Supplementary Material (ESI) for Chemical Communications

Supporting Information

Dual-Host Approach for Liquid-Liquid Extraction of Potassium Fluoride/Chloride *via* Formation of an Integrated 1-D Polymeric Complex

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MATERIALS AND METHODS

Materials: Tris-(2-aminoethyl)-amine (TREN), pentafluorobenzoyl chloride, 18-crown-6, hexafluorobenzene, tetrabutylammonium salts of fluoride and chloride, were purchased from Sigma-Aldrich and were used as received. Tetrahydrofuarn (THF) was freshly distilled over potassium and benzophenone. Triethylamine, dichloromethane and chloroform were distilled over calcium hydride and acetonitrile was dried over phosphorous pentoxide prior to use by usual procedure. De-ionized water was used for crystallization and extraction. Potasssium fluoride and Potassium chloride were purchased from Spectrochem, India. All solvents were procured from Merck. Buffer capsules for pH 4.0 and 9.0 are purchased from Merck Ltd.

Methods: Melting points of receptor $\mathbf{L^2}$ and complexes were determined on a BioCote melting point apparatus. FTIR was recorded on SHIMADZU FTIR-8400S infrared spectrophotometer with KBr pellets. HRMS experiment was carried out on a Water's QtoF Model YA 263 mass spectrometer in positive ESI mode. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a 300 MHz and 75 MHz Bruker DPX-300 MHz NMR Spectrometer. ^{19}F-NMR and ^{35}Cl-NMR spectra were obtained on a 500 MHz Bruker DPX-500 MHz NMR spectrometer. Hexafluorobenzene was used as internal standard in ^{19}F-NMR studies. Powder X-ray diffraction (PXRD) analysis were performed using a Bruker axs (D8 Advance) diffractrometer supported by LynxEye super-speed detector and Ni-filtered CuKα (λ = 0.154 nm) radiation generated at 40 kV/40 mA. Energy Dispersive X-ray (EDX) analyses were carried out on a field emission scanning electron microscope (FE-SEM) using JEOL, JSM-6700F equipment operated with the accelerating voltage 5 kV.

X-ray Crystallography: Crystals suitable for single crystal X-ray diffraction studies were selected from the crystallization vial and immersed in paratone oil and then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for the crystals **1**, **2**, **3** and **4** were collected using MoK_α (λ = 0.7107 Å) radiation on a Bruker SMART APEX II diffractometer equipped with CCD area detector. The data integration and reduction were processed with SAINT[2] software provided with the software package of SAMRT APEX II. An empirical absorption correction was applied to the collected reflections with SADABS[3]. The structures were solved by direct methods using SHELXTL[4] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97[5] program package. Graphics were generated using PLATON[6] and MERCURY 1.4.[7] The non-hydrogen atoms were refined anisotropically till the convergence. In cases of complexes **1**, **3**, and **4**, the hydrogen atoms were geometrically fixed at idealized positions. In the case of complex **2**, all the hydrogen atoms were located from the difference Fourier map and refined isotropically. In cases of complex **1** and **3**, even though the data was collected at 100 K, the hydrogen atoms attached to the lattice water molecule could not be located from the difference Fourier map. In complex **2**, the methyl group (C39) of tetrabutylammonium cation is disordered at two position

and the occupancy factors of these two positions were treated with FVAR command of the SHELXTL program and refined isotropically. The hydrogen atoms to these disordered atoms (C38 and C39) are not either located or fixed. The whole crown-ether moiety of complex **3** is disordered at two sites and the occupancy factors were refined using the FVAR command of the SHELXTL program and isotropically refined. The hydrogen atoms to these disordered atoms are not either located or fixed. The lattice water molecule (O4w) is refined isotropically and the hydrogen atoms attached to this molecule cannot be either located or fixed from difference Fourier Map. CCDC-701763 (**1**), CCDC-710731 (**2**), CCDC-732760 (**3**) and CCDC-743775 (**4**) contain the supplementary crystallographic data for this paper. Though the data quality of complexes **2**, **3** and **4** are poor, these are the best set of data available for the complexes (**2**, **3** and **4**) after several attempts of data collection from the crystals obtained from several batches. Different solvent systems acetonitrile-water mixture, ethylacetate, dichloromethane, methanol and methanol-water mixture (for complex **2**) and chloroform, acetonitrile, ethylacetate, methanol-chloroform mixture, acetonitrile-chloroform mixture and di-isopropyl ether diffusion in acetonitrile (for complexes **3** and **4**) were tried to grow crystals suitable for single crystal X-ray diffraction studies. Upon several efforts we could able to grow crystals for **2** only in acetonitrile-water mixture whereas for complexes **3** and **4** in chloroform. Rest of the solvent systems either resulted in even poor quality crystals or solid masses. Our effort to grow better quality crystals following different crystallization techniques like slow evaporation at room temperature and at 4°C in refrigerator or diffusion method was not successful. Data collections following different strategies by increasing the number of frames and exposure time per frame also did not provide better data sets.

Extraction Experiments:

73 mg (0.1 mmol) of $\mathbf{L^2}$ and 26.4 mg (0.1 mmol) of $\mathbf{L^1}$ in 10 ml of chloroform and 58.1 mg (1.0 mmol) of KF or 74.5 mg (1.0 mmol) of KCl dissolved in 10 ml of distilled water were placed in a 50 ml round bottom flask. The two layers were extensively mixed by stirring the solution at room temperature for 6 hrs. The two layers were transferred to a separating funnel and the separating funnel was allowed to settle for 1 hr to ensure that the two phases reached equilibrium, and then the organic phases in the two samples were collected and passed through silicone treated Whatmann 1PS filter paper. The organic layer was evaporated to dryness under reduced vacuum. The colorless solid was washed with cold diethyl ether (20 ml x 3 times) to remove un-reacted $\mathbf{L^1}$ and dried. This extracted mass was further subjected to various analyses. Competition experiments are performed under the same experimental conditions in the presence of KNO_3 (1.0 mmol).

Control Experiments:

73 mg (0.1 mmol) of $\mathbf{L^2}$ or 26.4 mg (0.1 mmol) of $\mathbf{L^1}$ in 10 ml of chloroform and 58.1 mg (1.0 mmol) of KF or 74.5 mg (1.0 mmol) of KCl dissolved in 10 ml of distilled water were placed in a 50 ml round bottom flask. The two layers were extensively mixed by stirring the solution at room temperature for 6

hrs. The two layers were transferred to a separating funnel and the separating funnel was allowed to settle for 1 hr to ensure that the two phases reached equilibrium, and then the organic phases in the two samples were collected and passed through silicone treated Whatmann 1PS filter paper. The organic layer was evaporated to dryness under reduced vacuum. The residue was washed with cold diethyl ether (20 ml x 3 times) to remove un-reacted $\mathbf{L^1}$ and dried. This residue was further subjected to various analyses.

Extraction Experiments at Different pH:

The experimental conditions are kept same as discussed earlier. The buffer systems potassium hydrogen phthalate and Boric acid/KCl/NaOH were employed to adjust the respective pH values ~4.0 and ~9.0.

SYNTHESES

Synthesis of Compound L^2: $\mathbf{L^2}$ is synthesized according to a modified procedure,[1] tris(2-amino-ethyl)amine, tren, (1 mL, 6.7 mmol) was taken in a 250 mL round bottomed flask, and dissolved in 75 mL of dry tetrahydrofuran (THF). About 3 mL (slight excess) of dry triethylamine was added to the homogeneous mixture. The mixture was allowed to stir at room temperature in nitrogen atmosphere for 15 min. 2.8 mL (20 mmol) of 2,3,4,5,6-pentafluorobenzoyl chloride was dissolved in another 50 mL of dry THF and taken in a 100 mL pressure equalizing funnel. This solution was added dropwise for a period of 1 hour at constant stirring in room temperature. After the addition, the reaction mixture was allowed to stir at room temperature in nitrogen atmosphere for another 14 h. The white precipitate (triethylammonium chloride) formed was filtered out, and washed three times with cold THF. The solvent was removed by evaporation under reduced pressure at 40 ºC to yield light yellow oil. The yellow oil was redissolved in 50 mL of dichloromethane (DCM), which was washed once with saturated NaCl solution, and three times with 100 mL of distilled water. The organic phase was separated, and dried over anhydrous sodium sulfate. Then the solvent was evaporated in *vacuo* to yield the desired product as colorless solid. The colorless solid was redissolved in 10 mL of hot DCM, and allowed to evaporate at 4°C to yield the required product as colorless crystals (4.5 g, 92%). FTIR (cm^{-1}): 3249.83 (br, -NH, *str*), 1654.81 (br, -CO, *str*), 1519.8, 1500.52 (s, -NH, *ben*). HRMS (ESI): 728.9133 [M+H^+] and 750.8843 [M+Na^+]. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.72 (t, 6H, NCH_2, J = 6 Hz), 3.49 (t, 6H, NCH_2CH_2, J = 6 Hz), 7.23 (t, 3H, N*H*). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 38.41 (N*C*H_2), 54.47 (NCH_2*C*H_2), 111.29 (m of s, Ar, *C*C-F, J_{CCF} = 15Hz), 137.43 (m of d, Ar, *C*-F, J_{CF} = 252 Hz), 142.25 (m of d, Ar, *C*-F J_{CF} = 252 Hz), 144.79 (m of d, Ar, *C*-F, J_{CF} = 249 Hz), 158.77 (s, *C*=O). ^{19}F NMR (500 MHz, $CDCl_3$): δ -163.86 (t, 2Ar-*F*, J_{F-F} = 20 Hz), -155.42 (t, Ar-*F*, J_{F-F} = 20 Hz), -143.98 (d, 2 Ar-*F*, J_{F-F} = 20 Hz). Melting Point: 175-176ºC. Elemental analysis: Calculated:- C-44.52, H-2.08, N-7.69 %, Experimental:- C-44.97, H-1.82, N-7.56 %.

Synthesis of Complex 1: 60 mg (0.08 mmol) of $\mathbf{L^2}$ was dissolved in 10 ml of H_2O or CH_3CN/H_2O (1:1 v/v) and then 63 mg (0.24 mmol) of *n*-$Bu_4N^+F^-$ was added to the above solution. Then the mixture was stirred at room temperature for 10 minutes and heated to 60ºC. Then, the mixture was filtered at room temperature and allowed to evaporate for crystallization. After a week, colourless crystalline solid of the complex was obtained in 75% yield. Upon re-crystallisation acetonitrile/water few colourless crystal of complex [$\mathbf{L^2}$(F^-)·H_2O]·*n*-Bu_4N^+ (**1**) suitable for X-ray diffraction studies were obtained upon slow and complete evaporation of the solvent. Melting Point: 120-122ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, 3H, $NCH_2CH_2CH_2CH_3$, J = 7.2 Hz), 1.42 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.93 (m, 2H, $NCH_2CH_2CH_2CH_3$), 2.56 (t, 6H, NCH_2CH_2, J = 4.8 Hz), 3.17 (m, 2H, $NCH_2CH_2CH_2CH_3$), 3.43 (t, 6H, NCH_2CH_2, J = 4.8 Hz), 11.73 (br, 3H, N*H*). ^{19}F NMR (500 MHz, $CDCl_3$): δ -165.26 (br, 2Ar-*F*), -158.48 (br, Ar-*F*), -145.38 (br,

2 Ar-*F*), -110.22 (br, 1-F^-). Elemental analysis: calculated: C – 51.24%, H – 5.30%, N – 6.95% and experimental: C – 51.94%, H – 5.93%, N – 6.70%.

Synthesis of Complex 2: 60 mg (0.08 mmol) of $\mathbf{L^2}$ was dissolved in 10 ml of CH_3CN/H_2O (1:1 v/v) mixture and then 67 mg (0.24 mmol) of *n*-$Bu_4N^+Cl^-$ was added to the above solution. The reaction mixture was further stirred at room temperature for 10 minutes. Then, mixture was filtered at room temperature and the filtrate was allowed for crystallization. After a week, colourless crystalline solid of the complex was obtained in ~60% yield. Upon re-crystallisation acetonitrile/water few colourless crystal of complex [$\mathbf{L^2}(Cl^-)$]·*n*-Bu_4N^+ (**2**) suitable for X-ray diffraction studies were obtained upon slow and complete evaporation of the solvent. Melting Point: 114-116ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, 3H, $NCH_2CH_2CH_2CH_3$, J = 7.2 Hz), 1.38-1.43 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.90 (m, 2H, $NCH_2CH_2CH_2CH_3$), 2.56 (t, 6H, NCH_2CH_2, J = 4.8 Hz), 3.26 (m, 2H, $NCH_2CH_2CH_2CH_3$), 3.47 (t, 6H, NCH_2CH_2, J = 4.8 Hz), 9.76 (br, 3H, N*H*). Elemental analysis: calculated: C – 43.41%, H – 4.29%, N – 5.62% and experimental: C–43.23%,H – 4.66%, N – 5.77%.

Synthesis of Complex 3: 73 mg (0.1 mmol) of $\mathbf{L^2}$ and 26.4 mg (0.1 mmol) of $\mathbf{L^1}$ were dissolved in 10 ml of chloroform. 58.1 mg (1.0 mmol) of KF was dissolved in 10 ml of distilled water and added to the above solution. The reaction mixture was further stirred at room temperature for 6 hrs. Then, organic layer was separated and allowed for crystallization at 4°C. The complex **3** was obtained by the removal of the solvent from the extracted mass under reduced pressure and followed by cold diethyl ether wash (5ml x 2) and room temperature drying. Yield = 48% (considering complex composition (L^1:L^2: KF = 1:1:1) therefore 100% extraction should results (26.4 + 73 + 5.8 mg = 105.4 mg of **3**). Upon re-crystallization of the complex in chloroform, few colorless single crystals of complex [$\mathbf{L^2L^1}(F^-)(K^+)(H_2O)$] (**3**) suitable for X-ray diffraction studies were obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.66 (m, 6H, NCH_2CH_2), 3.49 (m, 6H, NCH_2CH_2), 3.63 (s, 24H, Crown-NH_2) 11.42 (br, 3H, N*H*). ^{19}F NMR (500 MHz, $CDCl_3$): δ -165.25 (br, 2Ar-*F*), -158.47 (br, Ar-*F*), -145.37 (br, 2 Ar-*F*), -110.22 (br, 1-F^-).

Synthesis of Complex 4: 73 mg (0.1 mmol) of $\mathbf{L^2}$ and 26.4 mg (0.1 mmol) of $\mathbf{L^1}$ were dissolved in 10 ml of chloroform. 74.5 mg (1.0 mmol) of KCl was dissolved in 10 ml of distilled water and added to the above solution. The reaction mixture was further stirred at room temperature for 6 hrs. Then, organic layer was separated and allowed for crystallization at 4°C. The complex **4** was obtained by the removal of the solvent from the extracted mass under reduced pressure and followed by cold diethyl ether wash (5ml x 2) and room temperature drying. Yield = 44% (considering complex composition ($\mathbf{L^1}$:$\mathbf{L^2}$:KCl = 1:1:1) therefore 100% extraction should results (26.4 + 73 + 7.4 mg = 106.8 mg of **4**). Upon re-crystallization of the complex in chloroform, few colorless single crystals of complex [$\mathbf{L^2L^1}(Cl^-)(K^+)(H_2O)$] (**4**) suitable for X-ray diffraction studies were obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.61 (m, 6H, NCH_2CH_2), 3.49 (m, 6H, NCH_2CH_2), 3.62 (s, 24H, Crown-NH_2) 9.49 (br, 3H, N*H*). ^{35}Cl NMR (500 MHz, $CDCl_3$): δ 14.76 (br, Cl^-).

Figure 1S. ^{1}H-NMR Spectra of $\mathbf{L^2}$ in $CDCl_3$ at 25ºC.

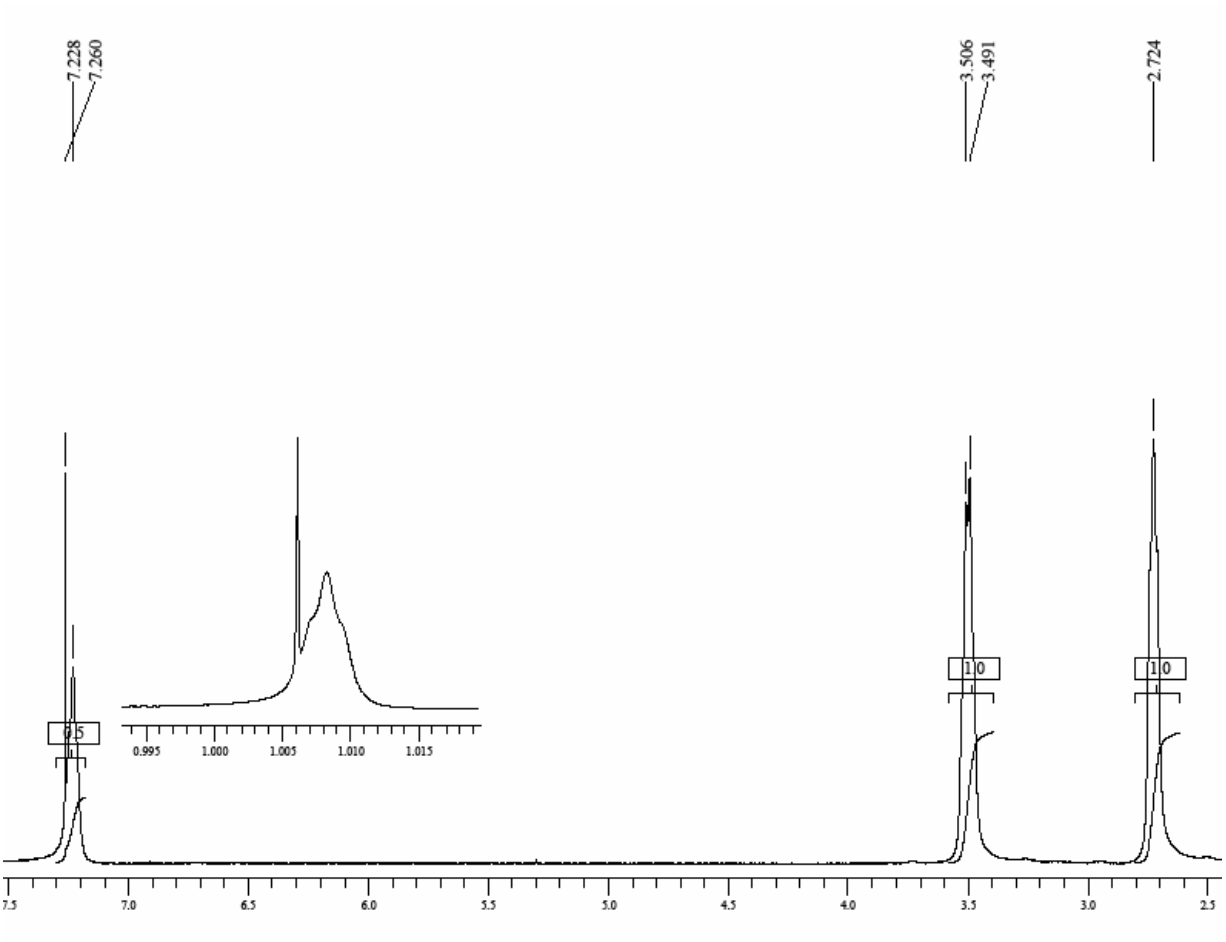


Figure 2S. ^{13}C-NMR Spectra of $\mathbf{L^2}$ in $CDCl_3$ at 25ºC.

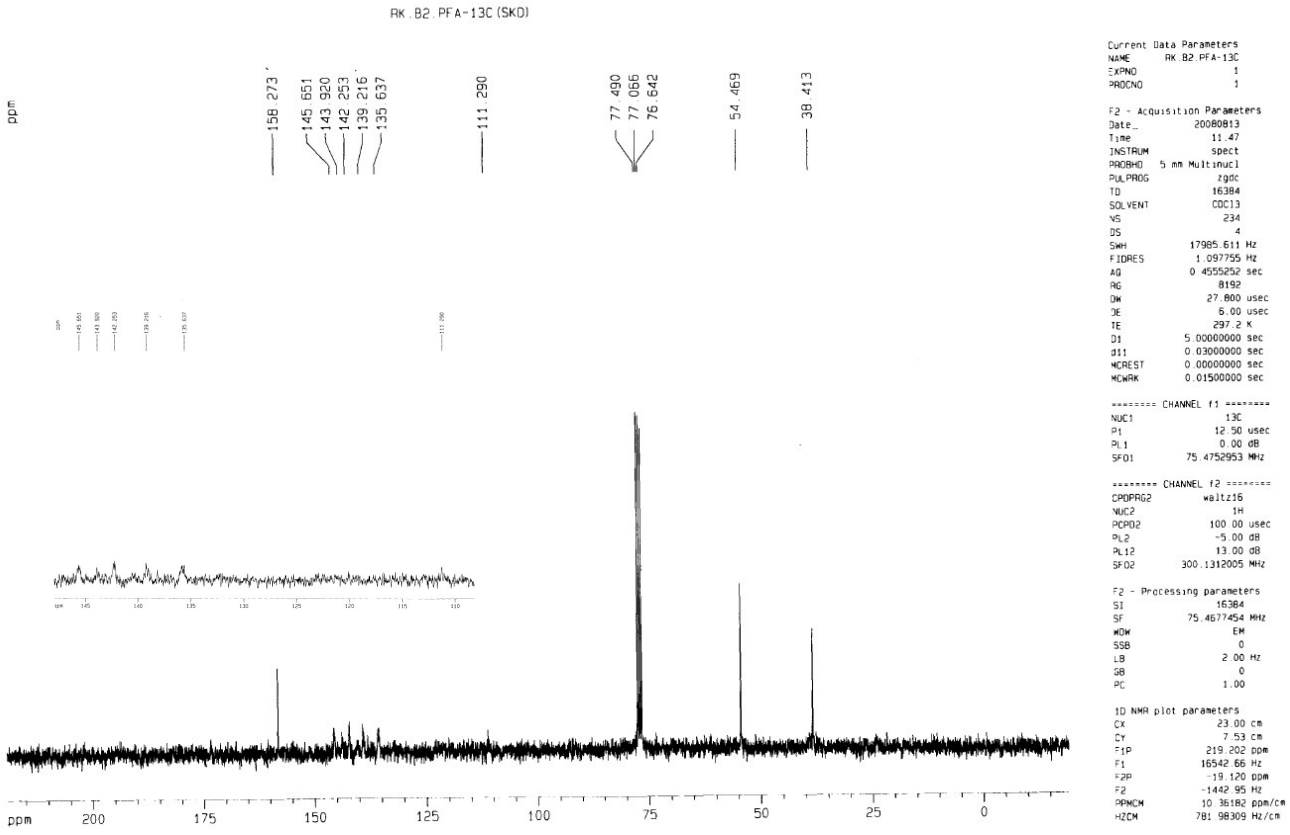


Figure 3S. ^{19}F-NMR Spectra of $\mathbf{L^2}$ in $CDCl_3$ at 25ºC.

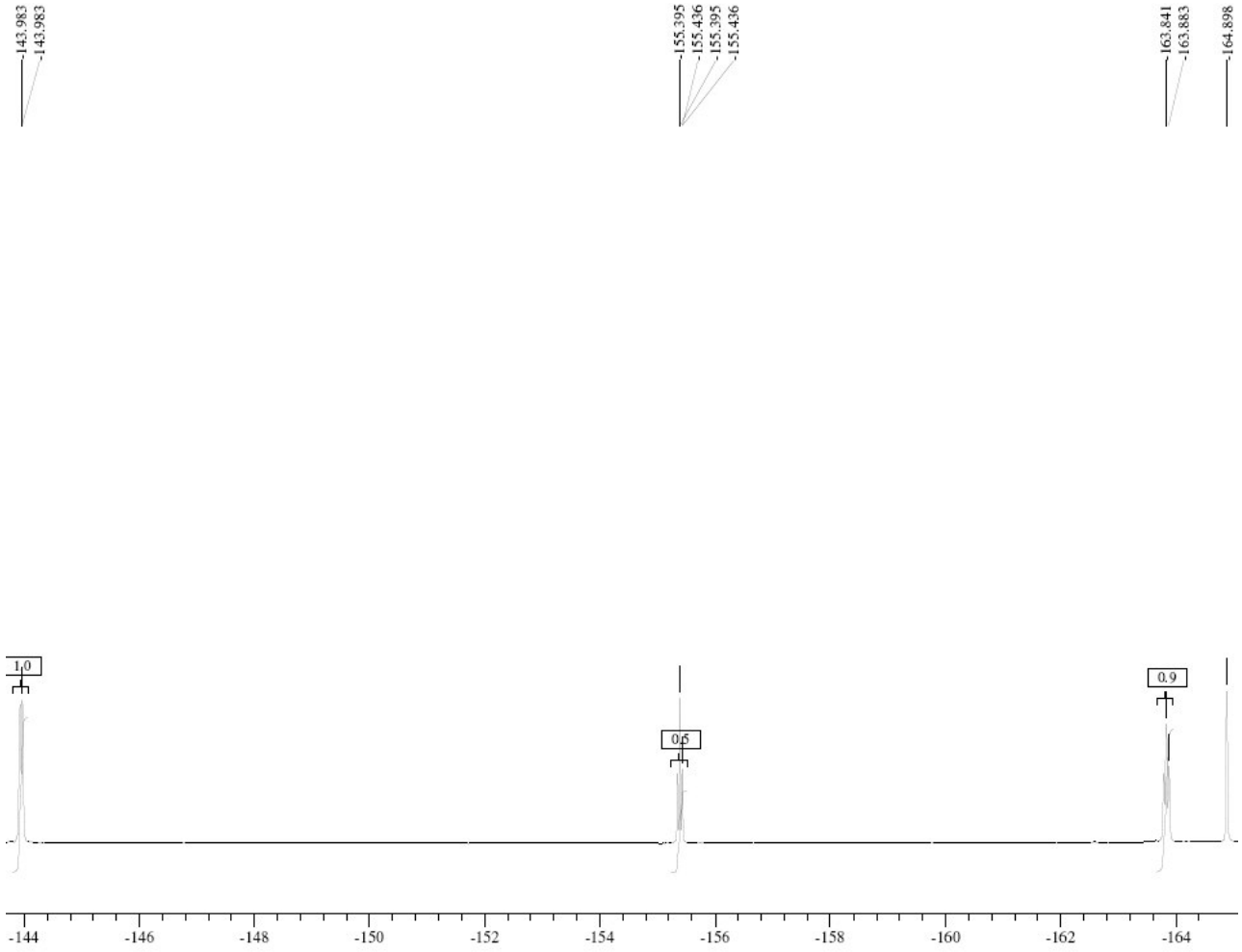


Figure 4S. HRMS of $\mathbf{L^2}$.

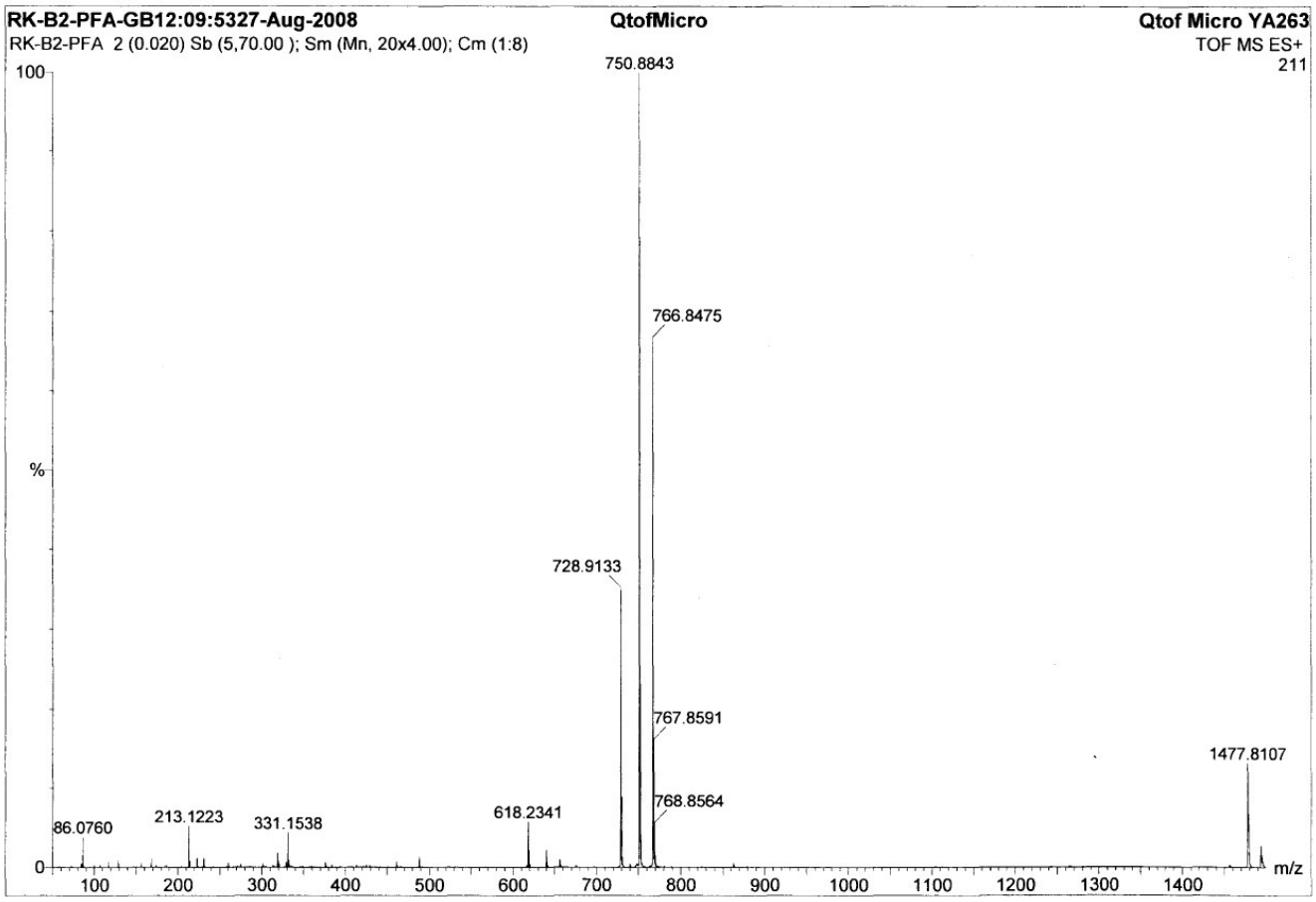


Figure 5S. ^{1}H-NMR Spectra of Complex **1** in $CDCl_3$ at 25ºC.

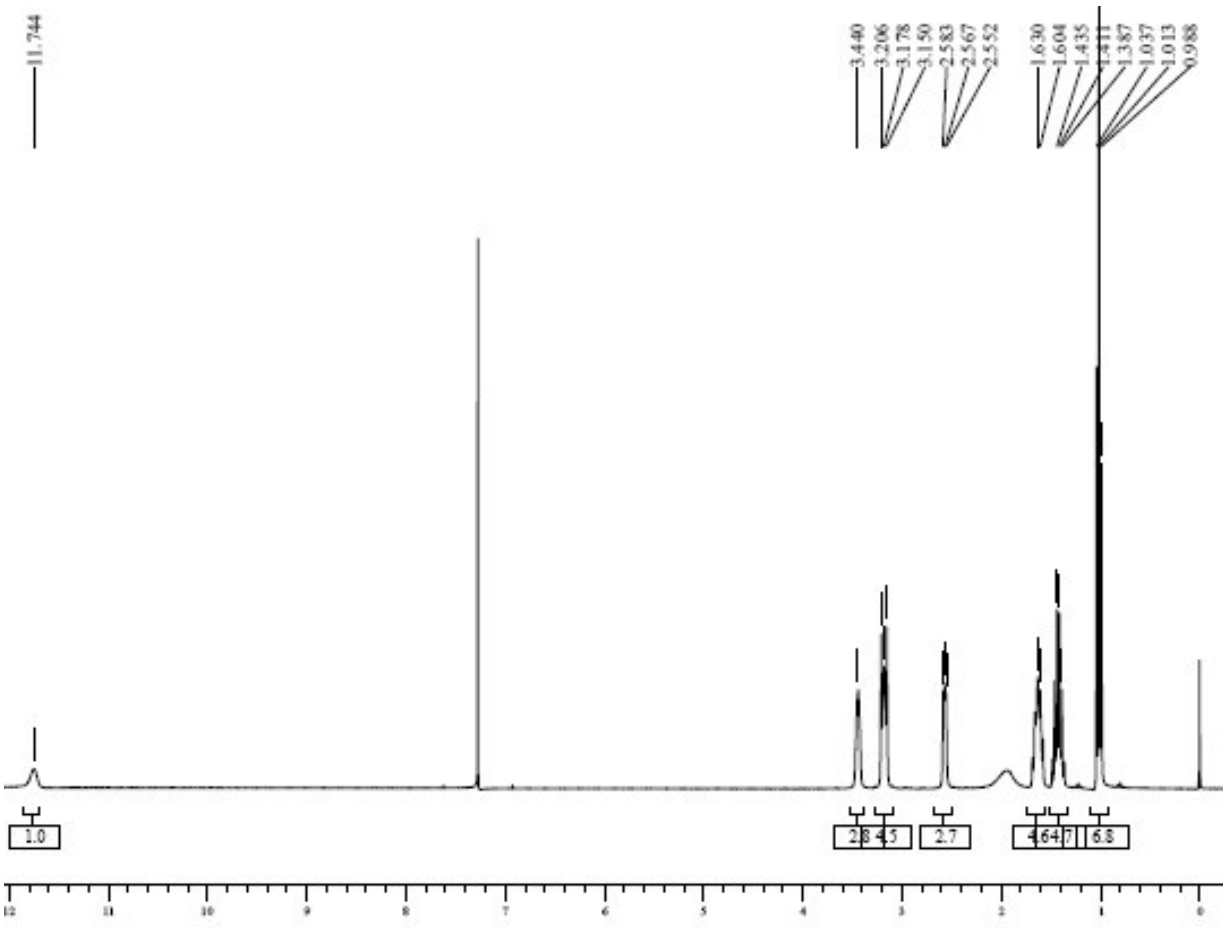


Figure 6S. ^{19}F-NMR Spectra of Complex **1** in $CDCl_3$ at 25ºC.

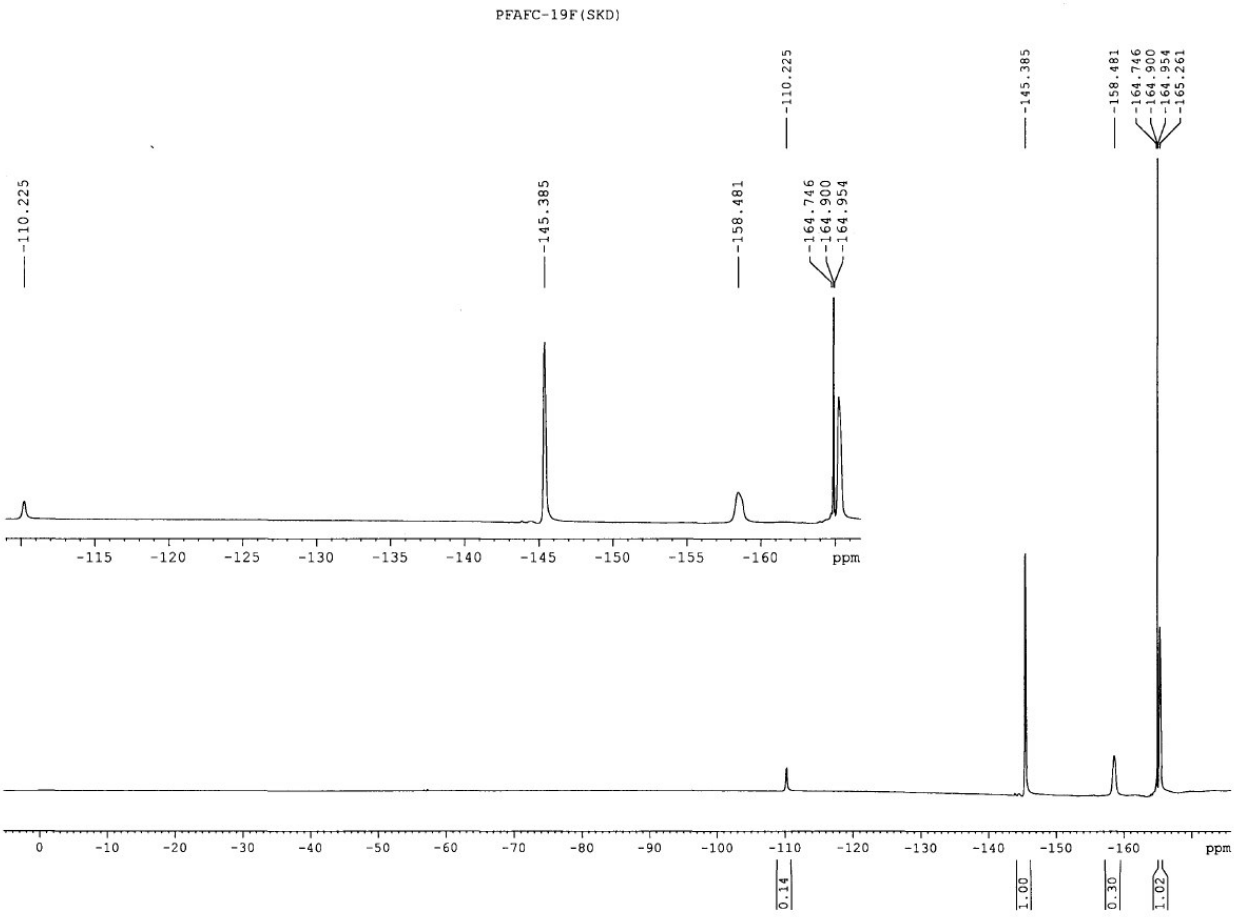


Table 1S. Crystallographic table of Complex **1**.

	1
Emprical formula	$C_{43}H_{52}F_{16}N_5O_4$
Formula weight	1006.88
Crystal system	Monoclinic
Space group	P21/n
a (Å)	16.3394(11)
b (Å)	13.3936(9)
c (Å)	23.0429(15)
α (deg)	90.00
β (deg)	104.689(2)
γ (deg)	90.00
V (Å^3)	4878.0(6)
Z	4
d_{calcd} (g/cm^3)	1.368
Crystal size (mm^3)	0.42 x 0.31 x 0.12
F(000)	2080
μ Mo Kα (mm^{-1})	0.129
T (K)	100 (2)
θ range (deg)	1.38-23.15
Reflections collected	28988
Independent reflections	6895
R(int)	0.0322
data/restraints/parameters	6895/0/617
R1;wR2	0.0665; 0.1883
GOF (F^2)	1.017
Residual electron density	0.806, -0.276

Figure 7S. Single crystal X-ray structure of complex **1,** (a) encapsulated F^- in the cavity of $\mathbf{L}^2$ and (b) space fill view of **1**

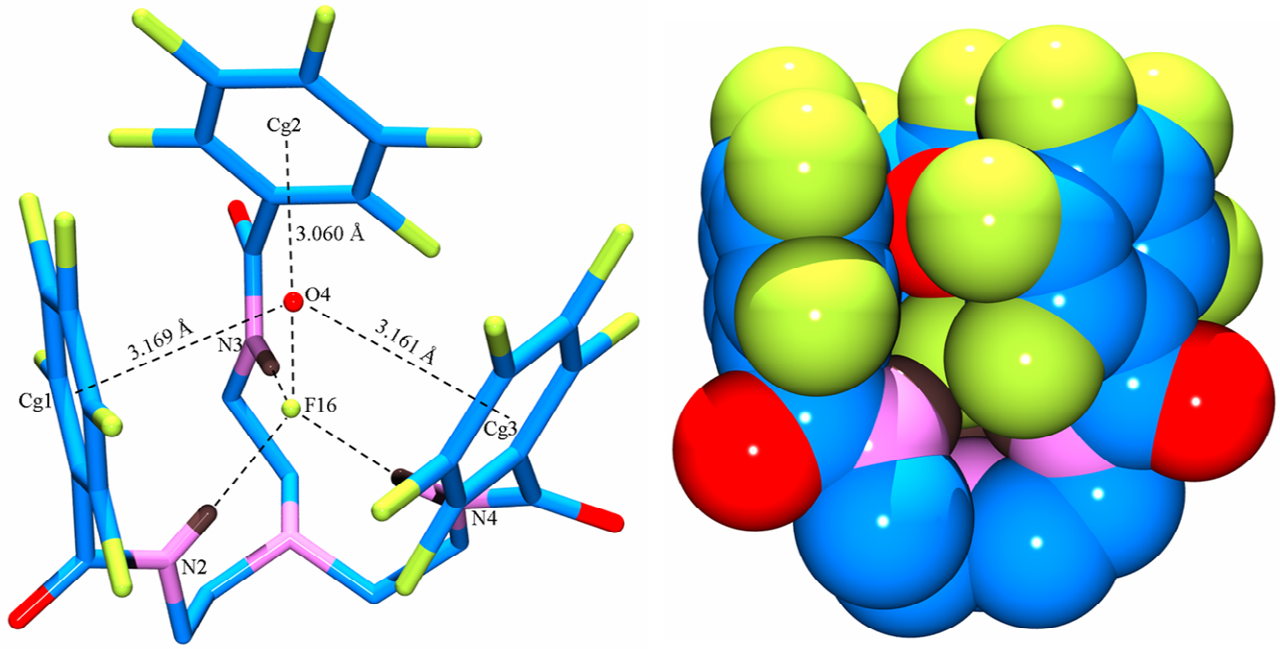
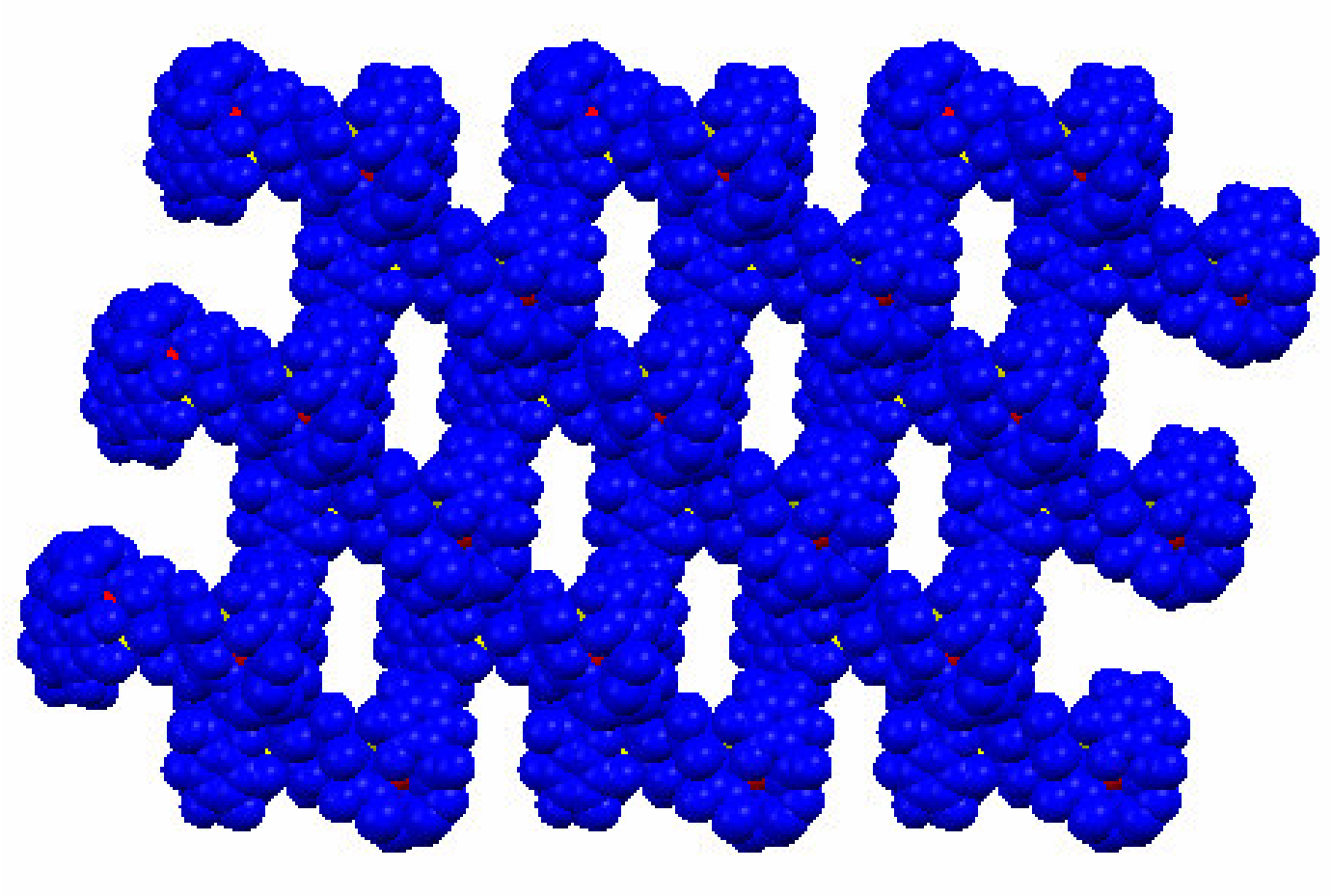


Figure 8S. Packing Diagram of Complex **1** along c-axis



Tetrabutylammonium cations and hydrogen atoms are omitted for clarity.

Figure 9S. ^{1}H-NMR Spectra of Complex **2** in $CDCl_3$ at 25ºC.

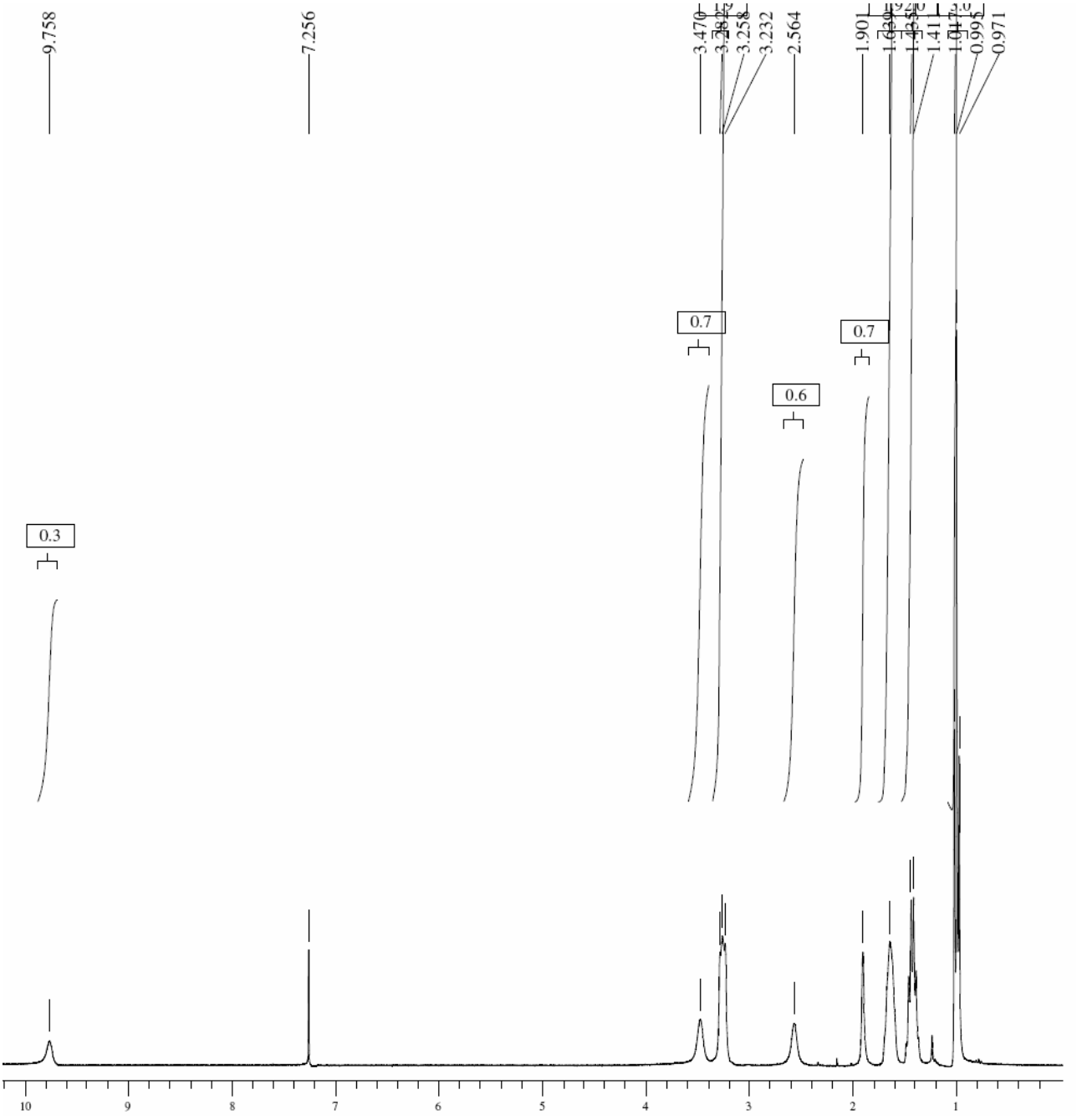
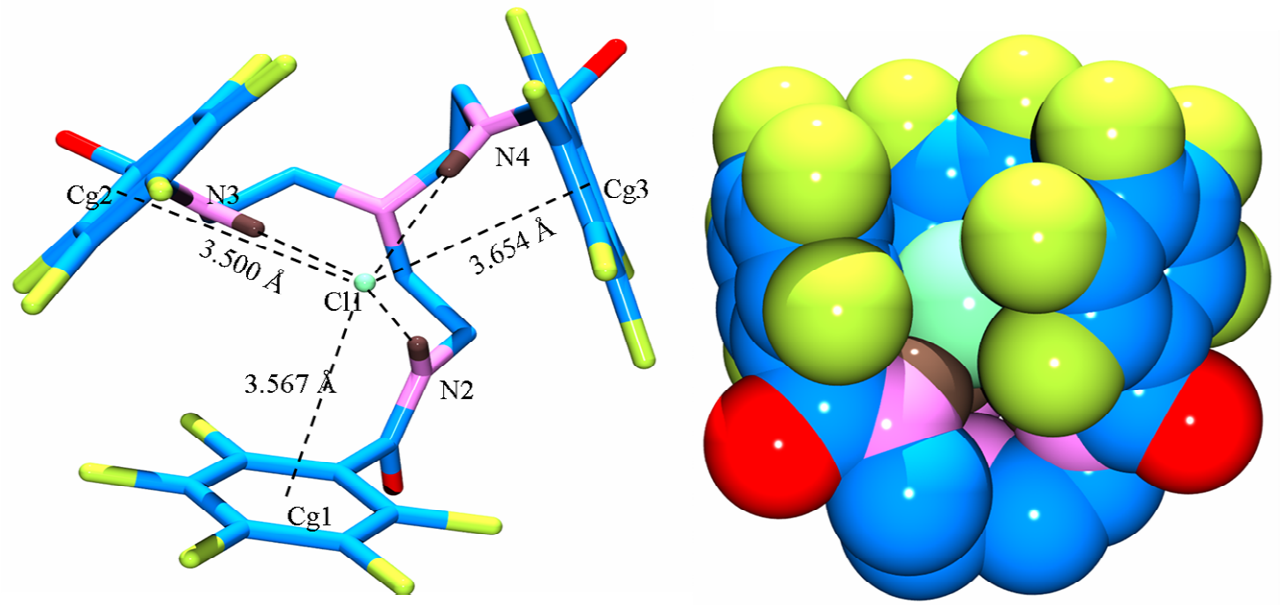


Table 2S. Crystallographic Table of Complex **2**.

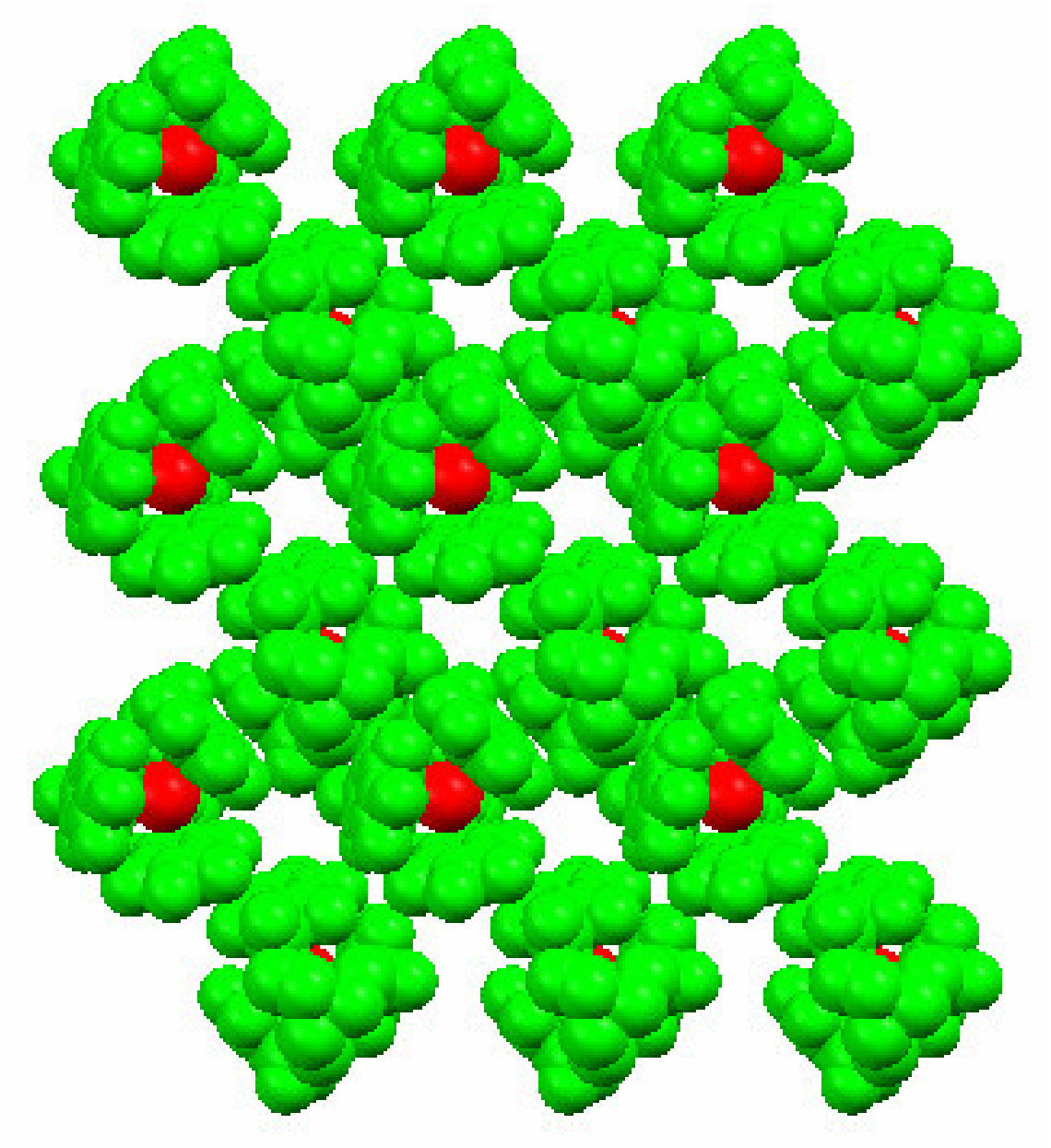
	2
Emprical formula	$C_{43}H_{51}ClF_{15}N_5O_3$
Formula weight	1006.34
Crystal system	Triclinic
Space group	P-1
a (Å)	11.7018(18)
b (Å)	14.141(2)
c (Å)	15.737(3)
α (deg)	88.438(6)
β (deg)	77.895(5)
γ (deg)	74.960(5)
V (Å^3)	2458.0(7)
Z	2
d_{calcd} (g/cm^3)	1.360
Crystal size (mm^3)	0.32 x 0.14 x 0.06
F(000)	1040
μ Mo Kα (mm^{-1})	0.177
T (K)	298 (2)
θ range (deg)	1.32-20.26
Reflections collected	14575
Independent reflections	4642
R(int)	0.0379
data/restraints/parameters	4642/0/601
R1;wR2	0.0624;0.1437
GOF (F^2)	0.964
Residual electron density	0.506, -0.204

Figure 10S. Single crystal x-ray structure of complex **2** (a) encapsulated Cl^- in the cavity of $\mathbf{L}^2$ (b) spacefill view of complex **2**



(a) (b)

Figure 11S. Packing Diagram of Complex **2** along a-axis



Tetrabutylammonium cations, and non-acidic hydrogen atoms are omitted clarity.

Figure 12S. ^{1}H-NMR Spectra of Complex **3** in $CDCl_3$ at 25ºC.

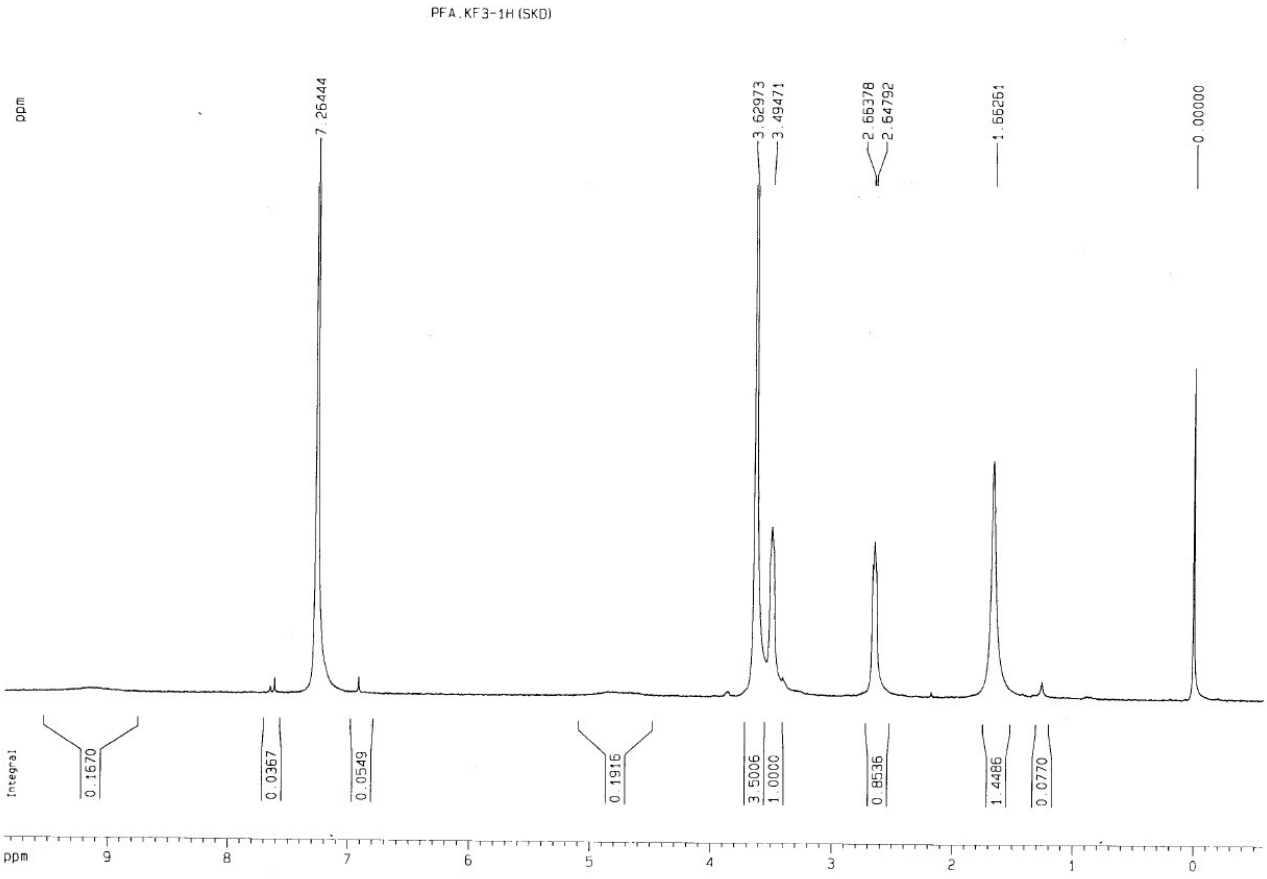


Figure 13S. ^{19}F-NMR Spectra of Complex **3** in $CDCl_3$ at 25ºC.

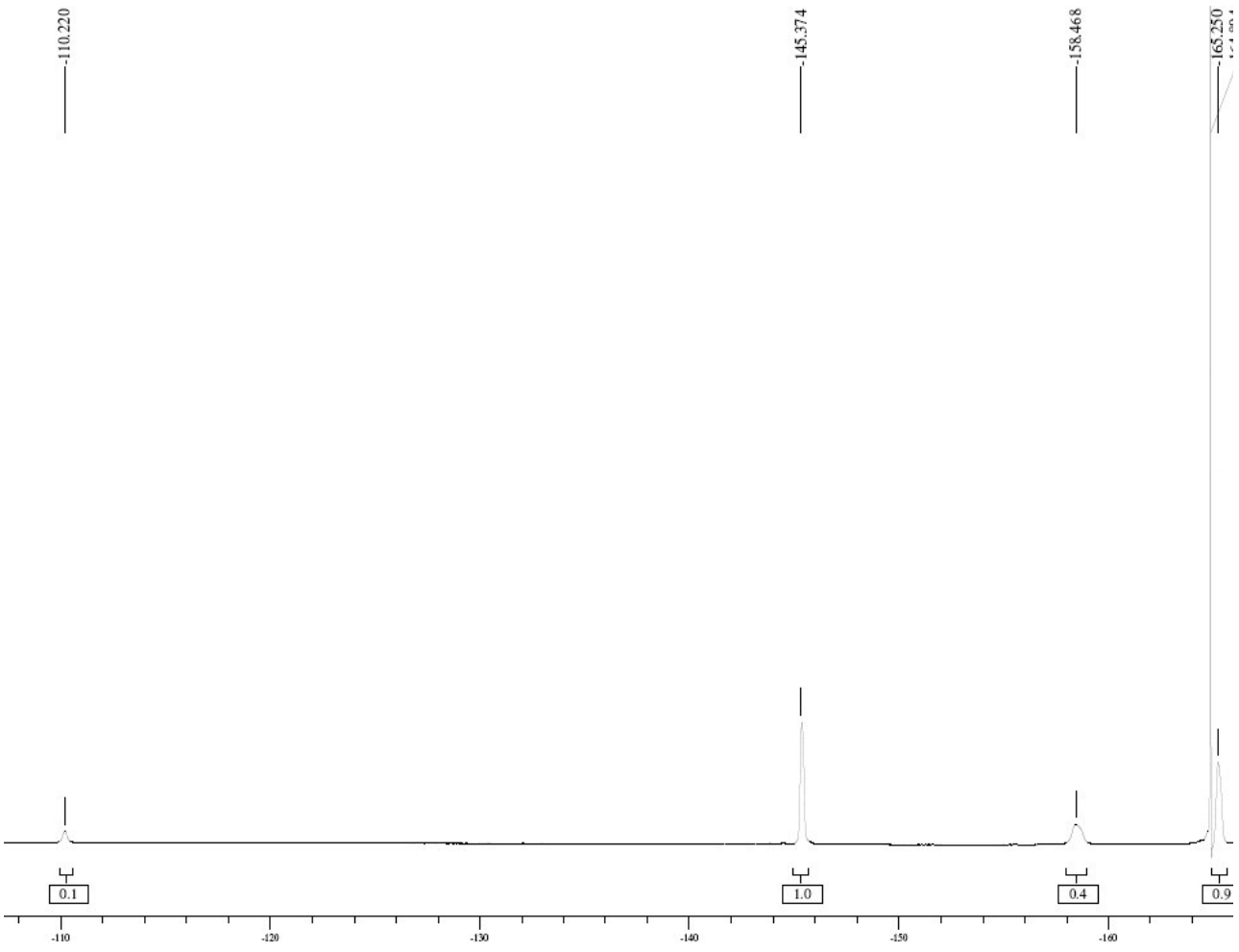


Table 3S. Crystallographic table of Complex **3**.

	3
Emprical formula	$C_{36}H_{41}F_{16}KN_4O_{10}$
Formula weight	1032.83
Crystal system	Monoclinic
Space group	P21/n
a (Å)	15.591(7)
b (Å)	19.049(8)
c (Å)	16.196(7)
α (deg)	90.00
β (deg)	93.954(6)
γ (deg)	90.00
V (Å^3)	4799.0(4)
Z	4
d_{calcd} (g/cm^3)	1.430
Crystal size (mm^3)	0.42 x 0.23 x 0.10
F(000)	2112
μ Mo Kα (mm^{-1})	0.226
T (K)	100 (2)
θ range (deg)	1.65-19.46
Reflections collected	26265
Independent reflections	4111
R(int)	0.1175
data/restraints/parameters	4111/80/574
R1;wR2	0.0832;0.2168
GOF (F^2)	1.038
Residual electron density	0.333, -0.395

Figure 14S. ^{1}H-NMR Spectra of Complex **4** in $CDCl_3$ at 25ºC.

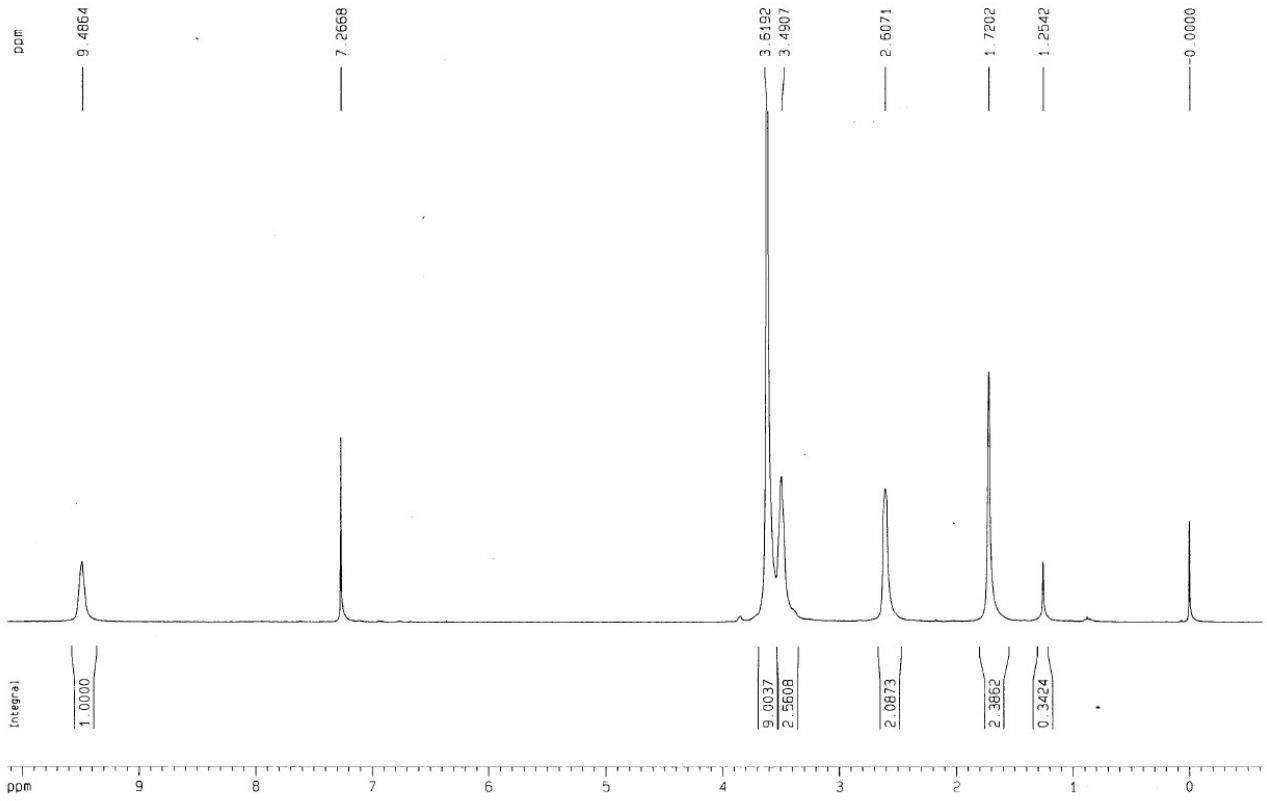


Figure 15S. ^{35}Cl-NMR Spectra of Complex **4** in CD_3CN at 25ºC.

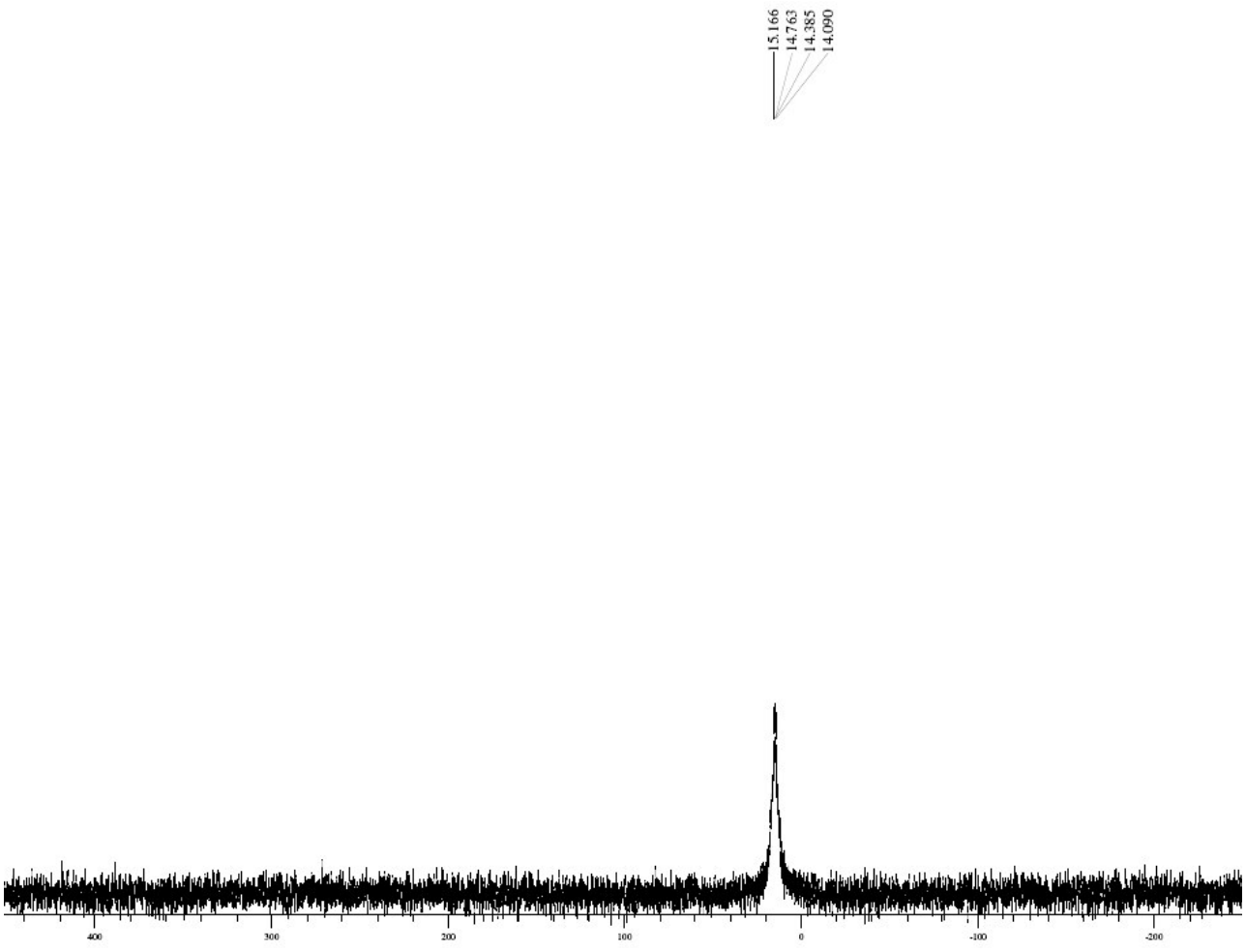
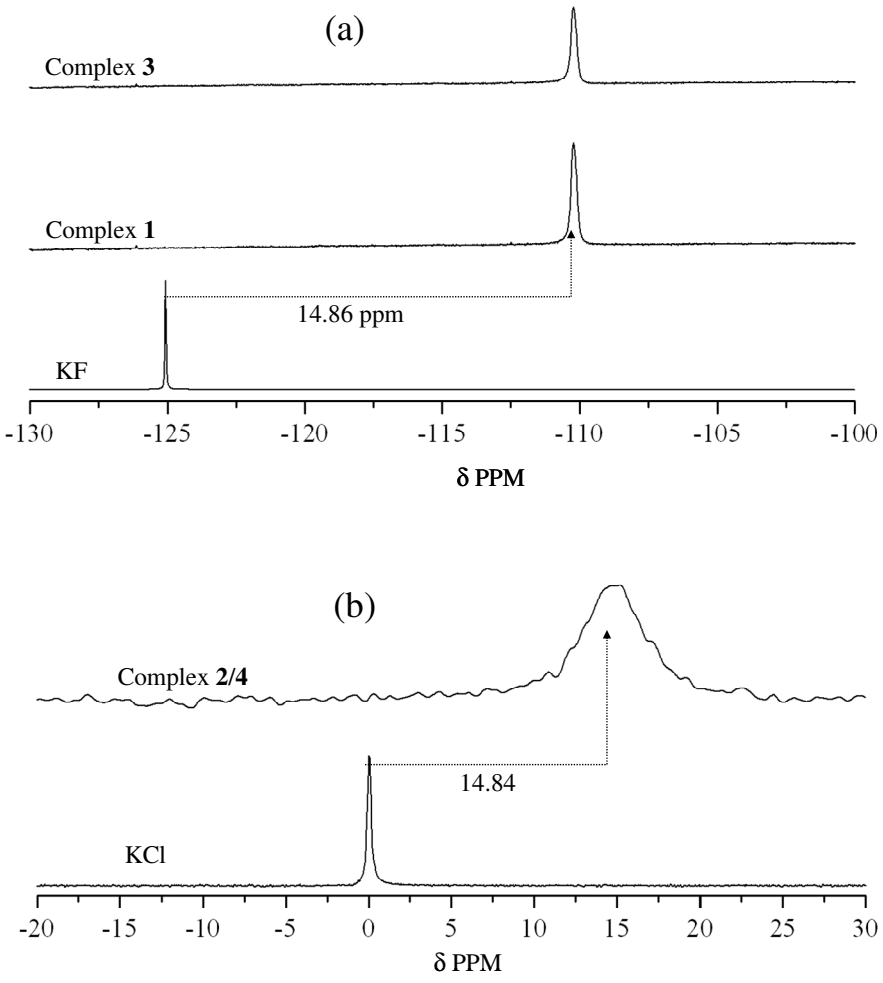
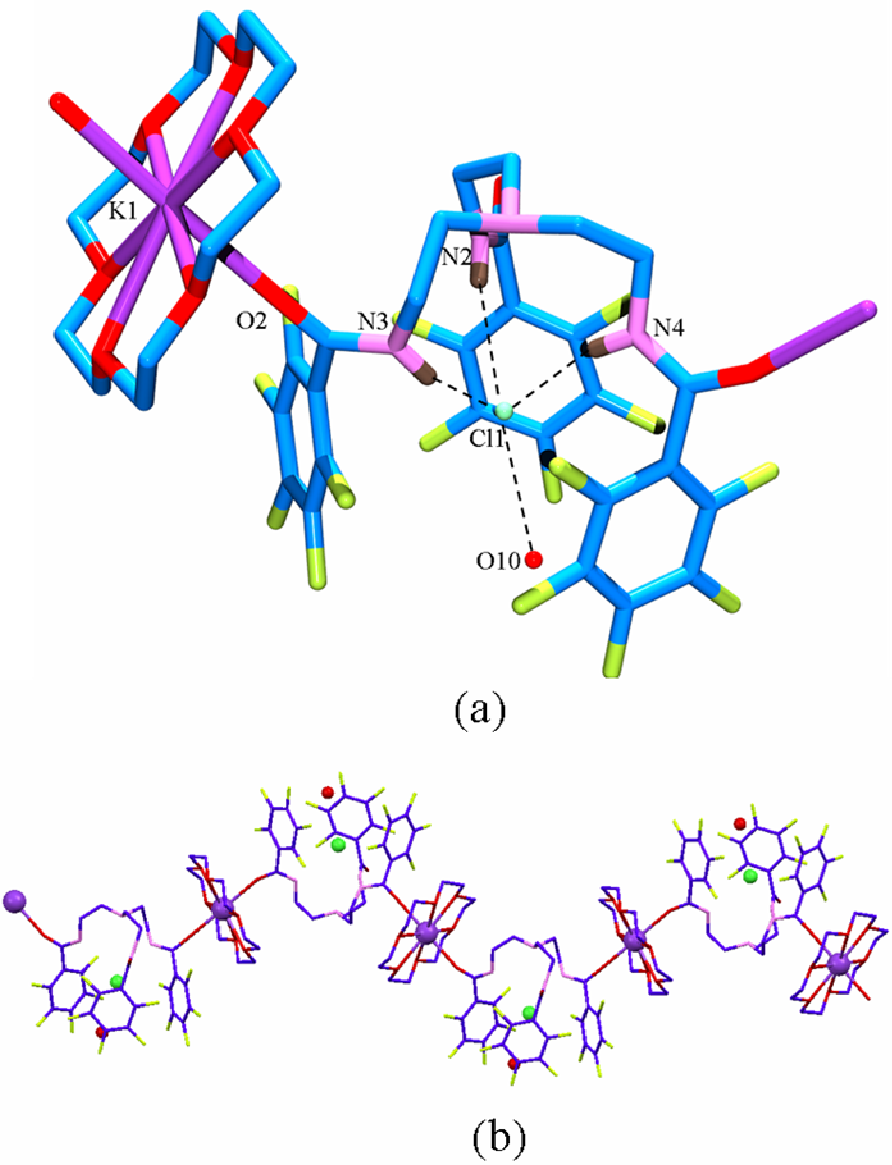


Figure 16S. Comparison of ^{19}F-NMR spectra of **1** & **3** and ^{35}Cl-NMR spectra of **2** & **4**.



(a) Partial ^{19}F-NMR spectra (500 MHz) of KF in D_2O and complexes **1** and **3** in $CDCl_3$. Hexafluorobenzene is added as an internal standard. (b) Partial ^{35}Cl-NMR spectra (500 MHz) of KCl in D_2O and complex **2/4** in $CDCl_3$ at 298 K.

Figure 17S. Single crystal x-ray structure of complex **4**

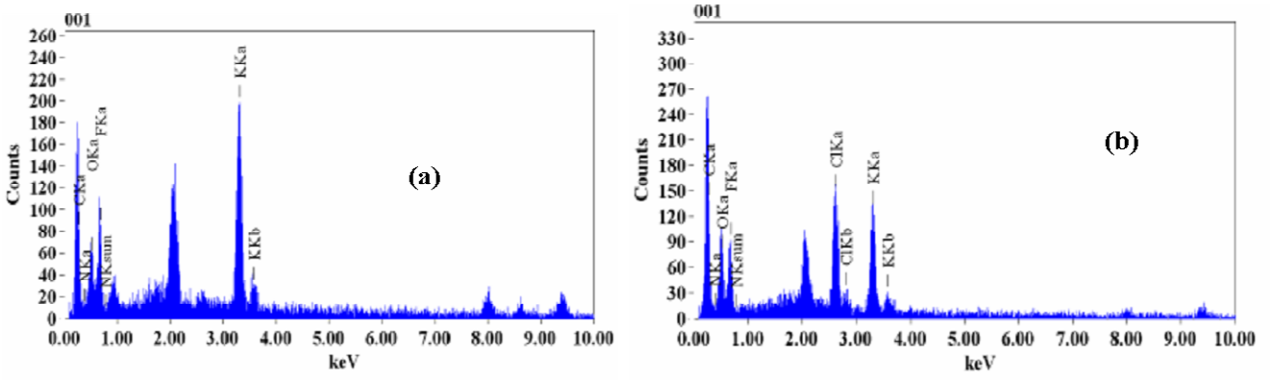


(a) Crystal structure of the monomer, (b) 1-D coordination polymer of **4**

Table 4S. Crystallographic Table of Complex **4**.

	4
Emprical formula	$C_{39}H_{41}ClF_{15}KN_4O_{10}$
Formula weight	1085.29
Crystal system	Monoclinic
Space group	P21/c
a (Å)	10.676(10)
b (Å)	24.66(2)
c (Å)	18.522(18)
α (deg)	90.00
β (deg)	98.094(11)
γ (deg)	90.00
V (Å^3)	4827(8)
Z	4
d_{calcd} (g/cm^3)	1.491
Crystal size (mm^3)	0.18 x 0.10 x 0.06
F(000)	2208
μ Mo Kα (mm^{-1})	0.280
T (K)	298 (2)
θ range (deg)	1.38-18.14
Reflections collected	21302
Independent reflections	3379
R(int)	0.0777
data/restraints/parameters	3379/0/631
R1;wR2	0.0738;0.1931
GOF (F^2)	1.232
Residual electron density	1.621, -0.317

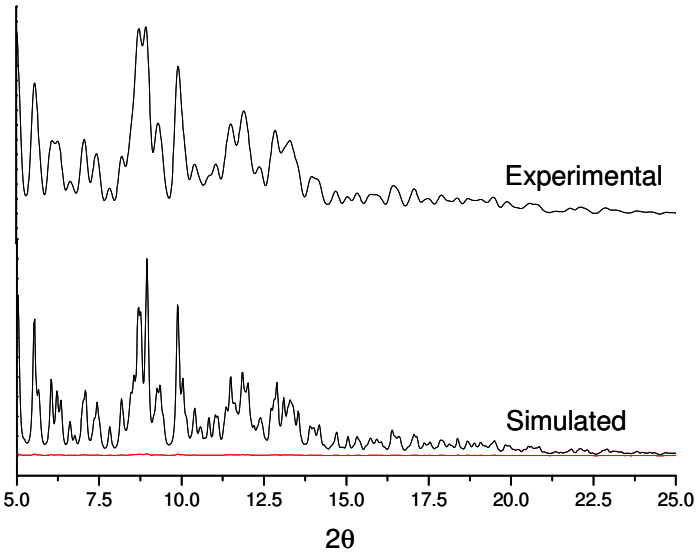
Figure 18S. Energy Dispersive X-ray spectroscopy (EDX) of complexes **3** and **4**



Energy Dispersive X-ray spectroscopy (EDX) of complexes **3** and **4,** depicting the presence of K^+, F^- (a) and K^+, Cl^- (b) ions, respectively

Figure 19S. Simulated and experimental powder X-ray patterns of complexes **3** and **4**.

Complex **3**



Complex **4**

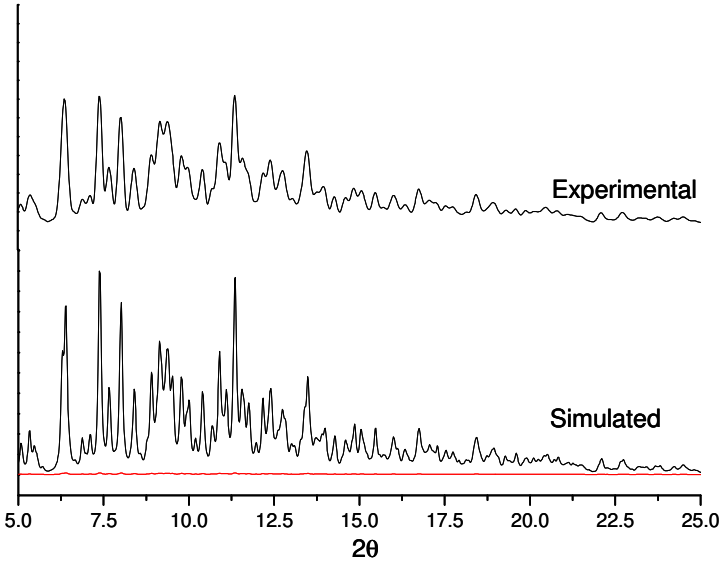


Figure 20S. 2-Dimensional diffusion ordered spectroscopy (2D-DOSY) ^{1}H-DOSY NMR spectra of a) $\mathbf{L^1}$ + $\mathbf{L^2}$ and b) $\mathbf{L^1}$ + $\mathbf{L^2}$ + KPF_6 c) $\mathbf{L^1}$ + $\mathbf{L^2}$ + KPF_6 + *n*-Bu_4NF and d) $\mathbf{L^1}$ + $\mathbf{L^2}$ + KPF_6 + *n*-Bu_4NCl in CD_3CN at 298 K.

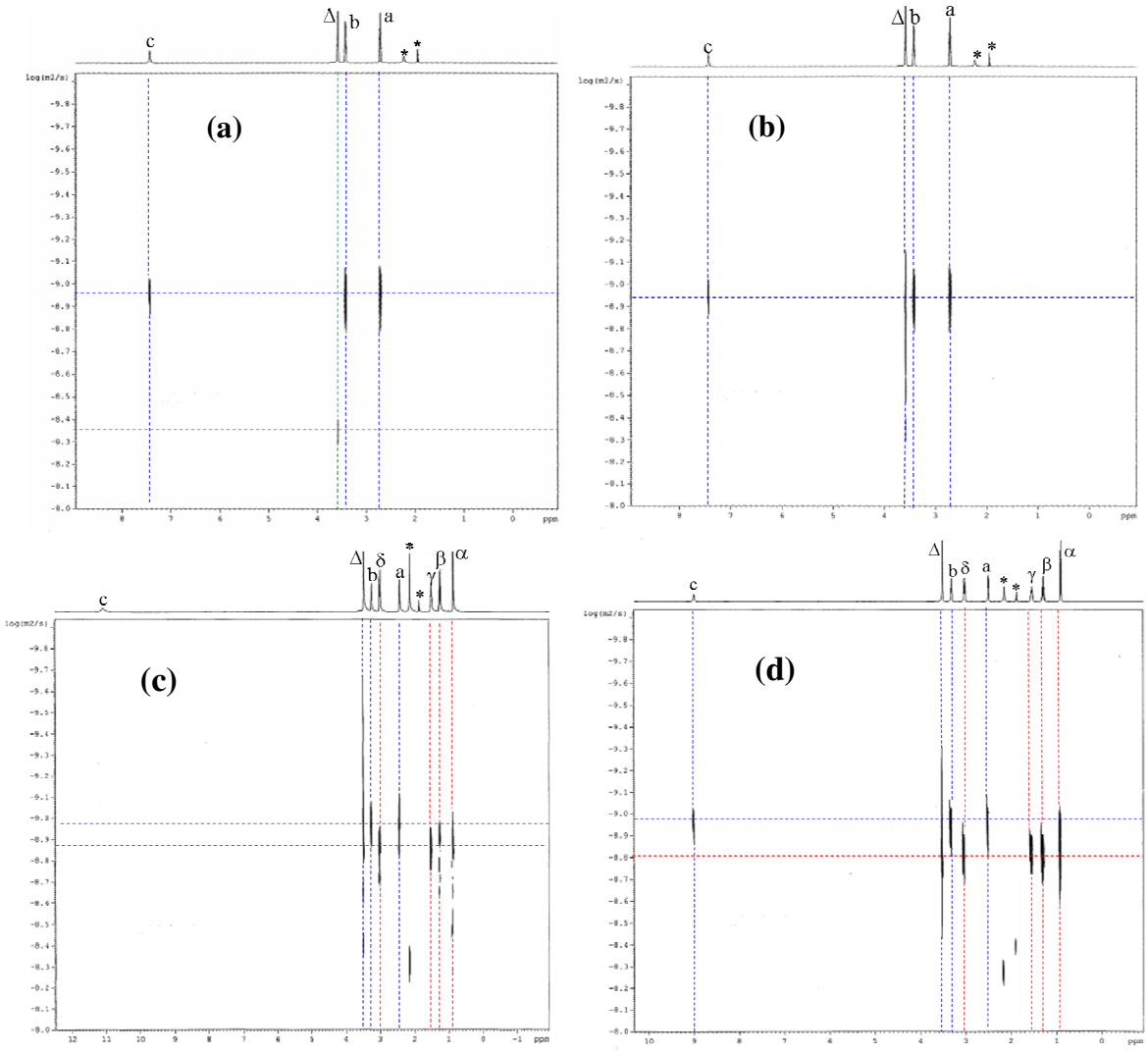


Table 5S. Interatomic Distances, and Angles for the H-bonding Interactions of the Encapsulated Fluoride-water in complex **1**.

D-H···A	d (H···A), Å	d (D···A), Å	< D-H-A º
N2-H2···F16	1.926(2)	2.771(4)	167.6(2)
N3-H3···F16	1.852(2)	2.707(4)	173.7(2)
N4-H4···F16	1.901(2)	2.752(4)	170.0(2)
O4···F16	-	2.475	-

Table 6S. Interatomic Distances, and Angles for the H-bonding Interactions of the Encapsulated Chloride in complex **2**.

D-H···A	d (H···A), Å	d (D···A), Å	< D-H-A º
N2-H2···Cl1	2.3155(15)	3.157(5)	166.2(3)
N3-H3···Cl1	2.3954(15)	3.235(6)	165.8(3)
N4-H4···Cl1	2.4385(14)	3.283(5)	166.9(4)

Table 7S. Interatomic Distances, and Angles for the H-bonding Interactions of the Encapsulated Fluoride-water in complex **3**.

D-H···A	d (H···A), Å	d (D···A), Å	< D-H-A º
N2-H2···F16	1.827(6)	2.685(11)	175.8(6)
N3-H3···F16	1.815(5)	2.664(10)	168.7(6)
N4-H4···F16	1.902(5)	2.738(10)	163.6(5)
O4w···F16	-	2.644	-

Table 8S. Interatomic Distances, and Angles for the H-bonding Interactions of the Encapsulated Chloride-water in complex **4**.

D-H···A	d (H···A), Å	d (D···A), Å	< D-H-A º
N2-H2···Cl1	2.548(3)	3.371(9)	160.3(6)
N3-H3···Cl1	2.423(3)	3.199(9)	150.3(5)
N4-H4···Cl1	2.464(3)	3.307(10)	167.1(6)
O10···Cl1	-	3.216	-

Figure 21S. Partial FT-IR spectra of **L**^{2}, Complexes **1**, **2**, **3** and **4** in KBr discs.

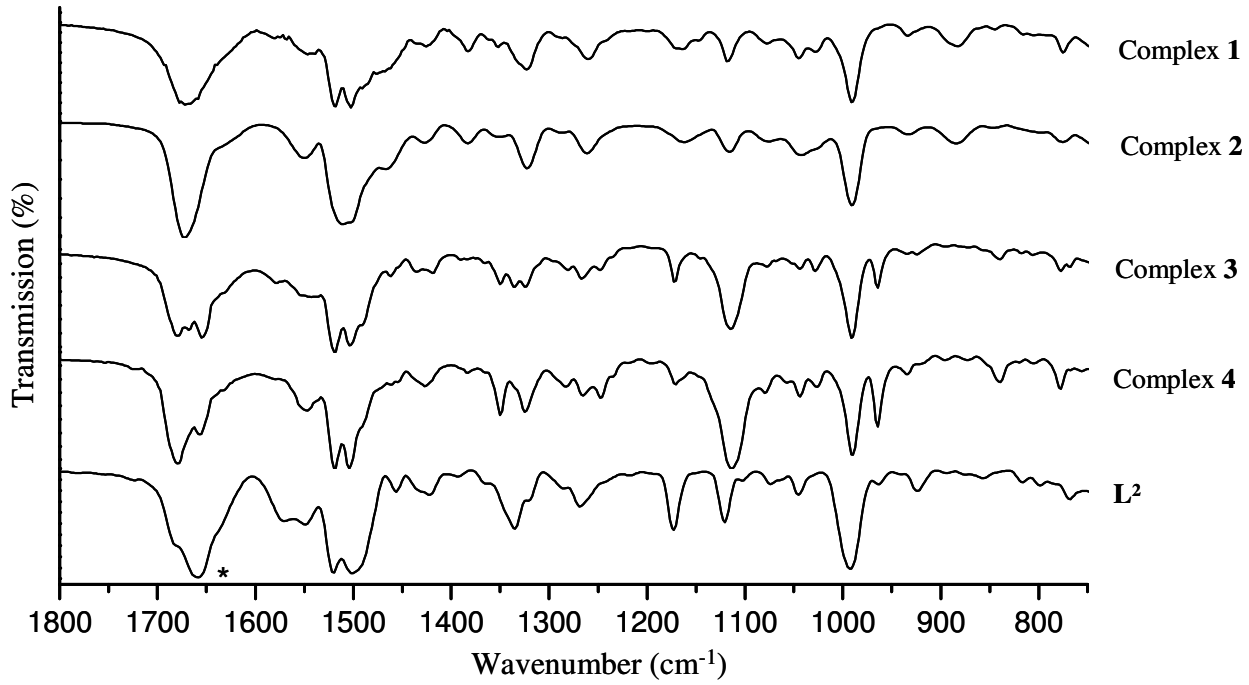


Figure 22S. ^{1}H-NMR spectra of $\mathbf{L^2}$ in $CDCl_3$ after exposure to KF.

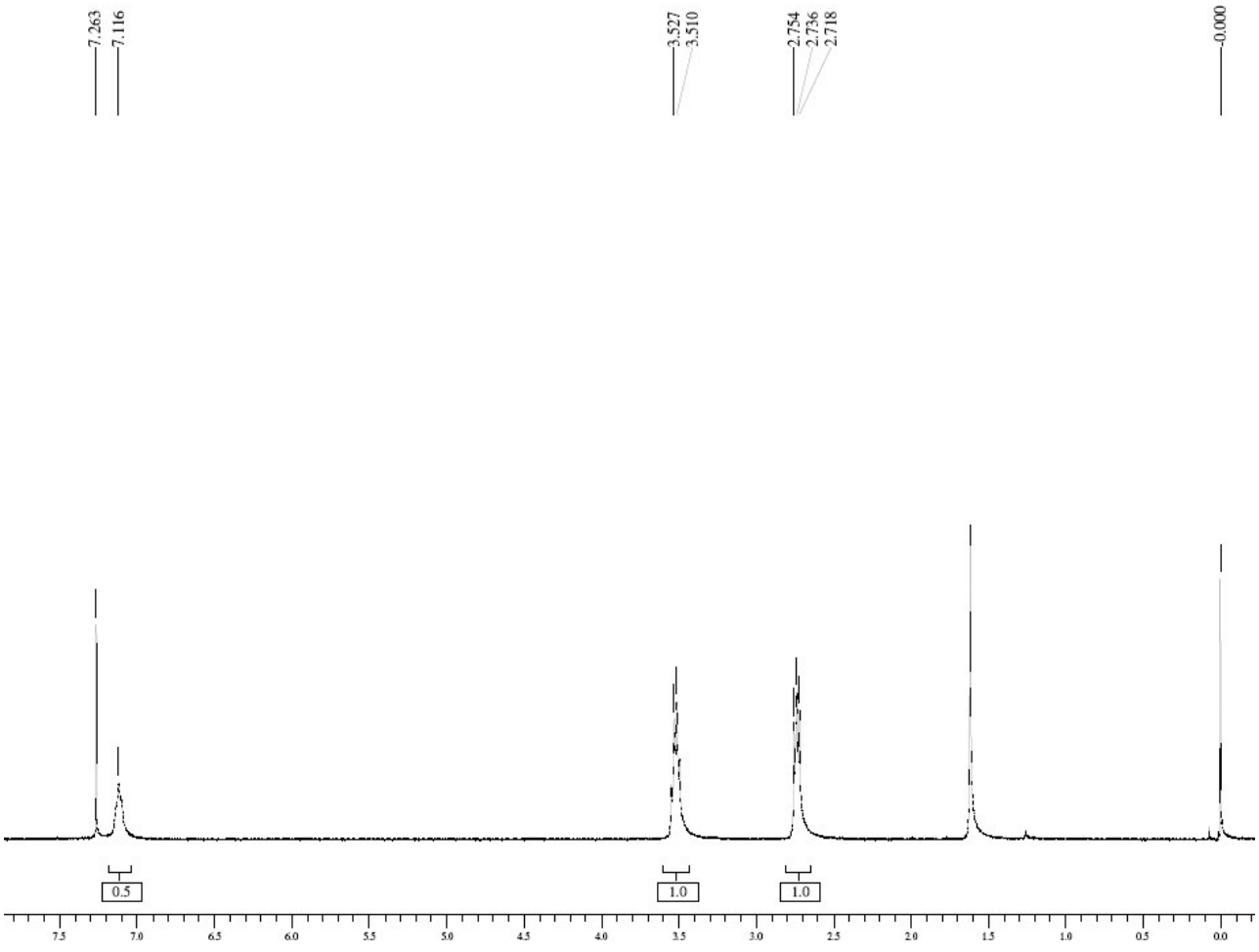


Figure 23S. ^{1}H-NMR spectra of $\mathbf{L^2}$ in $CDCl_3$ after exposure to KCl.

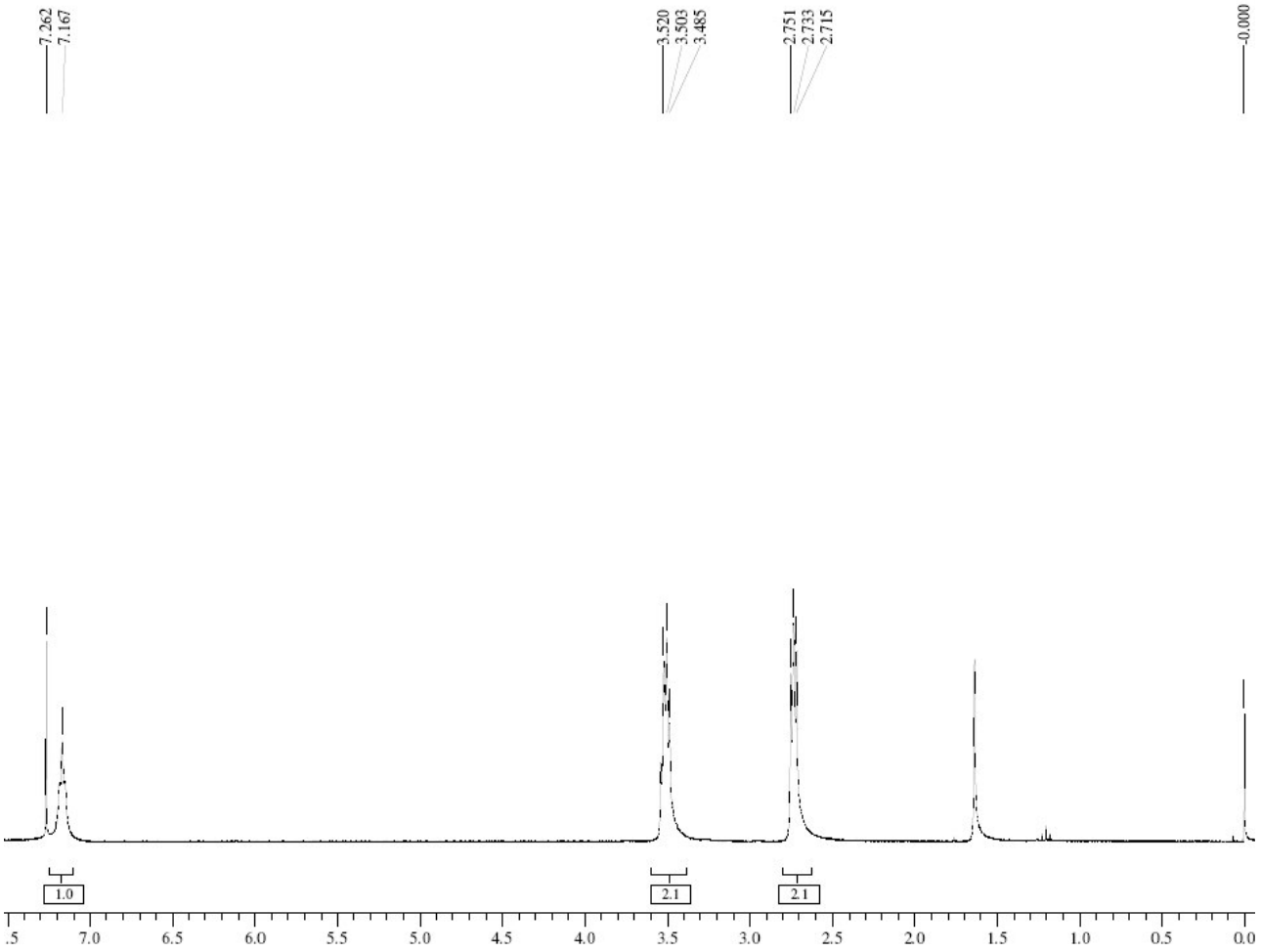


Figure 24S. ^{19}F-NMR spectra of Hexafluorobenzene in $CDCl_3$.

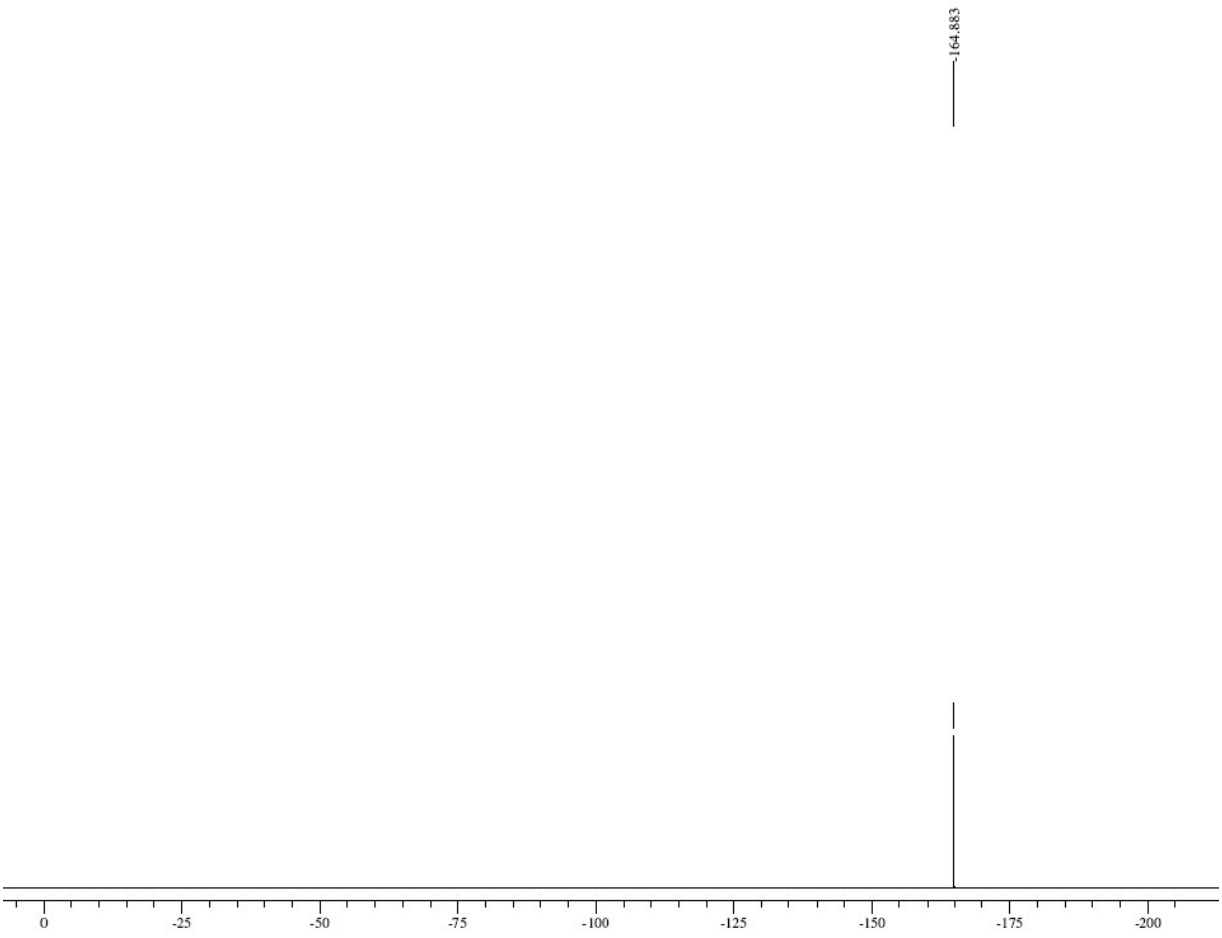


Figure 25S. ^{19}F-NMR spectra of KF in D_2O.

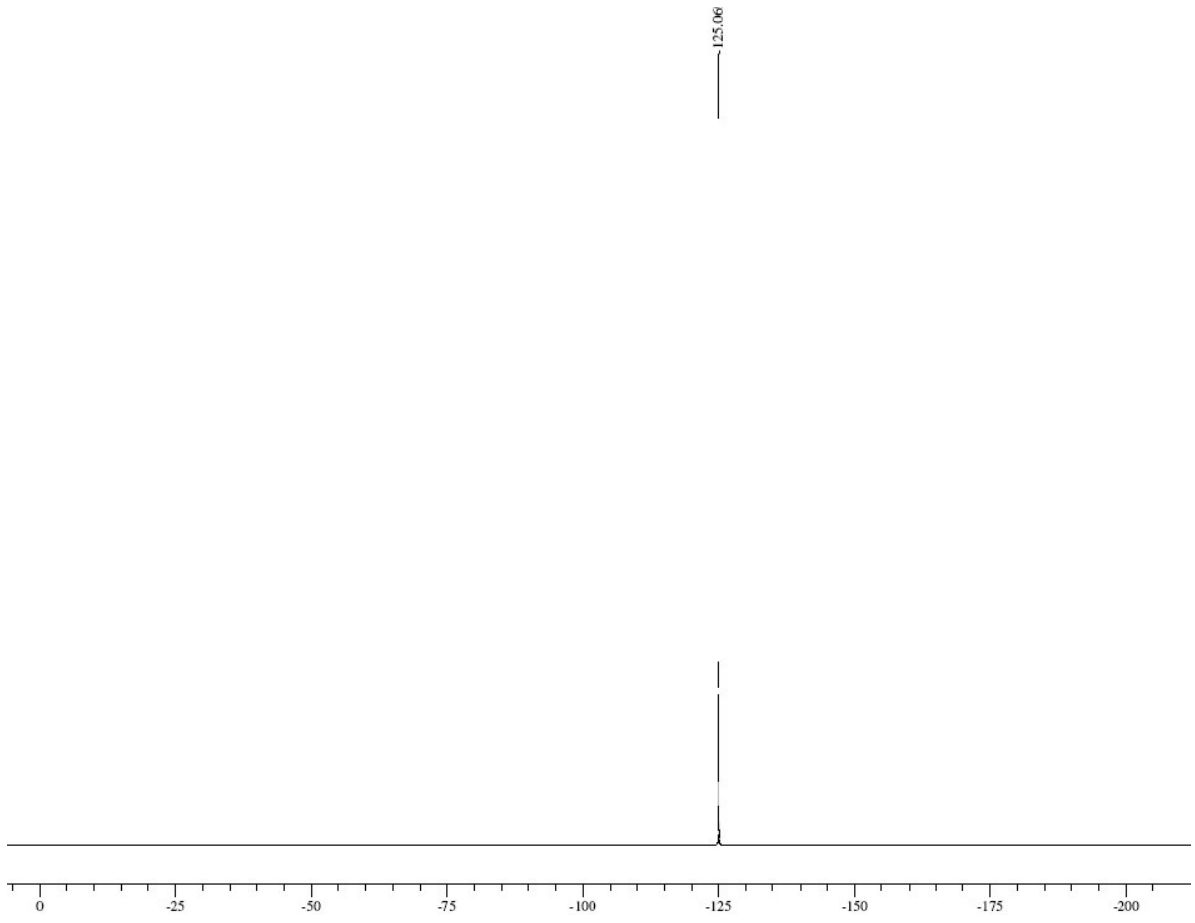


Figure 26S. ^{19}F-NMR spectra of *n*-$Bu_4N^+F^-$ in $CDCl_3$.

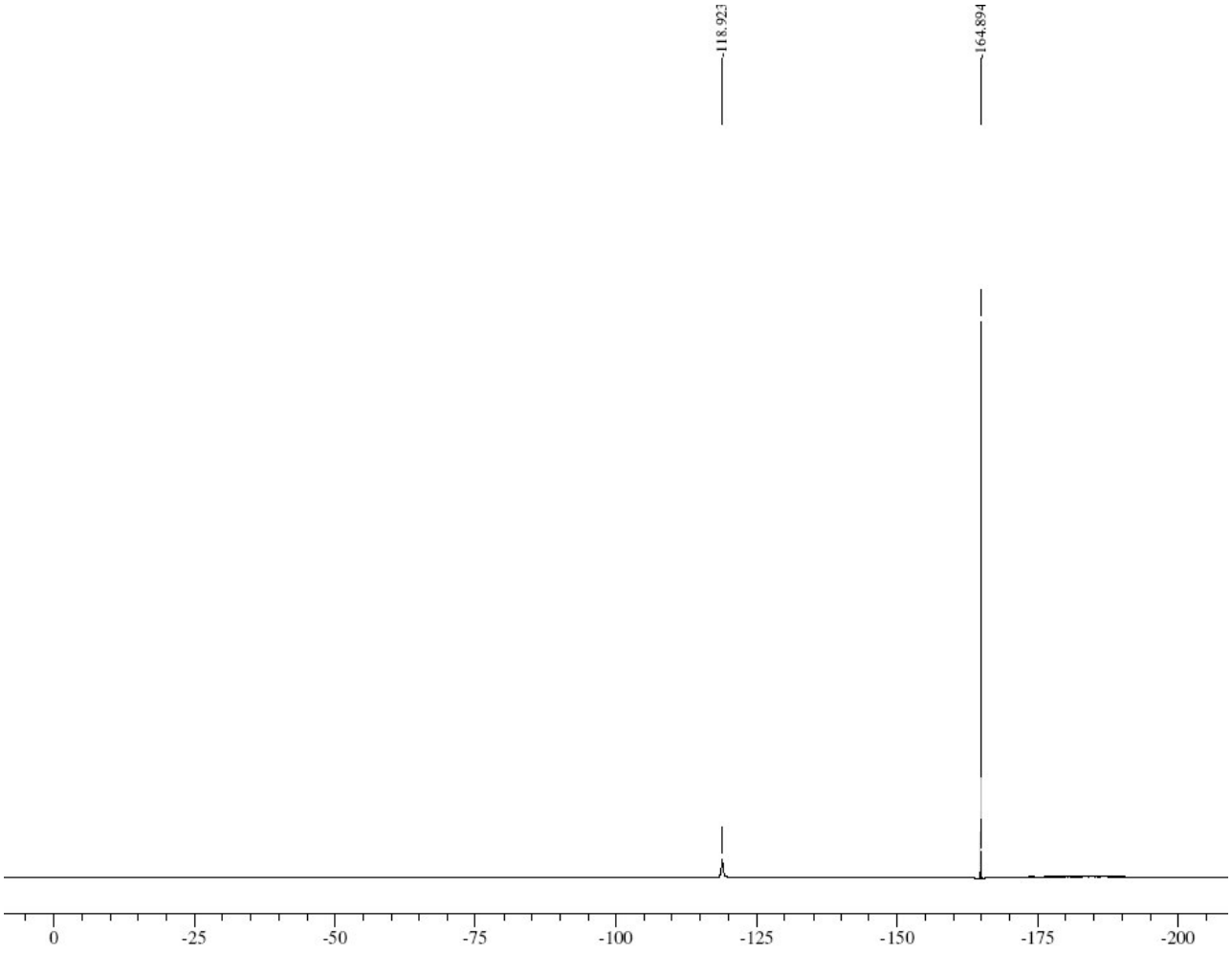


Figure 27S. ^{19}F-NMR spectra of $\mathbf{L^1}$ in $CDCl_3$ after exposure to KF.

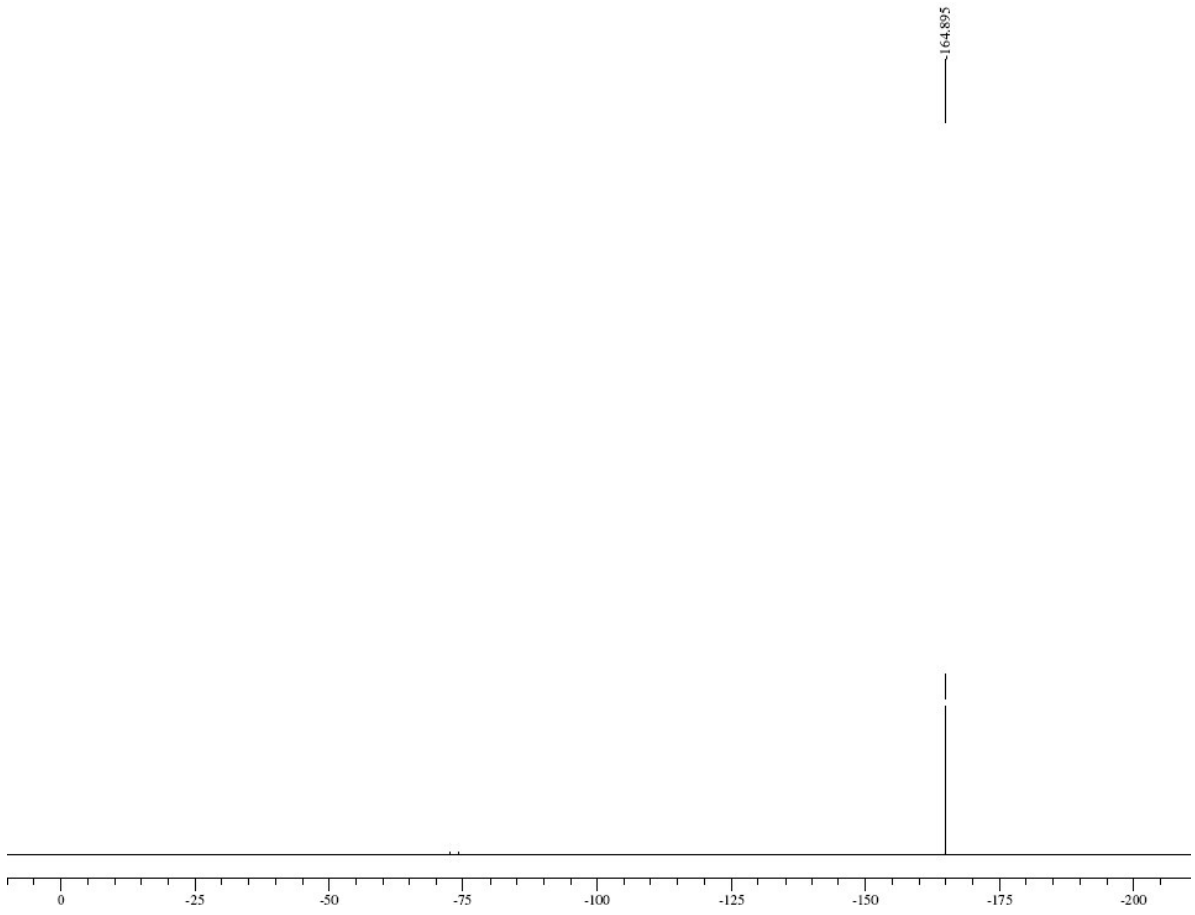


Figure 28S. ^{35}Cl-NMR spectra of KCl in D_2O.

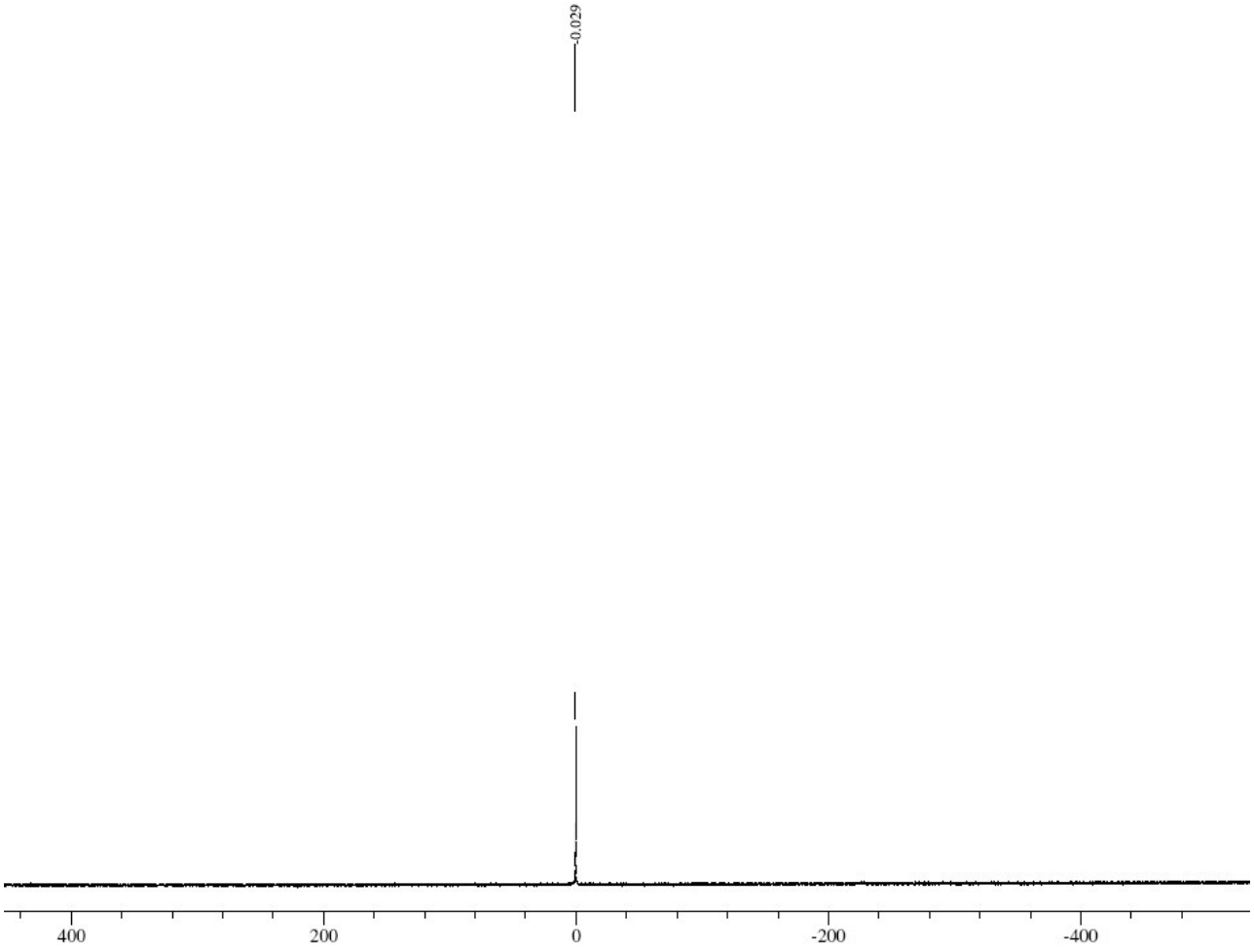


Figure 29S. ^{35}Cl-NMR spectra of *n*-$Bu_4N^+Cl^-$ in $CDCl_3$.

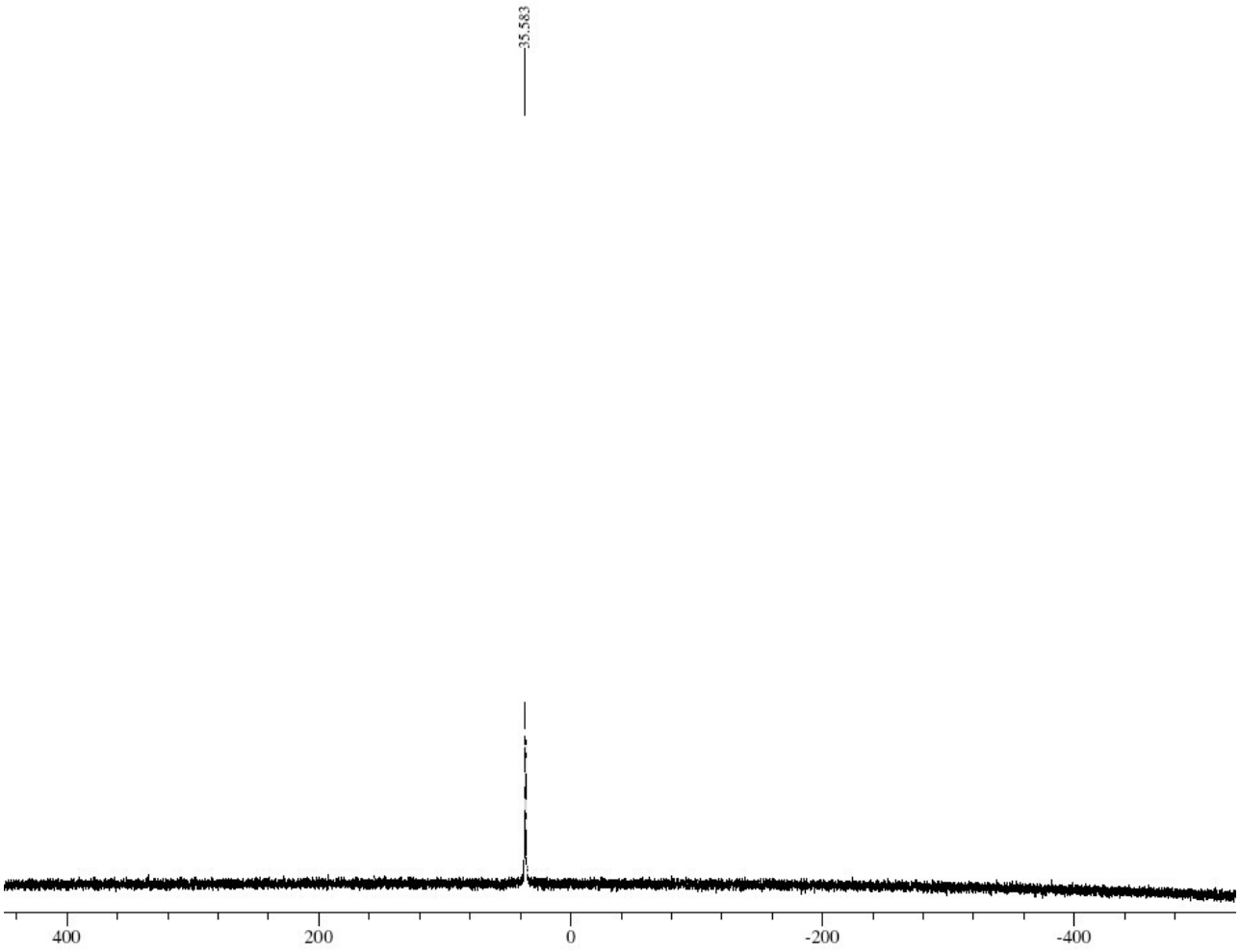


Table 9S. Summary of KF and KCl Extraction Efficiencies.

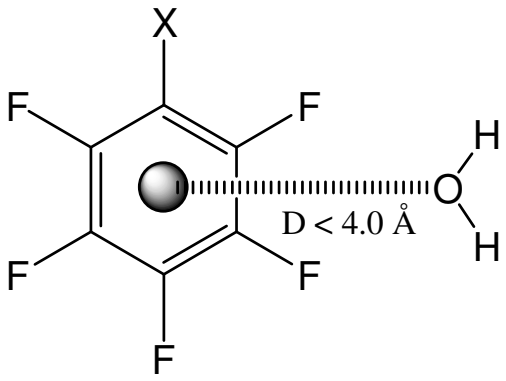
	% of KF Extracted	% of KCl Extracted
$\mathbf{L^1}$	NIL	NIL
$\mathbf{L^2}$	NIL	NIL
$\mathbf{L^1 + L^2}$	48	44

Table 10S. Summary of KF and KCl Extraction Efficiencies at different pH.

salts	% Extracted at pH 4.5	% Extracted at pH 6.3	% Extracted at pH 9.3
KF	45%	48%	NIL
KCl	43%	44%	NIL

CSD Search Results:

A CSD (Version 5.29 November 2007) search was performed with Conquest, version 1.9 for H_2O···pentafluorophenyl interaction. Search was performed by searching only X-C_6F_5 and water (as figure shown below) keeping intermolecular distance (D) between water oxygen and centroid of pentafluorophenyl moiety less than 4.0 Å and filtered using R factor< 10%, no errors and not disordered. Search results only 4 hits which show contact between H_2O and pentafluorophenyl moiety with the distances of 3.94 Å (DOLDEN), 3.783 Å (FEPJOA), 3.647 Å (GIWXAL) and 3.634 Å (IKIHIT).



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7) Mercury 2.2 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2003-2004.