iJRASET
International Journal For Research in Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 7 **Issue:** VI **Month of publication:** June 2019

DOI: http://doi.org/10.22214/ijraset.2019.6323

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International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.177
Volume 7 Issue VI, June 2019- Available at www.ijraset.com

Synthesis and Characterization of Supramolecular Cucurbituril, Molybdenum 2,2'- Bipyridyl Complex

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Abstract: ***Supra molecular Cucurbituril, Molybdenum2,2'-bipyridyl complex has been synthesized by precipitation followed by slow evaporation techniques. Changes in the physical properties of the ligand and the complex were characterized by melting point and solubility test . The absorption spectrum of the Cucurbituril, Molybdenum2, 2'-bipyridyl complex were studied by decreasing and increasing concentrations by using UV – Visible spectrophotometer and IR spectrophotometer. The interaction between the metal and ligands were studied by UV- visible spectral analysis. The functional groups and modes of vibration were identified by IR spectral analysis.***

Keywords: Cucurbituril, evaporation, precipitation, absorption, ligand, spectrophotometer.

I. INTRODUCTION

A Supramolecular assembly or "supramolecule" is a well defined complex of molecules held together by noncovalent bonds. Cucurbiturils are macrocyclic molecules consisting of glycouril repeating units. These supramolecular compounds are particularly interesting to chemists because they are molecular containers that are capable of binding other molecules within their cavities. The name is derived from the resemblance of this molecule with a pumpkin of the family of Cucurbitaceae. The cavity of cucurbituril has nanoscale dimensions with an approximate height of 9.1 A^0, outer diameter 5.8 A^0 and inner diameter 3.9 A^0. Cucurbiturils were first synthesized in 1905 by Behrend [1] but their structure was not elucidated until 1981[2]. Cucurbituril is a rigid molecule and posses a hydrophobic cavity. At each entrance to the cavity, six polar carbonyl groups are located. These conditions are ideal for complexation of positively charged organic molecules with hydrophobic groups. So the complexation of a large number of different ammonium ions by cucurbituril were studied first [3-8]. Cucurbituril is able to bind alkali and alkaline earth cations [9-11], rare earth metals and hydrogen bonded complexes of transition metal due to the presence of polarised carbonyl groups. Cucurbituril is used to remove reactive dyes from waste water produced from textile industry.. Key applications of this field are the construction of molecular sensors and catalysis.[12-15] . Freeman published the crystal structure of the first host-guest complex of Cucurbit[6]uril which incorporates the p-Xylene diammonium cation into the macrocyclic cavity. Researchers have shown that Cucurbit[6]uril acts as a catalyst in cyclo-addition reactions. Detailed examination has been done on the construction of supramolecular organic, inorganic compounds from macrocyclic cavitand cucurbit[6]Uril and mono and polynuclear aqua complexes. Cucurbit[6]uril is used in the construction of polyrotaxanes, supramolecular switches and fluorescent materials and in the removal of contaminants such as colourants from water or volatile organic molecules from air.

II. MATERIALS AND METHODS:

A. *Synthesis Of Cucurbituril*

1) *Materials:* Glyoxal, Urea, Formaldehyde, Concentrated hydrochloric acid, were of analytical grade. The mixture was stirred with water and again evaporated.

B. *Experimental Methods*

1) *Synthesis of Cucurbituril:* Cucurbituril is a cyclic condensation product of glycouril and formaldehyde.
2) *Preparation of Glycouril:* Glycouril was prepared by adding15g of urea with 5.8 ml of glyoxal and stirred well with 10 ml of distilled water. The pH was adjusted to 0-1 by adding concentrated hydrochloric acid.The solution was heated to 75^0C to get a creamy white precipitate which is insoluble in water. By using this quantity of urea, glyoxal and water we got the yield of about 3g of glycouril. The white precipitate was collected by filtering in a buckner flask.
3) *Synthesis of Cucurbituril:* About 3g of glycouril was dissolved in 12.5ml of hydrochloric acid. The solution was cooled to 0^0C and 4ml (40%) formaldehyde was added. The solution was mixed and then allowed to form a gel. After 1 hour the mixture

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was heated at 100^0C for about 3 hours. The mixture was allowed to cool to room temperature and then was evaporated to remove hydrochloric acid. A fractional crystallisation was performed by dissolving the solid in a minimum of concentrated hydrochloric acid and then adding water until the solution started to precipitate. The mixture was left over night and collected the precipitate.The filtrate was evaporated until all solid precipitates were collected. The product obtained was cucurbit[6]uril.Ordinarily multifunctional monomer such as cucurbituril undergoes a step-growth polymerisation that would give a distribution of products, but due to favourable strain and abundance of hydrogen bonding the cucurbit[6]uril was the only reaction product isolated after precipitation. Decreasing the temperatures of the reaction between 75^0C and 90^0C can be used to access other sizes of cucurbituril including cucurbit[5]uril, cucurbit[7]uril, cucurbit[8]uril, cucurbit[0]uril, cucurbit[10]uril. Although other ring sizes are still formed in smaller percentages than cucurbit[6]uril. The isolation of sizes other than cucurbit[6]uril requires fractional crystallization and dissolution cucurbit[5]uril, cucurbit[7]uril, and cucurbit[8]uril are all currently commercially available. The largest sizes are a particularly active area of research since they can bind larger and more interesting guest molecules thus expanding their potential applications.

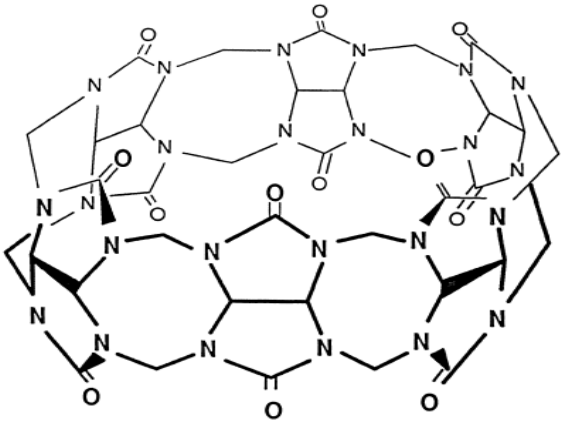
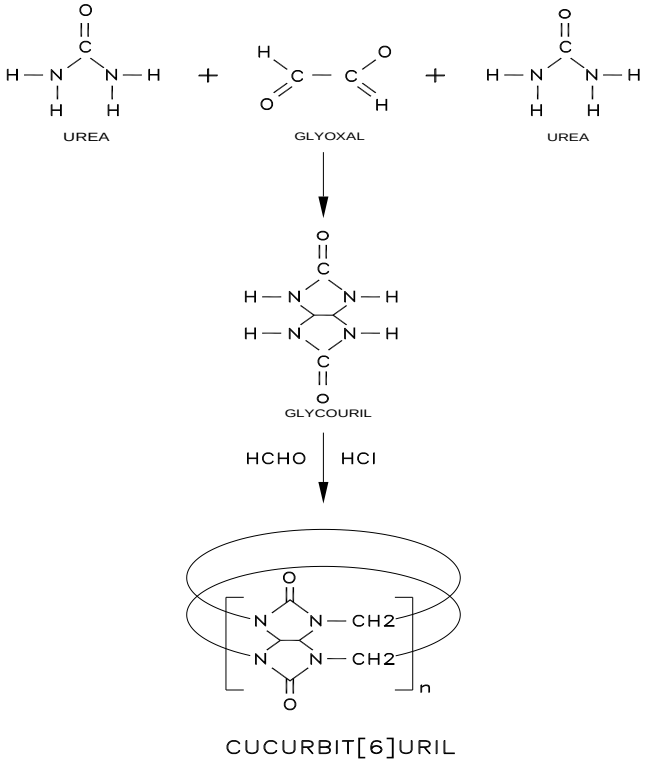


Fig. 1. Chemical structure of cucurbituril.

4) *Scheme I : The reaction can be represented as follows*



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C. Preparation Of Complex

1) Reagents Used: Cucurbituril, Molybdic acid, 2,2'-Bipyridyl, and aqueous HCl were of analytical reagent grade.

2) Synthesis of Molybdenum Cucurbituril 2,2'- Bipyridyl Complex: 10 ml solution of cucurbituril was added in aqueous HCl solution, 5 ml of Molybdic acid and 5 ml of 2, 2'- Bipyridyl in the same solvent. The amount of the solid ligand was high enough. The final green solution was mixed thoroughly and allowed to stand at room temperature. Slow evaporation was carried out by keeping in water bath. After two days, yellowish green crystals were separated out. The crystals obtained were filtered off, dried and the yield was obtained.

III. RESULTS AND DISCUSSION

A. Changes In The Physical Properties

Changes in the physical properties of the ligand and the complex were noted down by melting point and solubility tests.

S. NO	SAMPLE	DECOMPOSITION TEMPERATURE (°C)
1	Cucurbituril	247
2	Cucurbituril+ Molybdenum	210
3	Cucurbituril+ Molybdenum + 2, 2' Bipyridyl	260

Table 1: Decomposition temperature of Cucurbituril and its complexes.

B. Yield Obtained

S. No	Sample	Yield in %	Colour of the Sample
1	Cucurbituril	30%	White
2	Mixed ligand complex of Cucurbituril , Molybdenum 2,2'-Bipyridyl.	70 %	Fluorescent green.

Table 2: Yield obtained and Colour of cucurbituril and its complexes.

C. Absorption Spectroscopy

Absorption spectroscopy was carried out by keeping the concentration of metal and 2, 2' Bipyridyl constant and varying the concentration of cucurbituril. Stock solution of all the solutions 0.025M different ratios were taken 1:1:1, 1:2:1, 1:3:1, 1:4:1, 1:5:1, 1:6:1. All UV-Visible spectrphotometric measurements were carried out using Perkin Elmer UV-Visible spectrophotometer.

D. UV-Visible Spectroscopy

UV-Visible Spectroscopy is used to study the cucurbituril complexes. UV-Visible absorbance of cucurbituril increased form upon complexing with metal salts.

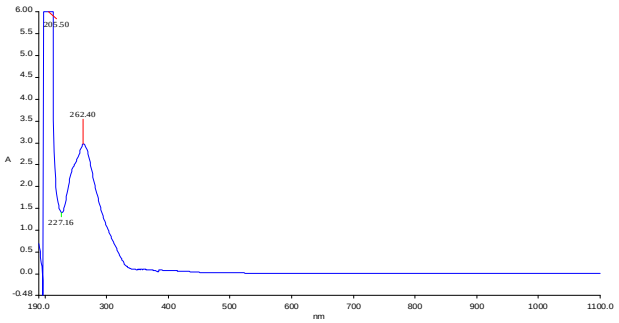


Figure-2 U.V. Absorption spectra of Cucurbituril

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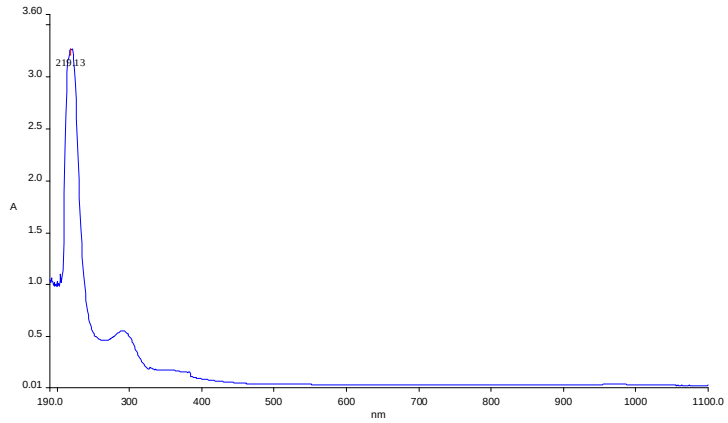


Figure-3 U.V. Absorption spectra of Cucurbituril + Molybdenum I + 2, 2' Bipyridyl complex with increasing concentration of Cucurbituril (concentrated).

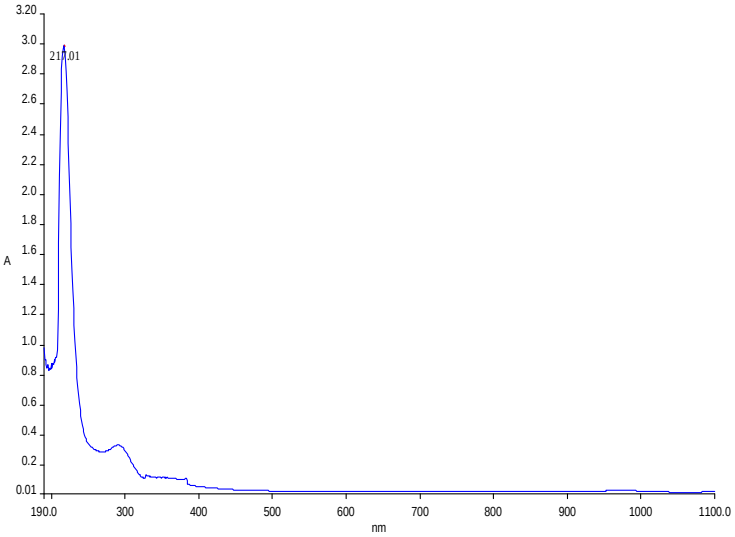


Figure-4 U.V. Absorption spectra of Cucurbituril + Molybdenum I + 2, 2'- Bipyridyl complex with decreasing concentration of Cucurbituril (diluted)

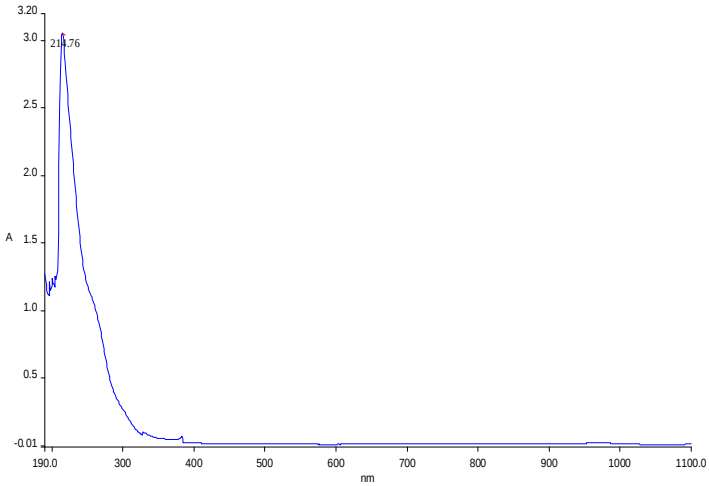


Figure-5 U.V. Absorption spectra of Cucurbituril + Molybdenum II + 2, 2'-Bipyridyl complex with increasing concentration of Cucurbituril (concentrated).

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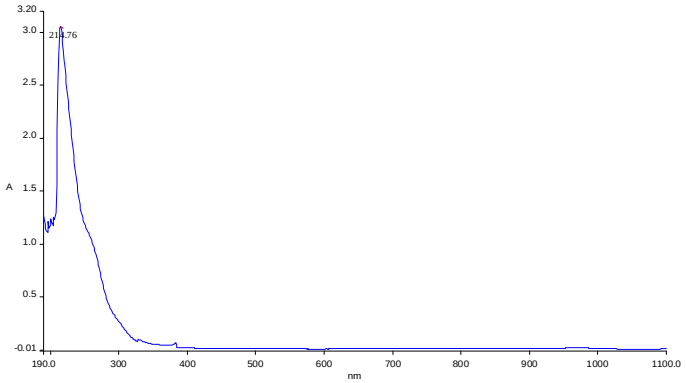


Figure-6 U.V. Absorption spectra of Cucurbituril + Molybdenum II + 2, 2'- Bipyridyl complex with decreasing concentration of Cucurbituril (diluted)

E. IR Spectroscopy

IR Spectra is a preliminary, primary tool that can be used for monitoring the reaction by absorbing the characteristic absorption peaks of the expected product according to the structure. IR Spectrophotometer was used to substantiate the format of the product in this study. The solid samples were mixed with KBr and made into a pellet to record a spectrum. All the spectra were recorded at a resolution of 4 cm^{-1} with a maximum of 100 scans. A background spectrum was run before recording a spectra.

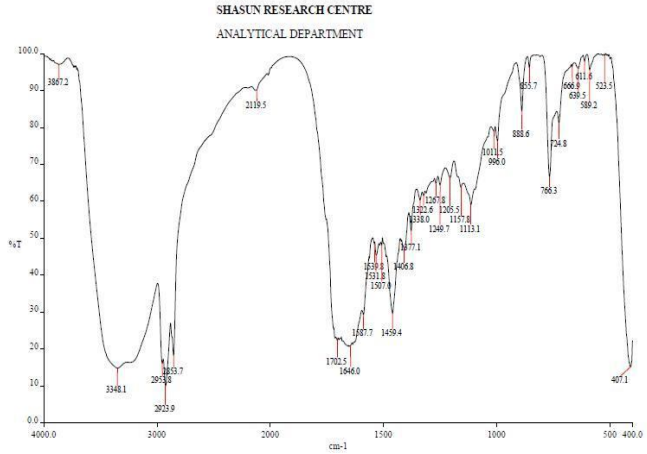


Figure-7 IR-spectra of Cucurbituril

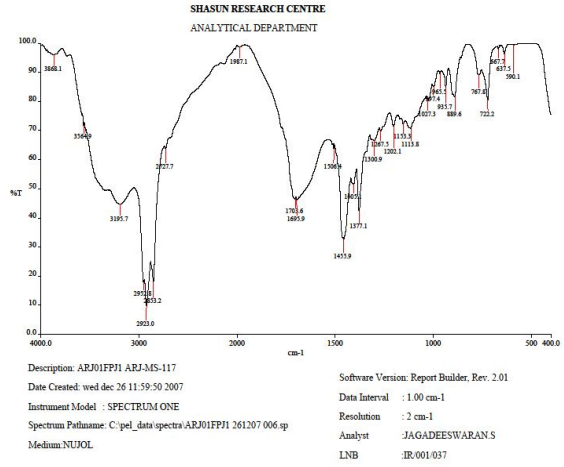


Figure-8 IR-spectra of mixed ligand complex of Molybdenum and 2, 2'- Bipyridyl complex with ratio of 1:2:1

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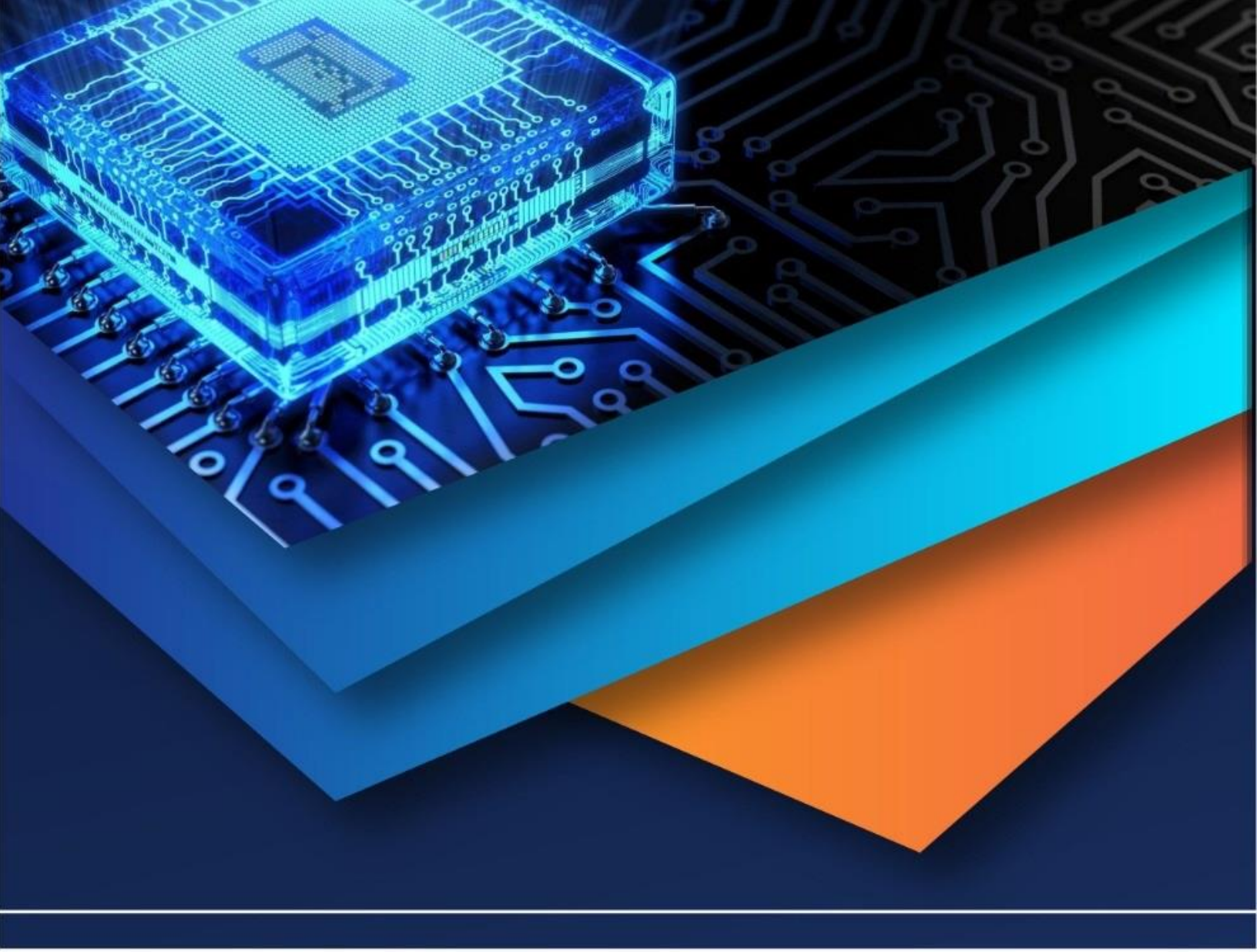
IV. SUMMARY AND CONCLUSION

From this work it is obvious that a better knowledge about the host guest complexation between metal Molybdenum + 2, 2' Bipyridyl and the host macrocyclic Cucurbituril have been obtained.The hydrophobic cavity of cucurbituril increases the complex stability by providing a barrier to decomplexation of charged species. Bipyridyls were chosen as the bulk of guests because they have the capability to bind as they are relatively small. UV-Visible IR techniques were employed to determine these interactions.

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