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ABSTRACT

This research aimed to study the detection of *para*-aminobenzoic acid (PABA) by calix[4]arene (C4) and calix[6]arene (C6) using the Langmuir technique and density functional theory (DFT). The necessity to develop a PABA nanosensor arises from the side effects associated with PABA. The Langmuir experiment followed by the Langmuir-Schaefer (LS) film deposition was carried out. Field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDX), carbon, hydrogen, nitrogen, sulphur elemental analyser (CHNS), ultraviolet-visible spectroscopy (UV-Vis), and Fourier transform infrared spectroscopy (FTIR) were used to characterise the LS films. DFT as a first-principle computational method was implemented to calculate the band gap (E_g) and binding energy (ΔE) using Quantum ESPRESSO (QE). The Langmuir findings demonstrated the optimum sensing of PABA by C4 and C6 existed at the 1:1 host-guest ratio. The FESEM study confirmed the successful fabrication of C4, C6, C4-PABA, and C6-PABA LS films. Their morphologies, elemental composition, and optical properties denoted the formation of novel C4-PABA and C6-PABA complexes with promising reactivity. In congruence with the Langmuir study, the identification of N-H bonds within the complexes proved PABA binding at the lower rim of C4 and C6. The negative ΔE and the E_g reduction further revealed the capability of calixarenes to form stable 1:1 host-guest complexes with promising reactivity. Based on the additional UV-Vis and DFT investigations, the use of a water-soluble calix[4]arene derivative, 4-sulfocalix[4]arene (SC4) as PABA nanosensor is recommended for future studies. In conclusion, the experimental and DFT findings confirmed the sensing ability of C4 and C6 towards PABA. The higher stability exhibited by the C4-PABA complexes suggests the better sensing capability of C4 towards PABA compared to C6. This study implies that PABA detection could be implemented and applied in the development of PABA nanosensors for various applications, including medicinal and environmental uses.

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KAJIAN LANGMUIR, LANGMUIR-SCHAEFER DAN PEMODELAN TEORI FUNGSI KETUMPATAN KALIKS[N]ARINA DAN KALIKS[N]ARINA-PABA UNTUK APLIKASI NANOPENDERIAAN DADAH

ABSTRAK

Penyelidikan ini bertujuan untuk mengkaji pengesanan asid *para*-aminobenzoik (PABA) oleh kaliks[4]arina (C4) dan kaliks[6]arina (C6) menggunakan teknik Langmuir dan teori fungsi ketumpatan (DFT). Pembinaan nanopenderia PABA diperlukan kerana terdapat kesan sampingan yang dibawa oleh PABA. Ujikaji Langmuir diikuti dengan pembentukan filem Langmuir-Schaefer (LS) telah dijalankan. Mikroskop pengimbasan elektron pancaran medan (FESEM), spektroskopi sinar-X penyebaran tenaga (EDX), penganalisis unsur karbon, hidrogen, nitrogen, sulfur (CHNS), spektroskopi ultraungu-tampak (UV-Vis), dan spektroskopi inframerah transformasi Fourier (FTIR) telah digunakan untuk mencirikan filem LS. DFT sebagai kaedah pengiraan prinsip pertama telah dilaksanakan untuk mengira jurang jalur (E_g) dan tenaga pengikat (ΔE) dengan menggunakan perisian Quantum ESPRESSO (QE). Dapatan Langmuir menunjukkan pengesanan optimum PABA oleh C4 dan C6 adalah wujud pada nisbah hos-tetamu 1:1. Berdasarkan kajian FESEM, pembentukan filem LS C4, C6, C4-PABA, dan C6-PABA adalah berjaya. Morfologi, komposisi unsur, dan sifat optik yang didapati telah menunjukkan pembentukan kompleks C4-PABA dan C6-PABA baharu secara kualitatif dengan kereaktifan yang baik. Pengenalpastian ikatan N-H baharu dalam kompleks telah membuktikan pembentukan C4-PABA dan C6-PABA dengan pengikatan PABA melalui rim bawah yang selaras dengan kajian Langmuir. ΔE yang negatif dan pengurangan E_g telah menunjukkan kemampuan kaliksarina untuk membentuk kompleks hos-tetamu yang stabil pada nisbah 1:1 dengan kereaktifan yang baik. Berdasarkan eksperimen UV-Vis dan pengiraan DFT tambahan, penggunaan terbitan kaliks[4]arina yang bersifat larut dalam air, 4-sulfokaliks[4]arina (SC4) sebagai nanopenderia PABA dicadangkan untuk kajian akan datang. Kesimpulannya, dapatan kajian ujikaji dan DFT telah mengesahkan keupayaan C4 dan C6 dalam pengesanan PABA. Kestabilan yang lebih tinggi telah ditunjukkan oleh kompleks C4-PABA. Hal ini menunjukkan keupayaan pengesanan lebih baik C4 dalam pengesanan PABA berbanding dengan C6. Kajian ini memberi implikasi bahawa pengesanan PABA boleh diusahakan dan diaplikasikan dalam pembangunan nanopenderia PABA untuk pelbagai aplikasi, termasuk kegunaan perubatan dan alam sekitar.

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CONTENTS

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LIST OF TABLES

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LIST OF FIGURES

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LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy
C	Carbon
C4	Calix[4]arene
C4-PABA	Calix[4]arene-PABA
C6	Calix[6]arene
C6-PABA	Calix[4]arene-PABA
CCDC	Cambridge Crystallographic Data Centre
CHNS	Carbon, Hydrogen, Nitrogen, Sulphur Elemental Analyser
CIF	Crystallographic Information File
DFT	Density Functional Theory
DI	Deionised
DOS	Density of State
EDX	Energy Dispersive X-Ray Spectroscopy
F	Fluorine
FESEM	Field Emission Scanning Electron Microscope
FIR	Far-Infrared
FTIR	Fourier Transform Infrared Spectroscopy
GGA	Generalised Gradient Approximation
H	Hydrogen

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IR	Infrared
KSV2000-2	Langmuir apparatus KSV 2000 System 2
LDA	Local Density Approximation
OH	Hydroxyl
HMDS	1,1,1,3,3,3-Hexamethyldisilazane
IUPAC	International Union of Pure and Applied Chemistry
LB	Langmuir-Blodgett
LS	Langmuir-Schaefer
MD	Molecular Dynamics
MIR	Mid-Infrared
N	Nitrogen
NA	Not Applicable
ND	Not Detectable
NIR	Near-Infrared
O	Oxygen
PABA	*Para*-Aminobenzoic Acid or 4-Aminobenzoic Acid
PBE	Perdew–Berke–Erzndof
QE	Quantum ESPRESSO
RO	Research Objective
SCF	Self-Consistent Field
S	Sulphur
SC4	4-Sulfocalix[4]arene
SC4-PABA	4-Sulfocalix[4]arene-PABA
SPOT	Surface Potential Sensor

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2-D	Two-Dimensional
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible Spectroscopy

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LIST OF SYMBOLS

A	Absorbance
AU	Absorbance Units
α	Absorption Coefficient
Å	Angstrom
E_g	Band Gap
ΔE	Binding Energy
$CHCl_3$	Chloroform
c	Concentration
μ	Dipole Moment
$\mu_\perp$	Effective Dipole Moment
$\mu_\perp$-A	Effective Dipole Moment-Area
$v_{eff}(r)$	Effective Potential Functional
$\rho(r)$	Electron Density
$\mathcal{E}_i$	Energy of the System of Non-Interacting Electrons
ρ_0	Ground State Density
E_{Guest}	Ground State Energy of Guest
E_{Host}	Ground State Energy of Host
$E_{Complex}$	Ground State Energy of Host-Guest Complex
m_e	Mass of Electron
$\mu_{\perp max}$	Maximum Effective Dipole Moment

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ΔV_{max}	Maximum Surface Potential
A_0	Mean Molecular Area
A	Molecular Area
M	Molar
ε	Molar Absorption Coefficient
ε	Monolayer Permittivity
l	Path Length
E	Photon's Energy
υ	Photon's Frequency
h	Plank's Constant
r	Radius
$\hbar$	Reduced Planck Constant
c	Speed of Light
ΔV	Surface Potential
ΔV-A	Surface Potential-Area
Π	Surface Pressure
Π-A	Surface Pressure-Area
γ	Surface Tension of Pure Subphase
γ_0	Surface Tension of the Subphase Covered with a Monolayer
N	Total Number of Electron
T	Transmittance
ε_0	Vacuum Permittivity
$\phi_i(r)$	Wavefunction
λ	Wavelength

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λ_{max}	Wavelength of Maximum Absorbance

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CHAPTER 1

INTRODUCTION

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1.1 Research Background

This research is based on the implementation of nanotechnology and the use of nanomaterials for drug nanosensor application via thin film fabrication. Nanotechnology is a field of the manipulation of individual atoms and molecules with the means provided to fabricate particular and sensitive platforms (Munawar et al., 2019). The utilisation of nanomaterials on the order of 1-100 nm has garnered a growing amount of attention over the past decade due to their wide range of applications in several fields as illustrated in Figure 1.1, that are employed in commonplace products. The use of nanomaterials reforms methods in several sectors, making them easier, safer, more affordable, and transportable (Titus, Samuel, & Roopan, 2019).

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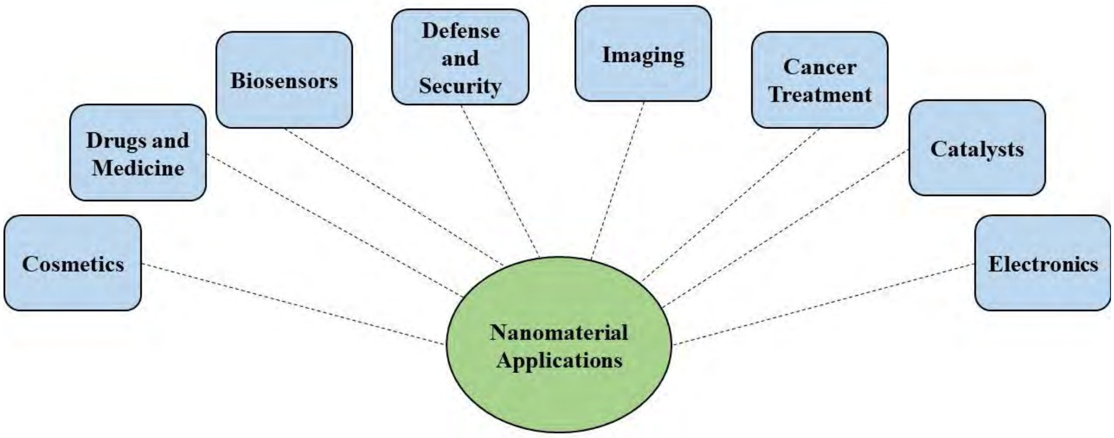

Figure 1.1. The Applications of Nanomaterials. Adapted from "Nanoparticle Characterization Techniques, by Titus, Samuel, and Roopan, 2019, *Green Synthesis, Characterization and Applications of Nanoparticles*. Copyright 2019 by Elsevier"

The implementation of nanotechnology in several fields, such as detecting small molecules, targeting drugs, and the fabrication and characterisation of nanomaterials have received notice in recent years. The distinctive properties of nanomaterials are also applied for sensing purposes. The sensitivity of nanosensors can be utilised in a variety of contexts, including environmental and industrial applications, as well as earlier detection of sickness, and toxins (Munawar et al., 2019).

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Nanomaterials are frequently used to develop nanosensors that are flexible, specific and sensitive. The uses of nanosensors are screening and measuring any changes related to a marker of interest and detecting important molecules. This is essential in clinical settings and industrial and environmental research development. Nanosensors are devices composed of nanoparticles and are capable of detecting signals at the nanoscale, including those generated by mechanical, electrochemical, or biological particles. The nanosensor specificity is transmitted by the targeting ligands.

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A particular marker of interest is attracted, depending on the functionality of the ligand (Shah, 2020; Munawar et al., 2019).

Host-guest interaction contributes to the advancement of nanosensor materials. In the field of supramolecular interaction, a chemical complex is formed during host-guest interaction, composed of at least two molecules that are held together in a unique structure, acting as a host molecule accommodating a guest molecule. The supramolecular complexes formed via host-guest interaction have been utilised in numerous applications, including nanosensors and drug delivery systems (Wagner, 2020; Gontero et al., 2017).

Calixarenes are known as the frequently studied host system and are used as nanosensors (Shah, 2020). Calixarenes are cavity-shaped cyclic molecules made up of phenol units linked via alkylidene groups with a micellar interior, internal nanopore and nanocage. Recently, calixarenes and their derivatives have received much attention. This is due to the outstanding characteristics of calixarenes which are able to interact with ions and neutral species (Cera, Arduini, Secchi, Credi, & Silvi, 2021; Fan & Guo, 2021; Farzin, Shamsipur, Sheibani, Samandari, & Hatami, 2019; Sanabria Español, & Maldonado, 2019).

The simplicity of calixarenes' synthesis is an additional benefit. Calixarenes are consistently defined as macrocycles that possess remarkable potential owing to their exceptional characteristics, which encompass adaptability and practicality as host molecules. The ability to change the initial molecular structure of calixarenes enables the development of novel functionalities (Wagner, 2020; Baroncini, Silvi, & Credi,

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2019; Iki & Miyano, 2001). In this context, calixarenes are easily functionalised at various sites on the upper and lower rims to construct vast modified three-dimensional structures. Furthermore, by modulating with appropriate groups, calixarenes are capable of self-assembly and may even assemble guest molecules into a variety of nanostructures. Moreover, calixarenes can form composite nanomaterials with both metals and non-metals. Multiple loading sites are provided by the calixarene-based associates for drugs (Fan & Guo, 2021).

Thus, through encapsulation and host-guest reactions, calixarene-based structures can be utilised to load drugs. Furthermore, calixarenes are a class of macrocyclic compounds that possess advantageous characteristics as drug carriers, such as low cytotoxicity and absence of hemolytic activity, which are crucial for safety purposes (Fan & Guo, 2021).

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The guest molecule in this research, 4-aminobenzoic acid known as *para*-aminobenzoic acid (PABA) is a vitamin. PABA is an organic molecule with two functional groups, which are amine and carboxyl. It is involved in the production of folic acid in bacteria, which is essential in drug synthesis (Sowinska, 2019; Drozd, Arkhipov, Boldyreva, & Perlovich, 2018). Furthermore, PABA is found as a structure in drugs that have numerous uses, including antibacterial functions and therapeutic uses (Chan et al., 2020; Sawalha, 2018). As an essential nutrient for many human pathogens, research has been conducted due to its biological and pharmaceutical properties (Krátký et al., 2020). Besides, PABA is an ultraviolet light-blocking agent used in sunscreen creams due to its chemical structure (Ozcan, 2019). However, evidence is provided at the molecular level regarding the harmful effect of PABA if used as a sunscreen

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ingredient. In simpler words, PABA causes DNA damage (Chan et al., 2020). Moreover, PABA has caused environmental pollution due to the constant release of PABA from personal care products into the aquatic environment (Khan et al., 2020; Tsoumachidou, Velegraki, & Poulios, 2016).

Since calixarenes are macrocyclic substances with excellent drug carrier properties, the use of calixarenes as a sensor to detect PABA is the focus of this research. The necessity of developing a PABA nanosensor is presented in the following section. The Langmuir behaviour, characterisation properties, and density functional theory (DFT) modelling of calixarenes and calixarene-PABA complexes were investigated in this study.

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1.2 Research Motivation

Nanosensors must be easy to handle in different environmental situations, affordable, and sensitive. Therefore, many attractive prospects have remained to be exploited in this area (Munawar et al., 2019). Furthermore, the developments of calixarenes in several areas are already known, including sensors, molecular machines, transport agents and molecular reactors. This shows that the developments of calixarenes could be considerable optimism in the future (Buttress et al., 2016; Baklouti, 2007).

This research is motivated to study the Langmuir behaviour and DFT modelling of calixarenes in detecting PABA because of the unique properties of both calixarenes and PABA. Furthermore, the structural developments in calixarenes are acknowledged

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(Sanabria Español & Maldonado, 2019). Previous research showed that calixarenes are attractive sensor materials for small molecule recognition. At the same time, an immense majority of calixarenes are investigated as sensing agents (Eddaif, Shaban, & Telegdi, 2019).

On the other hand, PABA, its unique properties, including pharmaceutical and biological properties, caused numerous scientific investigations to have been conducted for PABA as a drug (Drozd et al., 2018; Perillo & Atia, 2017). PABA is one of the main chemical ingredients contained in sunscreen products because of its potential power to absorb ultraviolet B (Singh, Čížková, Bišová, & Vítová, 2021). However, the sunscreen agent has become the common causative substance of photoallergic contact dermatitis (Snyder, Turrentine, & Cruz, 2019). The discovery of side effects caused by PABA is supported by various previous research, including photoallergic contact dermatitis, allergic contact dermatitis, and skin cancer (Nguyen & Yiannias, 2019; DeLeo, 2018; Gardner, 2014).

In the application of nanosensors, the information including the surface packing density, molecular orientation and stability is important to be determined. Concerning the use of the Langmuir technique, the way of interaction between molecules in the air-water interface could be studied. This technique is unique since the thin film fabrication of one molecule thickness can be done and their behaviour at the air-water interface can be investigated. The measurement of surface pressure (Π), mean molecular area (A_0) and surface potential (ΔV) can be studied to investigate the stability and conformation of the thin film (Paudyal et al., 2020).

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Moreover, DFT is used to study the structural and electronic properties of atoms, molecules and solids based on their electron density (Margraf & Reuter, 2021; Ranjan, Kumar, Chakraborty, Sharma, & Sharma, 2020). The extraordinary discovery regarding DFT won Walter Kohn the Nobel Prize in 1998 (Kohn, 1999). Recently, the structure and properties of molecules have been studied by some researchers using DFT. For instance, the electrochemical property and total interaction energy of calix[4]arene derivatives with guest molecules were studied for different purposes (Sharma, Sharma, Worthington, Shah, & Shrivastav, 2020; Ortolan et al., 2018).

Since calixarenes are macrocyclic substances with good drug carrier properties, the use of calixarenes as a nanosensor to detect the drug, which is PABA in a low concentration, is motivated. The Langmuir behaviour and DFT modelling of calixarenes in detecting PABA were focused on. Besides, several characterisation techniques were also utilised to investigate the structure and composition of the calixarene-PABA host-guest complex. This research is believed to be headed in future to a drug nanosensor as an application, which is crucial for safety purposes, and beneficial in various fields.

1.3 Problem Statement

Developing chemical and biological species using sensors is a fundamental issue in contemporary research. The difficulties entail a variety of complexities, including the synthesis to thin layer deposition, surface analysis technologies, and the use of computer-based data and signal processing, as well as their corresponding graphical

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representations (Bansal, Kumar, Karimi, Singh, & Kumar, 2020; Halay et al., 2019; McKervey, 1996). These are associated with the study conducted here.

Calixarenes have generated considerable attention, particularly in relation to the host-guest phenomenon, on account of their non-covalent capacity to ensnare guest molecules, such as ions and neutral molecules, as illustrated by the interactive structures adapted from Cambridge Crystallographic Data Centre (CCDC) in Figure 1.2 (Español & Villamil, 2019). Despite numerous previous research regarding macrocyclic calixarene, the sensing application of calixarenes is still a novel concept. On the other hand, the necessity of developing a PABA nanosensor is due to its role as a drug and its detrimental effect if used as a sunscreen ingredient (Chan et al., 2020; Sawalha, 2018). Besides, the development of a PABA nanosensor contribute to solving the environmental pollution caused by PABA in future. This development can be approached by studying the construction of novel calixarenes-PABA complexes.

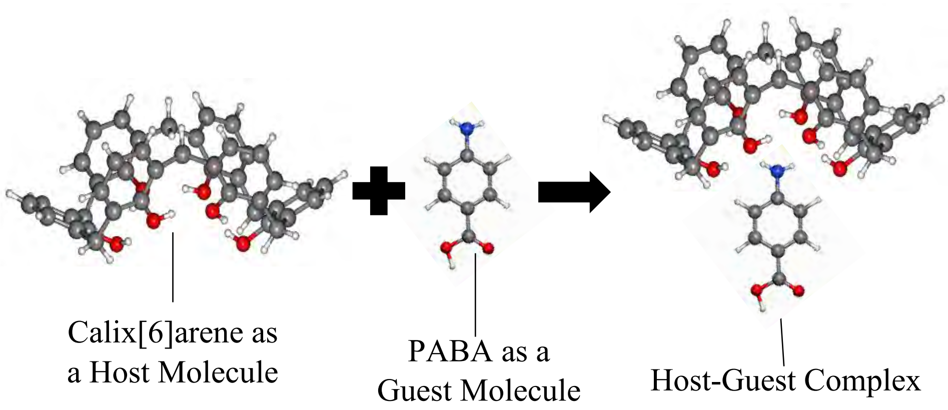

Figure 1.2. The Complexation Process of Calix[6]arene Macrocycle with PABA Molecule

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The encapsulation of PABA by macrocyclic substances has been explored in previous research. For instance, the complexation phenomena of PABA with cyclodextrin had been investigated by Kossay (2013). Besides, the optical property and Langmuir behaviour of calix[4]arene and its PABA host-guest complex were studied (Abd Karim, Supian, Wong, & Musa, 2023; Abd Karim et al., 2023).

Despite previous research regarding the interaction between PABA and macrocyclic substances, there is a lack of investigation of the host-guest interaction in the formation of calixarene-PABA complexes. The studies of the host-guest interaction including the morphology, elemental composition, and the formation of bonding are essential. This is because the structural studies of calixarenes are important (Coletta et al., 2020). In addition, there is great potential to be obtained beyond the molecule consideration (Asfari et al., 2004). Furthermore, there are neither Langmuir investigation, morphological, elemental, optical, nor binding studies of PABA trapped by calix[6]arene. Therefore, further research regarding the host-guest phenomena of calixarene and PABA as host and guest molecules, respectively, in the aspects stated above would contribute to the application of calixarenes.

Furthermore, the reactivity and binding are significant in host-guest interaction (Petroselli, Chen, Rebek, & Yu, 2021). The reactivity and stability of complexes are indicated by band gap (E_g) and binding energy (ΔE) respectively. These studies can be carried out precisely by applying DFT as a computational study (Shi, Han, Chen, & Du, 2019; Shahabi & Raissi, 2018). DFT, in contrast to the experimental method, is a cost-effective and efficient computational method for investigating diverse materials, including computing the E_g and ΔE (Lucatto, Assali, Pela, Marques, & Teles, 2017;

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Wasim, Mahmood, & Ayub, 2016). Nevertheless, there is no E_g nor ΔE studies of calixarenes and PABA in detail, despite the fact that there are some previous studies on the calixarenes derivatives, as discussed in the coming chapter. This research was distinguished by its integration of laboratory and computational works, as opposed to the previously conducted studies in the ways of solitary laboratory or computation.

In this research, PABA was aimed to be detected since developing a PABA nanosensor is necessary. The most widely studied calixarenes, calix[4]arene (C4) and calix[6]arene (C6) were chosen as the sensing material because of their structural features, which made them ideal precursors for assembling with guest molecules (Ukhatskaya, Kurkov, Matthews, & Loftsson, 2013; Baklouti, 2007). Besides, 4-sulfocalix[4]arene (SC4) was tested as well as a sensing material since its water-soluble property makes it an excellent host molecule for drug encapsulation (Fahmy et al., 2020). This research is believed to head towards a drug nanosensor development by using calixarenes to contribute to medicine and environmental benefits.

1.4 Research Objectives

This research was carried out with the following objectives.

i. To investigate the surface pressure-area (Π-A) isotherm, surface potential-area (ΔV-A) isotherm, and effective dipole moment ($\mu_{\perp}$) of calix[n]arene and calix[n]arene-PABA (n=4,6) using Langmuir technique.

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ii. To fabricate the calix[n]arene and calix[n]arene-PABA (n=4,6) Langmuir-Schaefer (LS) thin films.

iii. To characterise the morphologies, elemental compositions, optical properties, and chemical bonding of calix[n]arene-PABA LS films and compare them to calix[n]arene (n=4,6) using field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDX), carbon, hydrogen, nitrogen, sulphur elemental analyser (CHNS), ultraviolet-visible spectroscopy (UV-Vis), and Fourier transform infrared spectroscopy (FTIR).

iv. To determine the band gap (E_g) and binding energy (ΔE) of calix[n]arene and calix[n]arene-PABA (n=4,6) using density functional theory (DFT).

v. To test the usability of a water-soluble calix[4]arene derivative, 4-sulfocalix[4]arene (SC4) as PABA sensing material by studying their E_g and ΔE.

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1.5 Research Questions

i. What is the behaviour pattern of calix[n]arene and calix[n]arene-PABA (n=4,6) in Π-A isotherm, ΔV-A isotherm, and $\mu_{\perp}$ using the Langmuir technique?

ii. How do the calix[n]arene and calix[n]arene-PABA (n=4,6) LS films be fabricated?

iii. How are the morphologies, elemental compositions, optical properties, and chemical bonding of calix[n]arene and calix[n]arene-PABA (n=4,6) LS films using FESEM, EDX, CHNS, UV-Vis, and FTIR?

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iv. What are the significances of the E_g and complexes' ΔE of calix[n]arene (n=4,6) and calix[n]arene-PABA (n=4,6)?

v. Is the 4-sulfocalix[4]arene suitable to be used as PABA sensing material?

1.6 Research Scope and Limitation

In this research consisting of experimental and computational parts, three types of calixarenes, calix[4]arene (C4), calix[6]arene (C6), and 4-sulfocalix[4]arene (SC4) were used. C4 and C6 were used primarily in the experimental and computational studies, whereas SC4 was used as an addition sensing material in UV-Vis and DFT studies.

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In the experimental part, C4 and C6 were studied based on the Langmuir investigation. Based on previous studies, the stability and unique three-dimensional structure of C4 make it a particular interest in research (Lo & Wong, 2008). This was supported by Halay et al. (2019) regarding the numerous applications of C4 found in various fields including drug carriers. Furthermore, C4 is the most stable calixarene in its macrocyclic family (Lins et al., 2021). However, C6 with two extra aryl moieties is more flexible than C4 because of the enlargement of the structure (Becher & Schaumburg, 2013). By the way, the C6 was chosen as well to provide a larger cavity for the framework (Gutsche, 2007). SC4 was not used in the formation of Langmuir film due to its water-soluble properties. Unlike the amphiphilic C4 and C6, SC4 was unable to form Langmuir film at the air-water interface. Thus, the Langmuir technique is not suitable to be used for SC4 in the formation of a thin film. This is because the

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amphiphilic property is essential for the application of the Langmuir technique (Ariga, 2020).

First, Langmuir techniques were applied to analyse Π - A isotherm, ΔV - A isotherm and $\mu_{\perp}$ calculation before the C4 and C6 were deposited onto the substrate using the LS technique. Then, the spreading volume of C4 and C6, and the concentration of PABA, were determined. After the deposition of LS film, the studies of morphology and elemental analysis of the deposited C4, C6, C4-PABA, and C6-PABA thin film samples were carried out by using characterisation techniques including FESEM, EDX, CHNS, UV-Vis, and FTIR. In addition, the characterisation of C4, C6, C4-PABA, and C6-PABA solutions was carried out using UV-Vis to study their host-guest interaction as well as E_g. The same UV-Vis study was carried out for SC4 and SC4-PABA solutions in order to compare the experimental results with the computational outcomes.

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In the computational part, DFT calculation was carried out by inputting a crystallographic information file (CIF) obtained mainly from the Cambridge Crystallographic Data Centre (CCDC). Besides C4 and C6, the water-soluble SC4 was selected as the host molecule in the computational study as well due to its suitability as a drug carrier (Yuksel & Fellah, 2021). All of these calixarene members acted as sensing materials in this work, whereas the tested drug was PABA. The E_g of PABA, C4, C6, and SC4 was investigated. Furthermore, the ΔE of the novel C4-PABA, C6-PABA, and SC4-PABA complexes was also studied. The computational E_g was then compared to the experimental value.

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1.7 Research Significance

This research is heading towards drug nanosensor development, using calixarenes for medicine and environmental benefits. There is excellent potential for developing calixarenes in sensing technology applications (Mei & Ahmad, 2021). Current research has been able to get closer to the development of sensors for the detection of drugs (Sosa-Hernández et al., 2018). Significant interest has been gained by the development of the detection of drugs. Therefore, the improvement of sensors should be carried out. This is not only for the development but also to ensure the safe use for the detection, especially those that are harmful. Furthermore, research in sensing systems for drugs brings numerous advantages and values in different fields (Lima et al., 2018). Thus, developing a sensor to detect drugs such as PABA even at a very low concentration is necessary. The development of PABA nanosensors is crucial since PABA is found as a structure in drugs that have numerous uses. At the same time, it brings detrimental effects if used as a sunscreen ingredient (Chan et al., 2020; Sawalha, 2018).

Langmuir method was applied in this research as it fabricated monolayer thin films of amphiphilic molecules at the air-water interface (Begletsova et al., 2020). Besides, the application of DFT as a new form of quantum mechanical consideration in this research to investigate the aspect of the electronic structure of molecules enhanced the findings of this research (Yu, Li, & Truhlar, 2016).

Despite the sensing of calixarenes' family having been studied by numerous researchers, the utility of calixarenes as a drug nanosensor is still considered a relatively novel concept. At the same time, the significance of developing a PABA sensor is

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necessary as discussed above. Thus, the experimental and computational research of host-guest interaction between calixarenes' members and PABA is worth studying. The positive results of this research would be a good reference for future research regarding drug sensing development. Furthermore, the hybrid approaches with the combination of experimental and computational studies in this research would give new insight into PABA sensing development in the future. This is believed to head towards a drug nanosensor development by using calixarenes for contributing to medicine and environmental applications.

1.8 Thesis Organisation

Five chapters were presented in the thesis after completing the research. First, Chapter 1 introduced the nanotechnology and nanosensors related to calixarenes. Then, the roles of calixarenes and PABA as host molecules and drugs, respectively, were explained in the context of host-guest interaction. Overall, this chapter consisted of the background, motivation, problem statement, objectives, scope, limitation, and significance of this research.

Then, Chapter 2 presented the background of the calixarenes, PABA, Langmuir film, LS technique, and DFT related to this research in detail as the literature review. The working principle of each characterisation technique was discussed as well. All the information was based on previous research and studies. The information and knowledge referred to were studied and applied in this research.

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Chapter 3 described the materials and methodology applied in carrying out this research. The methods were based on the previous experiments mentioned in the literature review according to the suitable experimental conditions. The details regarding the Langmuir investigation, experiment characterisation, and DFT study were stated. Each of the steps involved in the experiments and computation calculations was mentioned. The parameters were decided as well. Both the experimental and computational studies were related and discussed in Chapter 4.

Next, Chapter 4 presented the result and discussion after collecting the data. Π-A isotherm, ΔV-A isotherm and $\mu_{\perp}$ calculation of C4, C6, C4-PABA, and C6-PABA Langmuir films were presented and discussed. After the deposition of materials onto the substrates using the LS technique, the morphology, elemental analysis, optical property, and bonding formation of the deposited thin film sample carried out using FESEM, EDX, CHNS, UV-Vis, and FTIR were investigated and presented. Furthermore, the results of UV-Vis solution characterisation and DFT studies for C4, C6, SC4, C4-PABA, C6-PABA, and SC4-PABA based on DFT were displayed. All of the data was presented in the form of tables and graphs. The discussion for each finding was explained holistically in Chapter 4.

Last but not least, Chapter 5 discussed the conclusion and recommendation of this research according to the results obtained from the experiment and computation works. This chapter concluded the whole research and discussed the recommendations for research related to the host-guest complexion of C4, C6, SC4, and PABA that might be carried out in future.

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