Electronic Supporting Information

Imidazopyridine-Fluoride Interaction: Solvent-switched AIE Effect via S…O Conformational Locking

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Crystal data of C1, C2, C1.S, and C2.S and H-bonding data

Table S1. Crystal data

Compound	**C1**	**C2**	**C1.S**	**C2.S**
CCDC No.	2085440	2085441	2085442	2085443
Empirical formula	$C_{15}H_9ClN_4OS$	$C_{15}H_{10}ClN_5O$	$C_{31}H_{48}Cl\ N_5O_3S$	$C_{31}H_{49}Cl\ N_6O_3$
Formula weight	328.77	311.73	606.25	589.21
Temperature/K	292(2)	292(2)	292(2)	292(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	P-1	$P2/c$	$Pbcn$
a/Å	8.0687(8)	6.5832(8)	23.0412(9)	46.3890(18)
b/Å	6.5157(5)	7.6795(10)	9.3628(4)	9.2469(6)
c/Å	26.9123(17)	13.7007(13)	15.7390(7)	15.7793(9)
α/°	90	97.024(9)	90	90
β/°	90.204(7)	91.925(9)	98.319(4)	90
γ/°	90	96.046(10)	90	90
Volume/Å^3	1414.9(2)	682.87(14)	3359.6(2)	6768.6(6)
Z	4	2	4	8
ρ_{calc}g/cm^3	1.543	1.516	1.199	1.156
μ/mm^{-1}	0.424	0.289	0.213	0.151
F(000)	672.0	320.0	1304.0	2544.0
Crystal size/mm^3	0.13 × 0.12 ×0.11	0.068 × 0.056 × 0.044	0.056×0.045×0.033	0.150 ×0.140 ×0.110
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range/°	6.056 to 57.86	5.378 to 50.992	5.076 to 57.802	4.492 to 58.792
Index ranges	$-10 \le h \le 9$, $-8 \le k \le 7$, $-35 \le l \le 32$	$-7 \le h \le 7$, $-8 \le k \le 9$, $-16 \le l \le 16$	$-30 \le h \le 30$, $-10 \le k \le 12$, $-20 \le l \le 21$	$-63 \le h \le 59$, $-12 \le k \le 9$, $-17 \le l \le 21$
Reflections collected	15957	4948	39938	22943
Independent reflections	3260 [R_{int} = 0.0928]	2536 [R_{int} = 0.0266]	7806 [R_{int} = 0.0824]	8095 [R_{int} = 0.066]
Data/restraints/parameters	3260/0/204	2536/0/207	7806/0/390	8095/50/407
Goodness-of-fit on F^2	1.102	1.026	1.012	0.954
Final R indexes [I>=2σ (I)]	R_1 = 0.0902, wR_2 = 0.2512	R_1 = 0.0530, wR_2 = 0.1037	R_1 = 0.0560, wR_2 = 0.1362	R_1 = 0.0653, wR_2 = 0.1336
Final R indexes [all data]	R_1 = 0.1044, wR_2 = 0.2578	R_1 = 0.1089, wR_2 = 0.1274	R_1 = 0.0925, wR_2 = 0.1523	R_1 = 0.2003, wR_2 = 0.1890
Largest diff. peak/hole / eÅ^{-3}	0.55/-0.40	0.20/-0.24	0.24/-0.29	0.18/-0.28

Table S2: H-bonding data

Interactions	D-H	H···A (Å)	D···A (Å)	D–H···A (º)	Symmetry code
C1					
N3-H3 ...N2	0.97(8)	2.36(8)	2.744(8)	102(6)	x,y,z
C1-H1 ...N2	0.93	2.72	3.612(9)	162	-x+2,-y,-z+1
C2-H2...N4	0.93	2.86	3.735(10)	158	-x+2,-y,-z+1
C12-H12...O1	0.93	2.65	3.366(10)	134	-x+1,-y+2,-z+1
C2					
N2-H2...O1	0.83(3)	2.32(3)	2.810(3)	118(3)	x, y, z
N2-H2 ...O1	0.83(3)	2.46(3)	3.104(3)	136(3)	-x,-y+1,-z+1
C13-H13 ...N1	0.93	2.65	3.544(4)	162	-x+2,-y+2,-z+1
C14-H14 ...N5	0.93	2.71	3.610(4)	163	-x+2,-y+2,-z+1
C1.S					
O2-H101...O3	0.82(3)	2.02(3)	2.837(3)	176(3)	x, y, z
O3-H102 ...N3	0.86(3)	2.08(3)	2.909(3)	162(3)	x, y, z
C12-H12...O2	0.93	2.62	3.199(3)	121	-x+1,-y+1,-z+1
O2-H100...N2	0.83(3)	2.16	2.980(2)	169(3)	x,+y-1,+z
O3-H103...N1	0.81(3)	2.37(4)	3.071(2)	146(3)	x,+y-1,+z
C2.S					
O2-H2A ...N3	0.84(4)	2.17(4)	2.992(4)	166(4)	x, y, z
O2-H2B...O3	0.92(4)	1.98(4)	2.861(4)	160(4)	x, y, z
O3-H3C ...N5	0.83(4)	2.22(4)	2.925(4)	143(4)	x, y, z
N4-H4 ...O1	0.86	2.01	2.563(3)	121	x, y, z
O3-H3B ...N2	0.82(4)	2.16(4)	2.941(4)	162(4)	x,+y+1,+z
C2-H2 ...O2	0.93	2.64	3.240(5)	123	-x+1,-y+1,-z+2

Spectroscopic characterization of compounds

Figure S1. ^{1}HNMR (400MHz, $CDCl_3$) of compound **1**.

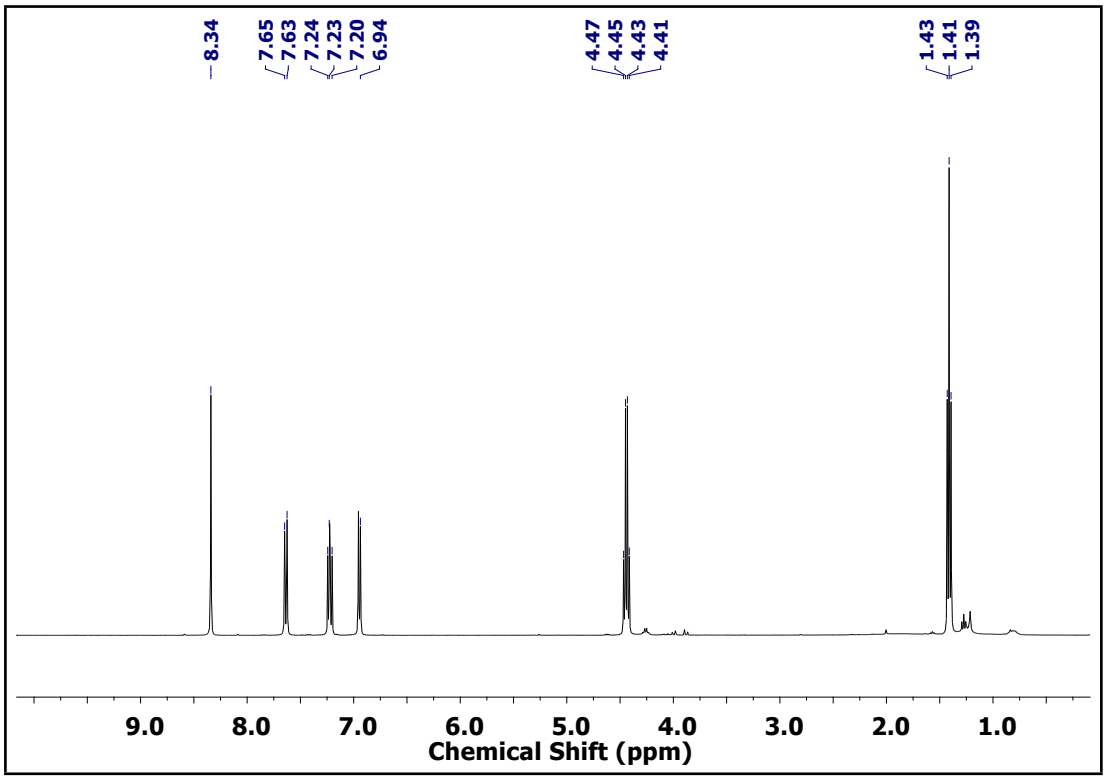


Figure S2. ^{13}CNMR (100 MHz, $CDCl_3$) of compound **1**.

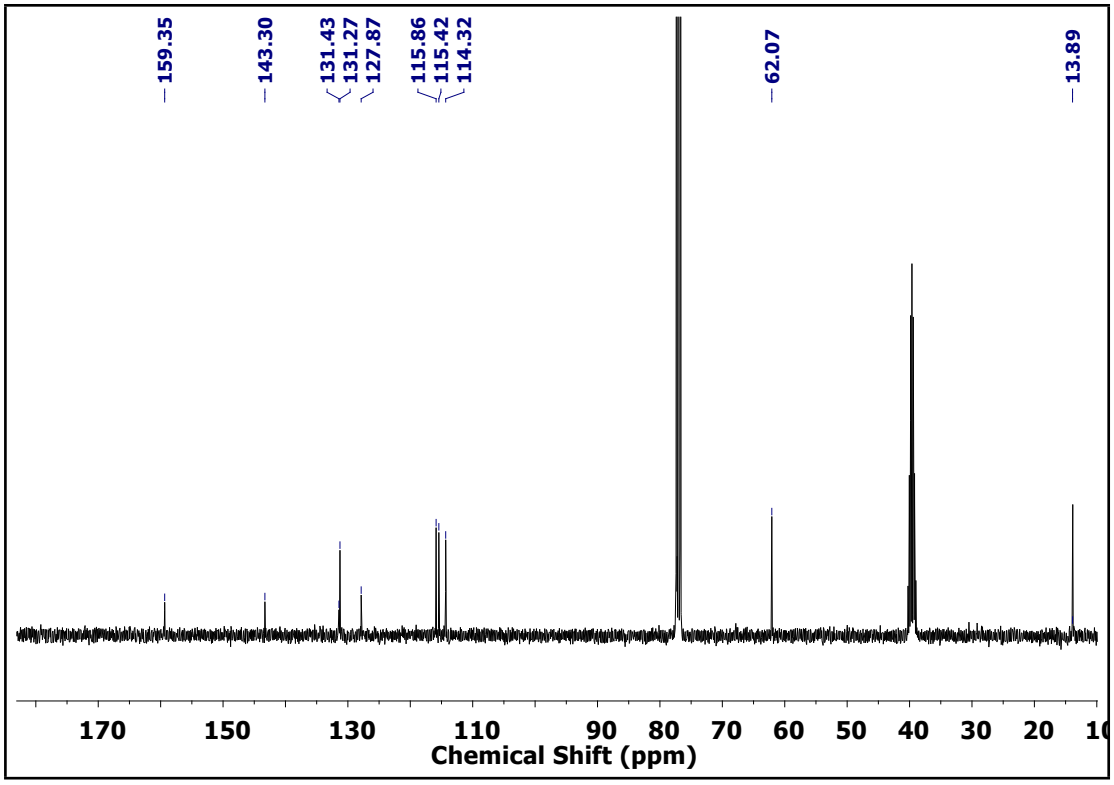


Figure S3. ^{1}HNMR (400 MHz, d_6-DMSO) of compound C1.

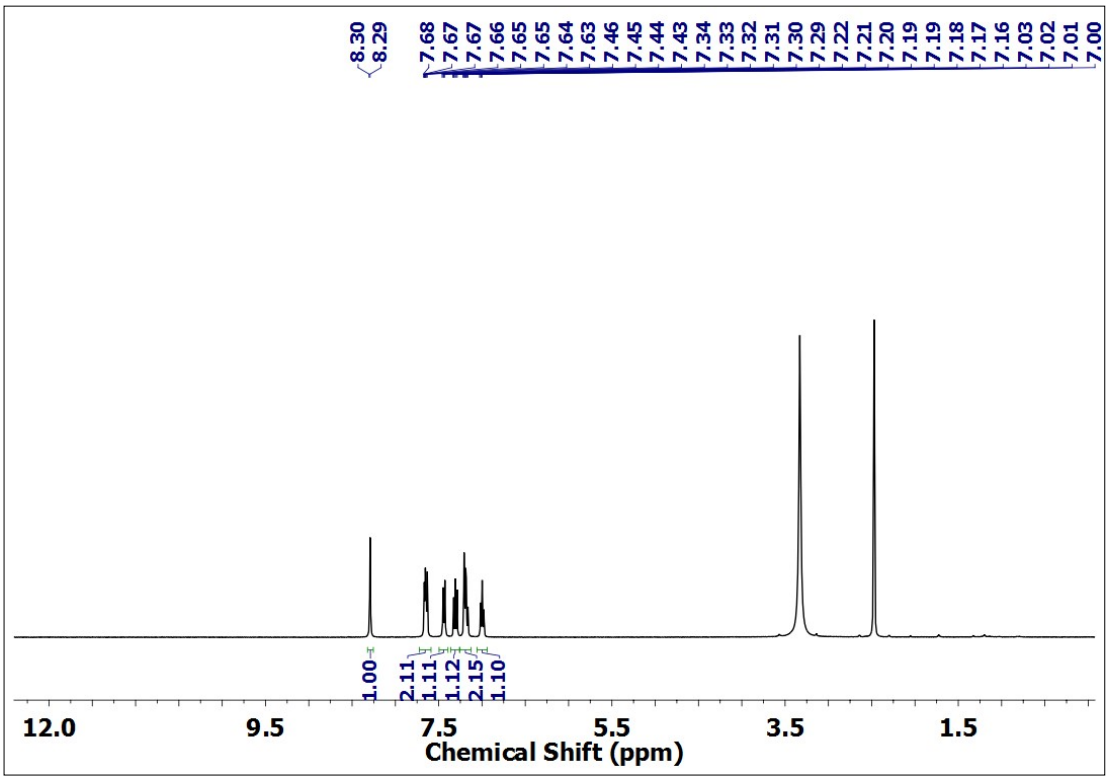


Figure S4. ^{13}CNMR (100 MHz, d_6-DMSO) of compound C1.

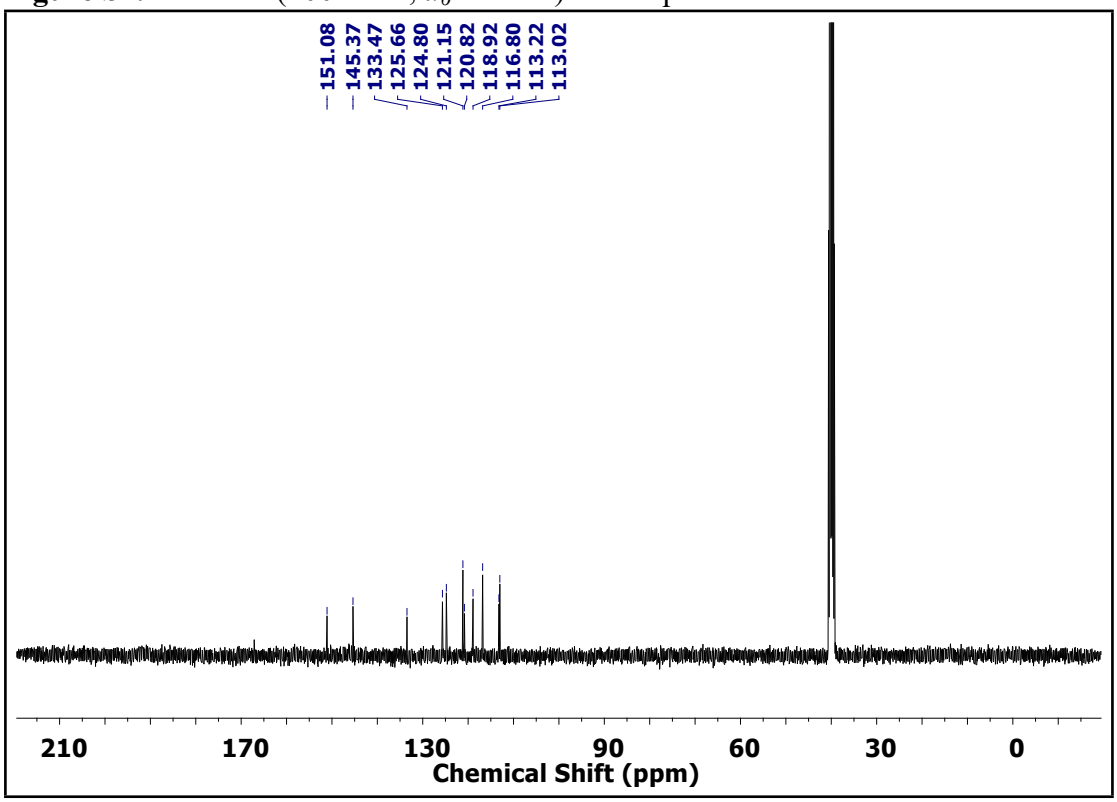


Figure S5. ^{1}HNMR (400 MHz, DMSO) of compound C2.

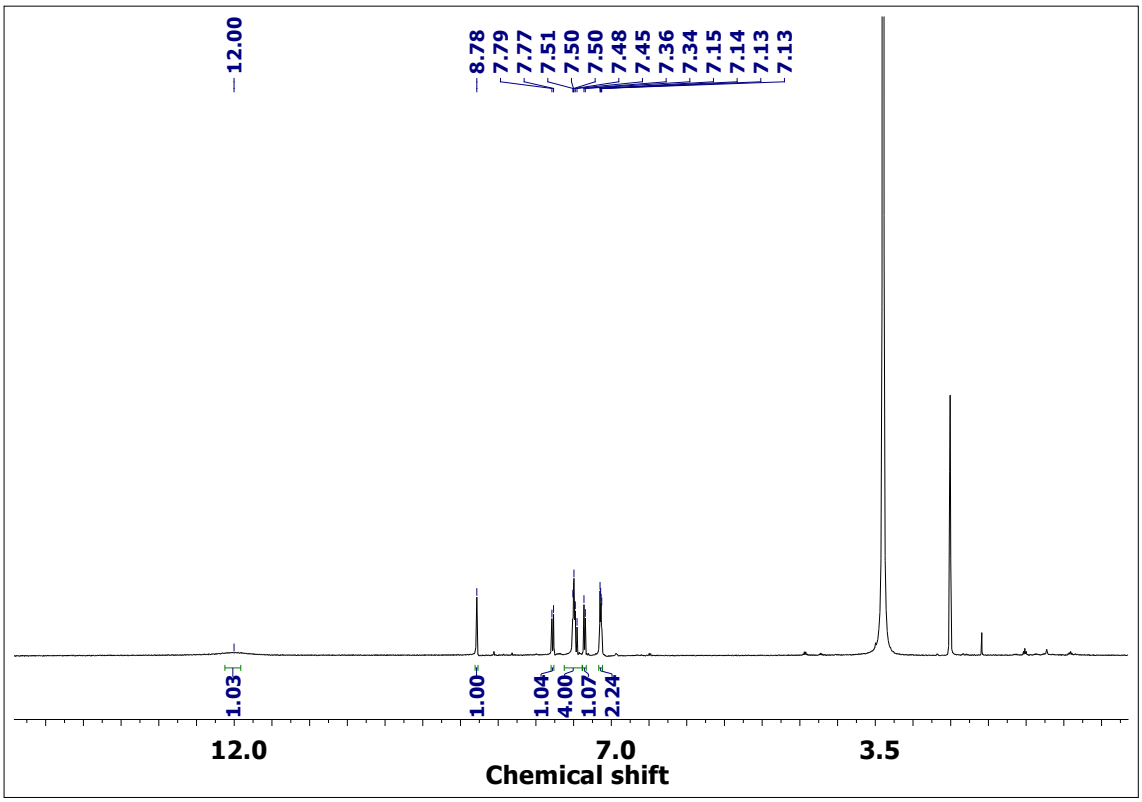


Figure S6. ^{1}HNMR (400 MHz, $CDCl_3$) of compound C2.

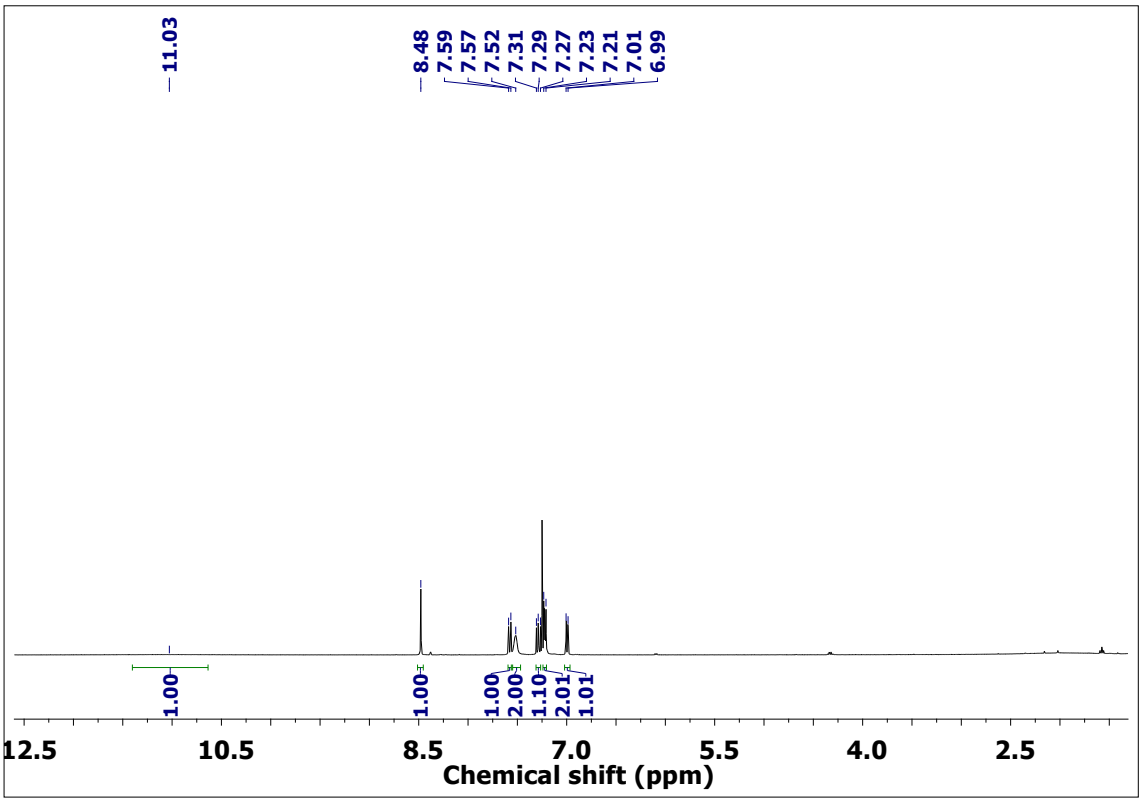


Figure S7. ^{13}CNMR (100 MHz, $CDCl_3$) of compound C2.

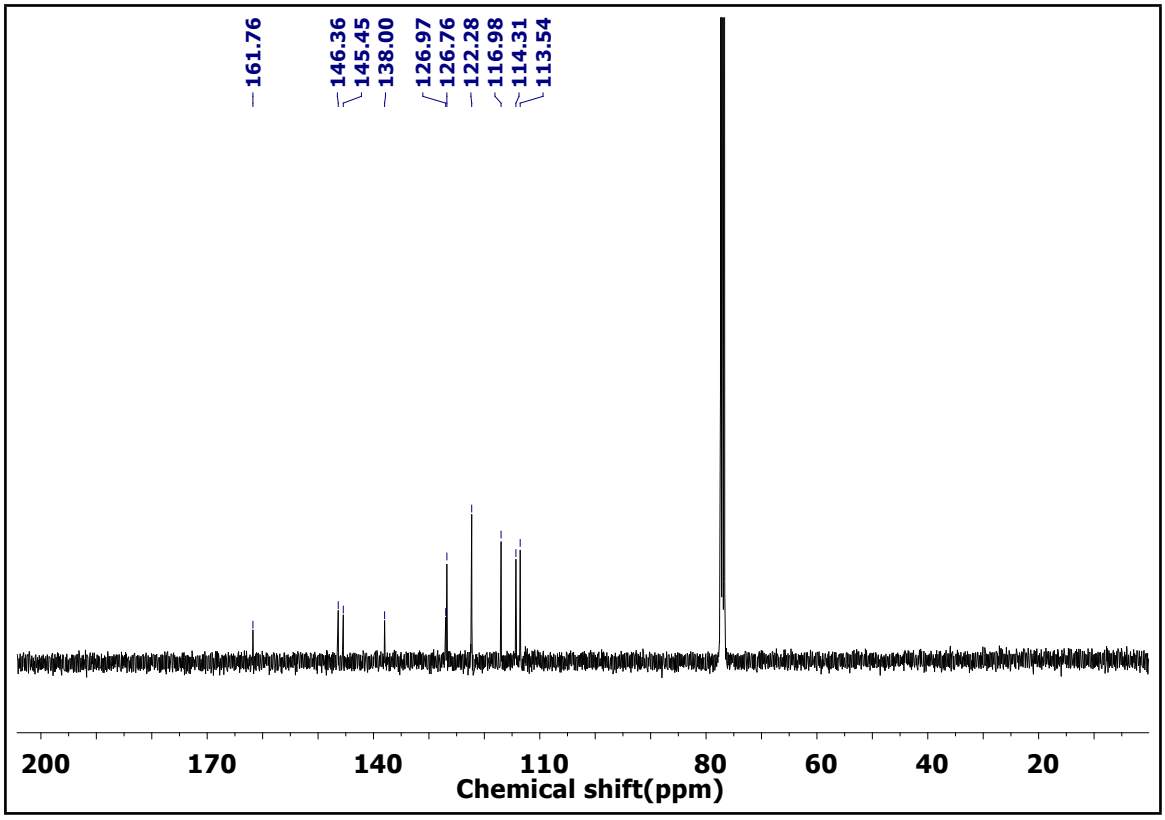


Figure S8. ESI-HRMS spectra of C1. The isotopic pattern at m/z= 351.0039can be attributed to [C1.Na$^+$] (m/zcalculated = 351.0078).

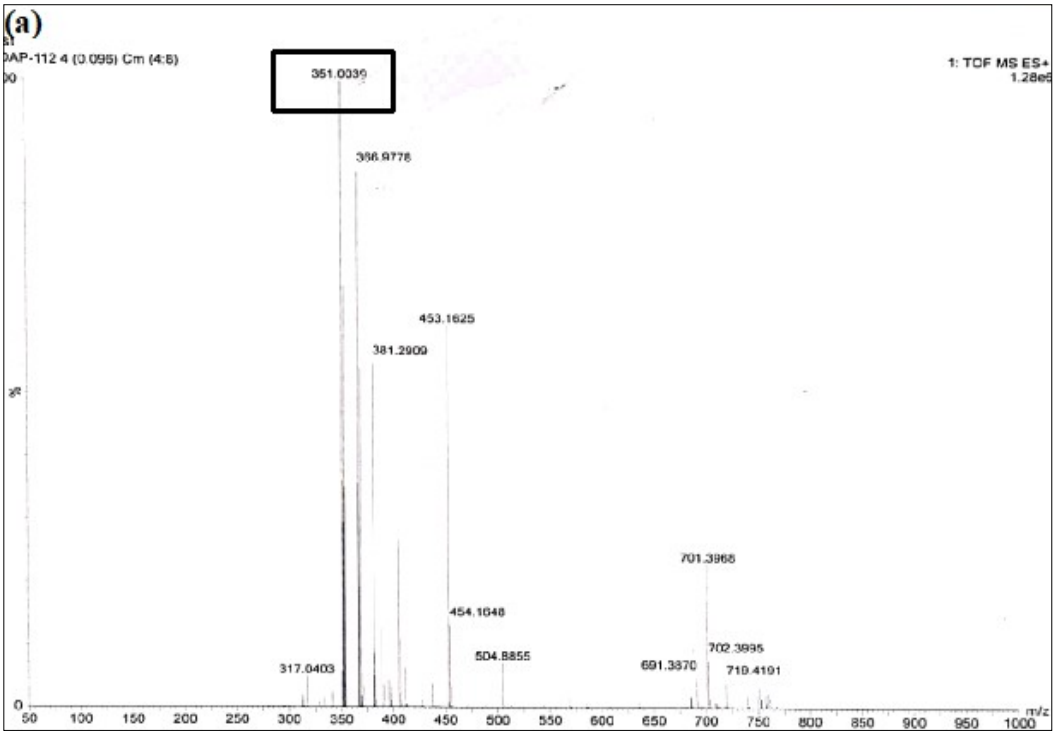
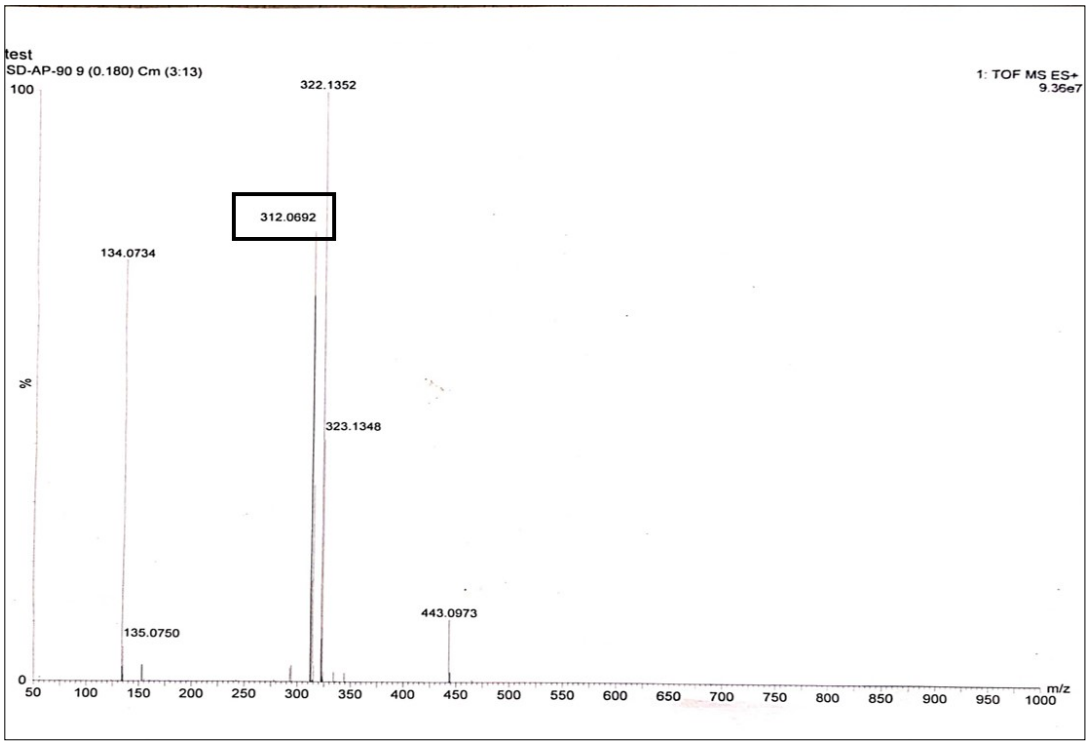


Figure S9. ESI-HRMS spectra of C2. The isotopic pattern at m/z= 312.0692 can be attributed to [C2.H$^+$] (m/zcalculated = 312.0647).



LOD, binding constant, and stoichiometry

Evaluating absorption and emission data collected after titration gives binding constant and limit of detection. Binding constant calculated by employing

Intercept/slope = Binding constant

Values obtained by linear fitting the importance of $1/\Delta\varepsilon$ vs. $1/[F^-]$.

LOD of compounds were obtained by placing the equation

2σ/slope

Here, σ stand for the stander deviation of the regression line and slope obtained by the emission intensity vs. concentration plot.

Figure S10. We are calibrating linear fit curve[1] of emission at 444nmof **C1** (Acetonitrile) to obtain (a) Binding constant (3.24×10^3) and (b) LOD (1.45×10^{-6}).

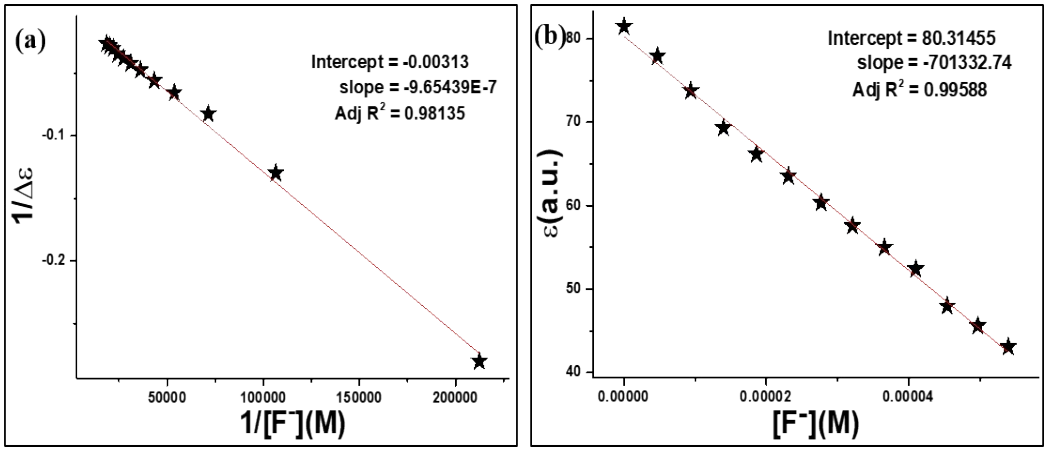


Figure S11. We are calibrating linear fit curve[1] of absorbance at 309nm of **C1** (Acetonitrile) to obtain (a) Binding constant ($1.55x10^4$) and (b) LOD ($2.46x10^{-4}$).

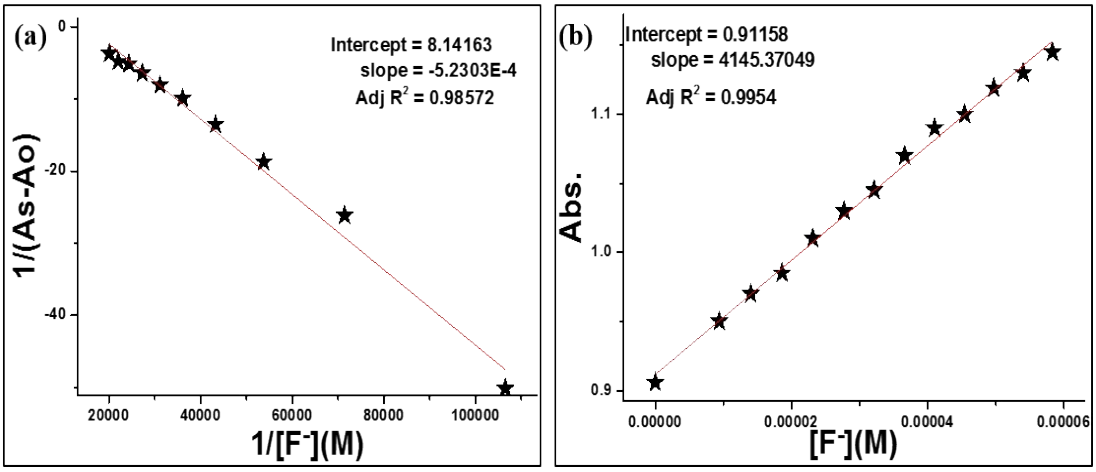


Figure S12. Calibrating linear fit curve[1] of emission at 422nm (water) of **C2**to obtain (a) Binding constant ($3.4x10^3$), (b) LOD ($9.8x10^{-8}$).

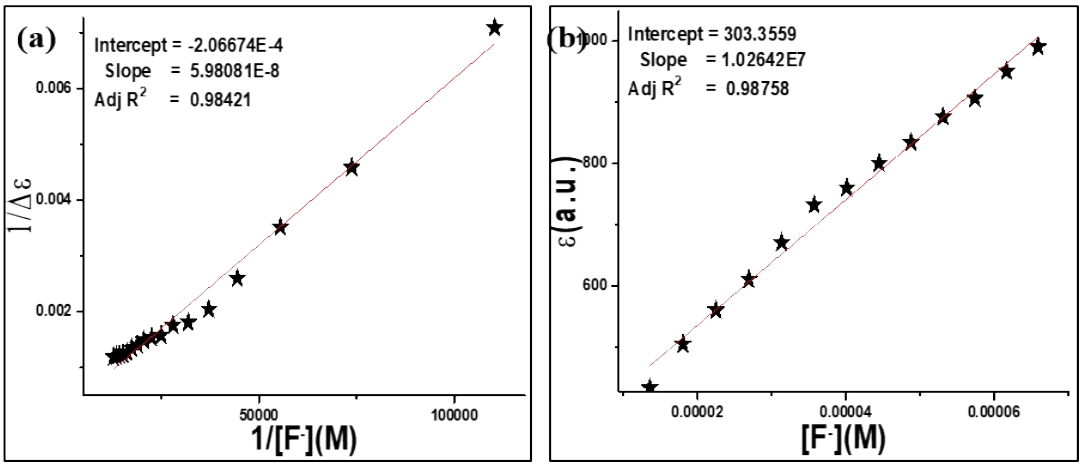
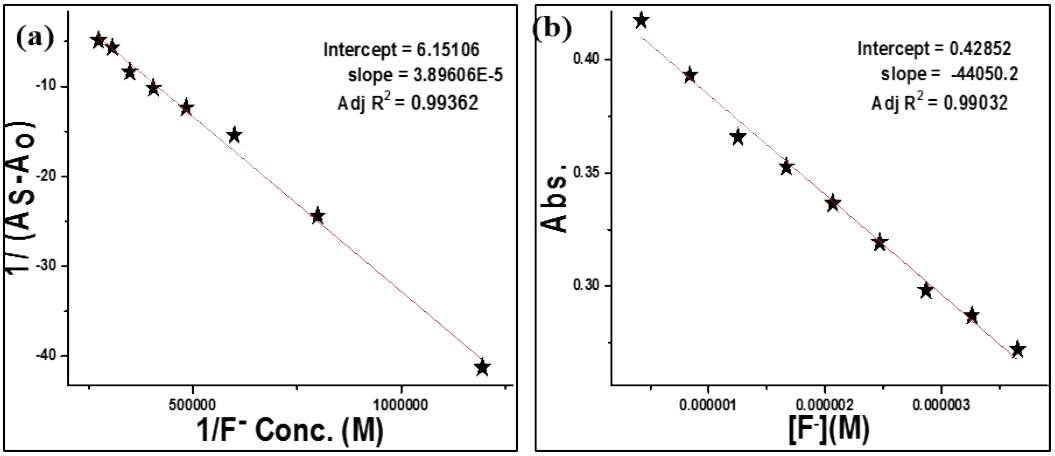


Figure S13. We are calibrating linear fit curve[1] of absorbance at 309nm of **C2** to obtain (a) Binding constant ($1.58x10^5$) and (b) LOD ($2.31x10^{-5}$).



Emission titration

Figure S14. Emission spectra of (a) **C1** in different solvents (b) **C1** in the presence of anions.

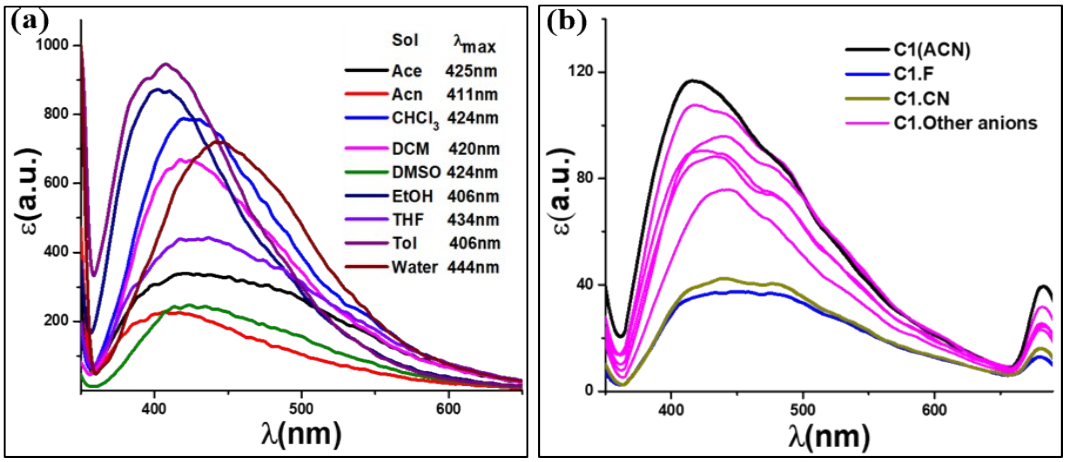


Figure S15. (a) Titration of **C1** with F^-(b) Titration of **C2** with F^- in acetonitrile. Emission spectra of C1.

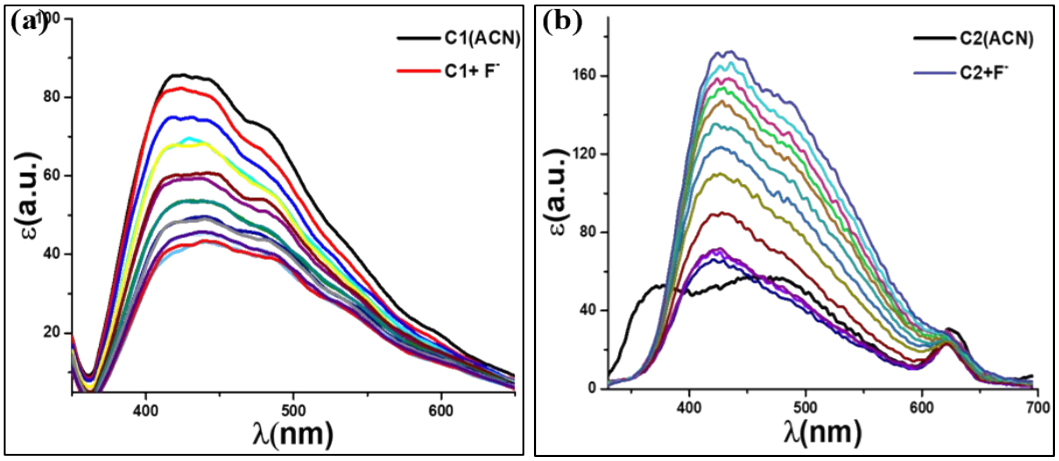


Figure S16. Depiction of change in absorbance of C1 and C2 with F^-.

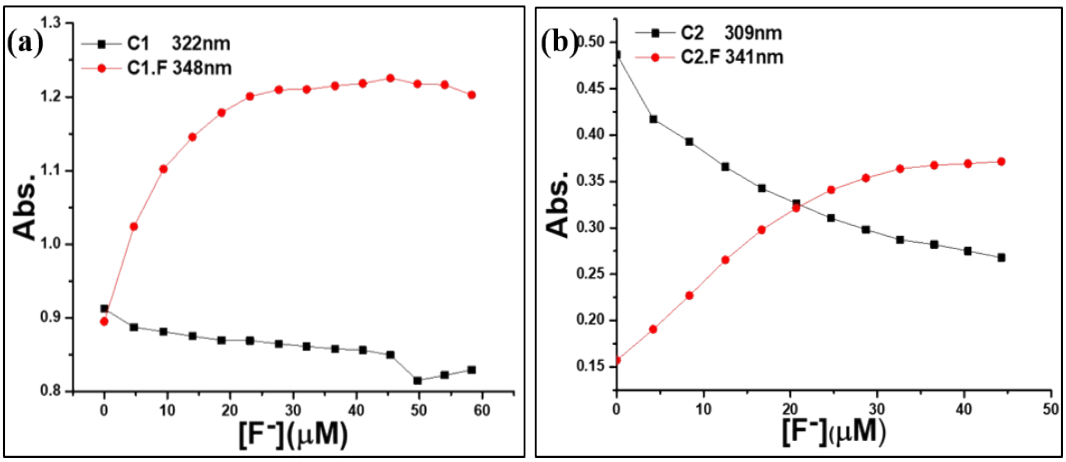
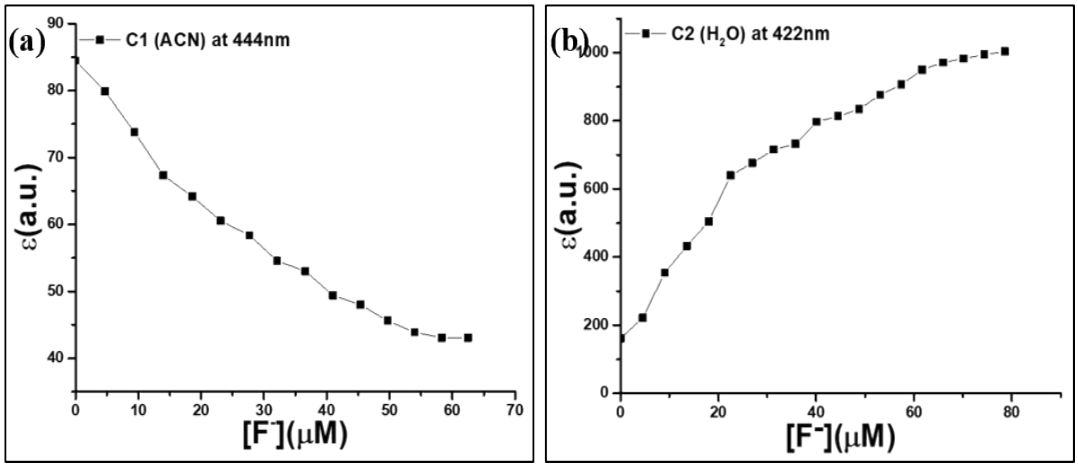
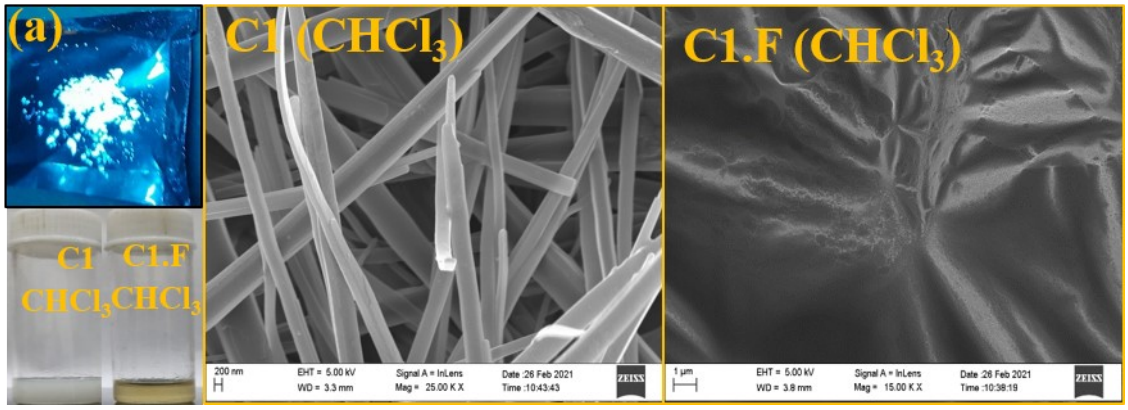


Figure S17. Depiction of change in emission intensity of C1 and C2 with F^-.



<u>Mysterious behavior of C1 in $CHCl_3$</u>

Figure S18. (a) Image of C1 powder in exposer to long-range light (white fluorescence in nature). FE-SEM and solution phase image support this behavior of C1 in CHCl3.



D_2O exchange of compounds in ^1H NMR

Figure S19. ^{1}HNMR (400MHz, DMSO) spectra of C1 (above) and C1 after D_2O addition (below). The peak at 7.28ppm shows D_2O exchange via reduced integration value.[2]

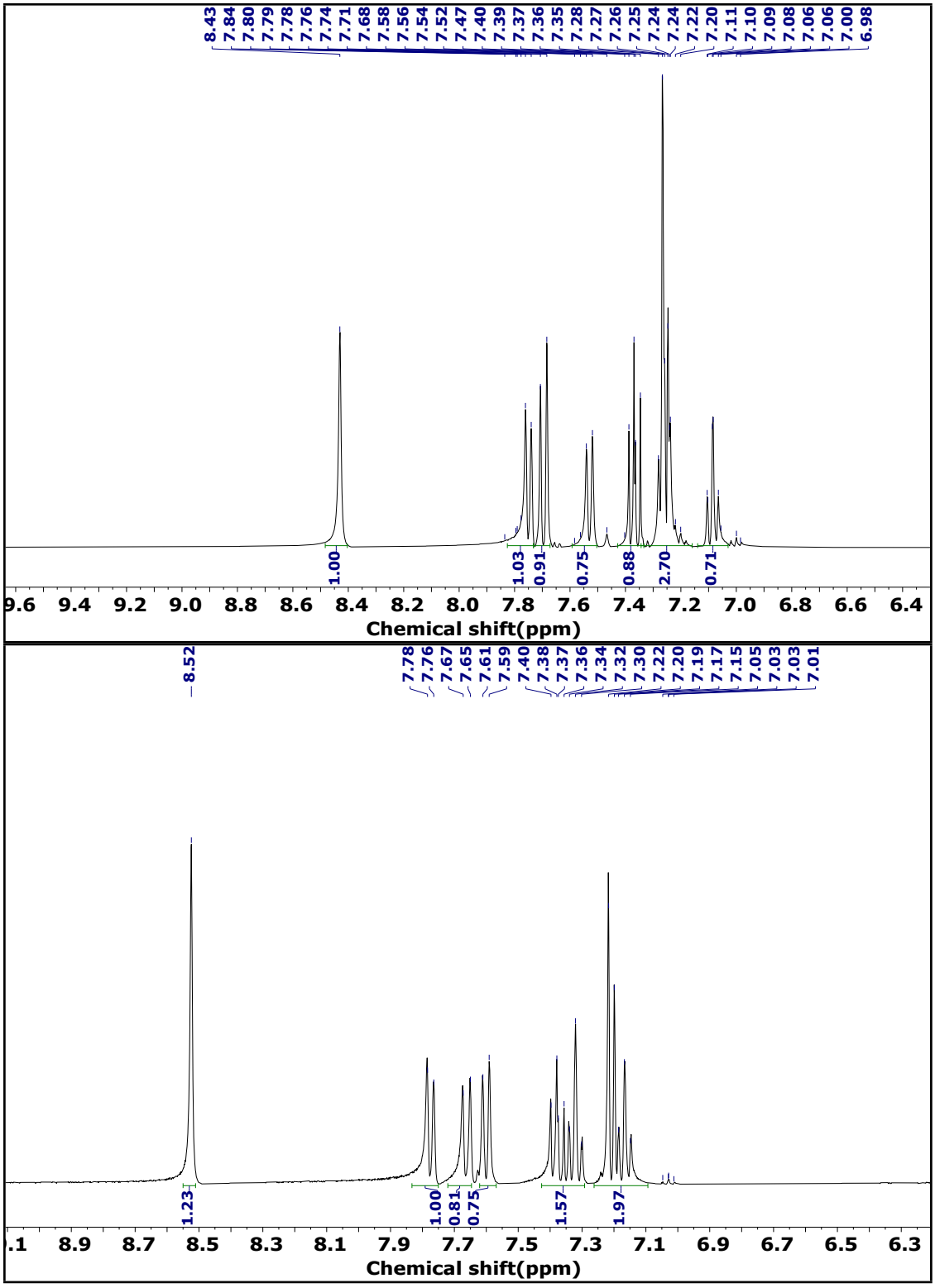
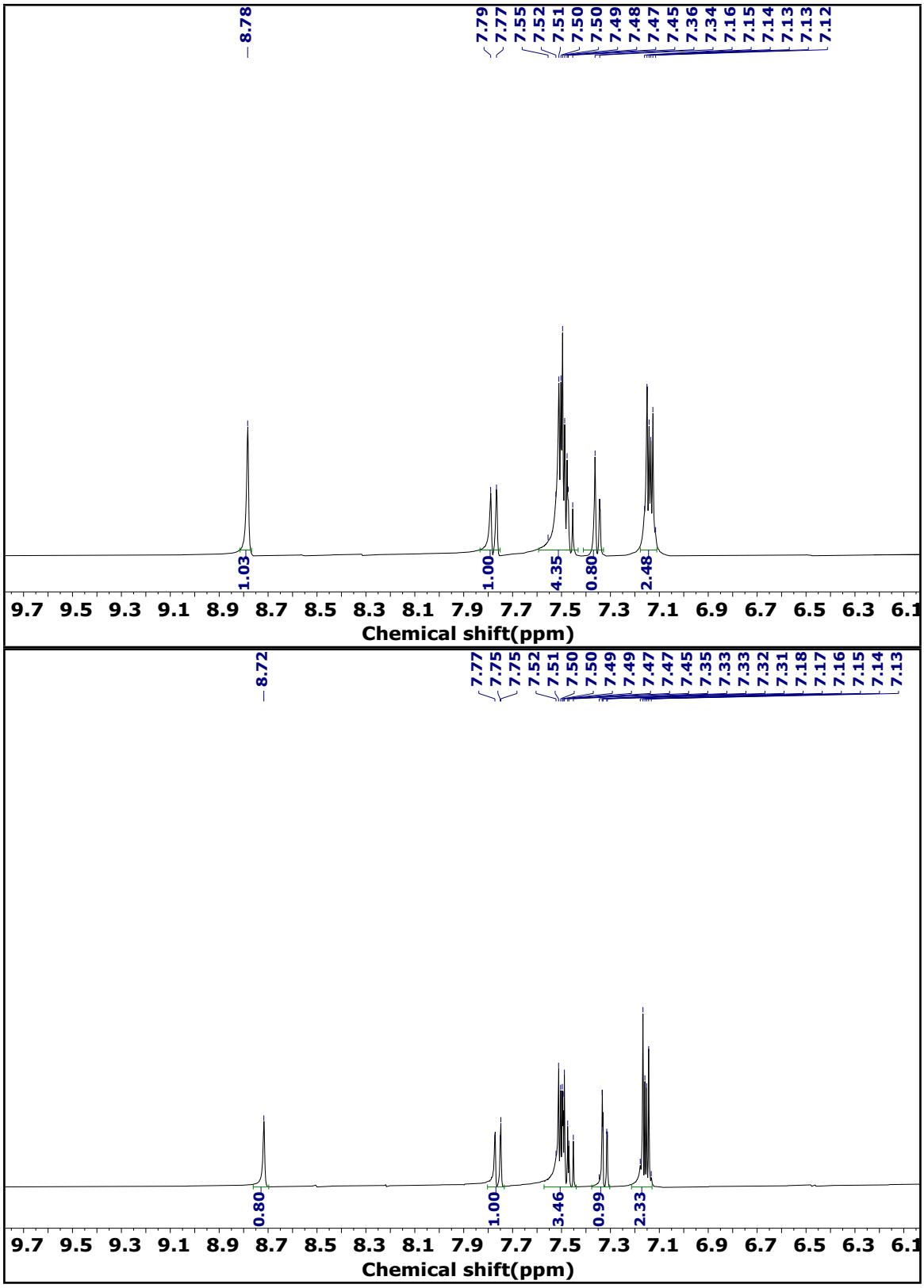


Figure S20. ^{1}HNMR (400MHz, DMSO) spectra of C2 (above) and C2 after D_2O addition (below). The peak at 7.55ppm shows a D_2O exchange reaction.[2]



^{1}H and ^{19}F NMR spectra of complexes

Figure S21. ^{1}HNMR(400 MHz, $CDCl_3$) of (a) C1.F^- and (b) C2.F^- having 20eq of F^-, up to a range of 13 to 19 ppm.[2,3]

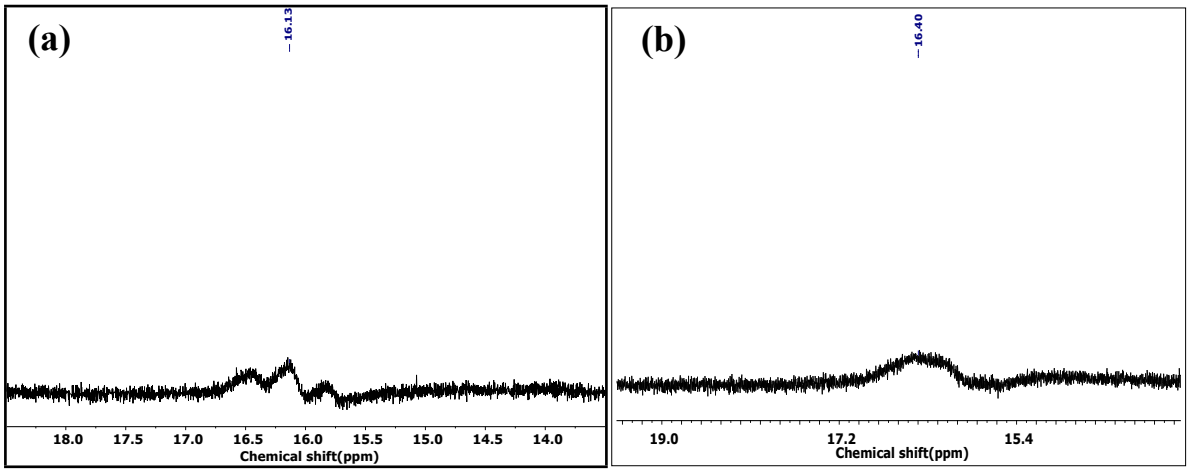


Figure S22. ^{19}FNMR (377 MHz, $CDCl_3$) spectra of C1.F^-. The desired triplet peak obtained at 144ppm signified that deprotonated fluoride ion [$H_2.F^-$].[3]

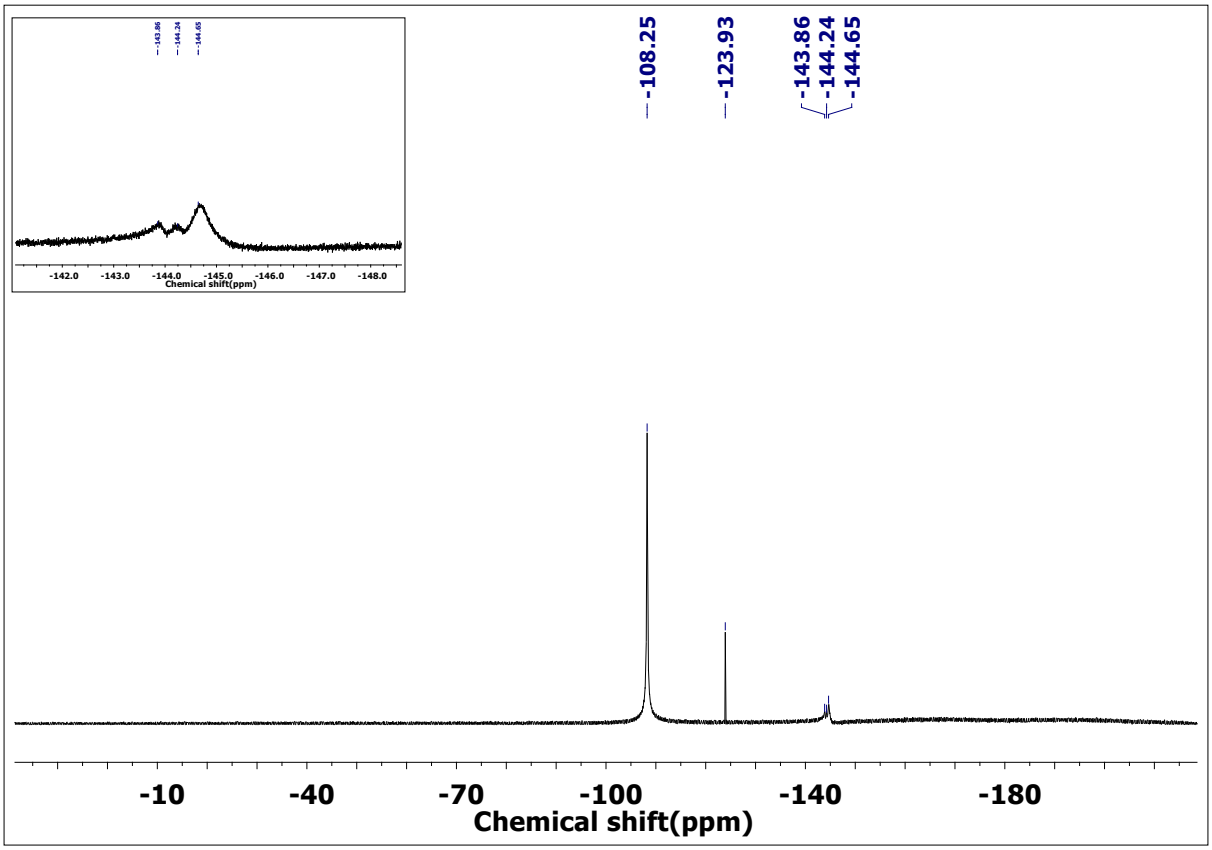


Figure S23. ^{19}FNMR (377 MHz, $CDCl_3$) spectra of C2.F$^-$. The desired peak between 130 to 170ppm obtained signified that deprotonated fluoride ion [H_2.F$^-$] formed.[3]

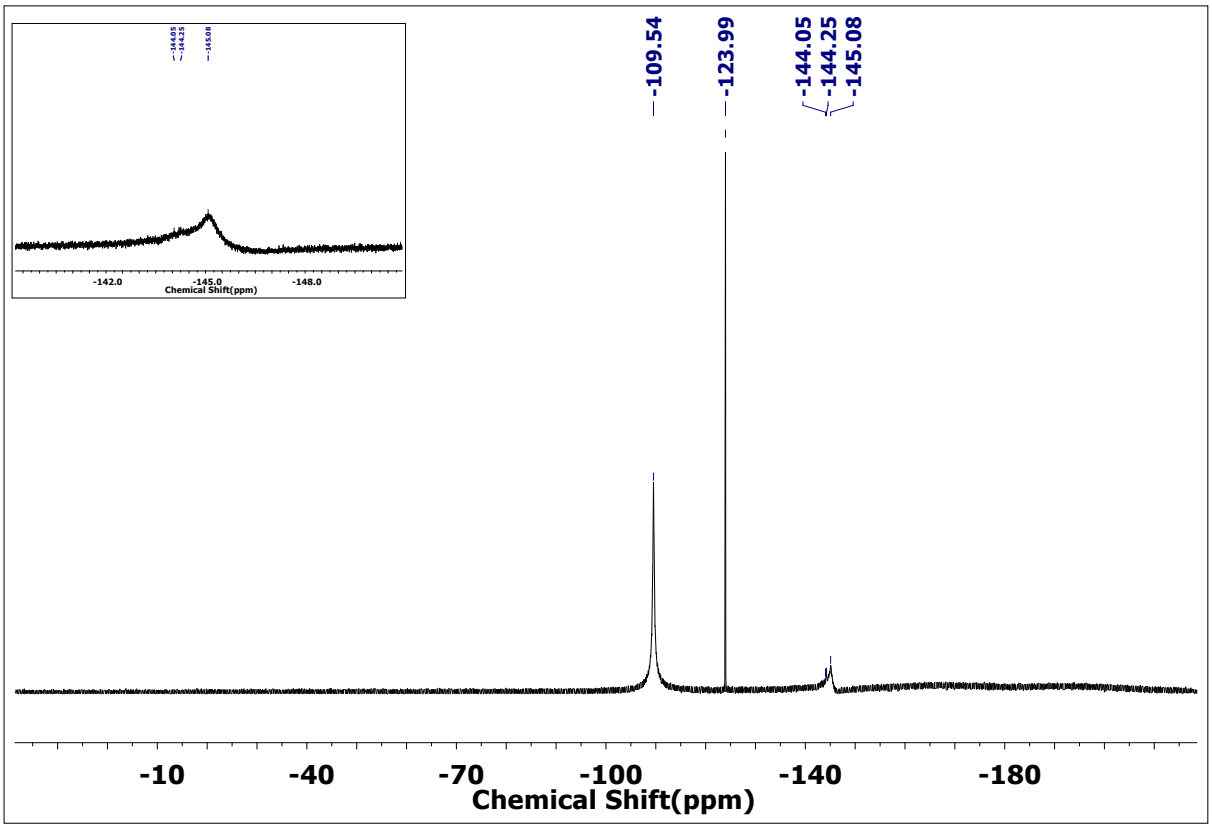


Figure S24. ^{19}FNMR (377 MHz, $CDCl_3$) spectra of TBAF$^-$. The desired peak was obtained at 124.62ppm.

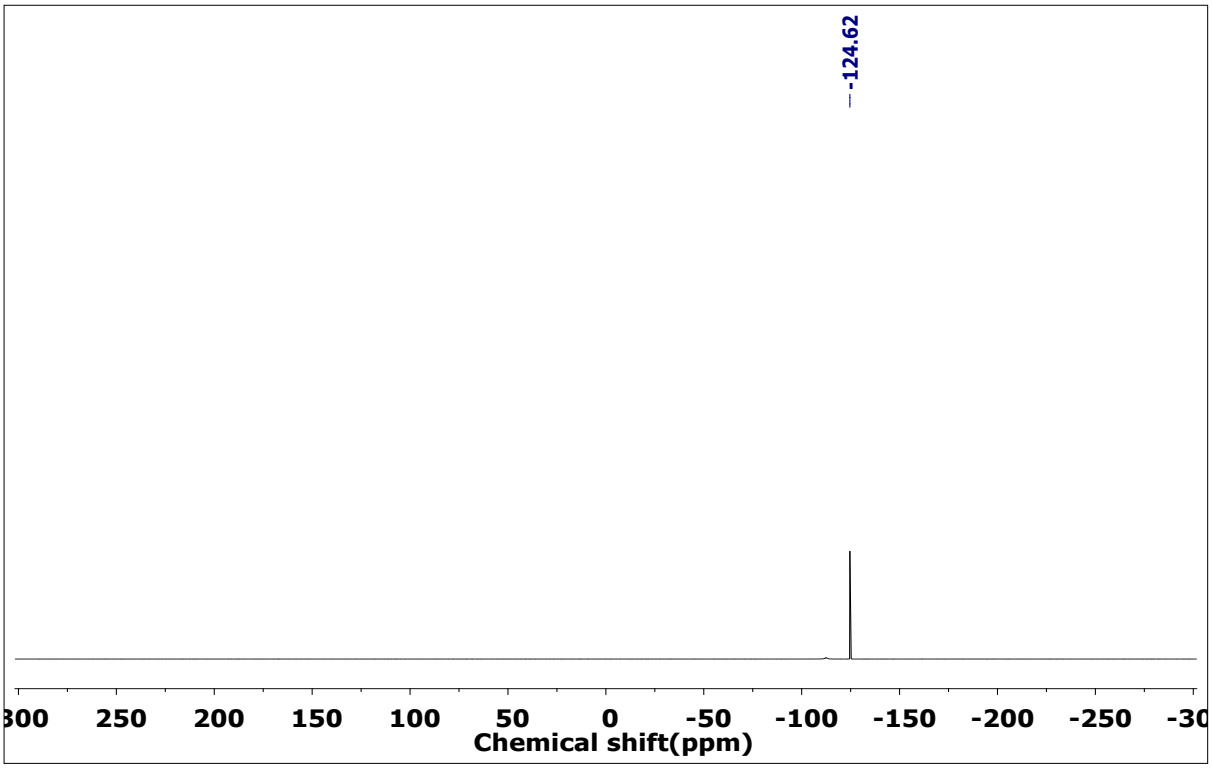
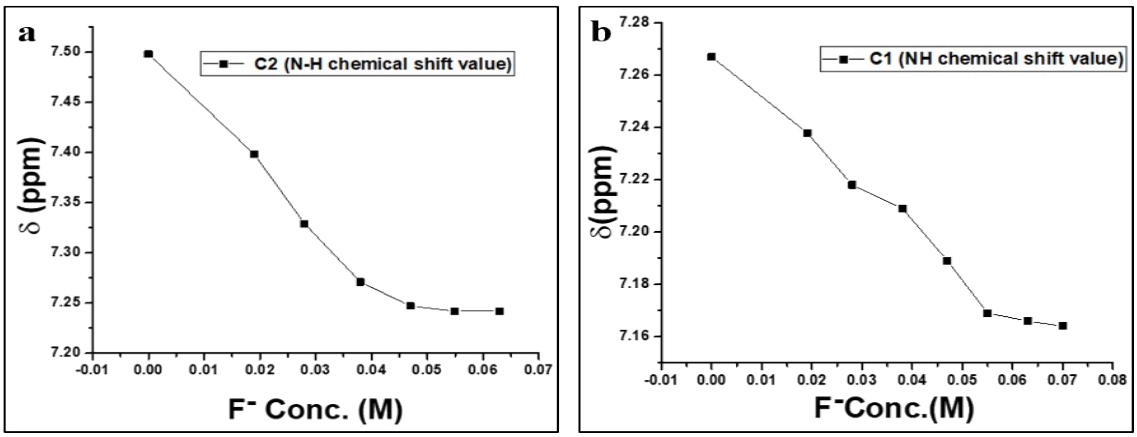
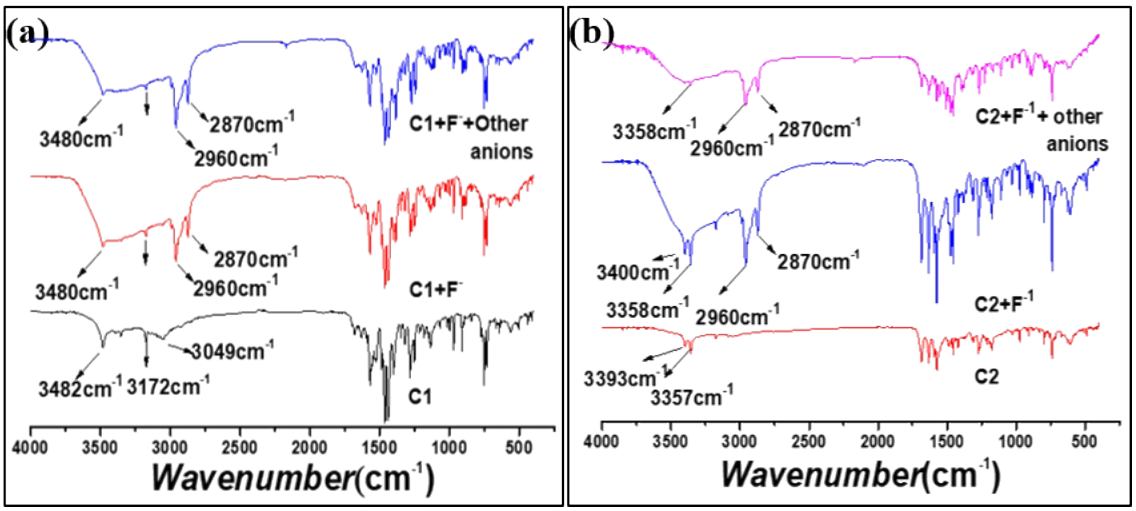


Figure S25. Fluoride anion concentration added versus chemical shift value of (a) **C1**and (b) **C2**.



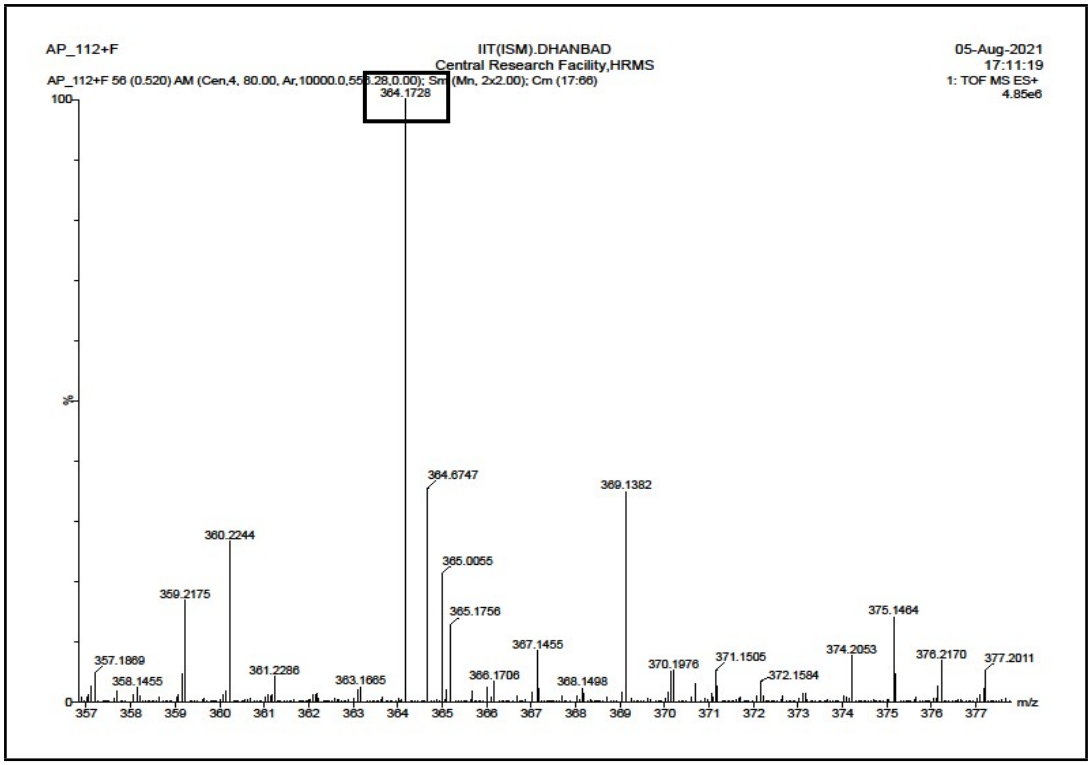
FT-IR spectroscopy

Figure S26. FT-IR plots of (a) **C1** and (b) **C2**.

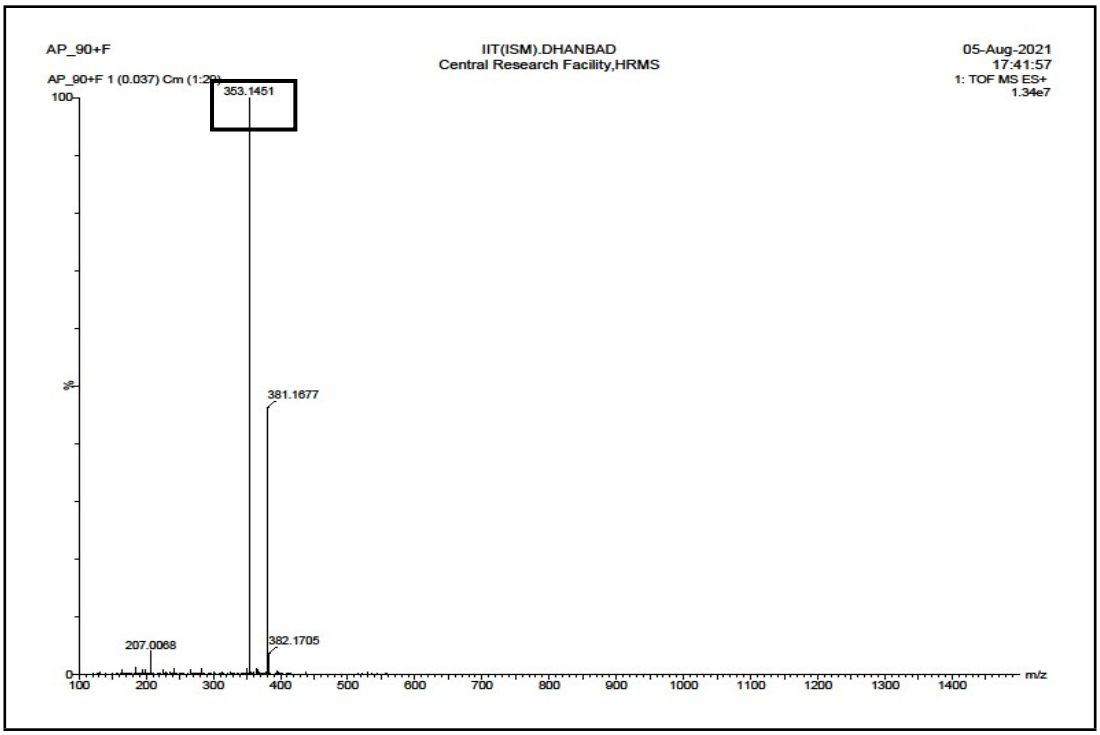


HR-MS spectrum of complexes

Figure S27. ESI-HRMS spectra of **C1.S** (m/z calculated for [C1+F+H_2O-H] = 364.0203 and obtained 364.1728)

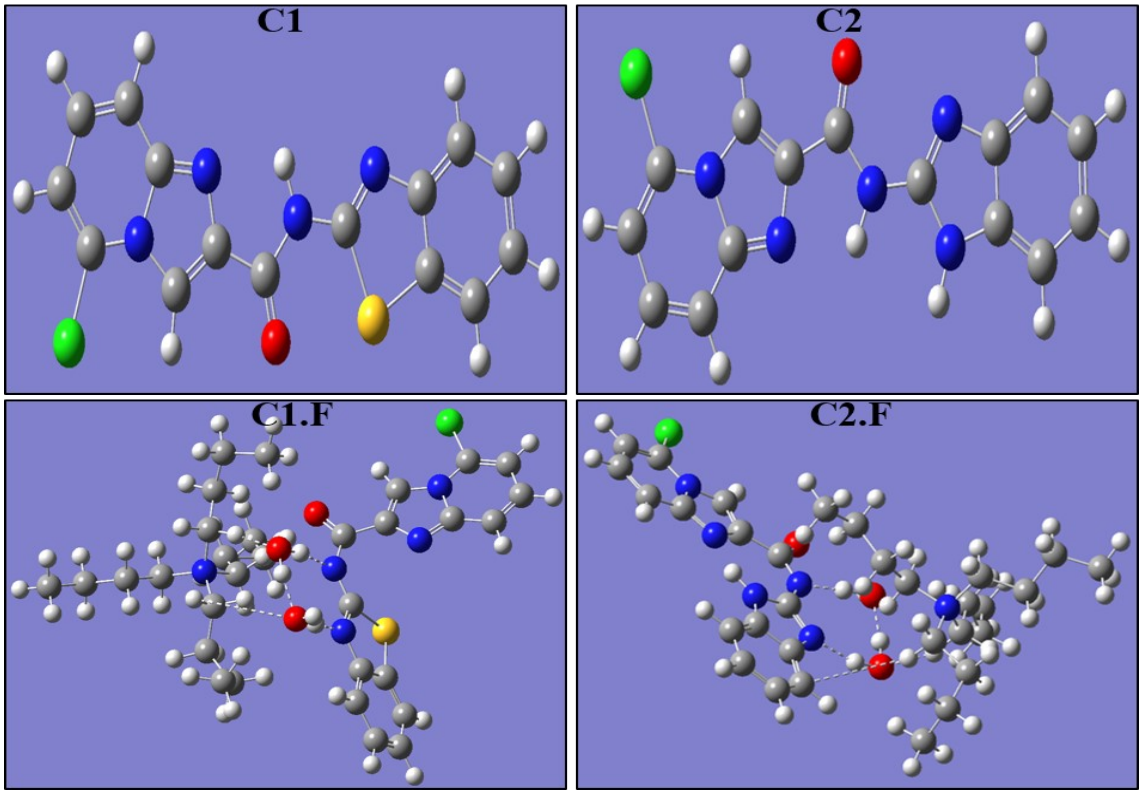


FigureS28. ESI-HRMS spectra of **C2.S** (m/z calculated for [C1+F+Na] = 353.0461 and obtained 353.1451).



DFT calculated optimized structure

Figure S29. DFT optimized **C1**, **C2**, **C1.S**, and **C2.S** using B3LYP /3-21G basis set on the Gaussian09 program.



Titration plot of carboxamide with CN^-

Figure S30. Absorption titration spectra of (a) **C1** and (b) **C2** with CN^-.

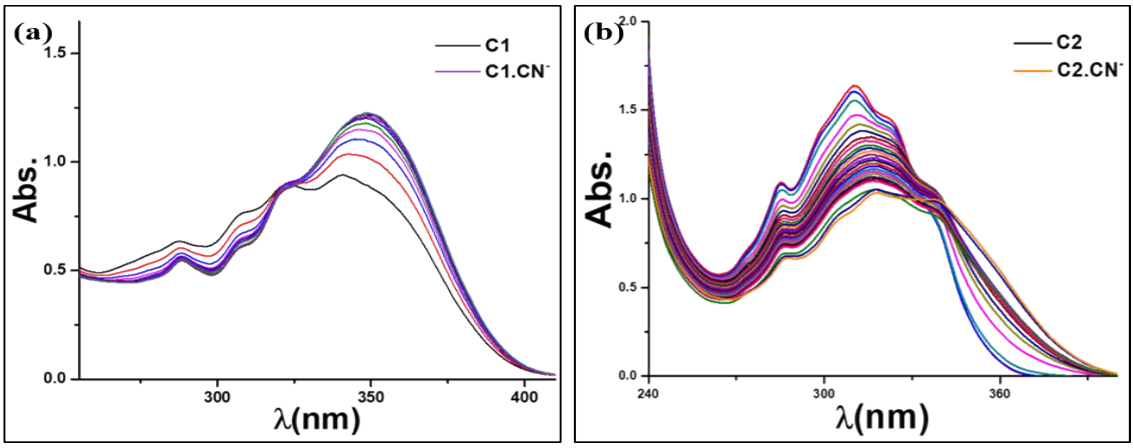


Figure S31. ^{1}H NMR titration profile of **C1** with cyanide anion.

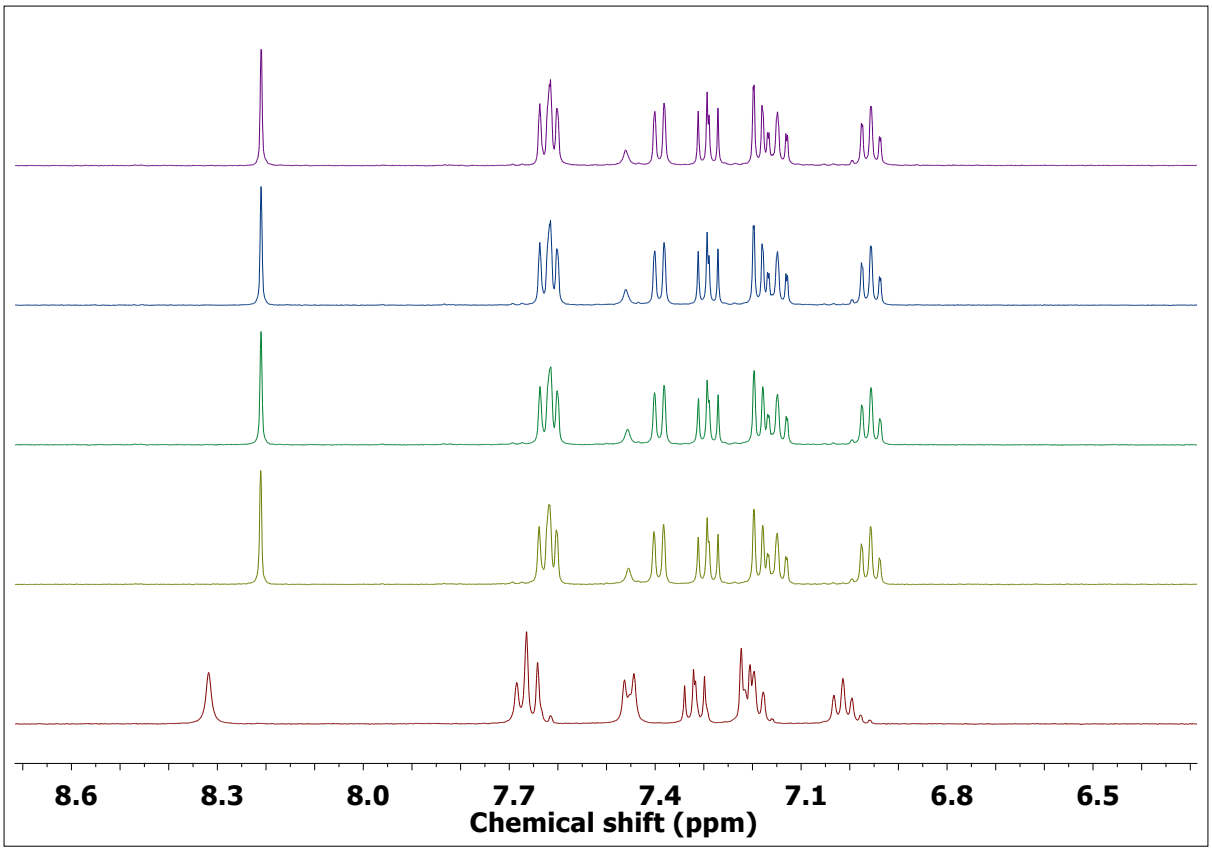
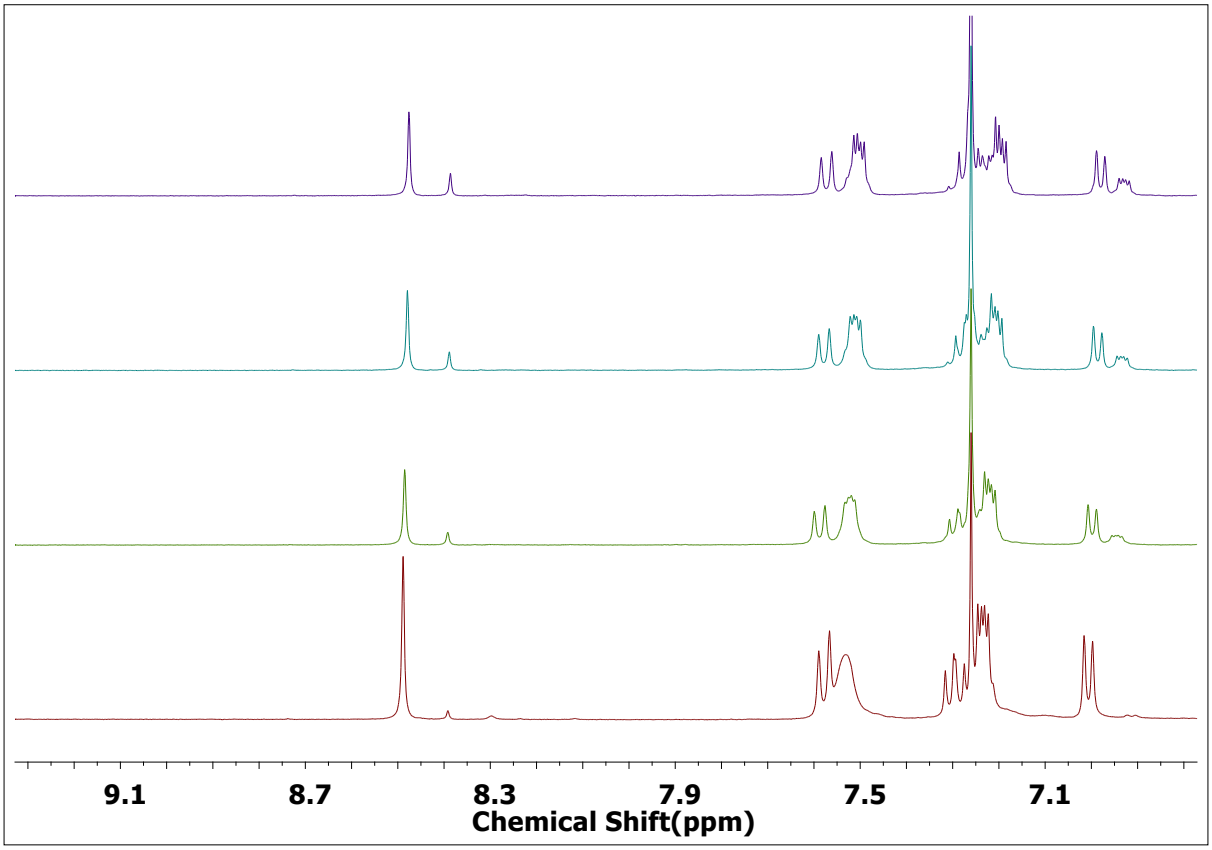
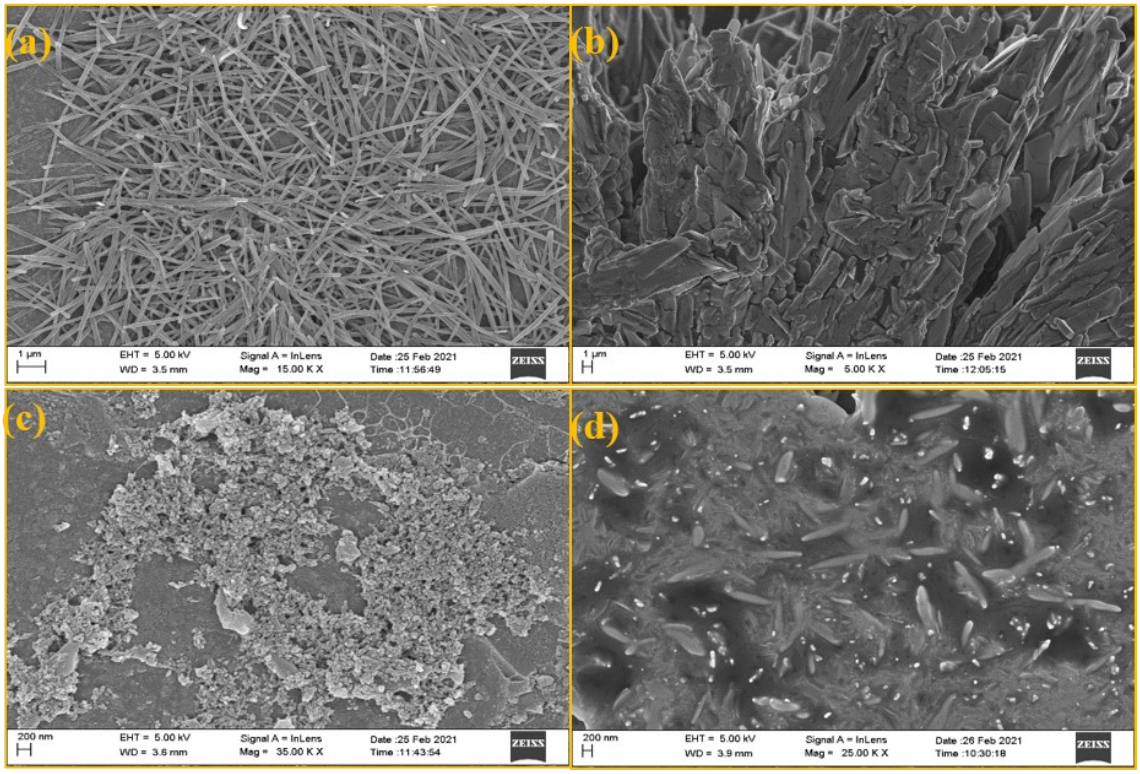


Figure S32. ^{1}HNMR titration profile of **C2** with cyanide anion.



FE-SEM image

Figure S33 FESAM image of (a) **C1**,(b) **C1.S**,(c) **C2**,and (d) **C2.S**. Sample prepared in DMSO for **C1** and **C1.S** and in water for **C2** and **C2.S** through drop caste method.



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