4: Singlet-A 2.9304 eV 423.10 nm f=0.6516 <S**2>=0.000*
396 -> 398 -0.32530
397 -> 399 -0.21622
397 -> 402 0.58053

*Excited State 5: Singlet-A 2.9311 eV 423.00 nm f=0.7282 <S**2>=0.000*
378 -> 398 0.10101
396 -> 399 -0.35118
397 -> 398 0.22924
397 -> 401 0.29206
397 -> 403 0.46860

*Excited State 6: Singlet-A 2.9906 eV 414.58 nm f=0.0573 <S**2>=0.000*
396 -> 399 0.10710
397 -> 401 0.63576
397 -> 403 -0.27003

*Excited State 7: Singlet-A 3.1226 eV 397.05 nm f=0.3047 <S**2>=0.000*
378 -> 398 -0.28500
396 -> 399 0.39099
396 -> 402 -0.14551
397 -> 398 -0.19834
397 -> 403 0.43231

*Excited State 8: Singlet-A 3.2058 eV 386.74 nm f=0.0068 <S**2>=0.000*
379 -> 398 0.64067
382 -> 398 -0.25753

*Excited State 9: Singlet-A 3.2335 eV 383.44 nm f=0.8456 <S**2>=0.000*
396 -> 398 0.43026
396 -> 403 0.22592
397 -> 399 0.28131
397 -> 402 0.37319

*Excited State 10: Singlet-A 3.3160 eV 373.90 nm f=0.0000 <S**2>=0.000*
396 -> 400 0.70272

*Excited State 11: Singlet-A 3.3621 eV 368.77 nm f=0.0185 <S**2>=0.000*
396 -> 401 0.69460

*Excited State 12: Singlet-A 3.3755 eV 367.31 nm f=0.0845 <S**2>=0.000*
378 -> 398 -0.42571
380 -> 398 -0.21807
396 -> 402 0.49167

*Excited State 13: Singlet-A 3.3974 eV 364.94 nm f=0.0017 <S**2>=0.000*
394 -> 398 0.50552
394 -> 399 -0.10405
395 -> 398 0.15409
395 -> 399 0.40663

*Excited State 14: Singlet-A 3.3978 eV 364.90 nm f=0.0012 <S**2>=0.000*
394 -> 398 -0.15615
394 -> 399 0.40892
395 -> 398 0.51378
395 -> 399 0.10471

*Excited State 15: Singlet-A 3.4135 eV 363.21 nm f=0.0022 <S**2>=0.000*
379 -> 399 -0.14326
392 -> 399 0.36095
393 -> 398 0.56286

*Excited State 16: Singlet-A 3.4139 eV 363.18 nm f=0.0007 <S**2>=0.000*
392 -> 398 0.58140
393 -> 399 0.36612

*Excited State 17: Singlet-A 3.4202 eV 362.51 nm f=0.0000 <S**2>=0.000*
379 -> 399 0.57246
382 -> 399 -0.28496
390 -> 399 0.12822
391 -> 398 0.11822
393 -> 398 0.16199

*Excited State 18: Singlet-A 3.4207 eV 362.45 nm f=0.2115 <S**2>=0.000*
378 -> 399 -0.23858
391 -> 399 -0.13425
396 -> 403 0.59787
397 -> 399 -0.10029
397 -> 402 -0.10001

*Excited State 19: Singlet-A 3.4312 eV 361.34 nm f=0.0383 <S**2>=0.000*
390 -> 398 0.46733
390 -> 403 0.11198
391 -> 399 0.40745
391 -> 400 0.10080
395 -> 398 0.10083
396 -> 403 0.17244

*Excited State 20: Singlet-A 3.4312 eV 361.34 nm f=0.0213 <S**2>=0.000*
379 -> 399 -0.14295
390 -> 399 0.39183
390 -> 400 0.10174
391 -> 398 0.46790
391 -> 403 0.11324
394 -> 398 0.13240

COMPUTED GEOMETRY OF MODEL COMPOUND 3m
Energy -4556.85949007a.u.

Table S4. Coordinates of **3m**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.008702	-0.000013	-0.000050
2	7	0	0.008561	-2.068752	0.036264
3	7	0	2.076997	-0.000025	-0.000054
4	6	0	2.480989	2.473341	0.007302
5	6	0	2.906289	1.122331	0.007406
6	6	0	4.297171	0.687076	-0.000266
7	1	0	5.154712	1.342814	-0.008192
8	6	0	4.297162	-0.687153	0.000165
9	1	0	5.154695	-1.342901	0.008097
10	6	0	2.906276	-1.122391	-0.007509
11	6	0	2.480961	-2.473396	-0.007394
12	6	0	1.129886	-2.898171	0.001998
13	6	0	0.693948	-4.287415	-0.067794
14	1	0	1.349954	-5.142660	-0.129839
15	6	0	-0.680424	-4.286487	-0.068122
16	1	0	-1.338637	-5.140314	-0.129089
17	6	0	1.129919	2.898131	-0.002083
18	6	0	3.542152	3.536959	0.023859
19	6	0	3.718962	4.400772	-1.082571
20	1	0	3.079930	4.284771	-1.954646
21	6	0	4.724407	5.379912	-1.073787
22	1	0	4.851960	6.015298	-1.947693
23	6	0	5.574830	5.569283	0.049497
24	6	0	5.368595	4.707541	1.161087
25	1	0	5.987376	4.828714	2.047380
26	6	0	4.389107	3.702194	1.144574
27	1	0	4.260176	3.054580	2.008396
28	6	0	3.542115	-3.537022	-0.023932
29	6	0	4.389064	-3.702293	-1.144646
30	1	0	4.260126	-3.054706	-2.008488
31	6	0	5.368553	-4.707638	-1.161134
32	1	0	5.987329	-4.828838	-2.047426
33	6	0	5.574798	-5.569342	-0.049515
34	6	0	4.724389	-5.379930	1.073771
35	1	0	4.851956	-6.015280	1.947701
36	6	0	3.718940	-4.400795	1.082528
37	1	0	3.079920	-4.284760	1.954608
38	7	0	0.008584	2.068726	-0.036351
39	7	0	-2.059881	-0.000001	-0.000037
40	6	0	-2.463909	-2.471871	-0.011217
41	6	0	-2.889333	-1.121772	-0.009460
42	6	0	-4.280358	-0.687165	-0.002025
43	1	0	-5.136800	-1.344580	0.003770
44	6	0	-4.280350	0.687189	0.001972
45	1	0	-5.136784	1.344615	-0.003816
46	6	0	-2.889320	1.121780	0.009396
47	6	0	-2.463880	2.471873	0.011155
48	6	0	-1.113892	2.896969	-0.000156
49	6	0	-0.680373	4.286469	0.068054
50	1	0	-1.338573	5.140304	0.129030
51	6	0	0.693999	4.287380	0.067722
52	1	0	1.350018	5.142616	0.129771
53	6	0	-1.113925	-2.896982	0.000083
54	6	0	-3.526860	-3.534639	-0.032225
55	6	0	-3.744091	-4.364129	1.092111
56	1	0	-3.136161	-4.222557	1.982436
57	6	0	-4.737388	-5.356054	1.069564
58	1	0	-4.877303	-5.984951	1.945771
59	6	0	-5.569279	-5.556019	-0.065704
60	6	0	-5.337683	-4.712099	-1.186024

61	1	0	-5.948564	-4.836603	-2.077551
62	6	0	-4.335915	-3.728941	-1.175996
63	1	0	-4.171532	-3.109859	-2.054672
64	6	0	-3.526822	3.534652	0.032185
65	6	0	-4.335859	3.728950	1.175969
66	1	0	-4.171468	3.109860	2.054637
67	6	0	-5.337617	4.712118	1.186021
68	1	0	-5.948482	4.836621	2.077559
69	6	0	-5.569224	5.556047	0.065711
70	6	0	-4.737350	5.356085	-1.069571
71	1	0	-4.877271	5.984992	-1.945770
72	6	0	-3.744063	4.364152	-1.092141
73	1	0	-3.136148	4.222582	-1.982477
74	5	0	-6.691341	6.657817	0.079891
75	6	0	-7.899095	6.508677	1.096413
76	6	0	-6.580158	7.872471	-0.934137
77	6	0	-8.188801	7.546533	2.040536
78	6	0	-8.722241	5.338471	1.104348
79	6	0	-5.445090	8.742579	-0.934514
80	6	0	-7.609195	8.104933	-1.906463
81	6	0	-9.251899	7.398365	2.955734
82	6	0	-7.354879	8.818501	2.116978
83	6	0	-9.796423	5.232385	2.015018
84	6	0	-8.510940	4.170779	0.145124
85	6	0	-5.349049	9.788326	-1.880422
86	6	0	-4.335249	8.660673	0.107336
87	6	0	-7.477725	9.149979	-2.843471
88	6	0	-8.848208	7.224341	-1.995720
89	6	0	-10.060348	6.249932	2.944098
90	1	0	-9.448933	8.191086	3.674626
91	1	0	-7.415922	9.395805	1.187186
92	1	0	-7.698781	9.459602	2.936523
93	1	0	-6.293797	8.599577	2.293529
94	1	0	-10.425610	4.344273	1.991986
95	1	0	-7.825300	3.427526	0.574037
96	1	0	-9.462405	3.663447	-0.056677
97	1	0	-8.084102	4.475827	-0.814797
98	6	0	-6.353521	9.993585	-2.835594
99	1	0	-4.479507	10.443523	-1.858447
100	1	0	-4.431878	9.481422	0.833332
101	1	0	-4.341385	7.723396	0.667347
102	1	0	-3.348772	8.762933	-0.363323
103	1	0	-8.261838	9.301819	-3.582520
104	1	0	-8.591706	6.183626	-2.236787
105	1	0	-9.404576	7.210080	-1.052168
106	1	0	-9.522458	7.582812	-2.781611
107	5	0	6.686886	6.680641	0.063245
108	6	0	7.248575	7.217279	-1.318388
109	6	0	7.211830	7.217020	1.460197
110	6	0	7.192723	8.612577	-1.636595
111	6	0	7.815946	6.325175	-2.282977
112	6	0	6.320746	7.797350	2.416706
113	6	0	8.597564	7.099964	1.812933
114	6	0	7.675657	9.077887	-2.877847
115	6	0	6.591504	9.633011	-0.678862
116	6	0	8.315945	6.825970	-3.504864
117	6	0	7.931825	4.821921	-2.048976
118	6	0	6.804329	8.224856	3.674041
119	6	0	4.849063	8.066956	2.124289
120	6	0	9.045862	7.525864	3.079906
121	6	0	9.622150	6.484363	0.869478
122	6	0	8.241640	8.193475	-3.810501
123	1	0	7.613366	10.139533	-3.108327
124	1	0	7.159440	9.689967	0.257118
125	1	0	6.584164	10.631237	-1.131055
126	1	0	5.555606	9.384010	-0.414283
127	1	0	8.763809	6.135754	-4.217592
128	1	0	7.022506	4.299100	-2.373862
129	1	0	8.772179	4.408399	-2.619820
130	1	0	8.084040	4.564707	-0.996290
131	6	0	8.157085	8.087745	4.012657

132	1	0	6.109538	8.670584	4.384296
133	1	0	4.679701	9.144736	1.983965
134	1	0	4.490419	7.556844	1.228225
135	1	0	4.217955	7.748654	2.964237
136	1	0	10.097961	7.416181	3.335114
137	1	0	9.402974	5.427602	0.663219
138	1	0	9.649481	7.003204	-0.094779
139	1	0	10.625928	6.528065	1.306781
140	5	0	6.686866	-6.680690	-0.063227
141	6	0	7.248602	-7.217233	1.318424
142	6	0	7.211784	-7.217140	-1.460162
143	6	0	7.192802	-8.612514	1.636712
144	6	0	7.815959	-6.325055	2.282951
145	6	0	6.320679	-7.797516	-2.416625
146	6	0	8.597506	-7.100081	-1.812944
147	6	0	7.675781	-9.077738	2.877979
148	6	0	6.591592	-9.633024	0.679053
149	6	0	8.316006	-6.825764	3.504854
150	6	0	7.931775	-4.821810	2.048866
151	6	0	6.804230	-8.225071	-3.673954
152	6	0	4.849002	-8.067109	-2.124161
153	6	0	9.045773	-7.526030	-3.079911
154	6	0	9.622114	-6.484427	-0.869547
155	6	0	8.241757	-8.193254	3.810569
156	1	0	7.613530	-10.139373	3.108521
157	1	0	7.159510	-9.690019	-0.256936
158	1	0	6.584294	-10.631224	1.131306
159	1	0	5.555681	-9.384072	0.414482
160	1	0	8.763861	-6.135491	4.217533
161	1	0	7.022444	-4.299006	2.373747
162	1	0	8.772128	-4.408225	2.619665
163	1	0	8.083951	-4.564646	0.996161
164	6	0	8.156976	-8.087962	-4.012613
165	1	0	6.109424	-8.670832	-4.384172
166	1	0	4.679640	-9.144885	-1.983800
167	1	0	4.490382	-7.556968	-1.228104
168	1	0	4.217873	-7.748831	-2.964103
169	1	0	10.097862	-7.416342	-3.335156
170	1	0	9.402898	-5.427677	-0.663276
171	1	0	9.649525	-7.003266	0.094708
172	1	0	10.625870	-6.528080	-1.306907
173	5	0	-6.691414	-6.657771	-0.079855
174	6	0	-7.899200	-6.508603	-1.096335
175	6	0	-6.580206	-7.872445	0.934146
176	6	0	-8.188953	-7.546440	-2.040465
177	6	0	-8.722325	-5.338381	-1.104229
178	6	0	-5.445163	-8.742585	0.934448
179	6	0	-7.609202	-8.104900	1.906517
180	6	0	-9.252075	-7.398239	-2.955629
181	6	0	-7.355052	-8.818419	-2.116955
182	6	0	-9.796532	-5.232263	-2.014866
183	6	0	-8.510969	-4.170703	-0.145000
184	6	0	-5.349102	-9.788352	1.880332
185	6	0	-4.335376	-8.660692	-0.107461
186	6	0	-7.477714	-9.149966	2.843498
187	6	0	-8.848191	-7.224280	1.995845
188	6	0	-10.060504	-6.249793	-2.943951
189	1	0	-9.449144	-8.190947	-3.674527
190	1	0	-7.416077	-9.395740	-1.187172
191	1	0	-7.698988	-9.459499	-2.936503
192	1	0	-6.293972	-8.599508	-2.293533
193	1	0	-10.425701	-4.344139	-1.991804
194	1	0	-7.825345	-3.427449	-0.573938
195	1	0	-9.462420	-3.663367	0.056857
196	1	0	-8.084083	-4.475767	0.814894
197	6	0	-6.353531	-9.993601	2.835551
198	1	0	-4.479580	-10.443573	1.858299
199	1	0	-4.432078	-9.481416	-0.833477
200	1	0	-4.341506	-7.723398	-0.667444
201	1	0	-3.348877	-8.763006	0.363139
202	1	0	-8.261794	-9.301801	3.582583

203	*1*	*0*	*-8.591653*	*-6.183574*	*2.236915*
204	*1*	*0*	*-9.404602*	*-7.209991*	*1.052319*
205	*1*	*0*	*-9.522413*	*-7.582747*	*2.781762*
206	*1*	*0*	*-10.886452*	*6.153052*	*3.645270*
207	*1*	*0*	*-6.266362*	*10.798305*	*-3.562413*
208	*1*	*0*	*8.623566*	*8.566131*	*-4.758526*
209	*1*	*0*	*8.517433*	*8.415144*	*4.985491*
210	*1*	*0*	*8.623718*	*-8.565843*	*4.758606*
211	*1*	*0*	*8.517300*	*-8.415396*	*-4.985444*
212	*1*	*0*	*-6.266358*	*-10.798336*	*3.562350*
213	*1*	*0*	*-10.886626*	*-6.152887*	*-3.645098*

Excitation energies and oscillator strengths:

```
Excited State   1:      Singlet-A      2.2384 eV  553.90 nm  f=0.0726  <S**2>=0.000
    401 -> 404        0.41340
    402 -> 403        0.56620
 Total Energy, E(TD-HF/TD-KS) =  -4556.77723132

Excited State   2:      Singlet-A      2.2387 eV  553.83 nm  f=0.0735  <S**2>=0.000
    401 -> 403       -0.41338
    402 -> 404        0.56614

Excited State   3:      Singlet-A      2.9534 eV  419.81 nm  f=0.8117  <S**2>=0.000
    401 -> 404        0.34379
    402 -> 403       -0.26374
    402 -> 405       -0.11530
    402 -> 407        0.53624

Excited State   4:      Singlet-A      2.9636 eV  418.36 nm  f=0.0212  <S**2>=0.000
    402 -> 405        0.69436

Excited State   5:      Singlet-A      2.9695 eV  417.53 nm  f=0.8674  <S**2>=0.000
    401 -> 403       -0.36119
    402 -> 404       -0.27423
    402 -> 406       -0.22441
    402 -> 408        0.48010

Excited State   6:      Singlet-A      3.0344 eV  408.60 nm  f=0.0467  <S**2>=0.000
    402 -> 406        0.66499
    402 -> 408        0.20269

Excited State   7:      Singlet-A      3.2008 eV  387.35 nm  f=0.5659  <S**2>=0.000
    401 -> 404       -0.39152
    401 -> 408        0.27877
    402 -> 403        0.24798
    402 -> 407        0.41666

Excited State   8:      Singlet-A      3.2063 eV  386.69 nm  f=0.4015  <S**2>=0.000
    401 -> 403        0.35616
    401 -> 407       -0.33537
    402 -> 404        0.21846
    402 -> 408        0.43276

Excited State   9:      Singlet-A      3.2618 eV  380.11 nm  f=0.0022  <S**2>=0.000
    401 -> 405        0.70333

Excited State  10:      Singlet-A      3.3051 eV  375.13 nm  f=0.0124  <S**2>=0.000
    401 -> 406        0.69684

Excited State  11:      Singlet-A      3.3795 eV  366.87 nm  f=0.5631  <S**2>=0.000
    385 -> 404       -0.11131
    401 -> 403        0.18701
    401 -> 407        0.60547
```

```
    402 -> 404       0.16867
    402 -> 408       0.17144

 Excited State  12:      Singlet-A      3.3988 eV  364.78 nm  f=0.4589  <S**2>=0.000
    385 -> 403       0.11215
    401 -> 404       0.15463
    401 -> 408       0.62771
    402 -> 403      -0.14656
    402 -> 407      -0.13572

 Excited State  13:      Singlet-A      3.4436 eV  360.04 nm  f=0.0033  <S**2>=0.000
    399 -> 403       0.46123
    399 -> 404       0.10650
    400 -> 403       0.12982
    400 -> 404      -0.45914

 Excited State  14:      Singlet-A      3.4440 eV  360.00 nm  f=0.0042  <S**2>=0.000
    399 -> 404      -0.46969
    400 -> 403       0.47564

 Excited State  15:      Singlet-A      3.4636 eV  357.96 nm  f=0.0008  <S**2>=0.000
    397 -> 403      -0.47004
    397 -> 405      -0.11464
    398 -> 404       0.48778
    398 -> 406       0.10705

 Excited State  16:      Singlet-A      3.4638 eV  357.95 nm  f=0.0033  <S**2>=0.000
    397 -> 404       0.48322
    397 -> 406       0.10698
    398 -> 403      -0.47375
    398 -> 405      -0.11471

 Excited State  17:      Singlet-A      3.4731 eV  356.98 nm  f=0.0021  <S**2>=0.000
    395 -> 403      -0.44540
    395 -> 405       0.12326
    395 -> 407       0.11997
    396 -> 404       0.45156
    396 -> 408      -0.13082

 Excited State  18:      Singlet-A      3.4734 eV  356.95 nm  f=0.0310  <S**2>=0.000
    395 -> 404      -0.44451
    395 -> 408       0.13054
    396 -> 403       0.45534
    396 -> 405      -0.12362
    396 -> 407      -0.11992
 Excited State  19:      Singlet-A      3.4952 eV  354.73 nm  f=0.0222  <S**2>=0.000
    393 -> 403       0.45341
    393 -> 405       0.15396
    394 -> 404      -0.45298
    394 -> 406      -0.14938
 Excited State  20:      Singlet-A      3.4980 eV  354.44 nm  f=0.0010  <S**2>=0.000
    382 -> 403       0.10555
    383 -> 404      -0.12825
    399 -> 403       0.47624
    400 -> 404       0.47604
```

References:

(1) P, C. A. Swamy.; Mukherjee, S.; Thilagar, P. *Chem. Commun.,* **2013**, *49*, 993. (Synthesis of 4-dimesitylborylbenzaldehyde)