UNIVERSITI TEKNOLOGI MARA

SYNTHESIS OF SYMMETRICAL AND UNSYMMETRICAL BENZOYLTHIOUREA LIGAND AS POTENTIAL CHEMOSENSOR FOR SELECTIVE DETERMINATION OF Cu(II) ION

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ABSTRACT

Design of a new specific colorimetric and fluorescence chemosensor for detection of Cu^{2+} is a challenge in the context of interference from coexisting metal ions in an aqueous solution. Therefore, new chemosensor were synthesized: symmetrical (L1, L2, L3) and unsymmetrical (L4, L5, L6, L7) benzoylthiourea ligand. The symmetrical ligands were synthesized by the reaction of benzoyl isothiocyanate with diethylenetriamine (2:1). The unsymmetical ligands were synthesized involving two steps. The first step was undergoing 1:1 condensation of 4-dimethylaminobenzaldehyde with diethylenetriamine. The reaction was completed by adding benzoyl isothiocyanate to form unsymmetrical ligands. All ligands were characterized by using Elemental Analysis (EA), Fourier Transform Infrared (FTIR) spectroscopy and proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy. For application, further study on selectivity, sensitivity, stoichiometry, binding constant, and the competition of ligands were conducted. Ultraviolet visible spectroscopy (UV-Vis) was used to study the symmetrical ligands and fluorescent emission spectroscopy (FES) was applied for all unsymmetrical ligands. All ligands showed more selective towards Cu^{2+} than other metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+} and Zn^{2+}). However, only L4 shows selective towards both Fe^{3+} and Cu^{2+} ions which is not a selective sensor. In conclusion, L1 is more sensitive (6.2×10^{-6} M) than L2 (1.5×10^{-6} M) and L3 (1.15×10^{-5} M) by forming a stable 1:2 (metal:ligand) complexes while for unsymmetrical ligand, L7 (9.7×10^{-6} M) is more sensitive than L5 (1.46×10^{-5} M) and L6 (9.7×10^{-5} M) by forming 2:1 (metal:ligand) complexes.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

Since 1970s, there has been growing concern over the diverse effects of heavy metals on humans and aquatic ecosystems (Amuda et al., 2006). Many heavy metals and their compound are toxic and very dangerous to the environment and human health. They accumulate in human body that can lead to various critical diseases such as cancers and dysfunction of organs (Zhang et al., 2015), cardiovascular diseases (Angelova et al., 2011) , and Alzheimer diseases (Duce & Bush, 2010). Heavy metals usually released from several industrial activities, such as mining, electroplating, aerospace, energy and fuel production, and catalysis.

Copper is the third most abundant trace mineral found in the human body. It is an essential trace element present in all living systems and is important for the function of many cellular enzymes (Lin et al., 2013). However, excess copper in human body can cause various intoxications (Yu et al., 2015; Udhayakumari et al., 2012). For example, the increasing concentration of copper cations in body causes imbalance in cellular processes resulting in pathogenesis. Therefore, the rational design and synthesis of efficient sensors that selectively recognize copper ion is an important topic in supramolecular chemistry. Although previous work has involved the development of a wide variety of chemical and physical sensors for the detection of copper, so far, improving the detection selectivity in the context of interference from coexisting metal ions has been challenging.

This heavy metal must be traced in an early stage before it becomes uncontrollable. Thus, there are many techniques can be used such as biosorbents (Siwin, 2017; Zhang et al., 2017), coagulant (Singh et al., 2017) and chemosensor. Adsorption strategy is the most efficient and cost-effective technique to remove low concentration Cr^{3+} ($\leq$100 mg/L) from aqueous solutions. However, the adsorptive removal of Cr^{3+} with low concentration is still challenging because the presence of other coexisting ions could significantly decrease the adsorption capacity of Cr^{3+} on adsorbent. Besides that, a range of pre-treatment methods can in theory be employed