# FABRICATION OF CALIXARENE FILMS USING LANGMUIR AND LANGMUIR-BLODGETT (LB) METHOD FOR HEAVY METAL ION SENSING

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## ABSTRACT

This study aims to develop novel calixarenes monolayer and multilayer films for sensing properties of heavy metals ion, namely $Pb^{2+}$ and $Cd^{2+}$, using Langmuir and Langmuir-Blodgett (LB) films techniques. Langmuir monolayer formation at the air-water interface was achieved by spreading amphiphilic molecules on water subphase and compressing them into an ordered arrangement. LB films were formed by transferring the floating monolayer molecules at the air-water interface onto a solid substrate. The properties of the calixarenes molecules developed from Langmuir film were discussed on terms of surface pressure-area (Π-A) isotherms, surface potential (ΔV) and effective dipole moment (μ) of the molecules in the absence and presence of metal ions. The calixarenes LB films were characterized by UV-visible spectroscopy to identify their optical properties. FTIR analysis yielded useful information regarding the specific interactions of calixarenes and the tested metal ions. Under the optimum experimental conditions, the lowest detectable concentration of $Pb^{2+}$ is $2.5x10^{-2}$ mM and $Cd^{2+}$ is $5.0x10^{-2}$ mM. Furthermore, calixarenes showed a well-defined response towards the $Pb^{2+}$ and $Cd^{2+}$ with good sensitivity and reproducibility. The detection mechanism of calixarenes with $Pb^{2+}$ and $Cd^{2+}$ ions in aqueous solution were also discussed. These findings are suitable to be applied for the development of optical sensors for the detection of heavy metal pollution in water.

# PENGHASILAN FILEM CALIXARENE MENGGUNAKAN KAEDAH LANGMUIR DAN LANGMUIR-BLODGETT (LB) UNTUK MENGESAN ION LOGAM BERAT

## ABSTRAK

Kajian ini bertujuan menghasilkan satu dan beberapa lapisan filem *calixarenes* bagi mengenalpasti ciri pengesanan ion $Pb^{2+}$ dan $Cd^{2+}$ dengan menggunakan kaedah Langmuir dan Langmuir-Blodgett (LB). Pembentukan filem Langmuir pada antara muka udara-air berlaku dengan menyebarkan molekul amfifilik tersebut pada sub-fasa air dan memampatkannya menjadi susunan yang teratur. Filem LB terbentuk dengan memindahkan lapisan filem terapung pada antara muka udara-air ke atas substrat. Sifat-sifat molekul *calixarenes* melalui penghasilan filem Langmuir dibincangkan dari segi isoterma tekanan permukaan-kawasan ($\Pi$-A), potensi permukaan ($\Delta$V) dan momen dwikutub berkesan ($\mu$) molekul dalam ketiadaan dan kehadiran ion-ion logam. Manakala pencirian filem LB *calixarenes* dilakukan dengan menggunakan spektroskopi penyerapan sinar ultra lembayung-cahaya nampak (*UV-visible spectroscopy*) untuk mengenalpasti ciri-ciri optik bahan tersebut. Analisis spektroskopi Fourier transformasi inframerah (FTIR) menghasilkan maklumat yang berguna mengenai interaksi tertentu *calixarenes* dengan ion logam yang diuji. Dalam keadaan yang optimum, kepekatan terendah untuk mengesan kehadiran ion $Pb^{2+}$ ialah $2.5x10^{-2}$ mM dan $Cd^{2+}$ ialah $5.0x10^{-2}$ mM. Tambahan pula, *calixarenes* menunjukkan tindak balas yang jelas ke arah ion $Pb^{2+}$ dan $Cd^{2+}$ dengan sensitiviti dan kebolehulangan yang baik. Mekanisme *calixarenes* mengesan ion $Pb^{2+}$ dan $Cd^{2+}$ dalam larutan *aqueous* turut dibincangkan dalam tesis ini. Hasil kajian ini sesuai diaplikasikan dalam pembangunan sensor optik bagi mengesan pencemaran logam berat dalam air.

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# LIST OF SYMBOLS

| | |
|---|---|
| $\Pi$ | Surface pressure |
| A | Mean molecular area |
| $A_0$ | Limitting area per molecule |
| $\gamma$ | Surface tension of water with monolayer |
| $\gamma_o$ | Surface tension of water |
| V | Electric potential |
| $\Delta V$ | Surface potential |
| $V_{acc}$ | Accelerating voltage |
| U | Potential energy |
| q | Charge |
| $\sigma$ | Charge density |
| d | Distance separated by two plates |
| W | Work done |
| $\mu$ | Dipole moment |
| $\mu_{\perp}$ | Effective dipole moment |
| $\varepsilon$ | Relative permittivity |
| $\varepsilon_o$ | Vacuum permittivity |
| T.R. | Transfer ratio |
| Pb | Lead |
| Cd | Cadmium |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| DI | Deionized |
| EPA | Environmental Protection Act |
| FTIR | Fourier Transform Infrared Spectroscopy |
| HMDS | Hexamethyldisilazane |
| IUPAC | International Union of Pure and Applied Chemistry |
| LB | Langmuir-Blodgett |
| LCAO | Linear combination of atomic orbitals |
| MO | Molecular orbitals |
| PTFE | Polytetrafluoroethylene |
| SPOT | Surface Potential Sensor |
| UV-Vis | Ultraviolet-Visible Spectroscopy |
| WHO | World Health Organization |

# CHAPTER 1

# INTRODUCTION

## 1.1 Introduction

The combination knowledge of Physics, Chemistry, Biology, Medicine, Material Science and Engineering lead to a new emerging scientific field which is called nanotechnology. This technological field provides outstanding potential to lead in the new discovery and invention for real life application. In recent years, many significant advances in the field of nanoscience and nanotechnology have emerged. The development of tools and devices to probe and manipulate matter at the atomic, molecular and macro-molecular levels are the significant part of research in nanotechnology.

Nanotechnology is defined as the engineering and utilization of functional structures designed at molecular scale with at least one characteristic dimension measured in nanometers (typically ranging from 1 to 100 nanometres). Nanotechnology can offer us a remarkable understanding of materials and devices that are useful in many kinds of fields. By tuning the structure on the nanoscale, a wide range of performance of existing chemicals and materials can be expended (Silva, 2006; Kim et al., 2012).

Nanotechnology has initiates the improvement of sensors suitable for measurements at the molecular level with high sensitivity and response time because of their high surface to volume ratio (Nano Connect Scandinavia, 2009). In short, most benefits of nanotechnology come from the possibility to modify the structures of materials at the nanoscale to obtain specific properties. Hence, the materials can be made to be stronger, lighter, more durable, more reactive, more sensitive, or better electrical conductors (Okwu & Onyeje, 2013). In fact, we also can produce a low-cost material and environment-friendly in order to keep the world a better place to live.

A nanosensor is a chemical or physical sensor, built on the nanoscale with the purpose of obtaining data on the atomic scale and convert them into data that can be easily analyzed. These sensors are very sensitive and able to detect even ultra-low concentrations of a substance that could be dangerous. There are many applications of nanosensors such as in the field of medical, environmental science, national security, aerospace, integrated circuits and so on. Furthermore, there are many types and a lot of ways to manufacture them but we are still facing with challenges to produce these nanosensors.

Calixarenes have been studied since 1970s which have been applied to extensive research in the development of electrode ionophores, waste water treatment, medical diagnosis and profoundly sensitive and selective sensors (Strobel et al., 2006). Calixarenes are example of supramolecular structures. Supramolecular structure can be defined as molecules of larger size formed together by grouping or bonding with the smaller molecules (Owens, 2005). Calixarenes are the third generation of supramolecular receptor after cyclodextrins and crown ethers (Shinkai et al., 1989) which can be functionalized at either upper rims or lower rims part to bind with cation or anion. By functionally modifying either the upper and/or lower rims it is possible to prepare various derivatives with differing selectivities for various guest ions and small molecules. Based on these interesting traits, calixarene is finally chosen as the sensing material in this work.

## 1.2 Motivation

The motivation behind the study of surface potential and effective dipole moment of calixarenes originates from their unique characteristics, which are capable for metal ions detection in aqueous environment. Due to their potential in capturing metal ions in water, it is believed that a metal ion sensor can be built by using Langmuir and Langmuir-Blodgett technique. Furthermore, calixarenes are non-toxic organic material. Therefore, the safety of using them as a receptor shall not be doubted. Although there are plenty of metal ion sensors have been produced (Shnek et al., 1995; Sun et al., 2011) it is rarely found a sensor that work based on the surface potential and effective dipole moment of the material. Hence, it is very exciting to explore the new scope of physics and chemistry which is compliment to each other.

This research focuses on the use of calixarene as organic sensor to detect heavy metals ion, namely $Pb^{2+}$ and $Cd^{2+}$ in a very low concentration. It is well known that lead and cadmium are toxic for living organisms, thus early detection in the environment is essential. The study of ion sensing plays an important role especially in industrial activity like manufacturing, mining, sewage treatment plant, and hazardous waste management facilities. In fact, food industry may also need the sensor to control the food quality and safety.

## 1.3 Problem statement

Heavy metals pollution have become a big worldwide environmental issue due to their tendency to accumulate in reservoir by biological and geochemical process and end up with entering the biological chain. The presence of heavy metals in the environment can naturally occur through weathering of rocks and volcanic activities (Liaghati, 2004). Besides that, heavy metals may occur due to human activities such as agriculture, industry and mining which can transport the contaminants to the river (Wang et al., 2007; Sany et al., 2013). Water contaminated by heavy metals may cause serious health problems and give a negative impact to our socio economy.

According to Lide (1992), heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water (1 at 4°C). Specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. For instance, cadmium (8.65), iron (7.9), lead (11.34) and mercury (13.546) (Thakur & Semil, 2013).

Lead (Pb) is one of the potentially toxic heavy metals when absorbed into the body. It is non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain and can be readily absorbed into the human body. The presence of Pb in drinking water even at low concentration level may cause diseases such as anemia, hepatitis and nephritic syndrome (Kumar & Gayathri, 2009). Pb is very harmful especially to children because children absorb 70% of Pb while adults only absorb 20% of it as in Figure 1.1 (Painter, 2013; Frisco Unleaded, 2013).

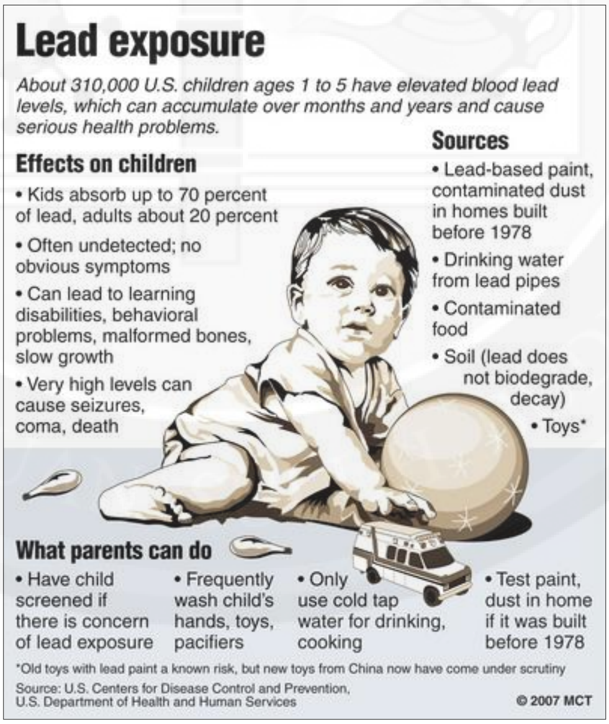


*Figure 1.1*. Lead exposure. Adapted from "U.S. Centers for Disease Control and Prevention, U.S. Department of Health and Human Services. Copyright 2007 by MCT.

If the level of Pb in the environment is not monitor and allowed to rise, it is afraid that it may cause long-term health risk to human and ecosystem. Therefore, the World Health Organization (WHO) has recommended an allowable concentration of Pb in drinking water, waste water and water used for daily purpose. The Environmental Protection Act (EPA) has established the drinking water standard for lead are 0.05 mg/L, but it is under review to decrease the level to 0.02 mg/L (Groffman et al., 1992) while the EPA has determined that the maximum contaminant level for cadmium in drinking water is 0.005 mg/L (Toxicological profile for Cadmium, 2012).

Based on the facts from WHO and EPA, it is very important to develop a sensor which can detect the presence of heavy metal even at a very low concentration. In this study, the aim is to detect two types of heavy metal ions, namely lead ion ($Pb^{2+}$) and cadmium ion ($Cd^{2+}$) in aqueous environment. Calix[4]arene is chosen as the sensing material because of the binding capabilities toward divalent cation and it is an organic material. Hence, it is believed that this study will be utilized in environmental analysis and medical diagnostic for early detection of heavy metal poisoning in humans.

## 1.4 Research objectives

This study was carried out with the following objectives:

i. To determine the Langmuir film characteristic such as surface pressure-area (Π-A) isotherm, limiting area per molecule ($A_0$) and isotherm phases of two types of calix[4]arene-based; Mat 3 and Mat 7.

ii. To determine the effective dipole moment (μ) of Langmuir film for Mat 3 and Mat 7.

iii. To compare Mat 3 and Mat 7 in terms of their size, surface potential (ΔV) and effective dipole moment (μ) in the absence and presence of $Pb^{2+}$ and $Cd^{2+}$ ions in aqueous solution.

## 1.5 Scope of research

In this study, two types of calix[4]arene were used as the sensing material namely Mat 3 and Mat 7. The study focus on the Langmuir and Langmuir-Blodgett (LB) technique to investigate the surface potential (ΔV) and effective dipole moment (μ) of calix[4]arene. The optimized parameters are ion concentration and spreading volume of calix[4]arene. The tested heavy metal elements used in this work are $Pb^{2+}$ and $Cd^{2+}$ metal cations. Several analysis such as surface pressure-area (Π-A) isotherm, surface potential (ΔV) measurement and effective dipole moment (μ) calculation were done on the ultra-thin film of calix[4]arene. Ultraviolet-visible spectroscopy were used to determine the optical properties of calix[4]arene sample in solution and thin films. The chemical bonding of the sample was determined using Fourier transform infrared spectrophotometer (FTIR).

A few challenges faced during the research period such as inability to conduct the experiment in a standard clean room. However, the cleanliness of the workplace and the instrument used are constantly monitored to minimized the contamination during the experiment. Besides that, the material of Mat 3 is insufficient to be tested with $Cd^{2+}$.

Thus, the surface pressure, surface potential and effective dipole moment of Mat 3 doped with $Cd^{2+}$ cannot be done.

## 1.6 Thesis organization

There are five chapters in this thesis and each chapter describes the sequence of this research. Chapter 1 presents a brief introduction of nanotechnology and its importance to humankind and the world. This chapter also presents the motivation to carry out the research, the problem statement, research objectives, scope of research and thesis organization. Chapter 2 covers an overview of related knowledge of Langmuir and Langmuir- Blodgett (LB) film. The applications of calixarene are reviewed in terms of ion sensing scope. Chapter 3 refers to the materials and methods describing the experimental procedure in the research. This chapter also covers the analysis and the characterization method of calixarene before and after incorporating with the ion. Chapter 4 presents the results and discussion covering heavy metals detection by calixarene. Chapter 5 refers to overall conclusions that are based on the findings obtained in the results and discussion (Chapter 4). Recommendations for future research were also given in the chapter.