

*Electronic Supplementary information*

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

R. Selvakumar<sup>a</sup>, S.K. Ashok Kumar<sup>a\*</sup>, Kari Vijayakrishna<sup>a,d</sup>, Akella Sivaramakrishna<sup>a</sup>,  
C.V.S. BrahmmanandaRao<sup>b</sup>, N. Sivaraman<sup>b</sup>, and Suban K. Sahoo<sup>c</sup>.

<sup>a</sup> Department of Chemistry, School of Advanced Sciences, VIT University, Vellore-632014, Tamil Nadu, India.  
E-mail: ashokkumar.sk@vit.ac.in; ashok312002@gmail.com

<sup>b</sup> Indira Gandhi Centre for Atomic Research, Homi Bhabha National Institute, Kalpakkam-603102, Tamil Nadu, India.

<sup>c</sup> Department of Applied Chemistry, S. V. National Institute Technology, Surat-395007, Gujarat, India

<sup>d</sup> School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Arugul, Khurda, Odisha, India-752050 India

**ESI Captions**

**Figure 1S:** <sup>1</sup>H NMR of HQ-Al

**Figure 2S:** <sup>13</sup>C NMR of HQ-Al

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

**Figure 4S:** <sup>1</sup>H NMR of HQ-OH

**Figure 5S:** <sup>13</sup>C NMR of HQ-OH

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

**Figure 7S:** <sup>1</sup>H NMR of HQ-MeCl

**Figure 8S:** <sup>13</sup>C NMR of HQ-MeCl

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

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

**Figure 11S:** <sup>1</sup>H NMR spectra of L

**Figure 12S:** <sup>31</sup>P NMR spectra of L

**Figure 13S:** <sup>13</sup>C NMR spectra of L

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

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

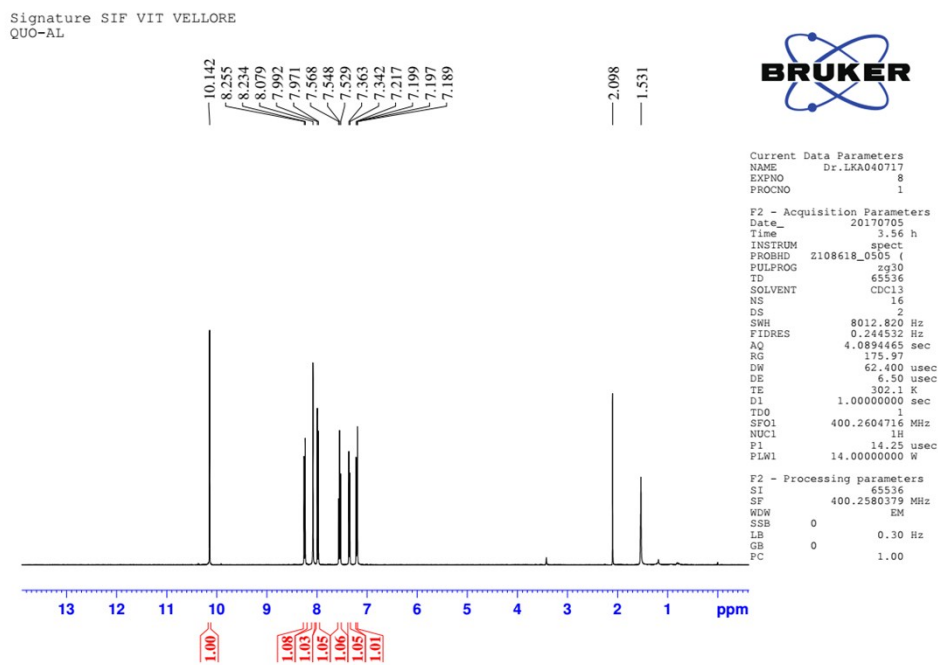
**Figure 16S.** TDDFT based excitation spectra of L and L<sub>2</sub>Th<sup>4+</sup>

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

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

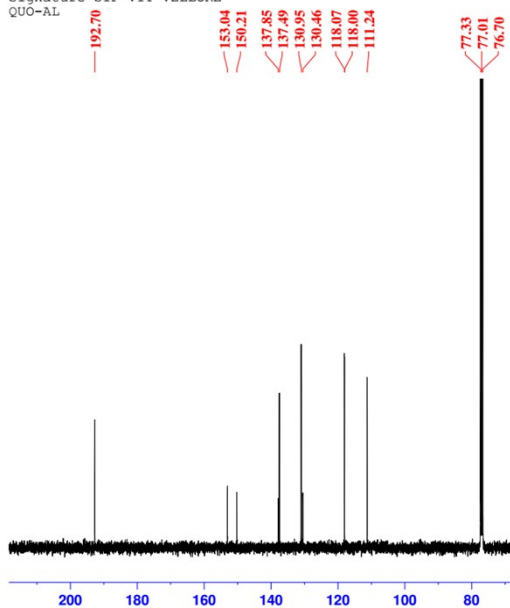
**Table 2S.** Analytical performance of ISE-10

**Table 3S.** Assessment of present Th<sup>4+</sup>-ISE with previously reported work.



**Figure 1S:** <sup>1</sup>H NMR of HQ-AI

Signature SIF VIT VELLORE  
QUO-AL



Current Data Parameters  
NAME: Dr.LKAO40717  
EXPNO: 9  
PROCNO: 1

F2 - Acquisition Parameters  
Date\_: 20170705  
Time: 4:24 h  
INSTRUM: spect  
PROBHD: e108618\_0505 (1  
PULPROG: zgpg30  
TD: 65536  
SOLVENT: CDCl3  
NS: 512  
DS: 4  
SWE: 24038.461 Hz  
FIDRES: 0.733596 Hz  
AQ: 1.3631486 sec  
RG: 112.69  
DW: 20.800 usec  
DE: 6.50 usec  
TE: 302.8 K  
D1: 2.0000000 sec  
D11: 0.0300000 sec  
TDO: 0.0000000 sec  
SFO1: 100.6550186 MHz  
NUC1: 13C  
P1: 9.80 usec  
PLM1: 58.0000000 W  
SFO2: 400.2536010 MHz  
NUC2: 1H  
CPCPRG12: waltz16  
PCPD2: 90.00 usec  
PLM2: 14.0000000 W  
PLM12: 0.25097000 W  
PLM13: 0.17654000 W

F2 - Processing parameters  
SI: 32768  
SF: 100.6449542 MHz  
WDW: EM  
SSB: 0  
LB: 1.00 Hz  
GB: 0  
PC: 1.40

Figure 2S: <sup>13</sup>C NMR of HQ-Al

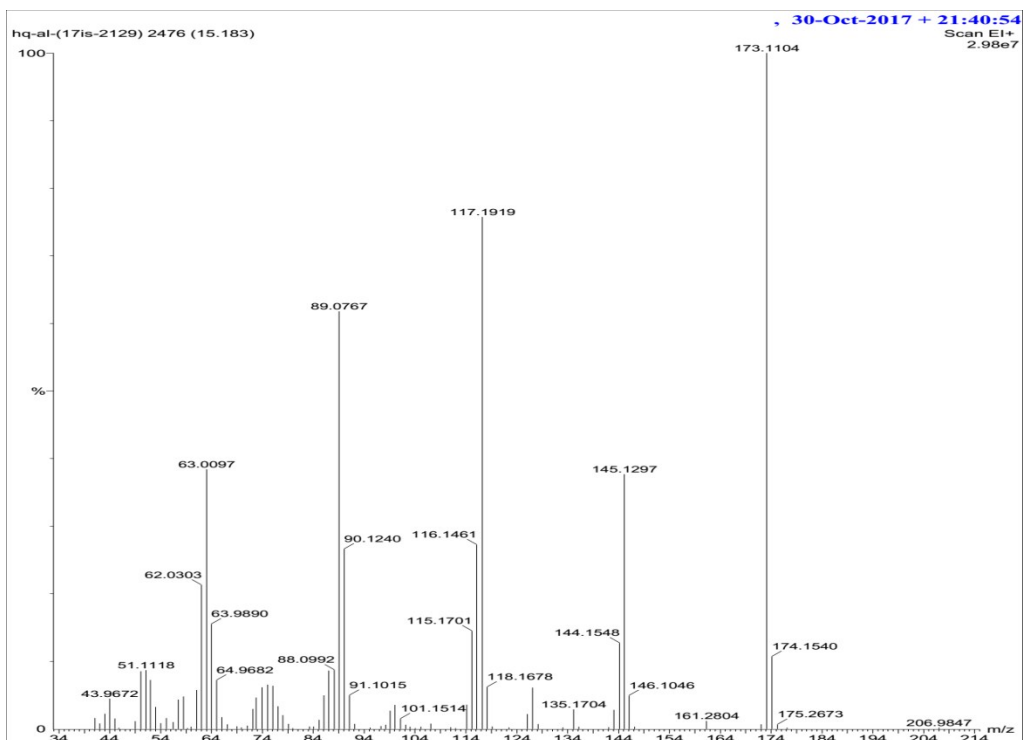


Figure 3S: Mass spectra of HQ-Al

Signature SIF VIT VELLORE  
HY-Q1

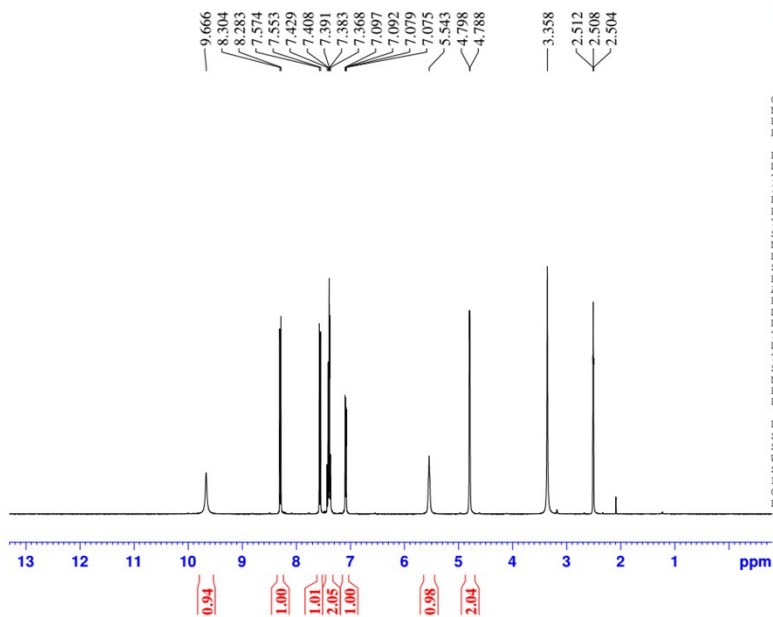


Figure 4S:  $^1\text{H}$  NMR of HQ-OH

Signature SIF VIT VELLORE  
HY-Q1

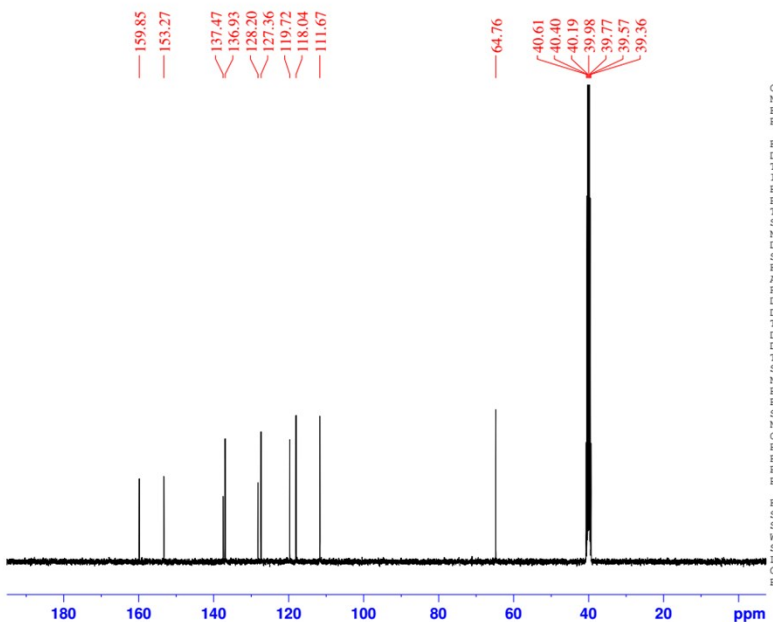


Figure 5S:  $^{13}\text{C}$  NMR of HQ-OH

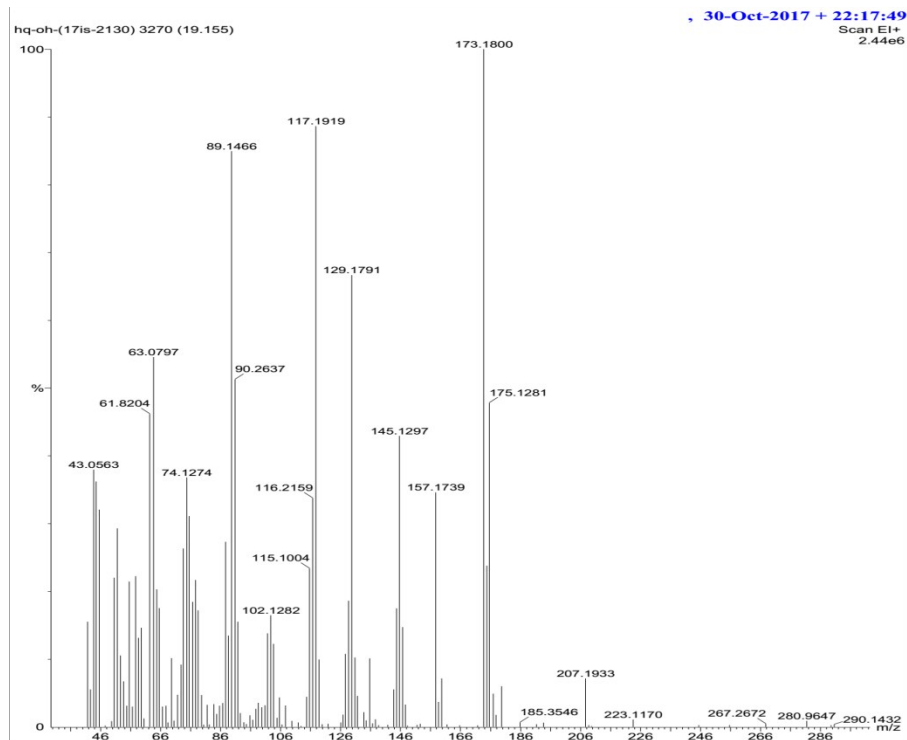


Figure 6S: Mass spectra of HQ-OH

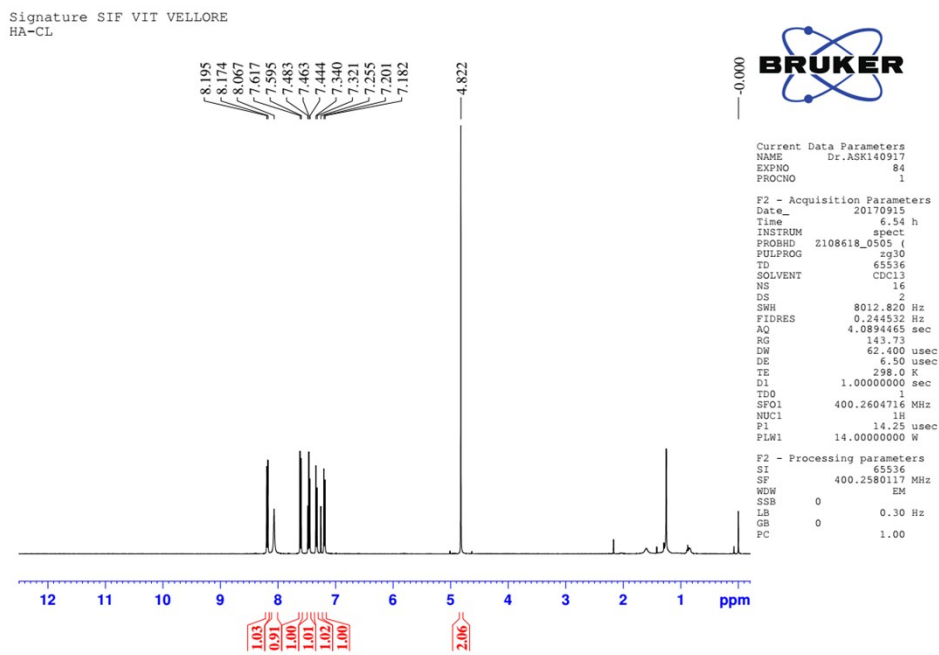


Figure 7S: <sup>1</sup>H NMR of HQ-MeCl

Signature SIF VIT VELLORE  
HA-CL

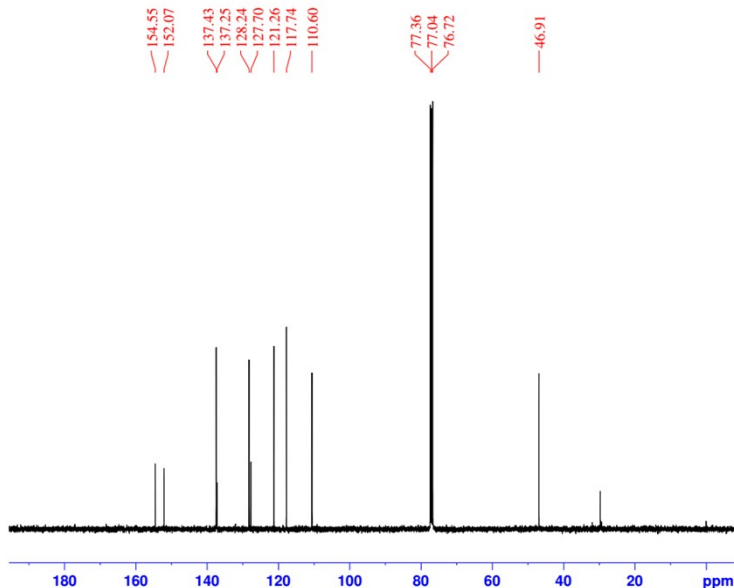


Figure 8S: <sup>13</sup>C NMR of HQ-MeCl

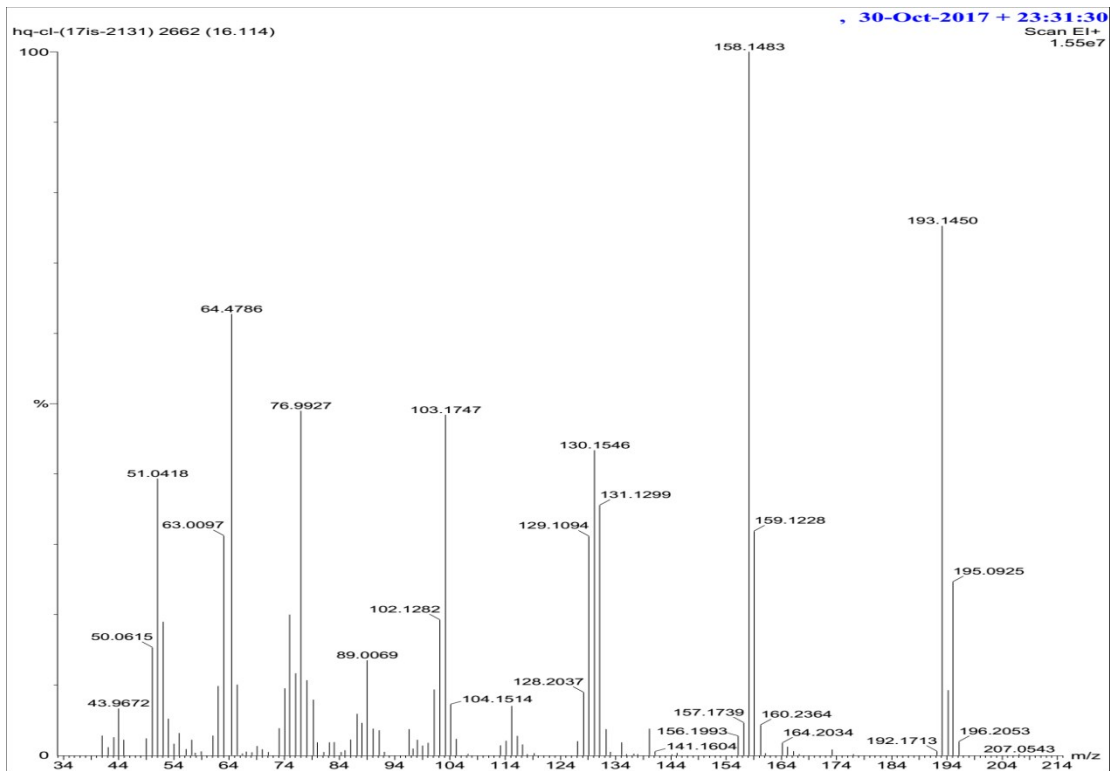


Figure 9S: Mass spectra of HQ-MeCl

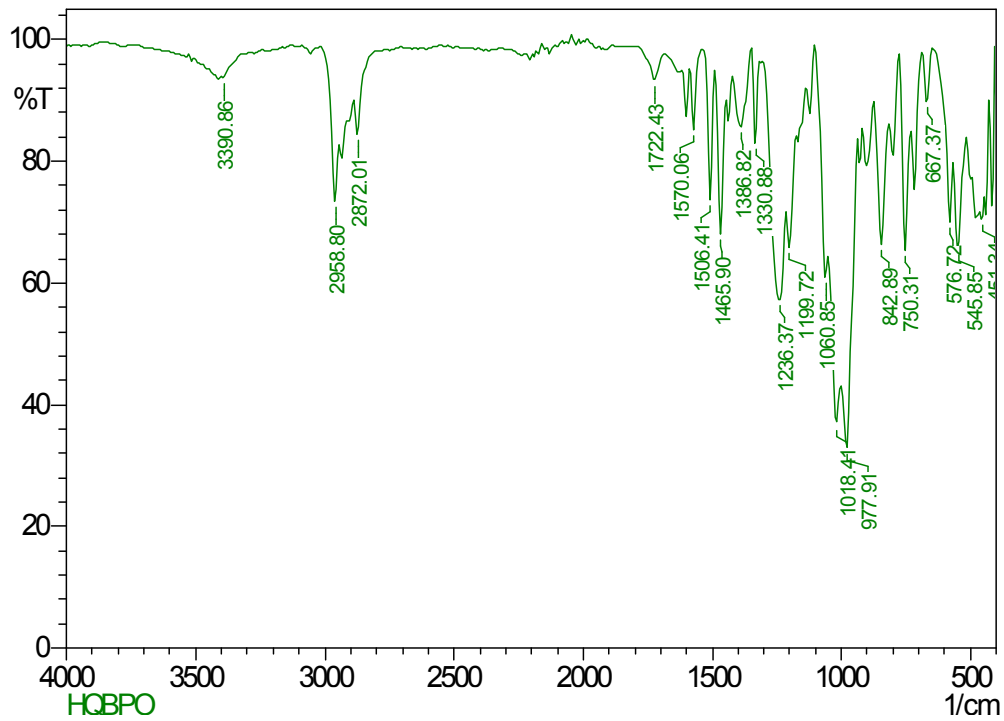


Figure 10S: FT-IR spectra of L

Signature SIF VIT VELLORE  
HQ-BPO

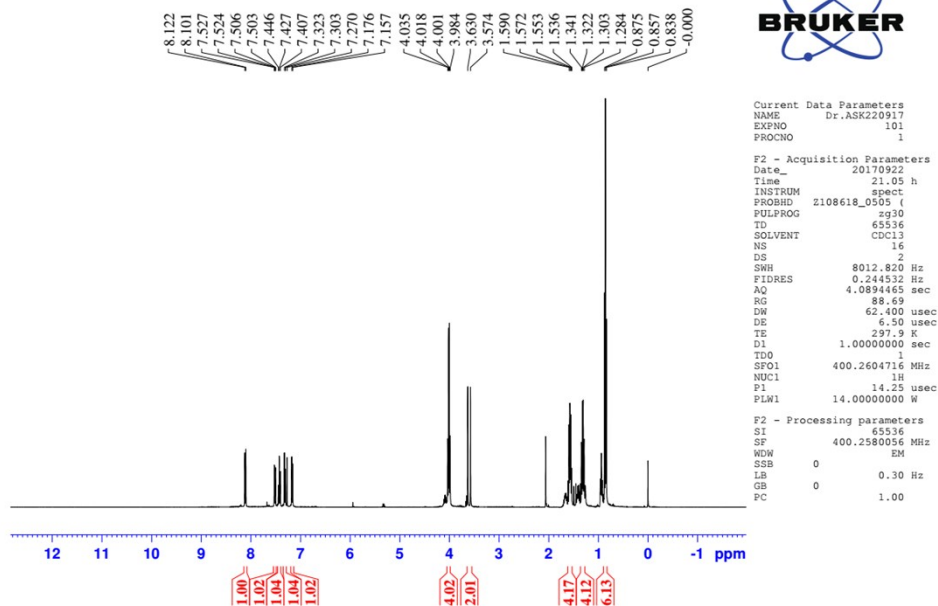


Figure 11S: <sup>1</sup>H NMR spectra of L

Signature SIF VIT VELLORE  
HQ-BPO

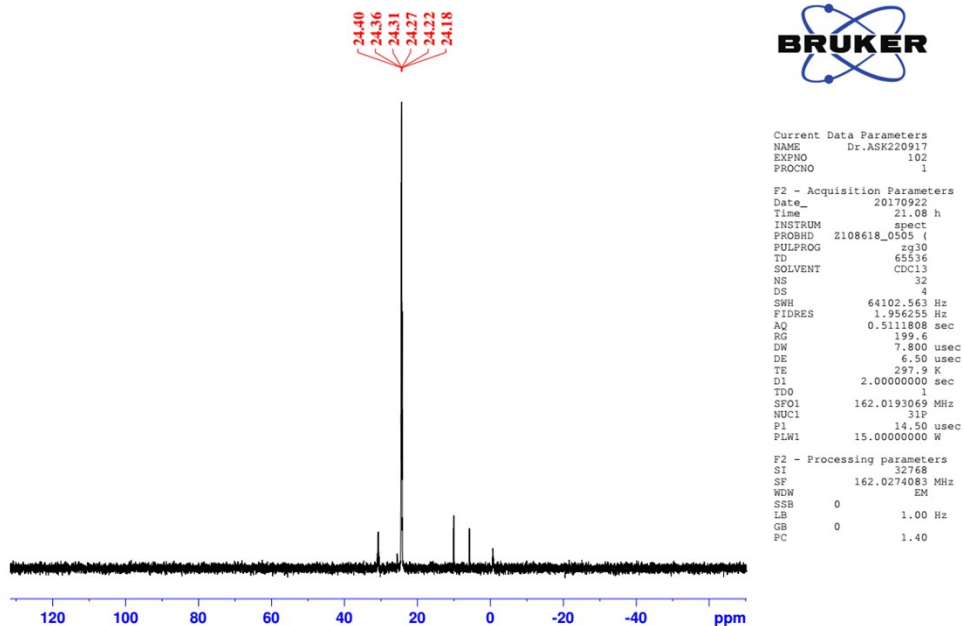


Figure 12S: <sup>31</sup>P NMR spectra of L

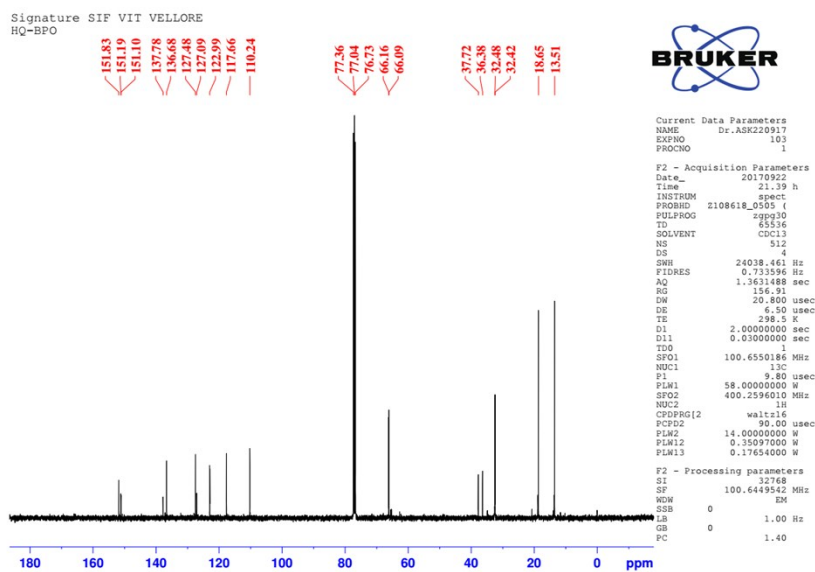


Figure 13S: <sup>13</sup>C NMR spectra of L



Signature SIF VIT VELLORE  
HQ-BPO

136.68  
136.66  
127.50  
127.49  
122.99  
122.96  
117.67  
117.65  
110.24

66.16  
66.09

37.72  
36.38  
32.48  
32.42

18.76  
13.52



Current Data Parameters  
NAME Dr.ASK270917  
EXPNO 104  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20170922  
Time 21.58 h  
INSTRUM spect  
PROBHD z108618\_0505 (PULPROG deptsp135  
TD 65536  
SOLVENT ccc13  
NS 256  
DS 8  
SNR 16129.032 Hz  
FIDRES 0.492219 Hz  
AQ 2.0316160 sec  
RG 199.6  
DW 31.000 usec  
DE 6.50 usec  
TE 298.2 K  
CHST2 145.000000 sec  
D1 2.00000000 sec  
D2 0.0034828 sec  
D12 0.0000200 sec  
TDO 1  
SFO1 100.6530057 MHz  
NUC1 13C  
P1 9.80 usec  
PL1 2000.00 usec  
PLA0 0 W  
PLM1 58.0000000 W  
SFOAM(5) Crp60comp.4  
SFOAL5 0.500  
SFOFFS5 0 Hz  
SFS4 8.51080036 W  
SFO2 400.2596010 MHz  
NUC2 1H  
CFOFFG[2] waltz16  
P3 14.25 usec  
P4 28.50 usec  
PCPD2 90.00 usec  
PLM2 14.0000000 W  
PLM12 0.35097000 W

F2 - Processing parameters  
SI 32768  
SF 100.6449542 MHz  
RGW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
CB 1.40

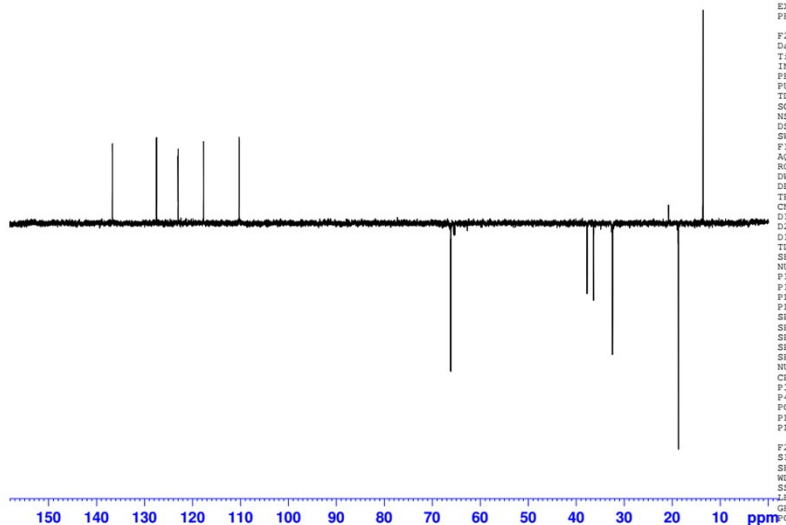


Figure 14S: DEPT-135 NMR spectra of L

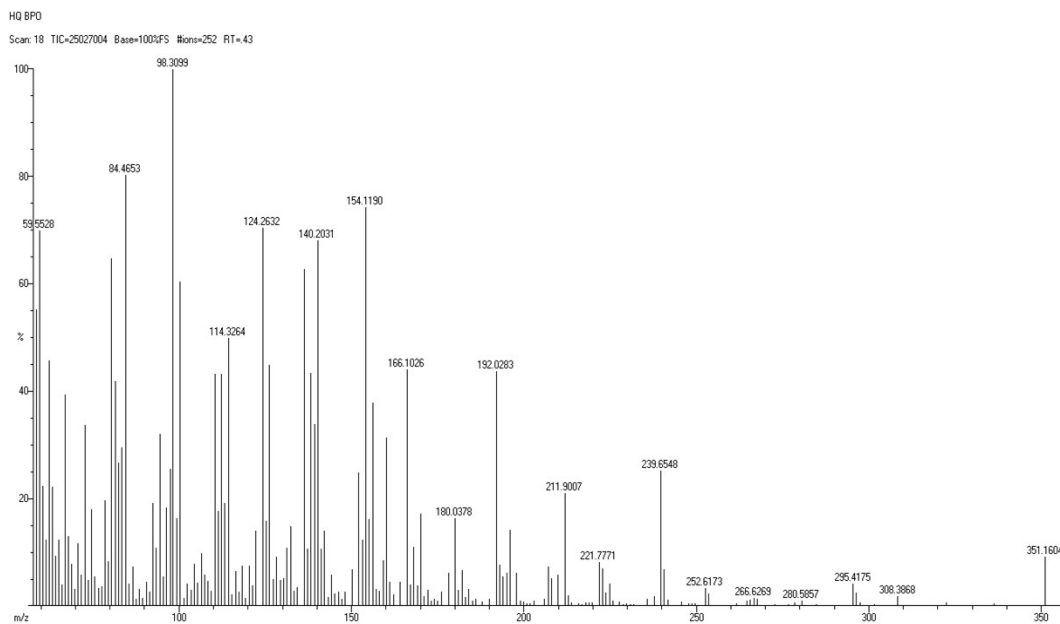


Figure 15S: HR-MS of L

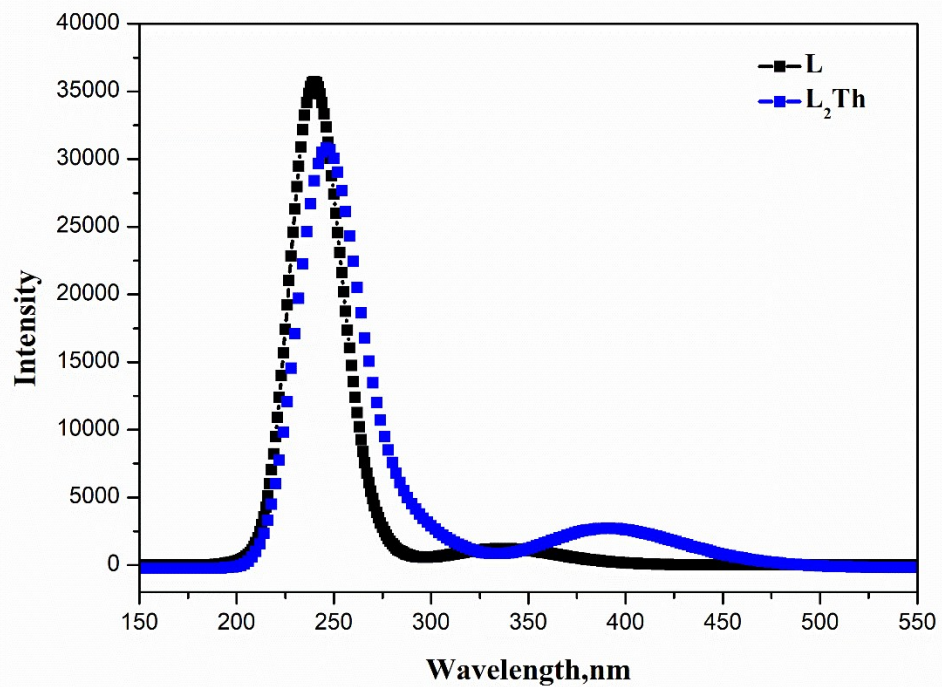


Figure 16S. TDDFT based excitation spectra of L and L<sub>2</sub>Th<sup>4+</sup>

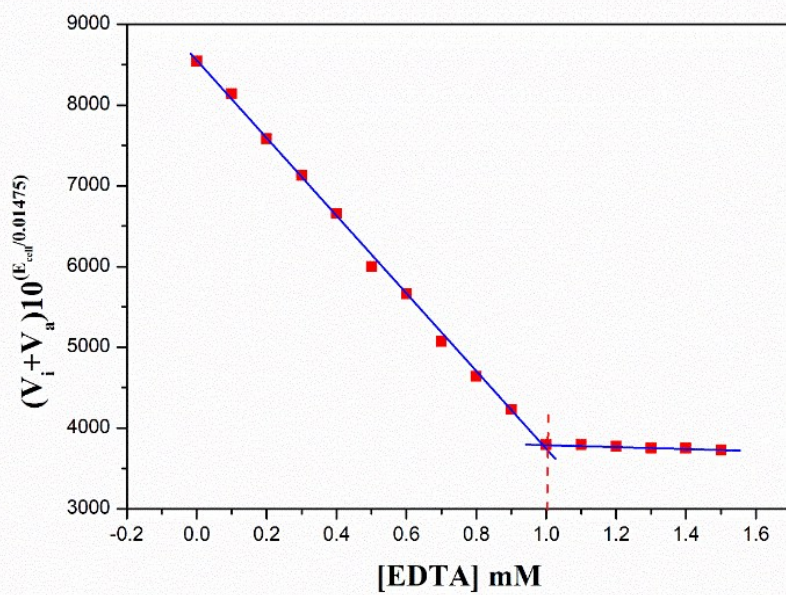


Figure 17S: Potentiometric titration plot represented using Gran's method

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

<b>Ligand and its complex</b>	<b>Experimental</b>		<b>Theoretical</b>			
	$\lambda_{\max}$ (nm)	$\epsilon$ (L M <sup>-1</sup> cm <sup>-1</sup> )	Excitation energy (nm)	Oscillator strength	Excited state	Key transitions
<b>L</b>	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%)
<b>L<sub>2</sub>Th<sup>4+</sup></b>	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<sup>4+</sup>-ISE with previously reported work.

S.No	Ionophore	Range (Mol) To 1x10 <sup>-1</sup> 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 <sup>-8</sup>	14.9 ±0.6	7	8.0 x10 <sup>-8</sup>	6	2.0 – 9.0
2	Thorium 8-hydroxyquinolate[21]	5.0 ×10 <sup>-6</sup>	15.5 ±0.5	30	1.6 x10 <sup>-6</sup>	2	3.0 – 5.0
3	Tin(IV) tungstoselenate Pyridine[22]	8.0 x 10 <sup>-6</sup>	14.2 ±1.0	15	6.0 x10 <sup>-6</sup>	***	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 <sup>-5</sup>	15.5 ±0.1	15	7.9 x10 <sup>-6</sup>	6	2.3 – 4.0
5	dithio-tetraaza macrocyclic compound [24]	1.0 x 10 <sup>-6</sup>	14.2 ± 0.3	10	8.0 ×10 <sup>-7</sup>	5	3.5 – 9.5
6	2-(diphenylphosphorothioyl)-N',N'-diphenyl acetamide[25]	1.0 x 10 <sup>-6</sup>	15.2 ± 0.5	30	6.3 x10 <sup>-7</sup>	1.5	3.0 – 9.0
7	Aliquat-336[41]	3.0 x 10 <sup>-5</sup>	-29.5 ± 0.3	40	1 x10 <sup>-5</sup>	***	***
8	trioctylphosphine oxide [26]	1.0 x 10 <sup>-6</sup>	-32.3 ±0.3	10	3.2 x10 <sup>-6</sup>	2.4	2.5 – 4.5
9	thorium toluate [27]	1.0 x 10 <sup>-6</sup>	-27.2 ±0.2	10	4.1 x10 <sup>-6</sup>	2.4	2.7 – 3.5
10	diphosphoryl-dicarboxylicacid-p-tert-butylcalix[4]arene [28]	2.0 x 10 <sup>-7</sup>	13.9	10	9.0 x10 <sup>-8</sup>	1.9	3.1 – 6.5
11	<b>Bibutyl (8-hydroxyquinolin-2-yl) methyl phosphonate (Present work)</b>	<b>1 x 10<sup>-7</sup></b>	<b>31.18 ±0.4</b>	<b>&lt;5</b>	<b>1 x10<sup>-8</sup></b>	<b>3</b>	<b>3.5 – 6.5</b>