OPTICAL TRAPPING AND MANIPULATION OF A SINGLE CALIX[4]ARENE MICROCLUSTER IN WATER

NUR IZZATI BINTI MAHADI

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

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NUR IZZATI BINTI MAHADI

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ABSTRACT

This research aimed to optically trap and manipulate a single calix[4]arene microcluster in water. The optically trapped microclusters were evaluated in terms of their optical stiffness and rotatability with respect to the variation of microclusters' effective radius and laser power density. The calixarene microclusters contained solution was prepared by sonicating a vial containing a mixture of 1.7 mg of calix[4]arene powder in 1 ml of deionised water for three minutes. Calix[4]arene microclusters in the effective radius range between 0.5 and 3.5 µm were optically trapped using a 976 nm laser at laser power densities between 0.67 and 2.30 MW/cm^2 with laser sport size 1.1 µm. A quadrant photodiode (QPD) collected the scattered light from a single trapped microcluster. The QPD signal was analysed using a custom-made program named OSCal to determine the corner frequency of the optical trap. A quarter waveplate was introduced to the laser path to change the laser polarisation state and induce microcluster rotation. The rotatability of the trapped microcluster was determined by analysing the QPD signal and particle tracking method. Results showed that as the laser power density increases, the corner frequency of the trapped microcluster also increases. Furthermore, the trapped microcluster rotated faster as the laser power density increased regardless of the microcluster's effective radius. To conclude, calix[4]arene in the form of a microcluster can be optically trapped and respond to the circularly polarised light. The strength of the optical stiffness and the magnitude of the rotatability of a trapped calix[4]arene microcluster depend on the laser power density. This research implies the broadening potential of light-manipulated calix[4]arene as a microprobe or microactuator in a liquid.

PEMERANGKAPAN DAN PEMANIPULASIAN OPTIK SATU MIKROGUGUSAN CALIX[4]ARENE TUNGGAL DI DALAM AIR

ABSTRAK

Kajian ini bertujuan untuk memerangkap dan memanipulasi secara optik satu mikrogugusan calix[4]arene tunggal di dalam air. Mikrogugusan yang terperangkap secara optik dinilai dari segi kekakuan optik dan kebolehputarannya berkenaan dengan variasi saiz berkesan mikrocluster dan ketumpatan kuasa laser. Larutan mikrogugusan di dalam vial telah disediakan dengan mensonikasikan campuran yang mengandungi 1.7 mg serbuk calix[4]arena dan 1 ml air ternyahion selama tiga minit. Mikrogugusan calix[4]arene dalam julat saiz berkesan antara 0.5 dan 3.5 µm diperangkap secara optik menggunakan laser 976 nm pada ketumpatan kuasa laser dari 0.67 hingga 2.30 MW/cm^2 dengan saiz titik laser 1.1 µm. Fotodiod Kuadran (QPD) mengumpul cahaya terserak daripada satu mikrogugusan tunggal yang terperangkap. Isyarat QPD dianalisis menggunakan perisian buatan khas bernama OSCal untuk menentukan frekuensi pepenjuru perangkap optik. Plat gelombang sukuan dimasukkan dalam laluan laser untuk menukar keadaan pengutuban laser dan mendorong putaran mikrogugusan. Kebolehputaran mikrogugusan yang terperangkap ditentukan dengan menganalisis isyarat QPD dan kaedah penjejakan zarah. Hasil analisis menunjukkan bahawa apabila ketumpatan kuasa laser meningkat, frekuensi penjuru mikrogugusan terperangkap juga meningkat. Tambahan pula, mikrokluster yang terperangkap berputar lebih cepat apabila ketumpatan kuasa laser meningkat tanpa mengira saiz berkesan mikrokluster. Sebagai kesimpulan, calix[4]arene dalam bentuk mikrogugusan boleh diperangkap secara optik dan bertindak balas kepada cahaya terkutub membulat. Kekuatan kekakuan optik dan magnitud kebolehputaran mikrocluster calix[4]arena yang terperangkap bergantung pada ketumpatan kuasa laser. Kajian ini memberi implikasi terhadap perkembangan potensi penggunaan calix[4]arene yang dimanipulasi cahaya sebagai mikroprob atau mikropenggerak di dalam bendalir.

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CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 METHODOLOGY

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LIST OF SYMBOLS

SYMBOLS	MEANING	UNITS
σ^2	variance	arbitrary
ρ	fluid's density	m^3/s
ρ'	probability density	---
U	trap potential energy	J
C	normalisation constant	---
T	absolute temperature	K
t	time	s
γ	coefficient of friction	N s/m
k_T	optical stiffness	pN/m
r^*	effective radius	m
Ƞ	fluid viscosity	Kg/m^3
f_c	corner frequency	Hz
F_g	gradient force	N
F_s	scattering force	N
λ	wavelength	m

LIST OF CONSTANTS

SYMBOLS	**MEANING**	**UNITS**
k_B	Boltzmann constant	J/K
π	Pi constant	---

LIST OF ABBREVIATIONS

ASCII	American Standard Code for Information Interchange
BS	Boltzmann Statistics
CCD	Charged Coupled Device
ET	Equipartition Theorem
NA	Numerical Aperture
OSCal	Optical Stiffness Calculator
OT	Optical Tweezers
PSD	Power Spectrum Density
QPD	Quadrant Photodiode
USB	Universal Serial Bus
WD	Working Distance

APPENDIX LIST

CHAPTER 1

INTRODUCTION

1.1 Introduction

This chapter gives a brief introduction to the research carried out. The chapter begins with the background of the research. Then followed up by a discussion of the problem statement. Several objectives have been identified to guide this research to address the challenge highlighted in the problem statement. Next, the research's significance and scope will also be discussed in this chapter. Finally, this chapter concludes with a summary of the dissertation.

1.2 Research Background

Arthur Ashkin was the first to establish optical tweezers (OT) in 1970, for which he received a Nobel Prize in 2018 (Ashkin, 1970). Optical tweezers were the preferred instrument for manipulating delicate nano and microparticle samples. There was no mechanical contact with the sample but only a tightly focused laser beam (X. Li & Sun, 2019; Ma et al., 2019, reducing the damage due to mechanical forces. Manipulating the particles with a tightly focused laser is called optical trapping. Two main forces are essential in optical trapping: gradient and scattering force.

The gradient force, F_g is a conservative force resulting from the difference in refractive index between particles and their surrounding medium that pulls the particle towards the area of maximum light intensity (Spesyvtseva & Dholakia, 2016). F_g creates an optical trapping potential for the particles while the scattering force, F_s tends to push the particles out of the trapping spot. F_g is proportional to the intensity gradient of the laser, while the F_s is proportional to the intensity of the laser. Therefore, F_g must be equal to or greater than F_s to establish a stable trap (Bormuth et al., 2008; Wu et al., 2017). These two illustrated forces are shown in Figure 1.1. The gradient force radially acts toward the laser beam, and the particle feels the resultant force toward the focal point of the laser.

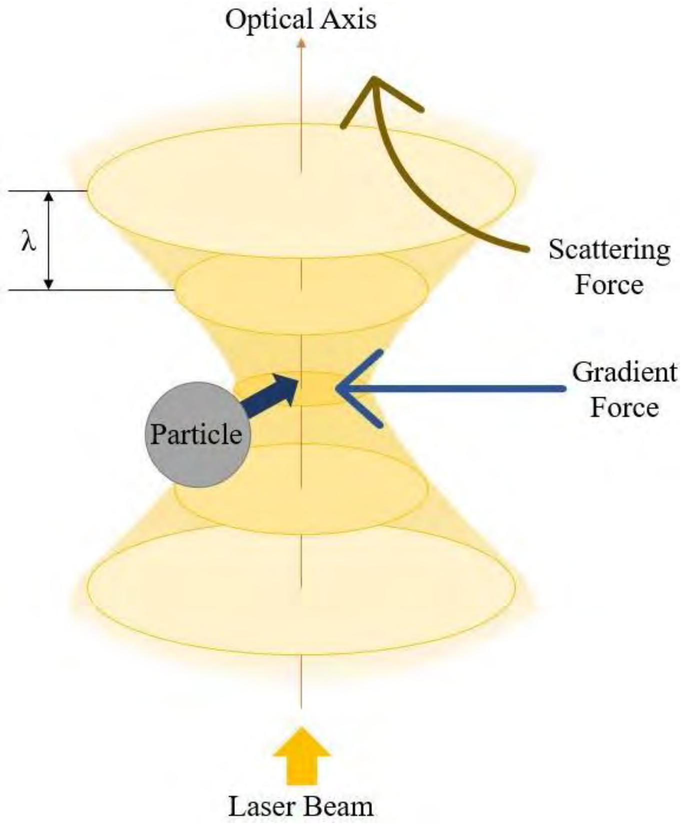

Figure 1.1. Gradient and scattering forces in an optical trap (Grier, 2003).

Optical tweezers have found their applications in many different research fields, such as physics (Suarez et al., 2021), chemistry (Lv et al., 2020), molecular biology (He et al., 2019), medicine (Konyshev et al., 2020), agricultural agriculture (Hawes et al., 2010) and many others. For example, optical tweezers have been used in the biological context to select and isolate a single cell (Keloth et al., 2018) and monitor bacteria's movement (Conteduca et al., 2019). Furthermore, the optical tweezers can also manipulate the lipid bilayer for membrane tension measurements (Dols-Perez et al., 2019). Optical tweezers can also study the interaction between red blood cells and viruses (Crick et al., 2014). Research on optical manipulation of a single particle or clusters of a regular shape (sphere, cylinder, oval, etc.) has been widely reported (Chang et al., 2006; Liu et al., 2016; Ranha Neves & Cesar, 2019). However, optical manipulation of a single irregular-shaped particle is still scarce and remains experimentally and theoretically challenging. On the other hand, optical manipulation by trapping a particle cluster with an irregular shape is quite interesting because of the possibility of broadening the trapping applications (Nieminen & Heckenberg, 2000; Yusof et al., 2020).

Calixarene was first introduced in 1870 but was ignored until Gutsche drew attention to the potential use of calixarene as a molecular receptor in 1970 (Mokhtari & Pourabdollah, 2013). During the last three decades, calixarene has been widely studied as a potential sensing element for sensor development, especially in heavy-ion detection in water (Gumpu et al., 2015; Mokhtari & Pourabdollah, 2013). Calixarene structures can be customed and differentiated by the number of phenolic units in their macrocyclic backbone (Gutsche & Bauer, 1985), as illustrated in Figure 1.2. Calixarene generally adopts a basket-shaped formation with the upper rim (hydrophobic) and lower rim (hydrophilic), as shown in Figure 1.3, and serves as host-guest molecules (H. Li et al., 2007; Morales et al., 2011). A hydroxyl group (-OH) in calixarene allows physical interaction with various functional groups. Therefore, the functional group can be used to detect the presence of ions. The promising applications of calixarene in heavy metal detection can be helpful in environmental sustainability. Toxic heavy metals can be found in air, soil, and water. It is harmful to humanity (Gumpu et al., 2015).

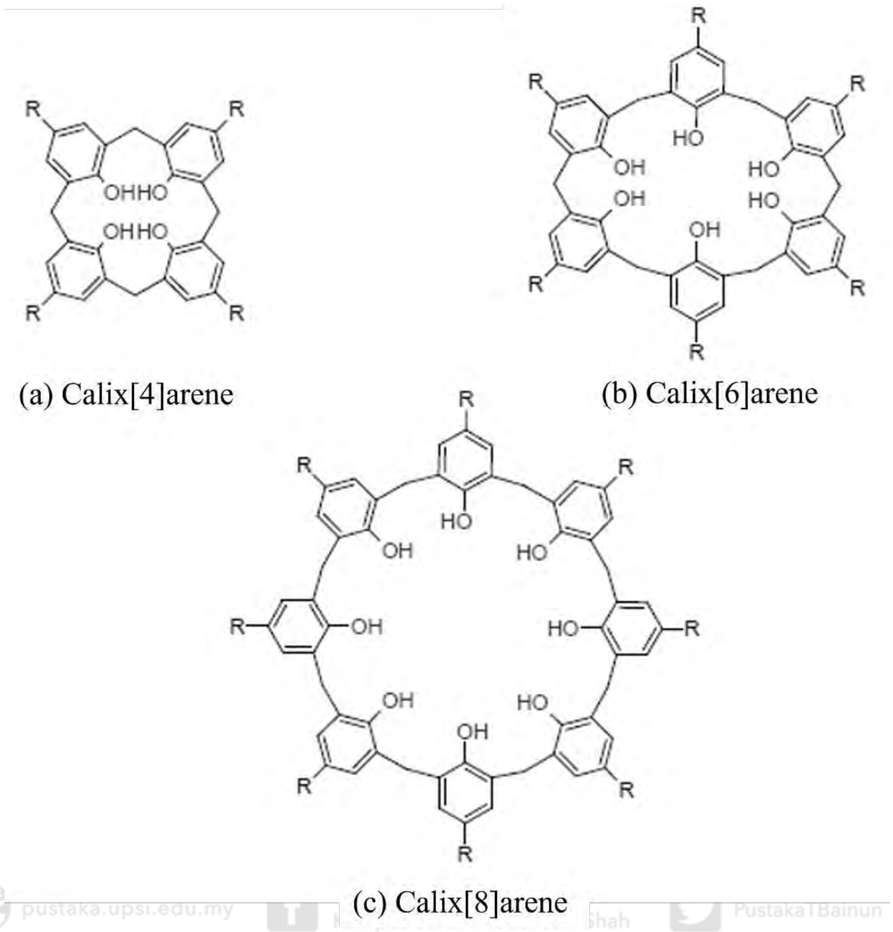

Figure 1.2. Calixarene was differentiated by the number of phenolic units in its macrocyclic backbone. (a) Calix[4]arene have four phenolic units, (b) calix[6]arene have six phenolic units, and (c) calix[8]arenes have eight phenolic units. (Español & Villamil, 2019)

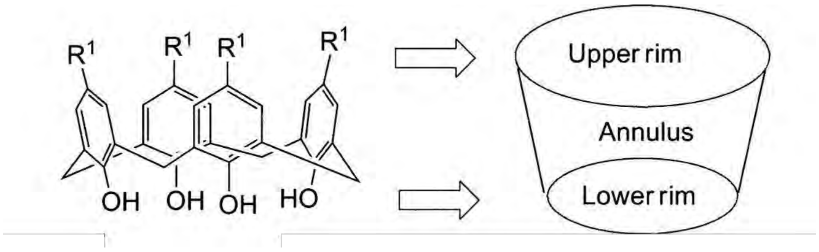

Figure 1.3. Calixarene generally adopts a basket-shaped formation with the upper rim (hydrophobic) and lower rim (hydrophilic) (Naseer et al., 2017).

This basket-shaped formation allows them to act as receptors for small ions and molecules by providing a rigid concave surface at their lower or upper rim, leading to their broader applications as a detector of metal ions (Satheeshkumar et al., 2004;

Toutianoush et al., 2005). Because of that, calixarene is more stood up among other supramolecular used to form sensors (Supian et al., 2017; Supian, Richardson, Deasy, Kelleher, et al., 2010). In addition, previous research has proven that calixarenes in thin-film and ion-selective electrodes are suitable for capturing metal ions in water using multiple parameters (Jin Mei & Ainliah Alang Ahmad, 2021; Supian, Richardson, Deasy, Kelleher, et al., 2010; Supian, Richardson, Deasy, Kelleher, et al., 2010).

Calixarene is made as a sensor element in the form of a thin film and electrodes in heavy-ion detection. This requires further steps in the sensor fabrication and post-detection analysis. This research explores another potential of using calixarene as an ion sensing element as a practical, functional heavy-ion detector by optically trapping and manipulating calix[4]arene microcluster in the water. Calix[4]arene was the most studied compared to other calixarenes because they are easy to synthesise and modify (Español & Villamil, 2019; Wenzel, 2012). Calix[4]arene also has shown the most selective recognition and complexation with heavy ions (Qureshi et al., 2009). In this research, calix[4]arene was tested as the starting basis for the possibility of extending its applicability using the optical trapping technique.

1.3 Problem Statement

In the last three decades, calixarenes have long been studied as ion detector sensors. The reason is that the calixarene's upper and lower rims can be modified to bond with specific ions or derivatives suited to the researcher's studies (Jin Mei & Ainliah Alang Ahmad, 2021; Mokhtari & Pourabdollah, 2013). However, most studies on calixarene as a sensor were on the water surface as a thin film and ion-selective electrodes. Because of the hydrophobic upper rims and hydrophilic lower rims, the researcher needs to add derivatives to make it a water-soluble structure (Español & Villamil, 2019). Typically, calixarenes form a thin film on the water surface for ion detection. A few types of research have been conducted on using calixarene as an ion detector in the water. However, some derivatives were added to make calixarene soluble in water. A review article by Jin Mei and Ainliah Alang Ahmad listed a few drawbacks of using derivatives. Therefore, this research proposed to trap optically and manipulate a single calix[4]arene microcluster in water without adding any derivatives.

However, trapping calix[4]arene microcluster in the water proved quite challenging as there were few studies on trapping irregular shapes using optical tweezers (Herranen et al., 2019). At the same time, extensive studies have been reported on trapping regular particles such as colloids and cells. Unfortunately, there is not much theory about irregular-shaped particles that could be used as references. The most crucial part of optical trapping is to have stable trapping. Optical stiffness is an indicator of whether the trapping is strong or weak. Optical stiffness can be determined by the corner frequency of the trapped microcluster. It can also show the strength of the optical tweezers' hold' on the trapped microcluster.

The microcluster can be extended if it can be free manipulated in 3-dimensional space. An optically trapped particle can be translated in x-, y-, and z- direction by moving the laser spot. However, the possibility of rotational control needs more consideration, such as the particle's polarizability and the laser's polarisation state. Therefore, this research will explore if the calix[4]arene microcluster can exhibit such a possibility in terms of its rotatability by changing the polarisation state of the applied laser.

1.4 Research Objectives

The objectives of this research were to optically trap and manipulate a single calix[4]arene microcluster. This research also aimed to evaluate the optical stiffness of the optical trap of calix[4]arene microclusters based on corner frequency, laser power density, and microcluster effective radius. Lastly, this research tried to determine the rotatability of the microcluster based on laser power density and microcluster effective radius. This research was done to broaden the potential of calix[4]arene as an ion detector application by proving that calix[4]arene can be used in water without adding any derivates.

Specifically, these research objectives are.

- To optically trap and manipulate a single calix[4]arene microcluster of calix[4]arene in water.
- To evaluate the optical stiffness of the optical trap of a single calix[4]arene microcluster based on the corner frequency, laser power density, and microcluster effective radius.
- To determine the rotatability of a single trapped calix[4]arene microcluster based on laser power density and microcluster effective radius.

1.5 Research Significant

For three decades, Calixarene has been studied and used as a specific metal ion detector. Although much research on calixarene as an ion detector was done on the water surface,no reported research about calixarene as an ion detector has been found in water because of calixarene's amphiphilic properties. This research aimed to confirm that a single calix[4]arene microclusters can be optically trapped and manipulated and possibly used as an ion detector in the water. This confirmation can broaden the potential of calixarene as an ion sensor detector. In addition, the stability of the optical as well as using it as microactuator trapping of the calix[4]arene microclusters was investigated in this research. This research could help other researchers study calixareneas an ion detector in the water.

1.6 Scope of Research

The optical tweezers used in this research were Modular Optical Tweezers, OTKB (/M) model. The wavelength of the laser used was 976 nm. The laser power densities were limited to five values: 0.67, 1.08, 1.48, 1.89, and 2.30 MW/cm^2. The calixarene used in this research was calix[4]arene. The trapping and manipulating process were performed only on the microclusters within an effective radius of 0.5 to 3.50 µm as the smaller microclusters were difficult to visualise by the camera using the current setup and larger microdroplets were challenging to be trapped. Besides calix[4]arene powder and deionised water, no additional surfactant or derivatives were added.

1.7 Dissertation Summary

This dissertation consists of five chapters. The first chapter explained the background of the research, problem statement, objectives, significance, and scope of the research. The second chapter briefly explained the principle behind the optical tweezers system, optical trapping and its applications, the PSD analysis method, k_T and f_c of a trapped particle, calixarene, and molecular sensor in the optical tweezers fields. Chapter 3 described the methodology for optical tweezers assembly and optical alignment, the preparation for calix[4]arene microcluster solution, the effective radius, optical stiffness, corner frequency, and angular velocity analysis of the trapped calix[4]arene microcluster. The next chapter, Chapter 4, presents the results obtained from this research. The calix[4]arene microcluster was produced and was optically trapped and manipulated using optical tweezers. The r^*, k_T, f_c and ω of the trapped microclusters were determined using the steps mentioned in the previous chapter. The final chapter concludes the research and provides recommendations for further studies that could beimproved based on this research.