

Thermodynamic Parameters of Complexation Calixpyrrole Derivative with Lanthanides Cations (Lu^{3+} , Ho^{3+} , Eu^{3+} and Pr^{3+}) in Nonaqueous Media

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Abstract: Calix [4] pyrrole derivative was used to target lanthanide cations. Meso tetramethyl-tetrakis-[(4-N, N-diethylacetamide) phenoxyethyl] calix [4] pyrrole, L2 was synthesised. This receptor constituted of hard donor atoms at the lower rim which interact with lanthanide cations being hard cations. ^1H NMR investigations showed that both, the pyrrolic N and the acetamide arm group provide sites for interaction with lanthanide metal cations. These findings are verified by conductance measurements in acetonitrile, plots of molar conductance against the ligand/metal cation ratio reveal the formation of 1:2 complexes between this ligand with lanthanide metal cations. Standard thermodynamics parameters of complexation ($\log K_s$, ΔH°_c , ΔS°_c , ΔG°_c) of L2 with lanthanide cations in acetonitrile were determined using the Nano ITC (isothermal titration calorimetry). The complexation process between these metal cations and the receptor L2 was enthalpically controlled.

Keywords: Calixpyrrole Receptor, Lanthanide Metal Cations, ^1H NMR Investigations, Conductance Measurements, Thermodynamic Studies

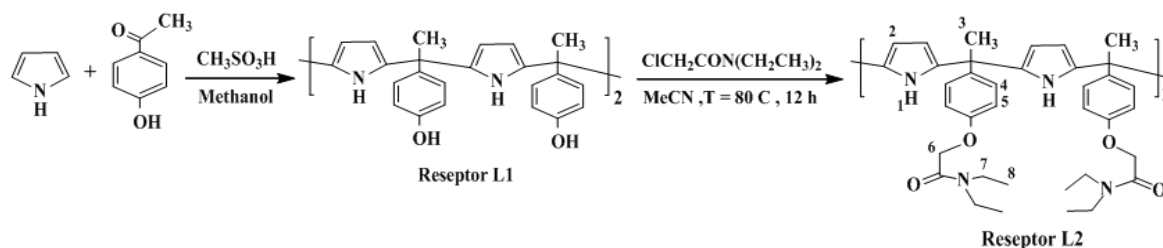
1. Introduction

Recently, supramolecular chemistry is one of the most advanced dynamic fields in chemistry. A key point is the molecular architecture and the selective recognition of molecules or ions by shape and size [1]. Metal recovery and separation of metal ions has been extensively used by industry in the past decades [2-5].

Research articles have been reported in the literature aiming to investigate the extraction for lanthanide cations from water to nonaqueous media. Lanthanides elements have gained a great attention because of their unique properties

and wide range of applications. These elements found much application in metallurgy, ceramic industry and nuclear fuel control [6,7]. Lanthanides are considered as one of the fission product and can cause risk if leaked to environment. It can be called as hazardous materials [8]. Floriani [9] work on the complexation of iron with the meso- octa methyl calix[4] pyrrole dating back to the early nineties is the only research in this area.

In this investigation, fully substituted, meso-tetra methyl tetrakis- [(4-N, N-diethylacetamide) phenoxyethyl] calix[4] pyrrole, L2, have been prepared for the detection of lanthanide metal cations (Scheme 1).



Scheme 1. Synthetic procedure used for the preparation L2.

We are, here, investigating the interaction of this receptor L2 with a number of cations, mainly lanthanides because of the prominent luminescence properties that these cations [10]. The aims of this paper are as follows:

- (i) To establish the presence or absence of interactions between Calix[4]pyrrole derivative (L2) and the lanthanide cations as well as the sites of interaction in acetonitrile at 298 K using ^1H NMR studies whenever possible. ^1H NMR studies were used to determine the interaction of this receptor with lanthanide metal cations by calculating the chemical shift changes after the addition of excess amounts of the lanthanides. The ^1H NMR studies provided evidence that significant chemical shift changes were observed for this receptor, L2, upon addition of these cations.
- (ii) Conductometric measurements were performed for receptor, L2, with the aim of determining a) the composition of the ligand-cations interaction and to gain information regarding the type and strength of interaction of the ligand with these metal cations in acetonitrile at 298 K. b) the degree of association of these cations in non-aqueous media.
- (iii) To characterize thermodynamically the complexation process involving calixpyrrole derivative (L2) and lanthanide cations in acetonitrile using Nano ITC (titration calorimetry).

2. Experimental

2.1. Chemicals

All starting materials and reagents used were purchased from Sigma-Aldrich and Fluka Company. All solvents were dried and purified as described in the literature [11]. Lutetium (III), Holmium (III), Europium (III) and Praseodymium (III) trifluoromethanesulfonate (triflate) were dried over P_4O_{10} under vacuum for several days before use.

2.2. Instrumentation

2.2.1. ^1H NMR Measurements

^1H NMR measurements were used to characterize the calix[4]pyrrole derivatives and to provide information about its interaction with lanthanide metal cations and whenever possible to establish the site of interaction of the ligand. ^1H NMR measurements were recorded at 298 K on A Bruker DRX-500 pulse Fourier Transform NMR Spectrometer. The operating conditions involved pulse or flip angle of 30° , spectra width (SW) of 15 ppm, spectral frequency (SF) of 500.150 MHz, delay time of 0.3 s, acquisition time (AQ) of 3.17s, and line broadening of 0.3 Hz. Solutions of the samples of interest ($1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) were prepared in the appropriate deuterated solvent. These were placed in 5mm NMR tubes using TMS (tetramethylsilane) as the internal reference.

2.2.2. Conductance Measurements

A Wayne-Kerr Autobalance Universal Bridge type B642 was used for conductometric measurements. The Wayne-Kerr is connected to a platinum glass bodied electrode housed in a cylindrical glass vessel where the reaction takes place. A thermostatic bath circulating water in the vessel jacket was used to maintain the temperature of the vessel at 298.15 K. A magnetic stirrer was used to keep homogeneous the solutions throughout the time of the experiment. The conductance cell was a Russell type glass bodied electrode with a cell constant (determined using $0.10 \text{ mol} \cdot \text{dm}^{-3}$ aqueous KCl solution). For these experiments, the vessel was filled with the lanthanide metal cations in the appropriate solvent (25 cm^3) and the conductance of the solution was measured. Then, a known volume of solution of calix [4] pyrrole derivative in the same solvent was added stepwise into the vessel and the conductance measured after each addition.

2.2.3. Nano ITC (Isothermal Titration Calorimetry)

The basic principle of ITC is simply to measure the heat released or absorbed in a liquid sample after the addition of another liquid sample. This heat is proportional to the total amount of binding that occurs within the calorimeter cell. The instrument has a pair of identical cells (1.4 ml), denoted as the reference and sample cells. These cells, along with access stems, are enclosed in a temperature-controlled thermal jacket. The reference and sample cells (and stems) are filled with identical ligand solutions. The power (or heat) difference between the sample and reference cells is used to determine n , K_a , and ΔH° .

To determine the accuracy of measurements carried out in the Nano ITC, a chemical calibration should be performed. The following equilibrium is established upon the addition of barium chloride to 18-crown-6 ether in water at 298.15 K [12]. The sample cell was filled with an aqueous solution of 18-Crown-6 (1 cm^3 , $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) and titrated incrementally from the burette stirring system with BaCl_2 ($0.015 \text{ mol} \cdot \text{dm}^{-3}$).

2.3. Synthesis

2.3.1. Synthesis of Meso-Tetramethyl-Tetrakis-(4-Hydroxyphenyl) Calix [4] Pyrrole, L1

Receptor L1 (Scheme 1) was synthesized and characterized as reported elsewhere [13].

2.3.2. Synthesis of Meso-Tetramethyl-Tetrakis-[(4-N, N-Diethylacetamide) Phenoxymethyl] Calix [4] Pyrrole, L2

Meso-tetramethyl-tetrakis-(4 hydroxyphenyl) calix [4] pyrrole, L1, (1.7 g , 2.26 mmol), potassium carbonate (2.5 g , 18.1 mmol) and 18-crown-6 (0.125 g) were vigorously stirred and refluxed for 1h in freshly refluxed acetonitrile (150 ml) and under a nitrogen atmosphere. Then N,N- diethyl chloro acetamide (2.46 ml , 17.9 mmol) was added dropwise and the mixture was refluxed overnight. The reaction was monitored by TLC using DCM/MeOH (9:1) as the developing solvent

system. After cooling down the reaction, the solvent was removed under pressure. The solid obtained was dissolved in dichloromethane and extracted several times with water to remove the excess of potassium carbonate. The dichloromethane phase was separated and dried over anhydrous magnesium sulphate, then filtered. Dichloromethane was rotary- evaporated and the oily product was recrystallized from acetonitrile to yield 70 % of white needle crystals. ^1H NMR (500 MHz), (CD_3CN)(298 K), δ (ppm): 7.97 (s, 4H, NH), 6.83 (d, 8H, ArH), 6.76 (d, 8H, ArH), 6.00 (d, 8H, pyrrole-H), 4.68 (s, 8H, O- CH_2 -CO), 3.36 (q, 16H, $\text{N}(\text{CH}_2\text{-CH}_3)_2$), 1.83 (s, 12H, CH_3 - bridge), 1.21(q, 12H, $\text{N}(\text{CH}_2\text{-CH}_3)_2$), 1.09(q, 12H, $\text{N}(\text{CH}_2\text{-CH}_3)_2$). Microanalysis was carried out ($\text{C}_{72}\text{H}_{88}\text{N}_8\text{O}_8$) calculated % were C, 72.46; H, 7.43; N, 9.39, O, 10.72. Found % = C, 71.76; H, 7.47, N, 10.1

3. Results and Discussion

3.1. ^1H NMR Studies on the Interaction of L2 with Lanthanide Metal Cations Deuterated Solvent at 298 K

^1H NMR spectra of the lanthanide metal cations - receptor complex at 298 K were recorded (Appendix A). The relevant ^1H NMR chemical shift changes of the protons observed by the addition of lanthanide metal cations to calixpyrrole derivative, in deuterated solvent at 298 K are listed in Table 1.

^1H NMR measurements involving the receptor L2 and lanthanide metal cations (Lu^{3+} , Ho^{3+} , Eu^{3+} and Pr^{3+}) as trifluoromethanesulfonates (no interaction was found between this anion and L2 in this solvent as shown by ^1H NMR) in CD_3CN were conducted in order to determine their contribution to the calixpyrrole framework and to assist with a detailed investigation of the cation-macrocyclic complexation process.

Table 1. ^1H NMR chemical shift changes observed via the addition of lanthanide metal cation salts to L2 relative to the free ligand in CD_3CN at 298 K

Proton	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8
δ_{Ref}	7.97	6.00	1.83	6.83	6.76	4.68	3.36	1.21
Lu^{3+}	8.00	7.02	7.11	4.91	3.38	1.15
$\Delta\delta$	-0.01	-0.20	-0.34	-0.23	-0.05	0.05
Ho^{3+}	7.69	1.80	6.61	6.73	4.89	3.63	1.33
$\Delta\delta$	0.29	0.03	0.21	0.04	-0.21	-0.29	-0.13
Eu^{3+}	7.94	5.86	1.90	6.97	7.06	4.85	3.41	1.16
$\Delta\delta$	0.04	0.14	-0.06	-0.15	-0.29	-0.17	-0.07	0.03
Pr^{3+}	7.86	6.01	1.87	6.89	6.95	4.88	3.53	1.18
$\Delta\delta$	0.13	-0.01	-0.03	-0.07	-0.17	-0.19	-0.19	0.02

Table 1 lists the chemical shift changes ($\Delta\delta$ ppm) observed in the ^1H NMR spectrum of L2 by the addition of lanthanide metal cations. These changes in CD_3CN indicate that both, the pyrrolic N and the acetamide arm group provide the sites of interaction with lanthanide metal cations. Approximately, all protons for ligand L2 have been affected upon the addition of Lu^{3+} , Ho^{3+} , Eu^{3+} and Pr^{3+} in CD_3CN at 298 K. Some protons have shielding effects and others have

deshielding effects.

It can be noted that the protons closest to the the acetamide arm group such as H-6, H-7 and H-8, have considerable chemical shift changes. This is an indication that the lower rim groups of the receptors interact with these metals. Protons such as H-1, H-2, H-3, H-4 and H-5 have been also affected as a result of this interaction.

3.2. Conductometric Measurements

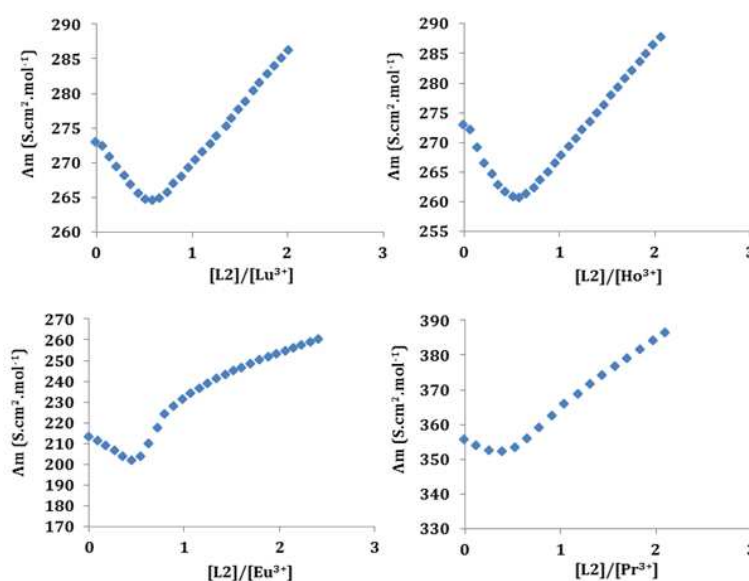


Figure 1. Conductometric curves for the titration of Lu^{3+} , Ho^{3+} , Eu^{3+} and Pr^{3+} (as trifluoromethanesulfonate) with L2 in acetonitrile at 298.15 K

Fig. 1, shows the conductometric curves (plots of Δ_m vs $[L2]/[Ln^{3+}]$) for the titration of lanthanide metal cations with the receptor L2 in acetonitrile at 298 K. A quick inspection of the titration curves for lanthanides and L2 in CD_3CN clearly reveals that all lanthanides form 1:2 (ligand: metal cation) complexes.

The shape of the titration curves for Lu^{3+} , Ho^{3+} , Eu^{3+} and Pr^{3+} have similar patterns. These cations form strong 1:2 (ligand: metal) complexes. The decrease in the conductivity observed in the case of Lu^{3+} , Ho^{3+} , Eu^{3+} and Pr^{3+} after addition of the ligand until a stoichiometry of $L2/M^{3+} = 0.5$ is due to the large size of the complexes metal-ion compared with the free solvated ion. After the break at 0.5 metal cation/ ligand ratio, one would expect a continuous decrease in the conductivity on addition of the ligand. However the opposite was observed. A possible explanation of this is that the presence of an excess of ligand, one metal cation from the 1:2 complex is transferred to the free ligand with the

corresponding increase in the conductance.

3.3. Thermodynamics of Complexation

Standard thermodynamics parameters of complexation ($\log K_s$, ΔH_c° , ΔS_c° , ΔG_c°) of the receptor L2 with lanthanide metal cations in MeCN were determined using the Nano ITC. For this purpose the instruments were electrically and chemically calibrated prior to measurements. Calorimetric titration curves for the titration of metal cations with the receptor L2 in acetonitrile at 298 K were recorded (Appendix B).

3.3.1. Calibration of the Nano ITC Instrument

The reaction of complexation of 18-C-6 and Ba^{2+} in aqueous medium was used as a standard reaction to check the accuracy and reliability of the Nano ITC instrument following the procedure described in the Experimental Part. Fig.2 show calorimetric titration curves for the titration of 18-crown-6 with Ba^{2+} in deionized water.

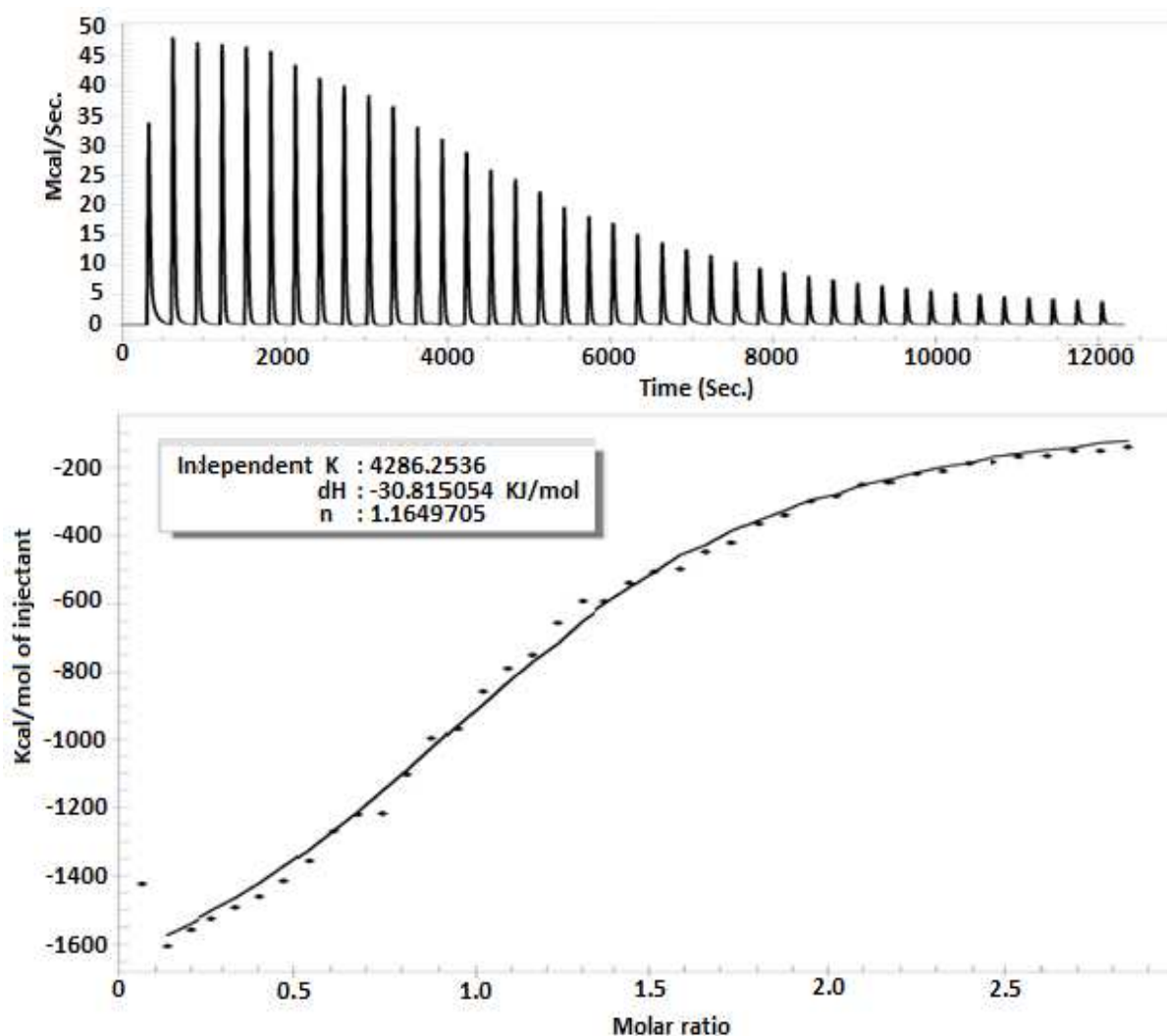


Figure 2. Representative calorimetric titration curves. The upper curve was obtained by titrating 18-crown-6 with Ba^{2+} in deionized water.

The stability constant (expressed as $\log K_s$), standard Gibbs energy, $\Delta_c G^\circ$, enthalpy, $\Delta_c H^\circ$ and entropy $\Delta_c S^\circ$ of complexation of 18-C-6 with Ba^{2+} in aqueous medium

obtained at 298.15 K from nanocalorimetric titrations are summarized in Table 2. For comparison purposes, values reported in the literature are also included.

Table 2. Thermodynamic parameters of BaCl_2 binding to 18-crown-6 by Nano-ITC in aqueous medium (deionized water) at 298.15 K

Log K_s	$\Delta_c H^\circ (\text{kJ. mol}^{-1})$	$\Delta_c G^\circ (\text{kJ. mol}^{-1})$	$\Delta_c S^\circ (\text{J. mol}^{-1} \cdot \text{K}^{-1})$	Ref
3.63	-30.82	-20.73	-33.8	This work
3.77	-31.39	-21.49	-33	[13]

The thermodynamic parameters for the complexation of Ba^{2+} with 18-C-6 in aqueous medium show a good agreement with the values reported in the literature by Briggner and Wadso [12].

3.3.2. Thermodynamic Parameters of Complexation of the Receptor 2 with Lanthanide Metal Cations in Acetonitrile at 298.15 K

Appendix B shows a Nano-ITC charts recorded for the titration of L2 with lanthanide metal cations which the thermal power is plotted against time. These graphs are typical for a 1:2 (ligand: lanthanide cation, Ln^{3+})

Table 3. Thermodynamics parameters for the complexation of lanthanides(III) cations (trifluoromethanesulfonate as counter ion) and L2 in acetonitrile at 298.15 K.

Metal	Ionic radius (pm)	Log K_s	$\Delta_c G^\circ (\text{kJ mol}^{-1})$	$\Delta_c H^\circ (\text{kJ mol}^{-1})$	$\Delta_c S^\circ (\text{kJ mol}^{-1} \text{K}^{-1})$	n
Lu^{3+}	84.80	5.12	-29.22	-51.50	-74.73	2.00
Ho^{3+}	89.40	5.04	-28.76	-48.90	-67.55	2.01
Eu^{3+}	95.00	4.98	-28.42	-45.10	-55.94	2.06
Pr^{3+}	101.30	4.80	-27.40	-39.70	-41.25	2.15

A general analysis of the thermodynamic parameters in Table 3 shows that the complexation process is favoured in terms of enthalpy (ΔH) but not in terms of entropy (ΔS). The complexation process is therefore enthalpically controlled. The data in Table 3 show that ΔG values obtained for L2 and various lanthanide cations in acetonitrile are close to each other.

Inspection of stability constant data (expressed as log K_s) shows that this ligand interacts selectively with Lu^{3+} , Ho^{3+} , Eu^{3+} and Pr^{3+} in acetonitrile following the sequence

$$\text{Lu}^{3+} > \text{Ho}^{3+} > \text{Eu}^{3+} > \text{Pr}^{3+}$$

It can be observed that the selective behavior of L2 for Lu^{3+} relative to other metal cations in this solvent.

4. Conclusion

From the above discussion, the following is concluded: ^1H NMR complexation experiments have demonstrated that Lutetium (III), Holmium (III), Europium(III) and Praseodymium (III) interact with L2 forming 1:2 complexes

complexation reaction. A plot of enthalpy changes during the nanocalorimetric titration against the ligand / lanthanide cation concentration ratio in acetonitrile at 298.15K is shown in these graphs.

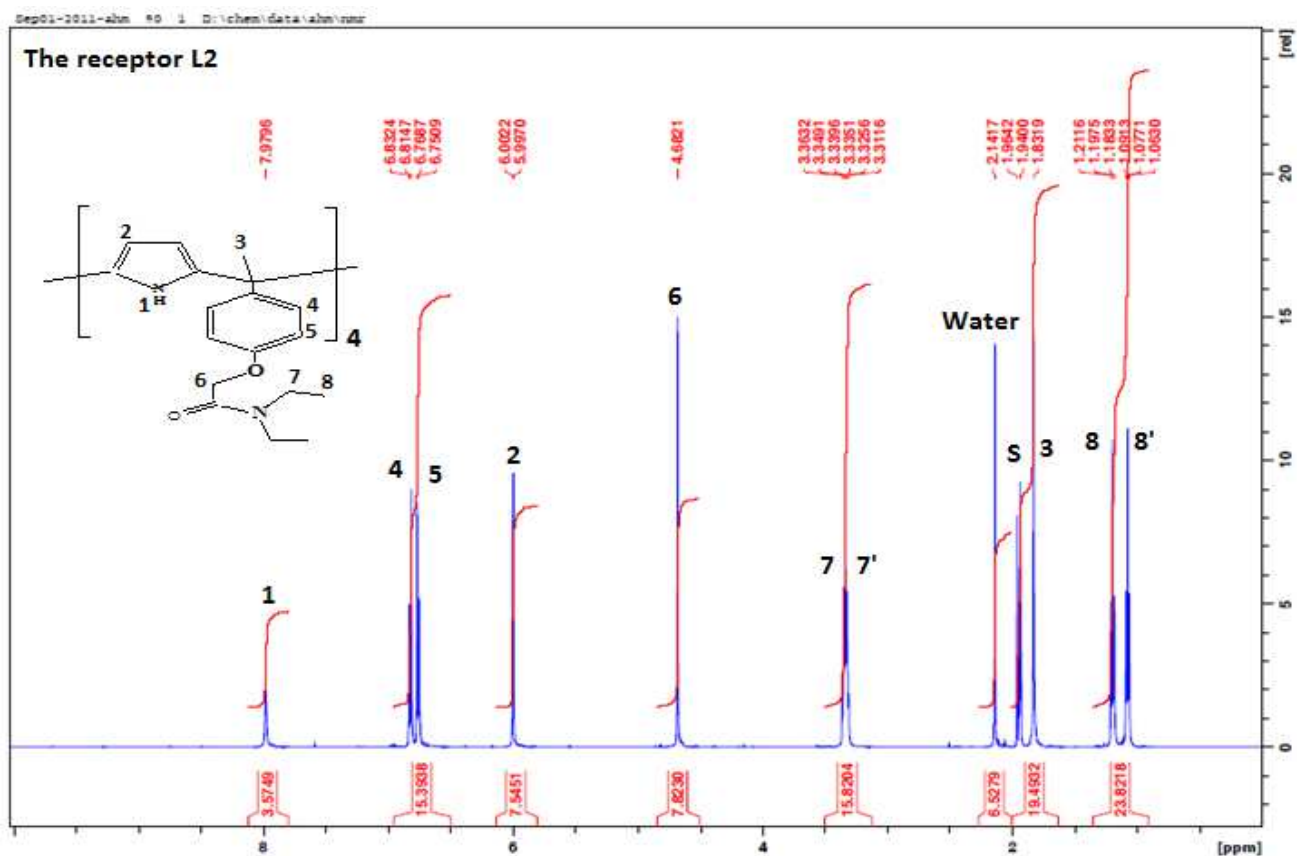
Titration calorimetry was used to obtain the log K_s and the enthalpy of complexation of L2 with cations in acetonitrile. Combination of Gibbs energies and enthalpies led to the calculation of the entropies associated to the complexation process. Thermodynamic data for the complexation of L2 with the cations in acetonitrile are summarized in Table 3.

in CD_3CN . The active sites of complexation are provided by the nitrogen and oxygen donor atoms. The large chemical shift changes observed for the protons of the acetamide groups suggested that both amide and possibly the pyrrolic N participate in the complexation process. Conductance data have shown that well-defined breaks in the titration curves demonstrated the formation of 1:2 complexes between L2 and lanthanide cations (Lu^{3+} , Ho^{3+} , Eu^{3+} and Pr^{3+}) in acetonitrile at 298.15 K. The thermodynamic data reported in this paper show that trivalent cations form 1:2 complexes in acetonitrile with L2. Ligand L2 forms complexes of similar stability constants in acetonitrile. Future work will involve the attachment of the receptor to solid support to generate recyclable materials for cations removal.

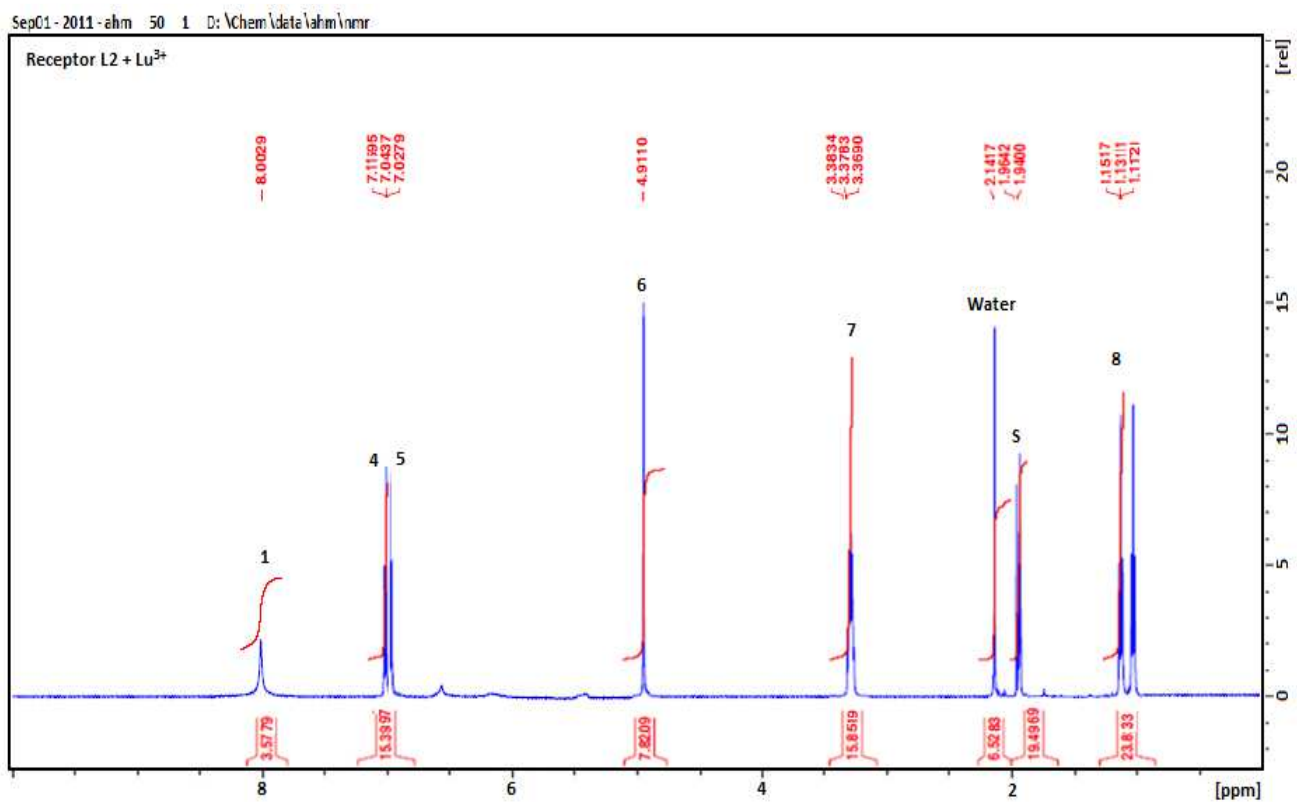
Acknowledgements

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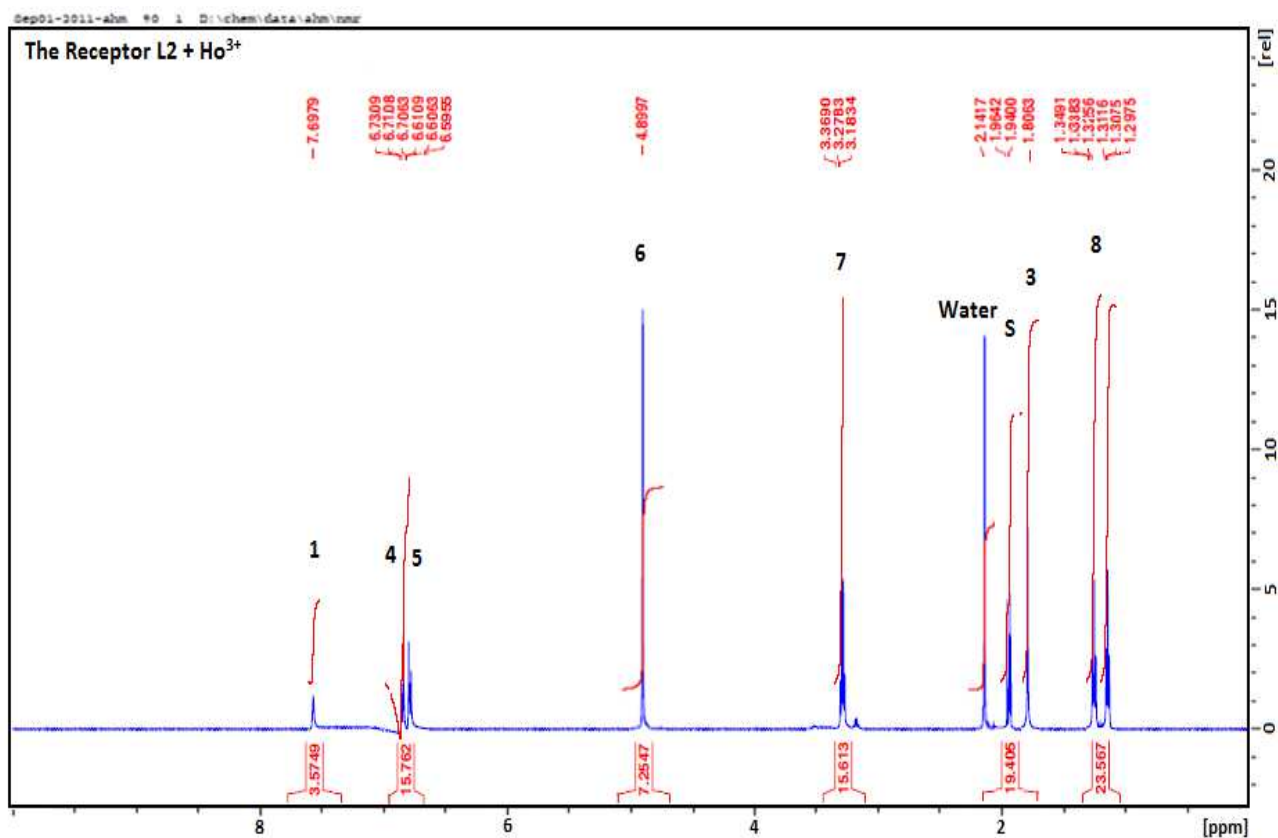
Appendix A



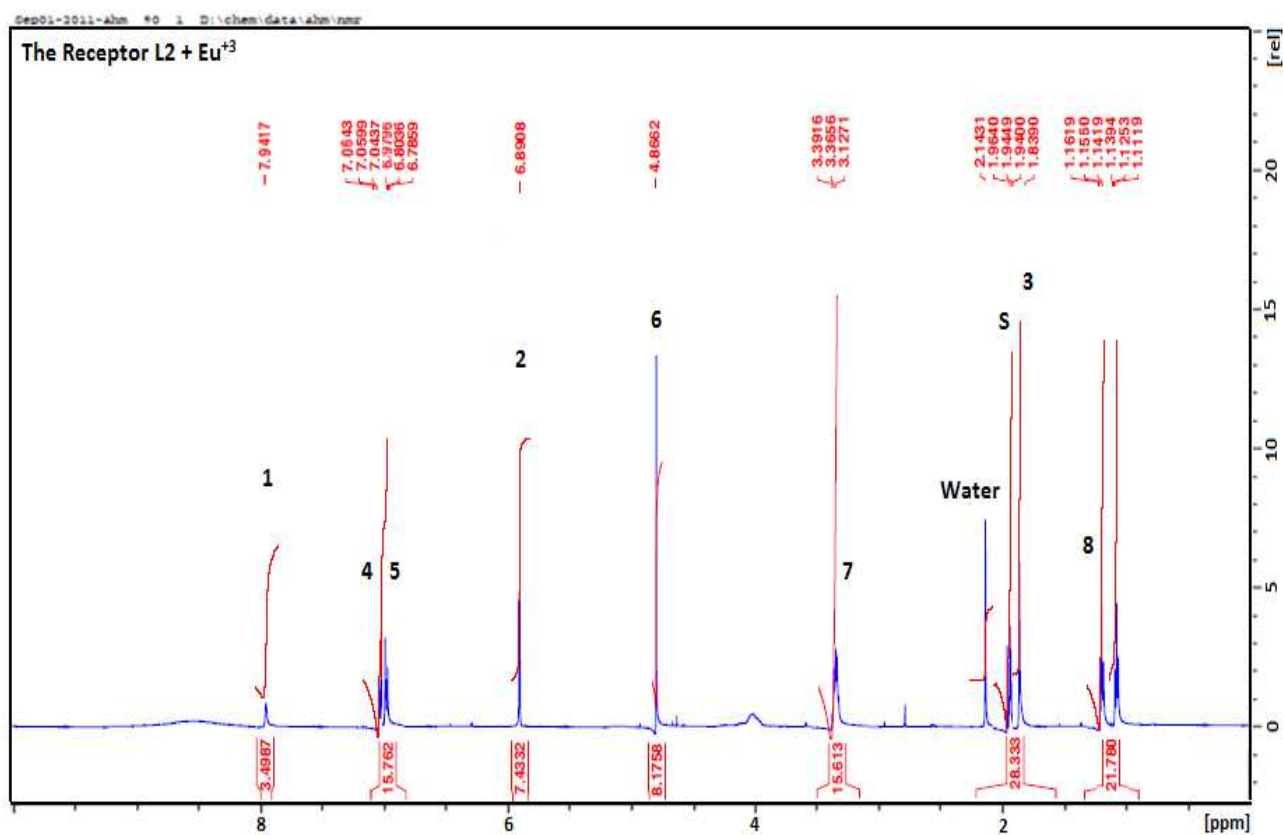
^1H NMR spectrum of L2 in CD_3CN at 298 K.



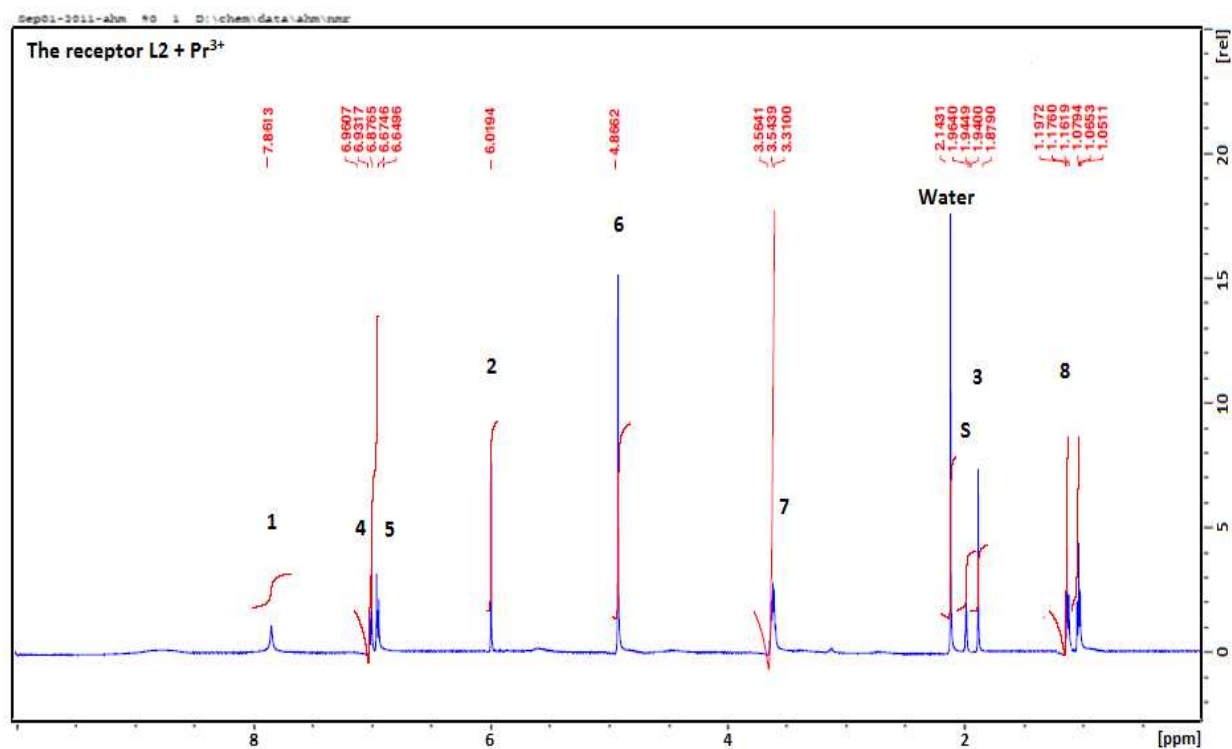
^1H NMR spectrum of L2 + Lu^{3+} in CD_3CN at 298 K.



^1H NMR spectrum of $\text{L2} + \text{Ho}^{3+}$ in CD_3CN at 298 K.

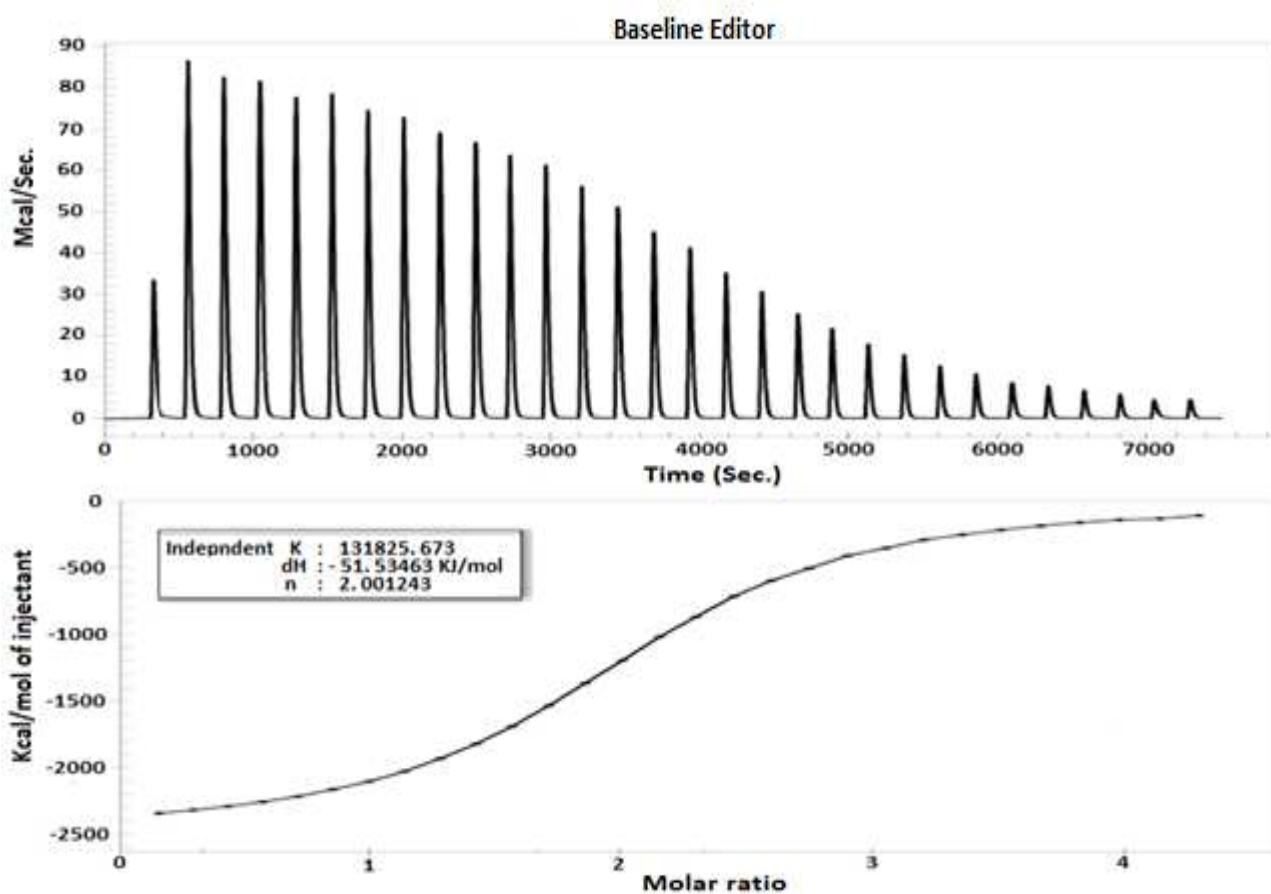


^1H NMR spectrum of $\text{L2} + \text{Eu}^{3+}$ in CD_3CN at 298 K.

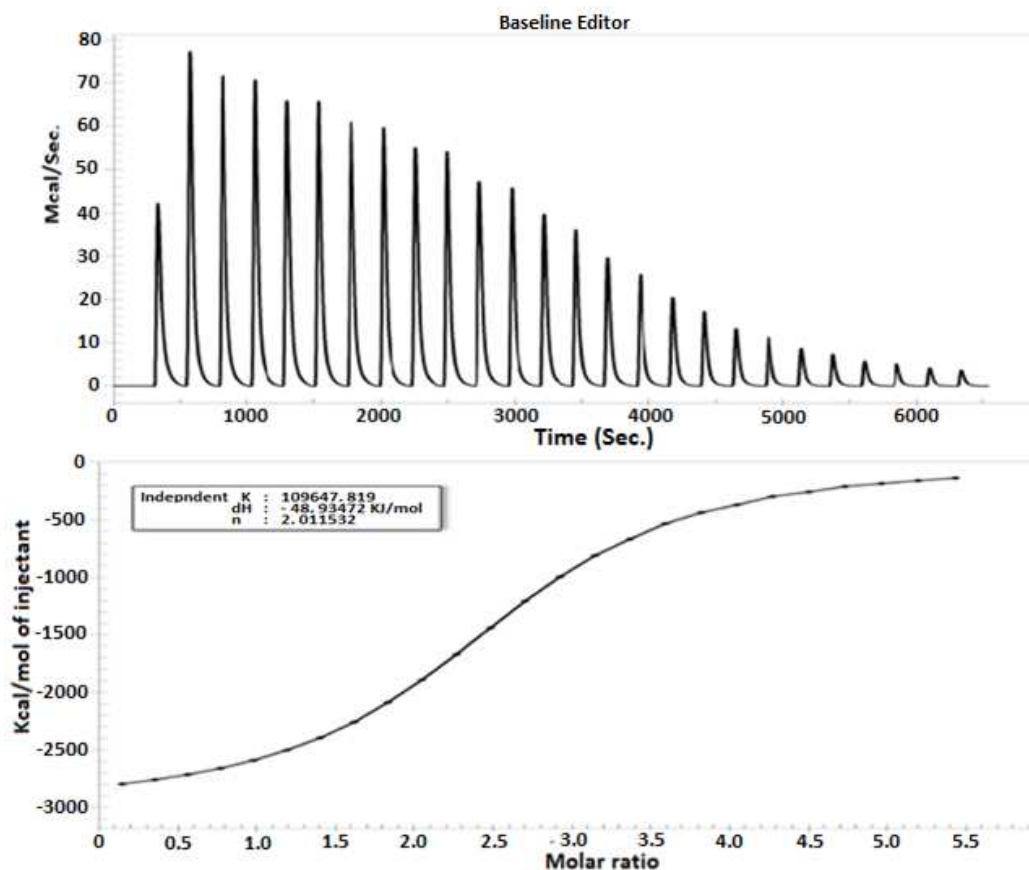


^1H NMR spectrum of L2 + Pr^{3+} in CD_3CN at 298 K.

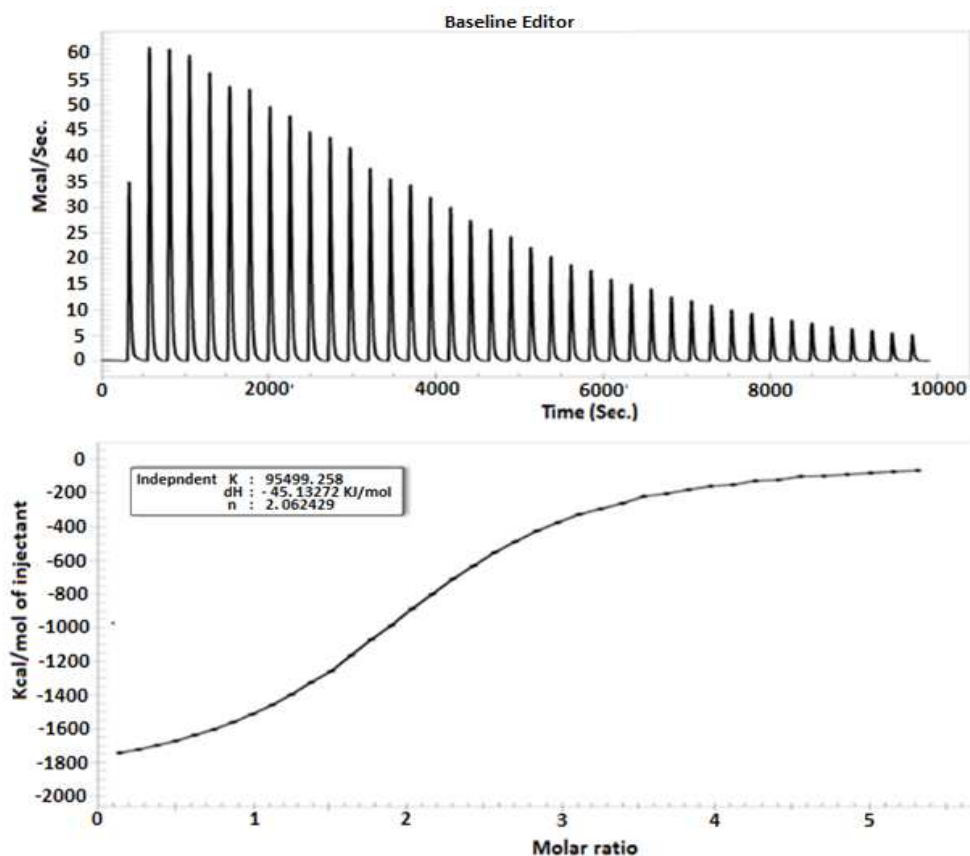
Appendix B



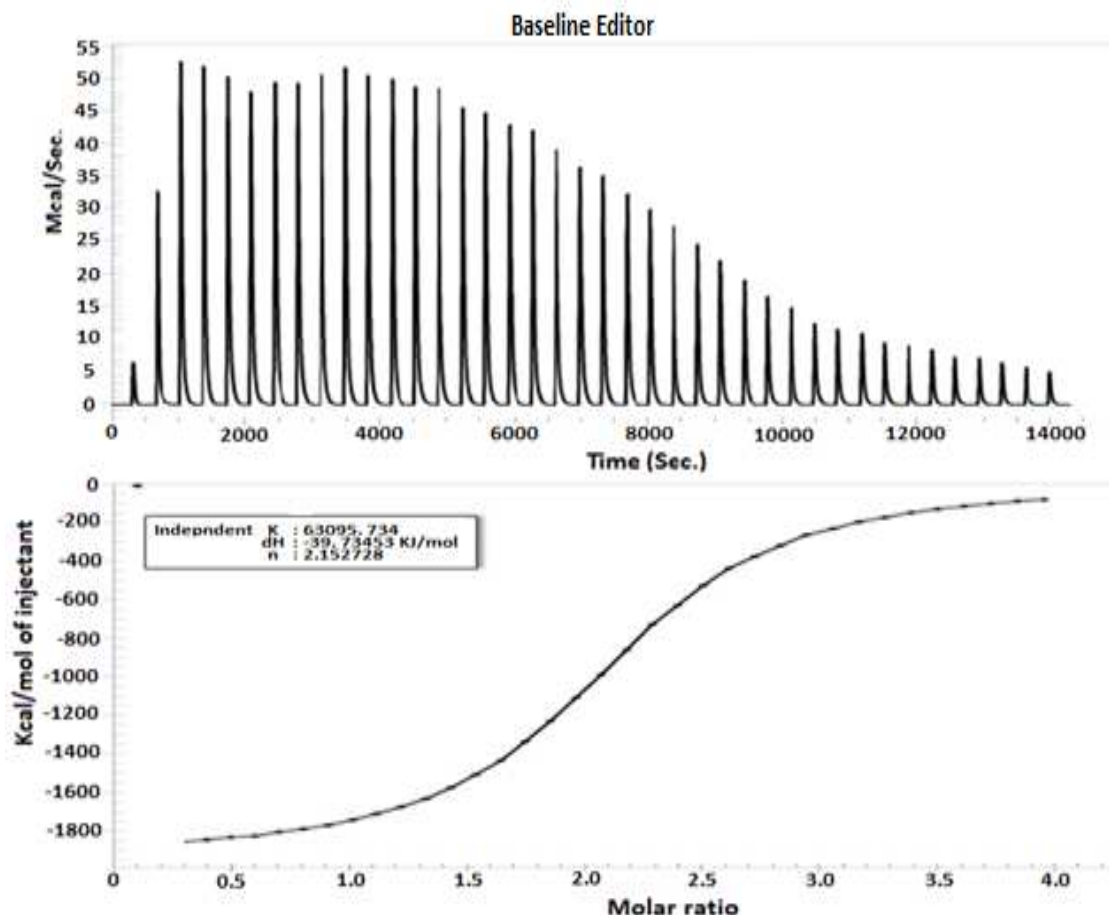
Representative calorimetric titration curves. The upper curve was obtained by titrating receptor L2 with Lu^{3+} in MeCN



Representative calorimetric titration curves. The upper curve was obtained by titrating receptor L2 with Ho^{3+} in MeCN



Representative calorimetric titration curves. The upper curve was obtained by titrating receptor L2 with Eu^{3+} in MeCN.



Representative calorimetric titration curves. The upper curve was obtained by titrating receptor L2 with Pr^{3+} in MeCN.

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