# UNIVERSITI TEKNOLOGI MARA

# UNSYMMETRICAL DIETHYLENETRIAMINE FLUORESCENT CHEMOSENSORS FOR SELECTIVE RECOGNITION OF Fe(lll) AND Zn(ll)

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# ABSTRACT

Fluorescent chemosensor have significant role in medical, environmental and biological applications. Receptor and signaling unit are important aspect in designing fluorescent chemosensor to selectively recognize metal ions for practical applications. In this study a series of chemosensors were synthesized for metal ions which bears diethylenetriamine and benzenyl derivatives as the receptor and dimethyl-phenyl-amine as fluorescence signal. Eight synthesized unsymmetrical ligands were prepared by using Schiff base technique that involved condensation of primary amine ($-NH_2$) with an aldehyde (HC=O) to produce azomethine group (RCH=NR). All ligands were fully characterized by Fourier Transform Infrared (FT-IR), Proton Nuclear Magnetic Resonance ($^1$H-NMR) and elemental analysis (CHNS). All ligands shown the characteristic FT-IR peak for C=N at 1596-1639 $cm^{-1}$ and the $^1$H-NMR signal for HC=N at 8.11-8.51 ppm confirmed the formation of Schiff base ligand. Sensing properties for six synthesized ligands N-(4-Dimethylamino-benzylidene)-N'-{2-[(3-nitro-benzylidene)-amino]-ethyl}-ethane-1,2-diamine (L1), N-(4-Dimethylamino-benzylidene)-N'-{2-[(4-nitro-benzylidene)-amino]-ethyl}-ethane-1,2-diamine (L2), 3-[(2-{2-[(4-Dimethylamino-benzylidene)-amino]-ethylamino}-ethylimino)-methyl]-phenol (L3), 4-[(2-{2-[(4-Dimethylamino-benzylidene)-amino]-ethylamino}-ethylimino)-methyl]-phenol (L4), N-(4-Dimethylamino-benzylidene)-N'-{2-[(pyridin-2-ylmethylene)-amino]-ethyl}-ethane-1,2-diamine (L5) and synthesis of N-(4-Dimethylamino-benzylidene)-N'-{2-[(pyridin-3-ylmethylene)-amino]-ethyl}-ethane-1,2-diamine (L6) were studied towards transition metal. The selectivity and sensitivity tests of ligands were conducted on several metal ions. The fluorescence measurements revealed that L5 was more selective towards $Zn^{2+}$ while L1-L6 were selective towards $Fe^{3+}$ ions and forms complexes in 1:1 ratio as evidenced by Job's plot analysis. The limit of detection for L5 was found to be $3.5 \times 10^{-5}$ M and L1-L6 were $1.42 \times 10^{-6}$ M, $3.76 \times 10^{-6}$ M, $1.58 \times 10^{-6}$ M, $5.37 \times 10^{-6}$ M and $6.49 \times 10^{-6}$ M respectively. These sensors also exhibit a very good fluorescence sensing ability towards $Zn^{2+}$ and $Fe^{3+}$ at pH 7.0. Therefore, this fluorescent sensor can be applied to monitor the presence of heavy metals both in environment and biology conditions.

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# CHAPTER ONE
# INTRODUCTION

## 1.1 Research Background

Chemical sensor is a device converting chemical information into physical recordable signal. The term chemosensor is defined as a molecule of abiotic origin that is able to bind with the presence change in the property of the system, such as redox potentials and absorption or luminescence spectra. The need for chemosensors nowadays is very evident, many efforts are devoted to the synthesis and a huge number of papers have been published [1],[2].

Generally, there are three different approaches in designing chemosensors which are: a) binding site-signalling approach b) displacement approach c) chemodosimeter approach. At the "binding site-signalling subunit" approach, the two parts are linked through a covalent bond. The interaction of the analyte with the binding site caused changes in the electronic properties of the signalling subunit, resulting sensing of the target anion.

The displacement approach is involves the displacement of the cation from the coordination sphere of the receptor upon the addition of a particular anion due to the strong affinity of anion for the metal ion, thereby reviving the optical signature of the free host [7]. In the chemodosimeter approach involves the use of specific chemical reactions upon binding with anions, which results in an optical signal [8]. The displacement approach is most popular approach involves covalently introducing binding sites and signaling subunits to the chemosensors.

In the last few years, great attention has been paid to fluorescent chemosensors and many new systems were synthesized [9]. Fluorescent chemosensor composed of two parts which are a receptor (recognition element) responsible for the molecular recognition of the analyte and a fluorophore (fluorescence reporter) which responsible of signaling the recognition event. Both are connected through a spacer or also known as a linker [10]. The basic concept of chemosensing is outlined in Figure 1.1. A receptor is connected to a fluorophore by a spacer, and when the targeted metal species is bound, the photophysical characteristic of the fluorophore (such as