# POLY (1-AMINONAPHTHALENE) AS A CHEMOSENSOR FOR SELECTIVE DETECTION OF IRON(III) ION

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# POLY (1-AMINONAPHTHALENE) AS A CHEMOSENSOR FOR SELECTIVE DETECTION OF IRON(III) ION

**by**

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| | |
|---|---|
| 1-AN | 1-Aminonaphthalene |
| $M_n$ | Average molecular number |
| $M_w$ | Average molecular weight |
| CPs | Conjugated polymers |
| EET | Electronic energy transfer |
| HOMO | Highest unoccupied molecular orbital |
| $\lambda$ | Wavelength |
| LOD | Limit of detection |
| LUMO | Lowest occupied molecular orbital |
| PET | Photoinduced electron transfer |
| $\pi$ | Pi |
| PAN | Poly (1-Aminonaphthalene) |
| PANI | Polyaniline |

# POLI (1-AMINONAFTALENA) SEBAGAI KEMOSENSOR BAGI PENGESANAN SELEKTIF ION FERUM (III)

## ABSTRAK

Kajian ini menghuraikan tentang sintesis poli (1-aminonaftalena) dan aplikasinya sebagai kemosensor untuk mengesan ion $Fe^{3+}$ dengan kaedah kolorimetrik dan fluorimetrik. Polimer tersebut telah disintesis menggunakan kaedah pempolimeran oksidatif kimia dengan menggunakan $FeCl_3$ sebagai mangkin. Pencirian polimer yang diperoleh telah dijalankan dengan menggunakan pelbagai kaedah spektroskopi termasuk spektroskopi inframerah jelmaan Fourier (FT-IR), resonans magnetik nuklear proton ($^1$H-NMR) dan kromatografi pemisahan gel (GPC). Gerak balas polimer terhadap pelbagai ion logam telah diselidik dengan kaedah pemerhatian kolorimetrik, spektrosopi ultra-lembayung nampak dan pendarflour. Polimer menunjukkan kepilihan dan kepekaan yang tinggi terhadap ion $Fe^{3+}$ berbanding dengan ion logam yang lain. Perubahan warna yang ketara daripada ungu kepada kuning boleh dilihat melalui mata kasar apabila penambahan ion $Fe^{3+}$ dengan gerak balas UV-Vis yang linear dalam julat kepekatan daripada 10 - 100 mg $L^{-1}$. Polimer ini turut menunjukkan kepilihan dan kepekaan pendarflour 'padam' yang tinggi terhadap ion $Fe^{3+}$ dan gerak balas linear yang baik diperoleh dalam julat kepekatan ion $Fe^{3+}$ daripada 10-50 mg $L^{-1}$ dengan had pengesanan 1.04 mg $L^{-1}$. Kemosensor yang dicadangkan telah diaplikasikan untuk pemulihan kandungan ion $Fe^{3+}$ dalam sampel air dan keputusan yang memberangsangkan telah diperoleh. Keputusan yang diperoleh menunjukkan bahawa polimer ini berpotensi digunakan sebagai kemosensor untuk pengesanan ion $Fe^{3+}$.

# POLY (1-AMINONAPHTHALENE) AS A CHEMOSENSOR FOR SELECTIVE DETECTION OF IRON (III) ION

## ABSTRACT

This study describes the synthesis of poly (1-aminonaphthalene) and its application as a chemosensor for the detection of $Fe^{3+}$ by colorimetric and fluorimetric method. The conjugated polymer was synthesized via chemical oxidative polymerization method using $FeCl_3$ as a catalyst. The obtained polymer was characterized by different spectroscopic methods including Fourier Transform Infrared (FT-IR), Proton Nuclear Magnetic Resonance ($^1$H-NMR) and Gel Permeation Chromatography (GPC). The response of the polymer towards various metal ions was investigated by colorimetric detection, ultra-violet visible and fluorescence spectroscopies. The polymer displayed a high selectivity and sensitivity towards $Fe^{3+}$ compared to other metal ions. A significant colour change from purple to yellow was observed by naked eye upon addition of $Fe^{3+}$ with a good linear UV-Vis relationship within the concentration of 10 - 100 mg $L^{-1}$. The polymer also shows high selectivity and sensitivity 'turn-off' fluorescence response towards $Fe^{3+}$ ion. A good linear response was obtained for the concentration of $Fe^{3+}$ in the range of 10 - 50 mg $L^{-1}$ with detection limit of 1.04 mg $L^{-1}$. The proposed chemosensor has been applied for the recovery of $Fe^{3+}$ content in water samples and satisfactory results were obtained. The results imply that the polymer can be used as a potential chemosensor for $Fe^{3+}$ detection.

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

In recent years, environmental pollution caused by heavy metals has gained a major concern due to their dangerous effects on the human health and environmental safety. Naturally found on the crust of the Earth, heavy metals are defined as elements that has a density of more than 5 g $cm^{-3}$ (Tchounwou et al., 2012; Tutic et al., 2015). It is widely used in industrial applications such as production of paints, pesticides, batteries and fertilizers (Ojedokun & Bello, 2016). Furthermore, trace amounts of metal ions are essential for many biological processes such as gene transcription, cellular metabolism, enzyme regulation and oxygen transportation. For example, iron and selenium plays a major role in transport of oxygen and hormone biosynthesis, respectively (Li et al., 2016; Schomburg et al., 2008).

Heavy metals cannot be degraded or destroyed therefore it tends to accumulate in living organisms. Natural and human activities including volcanic eruptions, mining, disposal of high metal wastes, leaded gasoline and paints are common sources of heavy metal pollution. Emissions of heavy metals to the environment can occur via a wide range of processes and pathways, including to the air for example during combustion, extraction and processing, to surface waters via runoff and releases from storage and transport and to the soil (and hence into groundwater's and crops). Therefore, they may enter human body through food intake, drinking water, air or absorption (Figure 1.1). As a result, prolonged exposure to heavy metals can cause serious effects to human health such as Alzheimer's disease, Parkinson's disease and kidney damage (Jarup 2003; Jan et al., 2015; Rehman et al., 2018).

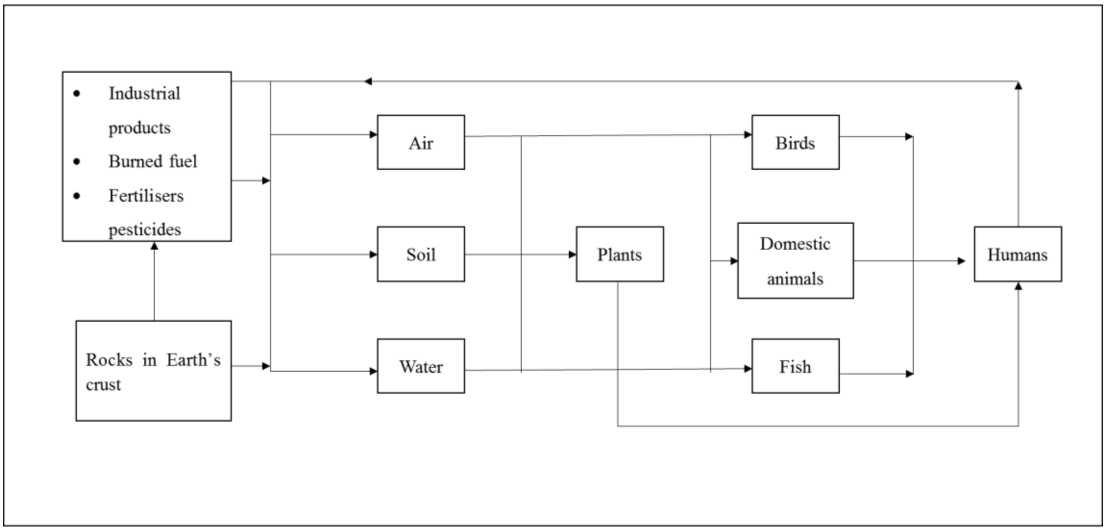

Figure 1.1 Sources of heavy metals and their cycle in the environment (Brady et al., 1994).

Iron is a silvery-white metal and the fourth most abundant element found in the Earth's crust (Frey & Reed 2012; Ilbert et al., 2013). It is commonly exists in nature in the form of oxides such as hematite and pyrite as it easily gets oxidized when in contact with atmospheric oxygen. As one of the transition elements in periodic table, iron has attractive properties such as durable, resistance to harsh conditions, ability to withstand both high pressure and temperature making it in high demand for many applications (Frey & Reed, 2012). Moreover, iron is fairly cheap compared to other metals and abundantly available on the surface of the Earth. These are among the reasons for which it is extensively utilized in manufacturing heavy machine, automobiles and production of steel as well as construction materials. Iron is also used as a catalyst in the chemical reaction of producing ammonia gas in the Haber process (Schlogl, 2003; McAulay et al., 2015).

Iron is also one of the essential trace elements in the human body and plays significant roles in various biological processes such as respiration, oxygen transportation, electron transfer and enzymatic reactions (Zhu & Jiang, 2011; Abbaspour et al., 2014; Gujar et al., 2018). Therefore, deficiency and surplus of iron may cause adverse impacts on human health. Iron deficiency is the most common mineral deficiency which could lead to anaemia (Zhu & Jiang, 2011; Jia et al., 2015; Li et al., 2016). Meanwhile, high level of irons within the permissible limit in the body have been associated with incidence of certain diseases such as hemochromatosis, liver problems, diabetes and heart failure (Narayamaswamy & Govindaraju, 2011; Hirayama & Nagasawa, 2017; Kumar et al., 2019).The permissible level of iron concentration in drinking water set by the World Health Organization(WHO) and Malaysian Ministry of Health (MOH) are 0.03 mg $L^{-1}$ and 0.2 mg $L^{-1}$ respectively (WHO, 1996; KAM, 2019). Thus, new sensor probes which are capable of showing selective sensing properties with iron ions at ppm level is important for human health.

## 1.2 Sensor

Nowadays, sensors are essential and extensively used in everyday life, which includes from the device we use at home to industrial equipment. According to the Oxford English Dictionary, a sensor is defined as a device that detects or measures a physical property and records, indicates or otherwise responds to it (Sensor, 2019). For example, pH meters, thermometers and smoke detectors are very common sensors used in our daily life.

Generally, a sensor is made up of three components: a receptor, a signal transducer and a read-out (Figure 1.2). The receptor is responsible for binding with a specific target substance known as analyte. Therefore, it should be selective and able to identify the analyte of interest. The transducer will then convert the input from the interaction of receptor with the analyte to a measurable and readable data. The read-out domain is the part responsible for reporting the binding event. The sensor's performance for real life application is determined by few factors such as selectivity, sensitivity, limit of detection, stability and cost (Zheng & Swager, 2005; Fegley et al., 2012).

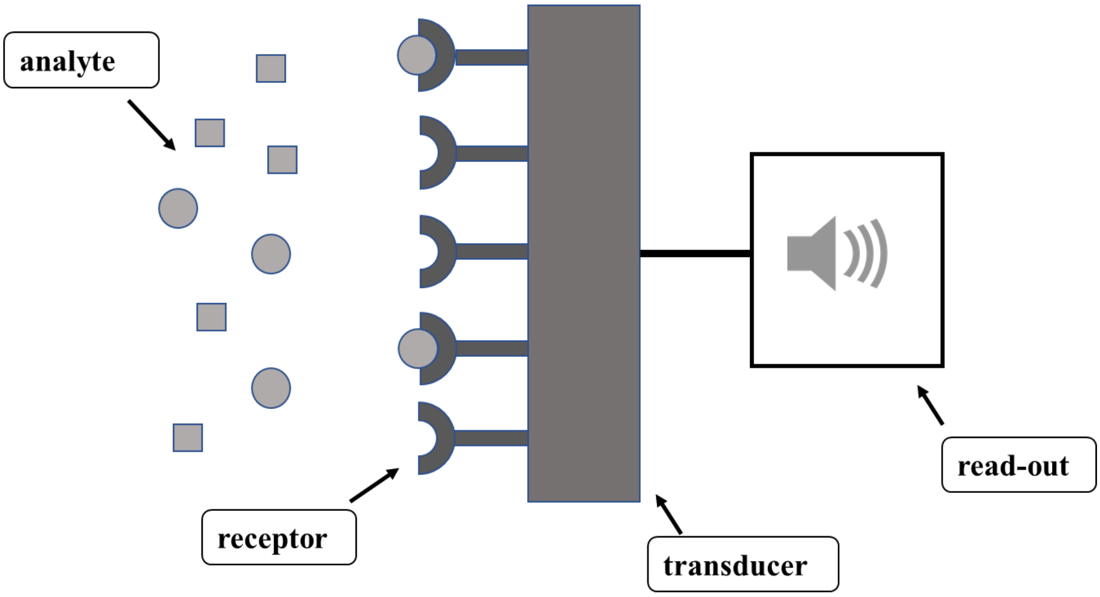

Figure 1.2 Schematic illustration of sensor device (Fan et al.,2009).

A chemical sensor also known as chemosensor is an analytical device that qualitatively or quantitatively detects the presence of specific chemical substances, a class of chemicals or a specific chemical reaction (Tu et al., 2016). Chemosensors based on changes of fluorescence signal are known as fluorescent chemosensors whereas colorimetric chemosensors referred to formation of a signal that is visible to the naked eye. Chemosensors has grown very rapidly and have been used for various detection of analytes such as cations, anions, neutral molecules and many more (Jun et al., 2006; Xu et al., 2007; Kim et al., 2011). This research will focus on colorimetric and fluorescent chemosensors for detection of heavy metal ions.

### 1.2.1 Colorimetric chemosensors

A colorimetric chemosensors is a method in which an intensity change or actual change in colour is observed when sensor interacts with a particular analyte, due to changes in their absorption properties (Upadhyay et al., 2018). Though colorimetric analyses are not sensitive as fluorescent approaches do, this method still showing a great significance and can be useful for early detection or preliminary qualitative detection. Colour-based diagnostic assays such as blood-glucose monitoring and early pregnancy test are some of the example of this method in real life applications.

Colorimetric chemosensors has been the most popular method for determination of metal ions due to its simplicity, inexpensive and easy to operate (Maity & Govindaraju, 2011; Jang et al., 2013; Choi et al., 2014; Song et al., 2015). Song et al. (2015) reported a visible colour change from colourless to yellow in solution containing a quinoxaline chromophore when reacts with $Co^{2+}$ and $Cu^{2+}$. Meanwhile, Maity and Govindaraju (2012) successfully developed colorimetric chemosensors $Co^{2+}$ based on coumarin-conjugated thiocarbanohydrazone. Upon the binding of ligand to the cation, a visible colour change observed from light yellow to deep pink. Choi et al. (2013) have reported instantaneous colour change from colourless to orange and to purple in the presence of $Fe^{2+}$ and $Fe^{3+}$ respectively in a solution containing juloidine-imidazole moieties. Jang et al. (2013) have successfully developed a chemosensor based on naphthol and quinoline moieties which exhibited selective recognition towards $Cr^{3+}$ by showing a colour change from yellow to colourless. However, the main drawback of this method compared to fluorescent approach is that they are less sensitive as single molecule detection is possible in fluorescent measurement .Furthermore, colorimetric method do not have low limit of detection compared to fluorescent approach where detection can be achieved at very low concentration.

### 1.2.2 Fluorescent chemosensors

A fluorescent sensor can be defined as a molecular machine capable of signalling the presence of analyte such as ions and molecules (Wang & Anslyn, 2011). There are components in fluorescence sensing approach; (i) signal moiety (the fluorophore) which acts as a signal transducer converting the recognition event into an optical response, (ii) recognition moiety (the receptor) which is responsible for binding to the target analyte in an efficient manner and (iii) a spacer (Figure 1.3). Usually, the signals moieties are linked to the receptor by a spacer that does not allow for any ground state $\pi$-$\pi^*$ or n-$\pi^*$ (Duke et al., 2010). In most cases, the spacer does not involve in the signal transduction. An important characteristic of fluorescent chemosensors is signal transduction of the binding of the analyte processed in a very short time by read-out. The outcome by the read-out can be either change of the fluorescence intensity or a shift in the emission wavelength, as well as the formation of new fluorescence band (Fan et al., 2009).

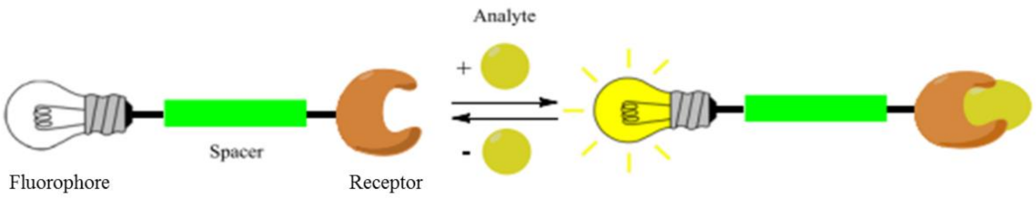

Figure 1.3 Schematic diagram of chemical sensor (Prodi et al., 2000).

For the past few years, fluorescent chemosensors are gaining increased attention among researchers due to their simplicity, cost-effectiveness, high sensitivity, selectivity and ease to operate (Li et al., 2010; Arulraj et al., 2015). Numerous works have been reported for detection of heavy metal ions using this approach (Lim et al., 2014; Nakajima & Kobayashi, 2016; Prabhu et al., 2015; Tang et al., 2011; Kim et al., 2014). Lim et al., (2014) have successfully synthesized a benzylidene polyester (BPE) as a fluorescent chemosensor for $Cu^{2+}$. The emission intensity of BPE was enhanced in the presence of $Cu^{2+}$ compared to other metal ions such as $Ni^{2+}$, $Zn^{2+,}$ $Ag^{+}$, $Cd^{2+}$, $Ca^{2+}$, $K^{+}$, $Pb^{2+}$, $Mn^{2+}$ and $As^{3+}$. The calixarene obtained from syringaldehyde were successfully synthesized by Nakajima and Kobayashi (2016) and used as fluorescence probe for detection of $Pb^{2+}$. The calixarene host was effectively quenched upon the addition of $Pb^{2+}$ in the concentration range of 0.25-2 μM. Prabhu et al., (2015) synthesized a simple anthracene based chalcone as fluorescent chemosensor which are capable of detecting $Pb^{2+}$ in aqueous media. Tang et al., (2011) have developed a new pyrrole Schiff base-containing rhodamine as a sensor for $Hg^{2+}$ and showed a relatively strong fluorescence. A Schiff base sensor exhibited a selective and sensitive recognition towards $Al^{3+}$ was synthesized by Kim et al., (2014) which displayed a significant fluorescence enhancement by 31-fold, suggesting that the polymer has a potential to detect $Fe^{3+}$ in the environmental samples. Table 1.1 shows the summarized of the reported fluorescent sensors.

Table 1.1: Summarized of recently reported chemosensors.

| Fluorophore | Analyte | Fluorescent mechanism | Concentration range of analyte | References |
|---|---|---|---|---|
| Benzylidene polyester (BPE) | $Cu^{2+}$ | Turn-on | 0.025 – 2.5 μM | Lim et al., 2014 |
| Calixarene | $Pb^{2+}$ | Turn-off | 0.25 – 2 μM | Nakajima & Kobayashi, 2016 |
| Anthracene based chalcone | $Pb^{2+}$ | Turn-on | 0.04 – 4 μM | Prabhu et al., 2015 |
| Pyrrole Schiff base-containing rhodamine | $Hg^{2+}$ | Turn-on | 0.125 – 10 μM | Tang et al., 2011 |
| Schiff base sensor | $Al^{3+}$ | Turn -on | 20 – 200 μM | Kim et al., 2014 |

### 1.2.3 Mechanism of analyte detection

The fluorescence signals from the probe upon binding with analytes can be observed in the form of enhancement (turn-on), quenching(turn-off) or red/blue shift in the fluorescence maxima of the probe (ratiometric). In fluorescence sensing, there are several well-known mechanisms such as photoinduced electron transfer (PET), electronic energy transfer (EET), photoinduced charge transfer (PCT), fluorescence resonance energy transfer (FRET) and excimer formation that have been applied to develop fluorescent probes for selective detection of various analytes, including $Fe^{3+}$ (Fan et al., 2009; Valeur et al., 2000; Formica et al., 2012). The majority of the reported $Fe^{3+}$-selective fluorescent probes garnered by fluorescence turn-off responses due to the paramagnetic nature of $Fe^{3+}$ which assisted photoinduced electron transfer (PET) and/or exited state de-excitation pathway via electronic energy transfer (EET). These two mechanisms are discussed because they are the most common mechanisms for fluorescence chemosensors. In this chapter, a concise overview of both mechanisms are discussed.

### 1.2.3 Photoinduced electron transfer (PET)

Photoinduced electron transfer (PET) is one of the most important mechanisms in fluorescence sensing describing the transfer of an electron from the HOMO of the donor in its ground state to a vacancy in the HOMO of the acceptor in its excited state. PET also can takes place in the opposite manner which is from the donor in its excited state. Originally developed by de Silva et al., this type of mechanism has been widely used in developing fluorescent sensors for a variety of analytes such as detection of cations, anions and neutral molecules (Alaei et al., 2012; Gunnlaugsson et al., 2003; Kowalcyzk et al., 2010; Kulatileke et al., 2006). In PET sensing, it features the 'fluorophore-spacer-receptor' design and could be classified into two categories: "turn-on" fluorescence or "turn-off" fluorescence. For fluorescence "turn-on" mechanism, the receptors usually contain a relatively high energy non-bonding electron pair. The fluorescence "turn-on" is observed upon the excitation of the fluorophore, an electron in highest occupied molecular orbital (HOMO) is then promoted to the lowest occupied molecular orbital (LUMO). This enables PET takes place from the HOMO of the donor to the fluorophore which causing a fluorescence quenching. Upon binding with the specific cation or anion, the HOMO of the receptor becomes lower in energy than the HOMO of the fluorophore, consequently creating a direct fluorescence emission pathway to the ground state. This decreases the driving force for the PET process and effectively stopping the quenching process which leads to the fluorescent enhancement as shown in Figure 1.4

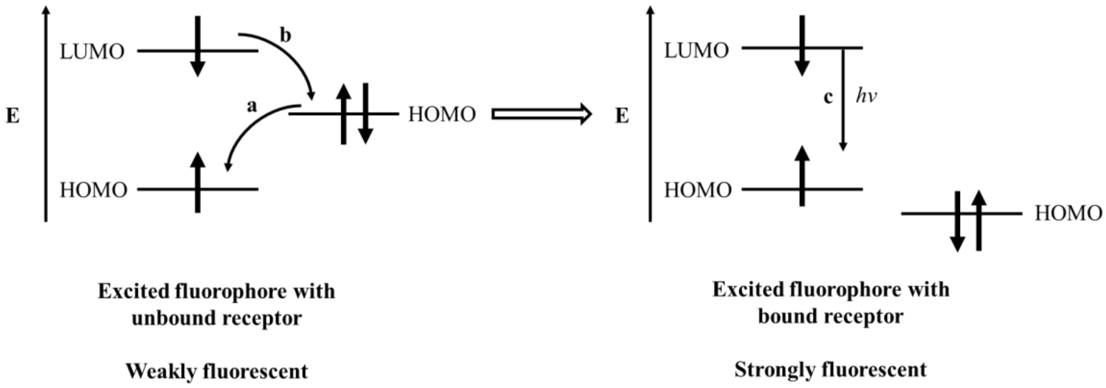

Figure 1.4 Orbital energy diagram for fluorescence "turn-on" PET sensors before and after binding cation with (a) forward electron, (b) backward electron transfer and (c) fluorescence emission processes (Fegley et al., 2012).

The "turn-off" fluorescence sensor occurred when the energy level of the LUMO specific cation or anion is between the energy level of HUMO and LUMO of the fluorophore. Thus, the binding of analytes by the receptor provides a non-radiative path to dissipate the excitation energy and resulting in fluorescence quenching (Figure 1.5).

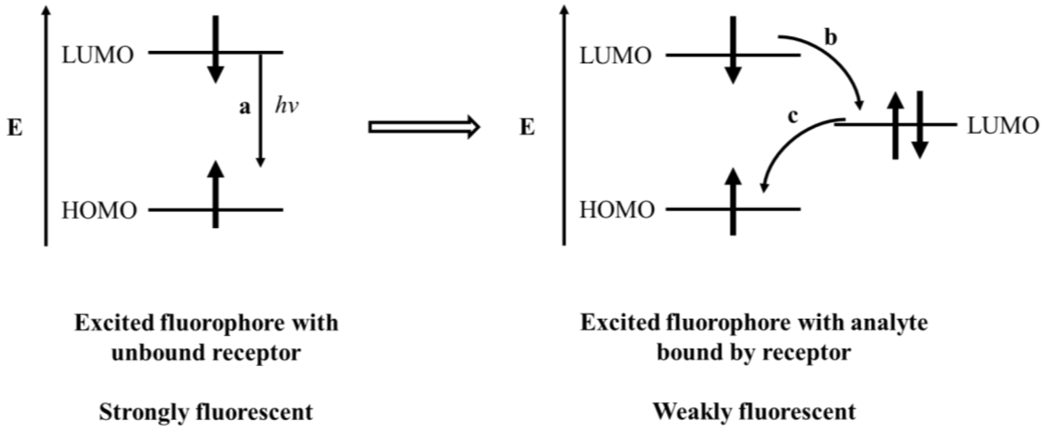

Figure 1.5 Orbital energy diagram for fluorescence "turn-off" PET sensors before and after binding cation with (a) fluorescence emission, (b) forward electron transfer and (c) backward electron transfer processes (Fegley et al., 2012).

As demonstrated, the main difference between the “turn-on” and “turn-off” mechanisms is that the PET process occurs either before or after the analyte binding. In the first case, the PET process participated in by the HOMO, LUMO of the fluorophore and the HOMO of the receptor before binding with the analyte. In the latter case, the PET process is created by the binding event.

### 1.2.4 Electronic energy transfer (EET)

Another mechanism involved fluorescence quenching upon cation binding is electronic energy transfer (EET). There are two types of EET mechanism: the double electron exchange (Dexter) energy transfer and the dipole-dipole coupling (Förster) energy transfer (Carter et al., 2014; Fan et al., 2009). Both of mechanisms involved exchange of two electrons and resulted in the same way. In Dexter energy transfer, the initially excited state of the fluorophore goes back to its ground state by a non-radiative decay. The differences between both mechanisms are Dexter electron energy transfer requires close distance between the fluorophore and the cations (Sasaki et al., 2016; Mako et al., 2018).

## 1.3 Conjugated polymers

Polymer is a large molecule composed of repeating structural known as monomer which are linked together by a covalent bond via chemical reaction called polymerization. The concept of polymers are built up of a linear molecule having high molecular weight was proposed by Hermann Staudinger in 1920 (Naka, 2014). More polymers have been subsequently been synthesized and can be categorized as homopolymers and copolymers. Polymers containing identical monomers units are known as homopolymers whereas copolymers are made up from two or more different types of monomers that are linked in the same polymer chain (McKeen, 2012).

Recently, conjugated aromatic organic polymers has gained great deal of attention for detection of a range of analytes such as anions and cations (Song et al., 2012; Chen et al., 2013; Kitazawa et al., 2012; Barbosa et al., 2016; Ye et al., 2017). Conjugated polymers (CPs) are macromolecules consisting of alternating single and double bonds and delocalized π electrons along their backbones. CPs can be classified into few categories such as conjugated polymer that has aliphatic, aromatic, heterocyclic and hetero-atom in their structure as shown in Figure 1.6.

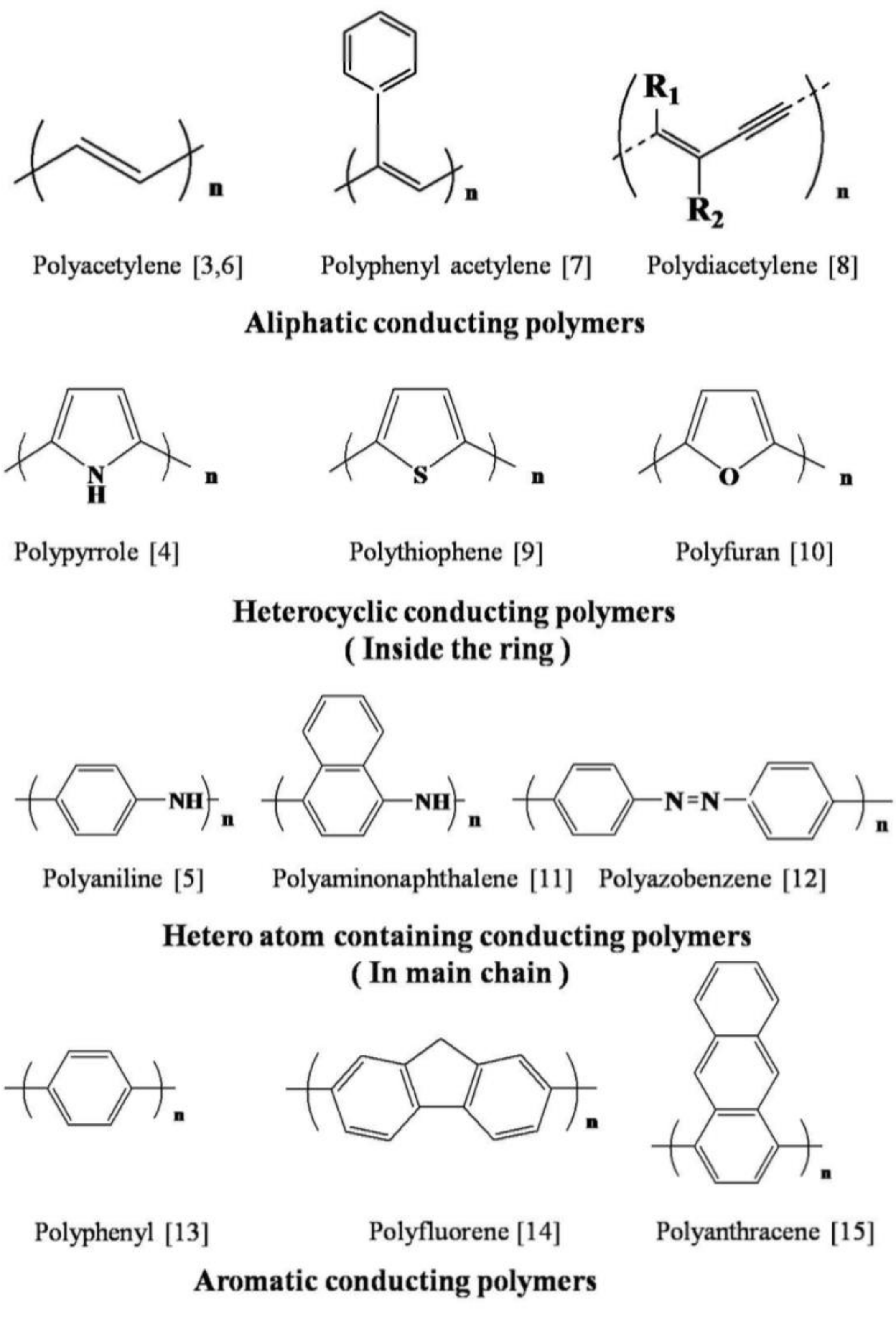

Figure 1.6 Classification of conjugated polymers (Wang et al, 2013).

Conjugated polymer could be conveniently synthesized by chemical oxidation polymerization which involves three significant stages which are oxidation of the monomer followed by radical coupling and formation of dimer and finally the chain growth shown in Figure 1.7 ( Wang et al., 2013).

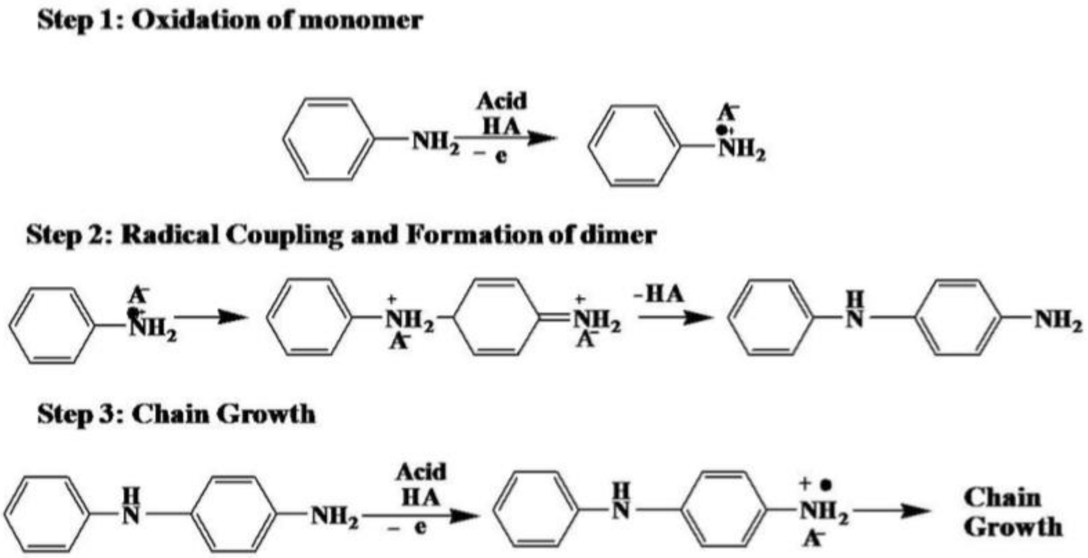

Figure 1.7 Mechanism of chemical oxidation polymerization of polyaniline (Wang, 2013).

Compared to small molecules, conjugated polymers have several advantages in sensing application. The repeated π-π conjugated unit along the backbone enhance the fluorescence signal therefore improve the sensitivity of the chemosensor (Fegley et al., 2012).Upon excitation, this electronic delocalization of π electrons provides a pathway for electron or hole mobility and can greatly amplify the fluorescence signal by the facile energy migration along the polymer backbone( Fan et al., 2009). This unique molecular structure of conjugated polymer offers attractive optical and electrical properties. For the past decades, conjugated polymers has gained great deal of attention as electrically conducting materials such as solid-state battery scheme using polyaniline, photovoltaic cells and light-emitting diodes made of an organic polymer (Anguera et al., 2014).

Among them, polyaniline (PANI) is one of the most studied conducting polymers owing to its properties of excellent stability, high electrical conductivity and ease preparation compared to others conducting polymers (Kumar et al., 2017). However, applications of this conducting polymer are restricted due to poor solubility in common organic solvents. The solubility of the polymer is important so that polymerization, purification, characterisation and processability of the conjugated polymer can be carried out in solution. Furthermore, the poor solubility of the polymer will limit the interaction between ligand and analyte in sensor application. Consequently, this leads to synthesized of new conducting polymers which have similar chemical structure to PANI e.g. aminoanthracene and aminonaphthalene (Moon et al., 1993; Roy et al., 2003; Li et al., 2005; Wang et al.,2013; Jadoun et al., 2017; Kumar et al., 2017).

### 1.3.1 Fluorescent Conjugated Polymers (CPs) as the chemosensor

Many CPs chemosensors have been used with great success in the past decade as fluorophores for detection of a range of analytes (Wang & Anslyn 2011). For instance, Wang et al., (2013) reported selective detection of $Pb^{2+}$ with conjugated poly-1-aminoanthracene. Cui et al., (2015) synthesized a CP containing 2,3-di(pyridine-2-yl) using Sonogashira coupling reaction for detection of $Ag^{+}$ with detection limit of $0.5\times10^{-6}$ µM. Chen et al*., (*2016) utilized thiourea based CP as a selective fluorescent chemosensor for $Cu^{2+}$ detection. However, there is no literature regarding polymer-based fluorescence containing aminonaphthalene for selective metal ion detection. The rationale behind the selection of conjugated poly 1-aminonaphthalene is it has a the repeated π-π conjugated unit along the backbone. Thus, it enhances the fluorescence signal and has a potential to be used as a chemosensor for metal ion Therefore, a conjugated poly 1-aminonaphtahelene was synthesized and its potential application as a fluorescent and colorimetric in detection metal ions were proposed.

## 1.4 Problem statements

Recently, CPs has gained great attentions as a sensing probes in many detecting fields such as metal ions and toxic chemicals owing to their unique properties such as having a backbone chain of alternating double and single bonds. Compared to smaller organic compounds, CPs is more sensitive in sensing applications due to the efficient mobility of excitation energy between the receptors along the backbone. Conjugated polymer such as polyaniline has gained great attention due to its thermal and pH stability which allowing wide temperature for processing in acidic and basic medium, low cost of monomer and less tedious steps of preparation. However, due to its poor solubility in common organic solvents have restricts their practical applications to some extent. Therefore, it is attractive to obtain polyaniline-like conjugated polymer with good solubility and use as a fluorescence probe in detection of metal ions.

Heavy metals are found naturally in the Earth and become concentrated which is resulted from the natural and anthropogenic processes such as volcanic eruptions, rock weathering, mining and industrial wastes. Despite of the fact that some of heavy metal ions are essential and play important roles in living systems, accumulation of these metal above the permissible limits can cause a serious environmental and health problems. Iron as example, plays a crucial role in biological system for instance as oxygen transportation and enzymatic reaction. However, it could also produce adverse effect to human health when in excessive or insufficient. Thus, the detection of $Fe^{3+}$ is an important goal in chemical sensor field.

In the past few years, several methods for detection $Fe^{3+}$ ions have been developed such as flow injection analysis (Measures et al., 2000; Anguiano et al., 2012), voltammetry (Berg, 2006), atomic absorption spectroscopy (Leao et al., 2016) and inductively coupled plasma mass spectroscopy (Jong et al., 2008). However, most of these methods are associated with many drawbacks including expensive, time-consuming and tedious job for sample preparation. On the other hand, fluorescence chemosensors stands out as a method of preference due to its selectivity and sensitivity, easy operation, cost effective and instantaneous response. There are few significance research on fluorescence chemosensors have been done for detection of $Fe^{3+}$ ions. However, only few reports combining of fluorescence sensing with colorimetric chemosensor. Therefore, these two methods shall be exploited as powerful approach for determination of $Fe^{3+}$ ions.

## 1.5 Objectives

Objectives of this study are:

i. To synthesize a conjugated (poly 1-aminonaphthalene) which is capable to exhibit chemosensing properties for selective detection of metal ion via a chemical oxidation polymerization.
ii. To characterize the obtained CP and to investigate its chemosensing behaviours via UV-Visible and fluorescence measurements.
iii. To apply the CP as an effective chemosensors for selective detection of $Fe^{3+}$ in a real sample.

## 1.6 Scope of study

In this study, the conjugated poly(1-aminonaphthalene) was synthesized via chemical oxidation polymerization method and the obtained CP was characterized via different spectroscopic methods including Fourier Transform Infrared (FT-IR), Proton Nuclear Magnetic Resonance ($^1$H-NMR) and Gel Permeation Chromatography (GPC). Next, the chemosensing behaviours of the CP towards metal ions were studied via colorimetric , UV-Vis and fluorescence spectroscopy. The selectivity and sensitivity of chemosensor towards metal ions were further studied. Finally, the chemosensor for metal ion detection was applied for real sample analysis in water samples.

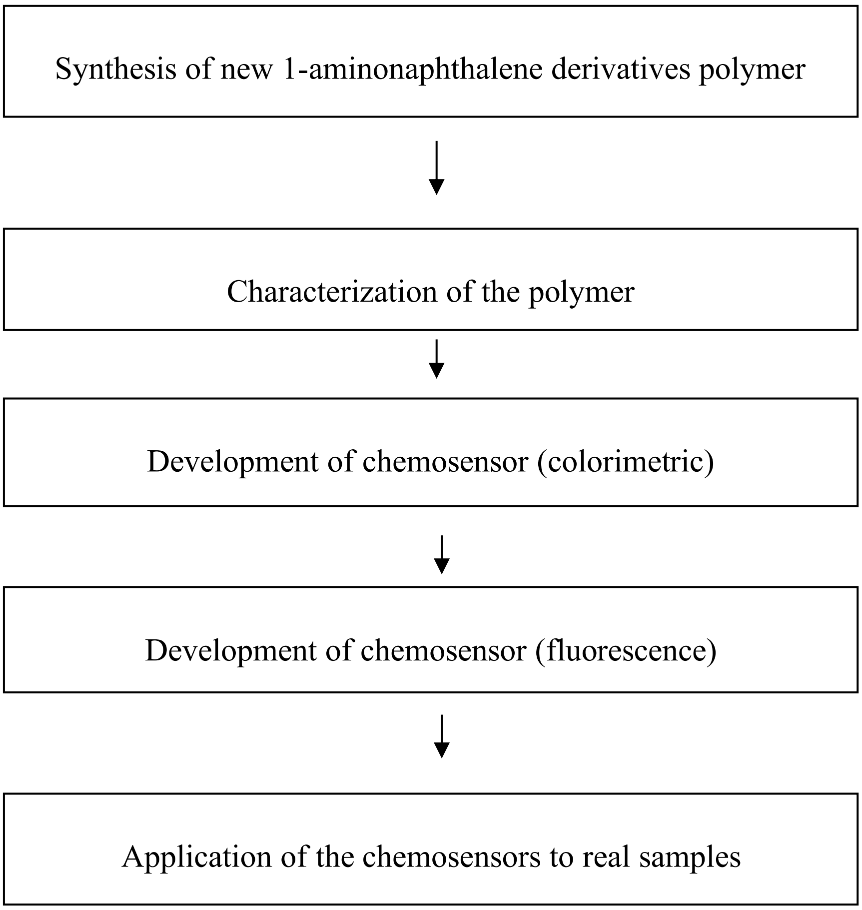

Figure 1.8 Flow chart of research

# CHAPTER 2

# LITERATURE REVIEW

This chapter will be divided into three sub-sections, review on the works on $Fe^{3+}$ detection, fluorescent and colorimetric chemosensors for detection of $Fe^{3+}$ and uses of conjugated polymer as a fluorescent probe for $Fe^{3+}$ detection. The first part of this chapter will be focused on the method of $Fe^{3+}$ detection. While the rest of this chapter, will cover on few literature examples which are appropriate for understanding on fluorescent and colorimetric approach as well as the uses of conjugated polymer as chemosensor for detection $Fe^{3+}$.

## 2.1 Method of detection for $Fe^{3+}$

In the past few decades and up to now, numerous analytical methods have been used for detection of $Fe^{3+}$ including solid phase extraction (SPE), flow injection analysis (FIA),flame atomic absorption spectrometry (FAAS), high performance liquid chromatography (HPLC) as well electrochemical methods such as voltammetry and potentiometric.

The most commonly method used for iron detection is FAAS. The main advantages of this method are the analysis is quite straightforward and inexpensive equipment required (Liang et al., 2003). This method involves two steps: (i) atomization of the sample and (ii) the absorption of radiation from light source by the free atom. Firstly, the solutions containing metal ion of interest are aspirated into nebulizer which converts the sample into a fine aerosol. The aerosol is then desolvated in the flame and subsequently vaporised and atomized. A new Schiff base, 5-((4-nitrophenylazo)-N-(2′,4′-dimethoxyphenyl)) salicylaldimine (L), has been synthesized by Shamspur et al., (2004) for the determination of $Fe^{3+}$ in aqueous samples using this method. The method has also been applied to determination of trace $Fe^{3+}$ in drinking water and river water samples with satisfactory results obtained. However, the main drawbacks of this method are lack of sensitivity due to the presence of other ions in solution, tedious sample pretreatment steps and affected by many conditions of samples such as salinity (Ahmed et al., 2015).

Due to the limitation of FAAS such as low sensitivity and high matrix interferences, a preliminary preconcentration step is necessary to enhance the detection limit and selectivity in determination of $Fe^{3+}$ at trace levels (Tang et al., 2016). To overcome this problem, several methods have been proposed including as ion exchange, solvent extraction and SPE (Baytak et al., 2006 ; Khayatian et al., 2012) Among the various preconcentration methods, SPE is widely utilized due to the several advantages such as higher enrichment factors, minimal costs due to low consumption of reagents and easy of automation (Elvan et al., 2013). Soleimani et al., (2007) have developed a solid phase extraction method using 2,2'-diamino-4,4'-bithiazole (DABTZ) as a ligand for the preconcentration of $Fe^{3+}$ in water samples prior to its determination by FAAS. The metal complex with DABTZ was retained on the column and then recovered with 2.5 mL of methanol. The $Fe^{3+}$ in effluent was then determined by FAAS. The limit of detection, sensitivity and correlation coefficient of the proposed method are 2 ppm, 0.05 ppm and 0.992 respectively. The results obtained shown that the method is highly sensitive. Even though the extraction method is highly sensitive but generally this method lack in simplicity as the extraction involves multiple steps and is time consuming.

Next technique which is useful in the detection of $Fe^{3+}$ is the FIA which involves injecting a plug of sample into a flowing stream of carrier solution which can be also a stream of reagent. This method is widely utilized owing to its several advantages like small sample size, high reproducibility, satisfactory reliability and ease of automation (Ramkumar & Chandramouleeswaran , 2017). Since the FIA method is dependent of the formation of a coloured species between $Fe^{3+}$ and chromophoric reagent, therefore the selection of chromophore reagent is one of factor should be taken into consideration. Previously, many flow-injections spectrophotometric methods have been developed for the determination of iron using different various reagents such as 1,10-phenantroline, salicylate, dphenylamine-4-sulfonic acid sodium salt (DPA-4-SA), 8-hydroxyquinoline, tiron and thiocyanate( Kass et al., 2002; Asan et al., 2012; Adebayo et al., 2011). However, many of the proposed reagents can be hazardous, not environment friendly or expensive (Jaikrajang et al., 2018). To overcome these problems, the use of natural reagents from plant extracts as a green analytical approach are much desirable. Several plants extract such as green tea, sweet potato root, guava leaves, Indian mulberry roots and pumpkins have been utilized as a natural reagent for the determination of $Fe^{3+}$ using a flow injection spectrophotometric method (Pinyou et al., 2010; Settheeworrarit et al., 2005; Tontrong et al., 2012; Supharoek et al., 2017). Natta et al., (2018) developed a FIA spectrophotometric method for determination of iron (III) by using a green reagent extracted from *Phyllanthus emblica* with a detection limit of 0.31 mg $L^{-1}$. Although the presented method provides an environmentally friendly approach; the main drawback of the method are high limit of detection and tedious procedures (Ensafi et al., 2004).

Alternatively, electrochemical methods such as voltammetry and potentiometry offers significant advantages such as high sensitivity and selectivity without pre-treatment procedures, low limit of detection and rapid response time (Sadak et al.,2017). In electrochemical methods, the most common used electrodes are either in solid-state or ionophore-free, ion-exchange electrodes and ionophore-based membrane (Bralic et al.,2012). The choice of electrode use in this method significantly can enhance the performance of sensor in term of detection limit. Anguiano et al., (2012) have proposed an electrochemical detection of $Fe^{3+}$ using a modified glassy carbon electrode that exhibits a good limit detection of 0.003 μM. Other types of electrodes such as chemically modified mercury free electrodes, modified gold nanoparticle electrode and bismuth alloy have shown a noteworthy low detection limit (Zakhrova et al.,2012 ; Merli et al.,2014 ; Liu & Wang ,2014 ; Lin et al., 2015). However, one of the disadvantage~~s~~ of this approach is the short lifetime of the electrode (Mashhadizadeh et al.,2004; Bralic et al.,2012). Therefore, a new method which are high sensitivity and selectivity, low cost and rapid response time need to be developed.

## 2.2 Fluorescent and colorimetric as chemosensor for detection of $Fe^{3+}$

Among the various methods used for detection of $Fe^{3+}$, colorimetric and fluorescent chemosensors have gained interest in recent years due to their simplicity, high sensitivity and selectivity, easy to operate and provide a real time measurement of target analyte at very low concentration without any pre-treatment of the sample (Narayanaswarny & Govindaraju, 2012 ; Nandhini et al.,2016). Various works have been reported for detection of $Fe^{3+}$ using these two approaches.

Devaraj et al., (2012) have synthesized a coumarin derivative for the detection of $Fe^{3+}$ and $Mg^{2+}$ in solution as a colorimetric and fluorescent sensor, respectively. The sensor exhibited highly selective and sensitive recognition towards $Fe^{3+}$ in $CH_3CN$ compared to other metal ions tested such as $Mg^{2+}$, $Cr^{3+}$, $Mn^{2+}$, $Co^{3+}$, $Ni^{2+}$, $Cu^{2+}$, $Ag^{+}$, $Cd^{2+}$, $Pb^{2+}$, $Ca^{2+}$ and $K^{+}$ ions. A visible colour change was observed upon the binding from colourless to brown. Moreover, the coumarin based receptor showed a significant fluorescence enhancement (70-fold) towards $Mg^{2+}$ in the mixture of solution $CH_3CN/H_2O$ (8:2, v/v). The reported coumarin derivative exhibits a dual chemosensing properties of new selective colorimetric chemosensor foe $Fe^{3+}$ and fluorescent sensor for $Mg^{2+}$.

Zhu et al., (2015) have designed and synthesized carbazole-based Schiff base which was utilized as a highly selective colorimetric and fluorescent chemosensor for $Fe^{3+}$ and $Cr^{3+}$, respectively. Upon the addition of different test metal cations ( $Na^{+}$, $Mg^{2+}$, $Cr^{3+}$, $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Cu^{2+}$, $Zn^{2+}$, $Cu^{2+}$ $Ag^{+}$, $Cd^{2+}$, $Pb^{2+}$, $Ca^{2+}$ and $K^{+}$), the chemosensor shows a selective recognition towards $Fe^{3+}$ by a significant colour change from yellowish green to colourless with a significant blue-shift from 410 nm to 378 nm. Furthermore, the addition of $Cr^{3+}$ causes a 11-fold fluorescence enhancement compared to other metal ions. The results indicate that the carbazole-based Schiff base is capable as a chemosensor for $Fe^{3+}$ and $Cr^{3+}$ recognition.

A fluorophore modulation of propranolol with sodium dodecyl sulphate (SDS) assemblies for highly selective and sensitive recognition of $Fe^{3+}$ over other metal ions was reported by Gujar et al., (2018). The fluorescence intensity was quenched upon the addition of $Fe^{3+-}$which indicates a turn-off fluorescence sensing with a detection limit of 2.7 $\mu$M. The fluorescence quenching can be attributed to the intramolecular (PET) process due to paramagnetic nature of $Fe^{3+}$. This method provided a simple but efficient recognition unit of $Fe^{3+}$ based on the PET mechanism that may be useful for developing chemosensor in the future.

Li et al., (2011) have synthesized a fluoranthene based fluorescent chemosensor 2-(7,10-diphenyl fluoranthene-8-yl)-pyridine for detection of $Fe^{3+}$ in ethanol solution. Upon the addition of $Fe^{3+}$, it exhibits a great decrease of emission intensity indicating an efficient $Fe^{3+}$-selective “off” behaviour. The mechanism proposed for fluorescence change may be due to the paramagnetic property of unfilled *d* shell of $Fe^{3+}$ led to the possibility of electron and/or energy transfer with the organic fluorophores opening a non-radiative deactivation channel, resulting in the decreasing of emission intensity.

Similar turn-off PET mechanism was reported by Joshi et.al (2015) whose synthesized a coumarin-triazole based probe which acts as a highly selective and sensitive fluorescence sensor for $Fe^{3+}$. Addition of 5 equiv. of $Fe^{3+}$ affected the fluorescence spectra dramatically and resulting a fluorescence quenching of ~95%. The limit of detection reported for this work was 0.473 μM. The possible mechanism of fluorescence quenching upon the addition of $Fe^{3+}$ may be explained on the favourable photoinduced electron transfer(PET ) mechanism between the probe and $Fe^{3+}$, transfer of the lone pair of electrons over electron donor nitrogen atom to vacant *d* orbital of $Fe^{3+}$ which led to formation of complex.