Electronic Supplementary Material (ESI) for Analytical Methods.
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Electronic Supplementary information

Development of Highly Selective Potentiometric Thorium (IV) Ion-selective Electrode: Exploration Supported with Optical and DFT Analysis

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ESI Captions

Table 1S. Comparison of experimental and theoretical UV-Vis spectral characteristics

Table 2S. Analytical performance of ISE-10

Table 3S. Assessment of present Th^{4+}-ISE with previously reported work.

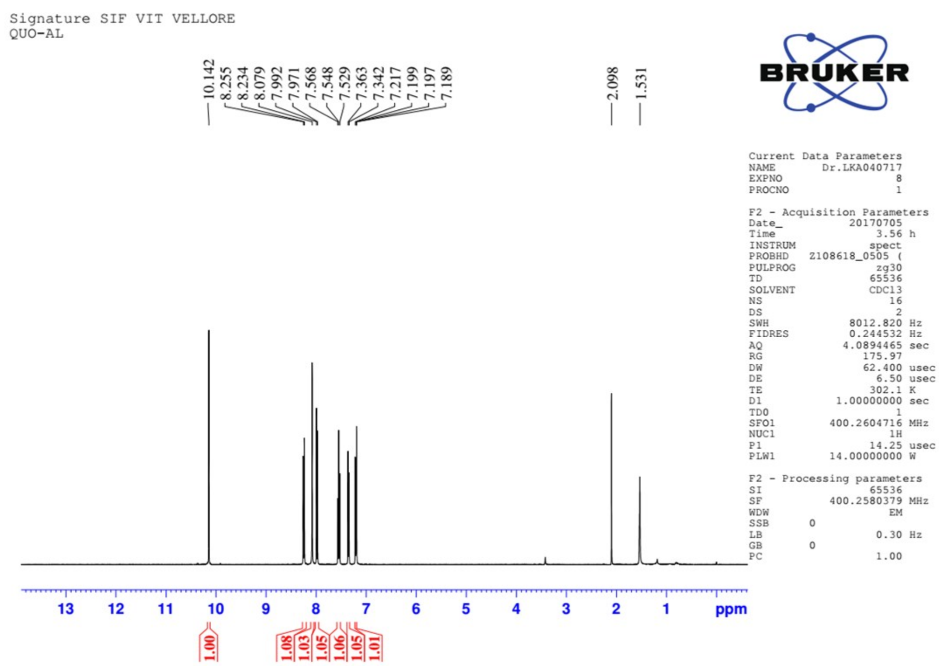

Figure 1S: ^{1}H NMR of **HQ-Al**

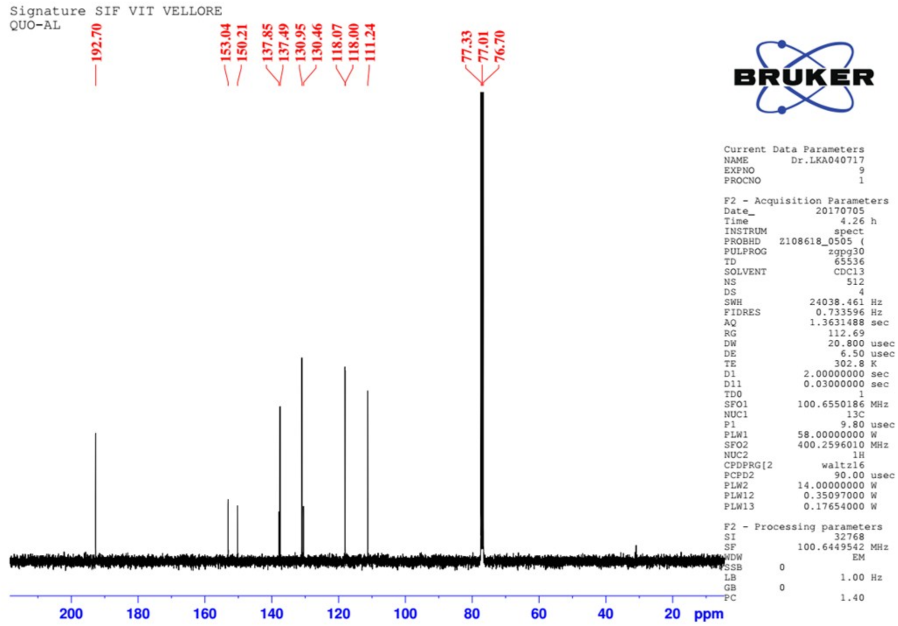

Figure 2S: ^{13}C NMR of **HQ-Al**

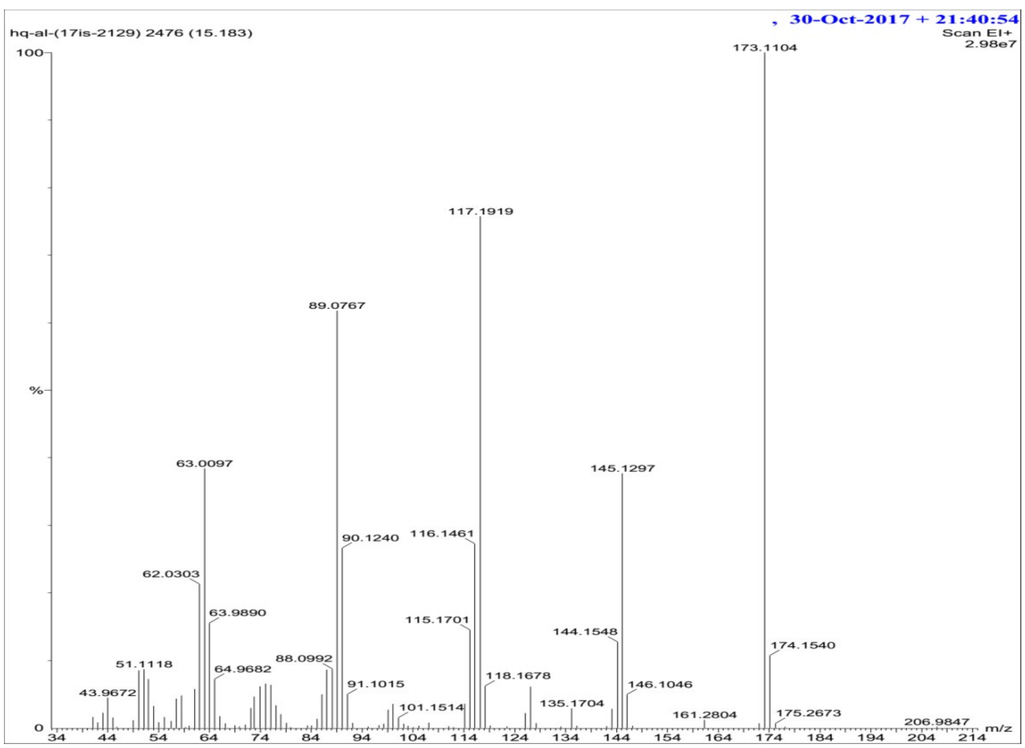

Figure 3S: Mass spectra of **HQ-Al**

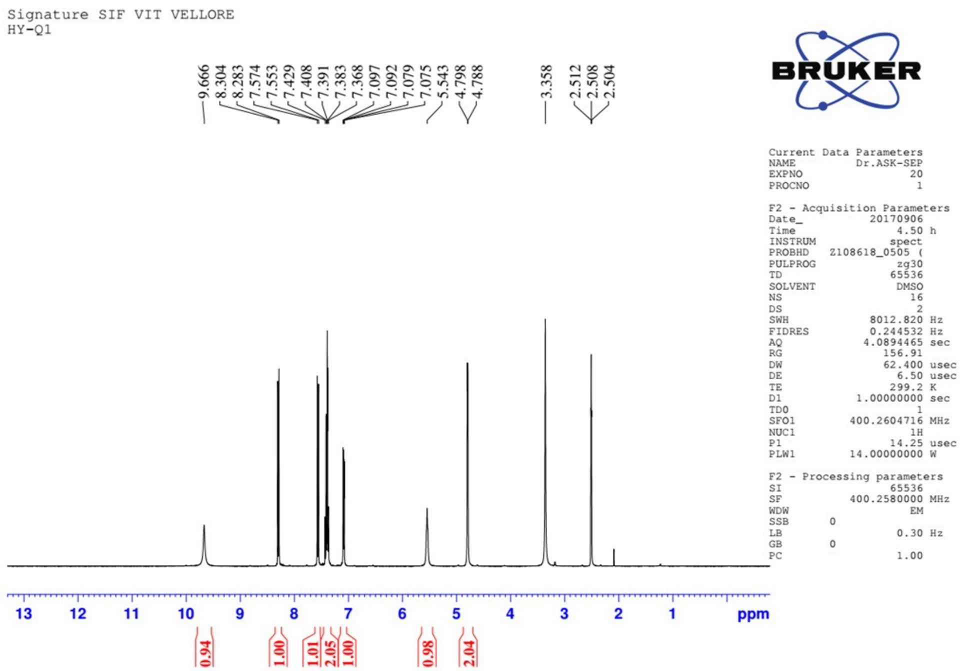

Figure 4S: ^{1}H NMR of **HQ-OH**

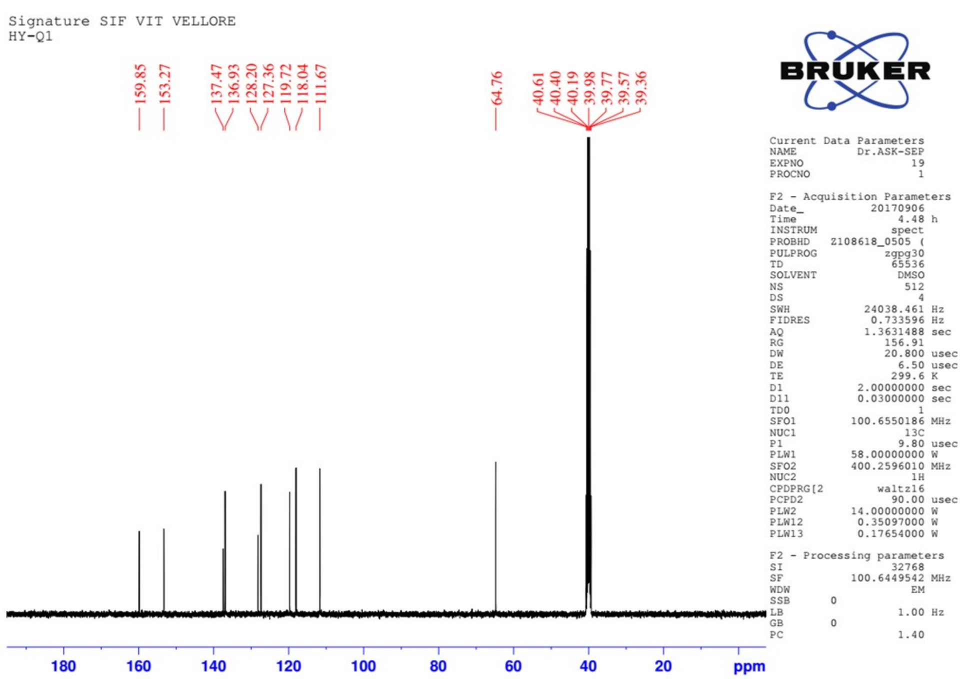

Figure 5S: ^{13}C NMR of **HQ-OH**

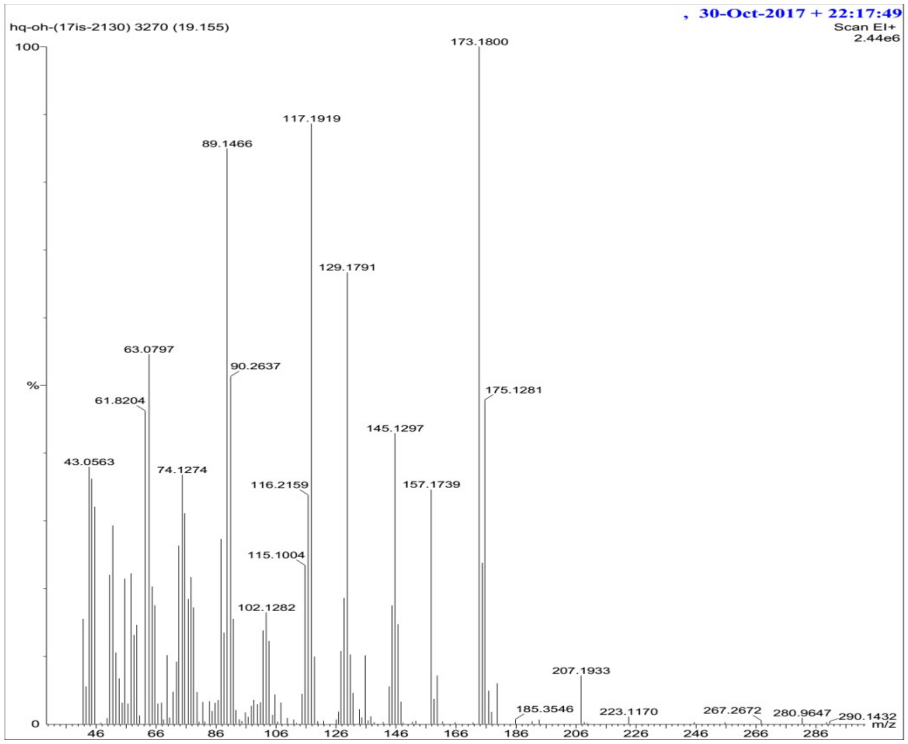

Figure 6S: Mass spectra of **HQ-OH**

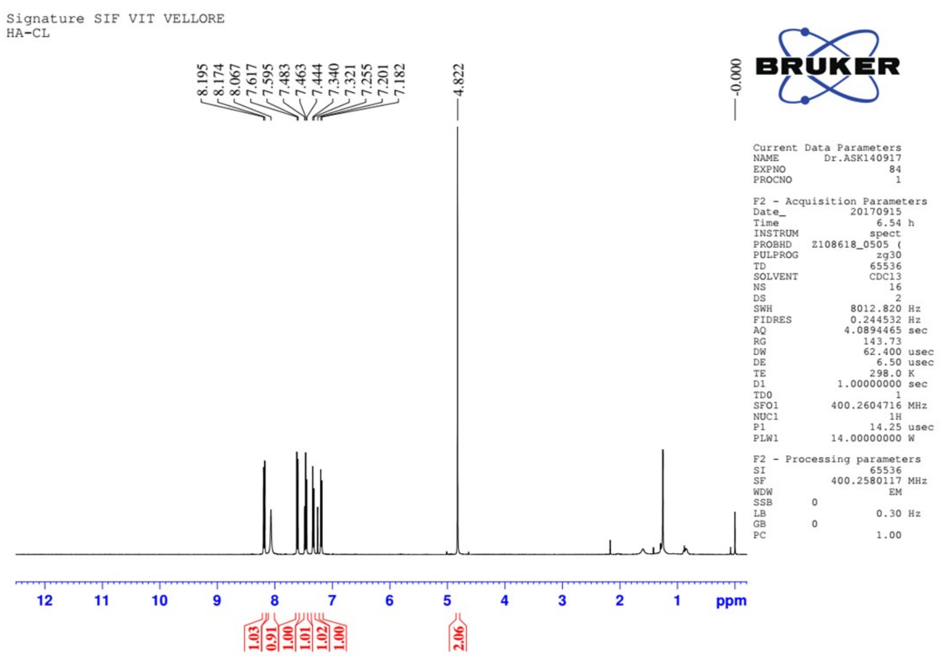

Figure 7S: ^{1}H NMR of **HQ-MeCl**

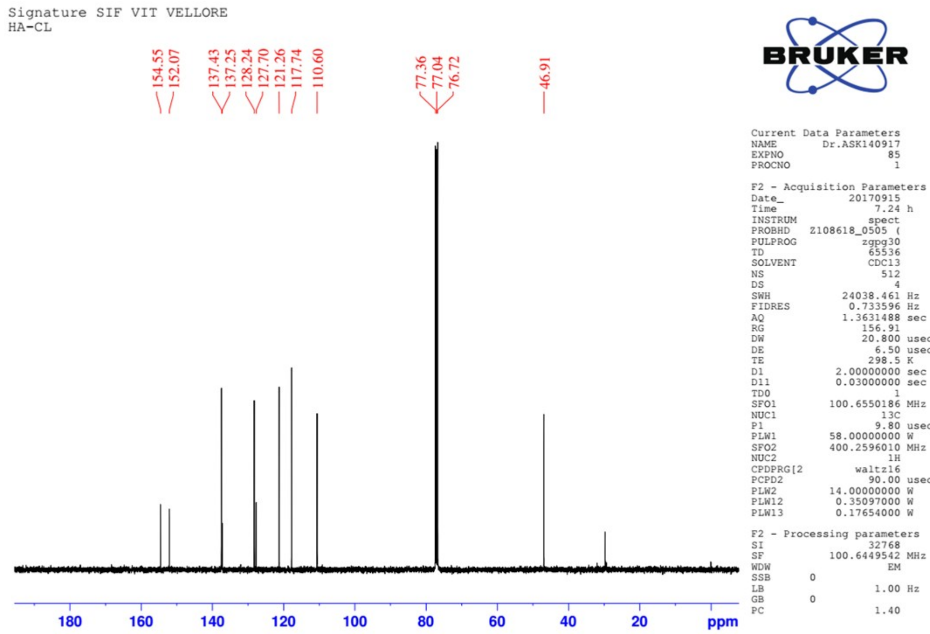

Figure 8S: ^{13}C NMR of **HQ-MeCl**

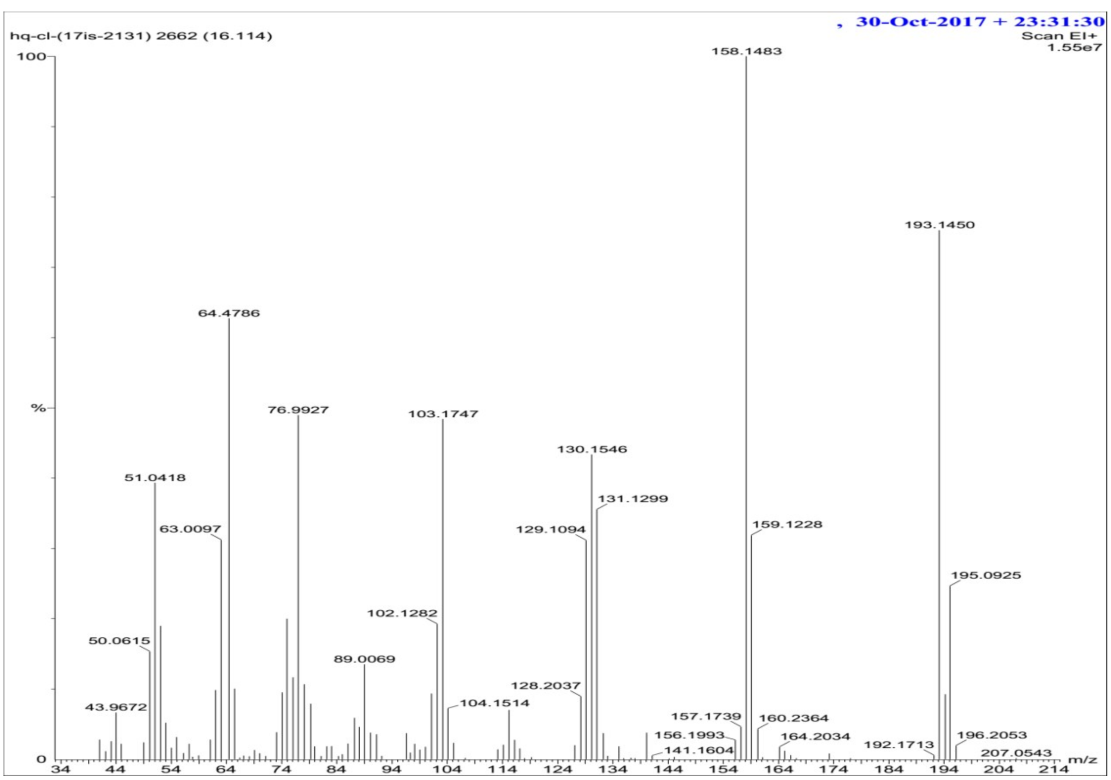

Figure 9S: Mass spectra of **HQ-MeCl**

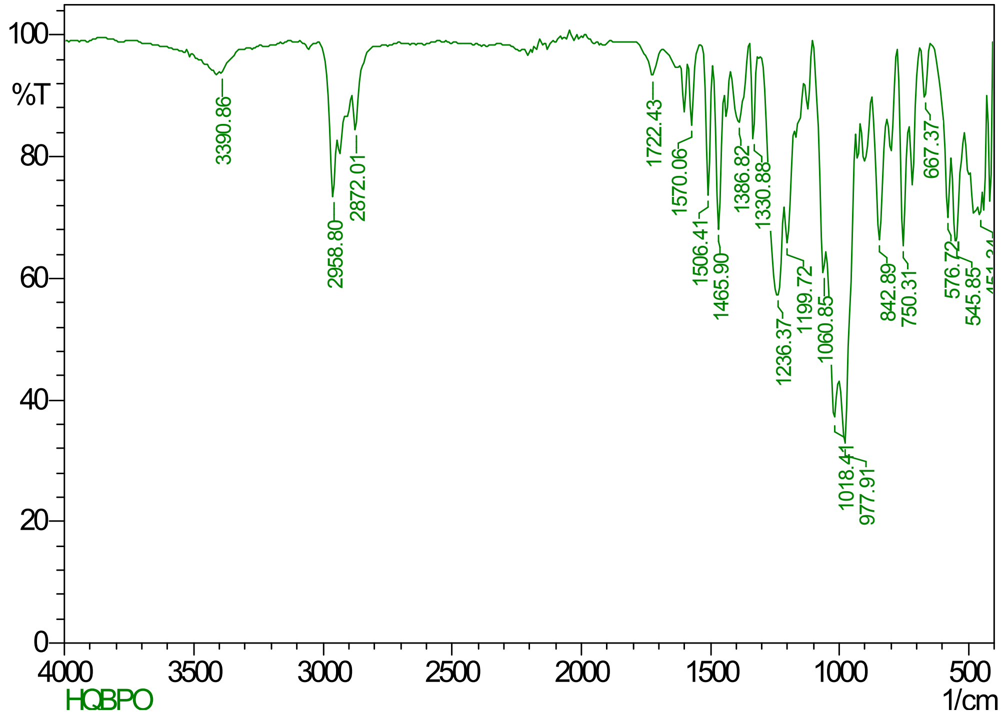

Figure 10S: FT-IR spectra of **L**

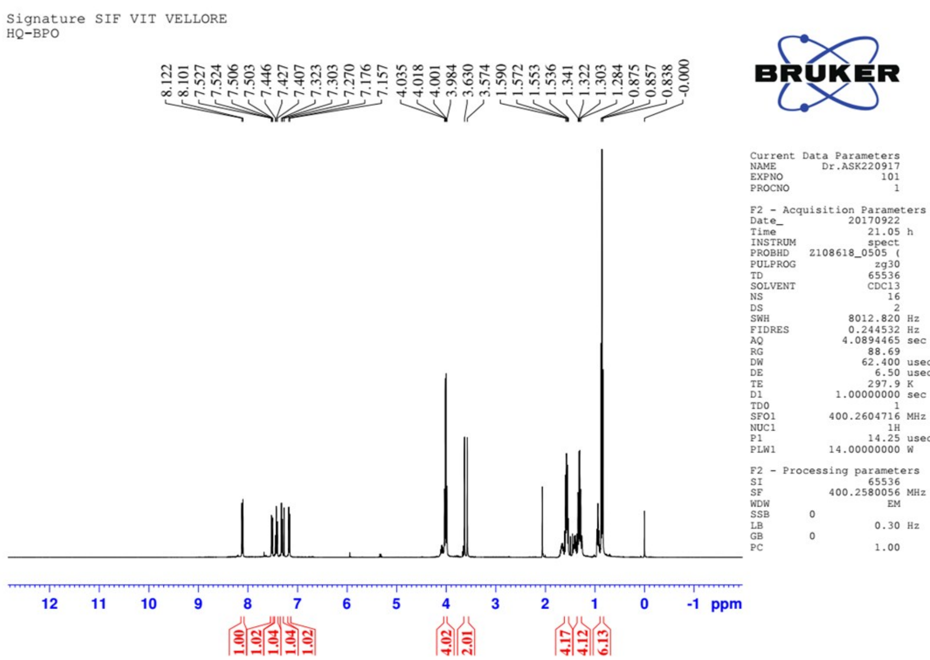

Figure 11S: [1]H NMR spectra of **L**

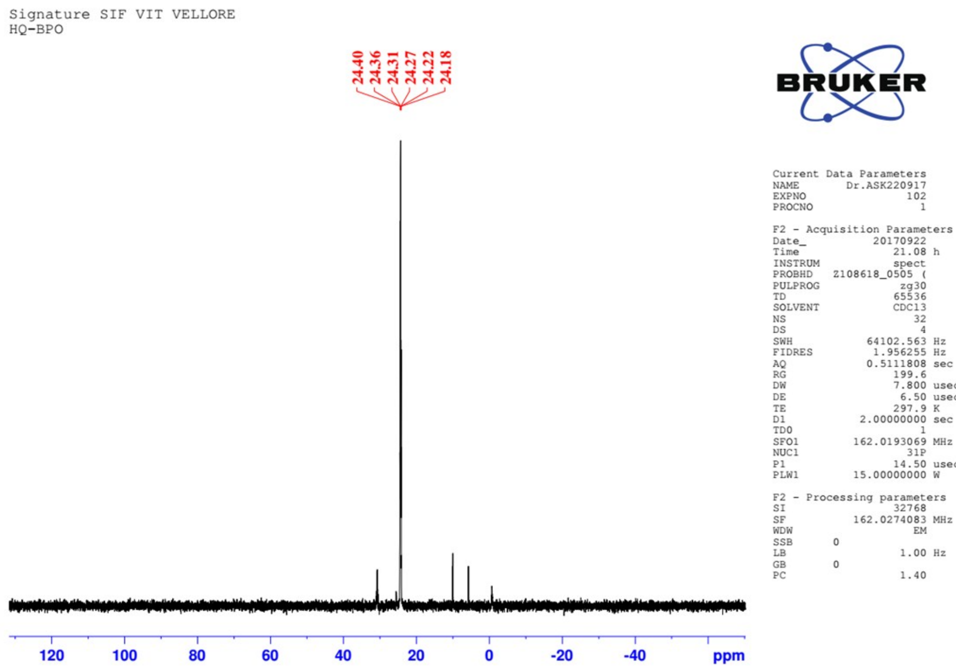

Figure 12S: ^{31}P NMR spectra of **L**

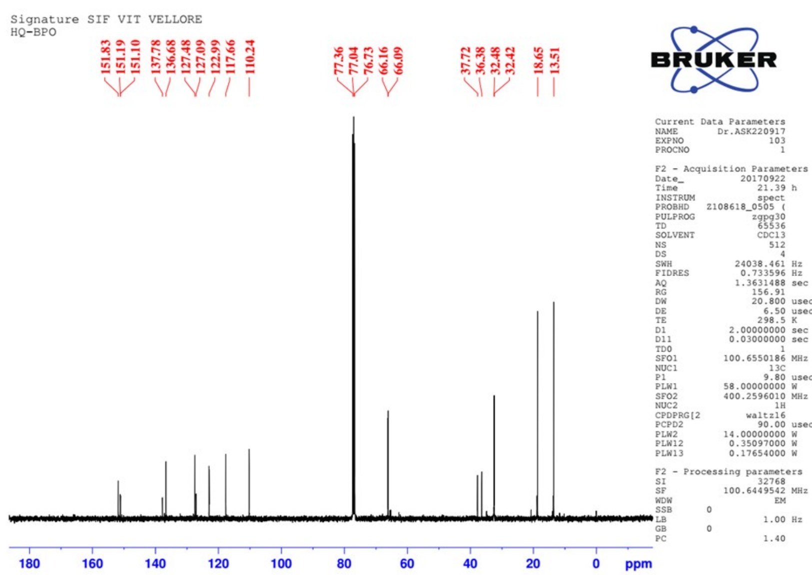

Figure 13S: ^{13}C NMR spectra of **L**

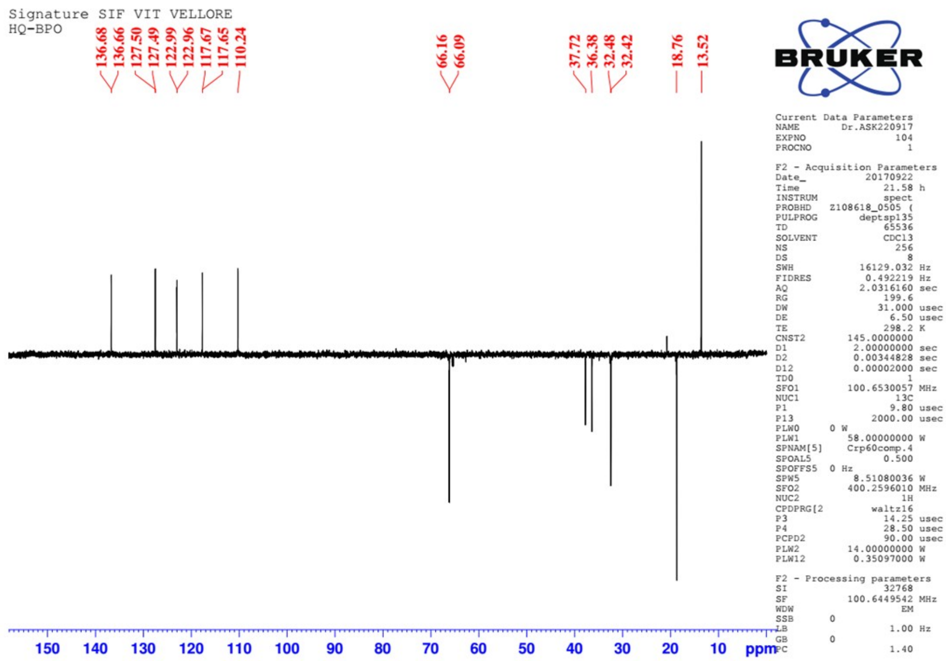

Figure 14S: DEPT-135 NMR spectra of **L**

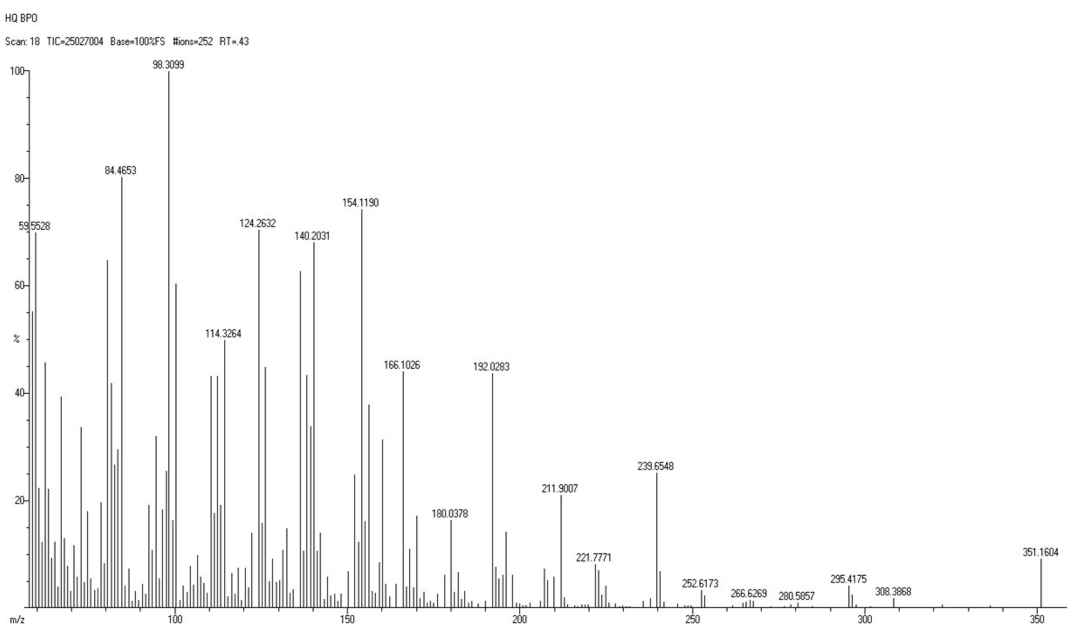

Figure 15S: HR-MS of **L**

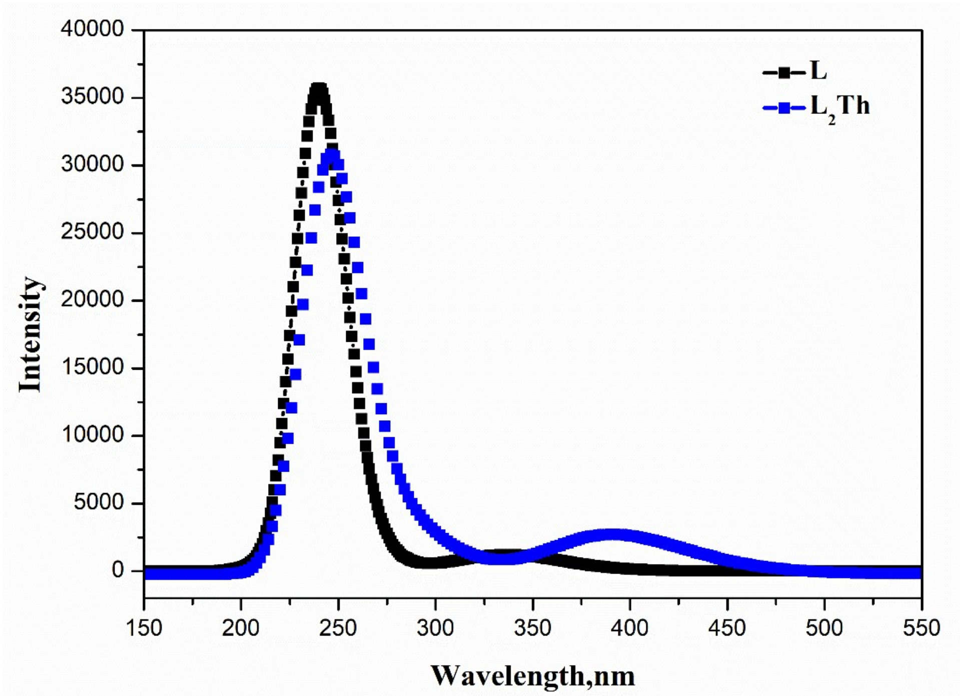

Figure 16S. TDDFT based excitation spectra of **L** and $\mathbf{L_2Th^{4+}}$

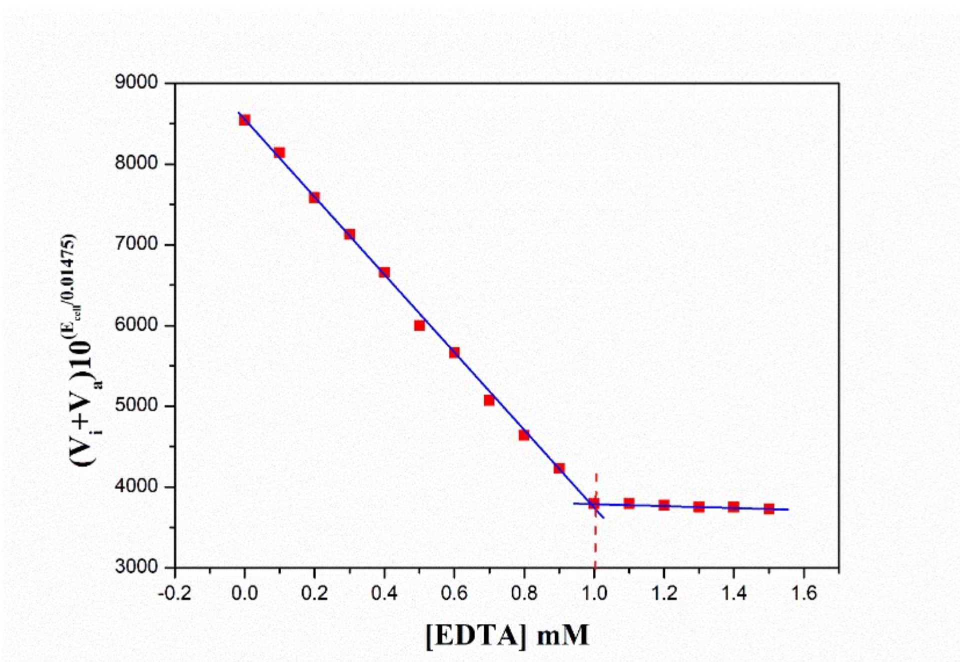

Figure 17S: Potentiometric titration plot represented using Gran's method

Table 1S. Comparison of experimental and theoretical UV-Vis spectral characteristics

Ligand and its complex	**Experimental**		**Theoretical**			
	λ_{max} (nm)	ε (L $M^{-1}cm^{-1}$)	Excitation energy (nm)	Oscillator strength	Excited state	Key transitions
L	245	10850	242.15	0.6495	S0 → S5	H-1 → L (37%), H → L+2 (19%), H → L+3 (10%),
	310	540	341.34	0.0298	S0 → S1	H → L (96%)
L_2Th^{4+}	260	5539	249.5 248.53	0.2493 0.2377	So → S25 So → S26	H-3 → L (20%), H → L+11 (20%)
	370	290	392.38	0.0699	S0 → S1	H → L (43%), H → L+1 (28%) H-1 → L+1 (20%)

Table 2S. Analytical performance of ISE-10

Sample	Thorium (IV) content (mg/L)					Deviation (SD)	Error (SE)	T-test	P value from t test	95%CI
	Added	R1	R2	R3	Mean					
Tap water	50	48.75	48.24	49.45	48.81	0.6074	0.3507	-3.3834	0.07735	[47.3042, 50.3224]
well water	50	47.65	48.57	46.57	47.60	1.0010	0.5779	-4.1583	0.05326	[45.1098, 50.0834]
DD water	50	49.52	49.14	49.57	49.41	0.23515	0.1357	-4.3456	0.04909	[48.8258, 49.9941]
Monazite sand	86.2	84.56	83.98	85.35	84.63	0.6876	0.3970	-3.9544	0.0584	[82.9217, 86.3382]
Gas mantle sample	24.1	21.58	23.45	23.89	22.97	1.2265	0.7081	-1.591	0.25626	[19.9264, 26.0202]

Table 3S. Assessment of present Th^{4+}-ISE with previously reported work.

S.No	Ionophore	Range (Mol) To $1x10^{-1}$ M	Slope (mV)	Response time (s)	Detection Limit (Mol)	Life time	pH Range
1	p-tert-butylthiacalix[4]arene derivative[20]	8.0 x 10^{-8}	14.9 ±0.6	7	8.0 x10^{-8}	6	2.0 – 9.0
2	Thorium 8-hydroxyquinolate[21]	5.0 ×10^{-6}	15.5 ±0.5	30	1.6 x10^{-6}	2	3.0 – 5.0
3	Tin(IV) tungstoselenate Pyridine[22]	8.0 x 10^{-6}	14.2 ±1.0	15	6.0 x10^{-6}	***	2.5 – 9.0
4	5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis (diphenylphosphinoylmethoxy) calix[4]arene[23]	1.0 x 10^{-5}	15.5 ±0.1	15	7.9 x10^{-6}	6	2.3 – 4.0
5	dithio-tetraaza macrocyclic compound [24]	1.0 x 10^{-6}	14.2 ± 0.3	10	8.0 ×10^{-7}	5	3.5 – 9.5
6	2-(diphenylphosphorothioyl)-N’,N’-diphenyl acetamide[25]	1.0 x 10^{-6}	15.2 ± 0.5	30	6.3 x10^{-7}	1.5	3.0 – 9.0
7	Aliquat-336[41]	3.0 x 10^{-5}	-29.5 ± 0.3	40	1 x10^{-5}	***	***
8	trioctylphosphine oxide [26]	1.0 x 10^{-6}	-32.3 ±0.3	10	3.2 x10^{-6}	2.4	2.5 – 4.5
9	thorium toluate [27]	1.0 x 10^{-6}	-27.2 ±0.2	10	4.1 x10^{-6}	2.4	2.7 – 3.5
10	diphosphoryl-dicarboxylicacid-p-tert-butylcalix[4]arene [28]	2.0 x 10^{-7}	13.9	10	9.0 x10^{-8}	1.9	3.1 – 6.5
11	**Bibutyl (8-hydroxyquinolin-2-yl) methyl phosphonate (*Present work*)**	**1 x 10^{-7}**	**31.18 ±0.4**	**<5**	**1 x10^{-8}**	**3**	**3.5 – 6.5**