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Supporting Information

Triarylborane conjugated dicyanovinyl chromophores: Intriguing Optical properties and colorimetric anion discrimination

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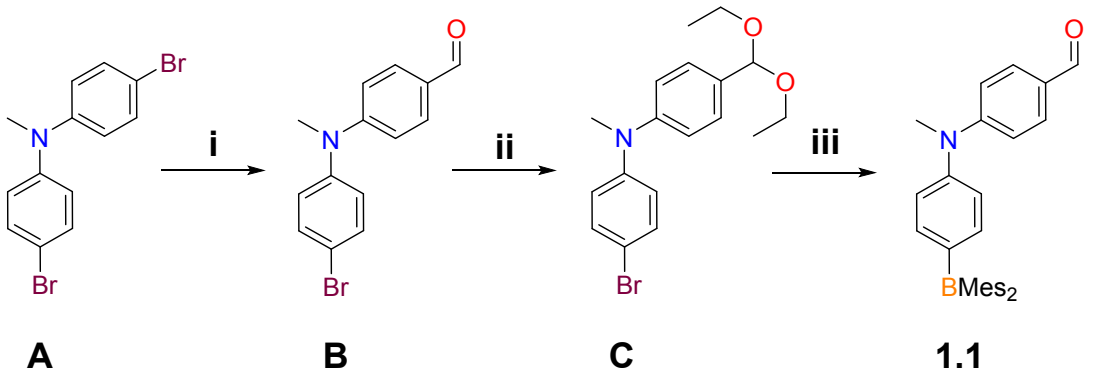


Scheme S1: (i) a) n-BuLi, b) DMF, c) dil. HCl (ii) $HC(OEt)_3$, H^+, Ethanol (iii) a) n-BuLi, b) $BFMes_2$, c) dil. HCl (iv) $CH_2(CN)_2$, piperidene, ethanol/DCM

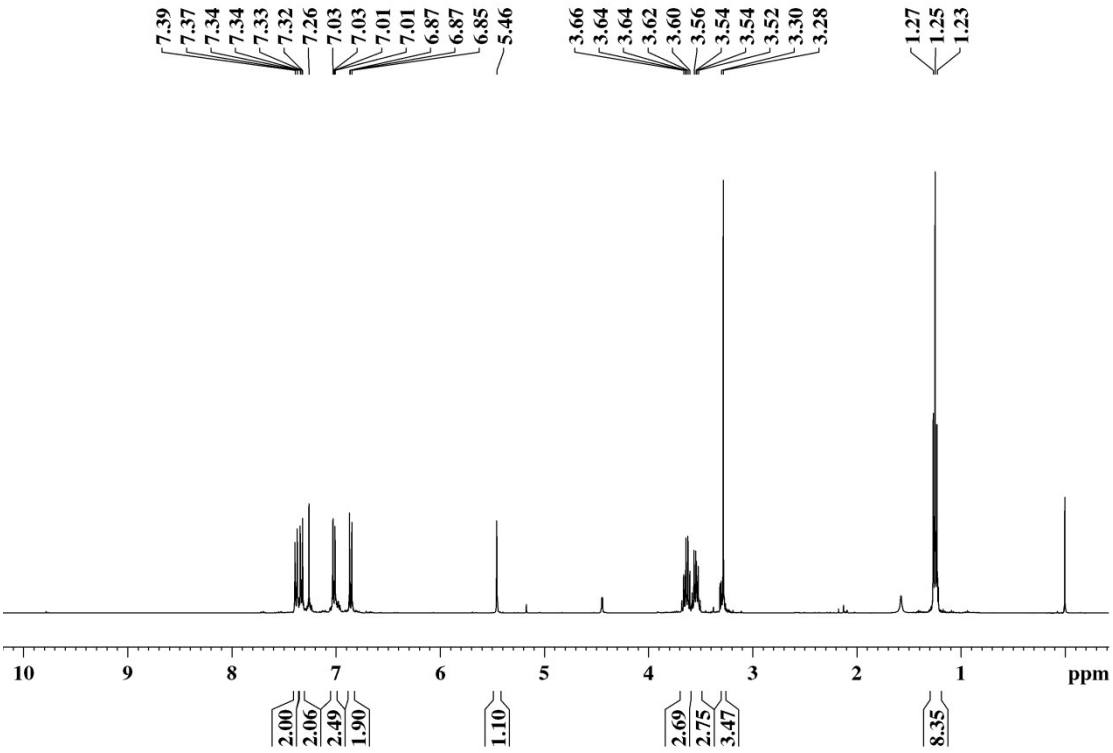


Figure S2: ^{1}H NMR spectrum of **C**

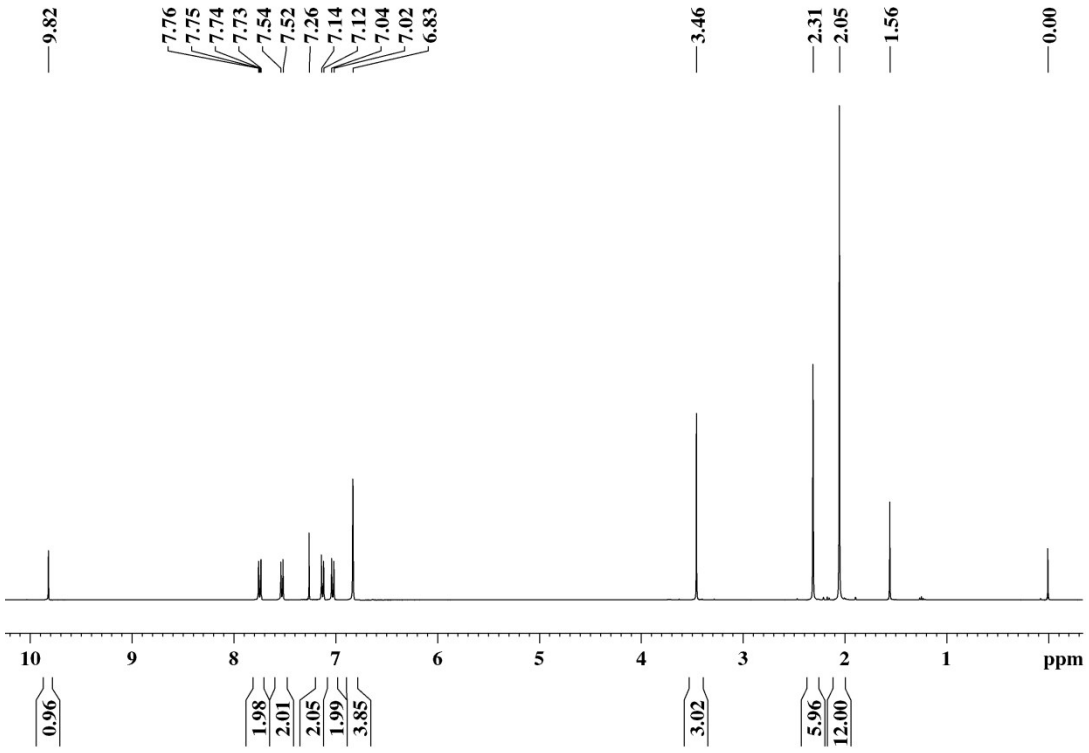


Figure S3: ^{1}H NMR spectrum of **1.1**

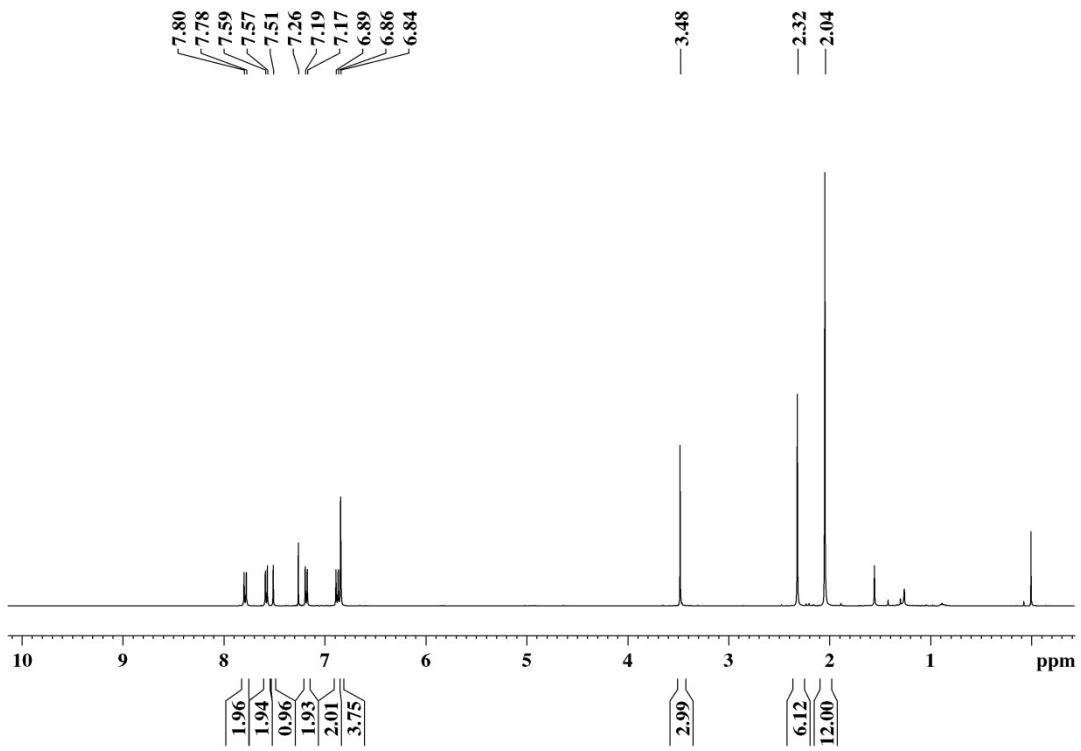


Figure S4: ^{1}H NMR spectrum of **1**

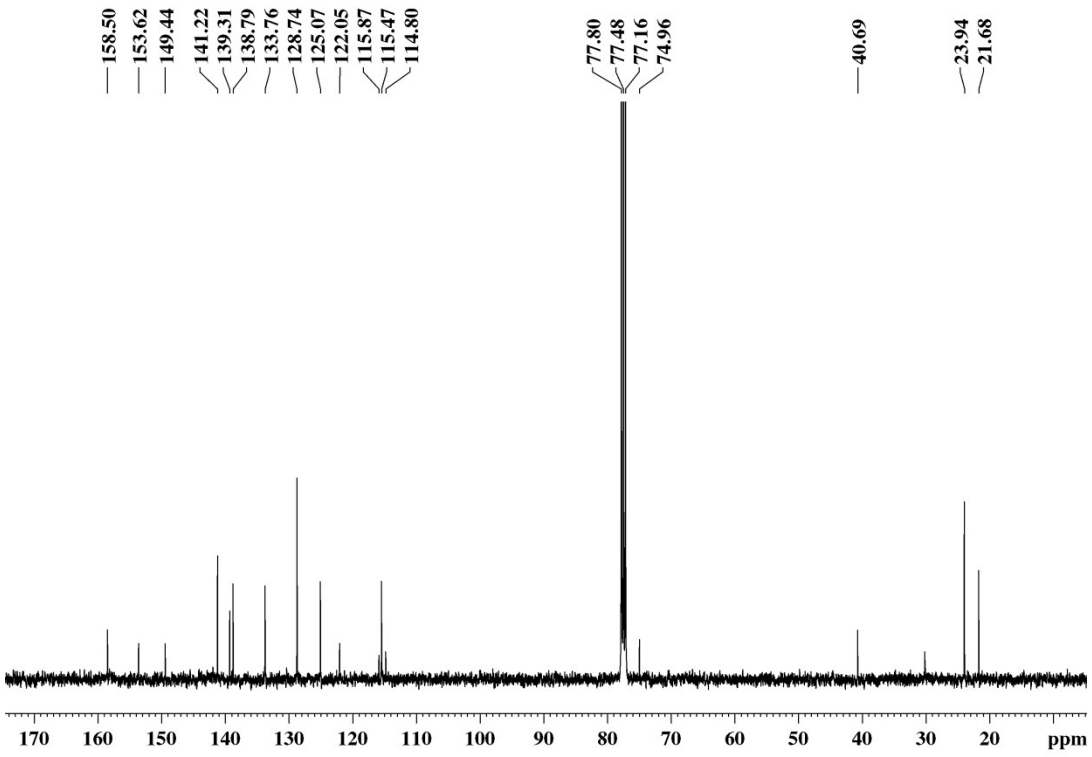


Figure S5: ^{13}C NMR spectrum of **1**

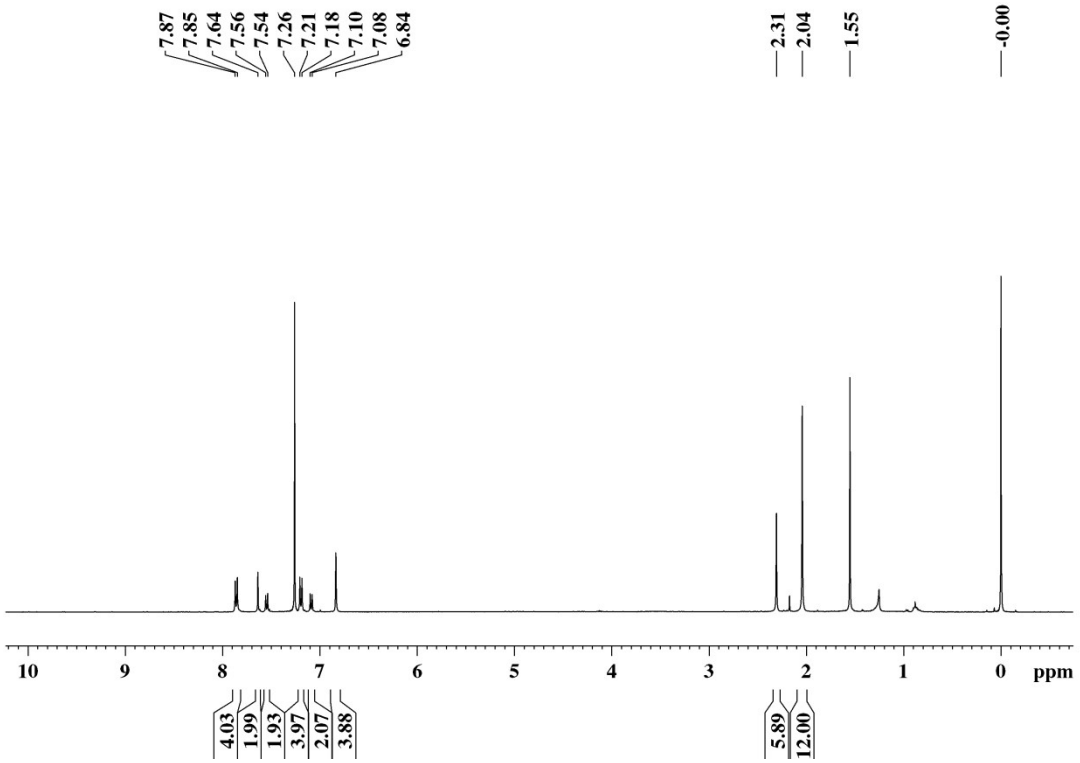


Figure S6: ^{1}H NMR spectrum of **2**

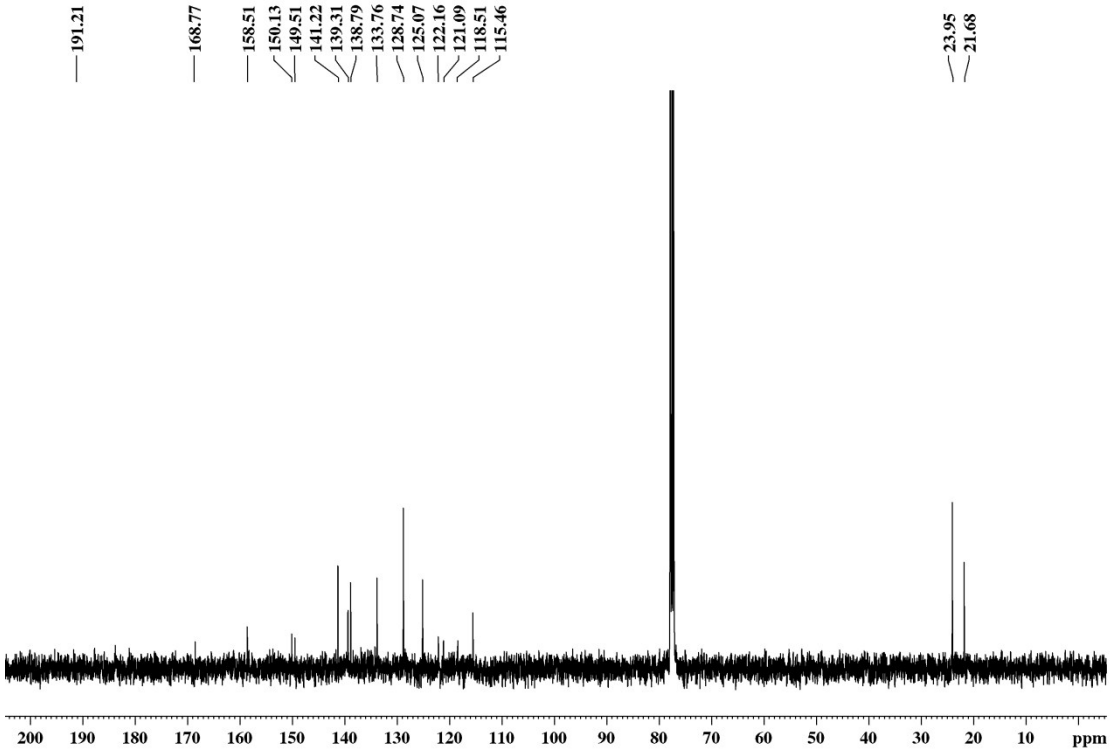


Figure S7: ^{13}C NMR spectrum of **2**

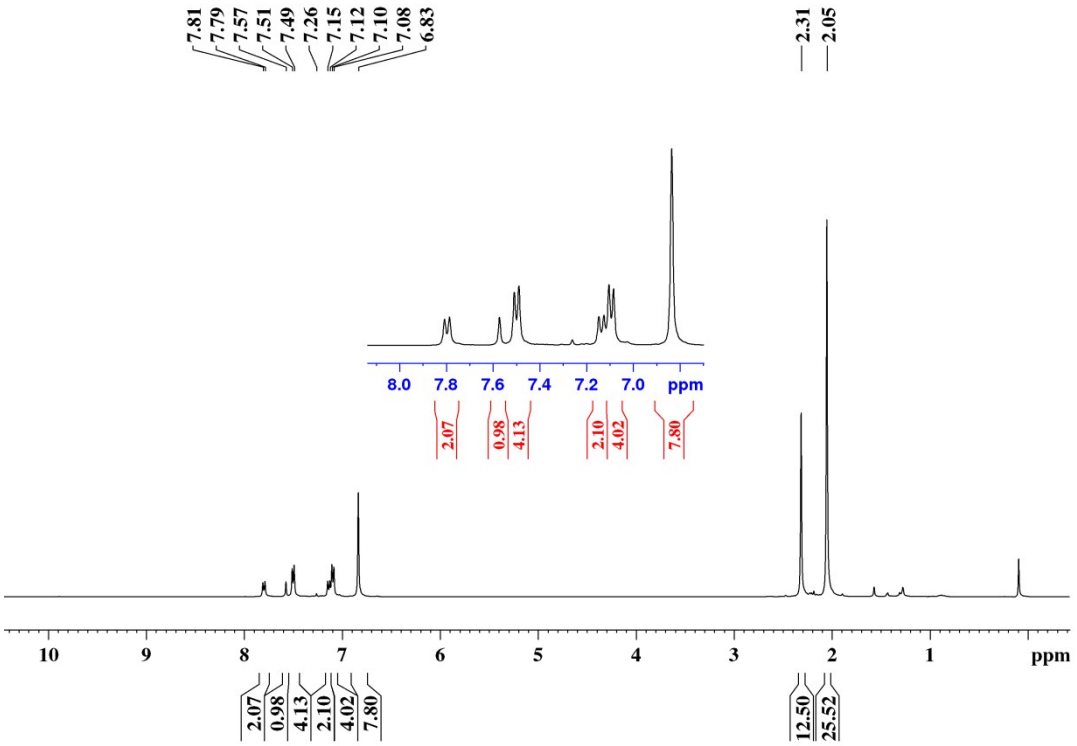


Figure S8: ^{1}H NMR spectrum of **3**

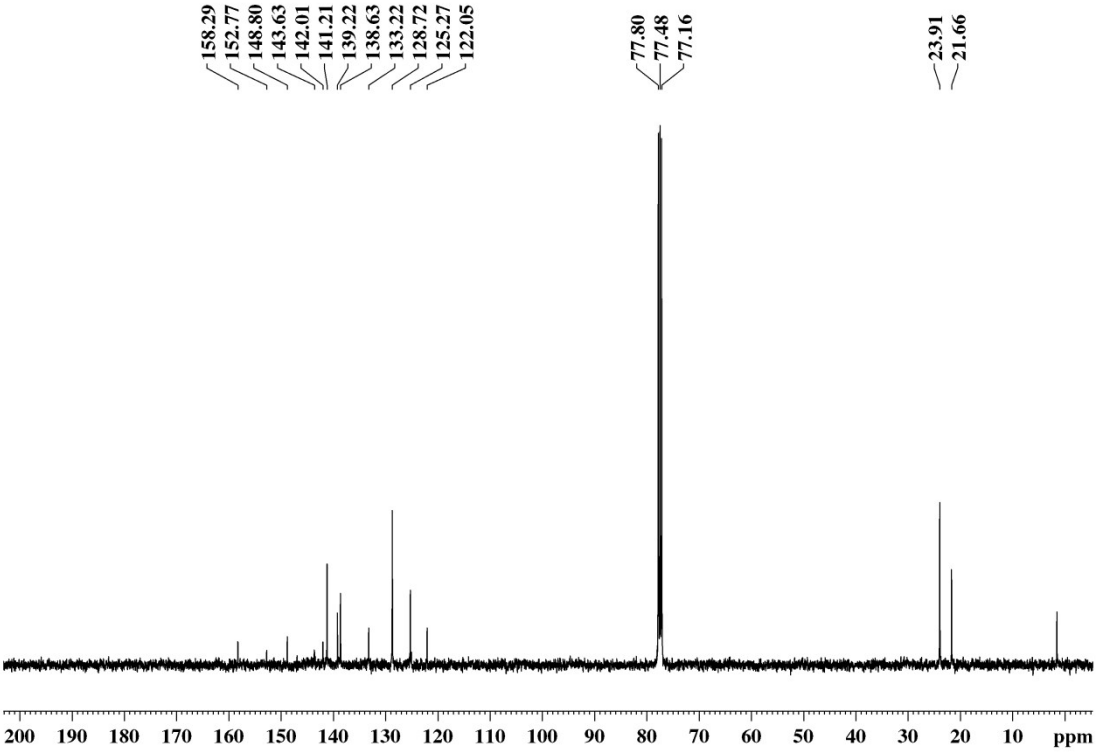


Figure S9: ^{13}C NMR spectrum of **3**

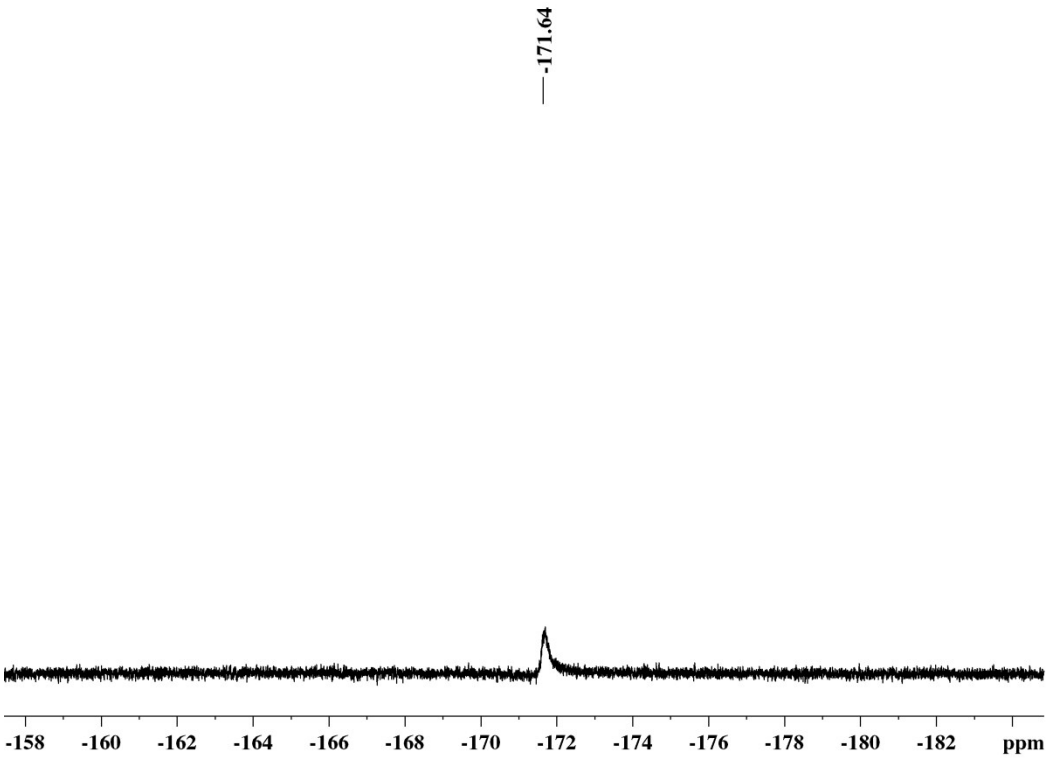


Figure S10: ^{19}F NMR spectrum of **1** in presence of TBAF in $CDCl_3$

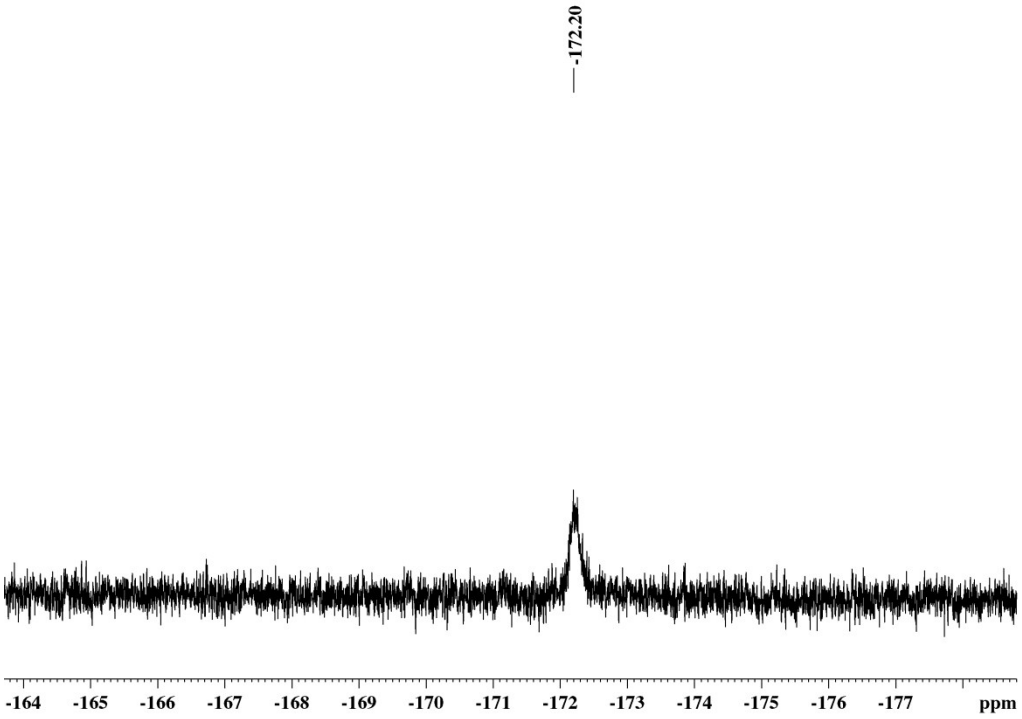


Figure S11: ^{19}F NMR spectrum of **2** in presence of TBAF in $CDCl_3$

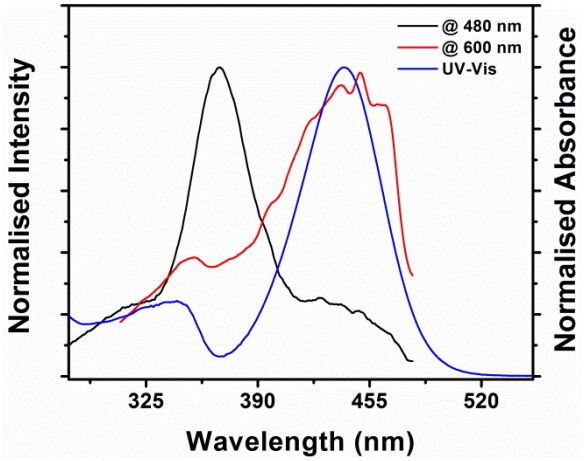


Figure S12: Excitation spectra monitored at two emission wavelengths (481 nm and 600 nm).

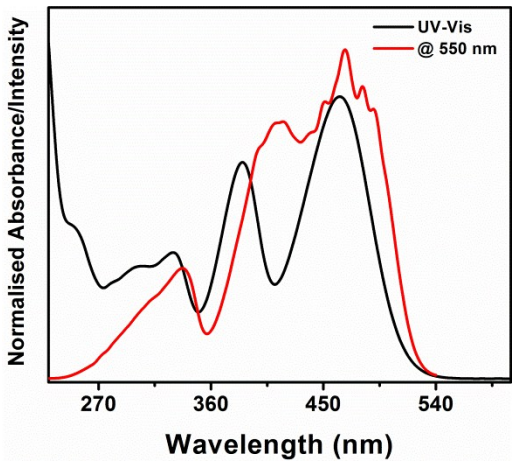


Figure S13: Excitation spectra of **2** nearly reproduced the respective absorption spectra. Concentrations 1×10^{-5} M in dichloromethane**.**

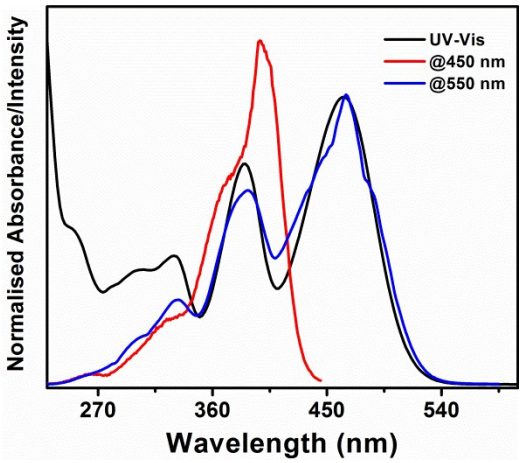


Figure S14: Excitation spectra of **3** nearly reproduced the respective absorption spectra. Concentrations 1×10^{-5} M in dichloromethane**.**

Life Time Measurement

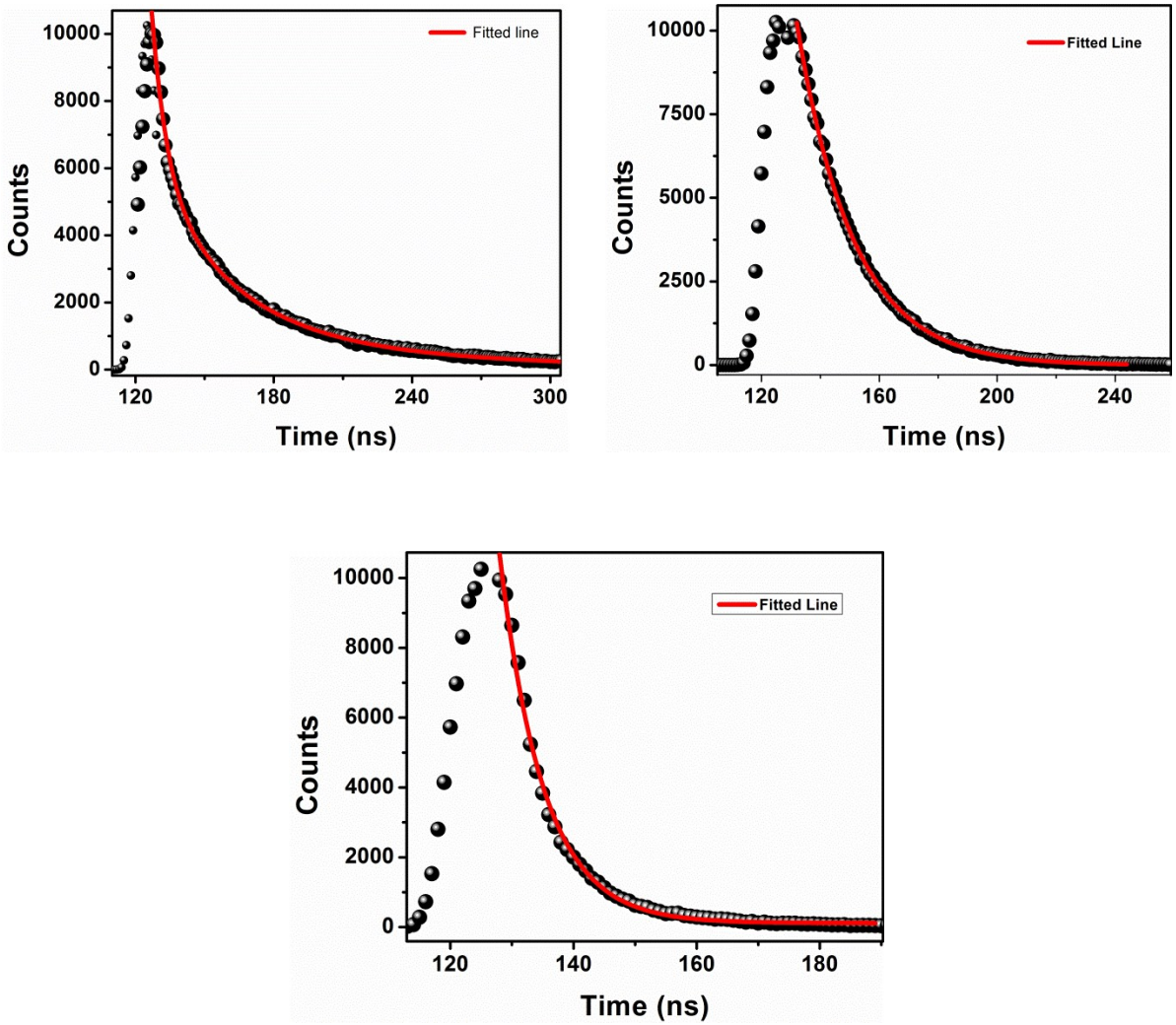


Figure S15: Time resolved fluorescence decay profiles of **1** (top left), **2** (top right) and **3** (bottom) in CH_2Cl_2

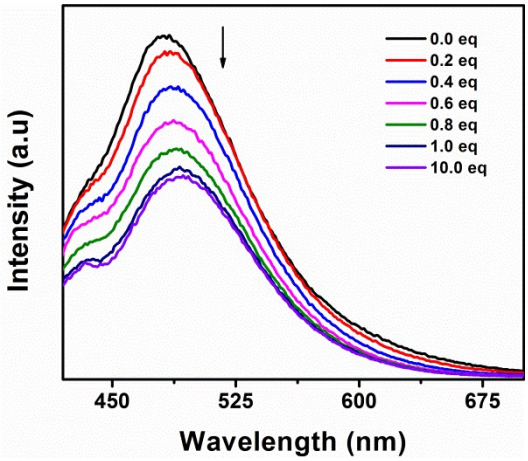


Figure S16: Changes in photoluminescence spectra of **1** (1×10^{-5} M) in presence of TBAF (2 µL = 1 eq) in dichloromethane**.**

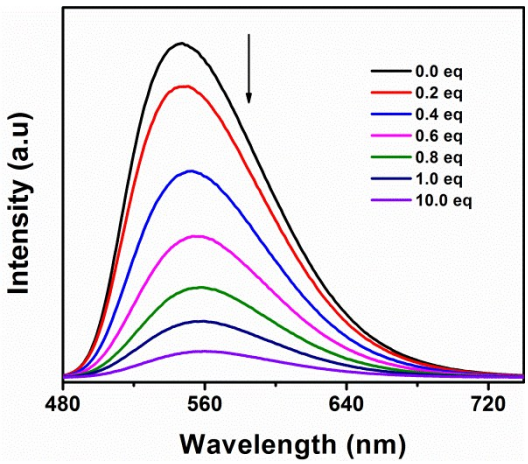


Figure S17: Changes in photoluminescence spectra of **2** (1×10^{-5} M) in presence of TBAF (2 µL = 1 eq) in dichloromethane**.**

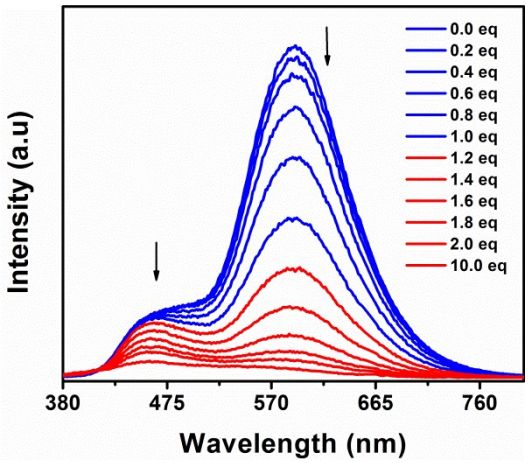


Figure S18: Changes in photoluminescence spectra of **3** (1×10^{-5} M) in presence of TBAF (2 µL = 1 eq) in dichloromethane**.**

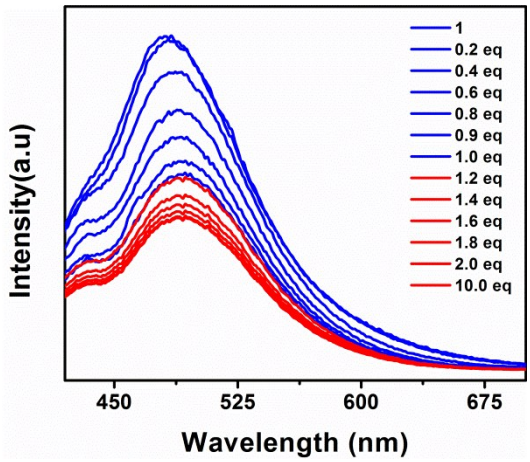


Figure 19: Changes in photoluminescence spectra of **1** (1×10^{-5} M) in presence of TBACN (2 μL = 0.1 eq) in dichloromethane.

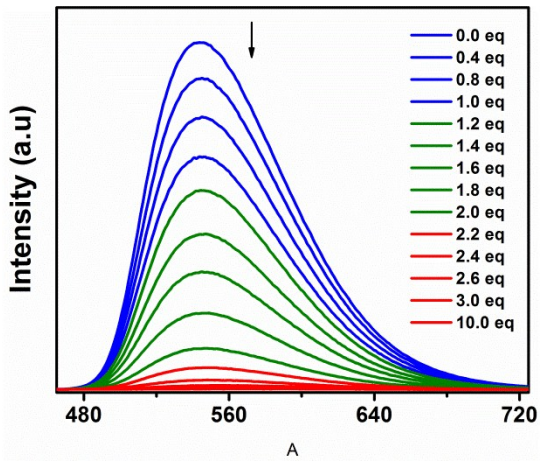


Figure 20: Changes in photoluminescence spectra of **2** (1×10^{-5} M) in presence of TBACN (2 μL = 0.1 eq) in dichloromethane. Since CN- binds concomitantly with both the receptor centre, quenching phenomenon is noted.

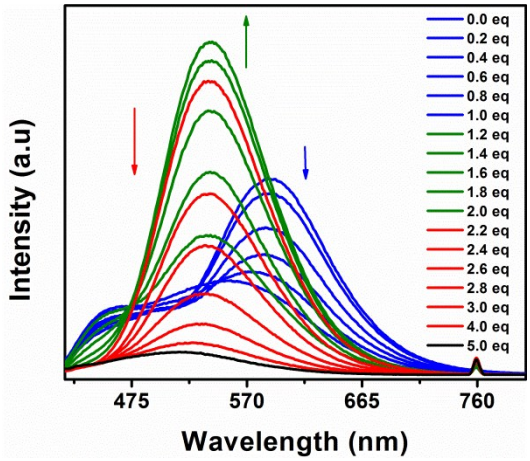


Figure 21: Changes in photoluminescence spectra of **3** (1×10^{-5} M) in presence of TBACN (2 µL = 0.1 eq) in dichloromethane. Since CN- binds concomitantly with both the receptor centre, quenching phenomenon is noted.

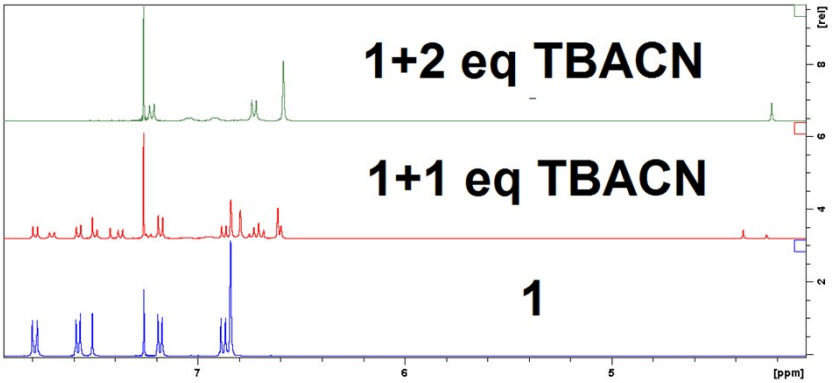


Figure S22: ^{1}H NMR titration of **1** (3.94×10^{-3} M, left) against TBACN (2 µL = 0.1 eq). In presence of 1 eq of TBACN, three species (SI) formed simultaneously and hence spectra looks complex. Excess eq of TBACN results in formation of a single molecule in which both the receptor cites are saturated by the anions.

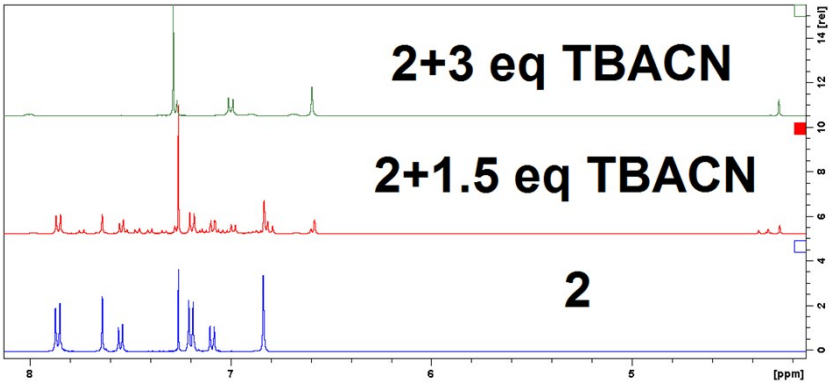


Figure S23: ^{1}H NMR titration of **2** (3.94×10^{-3} M, left) against TBACN (2 µL = 0.1 eq). In presence of 1 eq of TBACN, multiple species (SI) formed simultaneously and hence spectra looks complex. Excess eq of TBACN results in formation of a single molecule in which both the receptor cites are saturated by the anions.

Calculation of Detection Limits (fluoride)

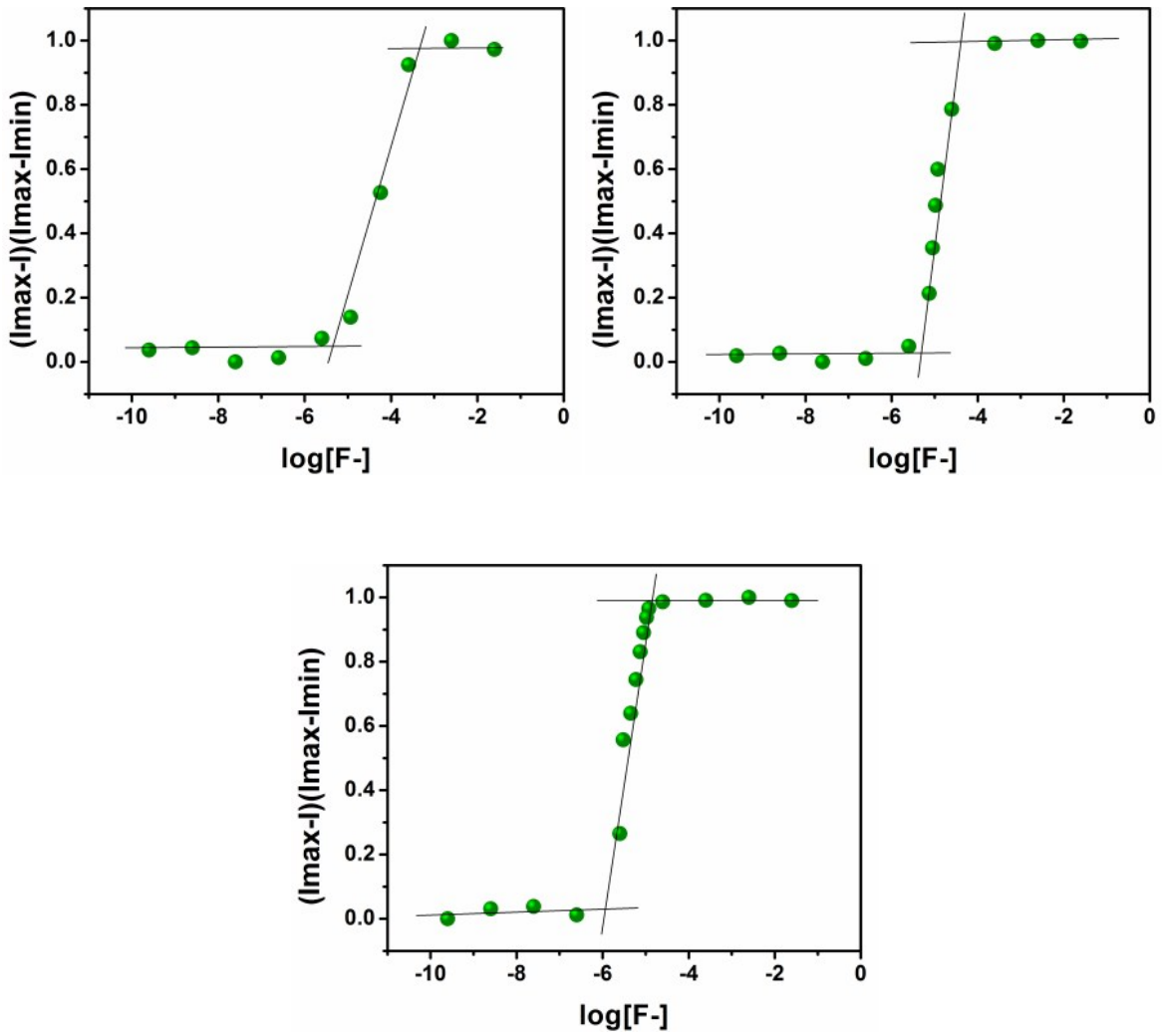


Figure S24: (Imax − I)/(Imax − Imin) vs log[F−] plots for **1** (top left), **2** (top right), and **3** (rbottom). The intercept on the X-axis shows the lowest concentrations of [F⁻] that can be detected by the respective sensors.

Calculation of Detection Limits (Cyanide)

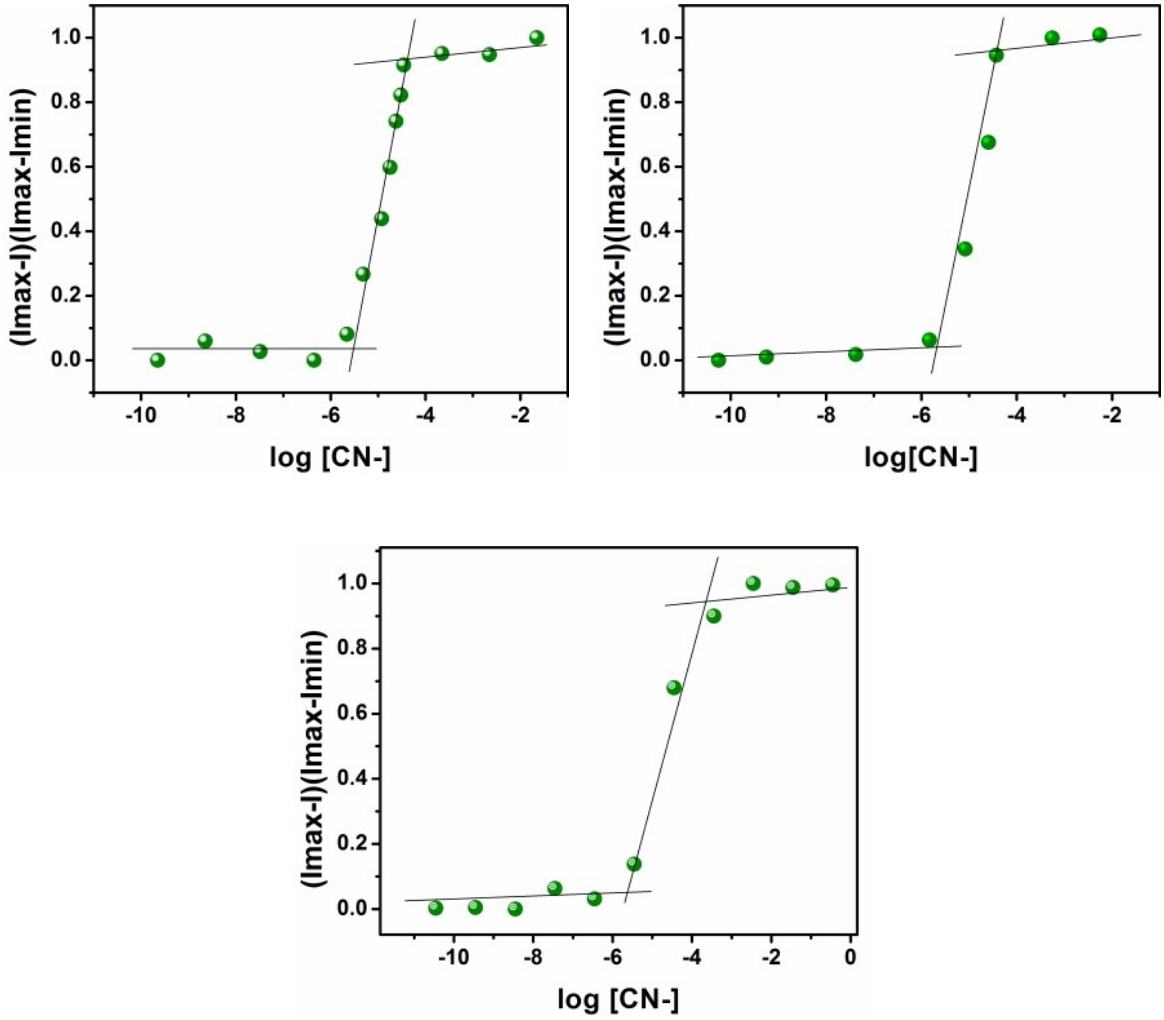


Figure S25: (Imax − I)/(Imax − Imin) vs log[F−] plots for **1** (top left), **2** (top right), and **3** (bottom). The intercept on the X-axis shows the lowest concentrations of [CN^-] that can be detected by the respective sensors.

Reversible anion binding behaviours of **2** and **3**

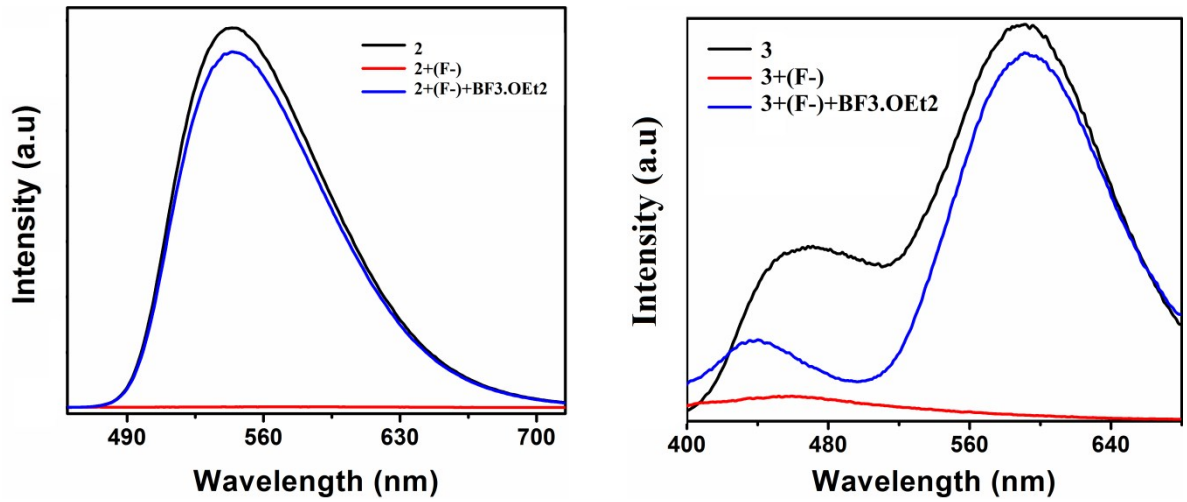


Figure S26: Reversible binding behaviour of **2** (left), and **3** (right) with fluoride in presence of $BF_3.OEt_2$. Enhancement of luminescence intensity after adding $BF_3.OEt_2$ clearly indicates that the probes are reversible towards fluoride.

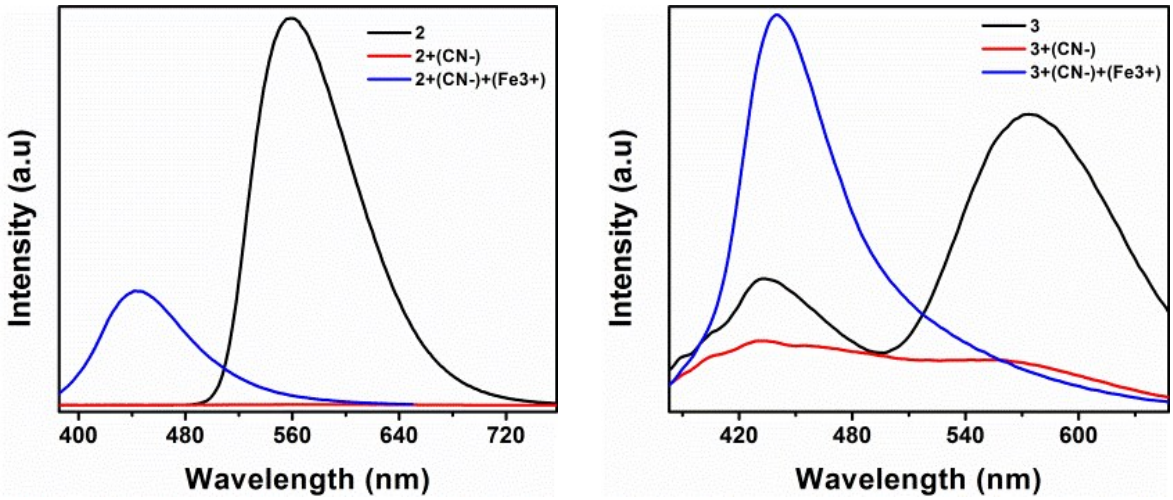


Figure S276: Reversible binding behaviour of **2** (left), and **3** (right) in THF with cyanide in presence of Fe^{3+} ions. Enhancement of higher energy luminescence intensity after adding Fe^{3+} clearly indicates that the probes are reversible towards cyanide ions at TAB receptor cite.

Selectivity of **1, 2** and **3** towards fluoride and cyanide

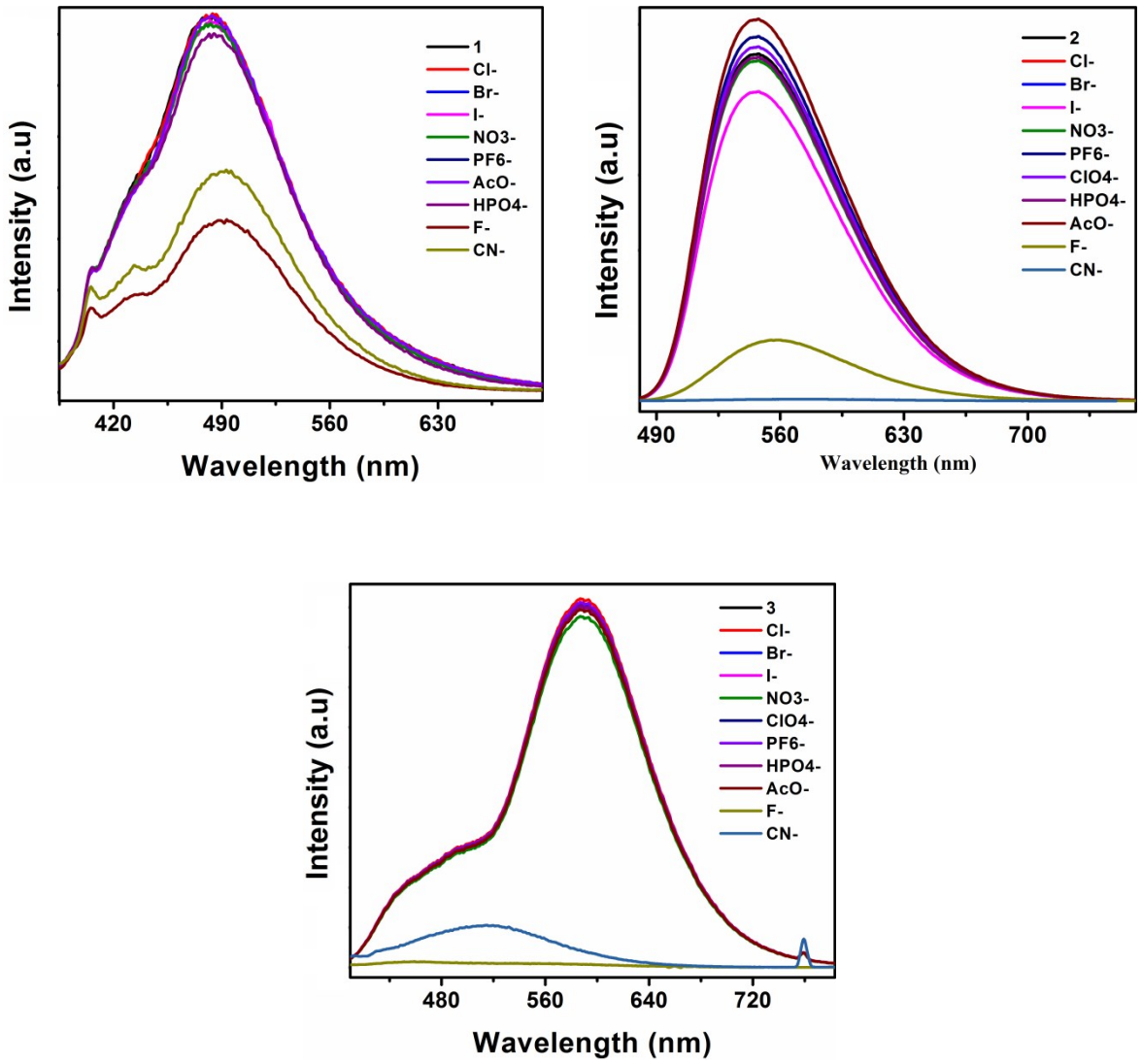


Figure S28: Changes in emission features of **1** (top left), **2** (top right) and **3** (bottom) in presence of various anions of 10 eq. All the reported probes are highly selective towards fluoride and cyanide ions.

Calculation of binding constants towards fluoride ions

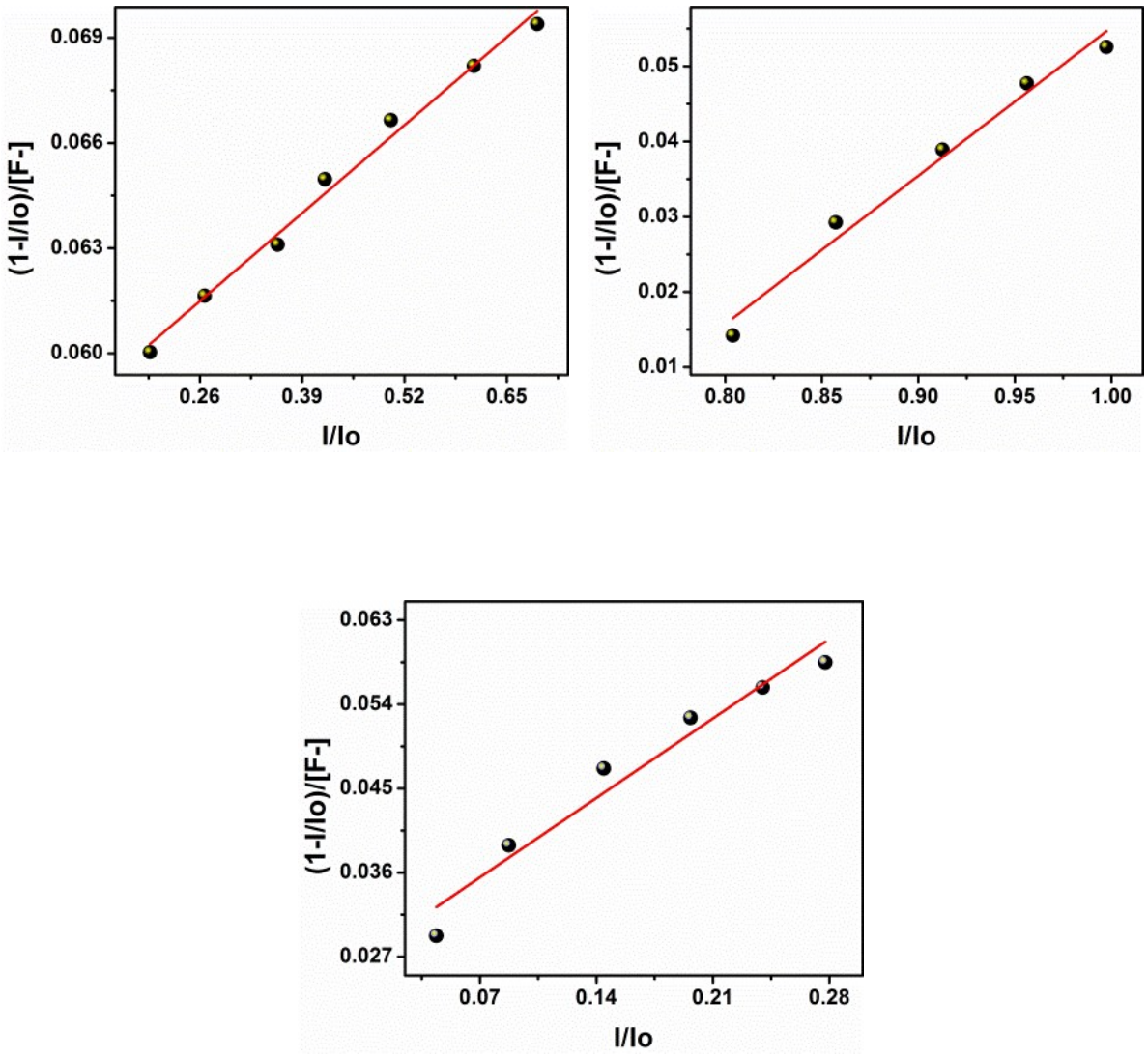


Figure S29: $(1-I/I_0)/[F^-]$ vs $\log[F^-]$ plots for **1** (top left), **2** (top right), and **3** (bottom). Slope of the plot gives the value of binding constants.

Calculation of binding constants towards cyanide ions

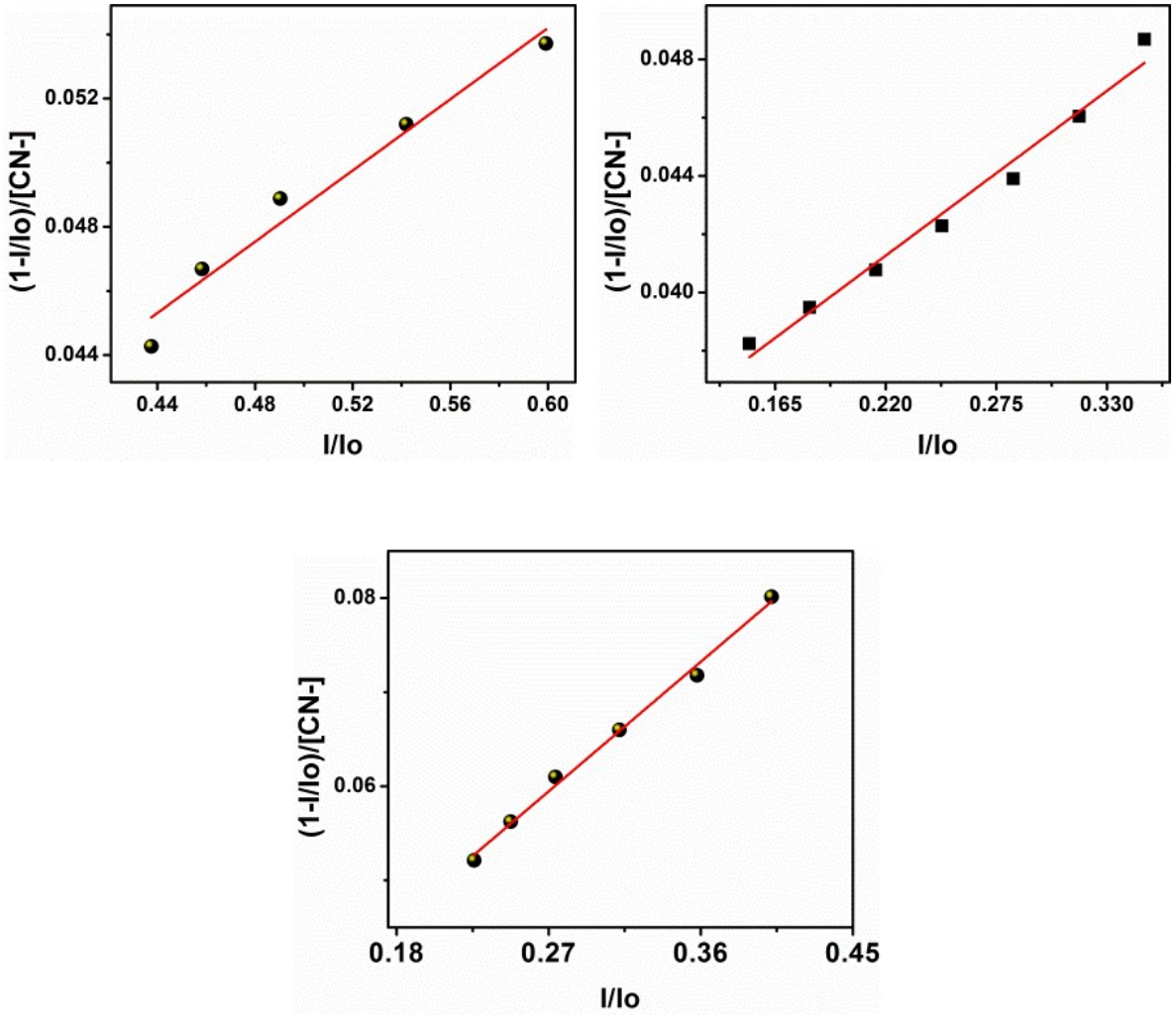
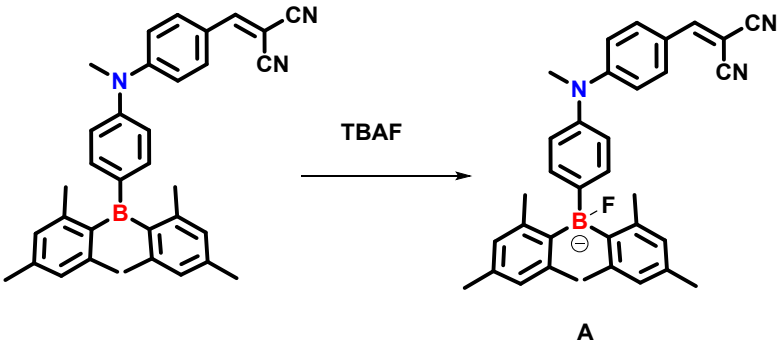
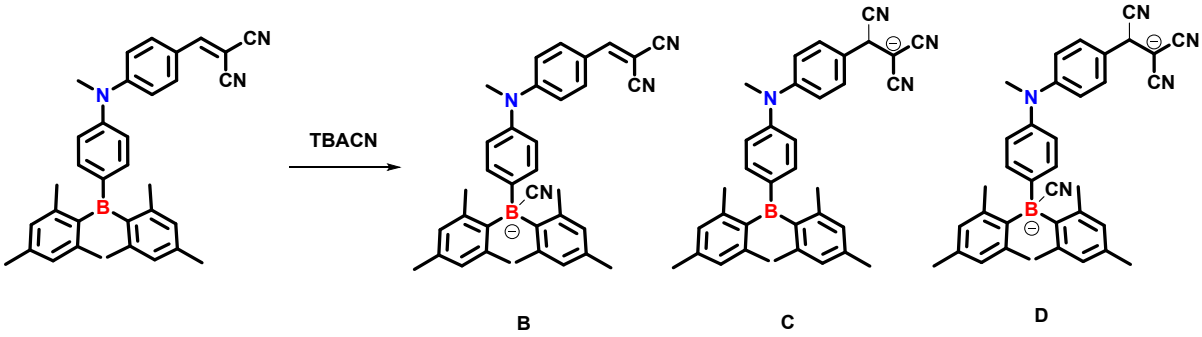


Figure S30: $(1-I/I_0)/[F^-]$ vs $\log[CN^-]$ plots for **1** (top left), **2** (top right), and **3** (bottom). Slope of the plot gives the value of binding constants.

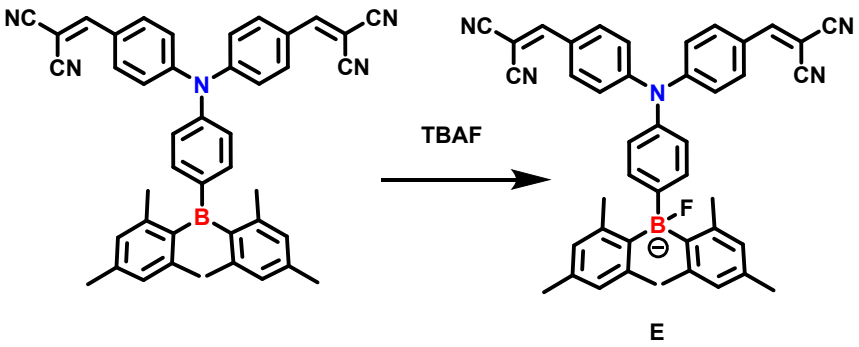
Binding modes of 1, 2 and 3 with possible species formed during anion sensing studies



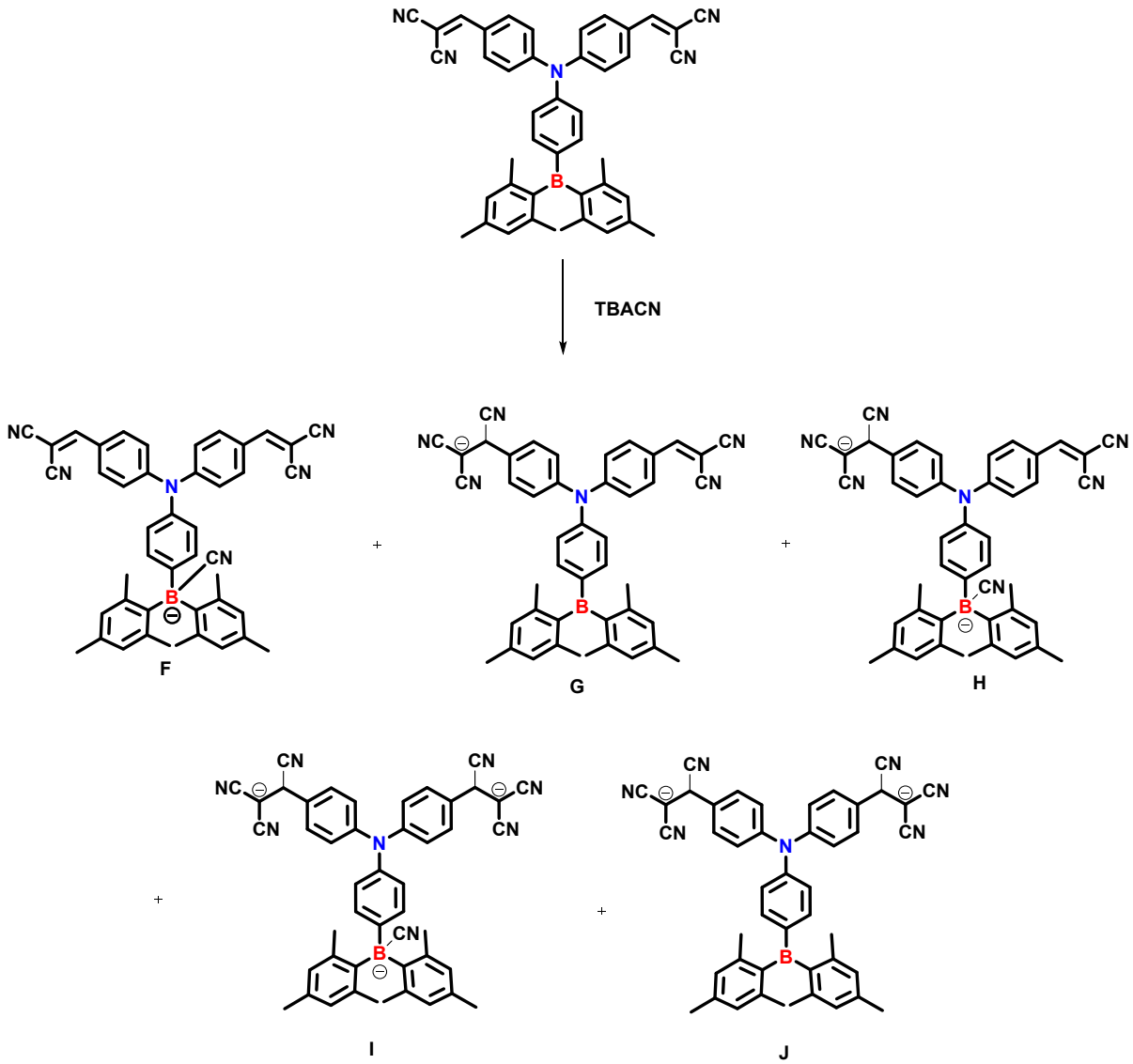
Scheme S2: Binding mode of **1** with fluoride ions



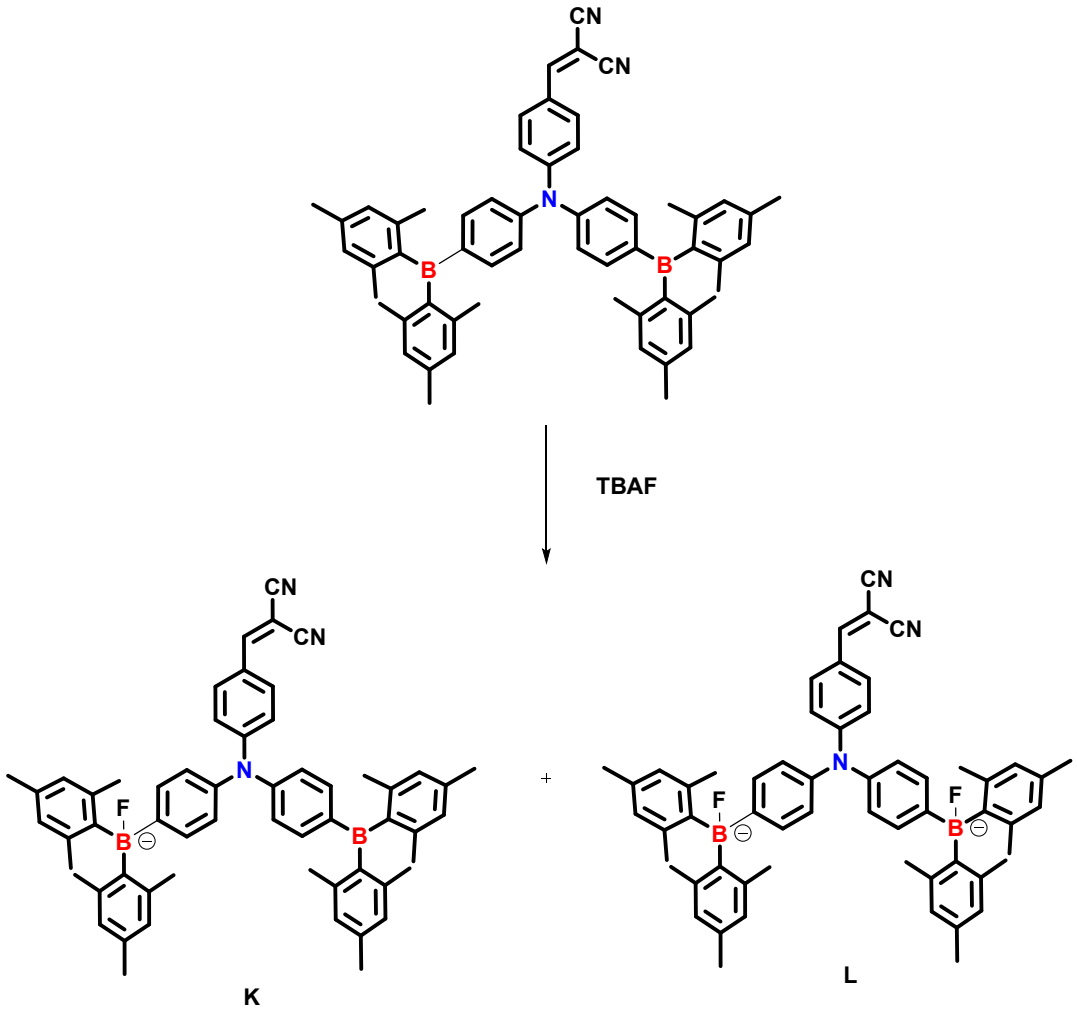
Scheme S3: Binding modes of **1** with cyanide ions



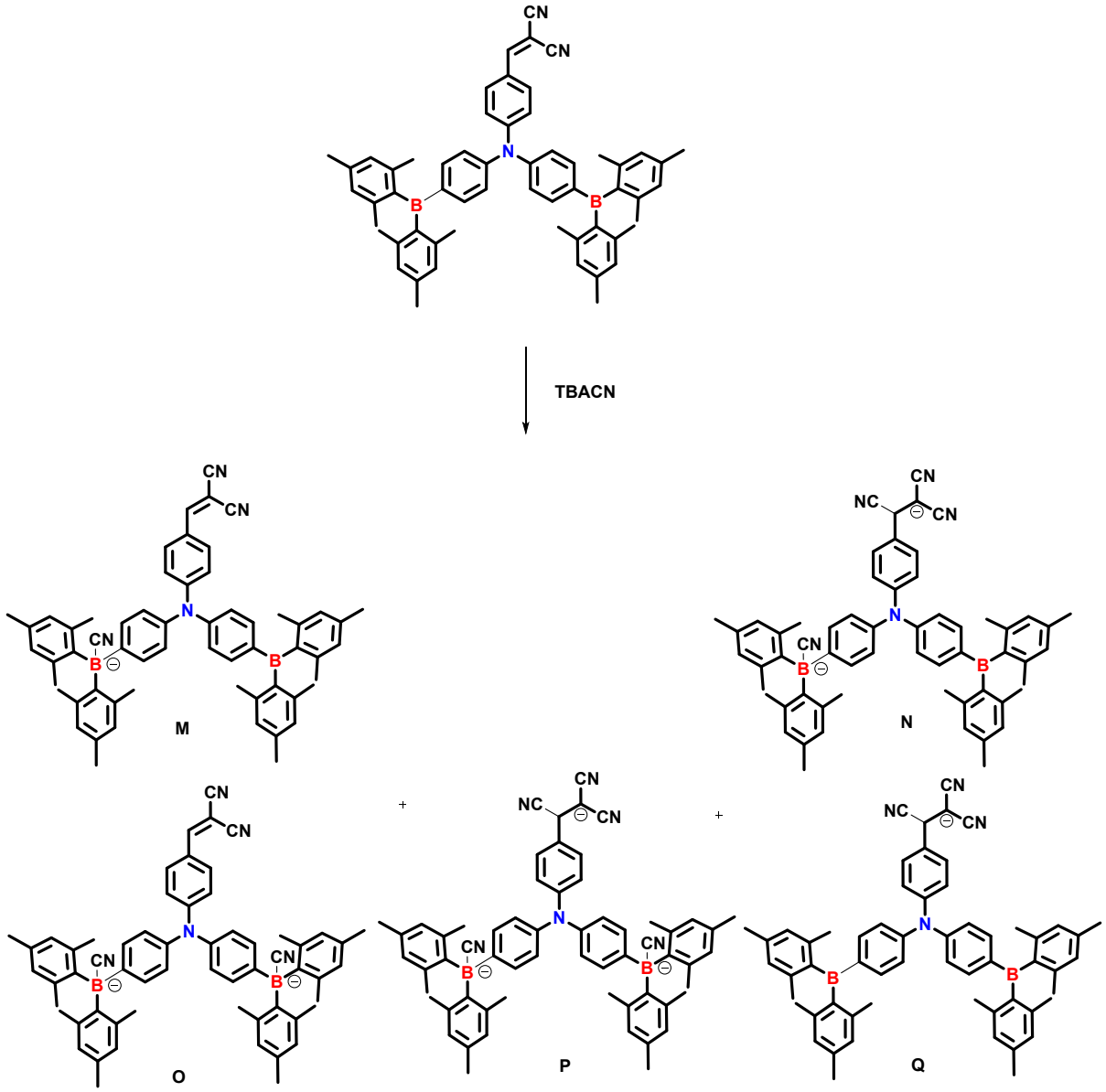
Scheme S4: Binding mode of **2** with fluoride ions



Scheme S5: Binding modes of **2** with cyanide ions



Scheme S6: Binding modes of **3** with fluoride ions



Scheme S7: Binding modes of **3** with cyanide ions

Table 1: Crystallographic data for **1**[1]

Empirical formula	C35 H34 B N3
Formula weight	507.46
Temperature	273(2) K
Wavelength	0.71073 Å
Unit cell	a = 8.2822(18) A α= 97.984(6)° b = 11.668(3) A β = 94.609(6)° c = 16.026(4) A γ = 101.200(6)°
Volume	1495.2(6) A^3
Z, Calculated density	2, 1.127 Mg/m^3
Absorption coefficient	0.065 mm^-1
F(000)	540
Crystal size	0.6 x 0.4 x 0.5 mm
Theta range for data collection	3.06 to 30.50°
Limiting indices	-11<=h<=11, -16<=k<=16, -22<=l<=22
Reflections collected / unique	32454 / 9059 [R(int) = 0.1456]
Completeness to theta = 27.51	99.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9059 / 0 / 428
Goodness-of-fit on F^2	0.964
Final R indices [I>2sigma(I)]	R1 = 0.0992, wR2 = 0.1718
R indices (all data)	R1 = 0.3028, wR2 = 0.2293
Largest diff. peak and hole	0.259 and -0.206 e.A^-3

Table 2. Anisotropic displacement parameters (A^2 x 10^3) for dcv1_0m. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	41(1)	36(1)	44(1)	2(1)	18(1)	6(1)
N(2)	102(3)	67(2)	274(6)	-24(3)	108(3)	6(2)
N(3)	77(2)	57(2)	75(2)	12(2)	-2(2)	-9(2)
C(34)	133(3)	70(2)	48(2)	7(2)	-19(2)	38(2)
C(30)	90(3)	39(2)	42(2)	-1(2)	-2(2)	31(2)
C(31)	56(2)	55(2)	54(2)	-11(2)	-8(2)	20(2)
C(32)	47(2)	46(2)	44(2)	-8(2)	1(2)	10(2)
C(27)	46(2)	31(2)	37(2)	-2(1)	5(1)	12(1)
C(15)	39(2)	30(2)	36(2)	0(1)	1(1)	5(1)
C(16)	53(2)	40(2)	30(2)	5(2)	5(1)	14(1)
C(17)	60(2)	39(2)	37(2)	8(2)	9(2)	22(2)
C(12)	37(2)	31(2)	38(2)	3(1)	12(1)	7(1)
C(8)	36(2)	37(2)	33(2)	3(1)	7(1)	6(1)
C(7)	36(2)	44(2)	48(2)	1(2)	16(2)	10(2)
C(6)	46(2)	35(2)	51(2)	-3(2)	12(2)	10(2)
C(5)	41(2)	38(2)	47(2)	2(1)	14(1)	6(1)
C(4)	44(2)	47(2)	49(2)	11(2)	16(2)	5(2)
C(3)	39(2)	35(2)	50(2)	9(2)	4(1)	4(1)
C(2)	58(2)	37(2)	119(3)	-2(2)	26(2)	6(2)

C(14)	56(2)	37(2)	42(2)	7(2)	1(2)	20(2)
C(13)	56(2)	46(2)	32(2)	6(2)	4(2)	17(2)
C(18)	40(2)	32(2)	36(2)	2(1)	9(1)	7(1)
C(19)	40(2)	35(2)	50(2)	4(1)	6(2)	5(1)
C(20)	40(2)	47(2)	57(2)	6(2)	-5(2)	5(2)
C(21)	43(2)	48(2)	62(2)	16(2)	9(2)	14(2)
C(25)	71(3)	72(3)	120(3)	30(2)	1(2)	30(2)
C(22)	56(2)	32(2)	65(2)	12(2)	23(2)	15(2)
C(23)	47(2)	29(2)	47(2)	4(1)	12(1)	5(1)
C(26)	72(3)	30(2)	94(4)	-4(2)	-5(3)	-2(2)
C(24)	51(2)	34(2)	78(2)	-3(2)	-7(2)	0(1)
C(35)	48(2)	90(3)	68(2)	-6(2)	7(2)	0(2)
C(29)	77(3)	46(2)	42(2)	8(2)	15(2)	21(2)
C(28)	57(2)	39(2)	41(2)	3(1)	9(2)	16(2)
C(33)	50(2)	93(3)	63(3)	25(3)	16(2)	6(2)
C(11)	47(2)	48(2)	44(2)	7(1)	20(2)	4(1)
C(9)	57(2)	39(2)	63(2)	0(2)	29(2)	13(2)
C(10)	49(2)	49(2)	64(2)	5(2)	29(2)	5(2)
C(1)	49(2)	48(2)	48(2)	8(2)	0(2)	6(2)
B(1)	36(2)	27(2)	46(2)	3(2)	9(2)	-4(1)

Table 3. Bond lengths [A] and angles [deg] for dcv1_0m.

N(1)-C(8)	1.367(3)
N(1)-C(12)	1.435(3)

N(1)-C(11)	1.458(3)
N(2)-C(2)	1.126(4)
N(3)-C(1)	1.139(3)
C(34)-C(30)	1.506(4)
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600
C(30)-C(31)	1.378(4)
C(30)-C(29)	1.385(4)
C(31)-C(32)	1.390(4)
C(31)-H(13)	0.97(3)
C(32)-C(27)	1.408(4)
C(32)-C(35)	1.521(4)
C(27)-C(28)	1.413(4)
C(27)-B(1)	1.573(4)
C(15)-C(16)	1.392(4)
C(15)-C(14)	1.391(4)
C(15)-B(1)	1.564(4)
C(16)-C(17)	1.376(4)
C(16)-H(12)	0.94(3)
C(17)-C(12)	1.378(4)
C(17)-H(10)	1.02(3)
C(12)-C(13)	1.375(4)
C(8)-C(9)	1.404(4)
C(8)-C(7)	1.401(4)
C(7)-C(6)	1.359(4)
C(7)-H(5)	0.93(2)

C(6)-C(5)	1.402(4)
C(6)-H(3)	0.96(3)
C(5)-C(10)	1.396(4)
C(5)-C(4)	1.422(4)
C(4)-C(3)	1.343(4)
C(4)-H(1)	0.91(3)
C(3)-C(2)	1.402(5)
C(3)-C(1)	1.431(4)
C(14)-C(13)	1.380(4)
C(14)-H(11)	0.93(3)
C(13)-H(9)	0.94(3)
C(18)-C(23)	1.401(3)
C(18)-C(19)	1.416(4)
C(18)-B(1)	1.573(4)
C(19)-C(20)	1.380(4)
C(19)-C(24)	1.513(4)
C(20)-C(21)	1.373(4)
C(20)-H(16)	0.90(2)
C(21)-C(22)	1.370(4)
C(21)-C(25)	1.511(4)
C(25)-H(33)	0.9600
C(25)-H(34)	0.9600
C(25)-H(32)	0.9600
C(22)-C(23)	1.386(4)
C(22)-H(15)	0.93(3)
C(23)-C(26)	1.513(4)
C(26)-H(27)	0.93(4)

C(26)-H(28)	0.91(4)
C(26)-H(26)	1.06(4)
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(35)-H(35A)	0.9600
C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600
C(29)-C(28)	1.377(4)
C(29)-H(14)	0.94(3)
C(28)-C(33)	1.511(4)
C(33)-H(25)	0.99(4)
C(33)-H(23)	0.93(4)
C(33)-H(24)	1.07(4)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(9)-C(10)	1.355(4)
C(9)-H(4)	0.95(3)
C(10)-H(2)	0.96(3)

C(8)-N(1)-C(12)	121.4(2)
C(8)-N(1)-C(11)	121.0(2)
C(12)-N(1)-C(11)	117.6(2)
C(30)-C(34)-H(34A)	109.5
C(30)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5

C(30)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(31)-C(30)-C(29)	117.2(3)
C(31)-C(30)-C(34)	121.4(3)
C(29)-C(30)-C(34)	121.4(3)
C(30)-C(31)-C(32)	122.3(3)
C(30)-C(31)-H(13)	120.2(17)
C(32)-C(31)-H(13)	117.4(17)
C(31)-C(32)-C(27)	120.2(3)
C(31)-C(32)-C(35)	118.4(3)
C(27)-C(32)-C(35)	121.4(3)
C(32)-C(27)-C(28)	117.4(3)
C(32)-C(27)-B(1)	121.6(3)
C(28)-C(27)-B(1)	120.7(2)
C(16)-C(15)-C(14)	115.8(3)
C(16)-C(15)-B(1)	121.5(2)
C(14)-C(15)-B(1)	122.4(3)
C(17)-C(16)-C(15)	122.2(3)
C(17)-C(16)-H(12)	119.1(17)
C(15)-C(16)-H(12)	118.7(17)
C(16)-C(17)-C(12)	120.1(3)
C(16)-C(17)-H(10)	121.8(14)
C(12)-C(17)-H(10)	118.0(14)
C(13)-C(12)-C(17)	119.5(3)
C(13)-C(12)-N(1)	120.4(2)
C(17)-C(12)-N(1)	120.1(2)

N(1)-C(8)-C(9)	121.8(2)
N(1)-C(8)-C(7)	121.3(2)
C(9)-C(8)-C(7)	116.9(3)
C(6)-C(7)-C(8)	121.7(3)
C(6)-C(7)-H(5)	120.2(14)
C(8)-C(7)-H(5)	118.0(14)
C(7)-C(6)-C(5)	122.1(3)
C(7)-C(6)-H(3)	119.8(15)
C(5)-C(6)-H(3)	118.0(15)
C(10)-C(5)-C(6)	115.3(3)
C(10)-C(5)-C(4)	119.4(3)
C(6)-C(5)-C(4)	125.3(3)
C(3)-C(4)-C(5)	132.2(3)
C(3)-C(4)-H(1)	116.9(18)
C(5)-C(4)-H(1)	110.9(18)
C(4)-C(3)-C(2)	124.9(3)
C(4)-C(3)-C(1)	121.6(3)
C(2)-C(3)-C(1)	113.5(3)
N(2)-C(2)-C(3)	178.8(5)
C(13)-C(14)-C(15)	122.7(3)
C(13)-C(14)-H(11)	124.9(16)
C(15)-C(14)-H(11)	112.4(16)
C(12)-C(13)-C(14)	119.6(3)
C(12)-C(13)-H(9)	118.4(16)
C(14)-C(13)-H(9)	121.9(16)
C(23)-C(18)-C(19)	117.4(3)
C(23)-C(18)-B(1)	122.5(2)

C(19)-C(18)-B(1)	120.1(2)
C(20)-C(19)-C(18)	119.8(3)
C(20)-C(19)-C(24)	117.6(3)
C(18)-C(19)-C(24)	122.6(3)
C(21)-C(20)-C(19)	122.9(3)
C(21)-C(20)-H(16)	114.1(16)
C(19)-C(20)-H(16)	123.0(16)
C(22)-C(21)-C(20)	117.2(3)
C(22)-C(21)-C(25)	122.2(3)
C(20)-C(21)-C(25)	120.7(3)
C(21)-C(25)-H(33)	109.5
C(21)-C(25)-H(34)	109.5
H(33)-C(25)-H(34)	109.5
C(21)-C(25)-H(32)	109.5
H(33)-C(25)-H(32)	109.5
H(34)-C(25)-H(32)	109.5
C(21)-C(22)-C(23)	122.7(3)
C(21)-C(22)-H(15)	117.2(16)
C(23)-C(22)-H(15)	120.2(16)
C(22)-C(23)-C(18)	120.1(3)
C(22)-C(23)-C(26)	119.1(3)
C(18)-C(23)-C(26)	120.8(3)
C(23)-C(26)-H(27)	113(2)
C(23)-C(26)-H(28)	105(3)
H(27)-C(26)-H(28)	107(3)
C(23)-C(26)-H(26)	112(2)
H(27)-C(26)-H(26)	105(3)

H(28)-C(26)-H(26)	114(4)
C(19)-C(24)-H(24A)	109.5
C(19)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(19)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(32)-C(35)-H(35A)	109.5
C(32)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(32)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(28)-C(29)-C(30)	122.7(3)
C(28)-C(29)-H(14)	120.2(19)
C(30)-C(29)-H(14)	117.1(18)
C(29)-C(28)-C(27)	120.1(3)
C(29)-C(28)-C(33)	117.8(3)
C(27)-C(28)-C(33)	122.1(3)
C(28)-C(33)-H(25)	108(2)
C(28)-C(33)-H(23)	115(2)
H(25)-C(33)-H(23)	105(3)
C(28)-C(33)-H(24)	109(2)
H(25)-C(33)-H(24)	111(3)
H(23)-C(33)-H(24)	108(3)
N(1)-C(11)-H(11A)	109.5
N(1)-C(11)-H(11B)	109.5

H(11A)-C(11)-H(11B)	109.5
N(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(10)-C(9)-C(8)	120.3(3)
C(10)-C(9)-H(4)	125.6(17)
C(8)-C(9)-H(4)	113.9(17)
C(9)-C(10)-C(5)	123.8(3)
C(9)-C(10)-H(2)	118.2(16)
C(5)-C(10)-H(2)	117.8(16)
N(3)-C(1)-C(3)	178.6(4)
C(15)-B(1)-C(27)	118.1(2)
C(15)-B(1)-C(18)	118.5(2)
C(27)-B(1)-C(18)	123.2(2)

Table 4: Crystallographic data for **2**[1]

Empirical formula	C21.50 H18 B0.50 N3
Formula weight	323.79
Temperature	296(2) K
Wavelength	0.71073 Å
Unit cell	a = 20.669(3) Å α = 90° b = 13.905(3) Å β = 90° c = 12.406(2) Å γ = 90°
Volume	3565.7(10) A^3
Z, Calculated density	8, 1.206 Mg/m^3
Absorption coefficient	0.072 mm^-1
F(000)	1364
Crystal size	0.6 x 0.3 x 0.6 mm
Theta range for data collection	1.77 to 27.51°
Limiting indices	-26<=h<=26, -18<=k<=18, -16<=l<=16
Reflections collected / unique	51040 / 4085 [R(int) = 0.1260]
Completeness to theta = 27.51	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4085 / 0 / 231
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1146
R indices (all data)	R1 = 0.1165, wR2 = 0.1448
Largest diff. peak and hole	0.223 and -0.250 e.A^-3

Table 5. Anisotropic displacement parameters (A^2 x 10^3) for **2**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(11)	28(1)	20(1)	28(1)	0	-2(1)	0
N(1)	26(1)	24(1)	29(1)	0	1(1)	0
N(3)	65(2)	61(2)	58(1)	-1(1)	20(1)	23(1)
N(2)	51(1)	53(1)	57(1)	12(1)	19(1)	7(1)
C(22)	38(1)	41(1)	71(2)	-3(1)	10(1)	-4(1)
C(18)	36(1)	24(1)	49(1)	-4(1)	6(1)	-4(1)
C(17)	33(1)	23(1)	43(1)	3(1)	0(1)	-2(1)
C(16)	35(1)	24(1)	34(1)	0(1)	1(1)	-5(1)
C(15)	36(1)	22(1)	30(1)	-1(1)	0(1)	-4(1)
C(14)	28(2)	26(2)	29(2)	0	-6(1)	0
C(13)	27(1)	28(1)	38(1)	-3(1)	-5(1)	-4(1)
C(12)	24(1)	29(1)	37(1)	-2(1)	-5(1)	5(1)
C(8)	25(1)	23(1)	28(1)	-2(1)	-3(1)	-1(1)
C(7)	31(1)	24(1)	31(1)	4(1)	-1(1)	2(1)
C(6)	34(1)	30(1)	29(1)	2(1)	1(1)	-2(1)
C(5)	34(1)	26(1)	30(1)	-2(1)	1(1)	2(1)
C(4)	43(1)	31(1)	36(1)	0(1)	3(1)	7(1)
C(3)	38(1)	32(1)	40(1)	-2(1)	3(1)	2(1)
C(2)	50(2)	44(2)	45(1)	-2(1)	9(1)	7(1)
C(1)	34(1)	39(1)	42(1)	-4(1)	10(1)	1(1)
C(10)	43(1)	28(1)	35(1)	6(1)	-1(1)	7(1)
C(9)	36(1)	31(1)	30(1)	4(1)	4(1)	5(1)
C(20)	45(1)	32(1)	34(1)	1(1)	2(1)	-2(1)

C(19)	45(1)	37(1)	40(1)	-1(1)	12(1)	-8(1)
C(21)	41(1)	46(2)	40(1)	15(1)	2(1)	2(1)
C(23)	68(2)	56(2)	33(1)	10(1)	6(1)	6(1)
B(1)	41(2)	30(2)	21(2)	0	-6(2)	0

Table 6. Bond lengths [A] and angles [deg] for **2**.

C(11)-C(12)	1.394(2)
C(11)-C(12)#1	1.394(2)
C(11)-N(1)	1.428(3)
N(1)-C(8)	1.416(2)
N(1)-C(8)#1	1.416(2)
N(3)-C(2)	1.146(3)
N(2)-C(1)	1.143(3)
C(22)-C(18)	1.511(3)
C(22)-H(5)	0.9600
C(22)-H(4)	0.9600
C(22)-H(1)	0.9600
C(18)-C(19)	1.385(3)
C(18)-C(17)	1.390(3)
C(17)-C(16)	1.395(3)
C(17)-H(9)	0.9300
C(16)-C(15)	1.418(3)
C(16)-C(21)	1.515(3)
C(15)-C(20)	1.415(3)
C(15)-B(1)	1.577(3)
C(14)-C(13)	1.408(2)
C(14)-C(13)#1	1.408(2)

C(14)-B(1)	1.572(4)
C(13)-C(12)	1.386(3)
C(13)-H(2)	0.9300
C(12)-H(3)	0.9300
C(8)-C(9)	1.390(3)
C(8)-C(7)	1.392(3)
C(7)-C(6)	1.382(3)
C(7)-H(15)	0.9300
C(6)-C(5)	1.404(3)
C(6)-H(16)	0.9300
C(5)-C(10)	1.394(3)
C(5)-C(4)	1.451(3)
C(4)-C(3)	1.347(3)
C(4)-H(17)	0.9300
C(3)-C(1)	1.435(3)
C(3)-C(2)	1.445(3)
C(10)-C(9)	1.375(3)
C(10)-H(18)	0.9300
C(9)-H(14)	0.9300
C(20)-C(19)	1.404(3)
C(20)-C(23)	1.507(3)
C(19)-H(10)	0.9300
C(21)-H(6)	0.9600
C(21)-H(7)	0.9600
C(21)-H(8)	0.9600
C(23)-H(11)	0.9600
C(23)-H(13)	0.9600
C(23)-H(12)	0.9600
B(1)-C(15)#1	1.577(3)

C(12)-C(11)-C(12)#1	120.0(3)
C(12)-C(11)-N(1)	119.99(13)
C(12)#1-C(11)-N(1)	119.99(13)
C(8)-N(1)-C(8)#1	119.1(2)
C(8)-N(1)-C(11)	120.43(11)
C(8)#1-N(1)-C(11)	120.43(11)
C(18)-C(22)-H(5)	109.5
C(18)-C(22)-H(4)	109.5
H(5)-C(22)-H(4)	109.5
C(18)-C(22)-H(1)	109.5
H(5)-C(22)-H(1)	109.5
H(4)-C(22)-H(1)	109.5
C(19)-C(18)-C(17)	117.6(2)
C(19)-C(18)-C(22)	120.7(2)
C(17)-C(18)-C(22)	121.6(2)
C(18)-C(17)-C(16)	121.7(2)
C(18)-C(17)-H(9)	119.1
C(16)-C(17)-H(9)	119.1
C(17)-C(16)-C(15)	121.08(19)
C(17)-C(16)-C(21)	118.10(19)
C(15)-C(16)-C(21)	120.77(19)
C(20)-C(15)-C(16)	116.80(19)
C(20)-C(15)-B(1)	121.29(17)
C(16)-C(15)-B(1)	121.60(17)
C(13)-C(14)-C(13)#1	116.7(3)
C(13)-C(14)-B(1)	121.64(13)
C(13)#1-C(14)-B(1)	121.64(13)
C(12)-C(13)-C(14)	121.99(19)

C(12)-C(13)-H(2)	119.0
C(14)-C(13)-H(2)	119.0
C(13)-C(12)-C(11)	119.62(19)
C(13)-C(12)-H(3)	120.2
C(11)-C(12)-H(3)	120.2
C(9)-C(8)-C(7)	118.59(18)
C(9)-C(8)-N(1)	119.42(17)
C(7)-C(8)-N(1)	122.00(17)
C(6)-C(7)-C(8)	120.67(19)
C(6)-C(7)-H(15)	119.7
C(8)-C(7)-H(15)	119.7
C(7)-C(6)-C(5)	120.97(19)
C(7)-C(6)-H(16)	119.5
C(5)-C(6)-H(16)	119.5
C(10)-C(5)-C(6)	117.49(18)
C(10)-C(5)-C(4)	115.87(18)
C(6)-C(5)-C(4)	126.58(19)
C(3)-C(4)-C(5)	132.5(2)
C(3)-C(4)-H(17)	113.7
C(5)-C(4)-H(17)	113.7
C(4)-C(3)-C(1)	125.1(2)
C(4)-C(3)-C(2)	119.7(2)
C(1)-C(3)-C(2)	115.20(19)
N(3)-C(2)-C(3)	178.8(3)
N(2)-C(1)-C(3)	177.9(2)
C(9)-C(10)-C(5)	121.53(19)
C(9)-C(10)-H(18)	119.2
C(5)-C(10)-H(18)	119.2
C(10)-C(9)-C(8)	120.73(19)

C(10)-C(9)-H(14)	119.6
C(8)-C(9)-H(14)	119.6
C(19)-C(20)-C(15)	120.4(2)
C(19)-C(20)-C(23)	117.8(2)
C(15)-C(20)-C(23)	121.7(2)
C(18)-C(19)-C(20)	122.1(2)
C(18)-C(19)-H(10)	118.9
C(20)-C(19)-H(10)	118.9
C(16)-C(21)-H(6)	109.5
C(16)-C(21)-H(7)	109.5
H(6)-C(21)-H(7)	109.5
C(16)-C(21)-H(8)	109.5
H(6)-C(21)-H(8)	109.5
H(7)-C(21)-H(8)	109.5
C(20)-C(23)-H(11)	109.5
C(20)-C(23)-H(13)	109.5
H(11)-C(23)-H(13)	109.5
C(20)-C(23)-H(12)	109.5
H(11)-C(23)-H(12)	109.5
H(13)-C(23)-H(12)	109.5
C(14)-B(1)-C(15)#1	116.96(13)
C(14)-B(1)-C(15)	116.96(13)
C(15)#1-B(1)-C(15)	126.1(3)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2

TD-DFT Results

Compound 1

Excited State 1: Singlet-A 3.0537 eV 406.02 nm f=1.0626 <S**2>=0.000
135 ->136 0.65248
135 ->137 -0.24281
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1543.19609887
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.3801 eV 366.81 nm f=0.0479 <S**2>=0.000
134 ->136 0.59029
134 ->137 -0.38190

Excited State 3: Singlet-A 3.4913 eV 355.12 nm f=0.0227 <S**2>=0.000
133 ->136 0.50149
133 ->137 -0.22698
135 ->136 -0.10265
135 ->137 -0.41752

Excited State 4: Singlet-A 3.5041 eV 353.83 nm f=0.0760 <S**2>=0.000
132 ->136 -0.15433
133 ->136 0.37322
133 ->137 -0.22217
135 ->136 0.20139
135 ->137 0.48415

Excited State 5: Singlet-A 3.5657 eV 347.71 nm f=0.0095 <S**2>=0.000
131 ->136 -0.11562
132 ->136 0.60460
132 ->137 -0.29086
135 ->136 0.10618
135 ->137 0.11569

Excited State 6: Singlet-A 3.6192 eV 342.57 nm f=0.0097 <S**2>=0.000
131 ->136 0.61490
131 ->137 -0.31697
132 ->136 0.10629

Excited State 7: Singlet-A 3.7162 eV 333.63 nm f=0.0396 <S**2>=0.000
134 ->136 0.38642
134 ->137 0.58666

Excited State 8: Singlet-A 3.8212 eV 324.47 nm f=0.0076 <S**2>=0.000
133 ->136 0.32218
133 ->137 0.62076

Excited State 9: Singlet-A 3.8837 eV 319.24 nm f=0.0373 <S**2>=0.000
132 ->136 0.30180
132 ->137 0.62639

Excited State 10: Singlet-A 3.9415 eV 314.56 nm f=0.0075 <S**2>=0.000
131 ->136 0.32461
131 ->137 0.61908

Compound **2**

Excited State 1: Singlet-A 2.6535 eV 467.25 nm f=0.7739 <S**2>=0.000
170 ->171 0.70605
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1996.83037800
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.9357 eV 422.34 nm f=0.5605 <S**2>=0.000
170 ->172 0.67890
170 ->173 -0.12285

Excited State 3: Singlet-A 3.0143 eV 411.32 nm f=0.0069 <S**2>=0.000
169 ->171 0.70449

Excited State 4: Singlet-A 3.0894 eV 401.32 nm f=0.0072 <S**2>=0.000
168 ->171 0.70286

Excited State 5: Singlet-A 3.1422 eV 394.57 nm f=0.0190 <S**2>=0.000
167 ->171 0.69740

Excited State 6: Singlet-A 3.2004 eV 387.40 nm f=0.0010 <S**2>=0.000
166 ->171 0.70111

Excited State 7: Singlet-A 3.2096 eV 386.30 nm f=0.0326 <S**2>=0.000
169 ->172 0.64125
169 ->173 -0.27244

Excited State 8: Singlet-A 3.3164 eV 373.85 nm f=0.0007 <S**2>=0.000
168 ->172 0.65993
168 ->173 -0.22523

Excited State 9: Singlet-A 3.3789 eV 366.94 nm f=0.0091 <S**2>=0.000
167 ->172 0.66342
167 ->173 -0.20739

Excited State 10: Singlet-A 3.4306 eV 361.40 nm f=0.0037 <S**2>=0.000
166 ->172 0.66728
166 ->173 -0.22135

Excited State 11: Singlet-A 3.5061 eV 353.62 nm f=0.1292 <S**2>=0.000
165 ->171 0.23235
170 ->173 0.64567

Excited State 12: Singlet-A 3.6544 eV 339.27 nm f=0.0496 <S**2>=0.000
169 ->172 0.27750
169 ->173 0.64537

Excited State 13: Singlet-A 3.7724 eV 328.66 nm f=0.0001 <S**2>=0.000
168 ->172 0.22568
168 ->173 0.65977

Excited State 14: Singlet-A 3.8433 eV 322.59 nm f=0.0093 <S**2>=0.000
167 ->172 0.20187
167 ->173 0.65930

Excited State 15: Singlet-A 3.8850 eV 319.14 nm f=0.0070 <S**2>=0.000
166 ->172 0.22140
166 ->173 0.66125

Compound **3**

Excited State 1: Singlet-A 2.7575 eV 449.62 nm f=0.8439 <S**2>=0.000

218 -> 219 0.69673

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2458.41347278

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.0996 eV 400.00 nm f=0.5192 <S**2>=0.000

218 -> 220 0.68969

Excited State 3: Singlet-A 3.1774 eV 390.20 nm f=0.0256 <S**2>=0.000

217 -> 219 0.66888

217 -> 220 -0.18736

217 -> 221 -0.10532

Excited State 4: Singlet-A 3.2388 eV 382.81 nm f=0.0245 <S**2>=0.000

216 -> 219 0.66559

216 -> 220 0.18867

216 -> 221 -0.11964

Excited State 5: Singlet-A 3.2889 eV 376.98 nm f=0.0013 <S**2>=0.000

215 -> 219 0.67542

215 -> 220 -0.13995

Excited State 6: Singlet-A 3.3280 eV 372.55 nm f=0.0023 <S**2>=0.000

214 -> 219 0.67716

214 -> 220 0.12747

Excited State 7: Singlet-A 3.3571 eV 369.32 nm f=0.0041 <S**2>=0.000

211 -> 219 -0.10186

213 -> 219 0.67300

Excited State 8: Singlet-A 3.3930 eV 365.41 nm f=0.0053 <S**2>=0.000

212 -> 219 0.67196

212 -> 220 0.10077

Excited State 9: Singlet-A 3.4208 eV 362.44 nm f=0.0045 <S**2>=0.000

211 -> 219 0.66990

211 -> 220 -0.13770

213 -> 219 0.11285

Excited State 10: Singlet-A 3.4485 eV 359.54 nm f=0.0033 <S**2>=0.000

210 -> 219 0.67389

210 -> 220 0.13898

212 -> 219 0.10212

Excited State 11: Singlet-A 3.4748 eV 356.81 nm f=0.0644 <S**2>=0.000

217 -> 219 0.21923

217 -> 220 0.60801

217 -> 221 0.26659

Excited State 12: Singlet-A 3.5486 eV 349.39 nm f=0.0625 <S**2>=0.000

216 -> 219 -0.22567

216 -> 220 0.60329

216 -> 221 -0.28046

Excited State 13: Singlet-A 3.5737 eV 346.93 nm f=0.0250 <S**2>=0.000

209 -> 219 0.15113

215 -> 220 0.22104

218 -> 221 0.61600

Excited State 14: Singlet-A 3.6192 eV 342.58 nm f=0.0009 <S**2>=0.000

215 -> 219 0.16240

215 -> 220 0.58957

215 -> 221 0.23509

218 -> 221 -0.22212

Excited State 15: Singlet-A 3.6734 eV 337.52 nm f=0.0005 <S**2>=0.000

214 -> 219 -0.16242

214 -> 220 0.61322

214 -> 221 -0.25179

218 -> 221 0.11876

Excited State 16: Singlet-A 3.7074 eV 334.43 nm f=0.0195 <S**2>=0.000

213 -> 219 0.12413

213 -> 220 0.62593

213 -> 221 0.21516

Excited State 17: Singlet-A 3.7383 eV 331.66 nm f=0.0064 <S**2>=0.000

211 -> 219 0.16141

211 -> 220 0.62543

211 -> 221 0.24465

Excited State 18: Singlet-A 3.7453 eV 331.04 nm f=0.0184 <S**2>=0.000

212 -> 219 -0.13758

212 -> 220 0.61867

212 -> 221 -0.23092

213 -> 221 -0.10321

Excited State 19: Singlet-A 3.7840 eV 327.65 nm f=0.0090 <S**2>=0.000

210 -> 219 -0.16486

210 -> 220 0.62748

210 -> 221 -0.26102

Excited State 20: Singlet-A 3.9910 eV 310.66 nm f=0.0039 <S**2>=0.000

205 -> 219 0.19623

207 -> 219 -0.39310

208 -> 219 0.12195

218 -> 222 0.51450

Reference

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann *J. Appl. Cryst*. **2009**. *42*, 339-341.