UNIVERSITI TEKNOLOGI MARA

SYNTHESIS OF UNSATURATED APPENDED NAPHTHALENE MACROCYCLIC LIGANDS AS CHEMOSENSOR

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ABSTRACT

Macrocyclic ligand is defined as cyclic molecules that contain of heteroatoms and capable to bind substrates. Six new macrocyclic ligands were synthesized by the reaction of 1,2-bis(2-carboxyaldehyde phenoxy)butane and various diamines. The macrocyclic ligands were synthesized involving two steps. The first step is the reaction of salicylaldehyde with 1,2-dibromoethane, 1,3-dibromopropane or 1,4-dibromobutane to produce precursor, then cyclisation were completed using Schiff base technique by adding diamines (naphthalene diamine). All ligands were characterized by using Elemental Analysis (EA), Fourier Transform Infrared (FT-IR) spectroscopy and proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy. The IR spectra of the precursor L1, L2, L3, L4 and L5 clearly demonstrated that the reaction was completed by the formation of υ(C-O-C) peak and disappearance of υ(OH) peak. The presence of υ(C-O-C) band peak appear in the range of 1267.84-1290.44 cm^{-1}. The IR spectra of the macrocyclic ligand L1a, L2a, L3a, L4a, L5a and L2b clearly demonstrated that the reaction was completed by the formation of υ(C=N) peak and disappearance of υ(C=O) of aldehyde. The presence of υ(C=N) band peak appear in the range of 1600.09 to 1637.53 cm^{-1}. The ^{1}H NMR spectra of the precursor L1, L2, L3, L4 and L5 shows the peak of O-$CH_2CH_2CH_2$-O in the range of 2.9 ppm and 4.6 ppm. Meanwhile, the ^{1}H NMR spectra of the macrocyclic ligand L1a, L2a, L3a, L4a, L5a and L2b shows the peak of δ(HC=N) at 9.1 ppm. Elemental analysis confirmed the theoretical and experimental value suggesting the attachment of diamine derivatives into the aldehyde precursor to form the macrocyclic. Attempt also made to produce saturated macrocyclic. The IR spectra of the ligand L6, L7 and L8 clearly shows the disappearance of the characteristic υ(-NH_2) that has been replaced with υ(-NH) peak at 3248 cm^{-1}, 3313 cm^{-1} and 3307 cm^{-1} respectively. For application, further study on selectivity, sensitivity, stoichiometry and binding constant were conducted. Ultraviolet visible spectroscopy (UV-Vis) was used to study the L3a and L2b ligands and fluorescent emission spectroscopic (FES) was applied for L1a and L2a ligands. Ligand L3a and L2b showed high selectivity towards Fe^{3+} ion than other metal ions Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. Thus Fe^{3+} was selected to study the fluorescence response profiles and detection limits. In conclusion, L2b is more sensitive (9.9 x 10^{-6} M) than L3a (6.689 x 10^{-6} M). Hence, the ligand and the Fe^{3+} synthesized in 2:1 ratio for further study of complexation. Ligand L1a and L2a showed more selective towards Fe^{3+} ion and Cu^{2+} than other metal ions. Thus Fe^{3+} and Cu^{2+} were selected to study the fluorescence response profiles and detection limits. The limit of detection L1a for Fe^{3+} is 1.08x10^{-6} M. The limit of detection L2a for Cu^{2+} is 1.2025x10^{-7} M. Ligand L1a and L2a were formed a stable 1:1 metal:ligand stoichiometry which is for further study of complexation.

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CHAPTER ONE
INTRODUCTION

1.1 Background of Study

Metals occur naturally in the crust, and their contents in the environment can vary between different regions resulting in spatial variation of background concentrations. The distribution of metals in the environment is controlled by the nature of metals and the influence of environmental factors (Lin et al., 2013). Of the 92 natural elements, about 30 metals and metalloids are potentially toxic to humans, Be, B, Li, Al, Ti, V, Cr, Mn, Co, Ni, Cu, As, Se, Sr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, W, Pt, Au, Hg, Pb, and Bi. Heavy metals are the generic term for metallic elements having an atomic weight higher than 40.04 (the atomic mass of Ca) (Misra et al., 2009). Heavy metals enter the environment in a natural and anthropogenic way. These sources include: natural release of crust, mining, land erosion, industrial discharge, urban runoff, sewage sludge, pest control or disease control used for plants, air pollution drops, and some others (Misra et al., 2009).

The main route of exposure to these toxic elements for most people is through the diet (food and water), even though some individuals are exposed to these contaminants at work. The contamination chain of heavy metals almost always following the order of cycles: industry, atmosphere, soil, water, foods and human. Although the poisoning and threats resulting to human health from any pollutants, of course, the focus function, it is known that chronic exposure to heavy metals and metaloids at relatively low levels can cause adverse effects (Lin et al., 2013). Hence, there is an increasing concern, especially in the developed world, about the exposure, and the absorption of heavy metals by humans. The population are increasingly demanding a cleaner environment in general, and reductions in the number of pollutants that reach humans due to increased human activity.

Heavy metal has been proven to be a major threat and there are several health risks associated with it. They sometimes act as a pseudo element of the body while at some point they may even interfere with metabolic processes. Some metals, such as aluminium, can be removed through removal activities, while some metals accumulated in the body and food chain, exhibiting a chronic properties. Various