Supporting Information

A Theoretical Study on Anion Sensing Mechanism of Multi-phosphonium Triarylboranes: Intramolecular Charge Transfer and Configurational Changes

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Table S1: Calculated Important Geometrical Parameters i.e, Bond lengths (in Å) and Bond angles (in degree) for the Fully Optimized Structures of **1** and **2** at CAM-B3LYP/6-31G(d) level

parameter	**1**[a]	**1**[b]	**2**[a]	**2**[b]
B1 C2	1.595	1.582	1.591	1.577
B1 C10	1.574	1.571	1.591	1.574
B1 C18	1.574	1.572	1.566	1.574
P26 C7	1.782	1.764	1.784	1.771
P30 C15	…..	…..	1.784	1.769
C2 B1 C10	119.1	119.1	118.1	122.7
C10 B1 C18	121.6	121.5	120.9	118.8
C2 B1 C18	119.1	119.3	120.9	118.4
C7 P26 H29	110.1	110.6	109.9	110.8
C7 P26 H28	112.3	112.6	112.6	112.0
C7 P26 H27	113.4	115.5	113.1	114.9
C4 C2 B1	120.5	121.2	119.6	121.6
C3 C2 B1	120.4	121.3	121.2	120.7

C11	C10	B1	121.7	122.4	121.2	120.8
C12	C10	B1	120.4	120.8	119.6	121.6
C19	C18	B1	120.4	120.8	121.0	121.4
C20	C18	B1	121.7	122.3	121.1	121.7
C38	C4	C2	…..	…..	122.7	121.5
C34	C3	C2	…..	…..	122.6	122.7
C34	C4	C2	122.4	122.1	…..	…..
C30	C3	C2	122.6	122.1	…..	…..
C42	C11	C10	…..	….	122.5	122.6
C46	C12	C10	…..	…..	122.8	121.5
C42	C12	C10	122.8	120.1	…..	…..
C38	C11	C10	122.7	121.5	…..	…..
C54	C20	C18	…..	…..	123.0	120.1
C50	C19	C18	…..	…..	123.0	119.9
C50	C20	C18	122.6	121.6	…..	…..
C46	C19	C18	122.8	120.1	…..	…..
C5	C7	P26	119.5	119.8	119.5	119.9
C6	C7	P26	120.0	120.4	120.0	120.5
C13	C15	P30	119.9	120.4	…..	…..
C13	C15	P30	119.6	119.8	…..	…..

[a] Implies Ground State (S_0); [b] Implies Excited State (S_1)

Table S2: Calculated Important Geometrical Parameters i.e, Bond lengths (in Å) and Bond angles (in degree) for the Fully Optimized Structures of **3** at CAM-B3LYP/6-31G(d) level; the Corresponding X-ray data[1](in parentheses)

parameter	**3**[a]	**3**[b]
B1 C2	1.585 (1.584)	1.605
B1 C10	1.585	1.560
B1 C18	1.585	1.560
P26 C7	1.787 (1.792)	1.780
P30 C15	1.787	1.782
P58 C23	1.787	1.782

C2 B1 C10	120.0 (120.0)	118.8
C10 B1 C18	119.9	122.3
C2 B1 C18	119.9	118.9
C7 P26 H29	110.0 (111.0)	110.1
C7 P26 H28	112.0	112.4
C7 P26 H27	113.0	113.6
C5 C7 P26	119.5	119.6
C6 C7 P26	119.9	120.1
C13 C15 P30	120.0	120.2
C14 C15 P30	119.4	119.6
C22 C23 P58	119.9	120.2
C21 C23 P58	119.5	119.6
C4 C2 B1	120.4	120.5
C3 C2 B1	120.4	120.5
C11 C10 B1	120.4	123.3
C12 C10 B1	120.4	119.5
C19 C18 B1	120.4	119.5
C20 C18 B1	120.4	123.3
C38 C4 C2	122.9	122.1
C34 C3 C2	122.9	122.2
C42 C11 C10	122.8	122.3
C46 C12 C10	122.9	121.0
C50 C19 C18	122.9	121.0
C54 C20 C18	122.8	122.3

[a] Implies Ground State (S_0); [b] Implies Excited State (S_1)

Table S3: Calculated Important Geometrical Parameters i.e, Bond lengths (in Å) and Bond angles (in degree) for the Fully Optimized Structures of **1F** and **2F** at CAM-B3LYP/6-31G(d) Level

parameter	**1F**[a]	**1F**[b]	**2F**[a]	**2F**[b]
B1 C2	1.678	1.681	1.660	1.657
B1 C10	1.664	1.671	1.672	1.665

B1 C18	1.665	1.667	1.674	1.676
P26 C7	1.771	1.764	…..	…..
P26 C15	…..	…..	1.772	1.774
B1 F62	1.460	1.461	1.454	1.454
P38 C23	…..	…..	1.773	1.775
C2 B1 C10	113.8	114.9	114.6	115.6
C10 B1 C18	115.3	117.4	113.9	114.9
C2 B1 C18	114.1	115.6	114.7	112.8
C7 P26 H29	110.3	110.8	…..	…..
C7 P26 H28	112.8	113.9	…..	…..
C7 P26 H27	114.6	115.5	…..	…..
C15 P26 H27	…..	…..	111.4	111.2
C15 P26 H28	…..	…..	114.8	114.6
C15 P26 H29	…..	…..	111.3	111.3
C23 P38 H31	…..	…..	114.5	114.3
C23 P38 H32	…..	…..	112.6	112.4
C23 P38 H33	…..	…..	110.4	110.4
C4 C2 B1	125.6	124.9	126.2	125.8
C3 C2 B1	117.5	118.3	117.8	118.1
C11 C10 B1	126.3	127.0	117.2	116.9
C12 C10 B1	117.8	118.2	125.8	125.9
C19 C18 B1	126.0	126.4	117.7	118.3
C20 C18 B1	118.1	119.7	125.3	126.8
C34 C4 C2	123.5	124.3	…..	…..
C30 C3 C2	123.2	124.0	…..	…..
C42 C4 C2	…..	…..	123.5	123.6
C46 C3 C2	…..	…..	123.1	123.4
C34 C12 C10	…..	…..	123.6	123.7
C42 C12 C10	122.8	123.4	…..	…..
C38 C11 C10	123.4	124.1	123.2	123.1
C54 C19 C18	…..	…..	123.2	123.7

C58 C20 C18	…..	…..	123.8	124.6
C50 C20 C18	123.0	123.8	…..	…..
C46 C19 C18	123.5	124.2	…..	…..
C5 C7 P26	119.8	120.3	…..	…..
C6 C7 P26	120.6	121.1	…..	…..
C13 C15 P26	…..	…..	120.2	120.1
C14 C15 P26	…..	…..	120.2	120.2
C21 C23 P30	…..	…..	120.6	120.5
C22 C23 P30	…..	…..	119.8	119.7
C2 B1 F62	102.7	103.3	104.8	106.2
C10 B1 F62	104.5	105.1	103.5	103.7
C18 B1 F62	104.2	104.9	103.2	101.5

[a] Implies Ground State (S_0); [b] Implies Excited State (S_1)

Table S4: Calculated Important Geometrical Parameters i.e, Bond lengths (in Å) and Bond angles (in degree) for the Fully Optimized Structures of **3F** at CAM-B3LYP/6-31G(d) level

parameter	**3F[a]**	**3F[b]**
B1 C2	1.669	1.670
B1 C10	1.669	1.663
B1 C18	1.669	1.666
P26 C7	1.774	1.776
P30 C15	1.775	1.776
P58 C23	1.775	1.776
B1 F62	1.449	1.448
C2 B1 C10	114.6	115.5
C10 B1 C18	114.5	115.4
C2 B1 C18	114.4	112.7
C7 P26 H29	111.1	111.0
C7 P26 H28	111.6	114.3
C7 P26 H27	114.5	111.6

C5 C7 P26	120.1	120.2
C6 C7 P26	120.3	120.1
C13 C15 P30	120.3	120.2
C14 C15 P30	120.0	120.0
C22 C23 P58	120.2	120.3
C21 C23 P58	120.1	119.9
C4 C2 B1	125.6	127.2
C3 C2 B1	117.3	117.8
C11 C10 B1	125.6	125.7
C12 C10 B1	117.3	117.0
C19 C18 B1	125.5	125.1
C20 C18 B1	117.3	117.6
C38 C4 C2	123.7	124.7
C34 C3 C2	123.4	123.7
C42 C11 C10	123.7	123.7
C46 C12 C10	123.4	123.3
C50 C19 C18	123.7	123.7
C54 C20 C18	123.4	123.7
C2 B1 F62	103.7	102.0
C10 B1 F62	103.7	104.0
C18 B1 F62	103.8	105.1

[a] Implies Ground State (S_0); [b] Implies Excited State (S_1)

Table S5: Calculated Important Geometrical Parameters i.e, Bond lengths (in Å) and Bond angles (in degree) for the Fully Optimized Structures of **1CN** and **2CN** at CAM-B3LYP/6-31G(d) level

parameter	**1CN**[a]	**1CN**[b]	**2CN**[a]	**2CN**[b]
B1 C2	1.681	1.670	1.669	1.665
B1 C10	1.672	1.658	1.677	1.671
B1 C18	1.673	1.654	1.679	1.678
P26 C7	1.773	1.717	…..	…..

P26 C15	…..	…..	1.777	1.776
B1 C62	1.625	1.673	1.622	1.622
P30 C23	…..	…..	1.775	1.774
C2 B1 C10	114.5	118.7	114.9	115.9
C10 B1 C18	115.1	115.5	114.3	115.2
C2 B1 C18	114.3	106.4	114.7	112.7
C7 P26 H29	111.1	110.2	…..	…..
C7 P26 H28	111.8	110.0	…..	…..
C7 P26 H27	114.5	113.7	…..	…..
C15 P26 H27	…..	…..	111.7	111.8
C15 P26 H28	…..	…..	114.4	114.3
C15 P26 H29	…..	…..	110.9	110.8
C23 P30 H31	…..	…..	114.3	114.3
C23 P30 H32	…..	…..	112.3	111.7
C23 P30 H33	…..	…..	110.6	110.8
C4 C2 B1	123.8	126.6	124.4	124.0
C3 C2 B1	119.8	117.5	119.9	120.1
C11 C10 B1	124.5	124.1	119.5	118.9
C12 C10 B1	119.8	119.9	124.0	124.3
C19 C18 B1	124.1	122.7	119.8	121.2
C20 C18 B1	120.3	119.5	123.6	124.8
C42 C4 C2	…..	…..	124.1	124.1
C46 C3 C2	…..	…..	123.9	124.3
C34 C4 C2	124.1	123.6	…..	…..
C30 C3 C2	123.9	123.2	…..	…..
C42 C12 C10	123.7	123.7	…..	…..
C38 C11 C10	124.0	124.1	124.0	123.9
C34 C12 C10	…..	…..	124.2	124.3
C54 C19 C18	…..	…..	124.1	124.5
C58 C20 C18	…..	…..	124.4	124.9
C50 C20 C18	123.9	123.6	…..	…..

C46	C19	C18	124.1	123.9	…..	…..
C5	C7	P26	120.3	121.7	…..	…..
C6	C7	P26	120.5	121.3	…..	…..
C13	C15	P26	…..	…..	120.1	120.0
C14	C15	P26	…..	…..	120.5	120.5
C21	C23	P30	…..	…..	120.6	121.5
C22	C23	P30	…..	…..	120.0	120.8
C2	B1	C62	102.8	105.1	104.3	106.2
C10	B1	C62	103.9	105.9	103.1	102.9
C18	B1	C62	103.9	103.6	103.3	101.7

[a] Implies Ground State (S_0); [b] Implies Excited State (S_1)

Table S6: Calculated Important Geometrical Parameters i.e, Bond lengths (in Å) and Bond angles (in degree) for the Fully Optimized Structures of **3CN** at CAM-B3LYP/6-31G(d) level

parameter	**3CN[a]**	**3CN[b]**
B1 C2	1.675	1.672
B1 C10	1.675	1.654
B1 C18	1.674	1.677
P26 C7	1.776	1.777
P30 C15	1.776	1.729
P58 C23	1.776	1.777
B1 C62	1.619	1.621
C2 B1 C10	114.5	111.4
C10 B1 C18	114.7	116.5
C2 B1 C18	114.5	115.3
C7 P26 H29	111.6	111.9
C7 P26 H28	111.1	110.7
C7 P26 H27	114.2	114.2
C5 C7 P26	120.3	120.5
C6 C7 P26	120.3	120.1

C13	C15	P30	120.0	124.0
C14	C15	P30	120.6	124.1
C22	C23	P58	120.2	120.3
C21	C23	P58	120.3	120.2
C4	C2	B1	123.9	123.8
C3	C2	B1	119.5	119.5
C11	C10	B1	123.8	126.1
C12	C10	B1	119.5	122.3
C19	C18	B1	123.8	124.1
C20	C18	B1	119.5	119.1
C38	C4	C2	124.3	124.4
C34	C3	C2	124.3	124.2
C42	C11	C10	124.3	124.3
C46	C12	C10	124.2	123.7
C50	C19	C18	124.3	124.4
C54	C20	C18	124.2	124.0
C2	B1	C62	103.5	106.1
C10	B1	C62	103.6	103.1
C18	B1	C62	103.6	102.5

[a] Implies Ground State (S_0); [b] Implies Excited State (S_1)

Table S7: The NPA Charge Distribution on Some Crucial Atoms of **1-3**, **1CN-3CN** and **1F-3F** in S_0 Calculated at CAM-B3LYP/6-31G(d) Level of Theory.

Molecule	**NPA charge distribution (Atom involved)**					
1	0.933 (B1)	-0.336 (C2)	-0.426 (C10)	-0.426 (C18)	0.861 (P26)	
1CN	0.274 (B1)	-0.176 (C2)	-0.252 (C10)	-0.255 (C18)	0.865 (P26)	0.169 (C62)
1F	0.757 (B1)	-0.216 (C2)	-0.298 (C10)	-0.300 (C18)	0.866 (P26)	-0.556 (F62)

2	0.941 (B1)	-0.350 (C2)	-0.350 (C10)	-0.445 (C18)	0.861 (P26)	
2CN	0.272 (B1)	-0.260 (C2)	-0.183 (C10)	-0.186 (C18)	0.865 (P26)	0.162 (C62)
2F	0.756 (B1)	-0.308 (C2)	-0.225 (C10)	-0.227 (C18)	0.865 (P26)	-0.552 (F62)
3	0.965 (B1)	-0.371 (C2)	-0.372 (C10)	-0.371 (C18)	0.859 (P26)	
3CN	0.271 (B1)	-0.193 (C2)	-0.193 (C10)	-0.193 (C18)	0.864 (P26)	0.155 (C62)
3F	0.756 (B1)	-0.236 (C2)	-0.236 (C10)	-0.236 (C18)	0.864 (P26)	-0.548 (F62)

Table S8: Calculated free energy changes (ΔG) for various Addition Products using CAM-B3LYP/6-31G(d) Level of Theory with Basis Set Superposition Error (BSSE) Corrections.

Molecule	**ΔG (Kcal/mol)**
1CN	-9.56
1F	-59.99
1Br	21.73
1Cl	28.22
1CH_3COO	4.08
1NO_3	18.96
1HSO_4	26.89
2CN	-17.43
2F	-69.52
2Br	12.90
2Cl	19.60
2CH_3COO	3.01
2NO_3	10.93
2HSO_4	19.61
3CN	-23.19

3F	-75.14
3Br	8.09
3Cl	13.50
3CH_3COO	10.55
3NO_3	5.63
3HSO_4	15.1

Table S9: Hybrids of **1-3**, **1CN-3CN** and **1F-3F** in Ground State Calculated by Employing the CAM-B3LYP/6-31G(d) Level of Theory.

Molecule	**Lewis-type NBOs**	**Hybrid[a]**	**AO (%)[b]**
1	$\sigma\,(B1-C2)$	$sp^{2.11}d^{0}$	s(32.12%) p(67.78%) d(0.10%)
	$\sigma\,(B1-C10)$	$sp^{1.95}d^{0}$	s(33.91%) p(66.00%) d(0.09%)
	$\sigma\,(B1-C18)$	$sp^{1.95}d^{0}$	s(33.92%) p(65.99%) d(0.09%)
1CN	$\sigma\,(B1-C2)$	$sp^{2.95}d^{0}$	s(25.26%) p(74.64%) d(0.10%)
	$\sigma\,(B1-C10)$	$sp^{2.78}d^{0}$	s(26.46%) p(73.45%) d(0.09%)
	$\sigma\,(B1-C18)$	$sp^{2.77}d^{0}$	s(26.51%) p(73.40%) d(0.09%)
	$\sigma\,(B1-C62)$	$sp^{3.58}d^{0.01}$	s(21.79%) p(78.09%) d(0.12%)
1F	$\sigma\,(B1-C2)$	$sp^{2.67}d^{0}$	s(27.18%) p(72.70%) d(0.12%)
	$\sigma\,(B1-C10)$	$sp^{2.51}d^{0}$	s(28.46%) p(71.43%) d(0.11%)
	$\sigma\,(B1-C18)$	$sp^{2.49}d^{0}$	s(28.62%) p(71.27%) d(0.11%)
	$\sigma\,(B1-F62)$	$sp^{3.43}d^{0.01}$	s(21.80%) p(78.10%) d(0.10%)
2	$\sigma\,(B1-C2)$	$sp^{2.06}d^{0}$	s(32.67%) p(67.23%) d(0.10%)
	$\sigma\,(B1-C10)$	$sp^{2.06}d^{0}$	s(32.67%) p(67.23%) d(0.10%)
	$\sigma\,(B1-C18)$	$sp^{1.89}d^{0}$	s(34.61%) p(65.31%) d(0.09%)

2CN	$\sigma\,(B1-C2)$	$sp^{2.72}d^{0}$	s(26.83%) p(73.08%) d(0.10%)
	$\sigma\,(B1-C10)$	$sp^{2.90}d^{0}$	s(25.61%) p(74.30%) d(0.09%)
	$\sigma\,(B1-C18)$	$sp^{2.89}d^{0}$	s(25.65%) p(74.26%) d(0.09%)
	$\sigma\,(B1-C62)$	$sp^{3.55}d^{0.01}$	s(21.94%) p(77.95%) d(0.12%)
2F	$\sigma\,(B1-C2)$	$sp^{2.47}d^{0}$	s(28.80%) p(71.10%) d(0.10%)
	$\sigma\,(B1-C10)$	$sp^{2.63}d^{0}$	s(27.55%) p(72.34%) d(0.11%)
	$\sigma\,(B1-C18)$	$sp^{2.61}d^{0}$	s(27.64%) p(72.24%) d(0.11%)
	$\sigma\,(B1-F62)$	$sp^{2.95}d^{0}$	s(27.05%) p(72.86%) d(0.10%)
3	$\sigma\,(B1-C2)$	$sp^{2.00}d^{0}$	s(33.32%) p(66.59%) d(0.10%)
	$\sigma\,(B1-C10)$	$sp^{2.00}d^{0}$	s(33.33%) p(66.58%) d(0.10%)
	$\sigma\,(B1-C18)$	$sp^{2.00}d^{0}$	s(33.31%) p(66.60%) d(0.10%)
3CN	$\sigma\,(B1-C2)$	$sp^{2.85}d^{0}$	s(25.96%) p(73.95%) d(0.09%)
	$\sigma\,(B1-C10)$	$sp^{2.84}d^{0}$	s(25.99%) p(73.92%) d(0.09%)
	$\sigma\,(B1-C18)$	$sp^{2.84}d^{0}$	s(25.99%) p(73.92%) d(0.09%)
	$\sigma\,(B1-C62)$	$sp^{3.52}d^{0.01}$	s(22.09%) p(77.80%) d(0.11%)
3F	$\sigma\,(B1-C2)$	$sp^{2.58}d^{0}$	s(27.90%) p(71.99%) d(0.11%)
	$\sigma\,(B1-C10)$	$sp^{2.58}d^{0}$	s(27.92%) p(71.97%) d(0.11%)
	$\sigma\,(B1-C18)$	$sp^{2.58}d^{0}$	s(27.91%) p(71.98%) d(0.11%)
	$\sigma\,(B1-F62)$	$sp^{2.87}d^{0}$	s(27.05%) p(72.86%) d(0.10%)

[a] Hybrid on A atom in the A-B Bond or otherwise as indicated.
[b] Percentage Contribution of Atomic Orbitals in NBO Hybrid.

Table S10: Calculated Electronic Excitation Energies and Corresponding Oscillator Strengths of Singlet Excited States of **1-3**, **1F-3F** and **1CN-3CN** at DFT/CAM-B3LYP/6-31G(d) Level

of Theory.

molecule	electronic transition[a]	energy (nm/eV)	f[b]	contrib.[c]	CI[d]
1	$S_0 \rightarrow S_1$	322(3.85)	0.1745	HOMO→LUMO	0.658
	$S_0 \rightarrow S_2$	302 (4.10)	0.0115	HOMO-1→LUMO	0.626
	$S_0 \rightarrow S_3$	284 (4.35)	0.0140	HOMO-2→LUMO	0.638
	$S_0 \rightarrow S_4$	279 (4.43)	0.0015	HOMO-3→LUMO	0.629
	$S_0 \rightarrow S_5$	264 (4.68)	0.0018	HOMO-4→LUMO	0.640
	$S_0 \rightarrow S_6$	255 (4.84)	0.0071	HOMO-5→LUMO	0.637
	$S_0 \rightarrow S_7$	232 (5.35)	0.0196	HOMO→LUMO+1	0.596
	$S_0 \rightarrow S_8$	225 (5.51)	0.0033	HOMO-1→LUMO+1	0.334
	$S_0 \rightarrow S_9$	224 (5.52)	0.0009	HOMO-2→LUMO+1	0.323
	$S_0 \rightarrow S_{10}$	220 (5.63)	0.0268	HOMO-7→LUMO	0.399
	$S_0 \rightarrow S_{11}$	216 (5.72)	0.0211	HOMO-6→LUMO	0.571
	$S_0 \rightarrow S_{12}$	213 (5.81)	0.0077	HOMO-1→LUMO+1	0.434
	$S_0 \rightarrow S_{13}$	211 (5.87)	0.0086	HOMO-4→LUMO+1	0.534
	$S_0 \rightarrow S_{14}$	205(6.05)	0.0045	HOMO-5→LUMO+1	0.413
	$S_0 \rightarrow S_{15}$	201 (6.15)	0.0124	HOMO-2→LUMO+1	0.504
1F	$S_0 \rightarrow S_1$	257 (4.80)	0.0021	HOMO→LUMO	0.592
	$S_0 \rightarrow S_2$	246 (5.02)	0.0082	HOMO-5→LUMO	0.601
	$S_0 \rightarrow S_3$	245 (5.05)	0.0126	HOMO-1→LUMO	0.485
				HOMO→LUMO	0.104
	$S_0 \rightarrow S_4$	235 (5.27)	0.0081	HOMO→LUMO+7	0.292
	$S_0 \rightarrow S_5$	234 (5.29)	0.0029	HOMO→LUMO+6	0.346
	$S_0 \rightarrow S_6$	230 (5.37)	0.0082	HOMO-1→LUMO	0.458
	$S_0 \rightarrow S_7$	217 (5.70)	0.0061	HOMO-2→LUMO	0.517
	$S_0 \rightarrow S_8$	216 (5.75)	0.0014	HOMO-3→LUMO	0.307
	$S_0 \rightarrow S_9$	215 (5.78)	0.0041	HOMO-3→LUMO	0.418
	$S_0 \rightarrow S_{10}$	214 (5.80)	0.0016	HOMO→LUMO+1	0.474
	$S_0 \rightarrow S_{11}$	211 (5.87)	0.0050	HOMO-6→LUMO	0.465
	$S_0 \rightarrow S_{12}$	209 (5.91)	0.0035	HOMO→LUMO+4	0.246
	$S_0 \rightarrow S_{13}$	204 (6.06)	0.0042	HOMO-7→LUMO	0.301
	$S_0 \rightarrow S_{14}$	202 (6.11)	0.0010	HOMO-7→LUMO	0.452
	$S_0 \rightarrow S_{15}$	200 (6.18)	0.0021	HOMO-4→LUMO+1	0.236

1CN	$S_0 \rightarrow S_1$	251 (4.93)	0.0040	HOMO-5→LUMO	0.514
	$S_0 \rightarrow S_2$	246 (5.03)	0.0019	HOMO-1→LUMO	0.523
	$S_0 \rightarrow S_3$	240 (5.15)	0.0046	HOMO→LUMO	0.515
	$S_0 \rightarrow S_4$	238 (5.20)	0.0143	HOMO-4→LUMO	0.550
				HOMO→LUMO	0.229
	$S_0 \rightarrow S_5$	236 (5.24)	0.0013	HOMO→LUMO+7	0.267
	$S_0 \rightarrow S_6$	235 (5.26)	0.0029	HOMO→LUMO	0.357
	$S_0 \rightarrow S_7$	219 (5.65)	0.0014	HOMO-2→LUMO	0.591
	$S_0 \rightarrow S_8$	216 (5.73)	0.0023	HOMO→LUMO+3	0.376
	$S_0 \rightarrow S_9$	214 (5.78)	0.0021	HOMO-3→LUMO	0.597
	$S_0 \rightarrow S_{10}$	211 (5.84)	0.0013	HOMO-1→LUMO+3	0.314
	$S_0 \rightarrow S_{11}$	208 (5.94)	0.0005	HOMO-1→LUMO+1	0.511
	$S_0 \rightarrow S_{12}$	201 (6.14)	0.0021	HOMO-4→LUMO+1	0.379
	$S_0 \rightarrow S_{13}$	200 (6.18)	0.0022	HOMO-7→LUMO	0.441
	$S_0 \rightarrow S_{14}$	198 (6.23)	0.0013	HOMO→LUMO+1	0.419
	$S_0 \rightarrow S_{15}$	197 (6.27)	0.0034	HOMO-5→LUMO	0.298
2	$S_0 \rightarrow S_1$	324 (3.82)	0.1955	HOMO→LUMO	0.664
	$S_0 \rightarrow S_2$	300 (4.13)	0.0187	HOMO-1→LUMO	0.622
	$S_0 \rightarrow S_3$	287 (4.30)	0.0200	HOMO-3→LUMO	0.464
	$S_0 \rightarrow S_4$	272 (4.55)	0.0018	HOMO-2→LUMO	0.553
	$S_0 \rightarrow S_5$	270 (4.58)	0.0071	HOMO-4→LUMO	0.522
	$S_0 \rightarrow S_6$	253 (4.88)	0.0195	HOMO-5→LUMO	0.667
	$S_0 \rightarrow S_7$	233 (5.31)	0.0083	HOMO→LUMO+1	0.603
	$S_0 \rightarrow S_8$	224 (5.53)	0.0026	HOMO-6→LUMO	0.374
	$S_0 \rightarrow S_9$	223 (5.55)	0.0077	HOMO→LUMO+7	0.379
	$S_0 \rightarrow S_{10}$	221 (5.60)	0.0104	HOMO-4→LUMO+1	0.370
	$S_0 \rightarrow S_{11}$	220 (5.62)	0.0014	HOMO-2→LUMO+1	0.437
	$S_0 \rightarrow S_{12}$	217 (5.70)	0.0205	HOMO-7→LUMO	0.414
	$S_0 \rightarrow S_{13}$	215 (5.76)	0.0053	HOMO-1→LUMO+1	0.624
	$S_0 \rightarrow S_{14}$	213 (5.81)	0.0116	HOMO→LUMO+2	0.569
	$S_0 \rightarrow S_{15}$	211 (5.86)	0.0051	HOMO-4→LUMO+1	0.366
2F	$S_0 \rightarrow S_1$	251 (4.92)	0.0066	HOMO→LUMO	0.525
	$S_0 \rightarrow S_2$	249 (4.97)	0.0012	HOMO→LUMO+1	0.329
	$S_0 \rightarrow S_3$	246 (5.02)	0.0035	HOMO-5→LUMO	0.396
	$S_0 \rightarrow S_4$	244 (5.07)	0.0068	HOMO→LUMO+1	0.392
	$S_0 \rightarrow S_5$	240 (5.14)	0.0149	HOMO-2→LUMO+1	0.552
				HOMO-1→LUMO+1	0.142
	$S_0 \rightarrow S_6$	236 (5.25)	0.0025	HOMO-2→LUMO	0.504

	$S_0 \rightarrow S_7$	233 (5.30)	0.0049	HOMO→LUMO+9	0.480
	$S_0 \rightarrow S_8$	221 (5.60)	0.0018	HOMO-3→LUMO	0.404
	$S_0 \rightarrow S_9$	218 (5.67)	0.0031	HOMO-3→LUMO+1	0.393
	$S_0 \rightarrow S_{10}$	216 (5.72)	0.0015	HOMO-1→LUMO	0.551
	$S_0 \rightarrow S_{11}$	213 (5.80)	0.0005	HOMO-1→LUMO+1	0.647
	$S_0 \rightarrow S_{12}$	212 (5.83)	0.0007	HOMO→LUMO+6	0.475
	$S_0 \rightarrow S_{13}$	207 (5.98)	0.0022	HOMO→LUMO+3	0.438
	$S_0 \rightarrow S_{14}$	205 (6.02)	0.0030	HOMO→LUMO+2	0.435
	$S_0 \rightarrow S_{15}$	201 (6.16)	0.0014	HOMO-7→LUMO	0.335
2CN	$S_0 \rightarrow S_1$	250 (4.94)	0.0046	HOMO-4→LUMO	0.405
	$S_0 \rightarrow S_2$	251 (4.95)	0.0034	HOMO-5→LUMO	0.329
	$S_0 \rightarrow S_3$	245 (5.04)	0.0017	HOMO→LUMO	0.524
	$S_0 \rightarrow S_4$	239 (5.18)	0.0159	HOMO-2→LUMO+1	0.431
				HOMO-3→LUMO	0.392
	$S_0 \rightarrow S_5$	236 (5.24)	0.0019	HOMO→LUMO+1	0.408
	$S_0 \rightarrow S_6$	235 (5.25)	0.0043	HOMO→LUMO+7	0.403
	$S_0 \rightarrow S_7$	233 (5.31)	0.0048	HOMO→LUMO+1	0.384
	$S_0 \rightarrow S_8$	220 (5.62)	0.0010	HOMO-1→LUMO	0.627
	$S_0 \rightarrow S_9$	217 (5.69)	0.0040	HOMO-3→LUMO+1	0.337
	$S_0 \rightarrow S_{10}$	213 (5.81)	0.0046	HOMO→LUMO+6	0.424
	$S_0 \rightarrow S_{11}$	212 (5.82)	0.0030	HOMO-1→LUMO+1	0.544
	$S_0 \rightarrow S_{12}$	209 (5.90)	0.0011	HOMO-2→LUMO+1	0.316
	$S_0 \rightarrow S_{13}$	205 (6.03)	0.0060	HOMO→LUMO+3	0.447
	$S_0 \rightarrow S_{14}$	201 (6.16)	0.0023	HOMO-2→LUMO+2	0.464
	$S_0 \rightarrow S_{15}$	200 (6.19)	0.0030	HOMO→LUMO+2	0.383
3	$S_0 \rightarrow S_1$	302 (4.10)	0.1433	HOMO-4→LUMO	0.485
	$S_0 \rightarrow S_2$	301 (4.11)	0.0015	HOMO-3→LUMO	0.529
	$S_0 \rightarrow S_3$	283 (4.37)	0.0082	HOMO-1→LUMO	0.467
	$S_0 \rightarrow S_4$	282 (4.40)	0.0080	HOMO-2→LUMO	0.463
	$S_0 \rightarrow S_5$	281(4.41)	0.0010	HOMO-4→LUMO	0.453
	$S_0 \rightarrow S_6$	255 (4.84)	0.0000	HOMO-5→LUMO	0.682
	$S_0 \rightarrow S_7$	227 (5.46)	0.0076	HOMO-2→LUMO+1	0.425
	$S_0 \rightarrow S_8$	226 (5.47)	0.0055	HOMO→LUMO+2	0.343
	$S_0 \rightarrow S_9$	225 (5.49)	0.0026	HOMO-2→LUMO+2	0.317
	$S_0 \rightarrow S_{10}$	223 (5.55)	0.0031	HOMO-6→LUMO	0.394
	$S_0 \rightarrow S_{11}$	222 (5.57)	0.0027	HOMO-7→LUMO	0.398
	$S_0 \rightarrow S_{12}$	213 (5.81)	0.0006	HOMO-3→LUMO+1	0.434
		211 (5.88)	0.0038	HOMO-7→LUMO	0.417

	$S_0 \rightarrow S_{13}$	210 (5.89)	0.0087	HOMO-6→LUMO	0.415
	$S_0 \rightarrow S_{14}$	209 (5.93)	0.0015	HOMO-3→LUMO+2	0.432
	$S_0 \rightarrow S_{15}$				
3F	$S_0 \rightarrow S_1$	248 (4.99)	0.0051	HOMO-2→LUMO	0.364
	$S_0 \rightarrow S_2$	248 (5.00)	0.0041	HOMO-2→LUMO+1	0.353
	$S_0 \rightarrow S_3$	247 (5.01)	0.0058	HOMO-1→LUMO+2	0.364
	$S_0 \rightarrow S_4$	240 (5.18)	0.0157	HOMO→LUMO+1	0.360
				HOMO-1→LUMO+1	0.349
	$S_0 \rightarrow S_5$	239 (5.19)	0.0055	HOMO→LUMO	0.366
	$S_0 \rightarrow S_6$	233 (5.31)	0.0020	HOMO→LUMO	0.373
	$S_0 \rightarrow S_7$	230 (5.39)	0.0016	HOMO-1→LUMO+2	0.438
	$S_0 \rightarrow S_8$	229 (5.40)	0.0002	HOMO→LUMO+2	0.463
	$S_0 \rightarrow S_9$	226 (5.46)	0.0037	HOMO→LUMO+1	0.417
	$S_0 \rightarrow S_{10}$	203 (6.12)	0.0042	HOMO-5→LUMO+2	0.395
	$S_0 \rightarrow S_{11}$	202 (6.13)	0.0027	HOMO-5→LUMO	0.501
	$S_0 \rightarrow S_{12}$	201 (6.14)	0.0008	HOMO-5→LUMO+1	0.477
	$S_0 \rightarrow S_{13}$	198 (6.28)	0.0034	HOMO→LUMO+4	0.292
	$S_0 \rightarrow S_{14}$	197 (6.29)	0.0028	HOMO→LUMO+4	0.349
	$S_0 \rightarrow S_{15}$	196 (6.30)	0.0017	HOMO-1→LUMO+3	0.299
3CN	$S_0 \rightarrow S_1$	251 (4.94)	0.0038	HOMO→LUMO+1	0.372
	$S_0 \rightarrow S_2$	250 (4.95)	0.0046	HOMO-2→LUMO	0.274
	$S_0 \rightarrow S_3$	249 (4.97)	0.0043	HOMO-5→LUMO	0.325
	$S_0 \rightarrow S_4$	238 (5.21)	0.0160	HOMO-3→LUMO+1	0.334
				HOMO-5→LUMO+1	0.116
	$S_0 \rightarrow S_5$	237(5.22)	0.0060	HOMO-3→LUMO+1	0.350
	$S_0 \rightarrow S_6$	228 (5.43)	0.0092	HOMO-1→LUMO	0.326
	$S_0 \rightarrow S_7$	221 (5.60)	0.0024	HOMO-1→LUMO+1	0.311
	$S_0 \rightarrow S_8$	217 (5.71)	0.0017	HOMO-2→LUMO+2	0.290
	$S_0 \rightarrow S_9$	216 (5.72)	0.0016	HOMO-1→LUMO+2	0.325
	$S_0 \rightarrow S_{10}$	204 (6.07)	0.0013	HOMO-3→LUMO+1	0.452
	$S_0 \rightarrow S_{11}$	203 (6.08)	0.0011	HOMO-3→LUMO	0.454
	$S_0 \rightarrow S_{12}$	201 (6.15)	0.0026	HOMO-3→LUMO+2	0.433
	$S_0 \rightarrow S_{13}$	200 (6.18)	0.0009	HOMO→LUMO	0.332
	$S_0 \rightarrow S_{14}$	199 (6.22)	0.0027	HOMO→LUMO+1	0.337
		198 (6.26)	0.0024	HOMO-2→LUMO+3	0.313

		$S_0 \rightarrow S_{15}$				

[a] Only the Selected Low-lying Excited States are Presented. [b] Oscillator Strength. [c] Only the Main Configurations are Presented. [d] The CI Coefficients are in Absolute Values.

Table S11: Calculated Electronic Excitation Energies and Corresponding Oscillator Strengths of the Low-Lying Singlet Excited States of **1-2, 1CN-2CN** and **1F-2F** by Employing Different Functionals.

functional	molecule	electronic transition[a]	energy (nm/eV)	f[b]	contrib.[c]	CI[d]
M06-2X	**1**	$S_0 \rightarrow S_1$	328 (3.77)	0.1572	HOMO→LUMO	0.665
		$S_0 \rightarrow S_2$	308 (4.01)	0.0197	HOMO-1→LUMO	0.591
		$S_0 \rightarrow S_3$	288 (4.29)	0.0059	HOMO-2→LUMO	0.621
		$S_0 \rightarrow S_4$	281 (4.41)	0.0098	HOMO-3→LUMO	0.649
		$S_0 \rightarrow S_5$	263 (4.69)	0.0638	HOMO-4→LUMO	0.647
		$S_0 \rightarrow S_6$	260 (4.76)	0.0309	HOMO-5→LUMO	0.623
M06-2X	**1F**	$S_0 \rightarrow S_1$	266 (4.65)	0.0069	HOMO→LUMO	0.589
		$S_0 \rightarrow S_2$	247 (5.00)	0.0017	HOMO-1→LUMO	0.566
		$S_0 \rightarrow S_3$	244 (5.06)	0.0329	HOMO-5→LUMO	0.592
		$S_0 \rightarrow S_4$	234 (5.29)	0.0042	HOMO-4→LUMO	0.403
		$S_0 \rightarrow S_5$	232 (5.32)	0.0024	HOMO-2→LUMO+3	0.319
		$S_0 \rightarrow S_6$	231 (5.35)	0.0013	HOMO-4→LUMO	0.348
M06-2X	**1CN**	$S_0 \rightarrow S_1$	254 (4.87)	0.0050	HOMO-1→LUMO	0.603
		$S_0 \rightarrow S_2$	247 (5.01)	0.0021	HOMO-5→LUMO	0.546
		$S_0 \rightarrow S_3$	244 (5.07)	0.0017	HOMO→LUMO	0.623
		$S_0 \rightarrow S_4$	236 (5.23)	0.0135	HOMO-4→LUMO	0.608

		$S_0 \rightarrow S_5$	235 (5.26)	0.0023	HOMO→LUMO+6	0.325
		$S_0 \rightarrow S_6$	235 (5.27)	0.0021	HOMO-1→LUMO+5	0.351
B3PW91	**1**	$S_0 \rightarrow S_1$	380 (3.25)	0.1207	HOMO→LUMO	0.701
		$S_0 \rightarrow S_2$	355 (3.48)	0.0603	HOMO-2→LUMO	0.690
		$S_0 \rightarrow S_3$	352 (3.51)	0.0204	HOMO-1→LUMO	0.696
		$S_0 \rightarrow S_4$	342 (3.62)	0.0596	HOMO-3→LUMO	0.699
		$S_0 \rightarrow S_5$	296 (4.18)	0.0374	HOMO-4→LUMO	0.691
		$S_0 \rightarrow S_6$	291 (4.25)	0.0713	HOMO-5→LUMO	0.655
B3PW91	**1F**	$S_0 \rightarrow S_1$	333 (3.72)	0.0046	HOMO→LUMO	0.697
		$S_0 \rightarrow S_2$	321 (3.85)	0.0016	HOMO-1→LUMO	0.703
		$S_0 \rightarrow S_3$	296 (4.17)	0.0143	HOMO-2→LUMO	0.703
		$S_0 \rightarrow S_4$	290 (4.26)	0.0001	HOMO-3→LUMO	0.703
		$S_0 \rightarrow S_5$	277 (4.47)	0.0022	HOMO-4→LUMO	0.688
		$S_0 \rightarrow S_6$	265 (4.66)	0.0012	HOMO→LUMO+1	0.671
B3PW91	**1CN**	$S_0 \rightarrow S_1$	321 (3.85)	0.0075	HOMO-1→LUMO	0.647
		$S_0 \rightarrow S_2$	320 (3.86)	0.0050	HOMO→LUMO	0.653
		$S_0 \rightarrow S_3$	300 (4.12)	0.0035	HOMO-2→LUMO	0.699
		$S_0 \rightarrow S_4$	291 (4.25)	0.0126	HOMO-3→LUMO	0.703
		$S_0 \rightarrow S_5$	264 (4.69)	0.0044	HOMO-4→LUMO	0.636
		$S_0 \rightarrow S_6$	263 (4.71)	0.0080	HOMO-5→LUMO	0.579
HCTH	**1**	$S_0 \rightarrow S_1$	442 (2.80)	0.1563	HOMO→LUMO	0.699
		$S_0 \rightarrow S_2$	423 (2.92)	0.0100	HOMO-2→LUMO	0.699
		$S_0 \rightarrow S_3$	422 (2.93)	0.0071	HOMO-1→LUMO	0.647
		$S_0 \rightarrow S_4$	409 (3.02)	0.0542	HOMO-3→LUMO	0.647
		$S_0 \rightarrow S_5$	335 (3.69)	0.0057	HOMO→LUMO+1	0.683
		$S_0 \rightarrow S_6$	327 (3.79)	0.0344	HOMO-1→LUMO+1	0.524

HCTH	**1F**	$S_0 \rightarrow S_1$	429 (2.88)	0.0032	HOMO→LUMO	0.704
		$S_0 \rightarrow S_2$	421 (2.93)	0.0083	HOMO-1→LUMO	0.702
		$S_0 \rightarrow S_3$	389 (3.18)	0.0187	HOMO-2→LUMO	0.706
		$S_0 \rightarrow S_4$	381 (3.24)	0.0001	HOMO-3→LUMO	0.705
		$S_0 \rightarrow S_5$	358 (3.46)	0.0018	HOMO-4→LUMO	0.694
		$S_0 \rightarrow S_6$	329 (3.76)	0.0068	HOMO-5→LUMO	0.692
HCTH	**1CN**	$S_0 \rightarrow S_1$	417 (2.97)	0.0020	HOMO→LUMO	0.706
		$S_0 \rightarrow S_2$	412 (3.00)	0.0076	HOMO-1→LUMO	0.706
		$S_0 \rightarrow S_3$	392 (3.15)	0.0023	HOMO-2→LUMO	0.706
		$S_0 \rightarrow S_4$	382 (3.24)	0.0181	HOMO-3→LUMO	0.706
		$S_0 \rightarrow S_5$	323 (3.83)	0.0012	HOMO→LUMO+1	0.706
		$S_0 \rightarrow S_6$	321 (3.85)	0.0014	HOMO-1→LUMO+1	0.706
LSDA	**1**	$S_0 \rightarrow S_1$	474 (2.61)	0.1687	HOMO→LUMO	0.686
		$S_0 \rightarrow S_2$	448 (2.76)	0.0381	HOMO-1→LUMO	0.687
		$S_0 \rightarrow S_3$	436 (2.84)	0.0245	HOMO-2→LUMO	0.646
		$S_0 \rightarrow S_4$	415 (2.98)	0.0703	HOMO-3→LUMO	0.645
		$S_0 \rightarrow S_5$	354 (3.49)	0.0518	HOMO→LUMO+1	0.638
		$S_0 \rightarrow S_6$	349 (3.54)	0.0313	HOMO-4→LUMO	0.583
LSDA	**1F**	$S_0 \rightarrow S_1$	446 (2.77)	0.0016	HOMO→LUMO	0.704
		$S_0 \rightarrow S_2$	431 (2.87)	0.0015	HOMO-1→LUMO	0.701
		$S_0 \rightarrow S_3$	397 (3.11)	0.0192	HOMO-2→LUMO	0.705
		$S_0 \rightarrow S_4$	379 (3.27)	0.0011	HOMO-3→LUMO	0.705
		$S_0 \rightarrow S_5$	357 (3.46)	0.0020	HOMO-4→LUMO	0.687
		$S_0 \rightarrow S_6$	338 (3.65)	0.0003	HOMO→LUMO+1	0.704

LSDA	**1CN**	$S_0 \rightarrow S_1$	427 (2.89)	0.0034	HOMO→LUMO	0.701
		$S_0 \rightarrow S_2$	422 (2.93)	0.0038	HOMO-1→LUMO	0.701
		$S_0 \rightarrow S_3$	395 (3.13)	0.0043	HOMO-2→LUMO	0.704
		$S_0 \rightarrow S_4$	375 (3.30)	0.0139	HOMO-3→LUMO	0.702
		$S_0 \rightarrow S_5$	331 (3.74)	0.0015	HOMO→LUMO+1	0.704
		$S_0 \rightarrow S_6$	328 (3.77)	0.0005	HOMO-1→LUMO+1	0.704
M06-2X	**2**	$S_0 \rightarrow S_1$	329 (3.76)	0.1856	HOMO→LUMO	0.666
		$S_0 \rightarrow S_2$	304 (4.07)	0.0235	HOMO-1→LUMO	0.580
		$S_0 \rightarrow S_3$	293 (4.22)	0.0440	HOMO-2→LUMO	0.486
		$S_0 \rightarrow S_4$	271 (4.56)	0.0532	HOMO-3→LUMO	0.625
		$S_0 \rightarrow S_5$	270 (4.58)	0.0042	HOMO-4→LUMO	0.547
		$S_0 \rightarrow S_6$	256 (4.82)	0.0111	HOMO-5→LUMO	0.669
M06-2X	**2F**	$S_0 \rightarrow S_1$	258 (4.79)	0.0087	HOMO→LUMO	0.526
		$S_0 \rightarrow S_2$	254 (4.87)	0.0029	HOMO→LUMO+1	0.481
		$S_0 \rightarrow S_3$	245 (5.06)	0.0033	HOMO-4→LUMO+1	0.338
		$S_0 \rightarrow S_4$	244 (5.07)	0.0045	HOMO-4→LUMO	0.334
		$S_0 \rightarrow S_5$	241 (5.14)	0.0143	HOMO-2→LUMO+1	0.552
		$S_0 \rightarrow S_6$	236 (5.25)	0.0026	HOMO-2→LUMO	0.521
M06-2X	**2CN**	$S_0 \rightarrow S_1$	253 (4.91)	0.0075	HOMO→LUMO	0.584
		$S_0 \rightarrow S_2$	248 (4.98)	0.0018	HOMO-4→LUMO	0.391
		$S_0 \rightarrow S_3$	247 (5.02)	0.0014	HOMO-5→LUMO	0.420
		$S_0 \rightarrow S_4$	241 (5.14)	0.0143	HOMO→LUMO+1	0.503
		$S_0 \rightarrow S_5$	236 (5.24)	0.0061	HOMO-3→LUMO	0.431
		$S_0 \rightarrow S_6$	235 (5.27)	0.0032	HOMO→LUMO+7	0.473

B3PW91	**2**	$S_0 \rightarrow S_1$	380 (3.25)	0.1527	HOMO→LUMO	0.699
		$S_0 \rightarrow S_2$	373 (3.32)	0.0074	HOMO-1→LUMO	0.702
		$S_0 \rightarrow S_3$	327 (3.78)	0.0306	HOMO-3→LUMO	0.466
		$S_0 \rightarrow S_4$	316 (3.92)	0.0230	HOMO-2→LUMO	0.538
		$S_0 \rightarrow S_5$	312 (3.96)	0.0464	HOMO-4→LUMO	0.624
		$S_0 \rightarrow S_6$	294 (4.20)	0.0277	HOMO→LUMO+1	0.703
B3PW91	**2F**	$S_0 \rightarrow S_1$	324 (3.81)	0.0052	HOMO→LUMO	0.695
		$S_0 \rightarrow S_2$	319 (3.87)	0.0032	HOMO→LUMO+1	0.695
		$S_0 \rightarrow S_3$	296 (4.18)	0.0004	HOMO-1→LUMO	0.704
		$S_0 \rightarrow S_4$	292 (4.23)	0.0010	HOMO-1→LUMO+1	0.700
		$S_0 \rightarrow S_5$	281 (4.40)	0.0112	HOMO-2→LUMO+1	0.590
		$S_0 \rightarrow S_6$	280 (4.41)	0.0079	HOMO-2→LUMO	0.585
B3PW91	**2CN**	$S_0 \rightarrow S_1$	324 (3.81)	0.0052	HOMO→LUMO	0.696
		$S_0 \rightarrow S_2$	319 (3.87)	0.0032	HOMO→LUMO+1	0.695
		$S_0 \rightarrow S_3$	296 (4.18)	0.0004	HOMO-1→LUMO	0.704
		$S_0 \rightarrow S_4$	292 (4.23)	0.0152	HOMO→LUMO+1	0.700
		$S_0 \rightarrow S_5$	281 (4.40)	0.0011	HOMO-2→LUMO+1	0.590
		$S_0 \rightarrow S_6$	280 (4.41)	0.0070	HOMO-2→LUMO	0.585
HCTH	**2**	$S_0 \rightarrow S_1$	452 (2.74)	0.1372	HOMO→LUMO	0.698
		$S_0 \rightarrow S_2$	445 (2.78)	0.0183	HOMO-→LUMO	0.695
		$S_0 \rightarrow S_3$	370 (3.34)	0.0035	HOMO→LUMO+1	0.696
		$S_0 \rightarrow S_4$	368 (3.37)	0.0002	HOMO-1→LUMO+1	0.701
		$S_0 \rightarrow S_5$	362 (3.42)	0.0203	HOMO-2→LUMO	0.631
		$S_0 \rightarrow S_6$	360 (3.44)	0.0376	HOMO-3→LUMO	0.634

HCTH	**2F**	$S_0 \rightarrow S_1$	417 (2.96)	0.0028	HOMO→LUMO	0.705
		$S_0 \rightarrow S_2$	412 (3.00)	0.0014	HOMO→LUMO+1	0.704
		$S_0 \rightarrow S_3$	387 (3.20)	0.0000	HOMO-1→LUMO	0.705
		$S_0 \rightarrow S_4$	382 (3.24)	0.0011	HOMO-1→LUMO+1	0.706
		$S_0 \rightarrow S_5$	354 (3.49)	0.0563	HOMO-2→LUMO	0.539
		$S_0 \rightarrow S_6$	352 (3.52)	0.0046	HOMO-2→LUMO+1	0.542
HCTH	**2CN**	$S_0 \rightarrow S_1$	415 (2.98)	0.0015	HOMO→LUMO	0.706
		$S_0 \rightarrow S_2$	397 (3.12)	0.0109	HOMO→LUMO+1	0.703
		$S_0 \rightarrow S_3$	393 (3.15)	0.0013	HOMO-1→LUMO	0.704
		$S_0 \rightarrow S_4$	377 (3.28)	0.0143	HOMO-1→LUMO+1	0.706
		$S_0 \rightarrow S_5$	328 (3.77)	0.0012	HOMO-2→LUMO	0.564
		$S_0 \rightarrow S_6$	319 (3.88)	0.0036	HOMO-2→LUMO+1	0.409
LSDA	**2**	$S_0 \rightarrow S_1$	450 (2.75)	0.1575	HOMO→LUMO	0.697
		$S_0 \rightarrow S_2$	424 (2.92)	0.0140	HOMO-1→LUMO	0.682
		$S_0 \rightarrow S_3$	389 (3.18)	0.0282	HOMO-2→LUMO	0.694
		$S_0 \rightarrow S_4$	384 (3.22)	0.0080	HOMO-3→LUMO	0.684
		$S_0 \rightarrow S_5$	346 (3.40)	0.0046	HOMO→LUMO+1	0.690
		$S_0 \rightarrow S_6$	361 (3.43)	0.0084	HOMO-4→LUMO	0.581
LSDA	**2F**	$S_0 \rightarrow S_1$	427 (2.90)	0.0044	HOMO→LUMO	0.670
		$S_0 \rightarrow S_2$	425 (2.91)	0.0008	HOMO→LUMO+1	0.669
		$S_0 \rightarrow S_3$	388 (3.19)	0.0001	HOMO-1→LUMO	0.694
		$S_0 \rightarrow S_4$	387 (3.20)	0.0051	HOMO-1→LUMO+1	0.698
		$S_0 \rightarrow S_5$	364 (3.40)	0.0574	HOMO-2→LUMO+1	0.540
		$S_0 \rightarrow S_6$	357 (3.46)	0.0042	HOMO-2→LUMO	0.530

LSDA	**2CN**	$S_0 \rightarrow S_1$	424(2.92)	0.0010	HOMO→LUMO	0.706
		$S_0 \rightarrow S_2$	403 (3.07)	0.0021	HOMO→LUMO+1	0.702
		$S_0 \rightarrow S_3$	394 (3.14)	0.0022	HOMO-1→LUMO	0.700
		$S_0 \rightarrow S_4$	377 (3.28)	0.0129	HOMO-1→LUMO+1	0.704
		$S_0 \rightarrow S_5$	337 (3.67)	0.0054	HOMO-2→LUMO	0.572
		$S_0 \rightarrow S_6$	327 (3.78)	0.0012	HOMO→LUMO+2	0.681

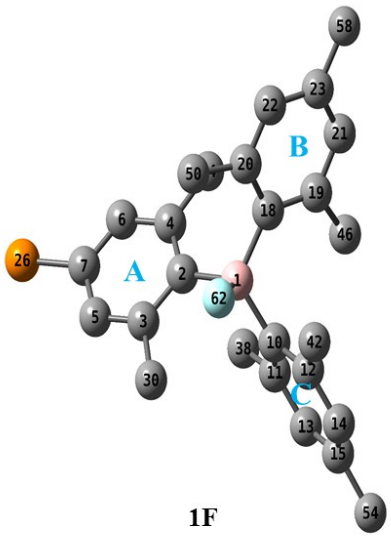
[a] Only the Selected Low-lying Excited States are Presented. [b] Oscillator sSrength. [c] Only the Main Configurations are Presented. [d] The CI Coefficients are in Absolute Values.

Table S12: Calculated Electronic De-Excitation Energies and Corresponding Oscillator Strengths of the Higher Singlet Excited States of **1F-3F** and **1CN-3CN** at DFT/CAM-B3LYP/631G(d) Level of Theory.

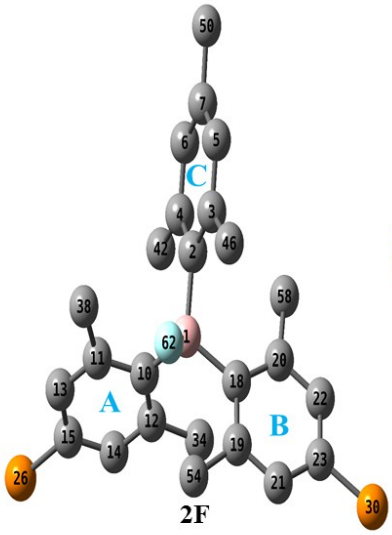
molecule	electronic de-excitation[a]	energy (eV)	f[b]	contrib.[c]	CI[d]
1F	$S_1 \leftarrow S_2$	0.74	0.0003	HOMO←LUMO	0.631
	$S_2 \leftarrow S_3$	0.70	0.0002	HOMO − 1←LUMO	0.565
1CN	$S_1 \leftarrow S_2$	0.49	0.0002	HOMO-1←LUMO	0.447
	$S_2 \leftarrow S_3$	0.41	0.0001	HOMO-5←LUMO	0.594
	$S_3 \leftarrow S_4$	0.30	0.0002	HOMO←LUMO	0.350
2F	$S_1 \leftarrow S_2$	0.42	0.0003	HOMO←LUMO	0.568
	$S_2 \leftarrow S_3$	0.31	0.0001	HOMO-1←LUMO	0.383
	$S_3 \leftarrow S_4$	0.23	0.0002	HOMO-1←LUMO	0.409
	$S_4 \leftarrow S_5$	0.19	0.0003	HOMO←LUMO+1	0.477
2CN	$S_1 \leftarrow S_2$	0.48	0.0003	HOMO-2←LUMO	0.631
	$S_2 \leftarrow S_3$	0.39	0.0001	HOMO-4←LUMO	0.509
	$S_3 \leftarrow S_4$	0.33	0.0002	HOMO←LUMO	0.677

	$S_1 \leftarrow S_2$	0.09	0.0002	HOMO←LUMO	0.657
3F	$S_2 \leftarrow S_3$	0.07	0.0004	HOMO-5←LUMO	0.421
	$S_3 \leftarrow S_4$	0.04	0.0002	HOMO-1←LUMO	0.602
	$S_1 \leftarrow S_2$	0.76	0.0003	HOMO←LUMO	0.693
3CN	$S_2 \leftarrow S_3$	0.51	0.0002	HOMO-1←LUMO	0.640
	$S_3 \leftarrow S_4$	0.33	0.0004	HOMO-4←LUMO	0.404

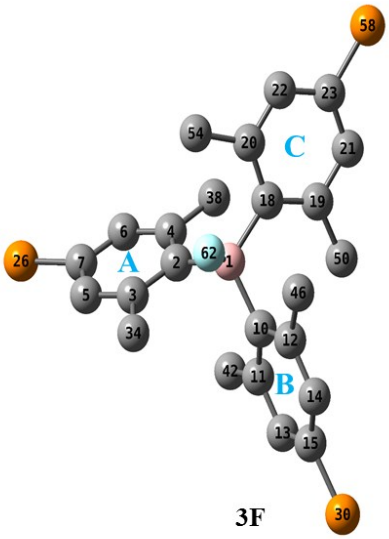
[a] Only the Selected Low-lying Excited States are Presented. [b] Oscillator sSrength. [c] Only the Main Configurations are Presented. [d] The CI Coefficients are in Absolute Values.



1F



2F



3F

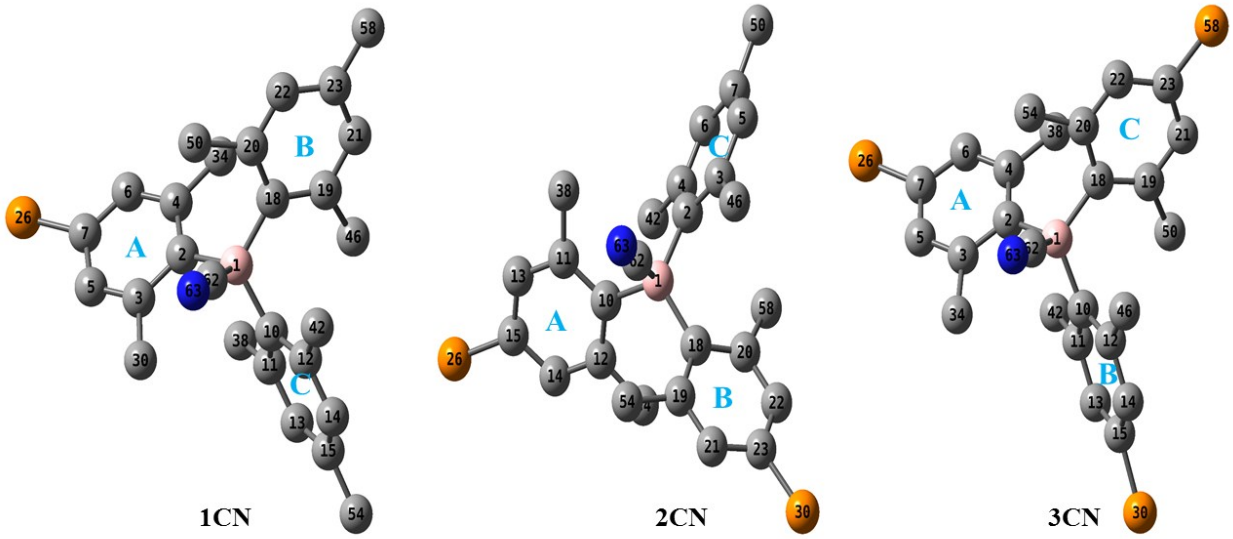
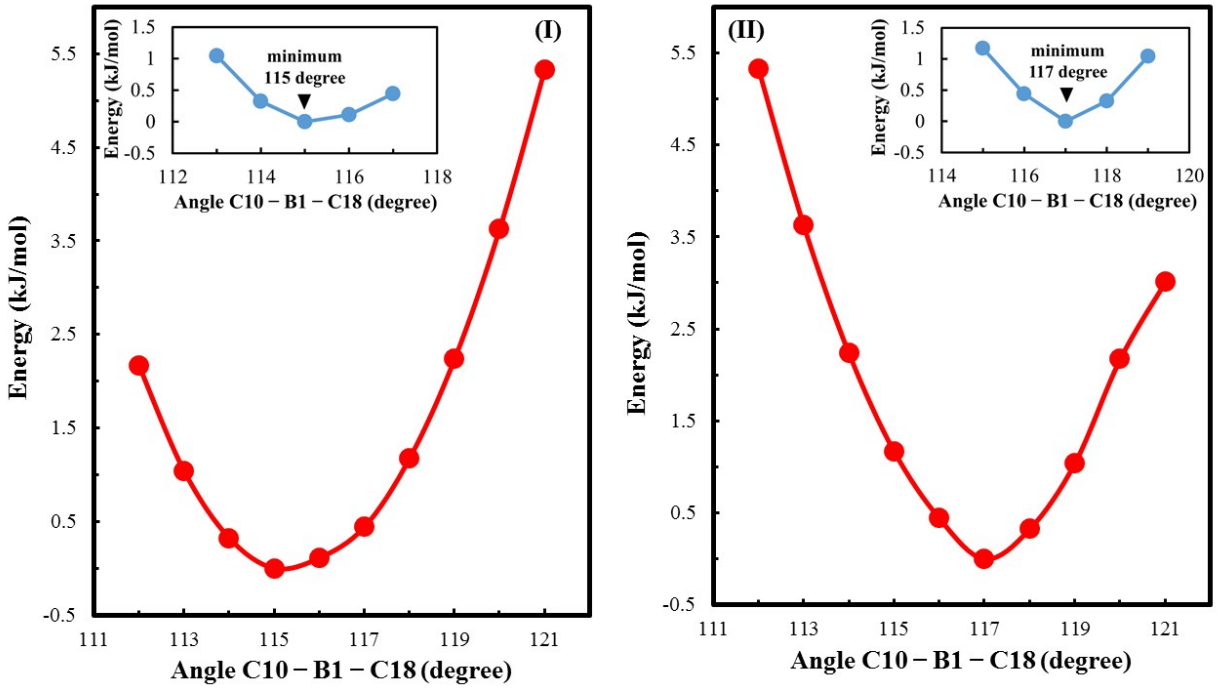


Figure S1: Ground state (S_0) optimized structures of **1F-3F** and **1CN-3CN** calculated at CAM-B3LYP/6-31G(d) level with the CPCM solvation model. Hydrogen atoms are omitted for clarity. In **1**, **2** and **3**, the cyanide and the fluoride ions are added at boron atoms with numbering 1. The numbering of atoms of added cyanide is C (62), N (63) and added fluoride is F (62). Geometry at boron centers in **1F-3F** and **1CN-3CN** is tetrahedral.



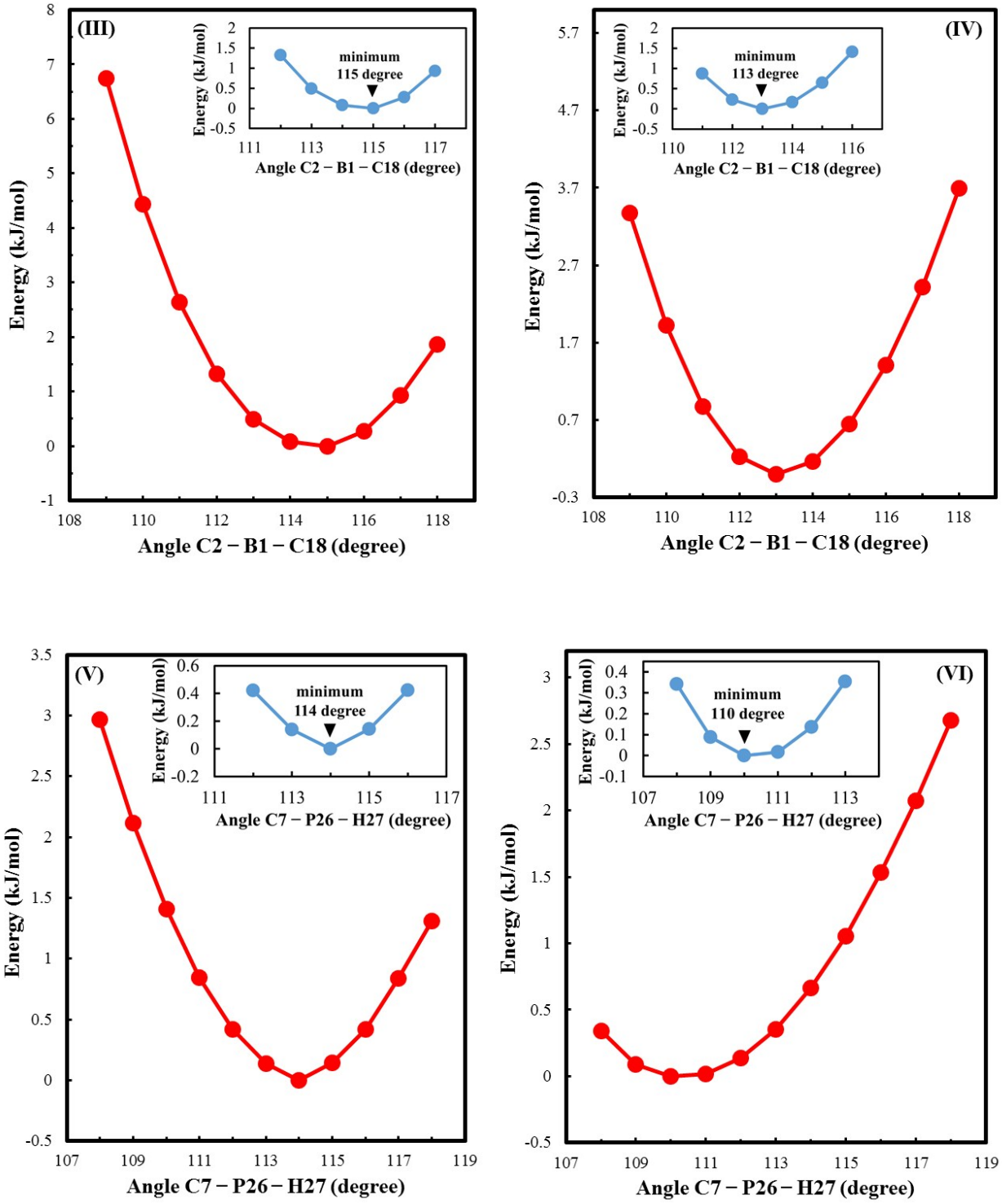


Figure S2: Potential energy curves of corresponding S_0 states of (I) **1F**, (III) **2F** and (V) **3F**; and corresponding S_1 states of (II) **1F**, (IV) **2F** and (VI) **3F** calculated at the CAM-B3LYP/6-31G(d) level with the CPCM solvation model as functions of the angles mentioned.

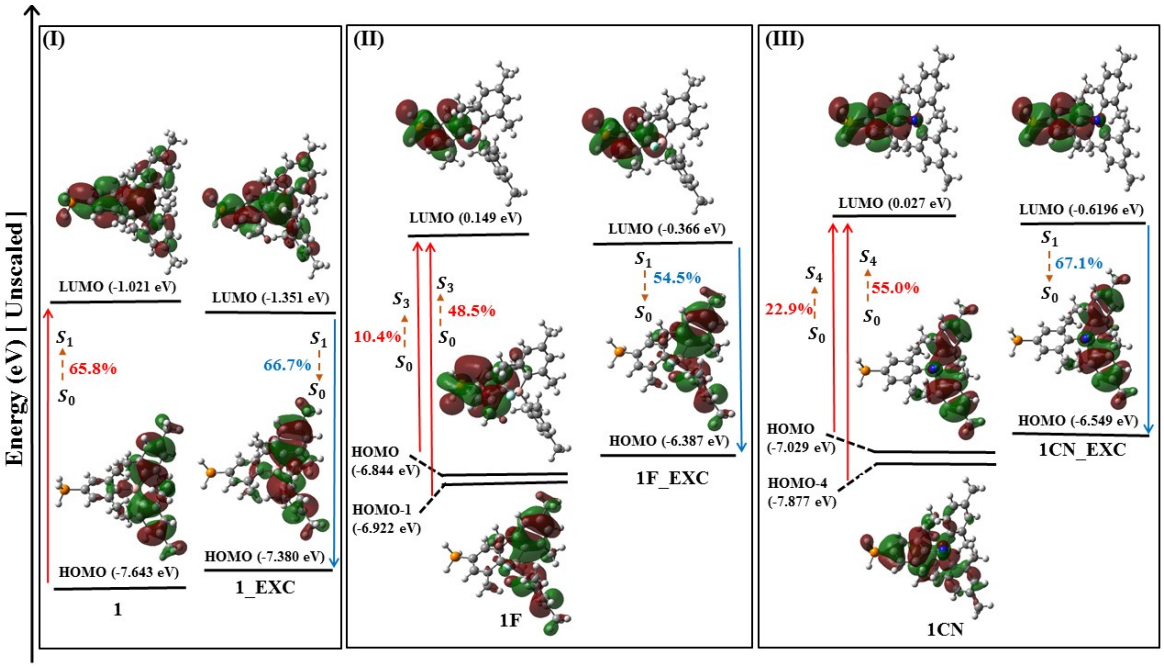


Figure S3: Calculated FMO energies for (I) **1** in ground state and excited state (**1_EXC**) (II) **1F** in ground state and excited state (**1F_EXC**) and (III) **1CN** in ground state and excited state (**1CN_EXC**) at CAM-B3LYP/6-31G(d) level using CPCM solvation model.

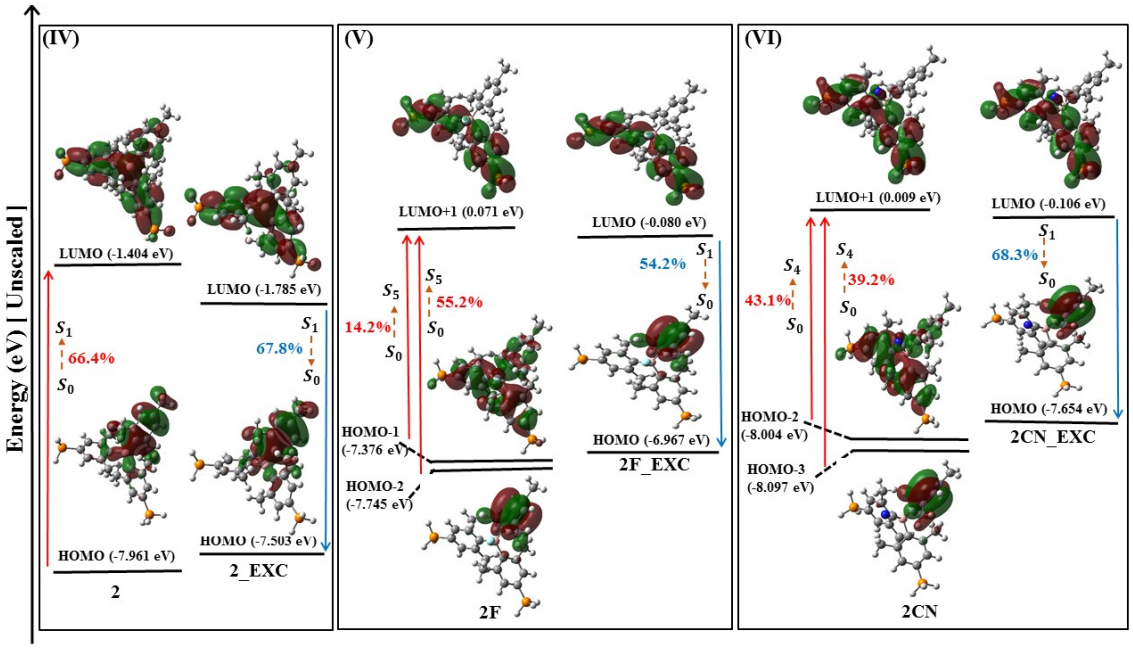


Figure S4: Calculated FMO energies for (IV) **2** in ground state and excited state (**2_EXC**) (V) **2F** in ground state and excited state (**2F_EXC**) and (VI) **2CN** in ground state and excited state (**2CN_EXC**) at CAM-B3LYP/6-31G(d) level using CPCM solvation model.

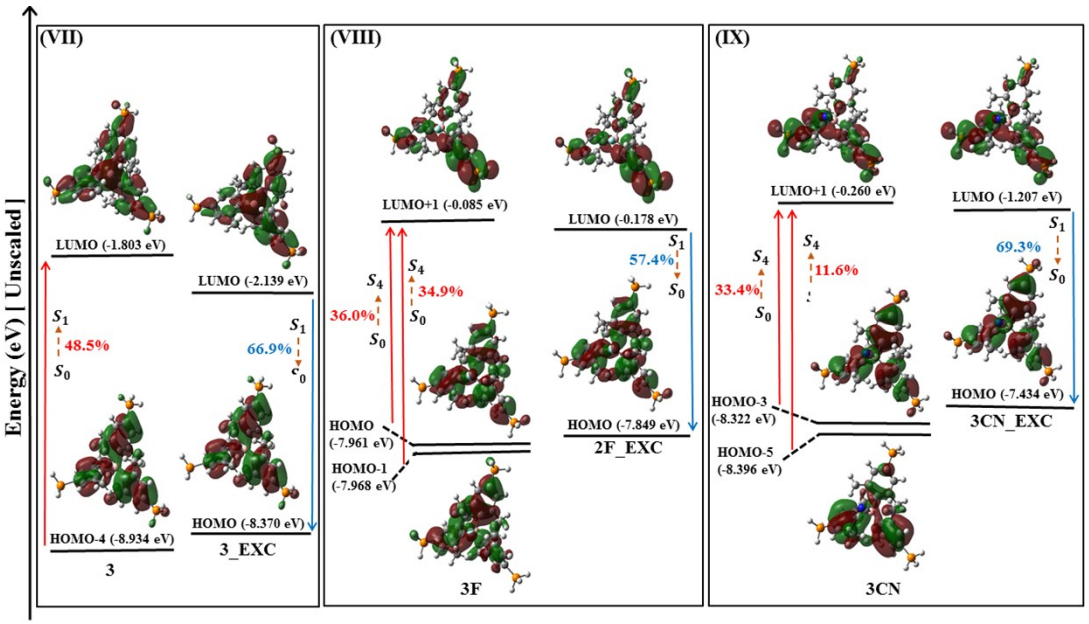
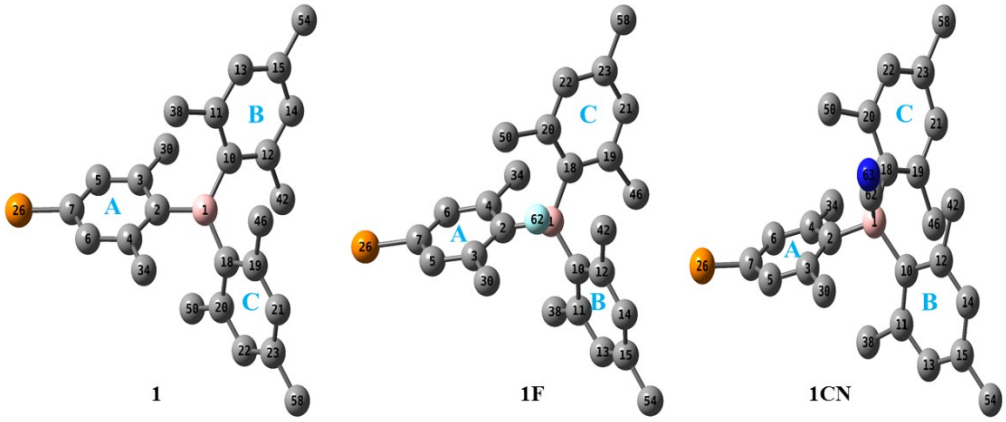


Figure S5: Calculated FMO energies for (VII) **3** in ground state and excited state (**3_EXC**) (VIII) **3F** in ground state and excited state (**3F_EXC**) and (IX) **3CN** in ground state and excited state (**3CN_EXC**) at CAM-B3LYP/6-31G(d) level using CPCM solvation model.



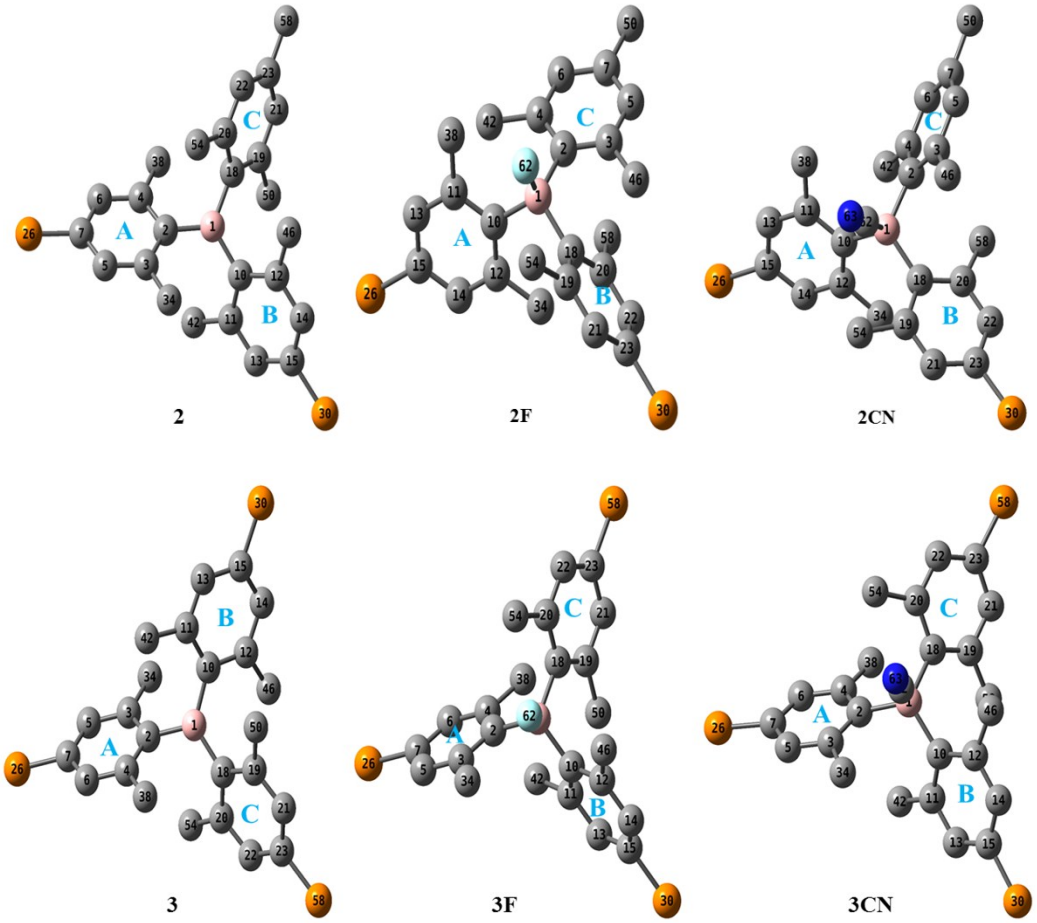


Figure S6: Excited state (S_1) optimized structures of **1**, **1F**, **1CN**, **2**, **2F**, **2CN**, **3**, **3F** and **3CN** calculated at CAM-B3LYP/6-31G(d) level with the CPCM solvation model. Hydrogen atoms are omitted for clarity. In **1**, **2** and **3**, the cyanide and the fluoride ions are added at boron atoms with numbering 1. The numbering of atoms of added cyanide is C (62), N (63) and fluoride is F (62). Geometry at boron centers in **1**, **2** and **3** is trigonal planar while as geometry at boron centers in **1F-3F** and **1CN-3CN** is tetrahedral.

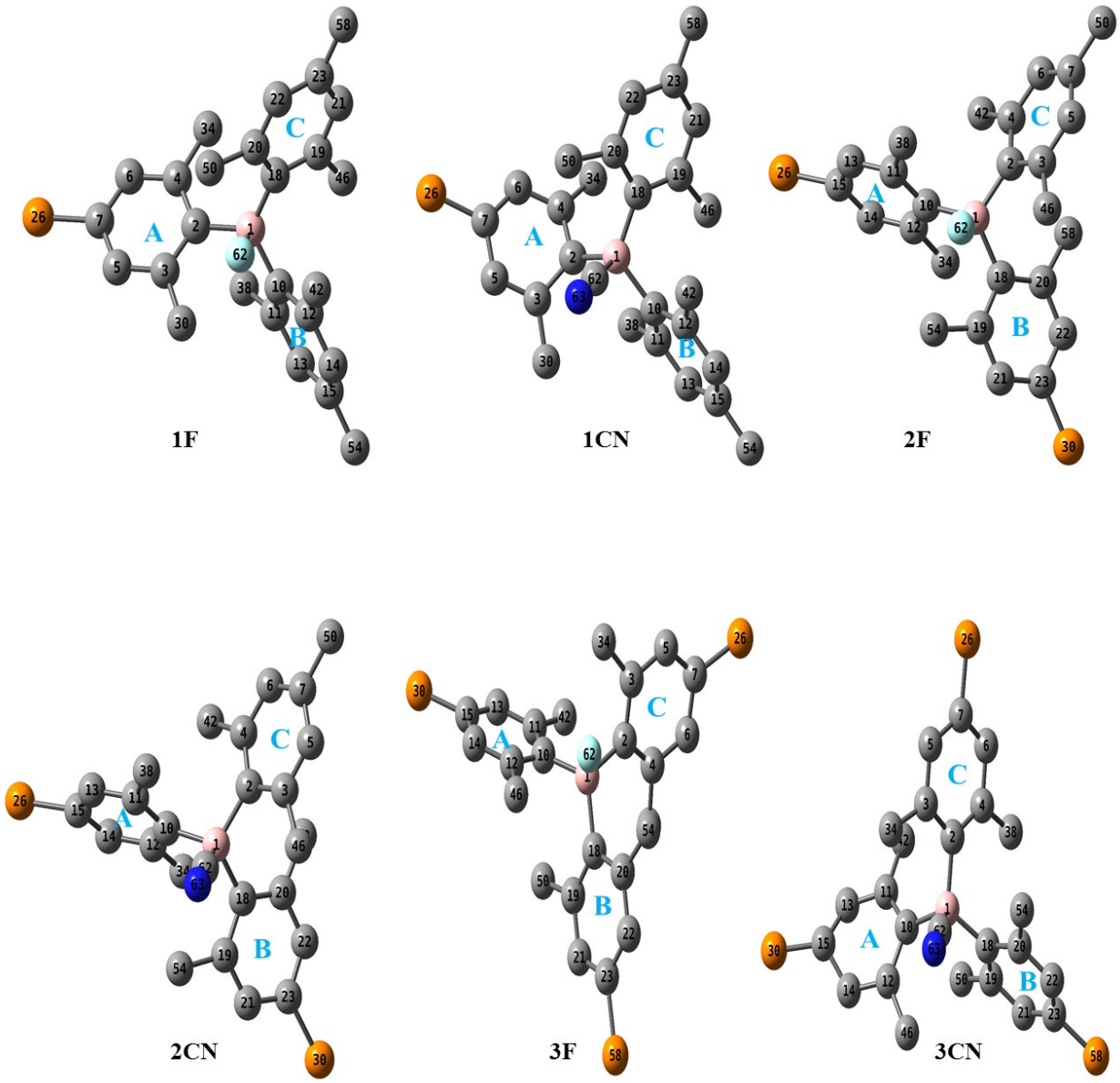


Figure S7: Excited state optimized structures of **1F** (third excited state, S_3), **1CN** (fourth excited state, S_4), **2F** (fifth excited state, S_5), **2CN** (fourth excited state, S_4), **3F** (fourth excited state, S_4) and **3CN** (fourth excited state, S_4) calculated at CAM-B3LYP/6-31G(d) level with the CPCM solvation model. Hydrogen atoms are omitted for clarity.

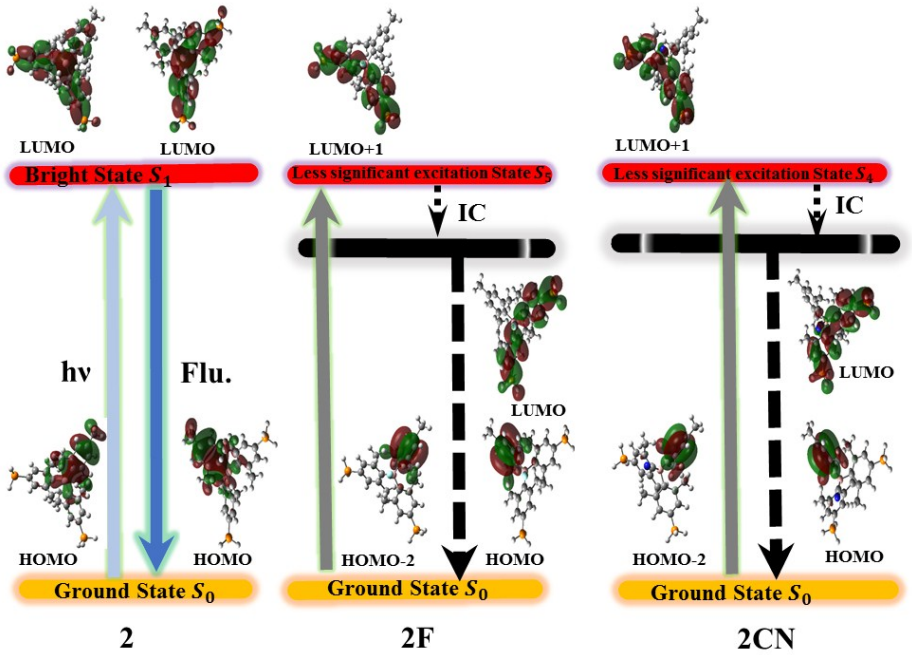


Figure S8: Scheme of the different mechanisms of fluorescence emission for **2**, **2F** and **2CN**.

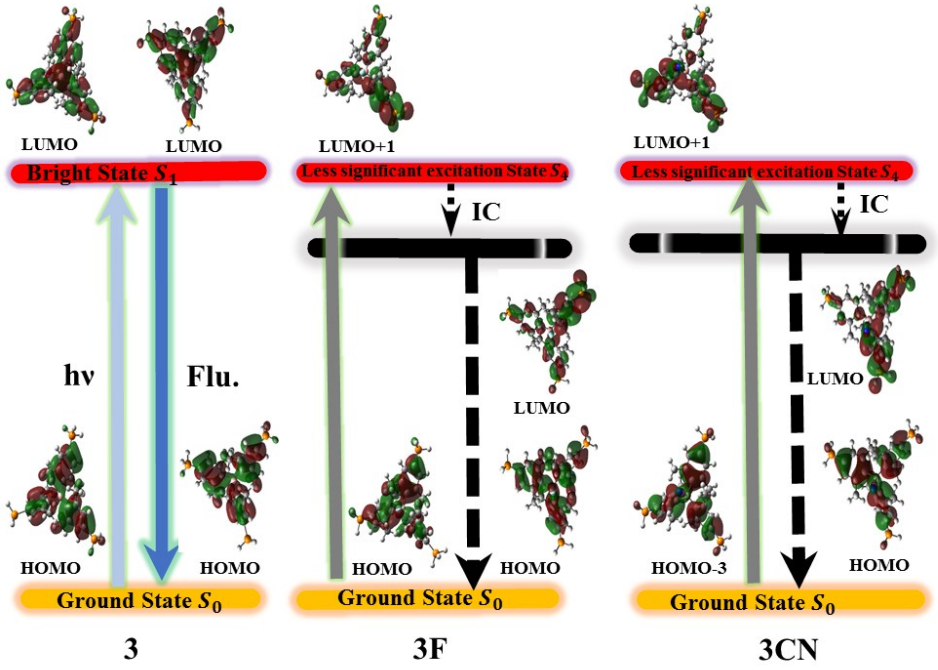


Figure S9: Scheme of the different mechanisms of fluorescence emission for **3**, **3F** and **3CN**.

References

(1) Song, K. C.; Lee, K. M.; Nghia, N. Van; Sung, W. Y.; Do, Y.; Lee, M. H. Synthesis and Anion Binding Properties of Multi-Phosphonium Triarylboranes: Selective Sensing of Cyanide Ions in Buffered Water at pH 7. *Organometallics* **2013**, *32*, 817–823.