Supplementary Information

Table of content

NMR Spectra of complexes

Table S 1 Table of 1H NMR spectra of the complexes.

	2FEu		3FEu	4FEu	2FSm	3FSm	4FSm	2FLa	4FLa
	$CDCl_3$	CD_3CN							
3Py	5.27 d 5.12 d	4.65 d 4.63 d	4.05 d	4.22 d	8.31 m	8.39 d	8.33 d	8.21 d 8.19 d	8.22 d
4Py	5.81 t 5.94 t	5.99 t 5.96 t	5.61 t	5.69 t	7.99 m	8.03 t	8.00 t	7.85 t 7.83 t	7.85 t
5Py	4.34 d 3.97 d	4.43 d 4.43 d	3.93 d	3.84 d	7.22 m	7.24 d	7.17 d	7.09 d 7.07 d	7.01 d
2Ar	-	-	7.40 br.s.	7.14 t	-	7.19 br.s	7.38 m	-	7.41 dd
6Ar	9.58 t 8.65 t	8.05 br.s 7.51 br.s	7.45 br.s		7.32 m	7.45 m		7.48 br.m. 7.44 t 7.32 t 7.27 t 7.24 t 7.17 t	
3Ar	7.27*	7.14 t 6.95 t	-	7.41 br.s	7.56 br.s.	-	7.22 m		7.19 t
5Ar	7.82 t 7.50 d	7.38 t 7.22 t	7.21 t		7.44 t 7.50 t	7.27 td			
4Ar	7.66 br.s 7.56 br.s	7.42 br.s	7.45 br.s	-	7.32 m	7.12 br.s	-		-
CH2	3.46 br.s 3.93 br.s 4.04 br.s 3.82 br.s	2.69 br.s 2.91 br.s 2.60 br.s	2.17 br.s	1.72 q	4.37 dd 4.45 dd	4.41 4.51 br.s	4.51 q	4.15 dq 3.89 dq	4.07 q
CH3	1.15 br.s 1.08 br.s	0.64 br.s 0.78 br.s	0.12 br.s	-0.02 t	1.35 t 1.39 t	1.46 t	1.48 t	1.22 - 1.32 m	1.26 t

*With the solvent signal.

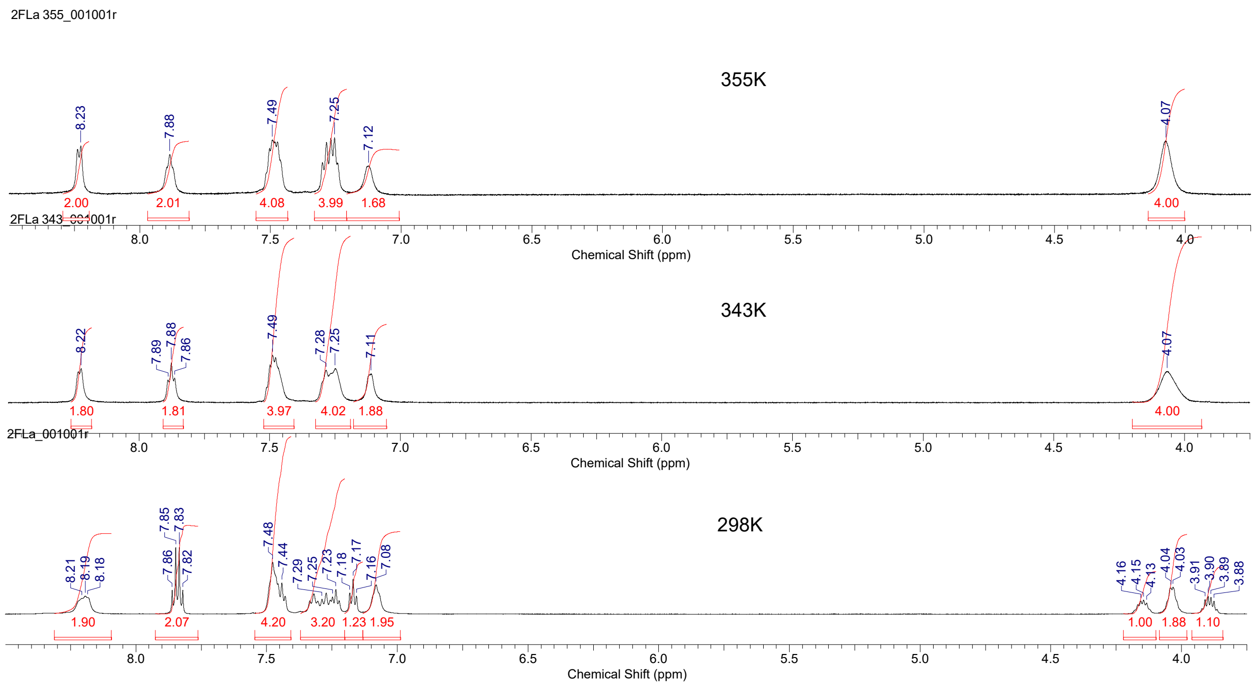

Fig 1 The temperature-dependent coalescence of the fluoroaromatic and methylene-groups protons in La2F$(NO_3)_3$ in acetonitrile

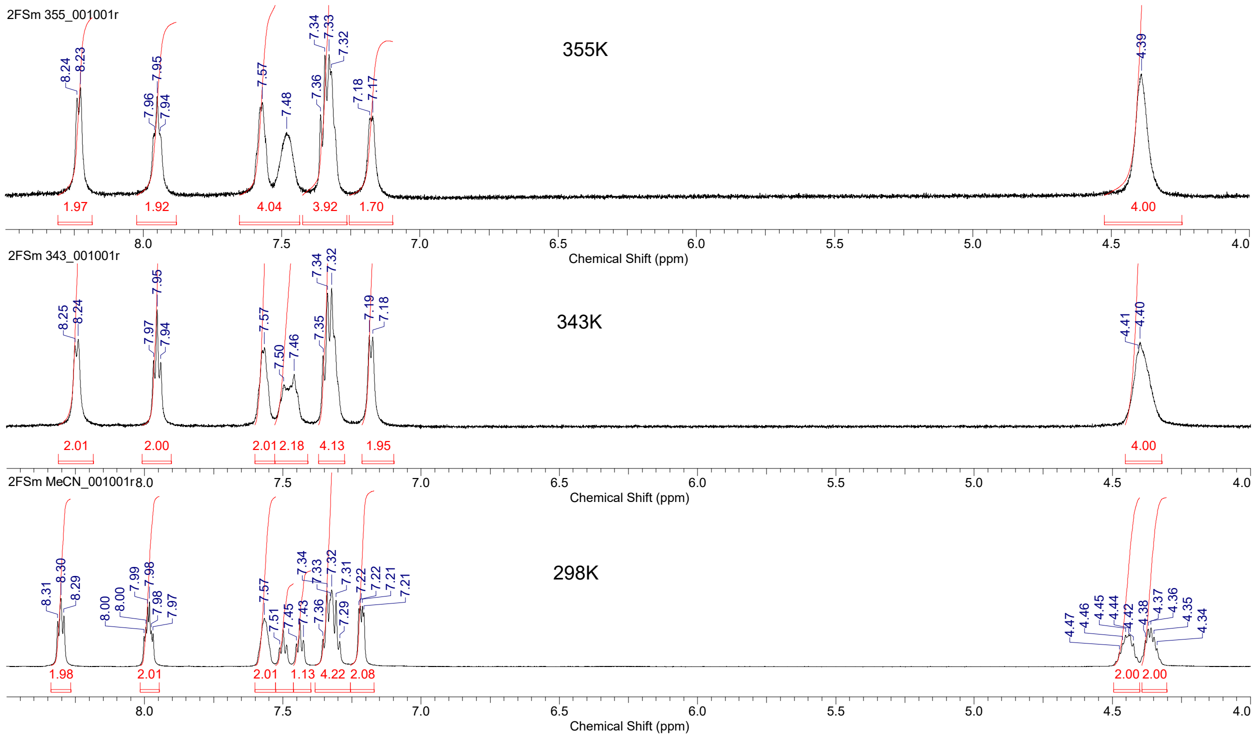

Fig 2 The temperature-dependent coalescence of the fluoroaromatic and methylene-groups protons in Sm2F$(NO_3)_3$ in acetonitrile

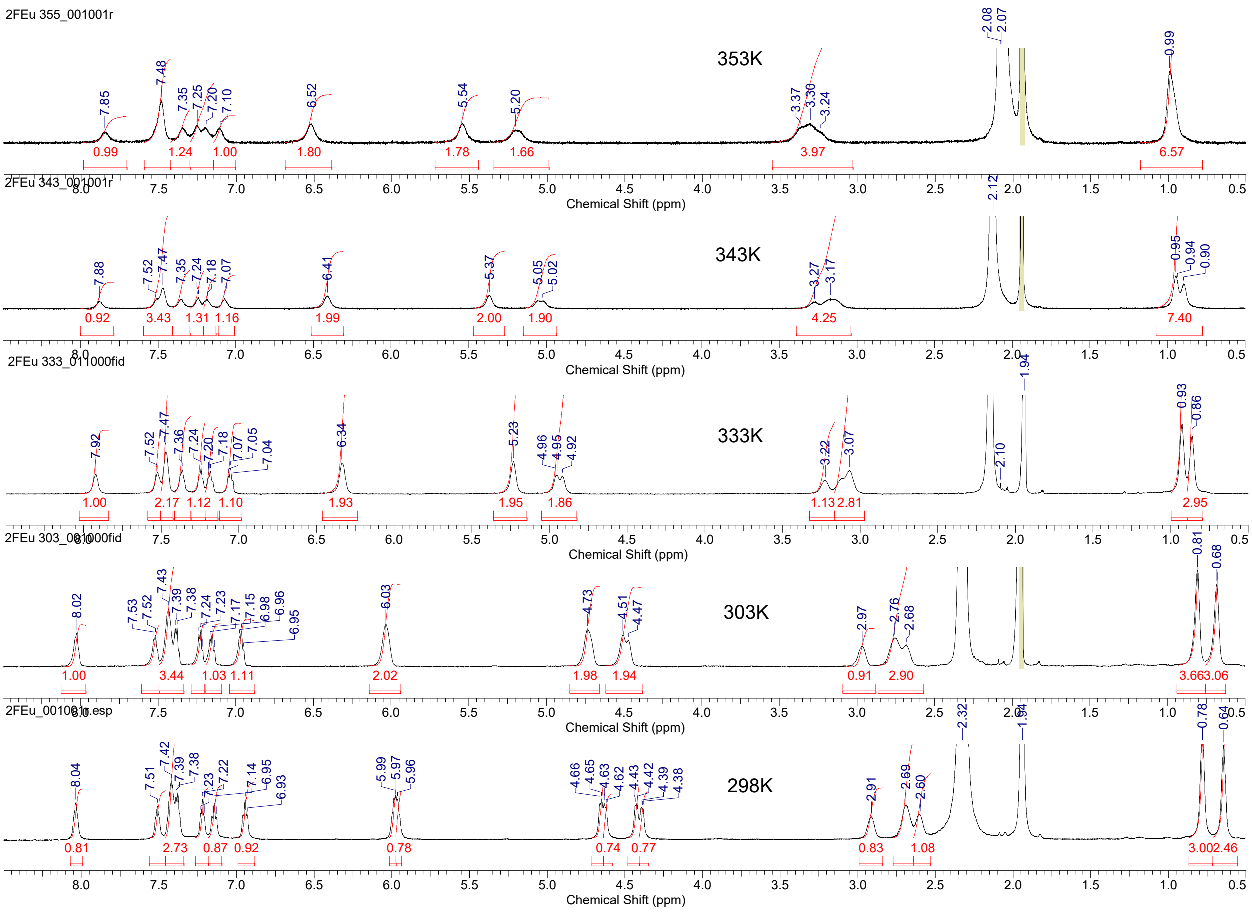

Fig 3 The temperature-dependent coalescence of the fluoroaromatic and methylene-groups protons in Eu2F(NO$_3$)$_3$ in acetonitrile

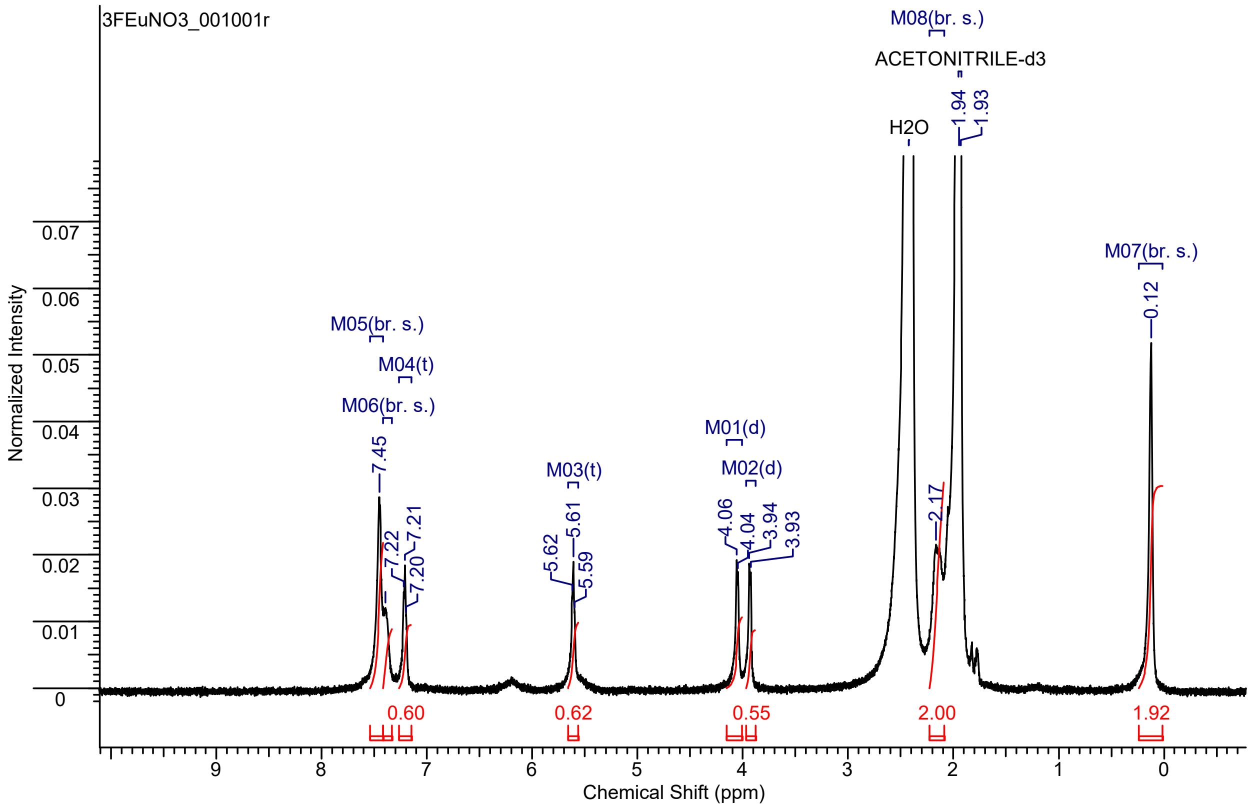

Fig 4 1H Spectrum of Eu3F(NO3)3 in acetonitrile

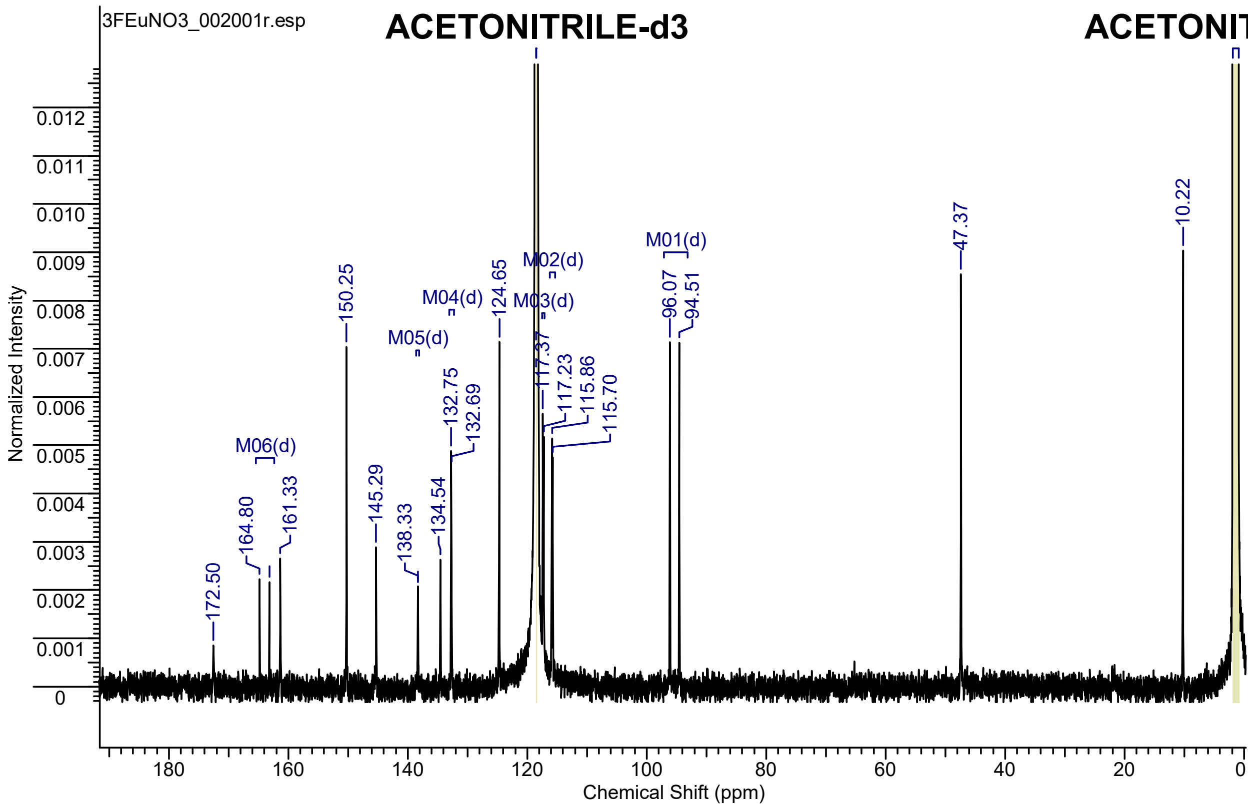

Fig 5 13C Spectrum of Eu3F(NO3)3 in acetonitrile

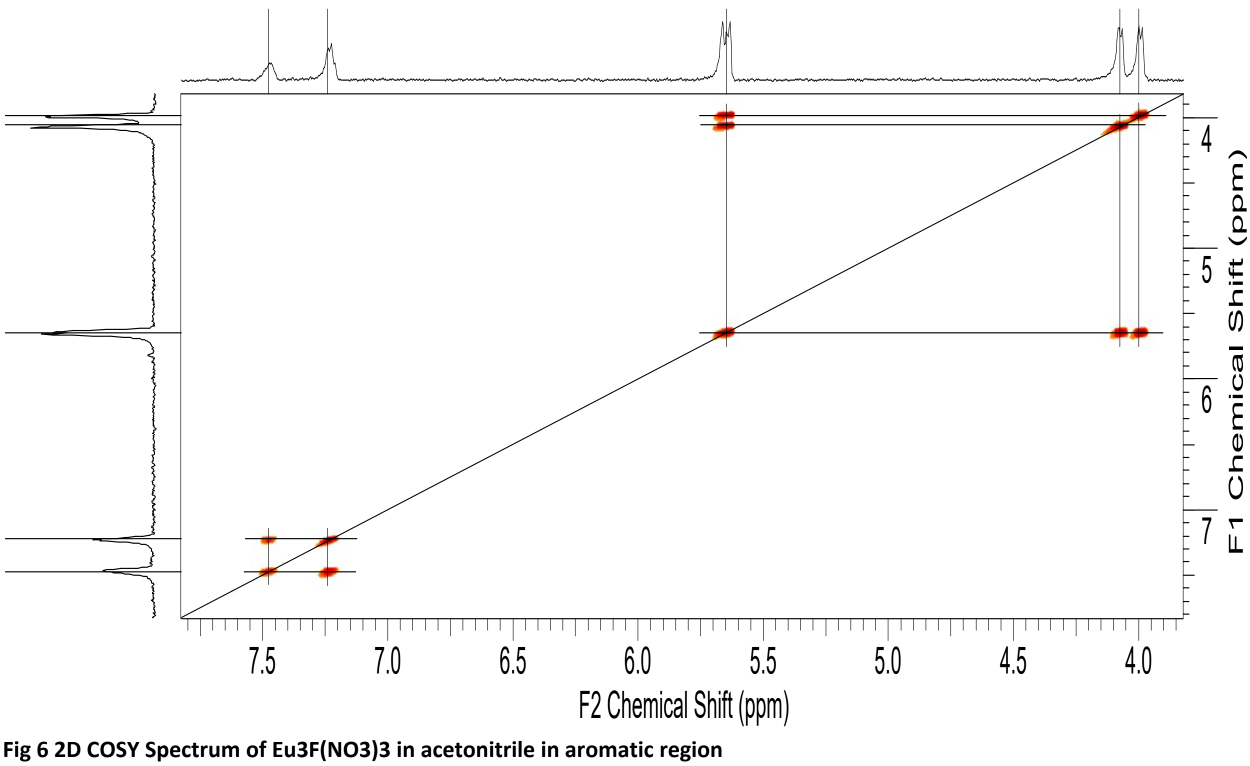

Fig 6 2D COSY Spectrum of Eu3F(NO3)3 in acetonitrile in aromatic region

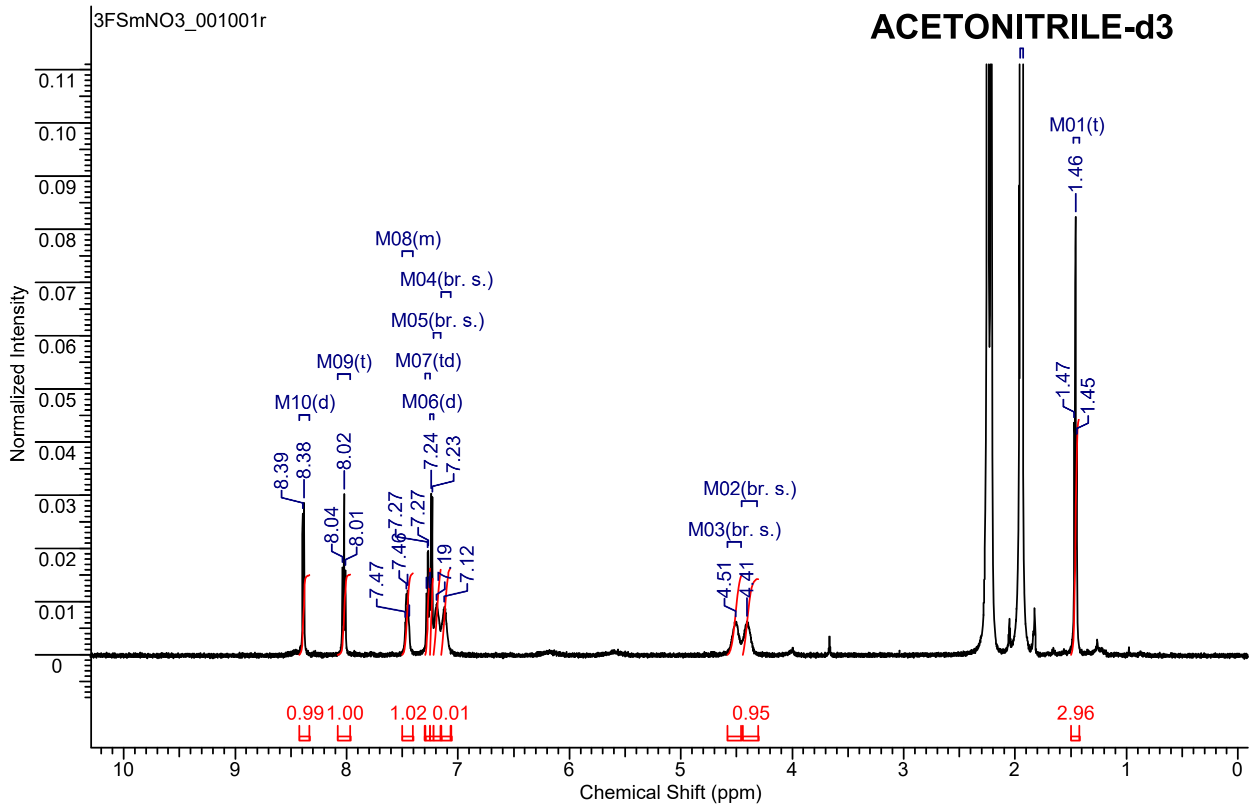

Fig 7 1H Spectrum of Sm3F(NO3)3 in acetonitrile

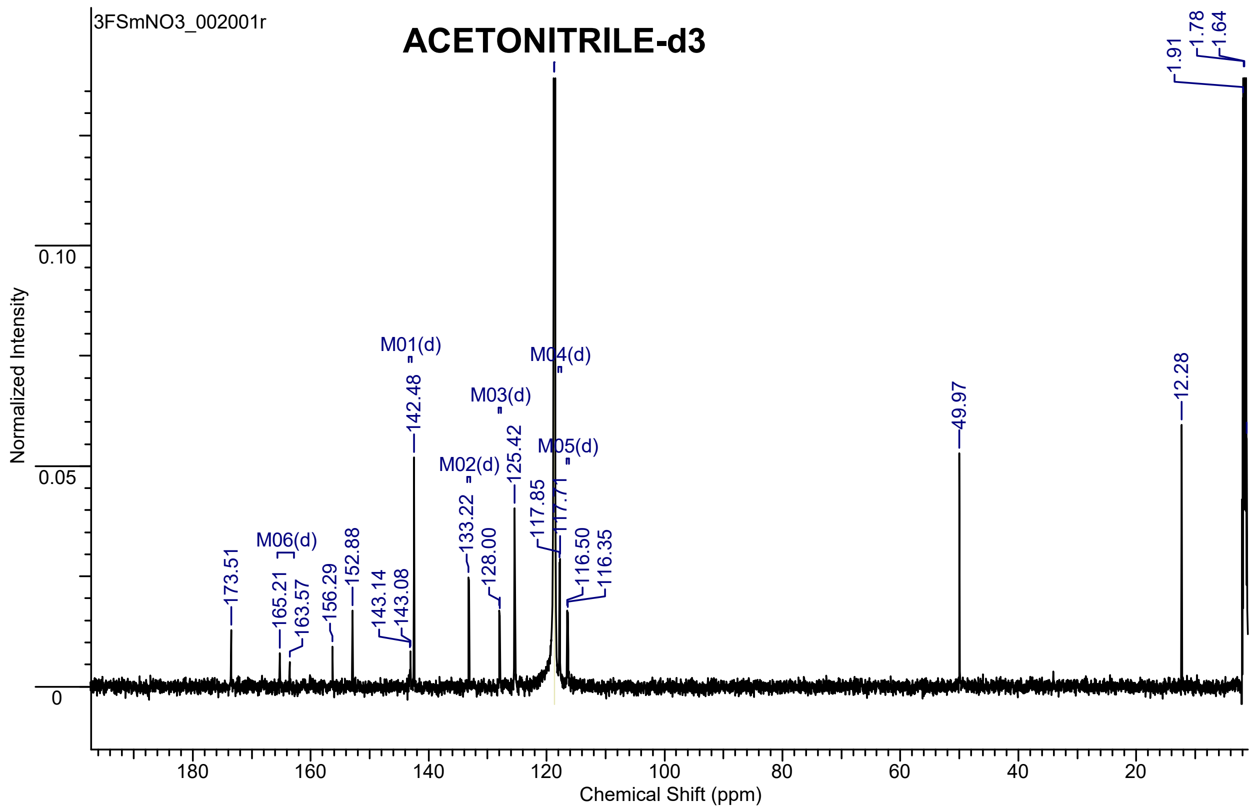

Fig 8 13C Spectrum of Sm3F(NO3)3 in acetonitrile

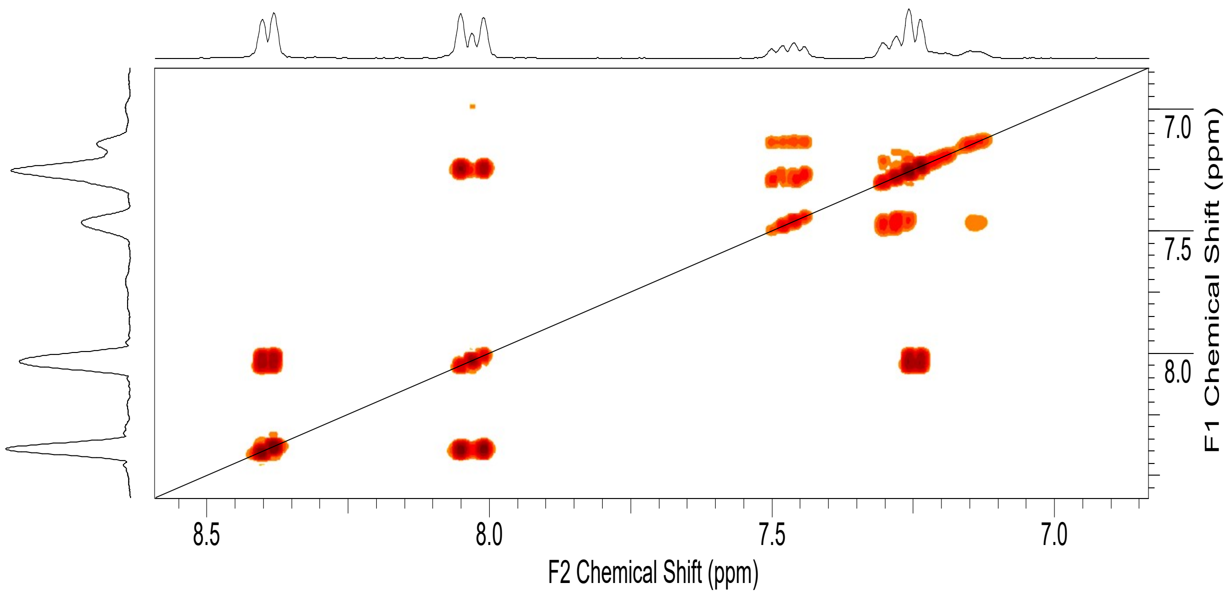

Fig 9 2D COSY Spectrum of Sm3F(NO3)3 in acetonitrile in aromatic region

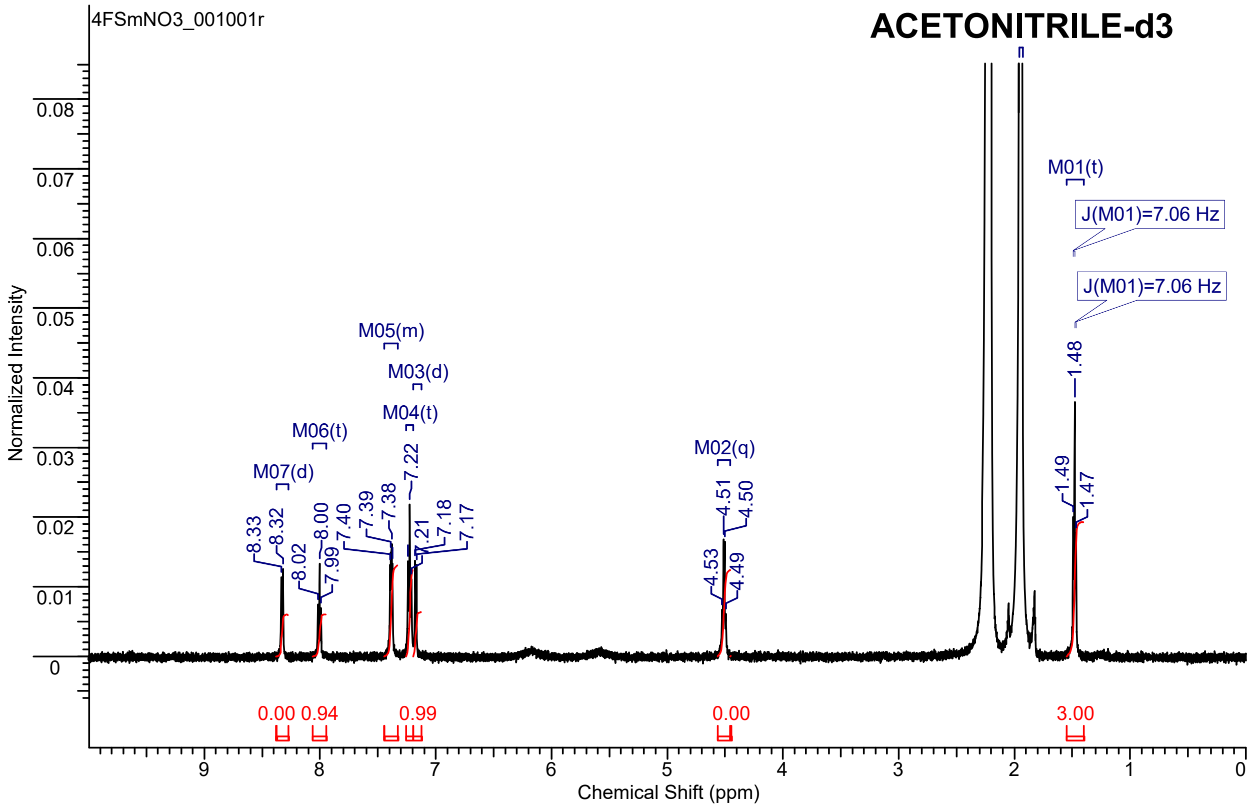

Fig 10 1H Spectrum of Sm4F(NO3)3 in acetonitrile

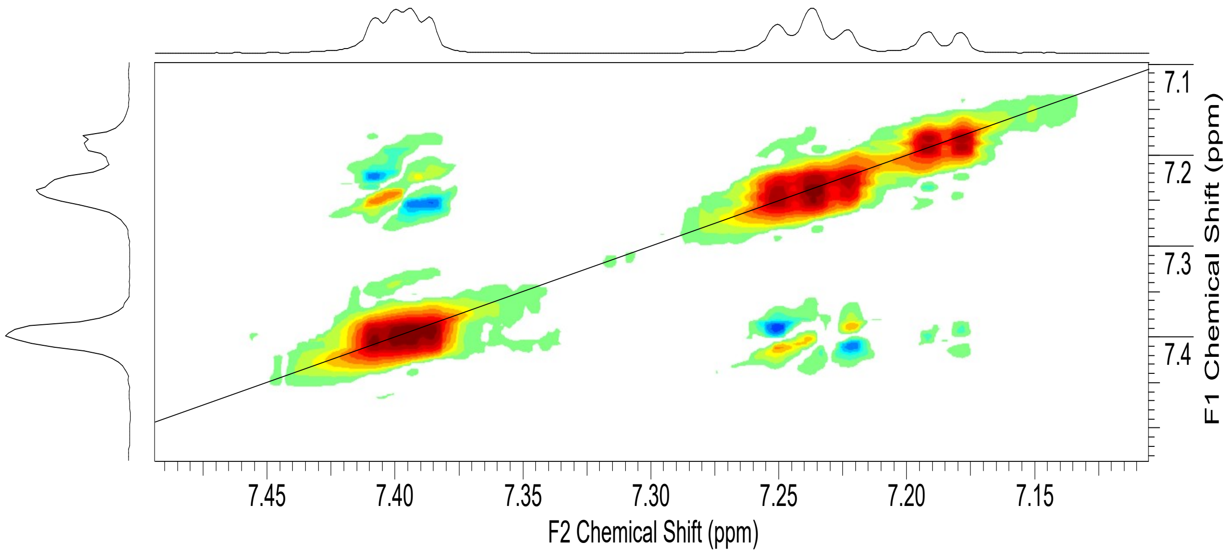

Fig 11 2D NOESY Spectrum of Sm4F(NO3)3. The aromatic region.

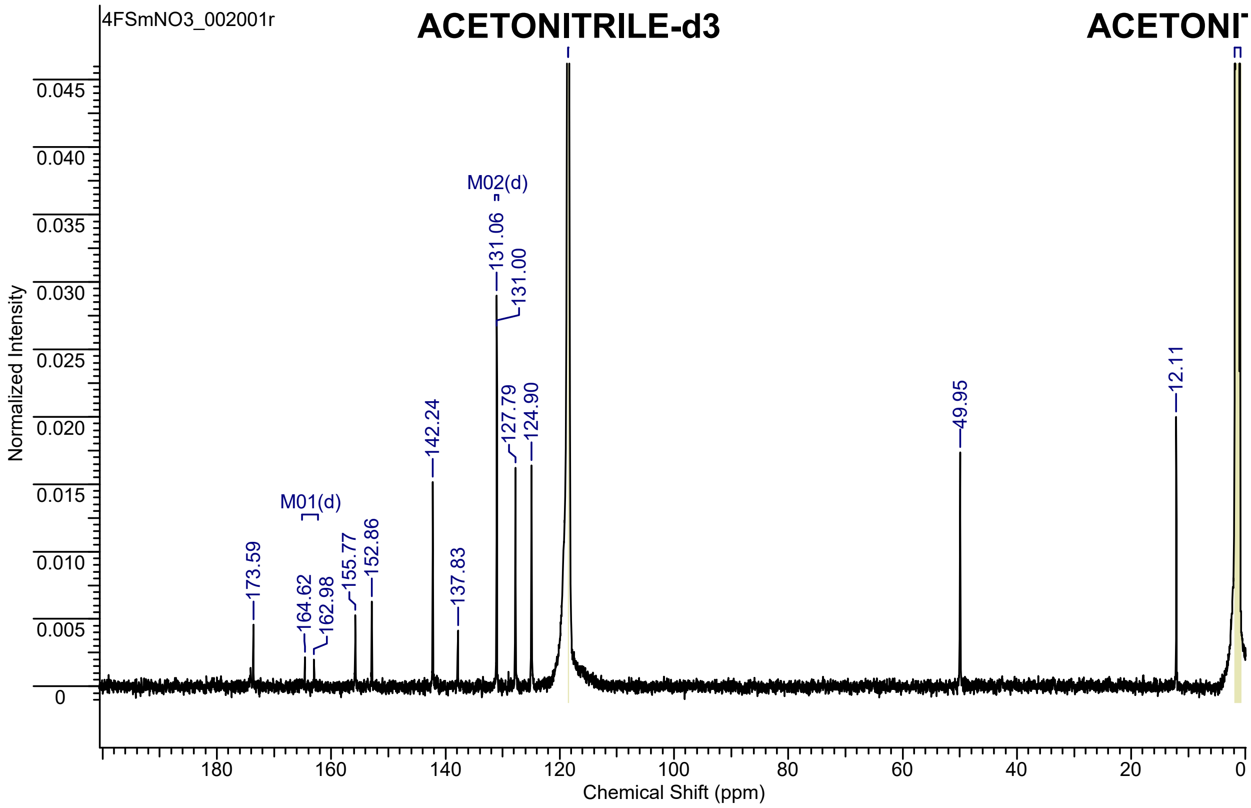

Fig 12 13C Spectrum of Sm4F(NO3)3 in acetonitrile

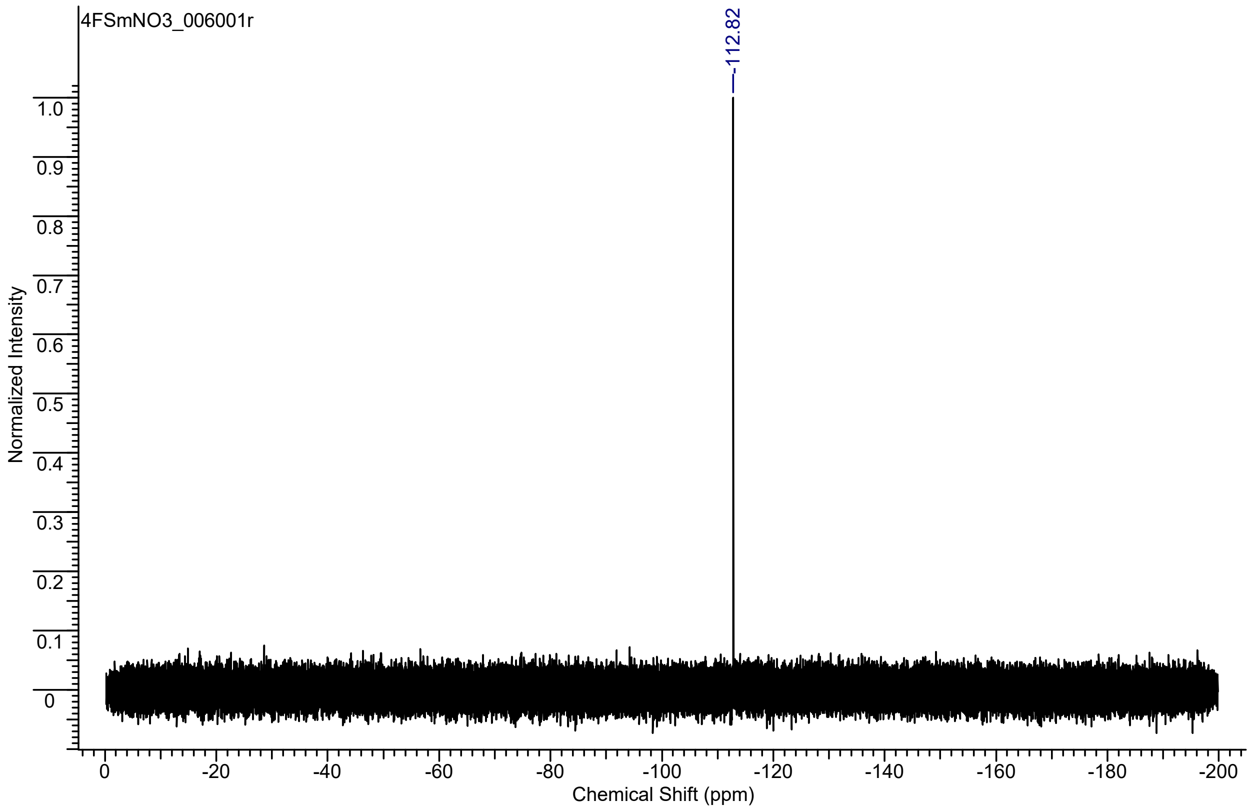

Fig 13 19F Spectrum of Sm4F(NO3)3 in acetonitrile

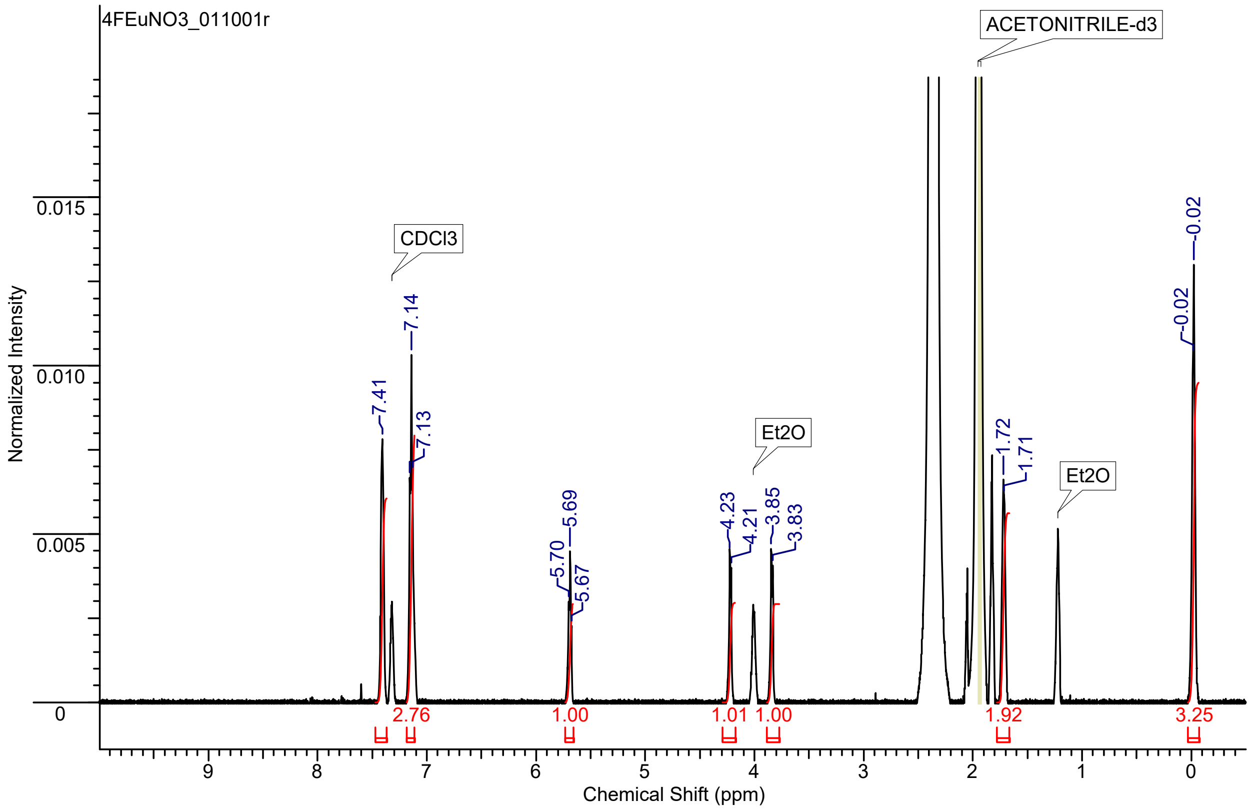

Fig 14 1H Spectrum of Eu4F(NO3)3 in acetonitrile

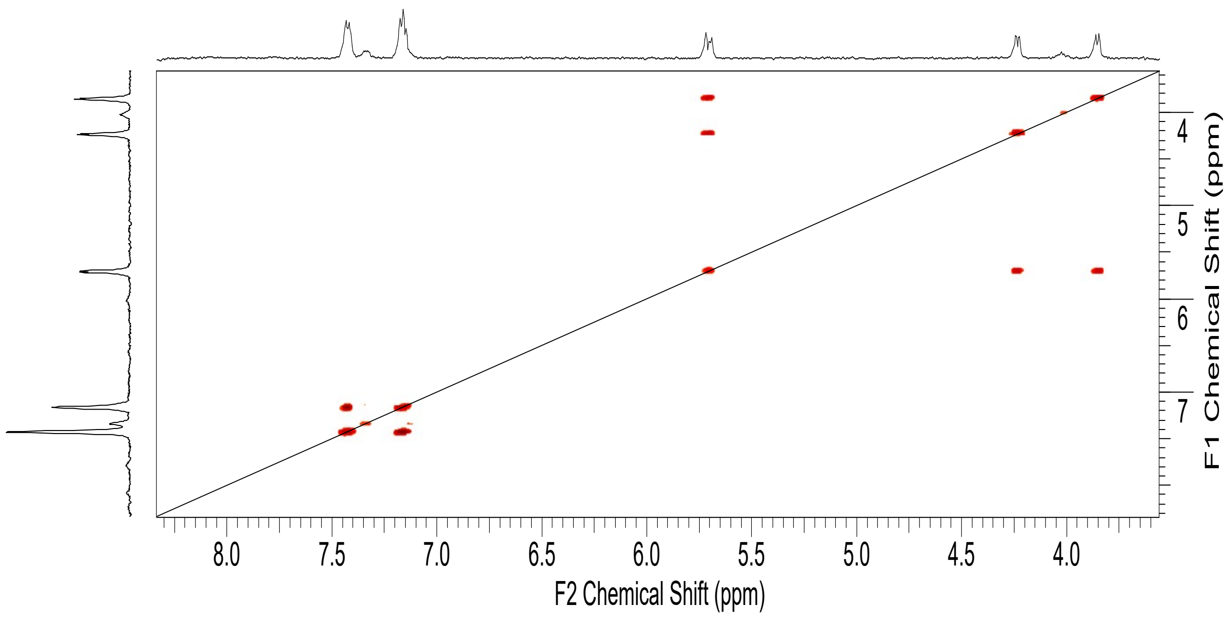

Fig 15 2D COSY Spectrum of Eu4F(NO3)3.

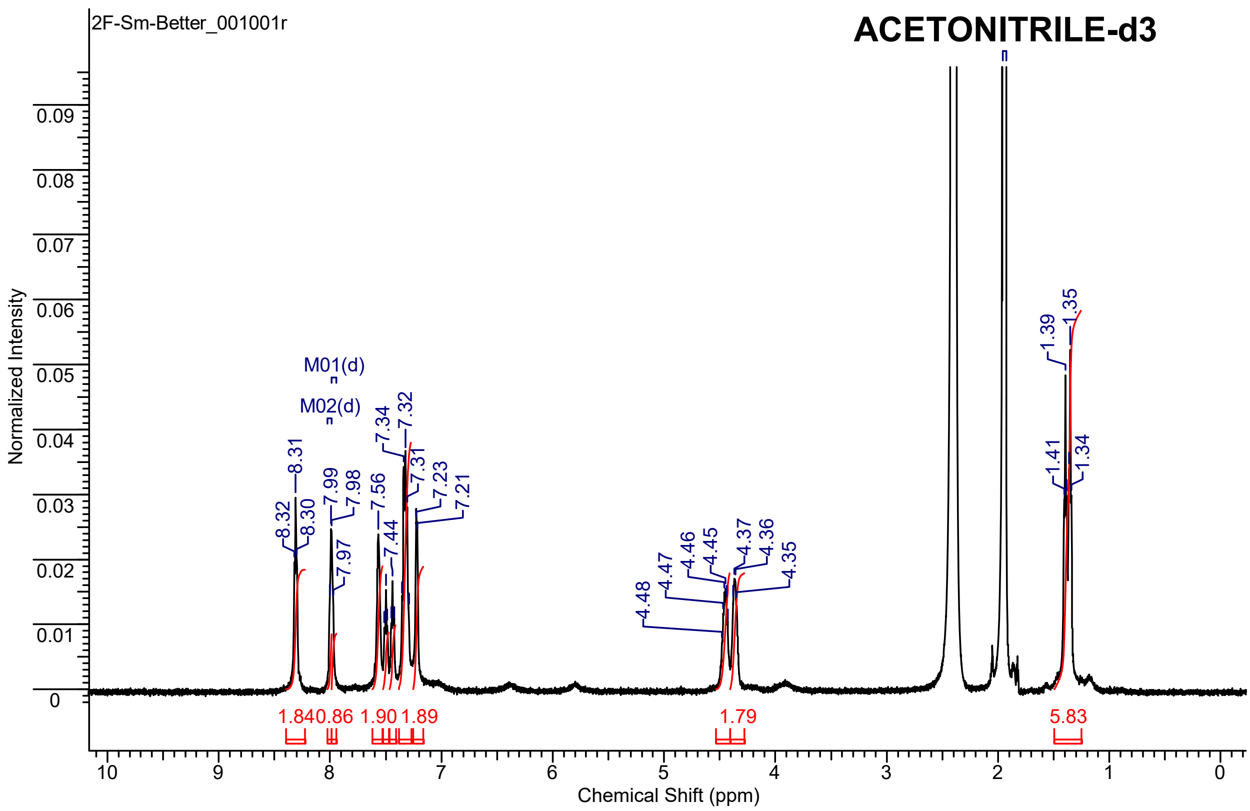

Fig 16 1H Spectrum of Sm2F(NO3)3 in acetonitrile

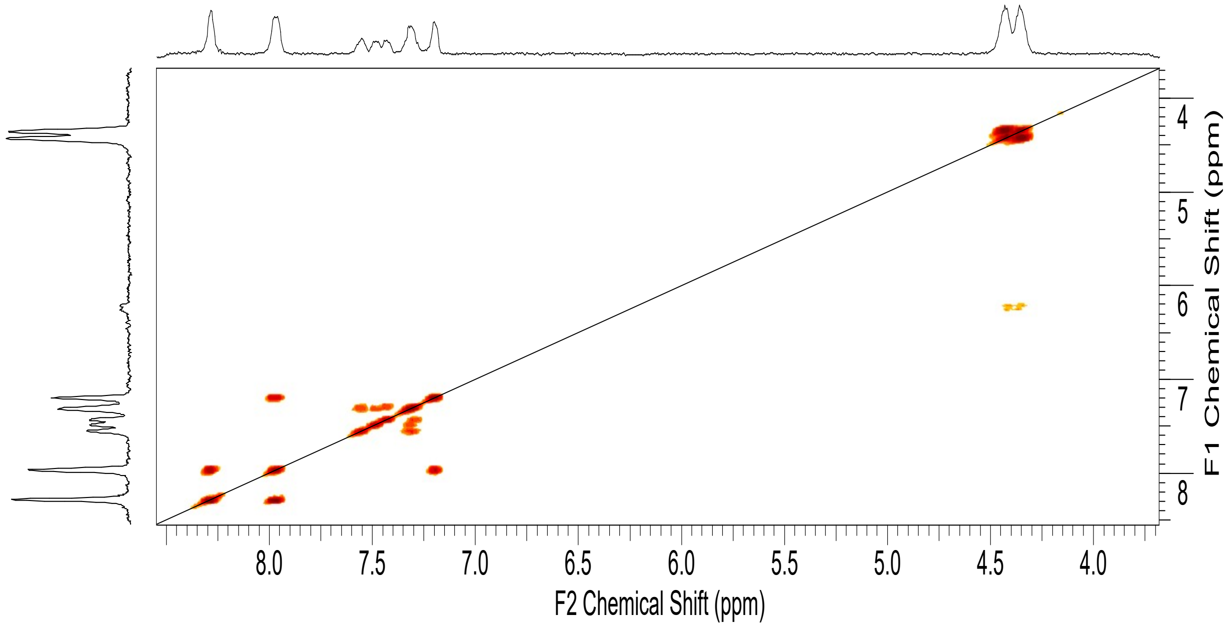

Fig 17 2D COSY Spectrum of Sm2F(NO3)3 in acetonitrile

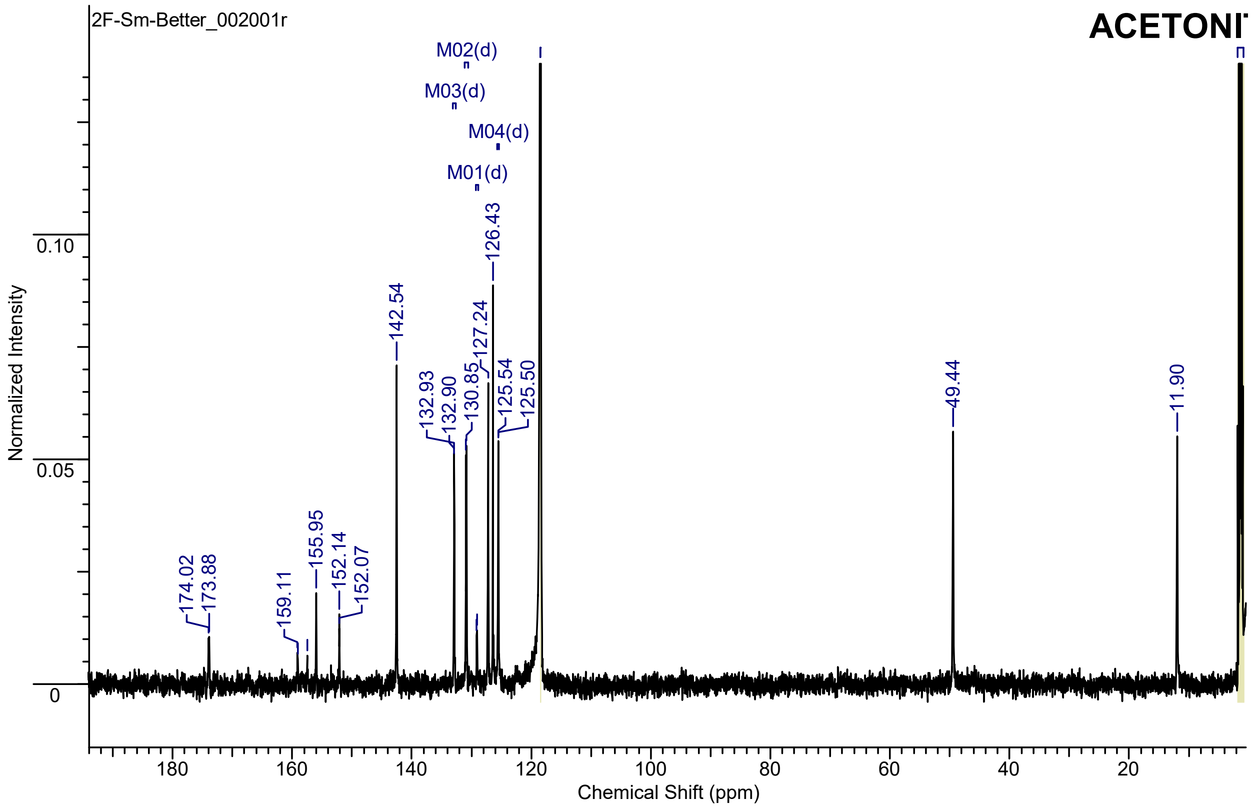

Fig 18 13C Spectrum of Sm2F(NO3)3 in acetonitrile

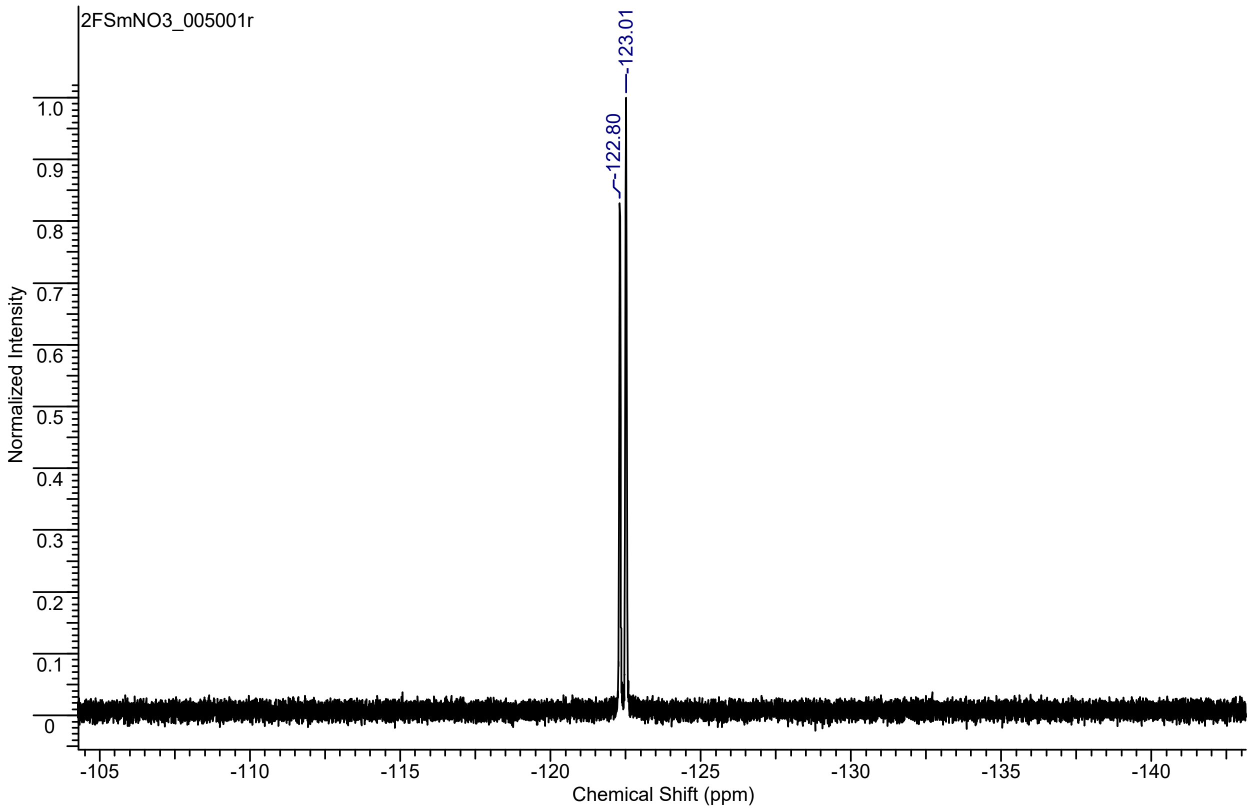

Fig 19 19F Spectrum of Sm2F(NO3)3 in acetonitrile

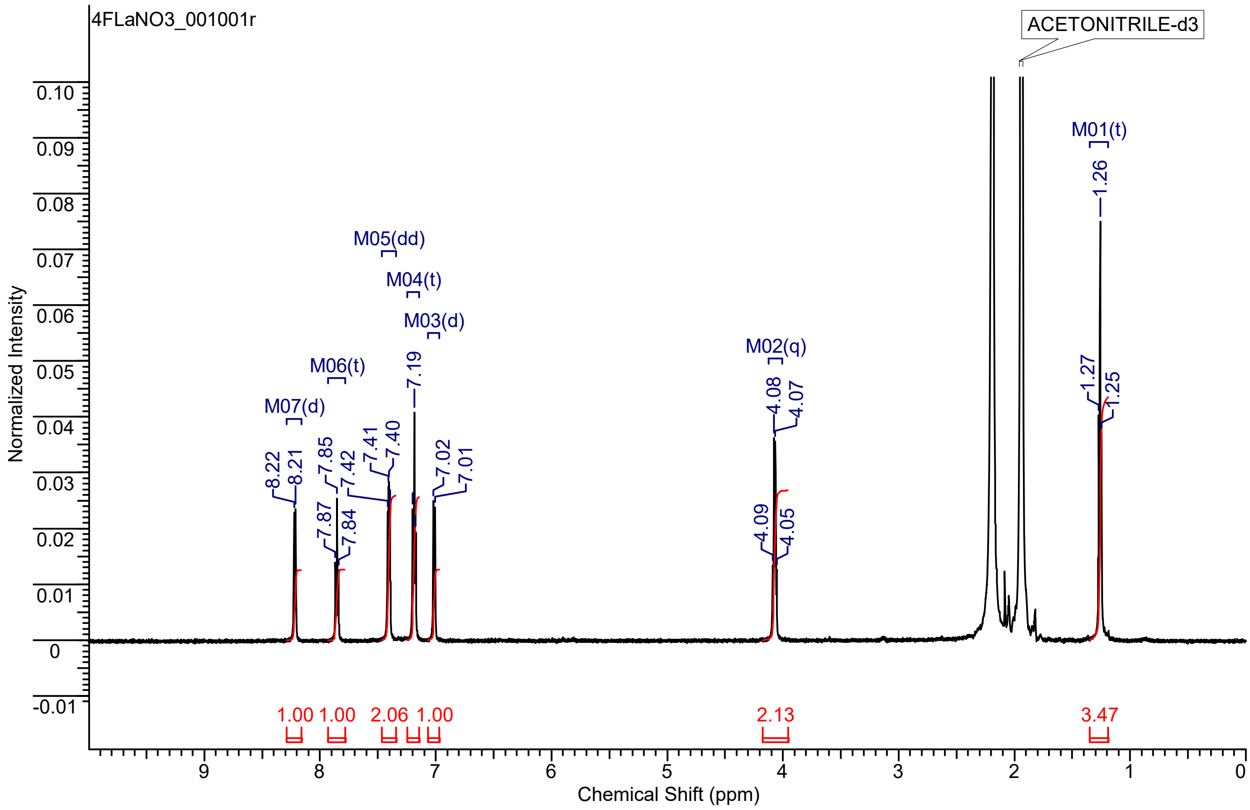

Fig 20 1H Spectrum of La4F(NO3)3 in acetonitrile

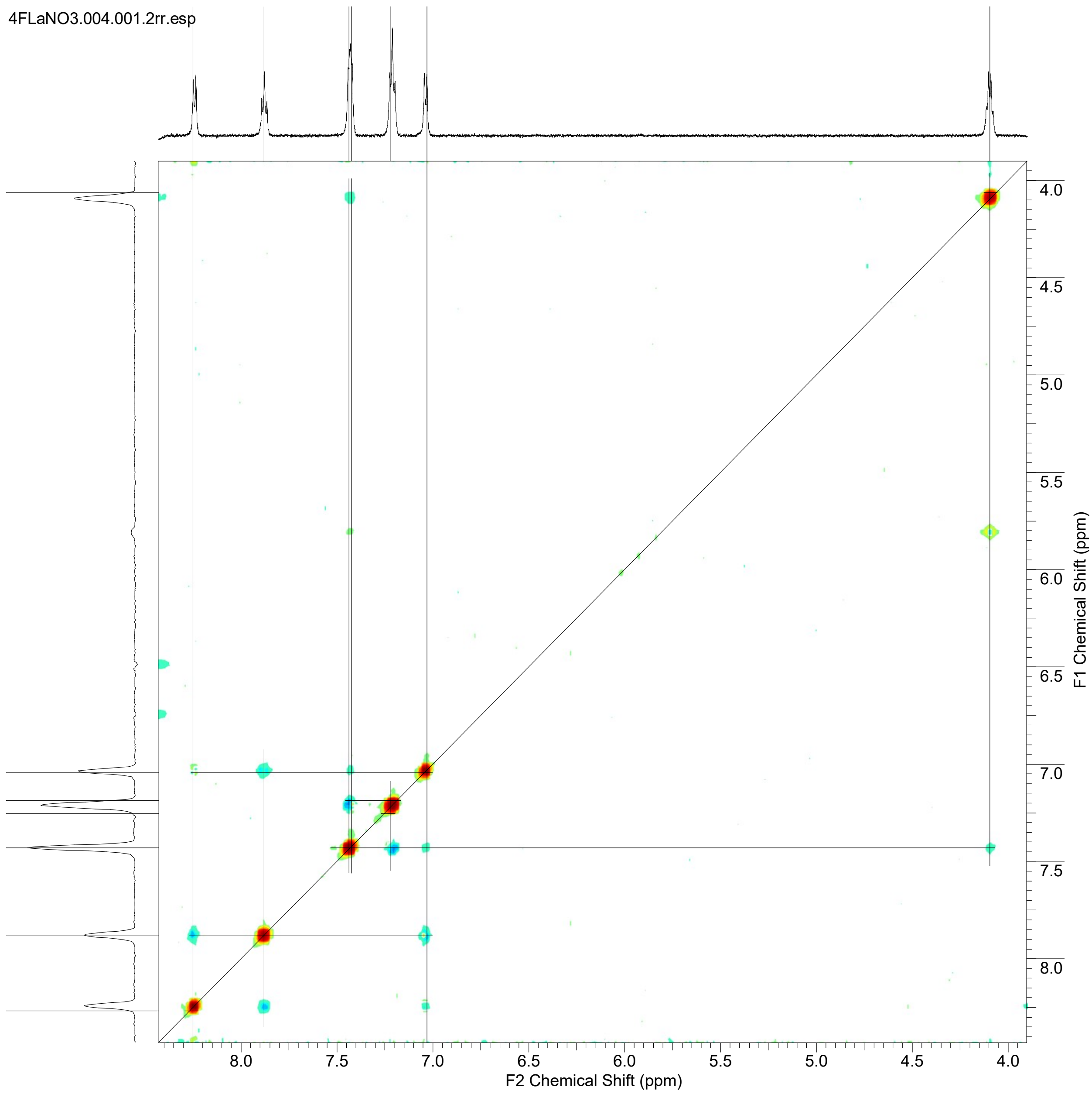

Fig 21 2D NOESY Spectrum of La4F(NO3)3 in acetonitrile

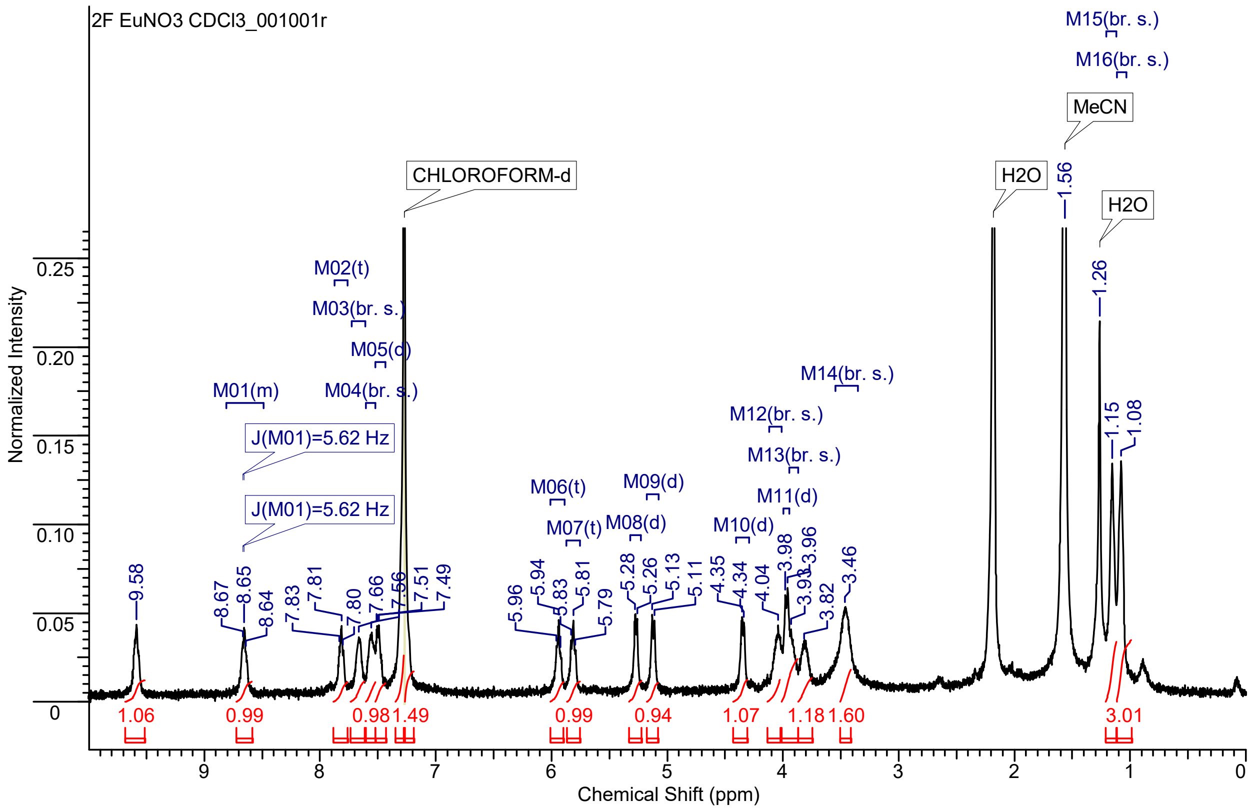

Fig 22 1H Spectrum of Eu2F(NO3)3 in acetonitrile

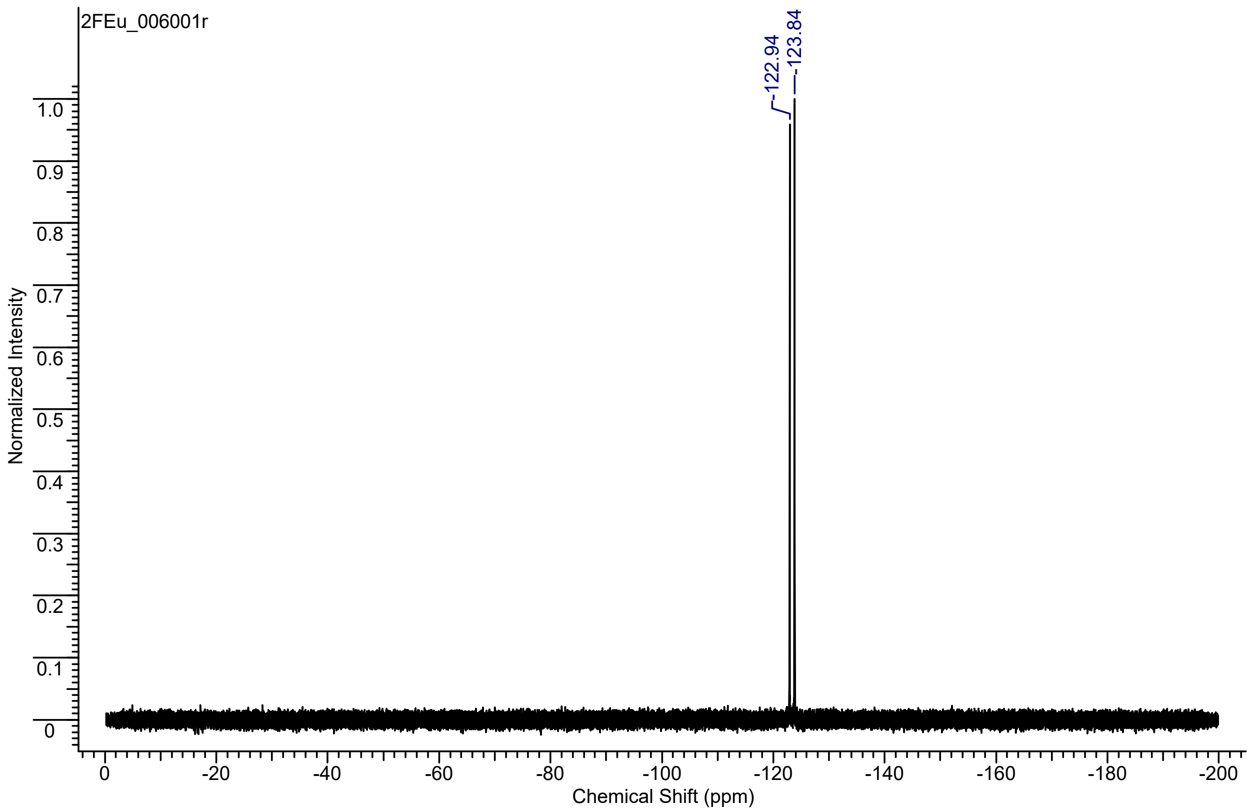

Fig 23 19F Spectrum of Eu2F(NO3)3 in acetonitrile

2F EuNO3 COSY CDCl3.001.001.2rr.esp

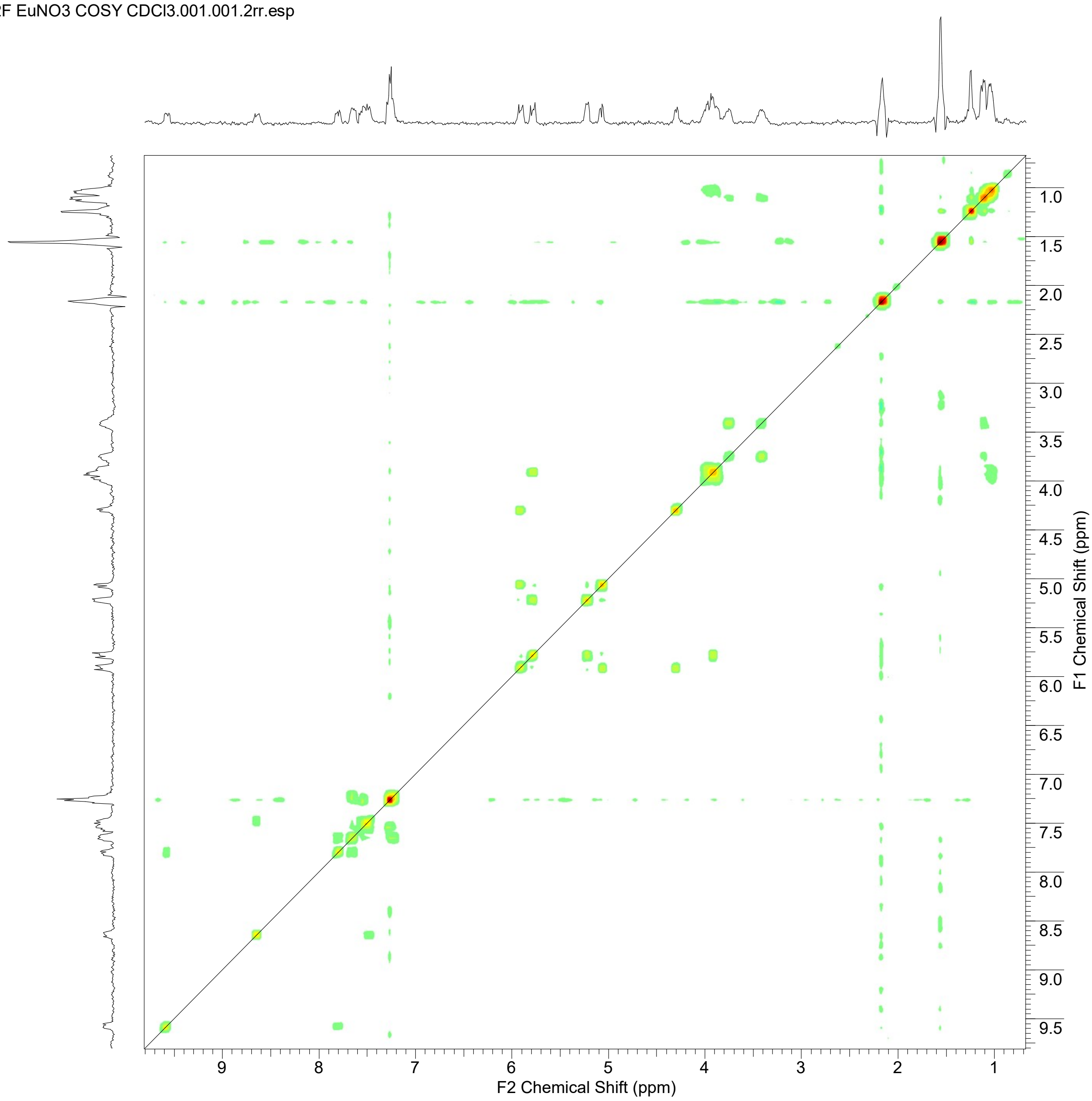

Fig 24 2D COSY Spectrum of Eu2F(NO3)3 in acetonitrile

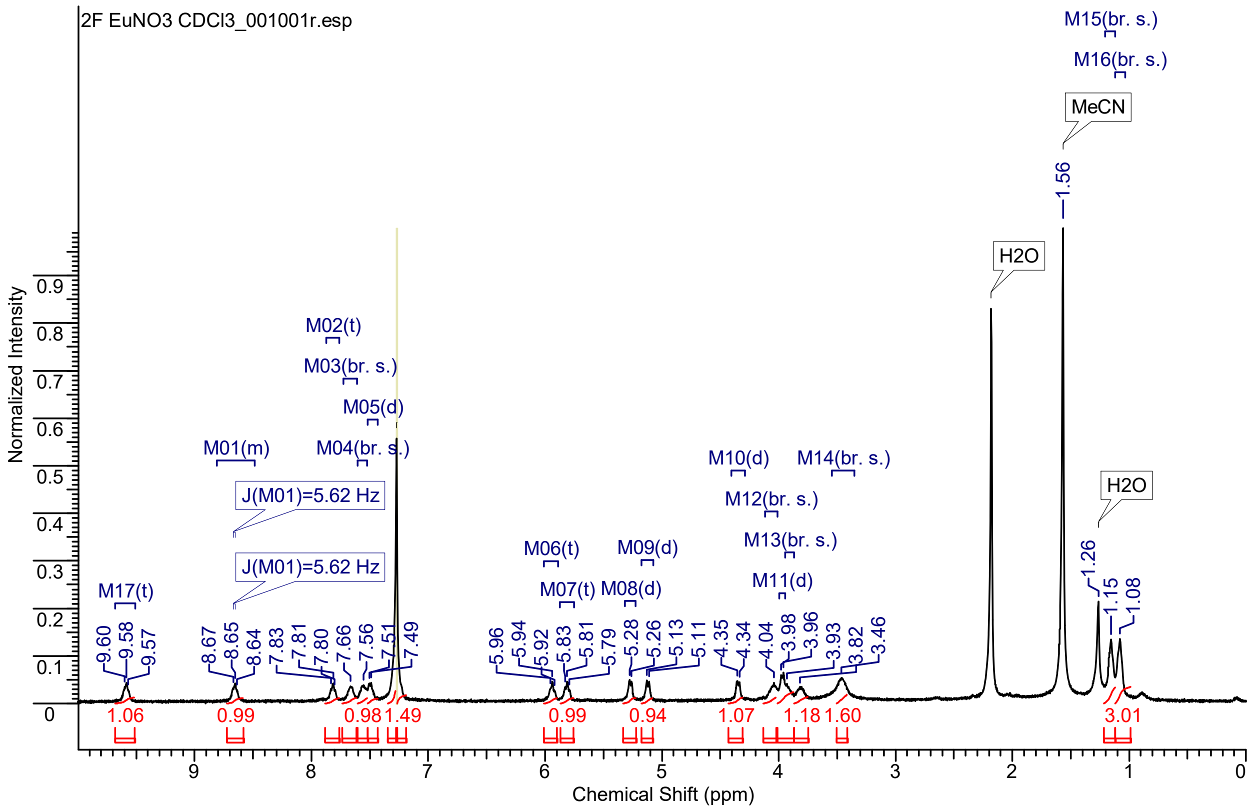

Fig 25 1H Spectrum of Eu2F(NO3)3 in CDCl3

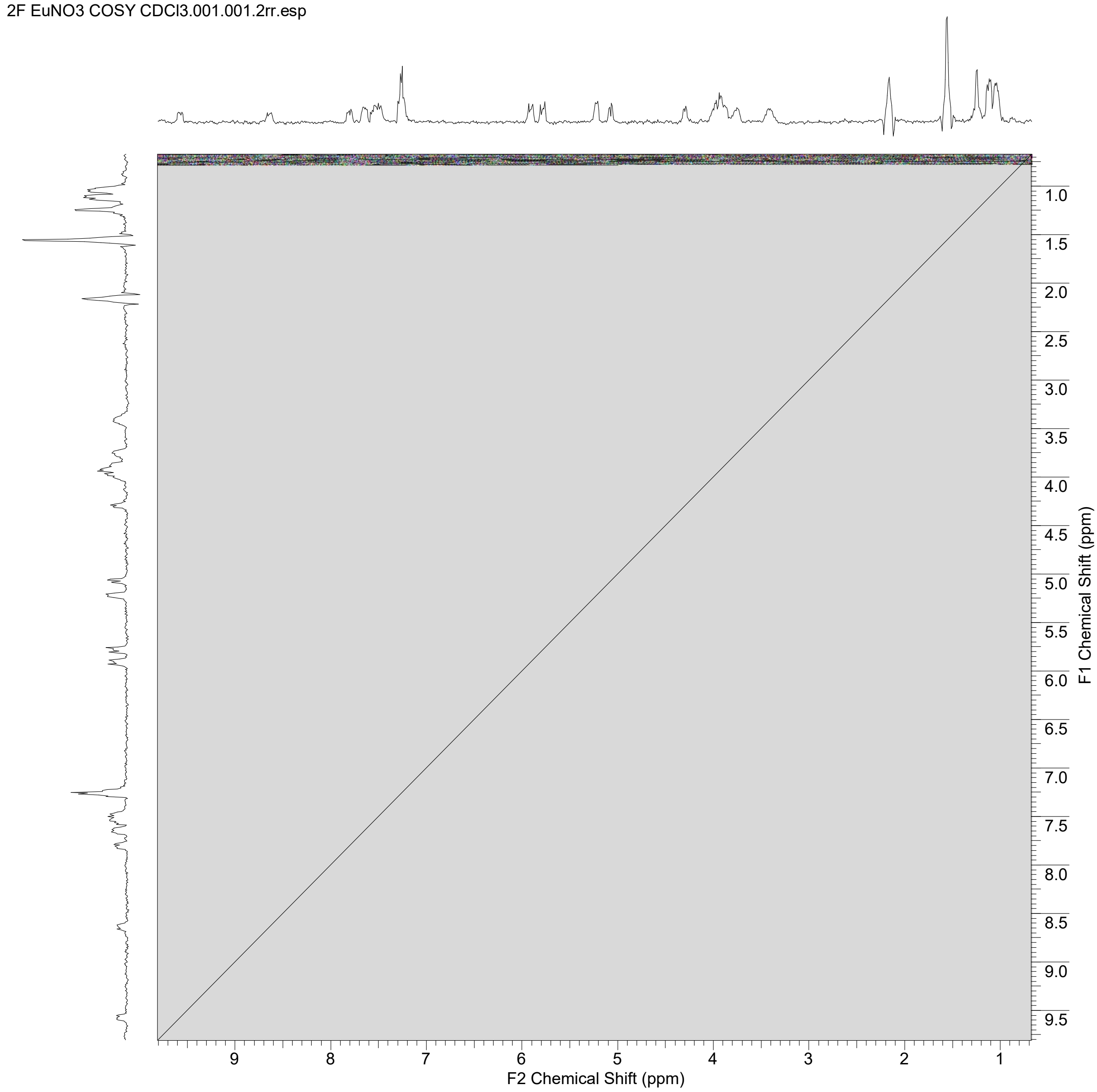

Fig 26 2D COSY Spectrum of Eu2F(NO3)3 in CDCl3

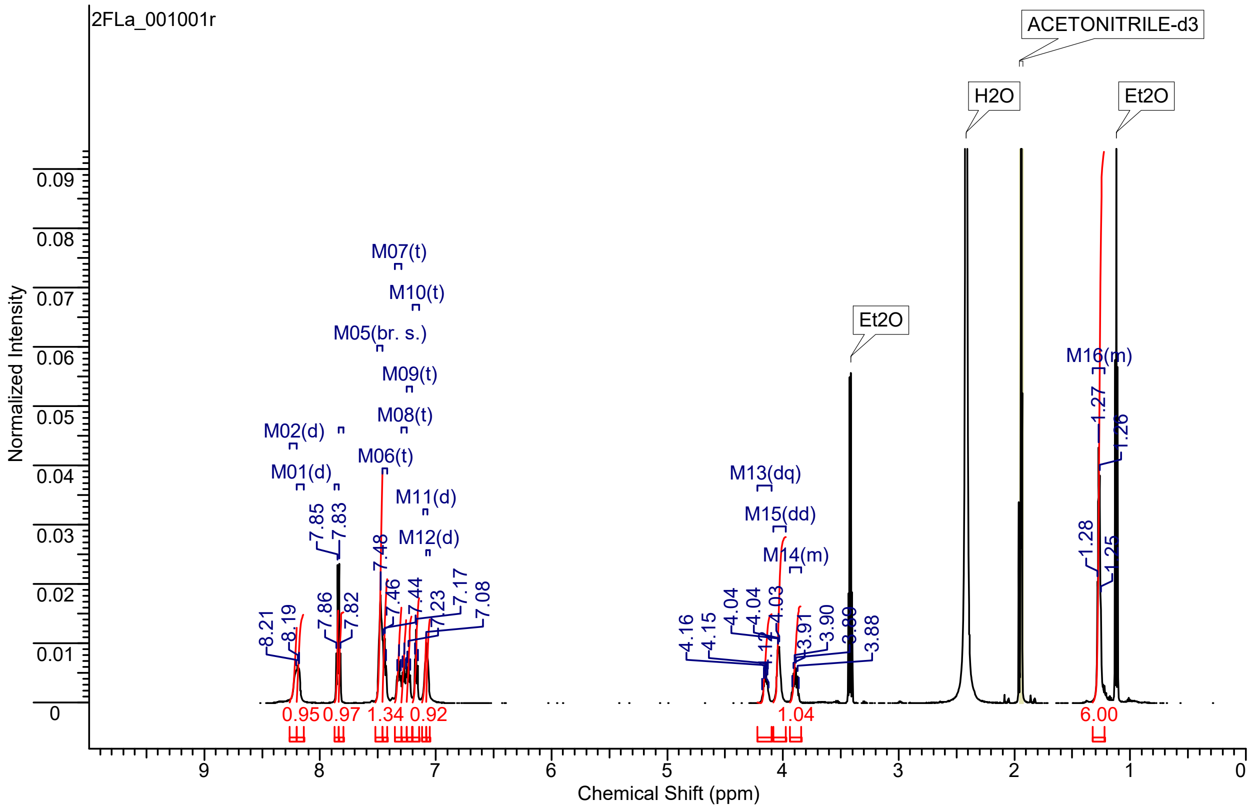

Fig 27 1H Spectrum of La2F(NO3)3 in acetonitrile

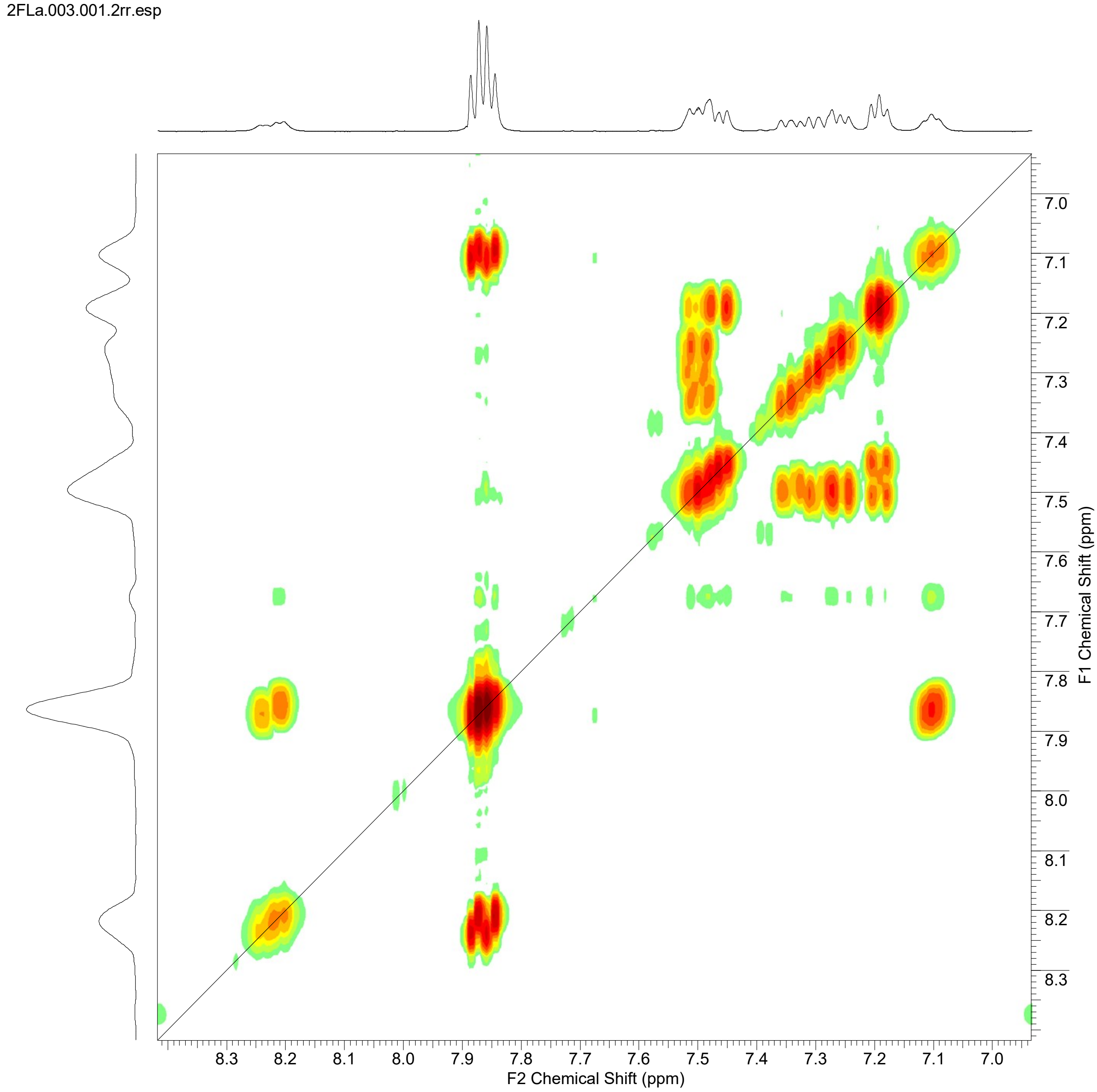

Fig 28 2D COSY Spectrum of La2F(NO3)3 (aromatic region) in acetonitrile

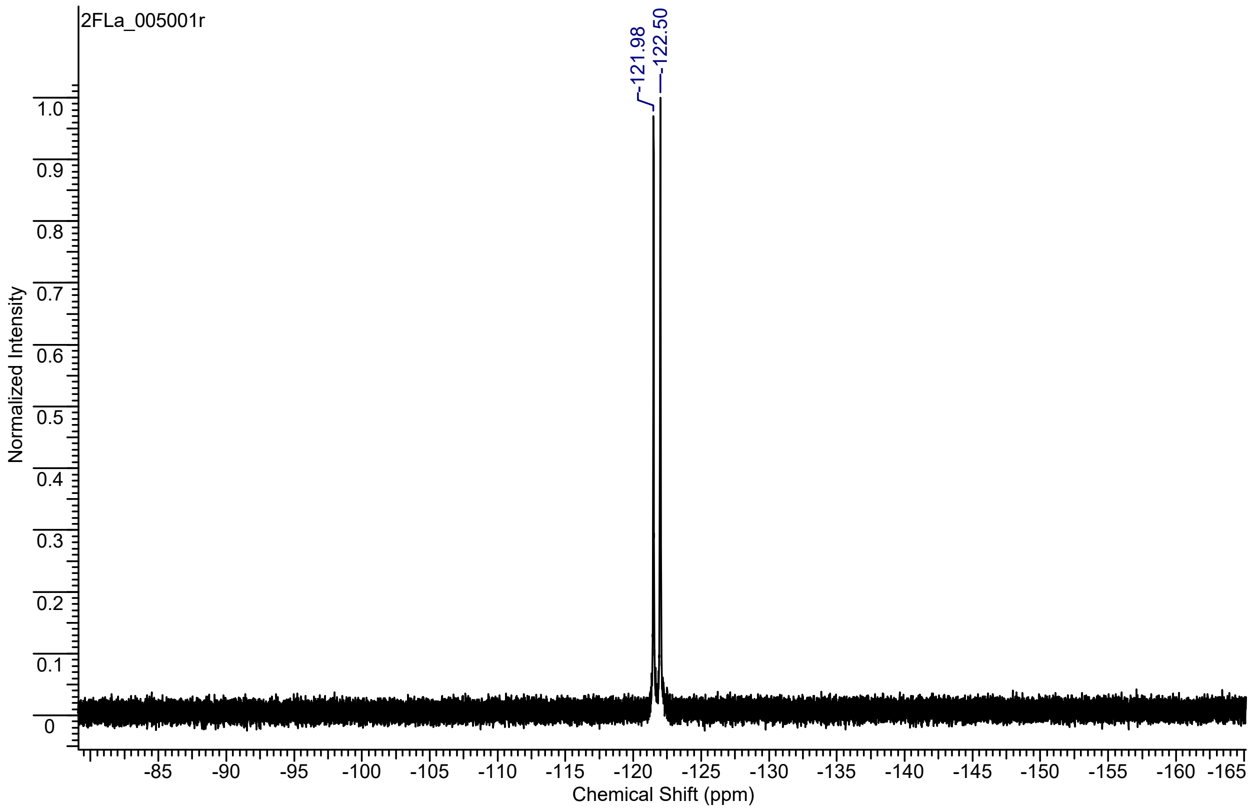

Fig 29 19F Spectrum of La2F(NO3)3 in acetonitrile

X-Ray structures data

Table S 2 Crystal data and structure refinements for complexes

Identification code	Eu**3F**$(NO_3)_3$	Gd**3F**$(NO_3)_3$	Eu**4F**$(NO_3)_3$	Sm**4F**$(NO_3)_3$	La**4F**$(NO_3)_3(H_2O)$·MeCN
Empirical formula	C28H24EuF2N7O11	C28H24F2GdN7O11	C28H24F2EuN7O11	C28H24F2SmN7O11	C30H29F2LaN8O12
Formula weight	824.50	829.79	824.50	822.89	870.52
Temperature	120(2) K			110(2) K	120(2) K
Wavelength	0.71073 Å				
Crystal system	Monoclinic				
Space group	C2/c		$P2_1/c$		$P2_1/c$
Unit cell dimensions	a = 43.8733(16) Å α= 90°	a = 43.8591(16) Å α = 90°	a = 23.6077(19) Å α = 90°	a = 23.577(4) Å α = 90°	a = 12.2480(11) Å α= 90°
	b = 8.4215(3) Å β= 106.3450(10)°	b = 8.4260(3) Å β = 106.2959(6)°	b = 8.6548(7) Å β = 97.558(2)°	b = 8.6260(16) Å β = 97.645(6)°	b = 10.8097(12) Å β= 93.008(3)°
	c = 17.8839(6) Å γ = 90°	c = 17.8675(7) Å γ = 90°	c = 15.7258(13) Å γ = 90°	c = 15.710(3) Å γ = 90°	c = 27.309(2) Å γ = 90°
Volume	6340.7(4) $Å^3$	6337.8(4) $Å^3$	3185.2(4) $Å^3$	3166.6(10) $Å^3$	3610.6(6) $Å^3$
Z	8		4		4
Density (calculated)	1.727 Mg/m^3	1.739 Mg/m^3	1.719 Mg/m^3	1.726 Mg/m^3	1.601 Mg/m^3

Absorption coefficient	2.061 mm^{-1}	2.175 mm^{-1}	2.051 mm^{-1}	1.937 mm^{-1}	1.264 mm^{-1}
F(000)	3280	3288	1640	1636	1744
Crystal size, mm^3	0.202 x 0.143 x 0.113	0.211 x 0.163 x 0.129	0.188 x 0.143 x 0.012	0.102 x 0.095 x 0.089	0.133 x 0.121 x 0.086
Theta range for data collection	1.935 to 30.000°.		2.509 to 29.999°	2.517 to 30.000°	2.03 to 30.000°
Index ranges	-61<=h<=60, -11<=k<=11, -21<=l<=25	-61<=h<=61, -11<=k<=11, -25<=l<=25	-33<=h<=33, -9<=k<=9, -22<=l<=22	-32<=h<=33, -12<=k<=12, -22<=l<=22	-17<=h<=16, -15<=k<=15, -36<=l<=36
Reflections collected	24832	39918	34478	32653	38328
Independent reflections	9211 [R(int) = 0.0226]	9245 [R(int) = 0.0246]	9285 [R(int) = 0.0766]	9221 [R(int) = 0.0758]	10499 [R(int) = 0.0606]
Completeness to theta = 25.242°	99.9 %				99.8 %
Absorption correction	Semi-empirical from equivalents				
Max. and min. transmission	0.815 and 0.670	0.778 and 0.642	0.982 and 0.681	0.6478 and 0.5576	0.5563 and 0.6487
Refinement method	Full-matrix least-squares on F^2				
Data / restraints / parameters	9211 / 0 / 454	9245 / 0 / 454	9285 / 0 / 444	9221 / 6 / 444	10499 / 0 / 489
Goodness-of-fit on F^2	1.040	1.058	1.013	0.993	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0214, wR2 = 0.0460	R1 = 0.0196, wR2 = 0.0430	R1 = 0.0439, wR2 = 0.0839	R1 = 0.0436, wR2 = 0.0899	R1 = 0.0342, wR2 = 0.0680
R indices (all data)	R1 = 0.0270, wR2 = 0.0486	R1 = 0.0234, wR2 = 0.0447	R1 = 0.0762, wR2 = 0.0962	R1 = 0.0630, wR2 = 0.0977	R1 = 0.0513, wR2 = 0.0730
Extinction coefficient	n/a				
Largest diff. peak and hole,	0.447 and -0.408 e/$Å^{-3}$	0.591 and -0.517 e/$Å^{3}$	1.423 and -2.062 e/$Å^{-3}$	1.655 and -1.296 e/$Å^{-3}$	0.500 and -0.529 e/$Å^{-3}$

Table S 3 Results of the SHAPE analysis for the Ln^{III} ions in complexes

Complex	Bicapped cube, *D4h*	Bicapped square antiprism, *D4d*	Metabidiminished icosahedron, *C2v*	Sphenocorona, *C2v*	Staggered dodecahedron, *D2*	Tetradecahedron, *C2v*	Hexadecaheron, *D4h*
Sm**4F**$(NO_3)_3$	11.222	4.530	8.340	**3.137**	3.379	3.433	8.486
Eu**4F**$(NO_3)_3$	11.027	4.259	8.219	**3.104**	3.470	3.532	8.780

Eu**3F**$(NO_3)_3$	8.169	4.305	6.631	3.986	4.287	**3.265**	5.478
Gd**3F**$(NO_3)_3$	8.279	4.216	6.822	3.838	4.351	**3.365**	5.627

UV-VIS Titration data

Table S 4 Log β_1 values for the stability of trivalent lanthanides ions with F ligands in acetonitrile with 40 ppm water content

Ln^{3+} Ligand	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
2-F	6.31 ±0.04	6.61 ±0.07	6.84 ±0.10	7.25 ±0.08	7.05 ±0.11	6.95 ±0.07	6.78 ±0.04	6.64 ±0.05	6.95 ±0.05	7.18 ±0.06	7.31 ±0.08	7.20 ±0.07	7.38 ±0.07	7.54 ±0.12
3-F	5.67 ±0.03	7.07 ±0.06	7.60 ±0.06	8.10 ±0.10	7.82 ±0.09	7.49 ±0.06	7.31 ±0.05	7.05 ±0.03	7.58 ±0.05	7.78 ±0.16	7.93 ±0.11	8.03 ±0.15	8.24 ±0.08	7.77 ±0.05
4-F	5.47 ±0.02	6.60 ±0.02	7.26 ±0.06	7.46 ±0.06	7.37 ±0.04	7.25 ±0.03	6.58 ±0.01	6.73 ±0.01	7.15 ±0.03	7.31 ±0.03	7.75 ±0.12	7.69 ±0.13	7.03 ±0.03	6.46 ±0.02

Table S 5 Log β_1 values for the stability of trivalent lanthanides ions with F-ligands in acetonitrile with 400 ppm water content

Ln^{3+} Ligand	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
2-F	5.93 ±0.03	5.61 ±0.03	5.60 ±0.03		6.30 ±0.04	6.15 ±0.05	6.01 ±0.05	6.33 ±0.04		6.68 ±0.05	
3-F	4.90 ±0.03	6.18 ±0.03	6.54 ±0.03				6.16 ±0.03	6.83 ±0.05			
4-F		4.76 ±0.10	5.63 ±0.02	5.66 ±0.02	5.40 ±0.02		5.63 ±0.02	5.17 ±0.03	5.31 ±0.02		5.80 ±0.01

Photophysical data

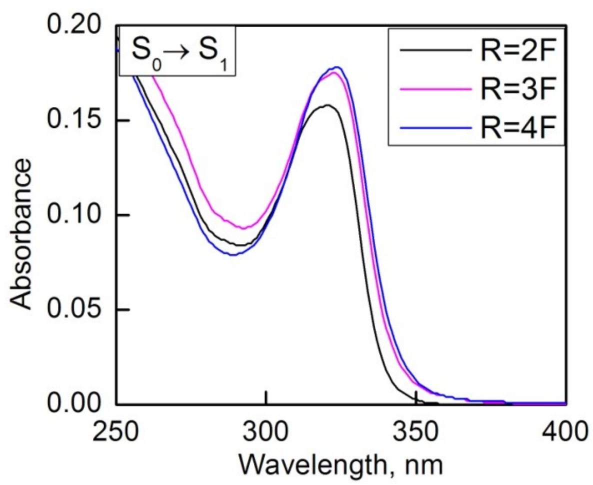

Fig 30 Absorption spectra of europium complexes with different fluoride-substituted ligands in acetonitrile, C=1·10^{-5} mol/l.

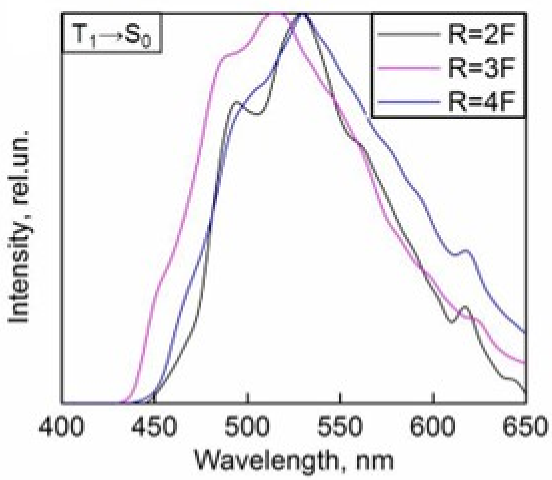

Fig 31 Normalized phosphorescence spectrum of gadolinium complexes with different fluoride-substituted ligands at 77 K.

Table S 6. Luminescence parameters of lanthanide complexes: the lanthanide resonance energy level (Erez, cm-1), ligand singlet energy level (E(S), cm-1), energy difference between ligand triplet level and lanthanide resonance level (ΔE(Tr-Rez), cm-1), luminescence quantum yield (QY, %) and luminescence lifetime (τ, ms). Data for the complexes with ligands without a substituent (R=H) are presented for comparison.

Parameter\Ln^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}
E_{Rez}, cm^{-1}	$^4G_{5/2}$ 17760±10	$^5D_0$ 17170±15	$^8S_{7/2}$ 32080[1]	$^5D_4$ 20340±80	$^4F_{9/2}$ 20770±90
			R=H		
			E(Tr)=21300 cm^{-1} [2,3]		
E(S), cm^{-1}	30960±190	30960±190	30960±190	30960±190	30960±190
ΔE(Tr-Rez), cm^{-1}	3540±200	4130±200	-10780±200	960±220	530±220
QY, %	< 0.01	8±2[3]	< 0.01	0.08±0.01	0.08±0.01
τ, ms	0.16±0.01	1.70±0.02[2]	n/a	0.41±0.02[2]	0.16±0.03
			R=2F		
			E(Tr)=19050 cm^{-1}		
E(S), cm^{-1}	31060±190	31250±200	31250±200	31380±210	31280±210
ΔE(Tr-Rez), cm^{-1}	1290±150	1880±150	-13030±150	-1290±180	-1720±180
QY, %	< 0.01	0.81±0.06	< 0.01	0.11±0.01	0.02±0.01
τ, ms	0.13±0.01	1.63±0.01	n/a	1.09±0.01	0.13±0.02
			R=3F		
			E(Tr)=19880 cm^{-1}		
E(S), cm^{-1}	31150±190	30960±190	31130±190	31150±190	31250±200
ΔE(Tr-Rez), cm^{-1}	2120±130	2710±130	-12200±130	-460±150	-890±160
QY, %	0.20±0.02	12±2	< 0.01	0.05±0.01	< 0.01
τ, ms	0.12±0.02	1.52±0.03	n/a	0.90±0.01	0.17±0.02
			R=4F		
			E(Tr)=18870 cm^{-1}		
E(S), cm^{-1}	30990±200	30960±190	30990±200	30990±200	30960±190
ΔE(Tr-Rez), cm^{-1}	1110±120	1700±120	-13210±120	-1470±150	-1900±150
QY, %	< 0.01	2.4±0.6	< 0.01	< 0.01	< 0.01
τ, ms	0.13±0.01	1.60±0.05	n/a	1.20±0.01	0.17±0.02

1. Daoud, M.; Zambon, D.; Mahiou, R.; Ammar, A.; Tanouti, B. Spectroscopic Properties of Trivalent Gadolinium in Diphosphate CsYP2O7. *Mater. Res. Bull.* **1998**, *33*, 597–603, doi:10.1016/S0025-5408(98)00012-9.
2. Borisova, N.E.; Kostin, A.A.; Eroshkina, E.A.; Reshetova, M.D.; Lyssenko, K.A.; Spodine, E.N.; Puntus, L.N. Lanthanide Complexes with Tetradentate N,N′,O,O′-Dipyridyl-Based Ligands: Structure, Stability, and Photophysical Properties. *Eur. J. Inorg. Chem.* **2014**, 2219–2229, doi:10.1002/ejic.201301271.
3. Borisova, N.E.; Sumyanova, T.B.; Kharcheva, A. V.; Matveev, P.I.; Ivanov, A. V.; Razumova, E.A.; Patsaeva, S. V. The Lanthanide Complexes of 2,2′-Bipyridyl-6,6′-Dicarboxylic Dimethylanilides: The Influence of a Secondary Coordination Sphere on the Stability, Structure, Luminescence and f-Element Extraction. *Dalt. Trans.* **2018**, *47*, 16755–16765, doi:10.1039/c8dt03734e.