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## CARBOXYLATE SELECTIVE LANTHANIDE IMPRINTED POLYMER SENSORS FOR SENSOR ARRAY

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CARBOXYLATE SELECTIVE LANTHANIDE IMPRINTED POLYMER SENSORS FOR  
SENSOR ARRAY

by

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Bachelor of Science  
University of South Carolina, 2010

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Submitted in Partial Fulfillment of the Requirements

For the Degree of Master of Science in

Chemistry

College of Arts and Sciences

University of South Carolina

2014

Accepted by:

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## DEDICATION

To my mom, dad

&

Ka Lit Lam

## ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor, Dr. Ken D. Shimizu, with my deepest gratitude for his guidance, advices and help in my graduate school years. You are greatly in helping me thinking critically and scientifically in a very patient way. I will never forget how you inspire me in the research and lead me become a deeper thinker and problem solver. Although revising my paper draft gives me a tough time, I learned so much about how to write a real science paper and I am sure this will benefit me for my lifetime. I am very grateful for all your training and effort on me.

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## ABSTRACT

A europium-based molecularly imprinted polymer (MIP) was developed and characterized, which combined the highly luminescent properties of europium and the recognition properties of molecularly imprinted polymers. The europium-based MIPs were used as selective sensors for different types of carboxylates. The ultimate goal of this work was to develop a europium-based sensor array to differentiate carboxylates anions. The polymer was synthesized by using a europium–salen complex as the monomer and ethylene glycol dimethacrylate (EGDMA) as the crosslinker. First, a europium containing non-imprinted polymer (NIP) and a series of europium containing MIPs imprinted with acetate, benzoate and phenylacetate were synthesized by free radical polymerization. All of the polymers were able to discriminate different analytes by their different fluorescence intensity responses. The MIPs were found to have different selectivities with changes in the structure of the imprinting templates, which is a very important feature for sensor array applications. Second, the poor solubility of the monomer in the polymerization solution, which can cause an uneven distribution of the europium in the polymer, was addressed. The solubility of the europium-salen complex monomer was improved by using Eu(III) triflate as the lanthanide source instead of Eu(III) nitrate. Third, the ability to reuse the polymer sensor was tested, and both NIP and MIPs were shown to be stable and provided consistent responses after several uses. The polymers were washed with sodium nitrate aqueous solution in order to eliminate the

decrease in binding efficiency after each use. Lastly, a new potential ligand, glycerol 1,3-diglycerolate diacrylate (polyalcohol), was investigated to create different coordination environment for binding analytes. The europium-polyalcohol containing polymer showed strong fluorescent intensity for the benzoate anion, which could be utilized in sensor arrays for identifying benzoate anions.

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# CHAPTER 1

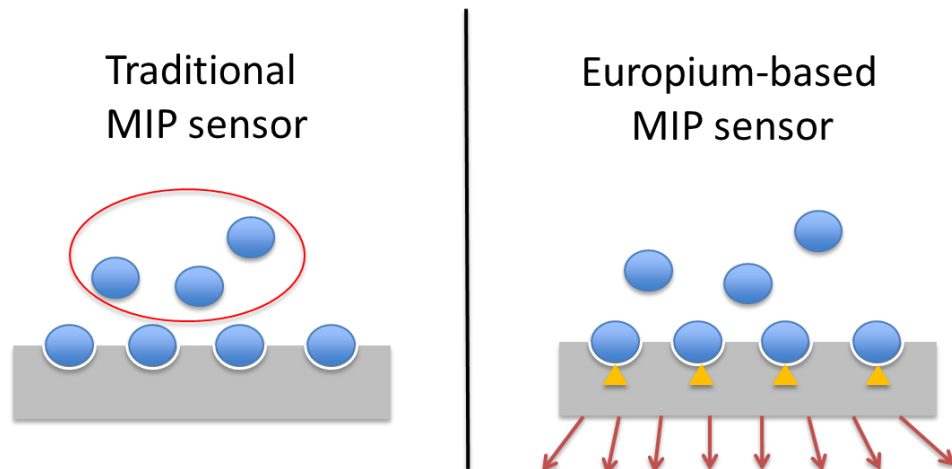
## INTRODUCTION TO EUROPIUM BASED MOLECULARLY IMPRINTED POLYMER

### 1.1 INTRODUCTION

The overall goal of this project is to develop a europium-based imprinted polymer sensor array that can sense and differentiate different types of carboxylate analytes. The development of luminescent materials for anion detection has been an active area of research.<sup>1-3</sup> In particular, lanthanide complexes have been widely investigated as sensing elements in chemosensors due to their narrow and sharp emission band, high luminescent efficiencies high coordination, and long fluorescent lifetimes.<sup>4-7</sup> Immobilization of the lanthanide sensors in a polymer matrix greatly reduces self-quenching (improving signal strength), improves stability and durability, and has better material properties for practical applications.<sup>4,8,9</sup> Sensors targeting carboxylates are of interest due to the importance of carboxylates in organic processes, biological systems and environmental contaminants.<sup>4</sup> To date, no lanthanide-based polymer sensor for carboxylates has been reported.

The difference in signaling efficiency between a traditional MIP sensor and a europium-based MIP sensor is illustrated in Scheme 1.1. The first advantage of the europium-based polymer sensor is the ability to easily and efficiently monitor binding

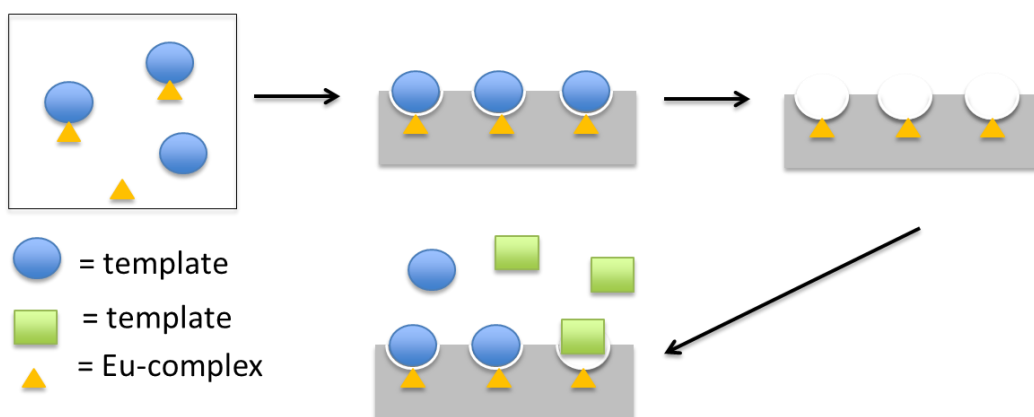
events in the polymer. The binding properties of a traditional MIP sensor are usually obtained indirectly by measuring the change in the analyte concentration in solvent. The europium-based polymer sensor incorporates the responsive europium unit into the polymer matrix and the binding events can be directly observed and quantified by monitoring the emission spectra of the polymer.<sup>10-12</sup> A second advantage of the europium-based polymer is that the europium provides a Lewis acidic recognition site in the polymer, which can coordinate a Lewis basic analyte.<sup>13</sup> The third advantage of the europium-based polymer is the ability to reuse the sensor, making it economically and environmentally friendly. The polymer sensor is in solid-state which is physically and thermally stable, and can be easily washed in an extraction process.



**Scheme 1.1.** Illustration of the differences of measuring the binding efficiency between a traditional sensor and a europium-based sensor. The gray blocks represent the polymer matrix, the blue circles represent analytes, the yellow triangles represent the europium binding sites, and the red arrows represent emission of the Eu-bound analytes.

The fluorescence properties of europium and the molecularly imprinting methodology polymer will be combined together to develop the sensing elements for a sensor array. The overall strategy to make and test the europium-based imprinted polymer is illustrated in Scheme 1.2. The templates and the polymerizable lanthanide

complex are combined and allow them to form a coordination complex, which is immobilized in a polymer matrix. After the templates are washed out, complementary binding sites are formed containing a lanthanide coordination site. In principle, only analytes with the same or very similar shape as the template molecule should be able to fit in the binding cavity and rebind to the lanthanide, leading to a change in the lanthanide's emission properties.<sup>14</sup> The magnitude of the fluorescence response can be used to determine the concentration of the analytes.



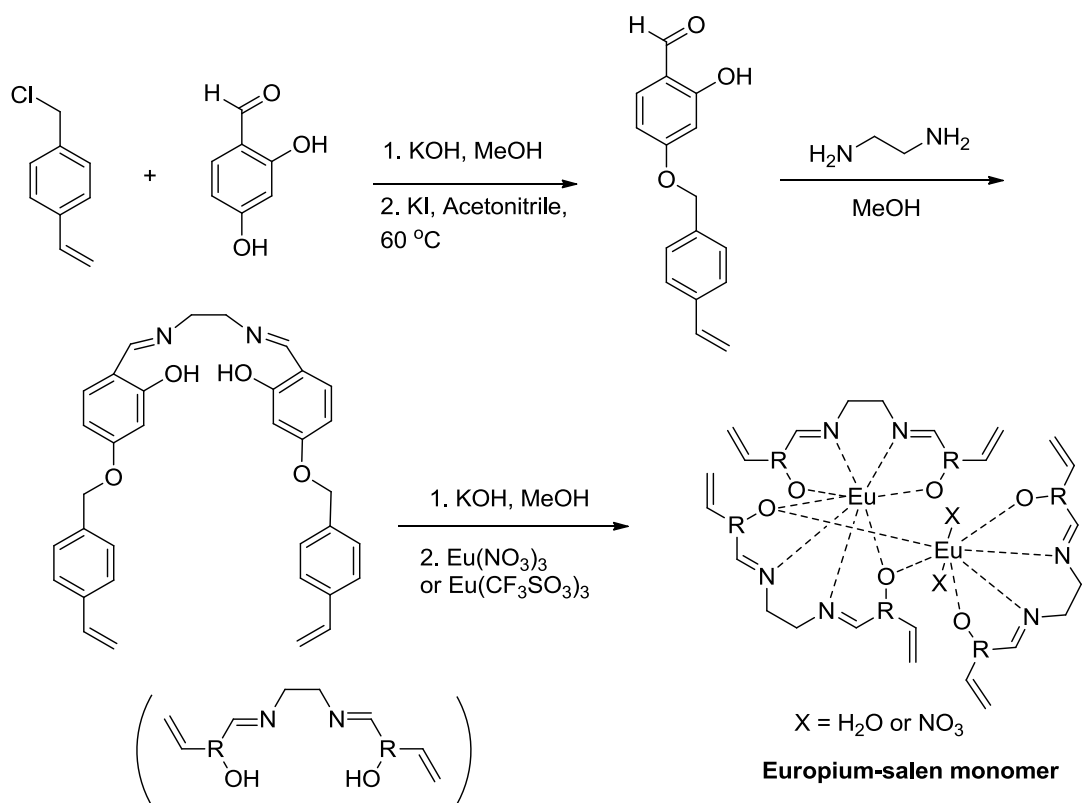
**Scheme 1.2.** Mechanism of europium-based imprinted polymer. The black box represents the polymerization solution, and the templates and europium complex are in free motion. The gray box represents the polymer matrix.

Previously, a europium-based “turn-on” polymer sensor targeting carboxylates was developed by Dr. Di Song from our group. The general strategy used to prepare the europium-based polymer is illustrated in Scheme 1.2. The europium complex was immobilized in the polymer matrix in order to improve the signal strength, stability and durability and prevent self-quenching.<sup>4,8,9</sup> The synthesis of the polymerizable europium complex followed a literature process, as shown in Scheme 1.3.<sup>5</sup> Modifications to the literature procedures included changing the base to potassium hydroxide instead of potassium methoxide, and using europium nitrate as europium source instead of europium triflate. Bis[2-hydroxy-4-(4-vinylbenzyloxy)benzaldehyde]ethylenediimine

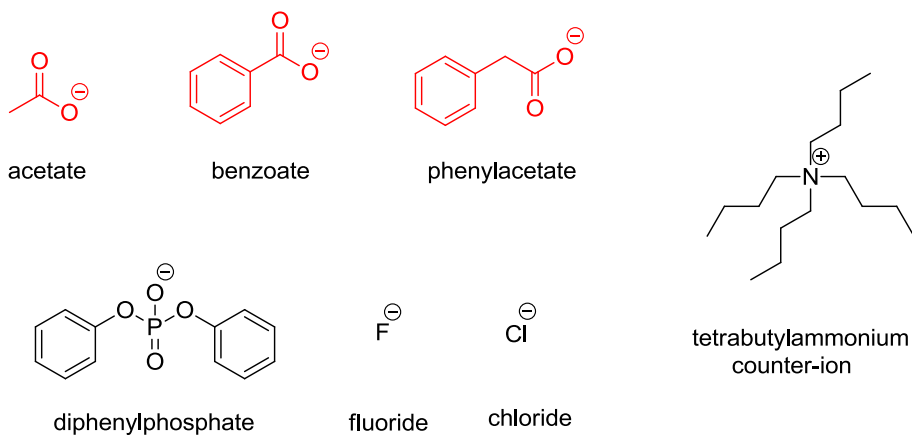
(salen) was chosen as the ligand because the corresponding Eu-complex displayed strong luminescent properties and was stable to the polymerization condition.<sup>4,15-17</sup> Also two vinyl groups on the ends of this ligand allow the complex to be covalently incorporated into the polymer framework.

A total of six analytes anions were tested including fluoride, chloride, diphenyl phosphate (DPP), acetate, benzoate and phenylacetate, and tetrabutylammonium was chosen as the counter-ion. The structures of the anions are shown in Scheme 1.4. The tetrabutylammonium cation was chosen because it is soluble in most organic and aqueous solutions. Acetate, benzoate and phenylacetate were chosen as representative non-aromatic, aromatic conjugated and aromatic non-conjugated to carboxylate analytes in order to test how the aromatic chromophore influence the fluorescent response and binding properties.





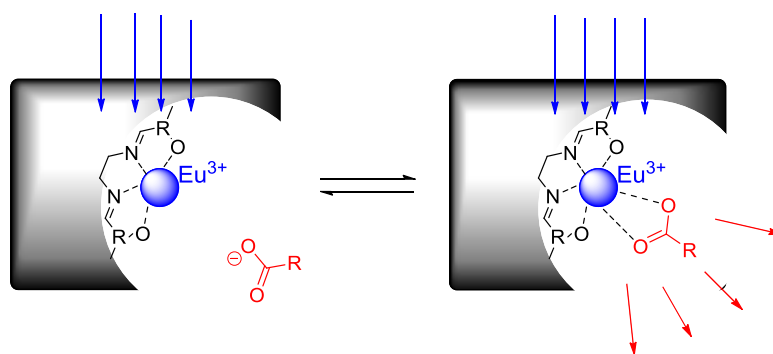
**Scheme 1.3.** Synthesis of the polymerizable europium-salen monomer.<sup>5</sup>



**Scheme 1.4.** List of anions and counter-ion used as templates and analytes for the polymer sensors.

In Dr. Di Song's work, only a responsive non-imprinted polymer was developed. The addition of carboxylate anions to the europium-polymer sensors was observed to enhance the intensity of the europium emission, and the sensor was a "turn-on" sensor in

acetonitrile. The advantage of a “turn-on” sensor is that they have a lower detection limits, because the fluorescence intensity of the “turn-on” sensor increases with increasing analyte concentration. The fluorescence intensity of a “turn-off” sensor decrease with increasing analyte concentration and therefore it can be difficult to detect small change at analytes concentration and also the very low emission intensities at high analytes concentrations. The new sensor could sense both aromatic and non-aromatic carboxylate anions but the intensity of the response were different for these two classed of analytes. The acetate showed the strongest fluorescent response and benzoate showed the lowest fluorescent response. The intensity of the responses appeared to correlate to the size of the analytes. Smaller carboxylates gave the strongest response, because the smaller analytes can the better access the binding sites. The sensor also showed a response to fluoride and an extremely low response to DPP and chloride. Differences were observed between the carboxylate and fluoride binding events. The polymer sensor was titrated with carboxylate and fluoride with series concentrations from 0.15 mM to 3mM. The fluorescent response to the carboxylate anions were all fit to a logarithmic trend line, and the fluorescence response to fluoride fit to an exponential trend line.



**Scheme 1.5.** Representation of europium containing polymer sensor. The gray blocks represent the polymer matrix. The blue spheres represent europium ion. The blue arrows represent absorption or excitation light, and the red arrows represent the emission light.

The ultimate goal of this project was to develop a sensor array that can differentiate carboxylate anions. In this work, several improvements to the previous work will be presented. First, a series of europium-based polymers with different selectivities was made by imprinting the polymers with different anion templates. Second, the poor solubility of the europium-salen monomer in the polymerization solution was improved resulting in a more even distribution of the europium binding sites in the polymers. Third, the re-usability of both the NIP and MIPs was assessed and optimized in order to make the sensor more economical and environmentally friendly. Lastly, in order to create an optimal coordination environment for binding analytes, a new polymerizable ligand for europium, glycerol 1,3-diglycerolate diacrylate, was studied and analyzed for more polymer sensor options.

## 1.2 REFERENCES

- (1) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094.
- (2) Martinez-Manez, R.; Sancenon, F. *Chem. Rev. (Washington, DC, U. S.)* **2003**, *103*, 4419.
- (3) Liu, Z.; He, W.; Guo, Z. *Chem. Soc. Rev.* **2013**, *42*, 1568.
- (4) Yang, C. L.; Xu, J.; Ma, J. Y.; Zhu, D. Y.; Zhang, Y. F.; Liyan, L. Y.; Lu, M. G. *Polymer Chemistry* **2012**, *3*, 2640.
- (5) Mitchell-Koch, J. T.; Borovik, A. S. *Chem. Mater.* **2003**, *15*, 3490.
- (6) Gunnlaugsson, T.; Harte, A. J.; Leonard, J. P.; Nieuwenhuyzen, M. *Supramol. Chem.* **2003**, *15*, 505.
- (7) Shinoda, S.; Tsukube, H. *Analyst* **2011**, *136*, 431.
- (8) Kawa, M.; Frechet, J. M. J. *Chem. Mater.* **1998**, *10*, 286.

- (9) Turkewitsch, P.; Wandelt, B.; Darling, G. D.; Powell, W. S. *Anal. Chem.* **1998**, *70*, 2025.
- (10) Shimizu, K. D.; Stephenson, C. J. *Curr. Opin. Chem. Biol.* **2010**, *14*, 743.
- (11) Stephenson, C. J.; Shimizu, K. D. *Polym. Int.* **2007**, *56*, 482.
- (12) Greene, N. T.; Shimizu, K. D. *J. Am. Chem. Soc.* **2005**, *127*, 5695.
- (13) Mehrotra, R. C.; Kapoor, P. N.; Batwara, J. M. *Coord. Chem. Rev.* **1980**, *31*, 67.
- (14) Rushton, G. T.; Furmanski, B.; Shimizu, K. D. *J. Chem. Educ.* **2005**, *82*, 1374.
- (15) Chen, H. Y.; Archer, R. D. *Macromolecules* **1996**, *29*, 1957.
- (16) Archer, R. D.; Chen, H. Y.; Thompson, L. C. *Inorg. Chem.* **1998**, *37*, 2089.
- (17) Chen, H. Y.; Archer, R. D. *Inorg. Chem.* **1994**, *33*, 5195.

## CHAPTER 2

### IMPROVEMENT AND CHARACTERIZATION OF THE EUROPIUM BASED IMPRINTED POLYMER

#### 2.1 ABSTRACT

The goal of this chapter is to modify and improve the research work on lanthanide-based polymer sensors, which was developed previously by Di Song. The specific goals of this project were: 1) to synthesize the europium-salen based non-imprinted polymer (NIP) form and molecularly imprinted polymer (MIP) forms, and characterize the selectivity of the MIPs for their corresponding analytes, including acetate, benzoate, and phenylacetate. 2) Improve the solubility of the europium-salen monomer in the polymerization solution. 3) Test the reusability of both the NIP and MIPs, improving the efficiency of reusing the polymers. 4) Investigate a new coordination environment at the binding sites by using a polymerizable polyalcohol as a new ligand.

#### 2.2 RESULT AND DISCUSSION

The europium-based polymer sensor model in this study was prepared using a slight modification of the literature procedure.<sup>1</sup> The europium-salen monomer and the ethylene glycol dimethacrylate (EGDMA) crosslinker were added to dichloroethane to make the polymerization solution. Due to the poor solubility of the complex, the pre-polymerization solutions were heated to 80 °C first in order to make sure all the

monomers were completely dissolved. Then azobisisobutyronitrile (AIBN) initiator was added to the pre- polymerization solution without cooling the solution down to start the polymerization.

After the polymerization, the polymers were grounded, sieved and washed. Then the polymer was weighted and suspended into a mix of chloroform and acetonitrile (5 to 1). Next, 10 mg of the polymers in the suspension were pipetted to each well on the 96-well plate. The polymer was air dried and put in oven at 80 °C for 10 min. Finally the polymers were titrated with anion analytes including chloride, fluoride, diphenylphosphate (DPP), acetate, benzoate and phenylacetate in acetonitrile. Tetrabutylammonium cation was chosen as the counter-ion for this work. Measurements of the fluorescent intensity were taken by using a microplate reader. In order to analyze and compare the NIPs and the MIPs, the relative intensity ( $I/I_0$ ), which is defined in Equation 2.1, was employed in this work.

$$\frac{I}{I_0} = \frac{\text{the fluorescence intensity of the polymer titrated with analyte (I)}}{\text{the fluorescence intensity of the polymer titrated with acetonitrile}(I_0)}$$

**Equation 2.1.** Definition of relative intensity used to compare the responses of the MIPs and NIPs.

### **2.3 CHARACTERIZATION OF THE RESPONSE OF EUROPIUM-BASED MOLECULARLY IMPRINTED POLYMERS TO THE ANALYTES**

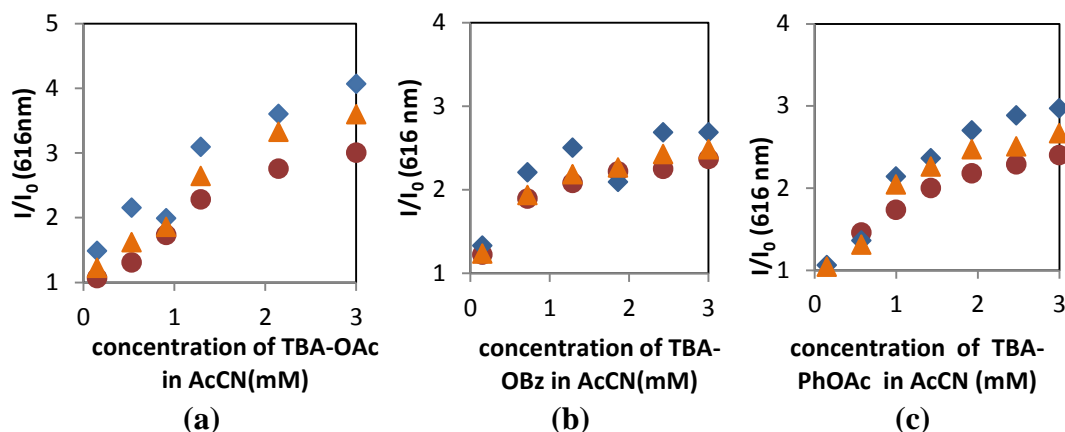
The first aim was to generate a series of Eu-containing polymers by using the molecular imprinting process. Each MIP will be used as a differential sensing element in a carboxylate sensing array. The first question was whether the imprinting process enhanced the binding efficiency of the polymers for the templates. For each template, a series of seven different polymers were made with different template to europium ratios.

(Table 2.1) Each set of polymers was titrated with their corresponding anion solution with concentrations from 0 mM to 3 mM.

**Table 2.1.** The pre-polymerization solution compositions for MIPs

template ratio to Eu	dichloroethane (solvent)	EGDMA	Eu-salen complex	template	AIBN
0				0 mmol	
1				0.052 mmol	
2				0.104 mmol	
3	3.5 mL	5.07 mmol	0.026 mmol	0.156 mmol	0.104 mmol
4		(97.5 mol%)	(0.5 mol%)	0.208 mmol	(2 mol%)
5				0.260 mmol	
6				0.312 mmol	

Normally, lanthanide metal ions prefer a coordination environment from 8 to 10, and the highest coordination number a europium ion can possibly reach is 12.<sup>2-4</sup> According to the published structure of Eu-complex monomer (Scheme 1.3),<sup>1</sup> the europium metal center already has seven fixed coordination sites, and two possible replaceable ligands. For each  $\text{Eu}_2(\text{salen})_3 \cdot 2\text{H}_2\text{O}$  complex, the ligand occupied 6 coordination positions from each europium. There are two X positions were occupied, but with two replaceable ligands. Therefore, the ratio of template to europium used in this work was 6 to 1. By comparing the NIP and MIPs with different ratios of europium and analytes shown in Figure 2.1, the results from all three sets of polymers showed that the relative fluorescent intensity (y-axis) at wavelength 616 nm with excitation at 350 nm increased as the template to europium ratio increased, and the binding efficiency of the MIPs was enhanced by the imprinting process. In order to completely saturate the Eu coordination sites, the highest mole ratio of template to europium of 6 to 1 was sufficient.



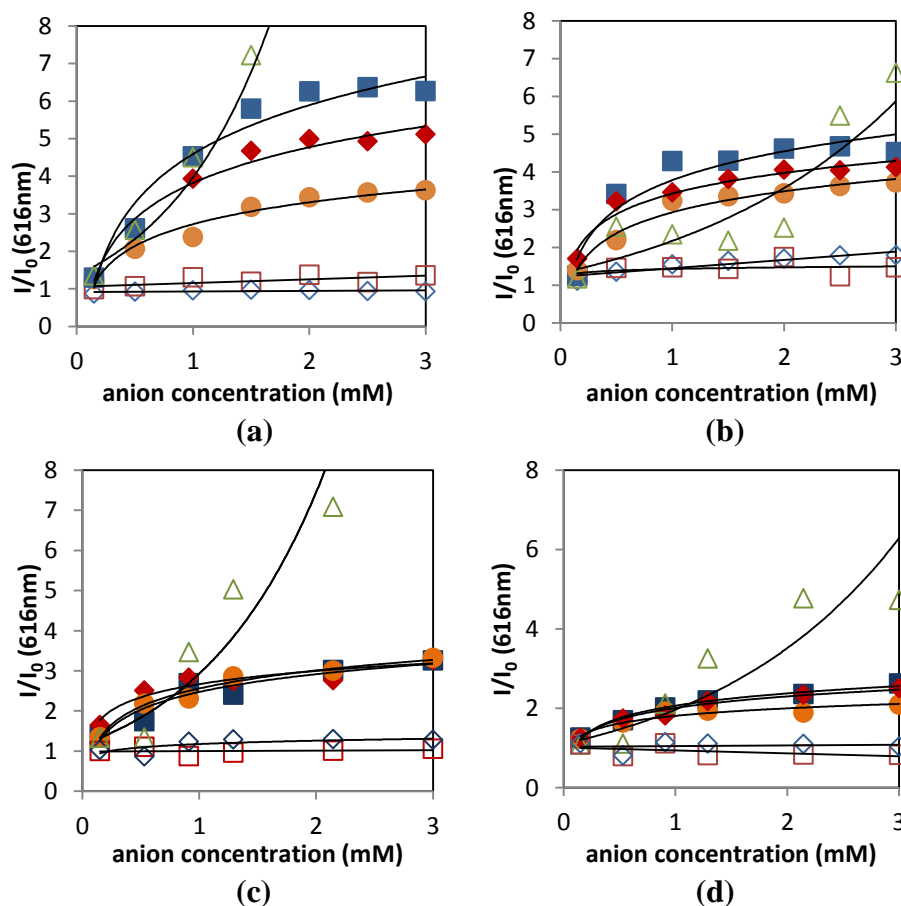
**Figure 2.1.** Comparison the relative fluorescent intensity at 616 nm (excitation at 350 nm) of MIPs (9.5 mg) and their corresponding NIP (9.5mg) in response to increasing concentration of corresponding anions in ranges 0 to 3 mM in acetonitrile (a) MIP with TAB-acetate template (b) MIP with TBA-benzoate template (c) MIP with TBA-phenylacetate template. MIP had template to europium ratios of 6:1 (blue diamond); MIP had template to europium ratios of 4:1 (yellow triangle); NIP had template to europium ratio of 0:1 (red circle).

The second question is: how do the specific templates affect the selectivity or sensing trends for other anions? Four sets of polymers were prepared. The first set was the NIPs, which were not prepared without any anion template. The other three sets of polymers were MIPs imprinted with acetate, benzoate, and phenylacetate templates at europium to template ratios of 6:1. Each set of polymers were titrated with anion analytes chloride, fluoride, diphenyl phosphate, acetate, benzoate and phenylacetate with concentrations from 0 mM to 3 mM.

By comparing the anion response profiles (Figure 2.2), the MIPs and NIP show different response patterns. The results indicate that MIPs made with different templates had different selectivities. The selectivity patterns appeared to be highly sensitive to the size of the template; benzoate, as the largest anion, showed a very high response on the polymer imprinted with benzoate, which is very close to the other two. For the phenylacetate imprinted polymer, the relative intensity with phenylacetate was drastically



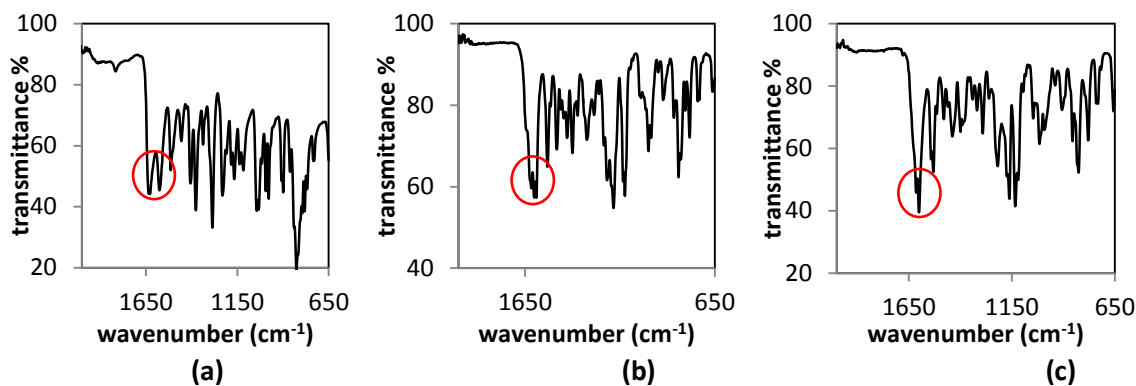
lower and the intensity of acetate is very close to the phenylacetate. The MIP imprinted with acetate, which is the smallest anion, only shows the decreasing in the relative intensity, but the response to carboxylates does not show an obvious preference to acetate. The response patterns from MIPs appear to be different, which is one of the features for the elements of sensor array. The templates were displaced the nitrate on the europium complex monomer, therefore the  $I_0$  of the MIP was higher than the  $I_0$  of the NIP. Ultimately, the MIPs made with different templates will combined and used in a series and eventually achieved a sensor array.



**Figure 2.2.** Comparison the relative fluorescent intensity at 616 nm(excitation at 350 nm) (a) NIP; (b) acetate anion imprinted polymer; (c) benzoate anion imprinted polymer; (d) phenylacetate anion imprinted polymer. Chloride anion (empty diamond), DPP anion (empty square), fluoride anion (empty triangle), acetate anion (solid square), benzoate anion (solid circle), phenylacetate anion (solid diamond)

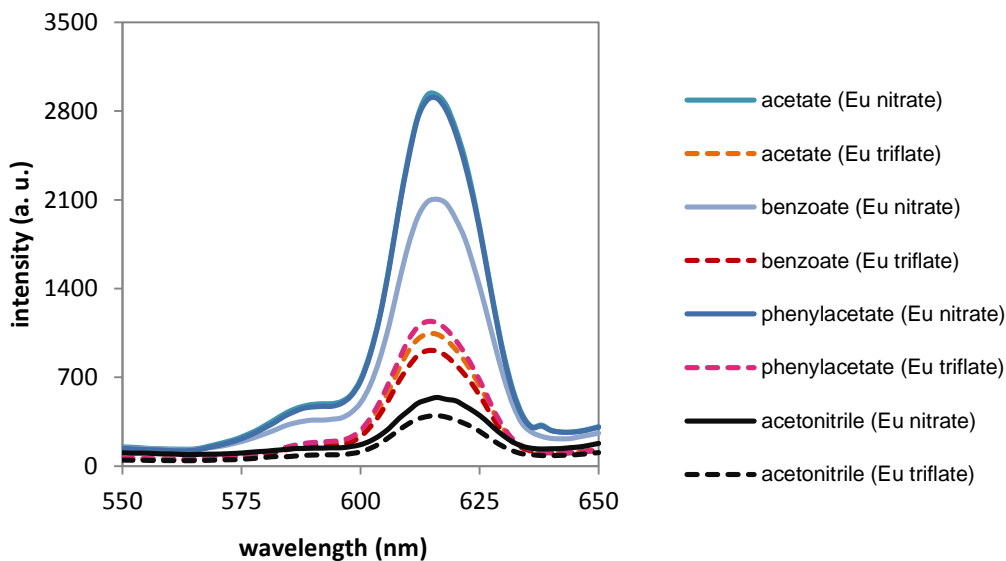
## 2.4 IMPROVEMENT OF THE SOLUBILITY OF EUROPIUM-SALEN MONOMER

During polymerization process, the original europium-salen complex showed very poor solubility in the pre-polymerization solution. The high variability in the test results and the poor detection limit may be due to the inefficient incorporation of the complex into the polymer. The low solubility of the complex in the polymerization solution reduces the actual amount of the complex immobilized in the polymer framework. Also, the poor solubility of the monomer in the polymerization solution can result in an uneven distribution of the binding sites in the polymer matrix. This can lead to an uneven distribution of the concentration of europium in each sample well. Since the solubilities of the europium-salen complex were improved by adding analytes into the pre-polymerization solution, this section will focus on improving the solubilities of the NIPs. In order to improve the solubilities of the europium-salen complex, the europium-salen complex was remade from europium trifluoromethanesulfonate (triflate) which showed a better solubility in dichloroethane than the original europium nitrate complex. Infrared spectroscopy was used to verify that the Eu(triflate)-salen complex had been successfully synthesized (Figure 2.3). The IR spectra of both Eu(nitrate)-salen complex and Eu(triflate)-salen complex shows that peaks at  $1650\text{cm}^{-1}$  (C=N bond) became sharper than the peak of salen at  $1650\text{cm}^{-1}$ .<sup>1</sup>



**Figure 2.3.** IR spectra for (a) salen; (b) europium nitrate – salen complex; (c) europium triflate – salen complex.

The europium triflate-salen complex showed improved solubility by completely dissolving in the pre-polymerization solution at 40 °C as opposed to 80 °C. After processing, the Eu(nitrate)-salen NIP and Eu(triflate)-salen NIP were titrated with TBA-acetate, TBA-benzoate, and TBA-phenylacetate at concentrations of 3 mM. The emission spectra of the two polymers are shown in Figure 4.



**Figure 2.4.** The emission spectra (excitation at 350 nm) of 10 mg of Eu(nitrate)-salen NIP (solid line) and 10 mg of Eu(triflate)-salen NIP (dash line). Both of NIPs titrated with 0.3 mL of TBA acetate, TBA benzoate and TBA phenylacetate at concentration of 3 mM in acetonitrile.

The NIP made with the europium triflate-salen polymer showed a smaller change in intensity in the presence of the analytes as compared to the polymer made with the europium nitrate-salen polymer. As shown in Figure 2.4, all the blue solid lines represent europium nitrate-salen complex and all the red lines represent europium triflate complex. The europium triflate-salen polymer shows a general trend of sensing acetate, benzoate and phenylacetate anions, where the response to acetate has highest fluorescent intensity and the response to benzoate has the lowest fluorescent intensity. This trend from europium triflate-salen polymer appears to be the same as the trend from europium nitrate-salen polymer. The magnitude differences of the response intensity between europium triflate-salen polymer and europium nitrate-salen polymer most likely due to the stronger binding of the triflate anion to the europium than the nitrate anion.

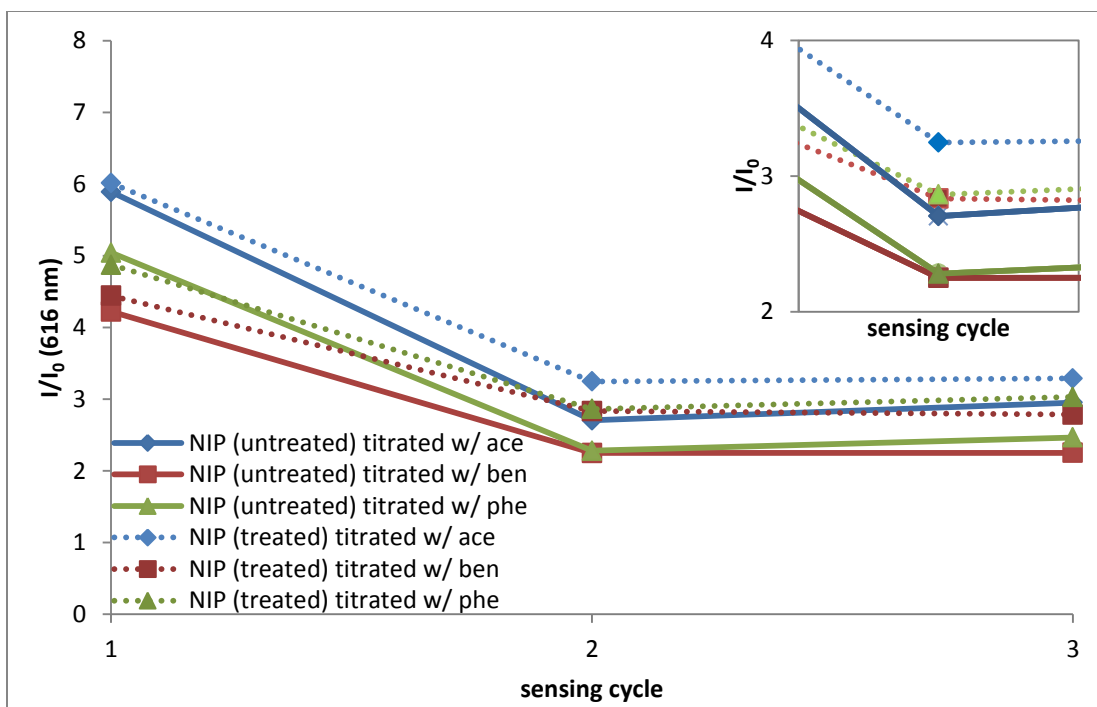
## **2.5 TESTING THE REUSABILITY OF THE POLYMER SENSORS AND OPTIMIZING THE REUSE OF THE POLYMERS**

The ability to reuse the polymer sensor is a very important property for future applications as it would make the sensor more economically and environmentally friendly. To investigate the polymers' reusability, the polymers were collected after each sensing cycle and washed with methanol for 12 hours, and then washed with mixture of methanol and acetonitrile (1:4) for another 12 hours in a Soxhlet extractor. The polymers were dried under vacuum for 6 hours. In each sensing cycle, the polymers were titrated with TBA-acetate, TBA-benzoate, or TBA-phenylacetate solutions in acetonitrile (3 mM). The acetate, phenylacetate, benzoate and nitrate anions are the conjugated bases of acetic acid, phenylacetic acid, benzoic acid and nitric acid which have pKa values of 4.8, 4.3, 4.2 and -1.3 respectively.<sup>5</sup> The acetate is the most basic anion and the nitrate is the

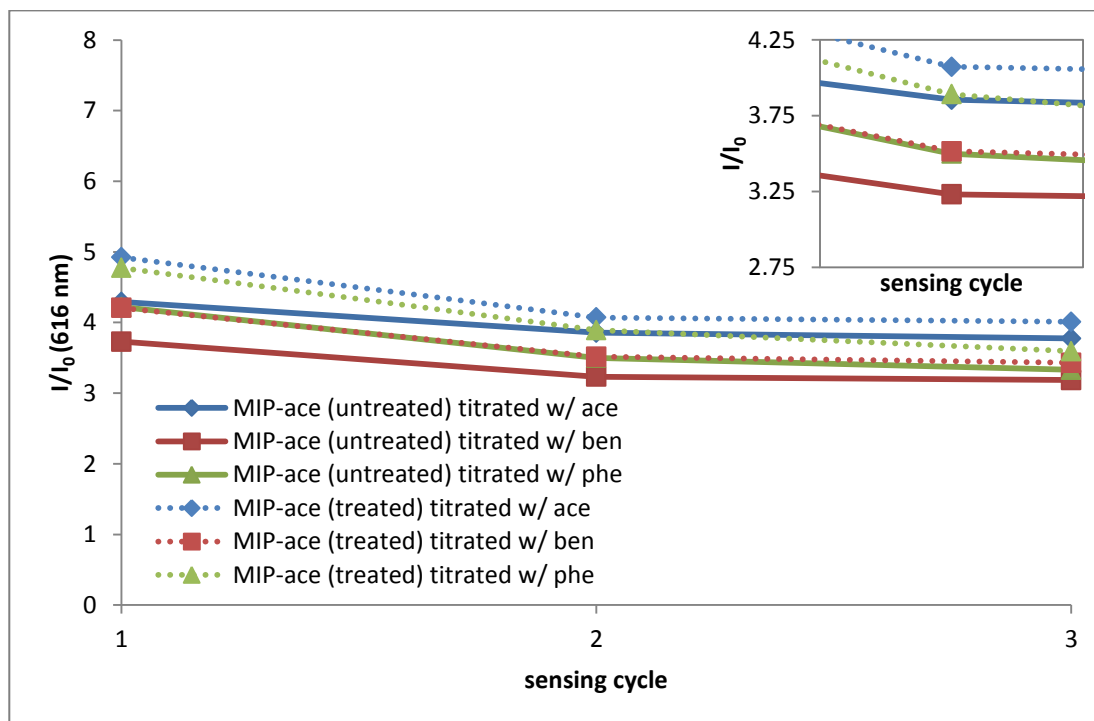
least basic. Therefore, we expected that the acetate would have the highest binding affinity for the Lewis acidic europium metal center and nitrate the weakest.<sup>6</sup>

Initially, the NIP, the MIP imprinted with benzoate, and the MIP imprinted with phenylacetate showed a fluorescent intensity drop of about 50% after the first use (Figure 2.5, solid lines). However, the fluorescent intensity of these polymers stabilized after the second sensing cycles. The decrease in fluorescent intensity after the first sensing cycle of the NIP was due to the presence of nitrate anions in the initial europium complex. The nitrate anion had a weaker binding affinity for europium than the carboxylate anions. After the first sensing cycle, the nitrate anions were replaced by carboxylate anions. The same anion substitution occurs in the MIPs where the anion templates are replaced with higher binding anions such as acetate.

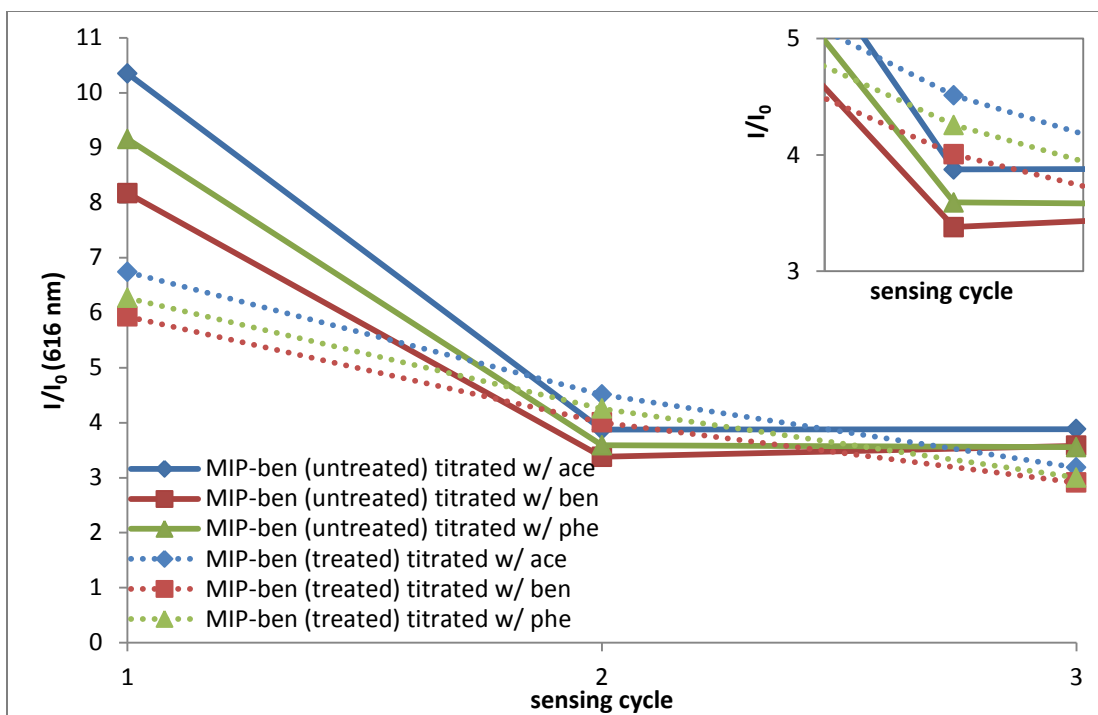
In order to have the same anion bound to the europium of all polymers, both the NIP and MIPs were washed with a 0.3 M concentration sodium nitrate aqueous solution. Nitrate was chosen as the common anion because the nitrate anion has the weakest binding affinity for europium and should be easily displaced by the more strongly binding carboxylate anions. All of the polymers washed with  $\text{NaNO}_3$  showed higher relative intensity than after the first use (Figure 2.5). There was only a small change in terms of relative intensity for MIP imprinted with acetate after the first sensing cycle. The MIP imprinted with acetate has the most basic acetate anion bond to the europium which is only partially replaced by any other anions. The MIP imprinted with benzoate (Figure 2.5c) shows a continuously decreasing relative intensity with an increasing number of cycles.



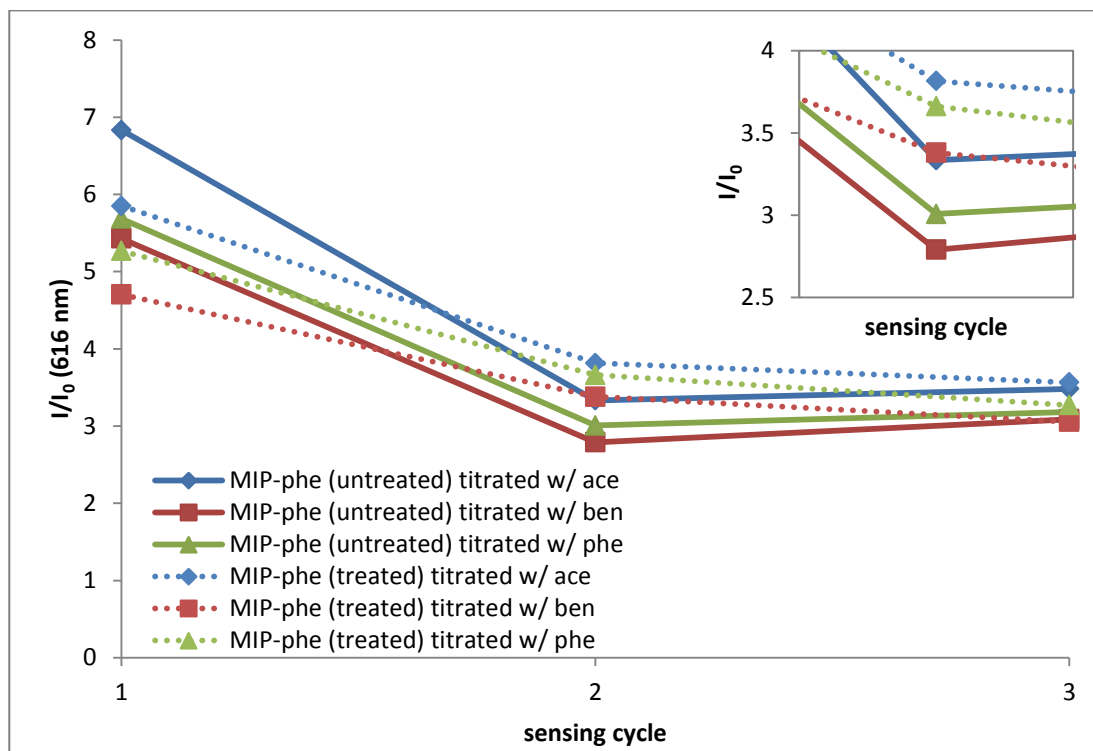
(a)



(b)



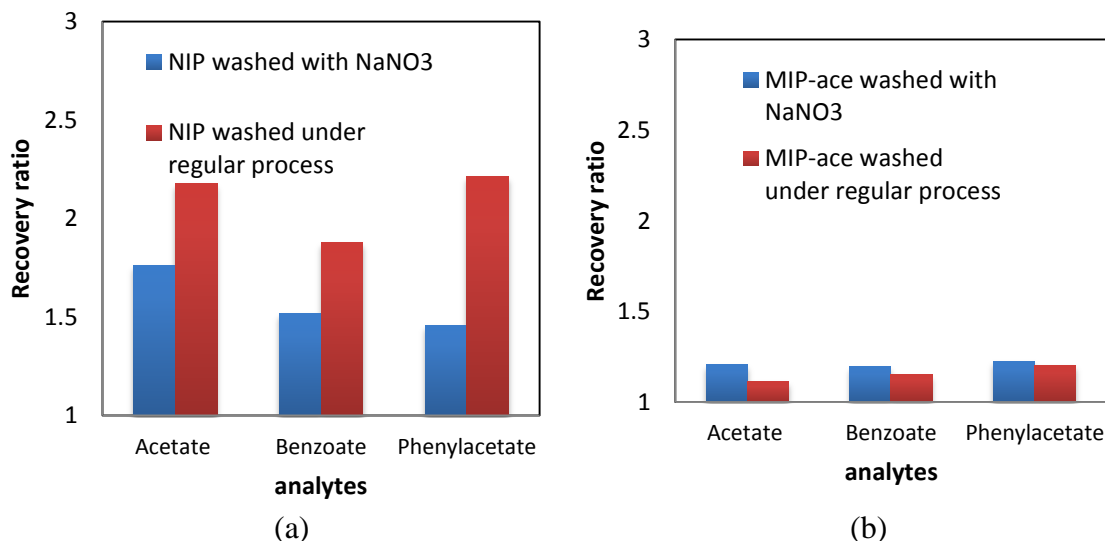
(c)



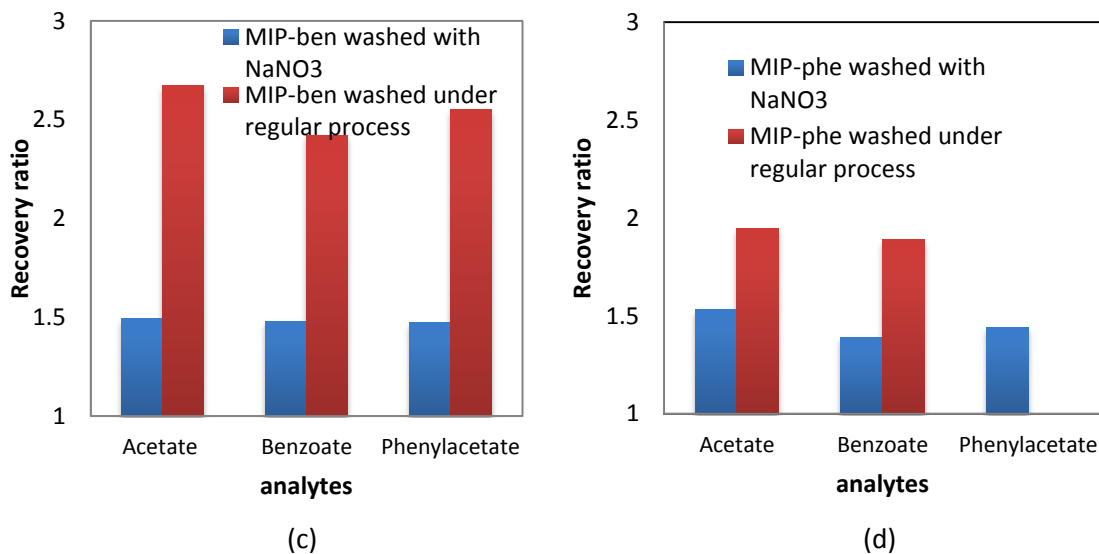
(d)

**Figure 2.5.** Changes in the relative fluorescent intensities at 616 nm (excitation at 350 nm) of Eu nitrate polymer (10 mg) (a) NIP; (b) TAB-acetate MIP; (c) TBA-benzoate MIP; (d) TBA-phenylacetate MIP, when tested with 300 $\mu$ L of 3 mM of acetate anion (blue), benzoate anion (red) and phenylacetate anion (green) in acetonitrile. The solid lines represent the polymers without washing with sodium nitrate and dash lines represent the polymers washed with sodium nitrate. The insert graph is magnified view of the second sensing cycle.

The recovery ratio, which was defined as the ratio of the relative intensity of the first use of the polymers to the relative intensity of the second use of the polymers, will be compared and used to indicate the effectiveness of the ion-exchange process. A recovery ratio closer to 1 indicates that the relative intensity was closer to the relative intensity of the first use of the polymer and the polymer was effectively washed. As shown in Figure 2.6, all the polymers show the differences between the polymer treated with sodium nitrate and the one without treatment. The polymers including NIP, MIP imprinted with benzoate and MIP imprinted with phenylacetate show a significant improvement in the recovery ratio after washing with the sodium nitrate aqueous solution.



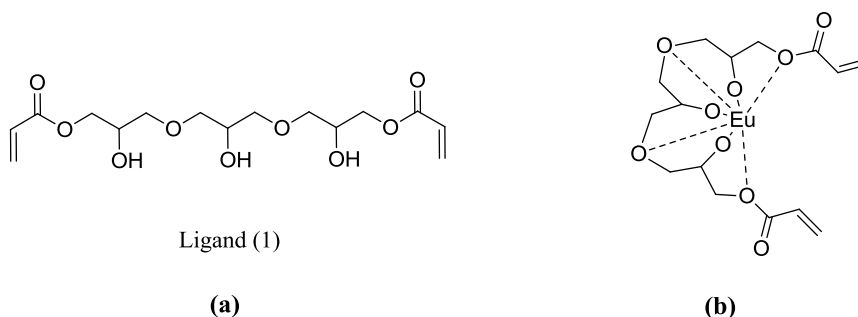




**Figure 2.6.** Comparison of the recovery ratio of the polymer washed with sodium nitrate and the polymer washed under regular process. (a) NIP; (b) MIP imprinted with acetate; (c) MIP imprinted with benzoate; (d) MIP imprinted with phenylacetate.

## 2.6 INVESTIGATION OF NEW BINDING ENVIRONMENT BY USING NEW LIGAND

The europium binding sites were shown to be very sensitive to the local binding environment. Two polymers were prepared by using same europium salt and ligand, but one polymer was prepared with base (Figure 2.8) and the other polymer (Figure 2.7) did not prepared with base. The response intensity patterns for two polymers are very different. Therefore, changing the ligand coordinated with the europium should change the binding environment and the fluorescence properties (relative intensity) of sensing the analytes. Polyalcohol (glycerol 1,3-diglycerolate diacrylate) (PA) was chosen and tested as potential monomer for preparing the europium-contained sensor. One of the advantages of this new ligand is that it is commercially available. Also, the polyalcohol ligand has three hydroxide groups and can fully coordinate with Eu at an oxidation state of +3, and forms a neutral system without any counter-ion, which can limit the inference of the counter-ion while testing analytes.



**Scheme 2.1.** Structure of polymerizable polyalcohol ligand (1) and possible coordination structure with europium.

Attempts to synthesize the complex involved, both europium nitrate and europium triflate were tested as well as both organic and inorganic bases, potassium hydroxide and triethyl amine.

**Table 2.2.** Mole ratios of polyalcohol, europium salt, base and co-ligand for making Eu-complex.

	ratio
<b>PA: Eu</b>	<b>4:1</b>
<b>PA:Eu:KOH</b>	<b>4:1:12</b>
<b>PA:Eu:Et<sub>3</sub>N</b>	<b>4:1:12</b>

To make the polymer, 0.025 mmol (1 mol%) europium salt was suspended in 1 mL acetonitrile, then 2.425 mmol (97 mol%) of crosslinker EGDMA was added to the suspension. The suspension was sonicated and heated to 60 °C. After all the complex dissolved, 0.05 mmol (2 mol%) AIBN as initiator was added to the polymerization solution, and allowed to polymerize at 60 °C for 8 hours. The resulting polymers were titrated with six anion analytes (fluoride, chloride, DPP, acetate, benzoate and phenylacetate) with tetrabutylammonium as the counter ion.

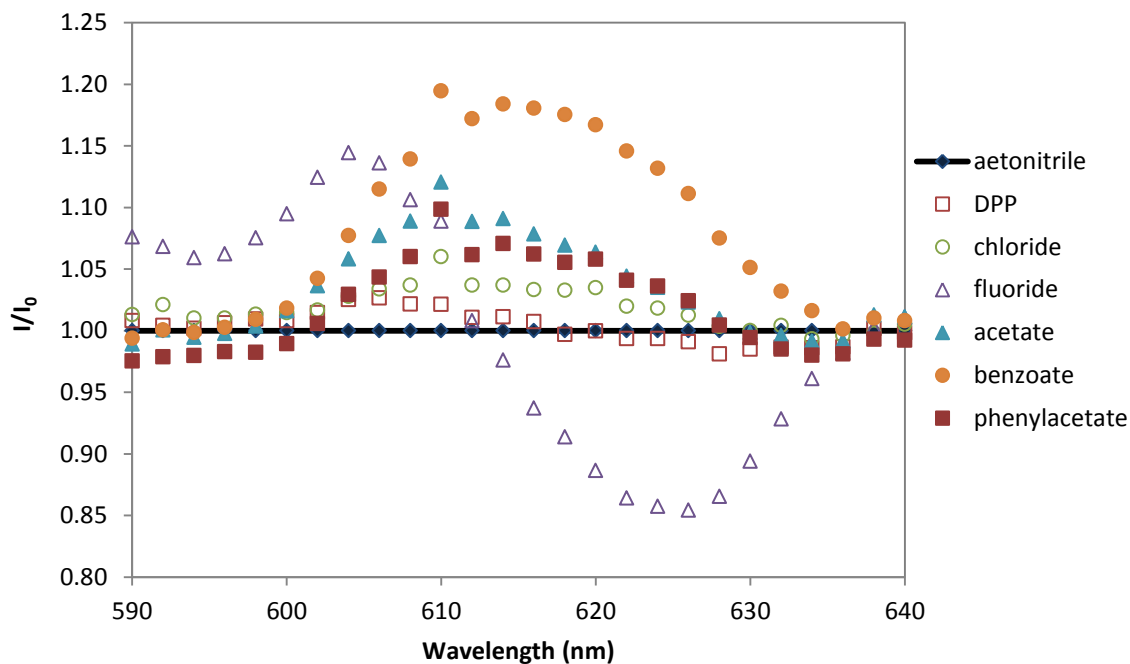
**Table 2.3.** The solubility of Eu-polyalcohol complex in acetonitrile as formed in different conditions.

<b>soluble</b>	<b>partially soluble</b>	<b>Insoluble</b>
	PA/Eu(nitrate)	PA/Eu(nitrate)/KOH
PA/Eu(triflate)	PA/Eu(nitrate)/Et <sub>3</sub> N	
PA/Eu(triflate)/Et <sub>3</sub> N	PA/Eu(triflate)/KOH	

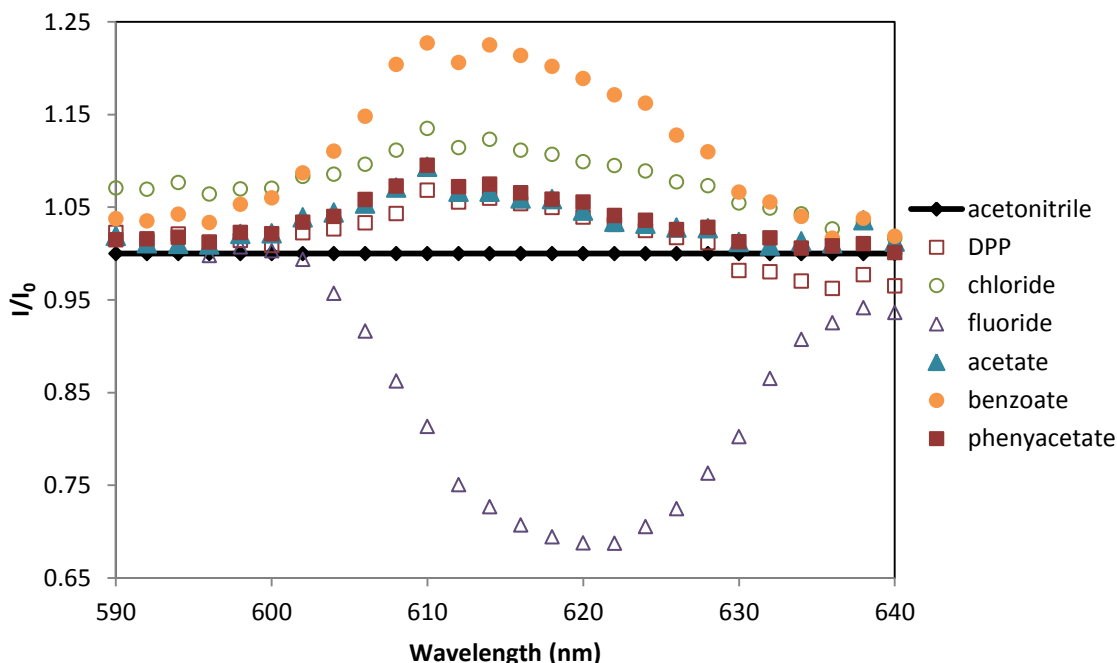
The solubility properties of all the monomers are shown in Table 2.3. Complexes formed by using inorganic bases showed very poor solubilities in the polymerization solution with solvent of acetonitrile. PA/Eu(nitrate)/KOH did not polymerize due to their extremely low solubilities even at 80 °C. Only two monomers, PA/Eu(triflate) and PA/Eu(triflate)/Et<sub>3</sub>N, were able to polymerize.

From previous study, the Eu-salen polymer had a turn-on response to acetate, benzoate, phenylacetate and fluoride, and has slightly to chloride and DPP. The relative intensity of acetate, benzoate, and phenylacetate are around 5. By comparison, the relative intensity of both the PA/Eu(triflate) polymer and the PA/Eu(triflate)/Et<sub>3</sub>N polymer are very small which is around 1.2 (Figure 2.7 and Figure 2.8). Small relative intensity may indicate that the ligand is not a very good chromophore. Both polymers had responses not only to carboxylates but to all anions. The responses to chloride, DPP, acetate and phenylacetate are very close, which cannot be used to distinguish carboxylate and other anions. The responses varied between turn-on response and turn-off response for fluoride. The PA/Eu(triflate) polymer and PA/Eu(triflate)/Et<sub>3</sub>N polymer showed mostly turn-on responses. Surprisingly, the intensity *I* after titrated with the fluoride anion are smaller than its *I*<sub>0</sub>, which means the polymers showed a turn-off response to fluoride anion. The property of turn-off response to the fluoride anion can be used to eliminate the interference of the fluoride ion in sensor arrays. Another discovery is that

the responses to benzoate were strongest and distinguishable from all other analytes tested. The possible reason for this observation is that the carboxylate group directly connects to a benzene ring, which enhances the energy transfer to the europium. Therefore, this polymer formed using polyalcohol as ligand will be very useful tool for distinguishing the benzoate anion and eliminate fluoride anion.



**Figure 2.7.** The fluorescent intensity (excitation at 350 nm) of Eu(nitrate)/PA polymer (10 mg) tested by acetonitrile solvent, chloride , DPP , acetate, benzoate, and phenylacetate at concentrations of 3 mM.



**Figure 2.8.** The fluorescent intensity (excitation at 350 nm) Eu(nitrate)/Et<sub>3</sub>N/PA polymer (10 mg) tested by acetonitrile solvent, chloride, DPP, acetate, benzoate, and phenylacetate at concentrations of 3 mM.

## 2.7 CONCLUSION

First, in comparison with NIP, the MIPs imprinted with different analytes showed different sensing response patterns. Thus, the MIPs have high potential to be used in a sensor array to discriminate carboxylates. Other different carboxylate anion with more distinguishable function group or larger size should be investigated as new analytes and eventually establish a complete sensor array system. Second, by using europium triflate to improve the solubility of the europium-salen complex in the polymerization solution, europium triflate-based polymer shows a similar trend of response to all types of analytes as europium nitrate. But the low fluorescent intensity obtained from europium triflate-based polymer might cause inaccurate measurements in future work. Next, the study of reusability of both NIP and MIPs showed a consistent and stable response after several uses, which ensured the possibility of practical applications. The NIP and the MIPs

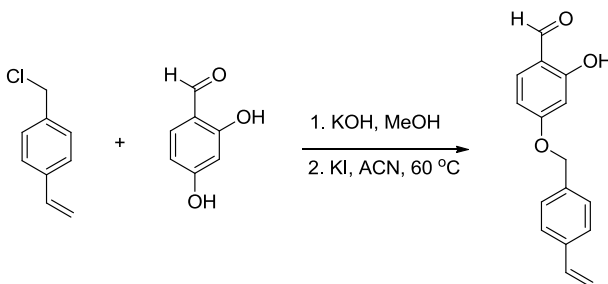
polymers treated with sodium nitrate aqueous solution showed significant recovery of the binding efficiency in terms of higher relative intensity than the NIP and MIPs without treatment. Lastly, the new ligand of polyalcohol showed its potential to be a coordination ligand in polymer based sensor, but much further study needed to be done by this point.

## 2.8 EXPERIMENTAL

### 2.8.1 General Experimental

NMR spectra were recorded on a Varian 300 MHz NMR at ambient temperature. UV measurements were obtained by using MDS SpectraMax M2 microplate reader. All the reagents were of commercial grade and purchased from Sigma-Aldrich and Fischer scientific without further purification. The synthesis of the monomer and polymer were followed a literature procedure with slightly modification.<sup>1,7-10</sup>

### 2.8.2 2-hydroxy-4-(4-vinylbenzyloxy) benzaldehyde

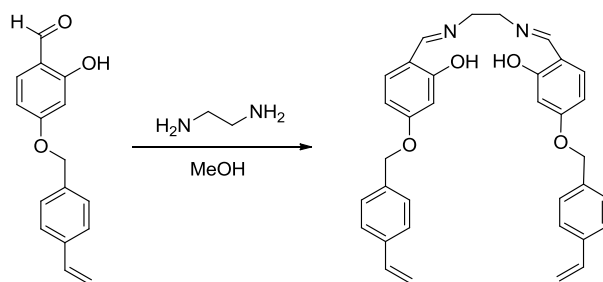


**Figure 2.9** Synthesis 2-hydroxy-4-(4-vinylbenzyloxy) benzaldehyde.

In 30 mL methanol, the 2,4-dihydroxybenzaldehyde (3.5 mmol) was dissolved and then 4.5 mmol of potassium hydroxide was added at room temperature. After 1 hour, the solvent was removed by rotary evaporator and light pink solid was collected. The solid was suspended in 40 mL of acetonitrile. The 4-vinylbenzyl chloride (4.0 mmol) was added to the suspension and then 1.2 mmol (30% of 4-vinylbenzyl chloride) of potassium iodide was added to the mixture. The reaction was heated at 60 °C for 24 hours under

reflux. The reaction suspension was filtered and the solution part with very dark red color was collected. The solvent of the solution was evaporated dried and the remaining was vacuum dried for 12 hours. The obtained solid was dissolved in mixture of 50 mL of water and 100mL of ethyl acetate mixture. Five drops of diluted HCl solution (0.1 mM) was added quickly when organic layer and aqueous layer were in emulsified stage (or adding HCl dropwise until the pH value of the aqueous layer reached 7). Both aqueous and organic layer were collected. The aqueous layer was washed with small amount ethyl acetate and the organic layer was collected and combined with original organic layer and the entire organic layer was washed with 3 wt% potassium carbonate aqueous solution three times. The dark red organic layer turned to yellow once mixed with potassium carbonate solution, and the organic layer was collected. Then the organic layer was washed with deionized water three times and the yellow organic layer was collected. Lastly, the organic layer was washed with 5 wt% citric acid aqueous solution three times. A very light yellow organic layer was observed and collected. The organic solution was dried by magnesium sulfate for 3 hours. The solvent was evaporated and the residue was recrystallized in ethyl acetate. A white crystalline solid (0.4274 g) was obtained as the final product with yield of 48%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.72 (s, 1 H), 7.42 (m, 5 H), 6.73 (dd,  $J = 17.7$  Hz,  $J = 10.8$  Hz, 1 H), 6.62 (dd,  $J = 8.7$  Hz,  $J = 1.8$  Hz, 1 H), 6.50 (m, 1 H), 5.75 (d,  $J = 17.7$  Hz, 1H), 5.27 (d,  $J = 10.8$  Hz, 1H), 5.10 (s, 2 H).

### 2.8.3 Bis[2-hydroxy-4-(4-vinylbenzyloxy)benzaldehyde]ethylenediimine (salen)



**Figure 2.10** Synthesis salen ligand.

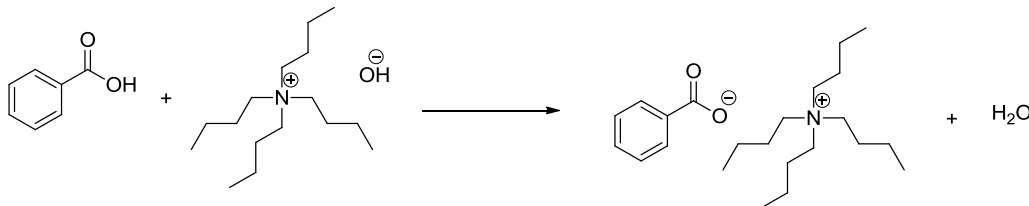
The 2-hydroxy-4-(4-vinylbenzyloxy) benzaldehyde (1.0 mmol) was suspended in 30 mL methanol in a round bottom flask cooled in an ice bath. The ethylenediamine (0.5 mmol) was dissolved in 3 mL methanol and the solution was slowly added to the suspension every 10 minutes in three separate portions. After adding ethylenediamine, the ice bath was removed and the reaction was stirred at room temperature for 12 hours. The precipitates was filtered and washed with ether. A neon yellow solid was collected and vacuum dried. The weight of the final product was 0.2576 g and yield was 96.7%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.20 (s, 2H), 7.38 (m, 8 H), 7.75 (d,  $J = 8.4$  Hz, 2 H), 6.68 (dd,  $J = 17.7$  Hz,  $J = 10.8$  Hz, 2 H), 6.45 (m, 4 H), 5.75 (d,  $J = 17.7$  Hz, 2H), 5.25 (d,  $J = 17.7$  Hz, 2H), 5.04 (s, 4 H), 3.84 (s, 4 H).

### 2.8.4 $\text{Eu}_2(\text{salen})_3(\text{H}_2\text{O})_2$ (salen-europium complex)

In 50 mL methanol, salen (0.3 mmol) was suspended, and then 0.6 mmol of potassium hydroxide was added to the suspension. The reaction was stirred for one hour at room temperature. Europium nitrate (or europium trifluoromethanesulfonate 0.21 mmol) was added to the suspension and reflux at 70  $^\circ\text{C}$  for 1 hour. The reaction was stirred at room temperature for 24 hours. A pale yellow precipitate was collected with weight of 0.1792 g and 92.8% yield.



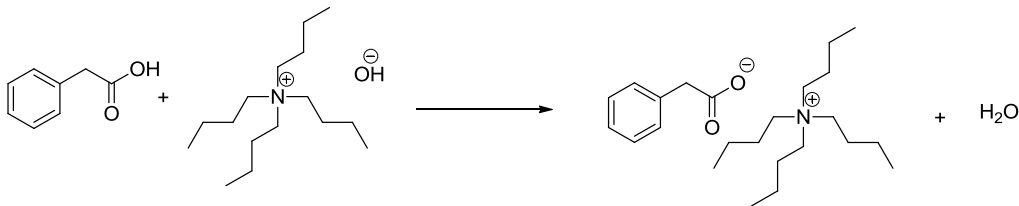
### 2.8.5 Tetrabutylammonium benzoate



**Figure 2.11.** Synthesis TBA benzoate analyte.

To 50 mL methanol, benzoic acid (4 mmol) was added, and then tetrabutylammonium hydroxide 30-hydrate (4 mmol) was added to the solution. The reaction was kept at room temperature for 6 hours. The solvent was removed using a rotary evaporator. The water was removed by adding toluene to the flask and dried by rotary evaporator, and this step was repeated several times. A light brown liquid was collected and dried under vacuum. Toluene was added and removed by rotary until the product was solidified under vacuum. A light brown solid was obtained with a 95% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 7.97 (m, 2 H), 7.28 (m, 3 H), 3.26 (m, 8 H), 1.63 (m, 8 H), 1.42 (m, 8 H), 0.98 (m, 12 H).

### 2.8.6 Tetrabutylammonium phenylacetate



**Figure 2.12.** Synthesis TBA phenylacetate analyte.

To 50 mL methanol, phenylacetate acid (4 mmol) was added, and then tetrabutylammonium hydroxide 30-hydrate (4 mmol) was added to the solution. The reaction was going under room temperature for 6 hours. The solvent was removed by rotary evaporator. The water was removed by adding excess of toluene to the flask and

dried by rotary evaporator, and this step was repeated for several times. A light brown liquid was collected and dried under vacuum. Toluene was added and removed by rotary until the product was solidified under vacuum. A light brown solid was obtained with a 97% yield.  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$ : 7.30 (d,  $J = 7.5$  Hz, 2 H), 7.22 (d,  $J = 7.2$  Hz, 2 H), 3.39 (m, 8 H), 3.21 (m, 3 H), 1.56 (m, 8 H), 1.38 (m, 8 H), 0.99 (m, 12 H).

### 2.8.7 Eu(salen) Polymers

To a 7 mL vial, dichloroethane (3.5 mL) and ethylene glycol dimethacrylate (EGDMA) (0.95 mL) were added. Europium salen complex (0.05 g) was weighted and added to the vial. Then the vial was set in oil bath at 80 °C until the complex completely dissolved. AIBN (0.104 mmol) was added to the solution in the vial and allowed to polymerize for 8 hours. After polymerization, the glass reaction vial was cracked and the polymer was collected and grounded to fine particles. The polymer was dried under vacuum for 2 hours and sieved by using the sieve with the opening size of 150  $\mu\text{m}$ . The polymer was first washed with methanol for 12 hours and then methanol acetonitrile mixture (1:4 ratio) for 12 hours by using a Soxhlet extraction system, and then vacuum dried to yield yellow NIP polymer. The MIP's were prepared under the same condition with addition of 0.052 mmol, 0.104 mmol, 0.156 mmol, 0.208 mmol, 0.260 mmol and 0.312 mmol of tetrabutylammonium acetate, tetrabutylammonium benzoate, and tetrabutylammonium phenylacetate to the polymerization solution. The MIPs were soaked in their corresponding 10 mM anion solutions for 30 minutes.

### 2.8.8 Eu(polyalcohol) complex

**Preparation without base:** To 30 mL of methanol, glycerol 1,3-diglycerolate diacrylate (1.2 mmol) was added. Then europium nitrate (0.3 mmol) or europium triflate

(0.3 mmol) was added to the solution and heated at 70 °C for 3 hours. Then, the reaction was stirred at room temperature for 12 hours. Solvent was evaporated and residue was vacuum dried.

**Preparation with base:** To 30 mL of methanol, glycerol 1,3-diglycerolate diacrylate (1.2 mmol) was added and then KOH (3.6 mmol) or triethyl amine (3.6 mmol) was added and reacted for one hour. Then europium nitrate (0.3 mmol) or europium triflate (0.3 mmol) was added to the solution and heated at 70 °C for 3 hours. Then, the reaction was stirred at room temperature for 12 hours. Solvent was evaporated and residue was dried under vacuum.

#### **2.8.9 Eu(polyalcohol) polymer**

Acetonitrile (1 mL) and EGDMA (0.472 mL) was added to a glass reaction vial. The europium polyalcohol complex (0.02 mmol) was added to the vial. Then the vial was set in water bath at 60 °C until the complex completely dissolved. AIBN (0.075 mmol) was added to the solution in vial and allowed to polymerize for 8 hours. The polymer was collected and grounded to fine particles. The polymer was first washed with methanol for 24 hours, and then with methanol acetonitrile mixture (1:4 ratios) for 24 hours, and then with vacuum dried to yield white polymer. Finally, the polymer sieved in a 150 micrometer sieve.

#### **2.8.10 Fluorescence Measurements**

To find the optimal ratio of chloroform and acetonitrile to suspend the polymer particles, the sieved polymer (0.1 g) was suspended in 1.5 mL of chloroform, and then acetonitrile was slowly (0.02 mL each time) added until a homogenous suspension was formed. The suspension was allowed to stand for 2 hours to confirm that the suspension

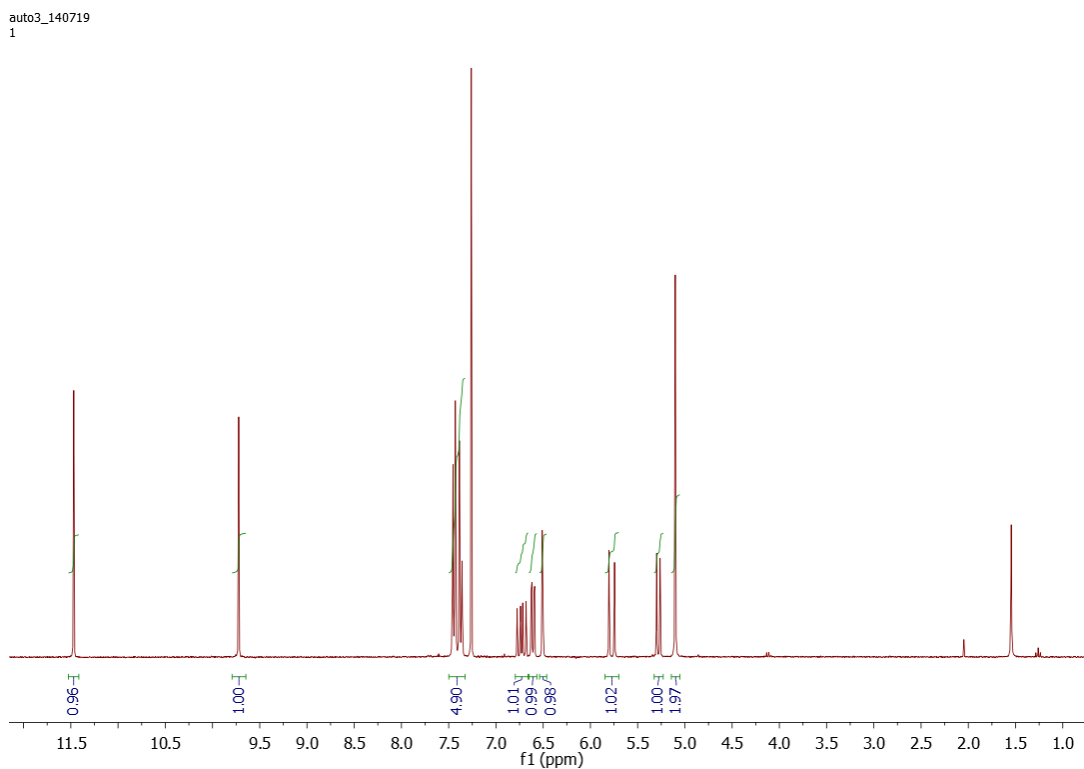
was stable. The optimal ratio of chloroform and acetonitrile to keep the polymer suspended was 5:1 (which is varied by batch). To transfer the polymer into the wells of a microtiter plate, total of 0.21 g of polymer was weighted and transferred into a 7 mL vial. To the vial, chloroform (3.5 mL) and acetonitrile (0.7 mL) was added. The vial was placed in sonicator for 1 min and shaken until a homogenous suspension formed. The suspension (0.2 mL) was transferred into each well by using a micropipette (100  $\mu$ L to 1000  $\mu$ L range). The solvent was dried by expose the polymer in the air and wait for several hours, and then the plate was put in oven for 10 min. After the plate was completely cooled down, the anion solution (0.3 mL) was pipetted into each well and wait for 15 min to allow them to equilibrium. The fluorescent properties (excited at 350 nm) were read and collected using MDS SpectraMax M2 microplate reader. The settings for the plate reader software were: (1) fluorescence reading from bottom; (2) excited at 350 nm; (3) reading range from 580 nm to 650 nm (depends on what kind spectrum is needed for the experiment); (4) reading steps was set at value of 2.

#### **2.8.11 Recycling Experiments**

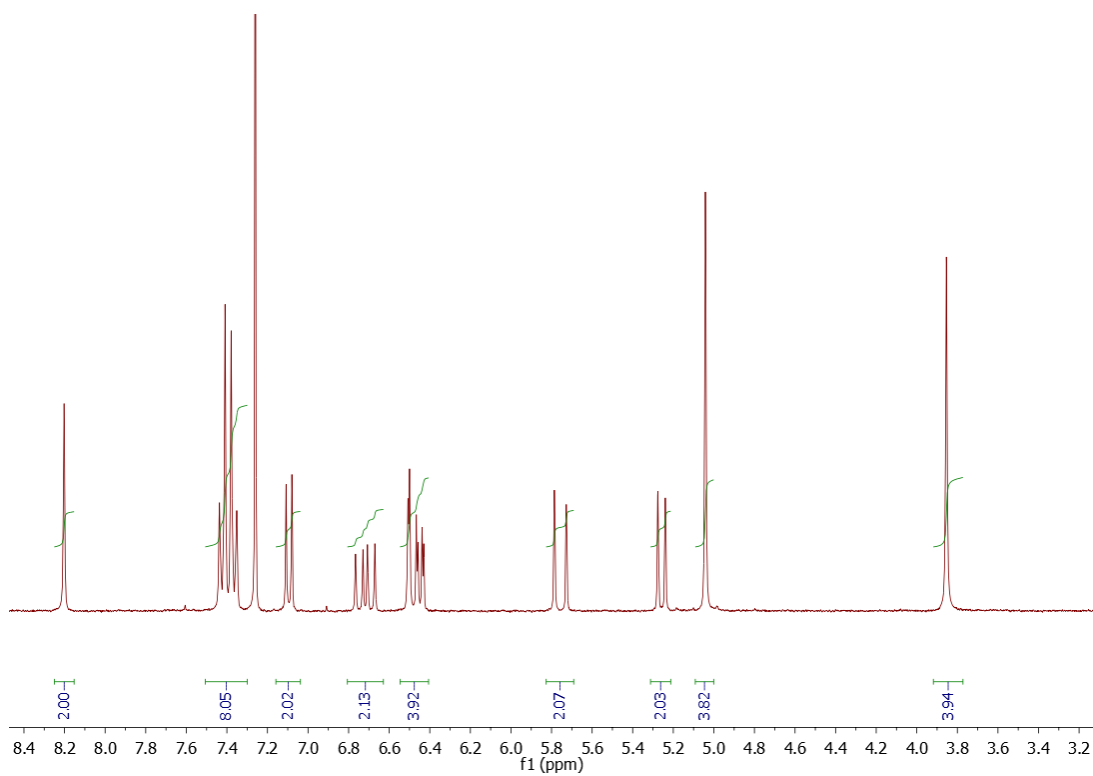
The polymer in the microtiter plate was collected after the titration experiment. The combined polymer was put in teabag and soaked in 300 mM sodium nitrate aqueous solution (200 mL) in a plastic bottle. Then the bottle was set on a shaker for 60 min. The solution was replaced with fresh sodium nitrate solution, and this washing procedure was repeated 3 times. Then the polymer was washed with water by setting the bottle on shaker for 15 min, and this was repeated 3 times. Next, the polymer was washed with methanol for 12 hours and then methanol acetonitrile mixture (1:4 ratio) for 12 hours by using a

Soxhlet extraction system. The polymer was dried under vacuum and ready to be used second time.

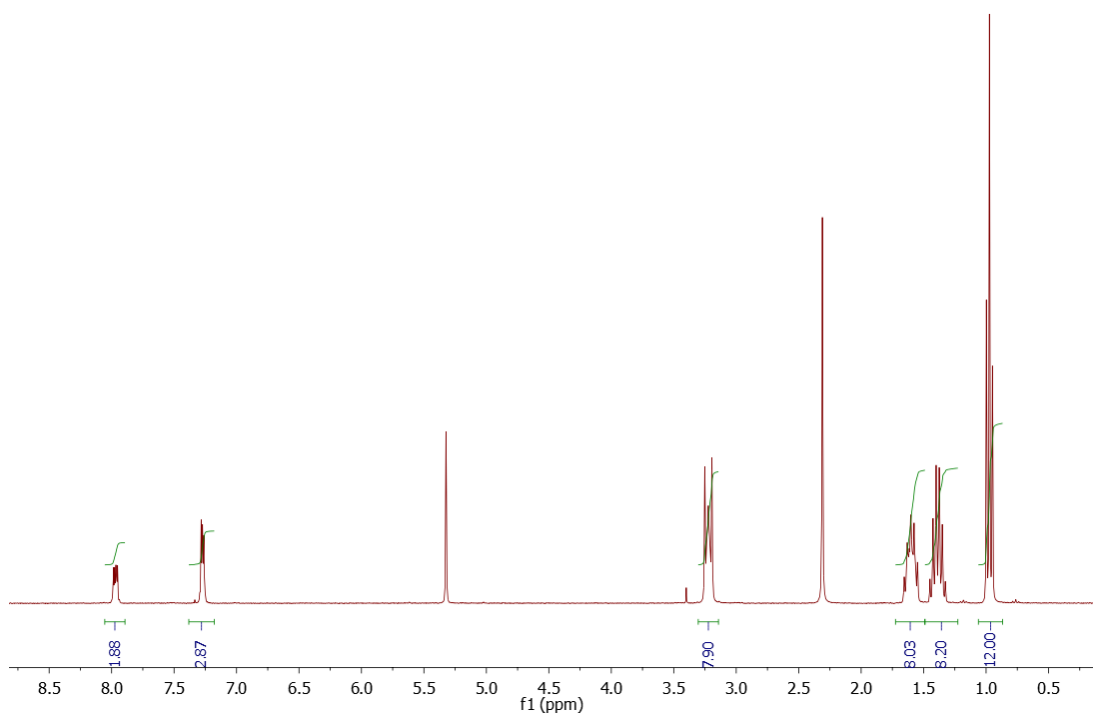
## 2.9 NMR SPECTRA



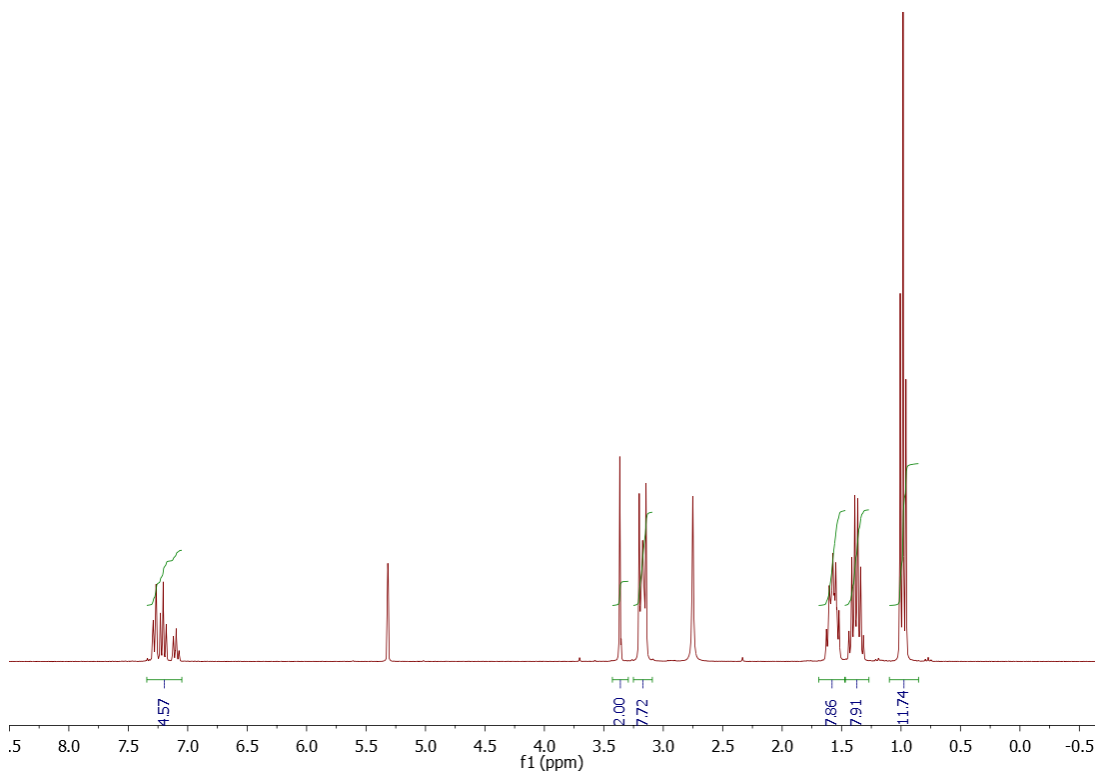
**Figure 2.13**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) of 2-hydroxy-4-(4-vinylbenzyloxy) benzaldehyde.



**Figure 2.14** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) of salen ligand.

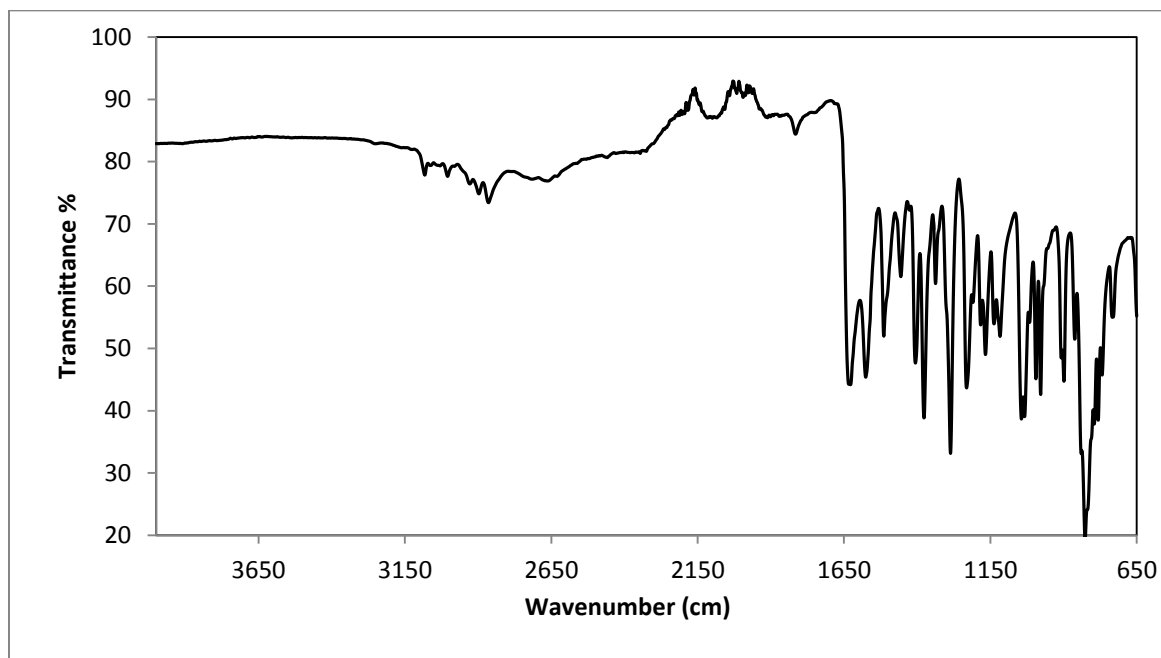


**Figure 2.15** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) of TBA benzoate analyte.

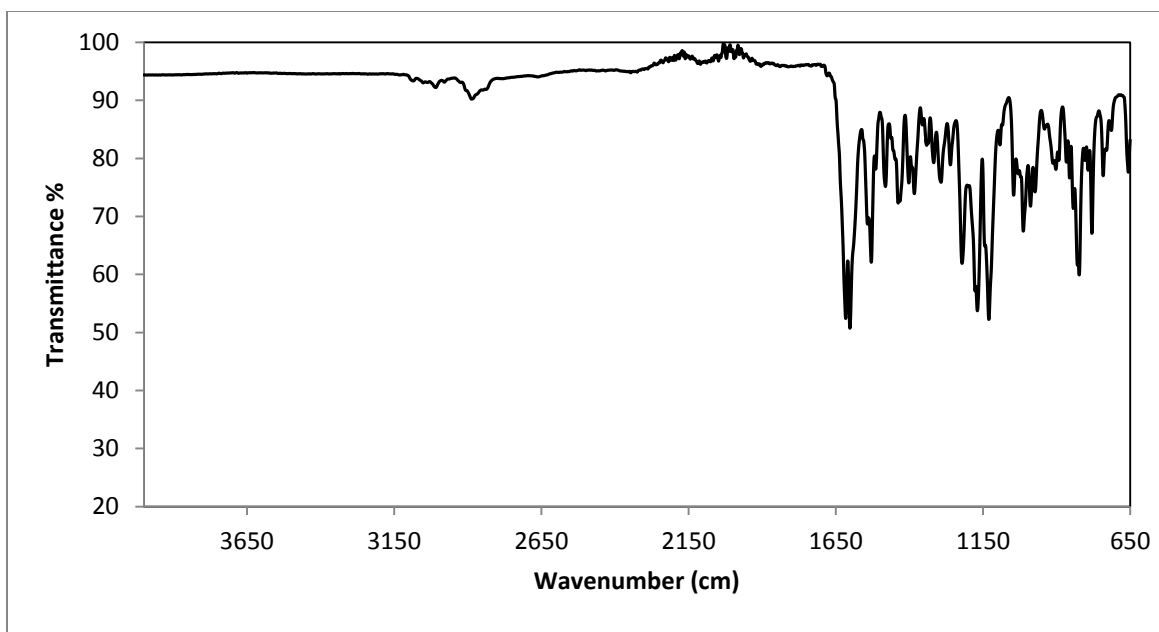


**Figure 2.16**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz) of TBA phenylacetate analyte.

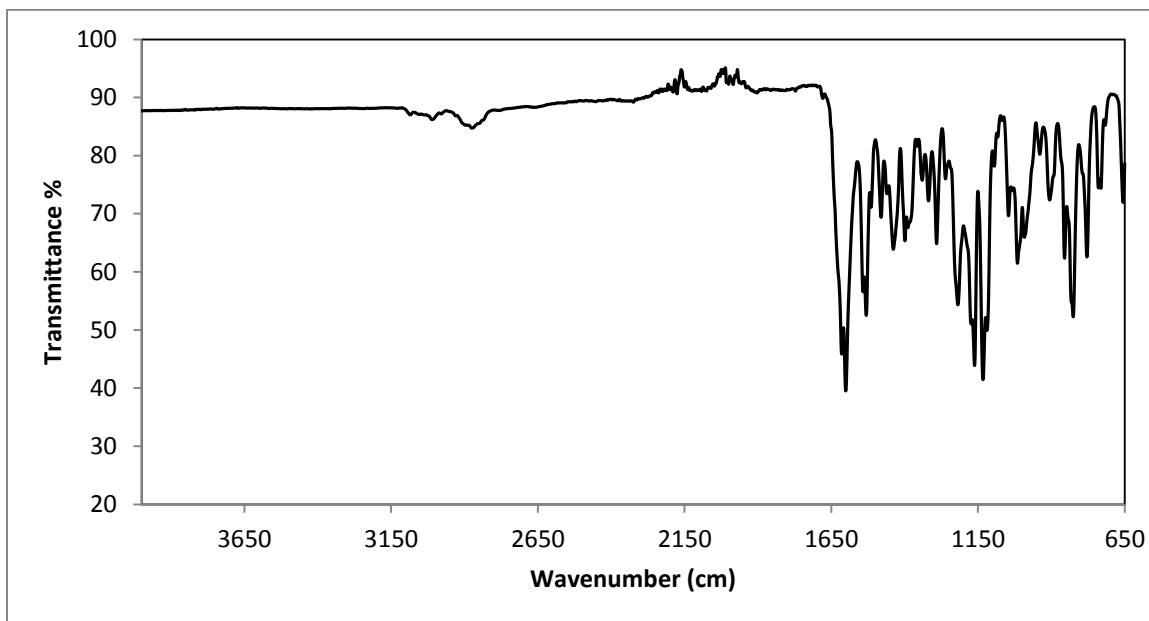
## 2.10 INFRARED SPECTROSCOPY



**Figure 2.17.** IR spectra of salen ligand.



**Figure 2.18.** IR spectra of europium nitrate-salen complex.



**Figure 2.19.** IR spectra of europium triflate-salen complex.

## 2.11 REFERENCES

- (1) Mitchell-Koch, J. T.; Borovik, A. S. *Chem. Mater.* **2003**, *15*, 3490.
- (2) Dehnicke, K.; Greiner, A. *Angew Chem Int Edit* **2003**, *42*, 1340.
- (3) Nicolo, F.; Bunzli, J. C. G.; Chapuis, G. *Acta Crystallogr C* **1988**, *44*, 1733.



- (4) Yan, C. H.; Zhang, Y. W.; Gao, S.; Li, B. G.; Huang, C. H.; Xu, G. X. *J. Alloys Compd.* **1995**, 225, 385.
- (5) Dewick, P. M. *Essentials of Organic Chemistry For Students of Pharmacy, Medicinal Chemistry and Biological Chemistry*; 2nd ed.; Wiley: Chichester, 2013.
- (6) Mehrotra, R. C.; Kapoor, P. N.; Batwara, J. M. *Coord. Chem. Rev.* **1980**, 31, 67.
- (7) Striegler, S.; Gichinga, M. G.; Dittelt, M. *Org. Lett.* **2008**, 10, 241.
- (8) Daly, J.; Witkop, B.; Horner, L. *J. Am. Chem. Soc.* **1961**, 83, 4787.
- (9) Fujii, Y.; Matsutani, K.; Kikuchi, K. *J Chem Soc Chem Comm* **1985**, 415.
- (10) Sharma, A. C.; Borovik, A. S. *J. Am. Chem. Soc.* **2000**, 122, 8946.