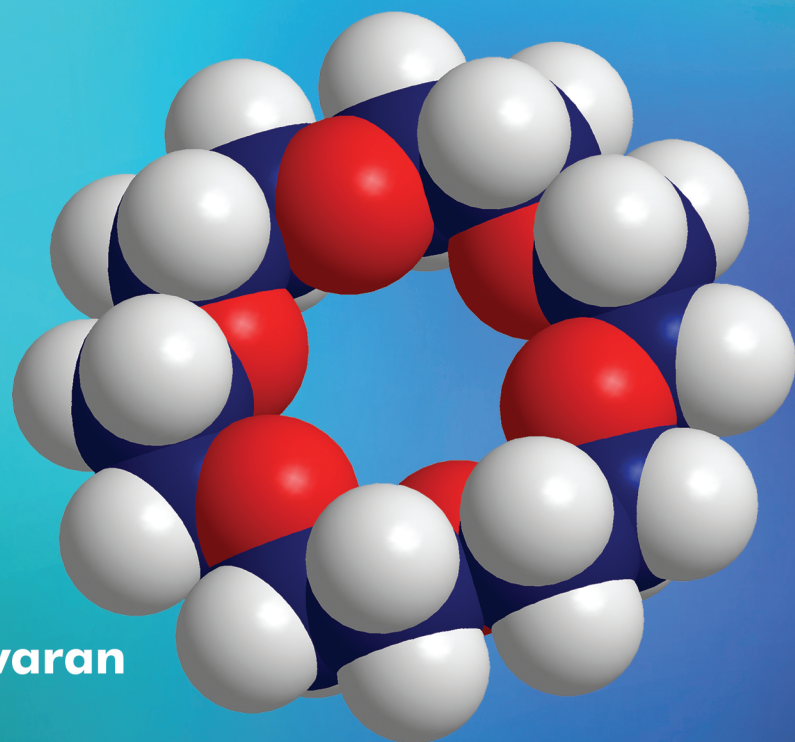
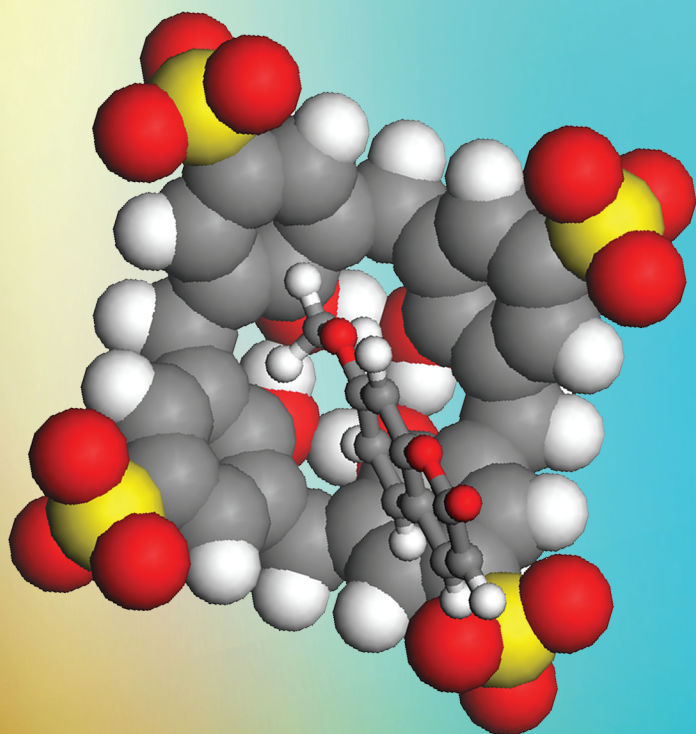


# PHOTOPHYSICS OF SUPRAMOLECULAR ARCHITECTURES



Editors:  
**Paulpandian Muthu Mareeswaran**  
**Palaniswamy Suresh**  
**Seenivasan Rajagopal**

**Bentham Books**

# **Photophysics of Supramolecular Architectures**

Edited by

**Paulpandian Muthu Mareeswaran**

*Department of Industrial Chemistry  
School of Chemical Sciences  
Alagappa University, Karaikudi – 630 003  
Tamilnadu, India*

**Palaniswamy Suresh**

*Department of Natural Products Chemistry  
School of Chemistry, Madurai Kamaraj University  
Madurai – 625 021, Tamilnadu, India*

&

**Seenivasan Rajagopal**

*Department of Physical Chemistry  
School of Chemistry, Madurai Kamaraj University  
Madurai – 625 021, Tamilnadu, India*

## **Photophysics of Supramolecular Architectures**

Editors: Paulpandian Muthu Mareeswaran, Palaniswamy Suresh and Seenivasan Rajagopal

ISBN (Online): 978-981-5049-19-0

ISBN (Print): 978-981-5049-20-6

ISBN (Paperback): 978-981-5049-21-3

© 2022, Bentham Books imprint.

Published by Bentham Science Publishers Pte. Ltd. Singapore. All Rights Reserved.

## **BENTHAM SCIENCE PUBLISHERS LTD.**

### **End User License Agreement (for non-institutional, personal use)**

This is an agreement between you and Bentham Science Publishers Ltd. Please read this License Agreement carefully before using the ebook/echapter/ejournal (“**Work**”). Your use of the Work constitutes your agreement to the terms and conditions set forth in this License Agreement. If you do not agree to these terms and conditions then you should not use the Work.

Bentham Science Publishers agrees to grant you a non-exclusive, non-transferable limited license to use the Work subject to and in accordance with the following terms and conditions. This License Agreement is for non-library, personal use only. For a library / institutional / multi user license in respect of the Work, please contact: [permission@benthamscience.net](mailto:permission@benthamscience.net).

### **Usage Rules:**

1. All rights reserved: The Work is the subject of copyright and Bentham Science Publishers either owns the Work (and the copyright in it) or is licensed to distribute the Work. You shall not copy, reproduce, modify, remove, delete, augment, add to, publish, transmit, sell, resell, create derivative works from, or in any way exploit the Work or make the Work available for others to do any of the same, in any form or by any means, in whole or in part, in each case without the prior written permission of Bentham Science Publishers, unless stated otherwise in this License Agreement.
2. You may download a copy of the Work on one occasion to one personal computer (including tablet, laptop, desktop, or other such devices). You may make one back-up copy of the Work to avoid losing it.
3. The unauthorised use or distribution of copyrighted or other proprietary content is illegal and could subject you to liability for substantial money damages. You will be liable for any damage resulting from your misuse of the Work or any violation of this License Agreement, including any infringement by you of copyrights or proprietary rights.

### ***Disclaimer:***

Bentham Science Publishers does not guarantee that the information in the Work is error-free, or warrant that it will meet your requirements or that access to the Work will be uninterrupted or error-free. The Work is provided "as is" without warranty of any kind, either express or implied or statutory, including, without limitation, implied warranties of merchantability and fitness for a particular purpose. The entire risk as to the results and performance of the Work is assumed by you. No responsibility is assumed by Bentham Science Publishers, its staff, editors and/or authors for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products instruction, advertisements or ideas contained in the Work.

### ***Limitation of Liability:***

In no event will Bentham Science Publishers, its staff, editors and/or authors, be liable for any damages, including, without limitation, special, incidental and/or consequential damages and/or damages for lost data and/or profits arising out of (whether directly or indirectly) the use or inability to use the Work. The entire liability of Bentham Science Publishers shall be limited to the amount actually paid by you for the Work.

### **General:**

1. Any dispute or claim arising out of or in connection with this License Agreement or the Work (including non-contractual disputes or claims) will be governed by and construed in accordance with the laws of Singapore. Each party agrees that the courts of the state of Singapore shall have exclusive jurisdiction to settle any dispute or claim arising out of or in connection with this License Agreement or the Work (including non-contractual disputes or claims).
2. Your rights under this License Agreement will automatically terminate without notice and without the

need for a court order if at any point you breach any terms of this License Agreement. In no event will any delay or failure by Bentham Science Publishers in enforcing your compliance with this License Agreement constitute a waiver of any of its rights.

3. You acknowledge that you have read this License Agreement, and agree to be bound by its terms and conditions. To the extent that any other terms and conditions presented on any website of Bentham Science Publishers conflict with, or are inconsistent with, the terms and conditions set out in this License Agreement, you acknowledge that the terms and conditions set out in this License Agreement shall prevail.

**Bentham Science Publishers Pte. Ltd.**

80 Robinson Road #02-00

Singapore 068898

Singapore

Email: [subscriptions@benthamscience.net](mailto:subscriptions@benthamscience.net)



## CONTENTS

<b>FOREWORD</b> .....	i
<b>PREFACE</b> .....	ii
<b>LIST OF CONTRIBUTORS</b> .....	iv
<b>CHAPTER 1 LUMINESCENT CYCLODEXTRIN SYSTEMS AND THEIR APPLICATIONS</b> .....	1
<i>Dqueq'Ej tkakp'Octkc'Ctrwj co 'Cuj y kp. 'Xgpnv'gucp'Ugy wt co cp'and'Rcwr cpf kcp'Owj w Octgguy ctcp</i>	
<b>INTRODUCTION</b> .....	1
<b>HOST-GUEST SYSTEMS</b> .....	2
<b>LUMINESCENT CYCLODEXTRINS</b> .....	7
<b>FLUORESCENT SENSORS</b> .....	13
<b>BIOSENSORS</b> .....	16
<b>THERAPEUTIC APPLICATION</b> .....	20
<b>CONCLUSION</b> .....	23
<b>CONSENT FOR PUBLICATION</b> .....	23
<b>CONFLICT OF INTEREST</b> .....	23
<b>ACKNOWLEDGEMENTS</b> .....	23
<b>REFERENCES</b> .....	23
<b>CHAPTER 2 CALIXARENE BASED LUMINESCENT SYSTEMS</b> .....	31
<i>Dqueq'Ej tkakp'Octkc'Ctrwj co 'Cuj y kp. 'Xgpnv'gucp'Ugy wt co cp'and'Rcwr cpf kcp'Owj w Octgguy ctcp</i>	
<b>INTRODUCTION</b> .....	31
<b>LUMINESCENT HOST-GUEST SYSTEMS</b> .....	32
Fluorescent Calixarene .....	33
<b>ION SENSING APPLICATIONS</b> .....	33
Anion Sensors .....	43
Solid State Sensor .....	44
<b>MOLECULAR RECOGNITION</b> .....	44
<b>LUMINESCENT LANTHANOID CALIXARENE COMPLEXES</b> .....	46
<b>CONCLUSION</b> .....	47
<b>CONSENT OF PUBLICATION</b> .....	48
<b>CONFLICT OF INTEREST</b> .....	48
<b>ACKNOWLEDGEMENTS</b> .....	48
<b>REFERENCES</b> .....	48
<b>CHAPTER 3 RESORCINARENE CROWNS AS VERSATILE HOST MOLECULES AND THEIR POTENTIAL APPLICATIONS</b> .....	58
<i>Ugræctcl'Fgk'Uqo cumpf etco 'Cpdw'Cplwi co 'Xcpfctmwj crk'and'Xcltcr gtwo cn'Vj eto ctcl</i>	
<b>INTRODUCTION</b> .....	58
Synthesis of Resorcinarenes .....	60
Selective Functionalization of Upper Rim Resorcinarene Crowns .....	63
Selective functionalization of lower rim resorcinarene crowns .....	64
<b>APPLICATIONS OF RESORCINARENE CROWNS</b> .....	65
Chemical Separations .....	66
Chemical Sensors .....	67
Catalytic Activity .....	68
Lithographic Application .....	69
Antioxidant and Antibacterial Applications .....	70

<b>CONCLUSION</b> .....	71
<b>CONSENT OF PUBLICATION</b> .....	71
<b>CONFLICT OF INTEREST</b> .....	71
<b>ACKNOWLEDGEMENTS</b> .....	72
<b>REFERENCES</b> .....	72
<b>CHAPTER 4 PILLARARENES: YOUNGER LUMINESCENT SUPRAMOLECULAR SYSTEMS</b> .....	77
<i>Rcrwpky co { 'Uwt guj 'and 'Lg{ctcl'Dgrkpf c' 'Cuj c</i>	
<b>INTRODUCTION</b> .....	77
Pillararenes .....	78
Structure of Pillararenes .....	79
Synthesis of Pillararenes .....	82
Host-Guest Binding Behaviours of Pillararenes .....	85
Photophysical Behaviours of Pillararenes .....	87
Pillararenes Based Luminescence Systems .....	87
Pillararenes in Sensors Applications .....	91
Pillararenes in Metal Ions Scavenging .....	98
Pillararenes Derived Stimuli Luminescent Materials .....	99
<b>CONCLUSIONS</b> .....	103
<b>CONSENT OF PUBLICATION</b> .....	104
<b>CONFLICT OF INTEREST</b> .....	104
<b>ACKNOWLEDGEMENT</b> .....	104
<b>REFERENCES</b> .....	104
<b>CHAPTER 5 CUCURBIT[N]URILS BASED MOLECULAR RECOGNITION WITH FLUORESCENCE SIGNALLING</b> .....	111
<i>NkwT0and'GOTclmo ct</i>	
<b>INTRODUCTION</b> .....	111
Cucurbituril CB[n] .....	113
Structural Features of CB[n]s .....	113
Physical Properties of CB[n]s .....	114
CB[n] Based Sensors .....	116
Detection Mechanism .....	117
Direct Binding Assay .....	117
Associative Binding Assay .....	118
Indicator Displacement Assay (IDA) .....	119
Detection of Metal Ions .....	121
Detection of Amino Acids and Peptide Molecules .....	123
Detection of Biomolecules .....	125
Detection of Organic Compound .....	126
Cucurbit[n]urils in Imaging and in Photodynamic Therapy .....	128
<b>CONCLUSION</b> .....	131
<b>CONSENT OF PUBLICATION</b> .....	131
<b>CONFLICT OF INTEREST</b> .....	132
<b>ACKNOWLEDGEMENT</b> .....	132
<b>REFERENCES</b> .....	132
<b>CHAPTER 6 RHENIUM(I)-BASED METALLACYCLES FOR SENSING APPLICATIONS</b> .....	137
<i>Owtwi gucp'Xgrv{wfj co 'and'Rqwpctcl'Vj cpcugnctcp</i>	
<b>INTRODUCTION</b> .....	137
Rhenium(I)-Based Metallacycles .....	140

Binuclear Re(I) Complex .....	141
Trinuclear Re(I) Complex .....	149
Tetranuclear Re(I) Complex .....	150
Hexanuclear Re(I) Complex .....	170
Octanuclear Re(I) Complex .....	173
<b>CONCLUSIONS</b> .....	174
<b>CONSENT FOR PUBLICATION</b> .....	175
<b>CONFLICT OF INTEREST</b> .....	176
<b>ACKNOWLEDGEMENTS</b> .....	176
<b>REFERENCES</b> .....	176
<b>CHAPTER 7 RECENT DEVELOPMENTS IN THE DYNAMICS OF FLUORESCENTLY LABELLED MACROMOLECULES</b> .....	181
<i>Mcpfj cwco l 'Fwtck'Owtwi cp.'Rcpf'k'Owj kwxp'and'Xllc{cpcpf 'Ej cpf t eugm t ep</i>	
<b>INTRODUCTION</b> .....	181
<b>POLY(ACRYLIC ACIDS) – STRUCTURAL TRANSITION AND DYNAMICS</b> .....	183
<b>PHOTOPHYSICS OF FLUOROPHORES IN POLYELECTROLYTES</b> .....	185
<b>PHOTOPHYSICS OF EXCITED STATE FLUOROPHORES</b> .....	185
<b>IMPORTANCE OF PHOTOPHYSICS AND PHOTOCHEMISTRY OF POLYMERIC MATERIALS</b> .....	186
<b>PHOTOPHYSICS AND CONFORMATIONAL DYNAMICS OF POLYELECTROLYTES</b> .....	188
<b>STEADY STATE FLUORESCENCE STUDIES AND FLUORESCENCE QUENCHING</b> .....	189
<b>EXCITED STATE ENERGY AND ELECTRON TRANSFER</b> .....	190
<b>EXCIMER AND EXCIPLEX FORMATION</b> .....	192
<b>TIME-RESOLVED FLUORESCENCE STUDIES AND SOLVATION DYNAMICS</b> .....	193
<b>POLYMER COMPLEXES</b> .....	198
<b>INTERPOLYMER COMPLEXES</b> .....	199
<b>HYDROGEN BONDED INTERPOLYMER COMPLEXES</b> .....	200
<b>CONCLUSION</b> .....	202
<b>CONSENT OF PUBLICATION</b> .....	202
<b>CONFLICT OF INTEREST</b> .....	202
<b>ACKNOWLEDGMENT</b> .....	203
<b>REFERENCES</b> .....	203
<b>SUBJECT INDEX</b> .....	234



## FOREWORD

The introduction of surfactants and micelles to study the photophysics and photochemistry of molecules opened up a new approach to mimic the reactions taking place in nature. The opening of new horizons in molecular science after the introduction of surfactants brought a new approach to the field of molecular assemblies. The intense research in the fields of photochemistry and its applications in understanding the photosynthetic processes and solar energy conversion via chemical routes led to the growth of 'supramolecular chemistry', known as 'chemistry beyond the molecule'. The last four decades witnessed an explosion of research activities in the application of supramolecular assemblies in photophysics and photochemistry of molecules and the importance of supramolecular chemistry was understood after the award of 1987 Nobel Prize for Chemistry (Nobel Laureates: Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen) in this area of research.

The editors have chosen the interesting theme of 'Photophysics of Supramolecular Architectures' and presented a collection of important topics covering a wide variety of molecular assemblies and their applications, in particular, in the field of sensors and allied topics. The senior editor Prof. S. Rajagopal with his four decades of intense research in the fields of electron transfer reactions and photochemistry and his experienced co-editors are able to bring together a spectrum of scientists working in the areas of supramolecular systems and their applications. The authors of eight chapters put their efforts to update the knowledge gained in the fields of supramolecular chemistry and their applications in photophysics and photochemistry. The scientists and the young researchers working in the areas of photophysics and photochemistry of molecules in supramolecular assembly can immensely benefit from the book 'Photophysics of Supramolecular Architectures 2021' published by the editors. The editors have made an effort to cover a wide range of supramolecular systems from the conventionally known cyclodextrin systems to calixarene, resorcinarene crowns, pillararene, cucurbit[n]urils, cavitands, metallacycles and fluorescently labelled macromolecules and presented their variety of applications related to photophysics and photochemistry, in particular, the luminescent sensor systems for a wide range of analyte molecules. This book is a single source of collection of literature on the chosen topic and will help the young researchers to understand the field of research, up-to-date literature and design their future plan of action in the areas of supramolecular systems and their applications in photophysics and photochemistry.

**Dr. R. Ramaraj**

Department of Physical Chemistry  
School of Chemistry  
Madurai Kamaraj University  
Madurai-625021, Tamilnadu  
India

## PREFACE

Supramolecular architectures, the prevalent architectures in nature, are designed through a variety of non-bonding interactions like hydrogen bonding,  $\pi$ - $\pi$  staking, self-assembly, *etc.* From physics to biology, the functionalities of supramolecular architectures play an important role. For example, life is not possible without a DNA folding or protein self-assembly. This book mainly focuses on cavities containing supramolecular hosts and their photophysical properties by attaching luminescent molecules as guests. The host-guest chemistry is a widely established subject that can expand as an individual field of research with respect to the cavitation. The host-guest chemistry is envisaged as mimic for enzymatic catalysis. Also, they are used as drug delivery vehicles for the targeted payload delivery in biochemistry and biotechnology. The study of the interaction of guest molecules with light in the presence of host molecule opens a research opportunity to develop advanced research like optical tweezers.

The recent studies of photophysics of guest molecules with various cavitation like cyclodextrin, calixarene and their derivatives, cucurbiturils are highlighted in this book. The cyclodextrin complexes having different cavities and encapsulation of fluorescent guest molecules and applications of these systems are elaborately discussed in Chapter 1. Chapter 2 deals with the interaction of fluorescent guest molecules with calixarenes and their applications towards (as) sensors. The photophysical properties of coordination complexes of calixarene-lanthanide systems are also discussed in this chapter.

Resorcinarenes, one of the important molecules in the calixarene family, receive importance for their hydroxyl group containing upper rim, which makes them suitable for catalysis applications. Chapter 3 mainly focuses on the upper rim modification at hydroxyl group to achieve crown ethers. Eventhough the crown ethers are separately known as supramolecules, this chapter discusses upper rim modified resorcinarene-crown and their applications using optical spectral techniques. Chapter 4 deals with the pillararenes, which are considered as young cavitation molecular system, reported only in 2008. This chapter focuses on the host-guest chemistry of pillararenes with fluorescent guest molecules. The self-assembly of pillararene derivative is also discussed to achieve sensor applications.

Chapter 5 is concerned with the molecular recognition of fluorescent guest molecules encapsulated cucurbiturils and their applications as sensors. The application of imaging and photodynamic therapy using cucurbiturils systems is also discussed. Chapter 6 deals with the control of photophysical properties and photochemical events of various cavities and capsules. Chapter 7 mainly focuses on the cavity containing rhenium(I) metallasupramolecules, i.e., metallacycles. The synthesis, photophysical properties and host-guest behavior of rhenium metallacycles ranging from simple to complex topologies are discussed in detail. Chapter 8 deals with the dynamics of macromolecules functionalized with fluorescent molecules. The macrocyclic environment acts as a host molecule and influences the optical properties of the functionalized fluorescent molecule. The folding and unfolding of macrocycles exhibit substantial variations in the fluorescent molecules.

This book strives to give collectively the applications of host-guest chemistry with recent applications. The recent advancements in the various host-guest systems will provide newer insights to readers into both conventional host molecules like cyclodextrin as well as young host molecules like pillararenes.

**Paulpandian Muthu Mareeswaran**  
Department of Industrial Chemistry  
School of Chemical Sciences  
Alagappa University, Karaikudi – 630 003  
Tamilnadu, India

**Palaniswamy Suresh**  
Department of Natural Products Chemistry  
School of Chemistry, Madurai Kamaraj University  
Madurai – 625 021, Tamilnadu, India

**&**

**Seenivasan Rajagopal**  
Department of Physical Chemistry  
School of Chemistry, Madurai Kamaraj University  
Madurai – 625 021, Tamilnadu, India

## List of Contributors

<b>Bosco Christin Maria Arputham Ashwin</b>	Department of Chemistry, Pioneer Kumaraswamy College, Nagercoil 629 003, Tamilnadu, India
<b>E. Rajkumar</b>	Biomimetic and Biosensor Lab, Department of Chemistry, Madras Christian College (Autonomous), Affiliated to University of Madras, Chennai-600 059, Tamilnadu, India
<b>Jeyaraj Belinda Asha</b>	Supramolecular and Catalysis Lab, Dept. of Natural Products Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625021, Tamilnadu, India
<b>Kandhasamy Durai Murugan</b>	Department of Bioelectronics and Biosensors, Alagappa University, Karaikudi-630003, Tamilnadu, India
<b>Liju R.</b>	Biomimetic and Biosensor Lab, Department of Chemistry, Madras Christian College (Autonomous), Affiliated to University of Madras, Chennai-600 059, Tamilnadu, India
<b>Murugesan Velayudham</b>	Department of Chemistry, Thiagarajar College of Engineering, Madurai-625015, Tamilnadu, India
<b>Palaniswamy Suresh</b>	Supramolecular and Catalysis Lab, Dept. of Natural Products Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625021, Tamilnadu, India
<b>Pandi Muthirulan</b>	Department of Chemistry, Lekshmpuram College of Arts and Science, (Affiliated to MS University, Tirunelveli), Neyyoor-629802, Tamilnadu, India
<b>Paulpandian Muthu Mareeswaran</b>	Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, Tamilnadu, India
<b>Pounraj Thanasekaran</b>	Department of Chemistry, Pondicherry University, Kalapet, Puducherry - 605 014, India
<b>Selvaraj Devi</b>	P. G. Department of Chemistry, Cauvery College for Women, Tiruchirappalli-620018, Tamilnadu, India
<b>Somasundaram Anbu Anjugam Vandarkuzhali</b>	Department of Chemistry, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences, Saveetha University, Chennai-600005, Tamilnadu, India
<b>Vairaperumal Tharmaraj</b>	Environmental Science and Technology Research Group, Department of Chemical Engineering, SRM Institute of Science and Technology, Kattankulathur-603203, Tamilnadu, India
<b>Venkatesan Sethuraman</b>	Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, Tamilnadu, India
<b>Vijayanand Chandrasekaran</b>	Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore-632014, Tamilnadu, India

## CHAPTER 1

# Luminescent Cyclodextrin Systems and Their Applications

Bosco Christin Maria Arputham Ashwin<sup>1</sup>, Venkatesan Sethuraman<sup>2</sup> and Paulpandian Muthu Mareeswaran<sup>2,\*</sup>

<sup>1</sup> Department of Chemistry, Pioneer Kumaraswamy College, Nagercoil 629 003, Tamilnadu, India

<sup>2</sup> Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, Tamilnadu, India

**Abstract:** This chapter explains the most recent development on different luminophore tethered cyclodextrin (CD), a cyclic polysaccharide and these applications in distinct areas. The host-guest inclusion complexation studies of CD with different guest molecules using fluorescence techniques are discussed. The hybrid materials of CD in the detection of biological analytes, toxic compounds and *in-vivo* bio-imaging applications are discussed. The compatibility nature of CD leads to its usage in drug delivery and the controlled drug dosage using CDs is explained. The interesting usage of CDs in counterfeit recognition and tunable emission are emphasised. The dimers and self-assemblies of CDs utilized for the enhancement of photophysical properties are discussed in detail. The CD hybrid materials exhibited numerous usage in essential needs.

**Keywords:** Aggregation, Amino acids, Anion, Bioimaging, Biomolecule, Cyclodextrin, Chemosensor, Dimer, Drug, Dye, Emission, Fluorescence, Host-guest, Interaction, Lanthanoids, Luminescence, Macrocyclic, Recognition, Nanocarrier, Nanoparticles.

## INTRODUCTION

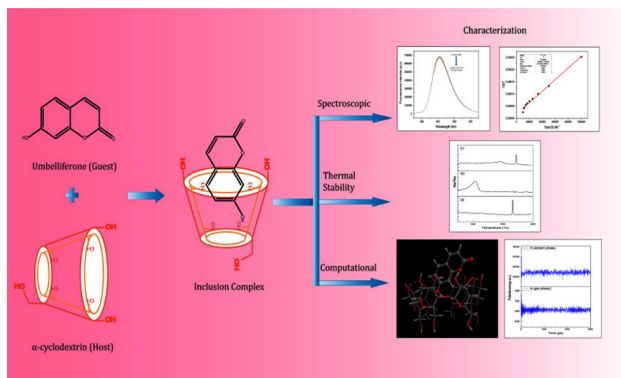
Cyclodextrin (CD) is a cyclic polysaccharide derived from enzymatic hydrolysis of starch [1]. CD has three native forms,  $\alpha$ -CD,  $\beta$ -CD and  $\gamma$ -CD containing six, seven and eight glucopyranose units, respectively. CD structure is a truncated cone with hydrophilic exterior and hydrophobic inner pocket, which makes it suitable for host guest inclusion complex formation [2]. The inner diameters of hydrophobic cavities of  $\alpha$ ,  $\beta$ , and  $\gamma$ -CDs are reported as 4.7–5.3, 6.0–6.5, and 7.5–8.3 Å, respectively [3]. Over the other supramolecular host molecules, CD

\* Corresponding author Paulpandian Muthu Mareeswaran: Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, Tamilnadu, India; Tel: +919790963437; E-mails: muthumareeswaran@gmail.com and mareeswaran@alagappauniversity.ac.in

attained wide interest and it was explored for its diverse functionalities in the therapeutic, biomedical, and food industries, as well as in biosensors/bio-imaging applications [4]. Despite CDs themselves being spectroscopically passive, by modification with appropriate chromophores, their derivatives are spectroscopically active [5]. Due to the non-luminescent nature of CDs, fluorescence spectral studies are prominent in studying its host-guest complex formation and binding orientation with luminescent dye molecules [6]. Due to the compatible nature of CD, recently, enormous studies were focused on CD and its derivatives to explore the utilisation of this assessible host molecule in different aspects. This chapter confers the new developments of luminescent CDs and the studies of CDs with luminescent guest molecules for top notch applications.

## HOST-GUEST SYSTEMS

Krishnan *et al.* [7] reported the aqueous mediated photophysical studies of resorcinol based acridinedione dyes with  $\beta$ -CD in the presence of urea. The urea and water hydrogen bonding self-assemblies led the formation of microspheres based on different environment, resulting in an effective displacement of dye from the hydrophobic nanocavity of  $\beta$ -CD. Roy *et al.* [8] explored the umbelliferone, a drug with  $\alpha$ -CD inclusion complex. The complex (Fig. 1) has been optimized by molecular docking and increased bioavailability with minimal dosage in the human body.



**Fig. (1).** Schematic representation of the studies of umbelliferone and  $\alpha$ -CD inclusion complex [8].

Periasamy *et al.* [9] studied the host-guest inclusion complex of  $\beta$ -CD and 4,4' - (1,4-phenylenediisopropylidene) bisaniline (PDB) in solid and solution states by numerous analytical techniques. UV and fluorescence spectral studies confirmed the 1:2 PDB:  $\beta$ -CD complex formation and the molecular docking studies also support this. A detailed spectroscopic investigation of the binding of pyrene with  $\beta$ -CD derivatives and their binary mixtures has been reported by Levine *et al.* [10]. Li *et al.* [11] studied the interaction between CDs and pullulanase. Enzyme

activity and kinetic studies exhibited that  $\alpha$ -CD,  $\beta$ -CD and  $\gamma$ -CD inhibited pullulanase in a vying manner and fluorescence spectroscopy suggested the formation of CD and pullulanase complexes. Visible-light responsive supramolecular gel (Fig. 2) has been fabricated by  $\beta$ -CD dimer and tetra-ortho-methoxy-substituted azobenzene dimer through the host-guest interaction. The substituted methoxy groups responsive to the shift in wavelengths of trans and cis forms led to the green and blue light regions, respectively [12].

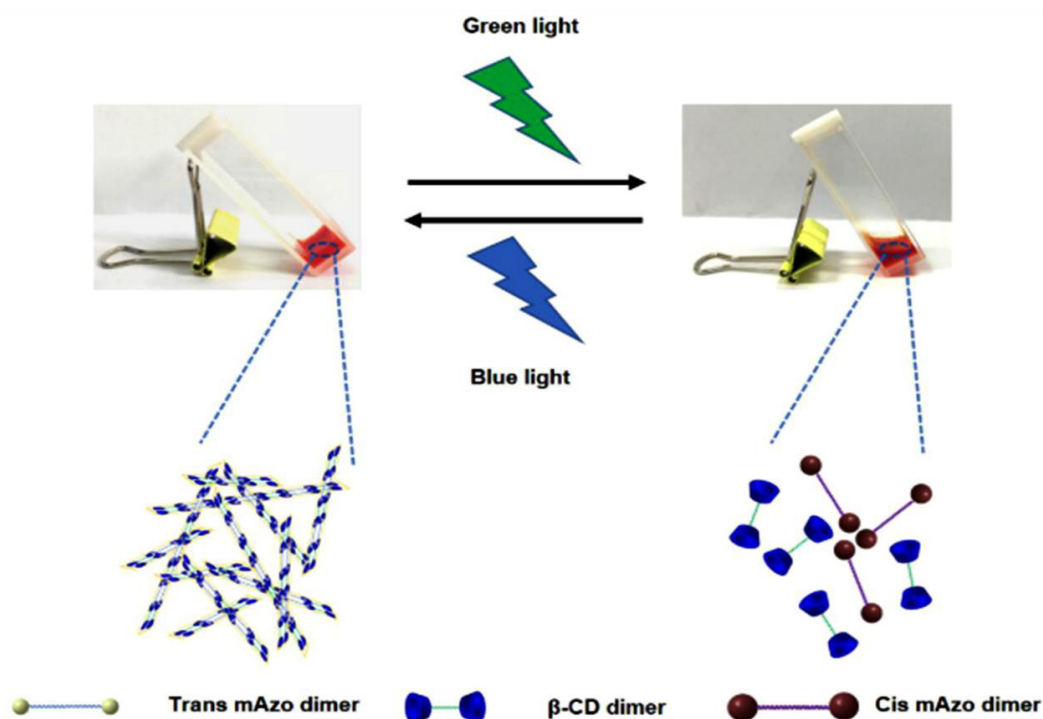


Fig. (2). Schematic representation of visible-light responsive  $\beta$ -CD dimer host-guest supramolecular gels [12].

Kim *et al.* [13] reported a synthetic strategy to form high yield CD based intranagap particles (Fig. 3) with a well-defined  $\sim 1$  nm interior gap. They incorporated 10 different fluorescent Raman dyes such as crystal violet, basic fuchsin, bromophenol blue, rhodamine B, methylene blue, Safranin O *etc.*, within the gap using the CD based host-guest chemistry.

## CHAPTER 2

## Calixarene Based Luminescent Systems

Bosco Christin Maria Arputham Ashwin<sup>1</sup>, Venkatesan Sethuraman<sup>2</sup> and Paulpandian Muthu Mareeswaran<sup>2,\*</sup>

<sup>1</sup> Department of Chemistry, Pioneer Kumaraswamy College, Nagercoil 629 003, Tamilnadu, India.

<sup>2</sup> Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, Tamilnadu, India

**Abstract:** This chapter focuses on the recent developments in calixarenes chemistry using luminescence aspect. This aspect comprises host guest system of luminescent guests with calixarenes as well as luminescent organic moieties tethered calixarene systems. The utilization of organic moieties tethered calixarene systems towards sensor applications for anions, cations and biomolecules is explored. The calixarene systems are used as a platform as well as convenient receptors for the luminescent sensor systems. The ease of modification in the rims of calixarenes renders numerous synthetic possibilities to recognise a particular target molecule and also to fabricate solid state luminescent sensor systems.

**Keywords:** Aggregation, Amino acids, Anion, Bioimaging, Biomolecule, Calixarene, Cation, Chemosensor, Device, Drug, Dye, Emission, Fluorescence, Host-guest, Interaction, Lanthanoids, Luminescence, Macrocycle, Nanoparticles, Recognition.

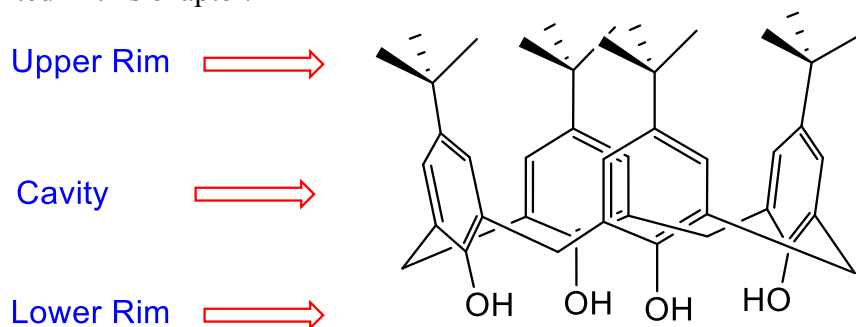
### INTRODUCTION

Calixarenes, the vase structured phenol-based macromolecules, have great attention among the most investigated scaffolds in supramolecular chemistry due to their easy modification as per the utilization [1, 2]. Calixarene is made up of phenol moieties connected by ethylene bridge [3]. They have more advantages especially (a) facile lower and upper rims functionalization, (b) a well-defined nonpolar cavity, (c) substituent and guest dependent definite conformations and (d) distinct target binding sites [4, 5]. The well-defined as well as flexible cavities are efficient to receive guest molecules [6,7]. The hydrophobic cavity can interact with guest molecules and ions by means of cation- $\pi$  interactions [8, 9]. The upper and lower rims can be synthetically tuned to target the specific guest molecules by

\* Corresponding author Paulpandian Muthu Mareeswaran: Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, Tamilnadu, India; Tel: +919790963437; E-mails: muthumareeswaran@gmail.com and mareeswaran@alagappauniversity.ac.in



means of desired interactions for the specific binding [10,11]. Calixarene itself is a non-luminescent molecule and the luminescent properties can be manipulated either by the inclusion of luminescent guest molecules or by tethering luminescent moieties on the rims of calixarenes (Fig. 1). The substituents enhanced the luminescent property of the calixarenes and have a variety of applications with specific targets than the guest induced luminescent systems. The recent research studies of the guest induced luminescent properties of calixarenes and predominantly luminescent moieties tethered calixarenes systems in detail are presented in this chapter.



**Fig. (1).** Structure of t-butyl calix [4]arene and their parts are represented. Most of the fluorophore guests were accommodated within the cavity.

## LUMINESCENT HOST-GUEST SYSTEMS

Studying the nature of non-bonding interactions and revealing the binding structure of the macrocyclic host molecule with guest molecules is an interesting and difficult one [12]. Utilizing the luminescent nature of the guest molecule of the host-guest complex with calixarene is a well preferred technique for understanding these aspects by means of the luminescence changes observed [13, 14]. In calixarene derivatives the aqueous soluble *p*-sulfonatocalix [4]arene has much reports with vast luminescent guest molecules [15] such as amino acids, proteins [16,17], curcumin [18], safranin T [14], viologen derivatives [19], 1,8-diaminonaphthalene [20], coumarin 460 [21], 7-methoxycoumarin [22], gallic acid [23], *n*-(4-hydroxyphenyl)-imidazole [24], vitamin E [25], thioflavin-T [26], triphenylpyrylium cation [27], diphenylamine [28], acenaphthene-1,2-dione [29] and more. Compared with advanced techniques developed, the studies based on luminescence change have great attraction due to quick and facile interpretations experimentally. Most of these findings support the theoretically stimulated results [22].

## Fluorescent Calixarene

Oueslati *et al.* [30] studied the luminescent nature of the elongated nanoporous micro crystals of distal calix [4]arene dimethylester derivative. The hydrogen bonds and van der Waals interactions within these molecules provided a stable linear nanoscale tubular polymeric structure. The crystals showed luminescence at room temperature due to the monomer fluorescence, dimer fluorescence and monomer phosphorescence with different excited state lifetimes. Zhu *et al.* [31] investigated the fluorescence properties of *p*-sulfonatocalix[n]arene (SC[n], n=4, 6 and 8)-cetyltrimethylammonium bromide (CTAB) supra-amphiphiles. Both SC[n] and CTAB were non-fluorescent but the formed SC[n]-CTAB complexes emitted fluorescence. When the molar ratio of CTAB to SC[n] reached the stoichiometry, the strongest fluorescence intensity was observed. An approach to inducing luminescence behaviour by incorporating dye molecules in calixarene has been reported [32]. Making use of this method as a solid-state sensor device consisting of calix [4]arene crafted on ruthenium dye doped silica nanoparticles has been reported [33]. It exhibited excellent recognition of glyphosate in an aqueous medium based on FRET [34].

## ION SENSING APPLICATIONS

The ion sensing applications using calixarene based luminescent systems is a widely studied aspect of sensor applications of cations. Kim *et al.* [35] synthesised a calixarene based calix [4]azacrown, a fluorescent molecule containing anthracenyl unit. It displayed chelation-enhanced fluorescence with Cs<sup>+</sup>, Rb<sup>+</sup> and K<sup>+</sup> metal ions. The interesting “molecular taekwondo” processes between metal ion pairs were observed by the change in fluorescence. The luminescence nature of a water soluble calix [4]arene derivative, 5,11,17,23-tetra-sulfonate-25,26,27,28-tetra-carboxymethoxycalix [4]arene with a lanthanoid ion (Tb<sup>3+</sup>) complexation has been studied in gelation medium. The calix [4]arene derivative formed an efficient energy transfer complex with Tb<sup>3+</sup> ion and the binding mechanism in gelatine was studied in detail by fluorescence [36].

In 2007 Kim *et al.* [37] reported a review of calixarene derived fluorescent probes. It exposed the luminescent calixarene sensors reported before in detail and the insight mechanisms were discussed. The unique topology of calixarenes offers a wide range of scaffolds, facilitating them to encapsulate plentiful different toxic cations and biologically relevant anions. Chang *et al.* [38] synthesised a triazole-modified calix [4]crown (**1**) in the 1,3-alternate conformation and studied sensing behaviour of metal ions. This chemosensor established that a metal ion exchange can trigger an on-off switchable fluorescent chemosensor (Fig. 2) for analyte ion.

## Resorcinarene Crowns as Versatile Host Molecules and Their Potential Applications

Selvaraj Devi<sup>1</sup>, Somasundaram Anbu Anjugam Vandarkuzhali<sup>2,\*</sup> and Vairaperumal Tharmaraj<sup>3,\*</sup>

<sup>1</sup> P. G. Department of Chemistry, Cauvery College for Women, Tiruchirappalli-620018, Tamilnadu, India

<sup>2</sup> Department of Chemistry, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences, Saveetha University, Chennai-600005, Tamilnadu, India

<sup>3</sup> Environmental Science and Technology Research Group, Department of Chemical Engineering, SRM Institute of Science and Technology, Kattankulathur-603203, Tamilnadu, India

**Abstract:** Resorcinarene crowns are significant building blocks for supramolecular chemistry. Resorcinarenes are part of the calixarenes family and are macrocyclic, bowl-shaped molecules. Derived from four resorcinol subunits, they have hydroxy groups at the wide rim of the bowl. These cavities were utilized for their potential recognition of racemic guests and catalysis applications. In this chapter, we focused on the overview of synthesis, conformational properties of resorcinarenes crown and their potential applications such as separation technique using high performance liquid chromatography (HPLC), gas chromatography (GC) and ion chromatography (IC). In addition, they are also used as chemo sensors, antibacterial and antioxidant agents, contrast agents, nanoparticles synthesis and catalytic systems. Finally, we concluded the chapter with the significance of resorcinarenes crown.

**Keywords:** Antibacterial and antioxidant activity, Catalysts, Resorcinarene crown, Sensors, Separation technique.

### INTRODUCTION

Resorcinarenes are a structurally versatile group of macrocyclic supramolecular host molecules that are closely related to the calixarenes. In 1940, Niederl and Vogel [1] proposed the structure of resorcinarenes with the molecular ratio of the aldehyde and the resorcinol as 4:4.

\* Corresponding author Vairaperumal Tharmaraj and Somasundaram Anbu Anjugam Vandarkuzhali: Environmental Science and Technology Research Group, Department of Chemical Engineering, SRM Institute of Science and Technology, Kattankulathur-603203, Tamil Nadu, India; Tel: +919789249631; and Department of Chemistry, Saveetha School of Engineering, Saveetha Institute of Medical and Technical Sciences, Saveetha University, Chennai- 600005, Tamilnadu, India; E-mails: tharmachem@gmail.com and anbu.anju@gmail.com

Finally, the structure of resorcinarene was proved in 1968 by single crystal X-ray analysis [2, 3] as shown in structure 1. The IUPAC name of the resorcinarene is 2,8,14,20-tetraalkylpentacyclo-[19.3.1.13,7.19,13.115,19]-octacos-1-(25),3,5,7(28),9,11,13(27),15,17,19(26),21, 23-dodecaene-4,6,10,12,16,18,22,24-octol.

Resorcinarenes have five different isomeric forms such as crown ( $C_{4v}$ ), boat ( $C_{2v}$ ), chair ( $C_{2h}$ ), diamond ( $C_s$ ) and saddle ( $D_{2d}$ ). Two major conformations such as chair ( $C_{2v}$ ) and crown ( $C_{4v}$ ) are preferred as shown in structure 2. The two resorcinol rings are almost vertical and the remaining two are aligned as horizontal, indicating the boat form of resorcinarene. The crown conformation is highly ordered with the formation of hydrogen bond network (Fig. (1)).

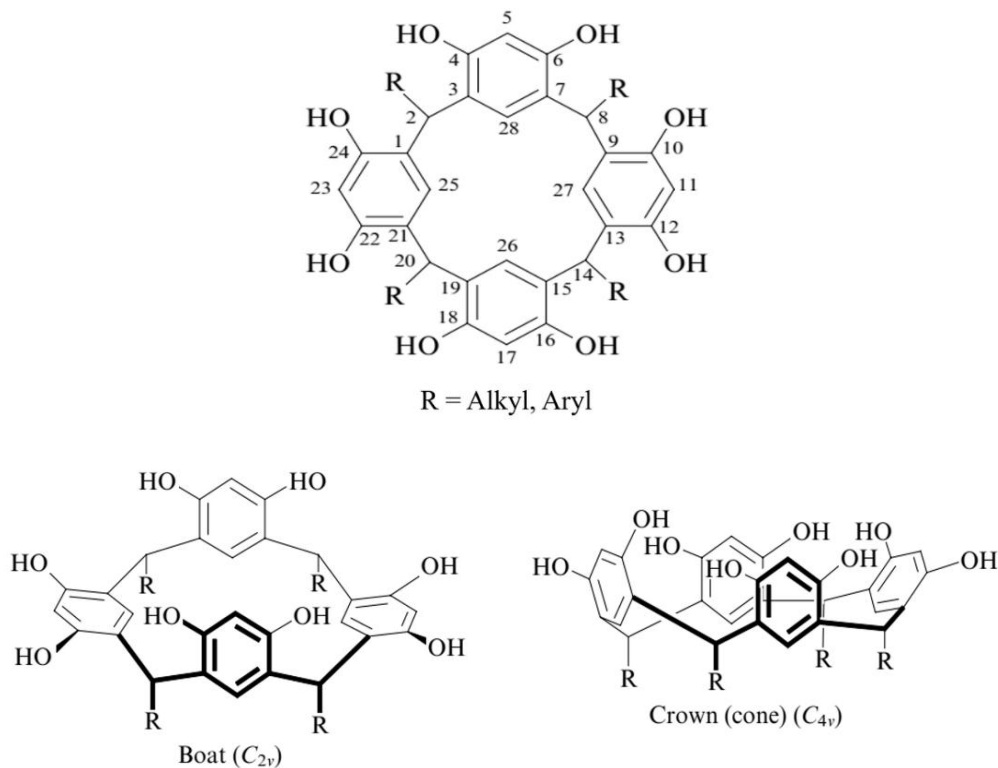


Fig. (1). Conformations of resorcinarenes.

The upper rim of resorcinarene cavity has a more hydrophilic nature because of the  $-OH$  group derived from the resorcinol. In addition, the upper rim is readily available for further functionalization with various molecules to improve the binding affinity and selectivity. Therefore, the major forms of Chair ( $C_{2v}$ ) and Crown ( $C_{4v}$ ) resorcinarenes have provided good binding properties but

comparatively crown form has more significance in functionalization, binding properties and structural features due to the hydroxyl groups of the upper rim having cavity structure. It is more suitable for modification with guest binding molecules [4].

Resorcinarenes crown, a macrocyclic supramolecular hosts molecule are capable of binding with various guest molecules or ions [5 - 7]. Therefore, resorcinarenes crown have been used in various fields of applications such as drug/ gene delivery [8, 9], catalyst [10], liquid crystals [11] and detection of volatile organic chemicals [12].

In addition, the host-guest properties of resorcinarenes crown allowed it to apply for environmental applications due to the changes in the structure of resorcinarenes from vesicles to micelles according to pH [13 - 15]. Resorcinarene crowns form complex with alkali and alkaline earth metal cations like  $K^+$ ,  $Cs^+$ ,  $Rb^+$  and  $Ag^+$ , *etc.* It shows many interesting structural properties and forms multilayers of capsules and nanomaterials [16 - 18]. This kind of nanomaterials based on resorcinarene crowns is used for antibacterial activity [19].

This chapter mainly focuses on the synthesis, structural conformation and complexation properties of selective functionalized resorcinarene crown. The potential applications of resorcinarene crowns in the construction of supramolecular assemblies, sensors and catalytic applications, *etc.* have been discussed. Finally, this chapter provides a conclusion with future perspectives on this field.

### **Synthesis of Resorcinarenes**

Resorcinarenes are a different form of calixarenes, constructed from resorcinol and various aliphatic or aromatic aldehydes by acid catalyzed condensation reaction as shown in Fig. (2).

In addition, all the possible functionalization has been designed and synthesized [20 - 26]. The upper and lower rims are readily available for functionalization with suitable functional groups either directly during the acid-catalyzed condensation reaction or after synthesis of basic resorcinarene to modify the lower rim.

## Pillararenes: Younger Luminescent Supramolecular Systems

Palaniswamy Suresh<sup>1,\*</sup> and Jeyaraj Belinda Asha<sup>1</sup>

<sup>1</sup> *Supramolecular and Catalysis Lab, Dept. of Natural Products Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625021, Tamilnadu, India*

**Abstract:** Since the development of supramolecular chemistry, synthetic macrocycles have also played an inevitable role in constructing the host-guest system. Among pillar[n]arenes, in short pillarenes, a decade-old younger member in the supramolecular family, after reported by Ogoshi *et al.* in 2008, has gained considerable attention. Due to the straightforward preparation methods, tunable cavity size, and symmetrical architecture makes it an ideal candidate in the supramolecular family. With this perspective, this chapter discusses a brief introduction to the synthesis, characterization, and structural features of different sizes of pillarenes. The presence of a confined hydrophobic and  $\pi$ -electron-rich cavity provided by a paraxyl ether or hydroquinone units offers a unique host-guest recognition capability towards positively charged and neutral molecules. Notably, the presence of a cavity with an aromatic wall provides a broad luminescent platform for various photophysical studies. This chapter elaborates on the contribution of pillarenes in tuning the photophysical properties of the small guest molecules and the formation of luminescent supramolecular materials. Further, the functionalization on the outer of the pillarenes has influenced the photophysical responses such as absorption and fluorescence, which paved a pathway for the development of supramolecular organic light-emitting functional material and novel sensor materials also discussed in this chapter. Finally, this chapter discusses all the progress and applications of luminescence pillarenes and their derivatives.

**Keywords:** Host, Host-Guest Chemistry, Luminescent materials, Pillararenes, Stimuli-Responsive.

### INTRODUCTION

The flourishing tailored interest from the biomolecules created a lot of attention with attraction in the development of various supramolecular systems, which are projected as bio-mimics [1]. The ever-growing attraction in supramolecular chemistry can be recognized from its versatile application in diverse platforms

\* **Corresponding author Palaniswamy Suresh:** Supramolecular and Catalysis Lab, Dept. of Natural Products Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625021, Tamilnadu, India; Tel: +919790296673; E-mail: suresh.chem@mkuniversity.ac.in

that span a broad spectrum of chemistry, physics, material science, nanoscience and nanotechnology, biotechnology, biomaterials, and other fields. Because of the importance of the novel macrocyclic architecture in supramolecular science, the designing and preparation of such supramolecules have grown considerably. In the continuous evaluation of the chemistry of supramolecules, several supramolecules such as crown ethers, cyclodextrins, cucurbiturils, calixarenes and their structurally similar scaffolds have been explored extensively in different aspects from the past couple of decades. Nevertheless, owing to the development of modern synthetic strategies and updated modern characterization techniques triggered the exploration of novel macrocyclic and polymeric systems, which are considered additional feathers in the crown of supramolecular chemistry. Molecular recognition is one of the unique properties of the supramolecular systems that involve host-guest interactions and plays a vital role in the life-sustaining biological process. The non-covalent interactions originate from the molecular recognition that arises from the various bonding and nonbonding interactions such as hydrogen bonding, charge transfer, and  $\pi$ - $\pi$  staking between molecules exhibiting molecular complementarity. To utilize such non-covalent interaction, understanding their role in the chemical reactions and exploring their applications in biomimetic systems, macrocyclic compounds provide a suitable platform. In the last century, after the Nobel award [2 - 5] Pederson, Lenn and Cram, the focus on the development of supramolecular chemistry has exponentially grown, and a spectrum of macrocyclic molecules have studied. However, owing to the remarkable molecular reorganization properties and mimicking the natural systems have drawn the attention of researchers and continuously focusing their engagement on the development of novel synthetic macrocyclic systems. In the continuous evolution of the synthetic supramolecular systems such as calixarene, cyclophane, crown ethers, and cucurbiturils, one more new type of columnar structural macrocyclic system with electron-rich cavities has been developed by Tomoki Ogoshi in 2008 [6] and named as 'pillararene'.

### **Pillararenes**

Pillararenes, a new type of macrocyclic synthetic supramolecule architected molecules, consist of substituted hydroquinone units connected by methylene bridges at the 2 and 5 positions [6]. In the macrocyclic systems, the chemical structure of the pillararenes has resembled those of the calixarenes [7, 8]. To understand this younger macrocyclic system, structural features have been compared with the well-established structures of calixarenes. While comparing the chemical structure of pillararenes with calixarenes, the critical difference between both was found in the connecting position of the methylene bridges. In calixarenes, the phenolic units are joined by methylene bridges at the *meta* position, which causes the shape difference between pillararenes and calixarenes

(Fig. 1). As a result, calixarenes show asymmetrical Calix-like structures, while pillararenes form symmetrical pillar-like structures. Indeed, the actual structure of pillararenes is different from that of typical calixarenes. Tomoki Ogoshi first reported about pillararenes as a *para*-bridge pillar-shaped novel host, pillar [5]arenes, formed by the condensation of 1,4-dimethoxybenzene (DMB) with paraformaldehyde in the presence of an appropriate Lewis acid catalyst.



Fig. (1). Comparison of chemical structures of pillar [5]arene [P5A] and calix [5]arene. (Adopted with permission from ref. 8).

### Structure of Pillararenes

In the cyclodextrins and calixarenes, the size of the ring is determined based on the number of monomer units such as glucose and phenol, respectively. In a similar manner, the pillararenes ring size is determined by the number of hydroquinone units. In the coined name “pillar[n]arene, the letter 'n' means the presence of the number of the hydroquinone units. For example, pillar [5]arene means a cyclopentamer with five hydroquinone units. Commonly three types of pillararenes, such as pillar [5]arenes, pillar [6]arenes and pillar [7]arenes, are popular [9]. In supramolecular chemistry, while dealing with molecular recognition, understanding the structural features of the novel host molecule is extremely important because their structural features directly influence their host-

guest binding properties, being different from the basket-shaped structure of the *meta*-bridged calixarenes, pillar [5]arene (P [5]A) has a unique, symmetrical architecture [10] X-ray crystal structure of 1,4-dipropoxypillar [5]arene (DP [5]A) confirmed that it has a pentagon from the upper view and a pillar structure from the side view (Fig. 2) [11]. The calculated average angle between the two-bridging carbon-carbon bonds is  $108^\circ$ , which is very close to the normal bond angle of the  $sp^3$  carbon atom,  $109^\circ 28'$ . Owing to the strain-free known bond angles P [5]A is conformationally stable. The diameter of the internal cavity of P [5]A was  $\sim 4.7$  Å (Table 1), which is close to that of cucurbit [6]uril ( $\sim 5.8$  Å) [12] and  $\alpha$ -cyclodextrin ( $\sim 4.7$  Å) [13]. From another study, the crystal structure of P [6]A, has a hexagon-like cyclic structure, and the diameter of its internal cavity is  $\sim 6.7$  Å, analogous to cucurbit [7]uril ( $\sim 7.3$  Å) [12] and  $\beta$ -cyclodextrin ( $\sim 6.0$  Å) (Fig. 3)



## Cucurbit[n]urils Based Molecular Recognition with Fluorescence Signalling

Liju R.<sup>1</sup> and E. Rajkumar<sup>1,\*</sup>

<sup>1</sup> *Biomimetic and Biosensor Lab, Department of Chemistry, Madras Christian College (Autonomous), Affiliated to University of Madras, Chennai-600 059, Tamilnadu, India*

**Abstract:** The development of fluorescence based supramolecules offering selectivity, sensitivity and detection in real time applications are of great interest. Cucurbit[n]urils (CB[n]), a macrocyclic synthetic host molecule consists of a varying number of glycoluril units bridged by methylene groups. CB[n]s easily forms host-guest complexes (inclusion complexes) with a wide range of analytes. The recognition of analytes in the presence of host molecules using fluorescence techniques received greater attention due to its rapid response, high sensitivity to the environment and robust adaptability. Exploiting the fluorescence properties of CB[n] based supramolecules by enhancing or quenching the fluorescence intensity in the presence of guest molecules by spectrofluorometric methods is discussed. A brief outlook on the development of fluorescence properties of CB[n] based supramolecules used for imaging and photodynamic therapy is presented and discussed.

**Keywords:** Binding affinity, Cucurbiturils, Fluorescence, Host-guest complex, Molecular Recognition, Non-covalent interactions, Supramolecules.

### INTRODUCTION

Molecular recognition is one of the fundamental supramolecular events. It is a process that involves the binding and selection of substrate (guest) by a given receptor (host)molecule with a specific function [1]. These two molecules exhibit molecular complementarity and have different combinations of non-covalent interactions such as hydrophobic interactions, electrostatic interactions,  $\pi$ - $\pi$  interactions, intermolecular hydrogen bonding, and van der Waals interactions, which are essential for the biological processes, supramolecules, molecular biology, and supramolecular assembly [2]. The greater the affinity that exists between host and guest by the combination of forces, the greater will be the selectivity of the host molecule.

\* **Corresponding author Eswaran Rajkumar:** Biomimetic and Biosensor Lab, Department of Chemistry, Madras Christian College (Autonomous), Affiliated to University of Madras, Chennai – 600 059, Tamilnadu, India; Tel: +919842303478; E-mail: rajjkumar@gmail.com

In 1894 Emil Fischer introduced the term “lock and key” for the double complementarity principle extending both the electronic and geometrical features to explain the selectivity and specificity of the specific enzymatic reactions. Supramolecular chemistry and host-guest chemistry are limited to the intermolecular processes, whereas “recognition” can apply to both inter and intra molecular phenomena [3].

Supramolecules are molecular assemblies that are held together by intermolecular forces rather than by covalent bonds. Supramolecules easily form a highly ordered system without any direct bond formation, which facilitates the development of rapid detection of analytes such as sensors. The relatively weak nature of the intermolecular interactions that present in supramolecular assemblies can change their configurations with respect to the variety of different external stimuli, including the introduction of the target analyte. The change in configurations with respect to the external stimuli can be measured by optical signals like fluorescence and absorption changes. The system can be reversed by removing the external stimuli, due to the presence of labile intermolecular interaction exist in the supramolecules. These inherent features of supramolecules are ideal candidates for use as chemosensors.

The detection of a variety of analytes in real time conditions is crucial for the different domains of scientific, medical and security fields [4]. There are several detection methods available for the detection of analytes varying from small organic molecules, anions, cations to whole cells and organisms. The following components are essential for the recognition/detection of analytes using chemosensors: (i) the analyte, defined as the target for recognition/detection (ii) the recognition element, defined as the part of the sensor that recognizes the analyte; (iii) the transducer, defined as the sensor component that responds to the presence of the analyte with changes in the signal.

For supramolecular chemosensors, there is a thermodynamic equilibrium established between the bound and free state, where the amount of complex formation depends on the concentration and the affinity of the analyte. The naturally occurring biological analytes such as amino acids, peptides, neurotransmitters, hormones and drugs are in the range of mM(millimolar) to nM(nanomolar) concentrations in aqueous media. The development of chemosensors with affinities ( $K_a$ )  $> 10^3 M^{-1}$  is commonly preferred. The calixarene or cyclodextrin based macrocycles rarely provide  $K_a$  values beyond  $10^3 M^{-1}$  in aqueous media unless particularly highly charged or hydrophobic analytes are targeted [5, 6]. Cucurbit[n]urils based macrocycles exhibit much higher binding affinity towards various guest molecules and they are inert towards many reagents/chemicals and are highly biocompatible. In this chapter, we are

highlighting the cucurbit[n]urils based system for the detection of various analytes using fluorescence techniques and the application of the selected supramolecules in cancer imaging and photodynamic therapy are discussed.

### Cucurbituril CB[n]

Cucurbit[n]urils ( $n=5,6,7,8,10,14$ ), a family of synthetic macrocyclic host molecules are composed of varying number of glycoluril units bridged by methylene groups, possess unique guest binding properties in aqueous media. In 1905, Berhend and coworkers [7] reported the polymeric product obtained from the condensation reaction between glycoluril units and formaldehyde in acidic solution; however, a complete characterization of the product was done by Mock and coworkers [2] in 1981, the product was successfully crystallized from the reaction; a macrocycle consisting of 6 glycoluril units bound together by 12 methylene bridges. The macrocycle resembled to a pumpkin, which belongs to the family of Cucurbitaceae, hence the name “Cucurbituril” was coined. In CB[n], “n” indicates the number of glycoluril building blocks that constitute the macrocycles. Kim *et al* [8, 9] and Day *et al* [10, 11] successfully synthesised and isolated the homologues series of CB[n] ( $n=5,6,7,8,10,14$ ) and the formation of a reaction mechanism of CB[n]s were reported by Isaacs *et al* [12 - 14].

### Structural Features of CB[n]s

The structural parameters of CB[n] ( $n=5,6,7,8,10$ ) such as cavity volume, cavity diameter, portal diameter and outer diameter are well explored, which are determined from the X-ray crystal analysis [8, 12] (Table 1). The portal diameter and cavity diameter of cucurbit [5]uril is 3.9 Å and 5.8 Å respectively. From the Table 1 and Fig. 1, it is clear that the structural parameters are increasing with increasing “n” value, though the CB[n]s have the same height of 9.1 Å. For example the inner cavity volume of CB [5] is 82 Å<sup>3</sup>, whereas the inner cavity volume of CB [10] is 870 Å<sup>3</sup>, which is approximately more than ten times of CB [5] inner cavity volume. All the CB[n] exhibits good aqueous solubility in acidic conditions. The CB[n]s, with “n” as odd numbers are soluble in neutral water, whereas with “n” as even numbers are poorly soluble. The solubility of CB[n] can be increased by complexing with metal cations or CB[n]: guest complexes in aqueous solution. CB[n], with  $n > 10$ , are less explored and larger cucurbituril are converted into hemicucurbituril or twisted/inverted CB[n] [16].

**Table 1. The structural and physical parameters of CB[n] [8, 12].**

	Mol. Weight	CB [5] <sup>a</sup>	CB [6] <sup>a</sup>	CB [7] <sup>a</sup>	CB [8] <sup>a</sup>	CB [10] <sup>b</sup>
Portal diameter (Å)	830	2.4	3.9	5.4	6.9	9.5- 10.6

# Rhenium(I)-Based Metallacycles for Sensing Applications

Murugesan Velayudham<sup>1,\*</sup> and Pounraj Thanasekaran<sup>2,\*</sup>

<sup>1</sup> Department of Chemistry, Thiagarajar College of Engineering, Madurai – 625015, Tamilnadu, India

<sup>2</sup> Department of Chemistry, Pondicherry University, Kalapet, Puducherry -605 014, India

**Abstract:** Coordination-driven self-assembly provides unique opportunities to prepare highly complex chemical systems from simple components and has led to significant progress in the construction of supramolecular materials with novel topologies and exploitable functions. During the past few decades, metallacycles have captured widespread interests due to their wide applications in catalysis, sensor, and biological relevant applications. Thus, exploring new metallacycles, studying their physical and chemical properties and applications have become one of the most attractive and exciting areas of inorganic chemistry and supramolecular chemistry. Among which, rhenium(I)-based metallacycles, constructed from the rhenium metal ions and a variety of aromatic ligands, have attracted considerable attention because of their unique potentials in light-harvesting, catalysis, sensing, biomedical, *etc.* In this chapter, we summarize the recent research progress in rhenium-based metallacycles with their synthesis, properties and potential application in host-guest chemistry.

**Keywords:** Aggregation induced emission, Aromatic molecules, Binding, Cages, Guest-Host, Hydrophobic interactions, Luminescence, Luminescent probes, Luminescent sensors, Metallacycles, Photophysics, Prisms, Quenching, Rectangle, Rectangular box, Rhenium, Self-assembly, Sensing, Weak interactions.

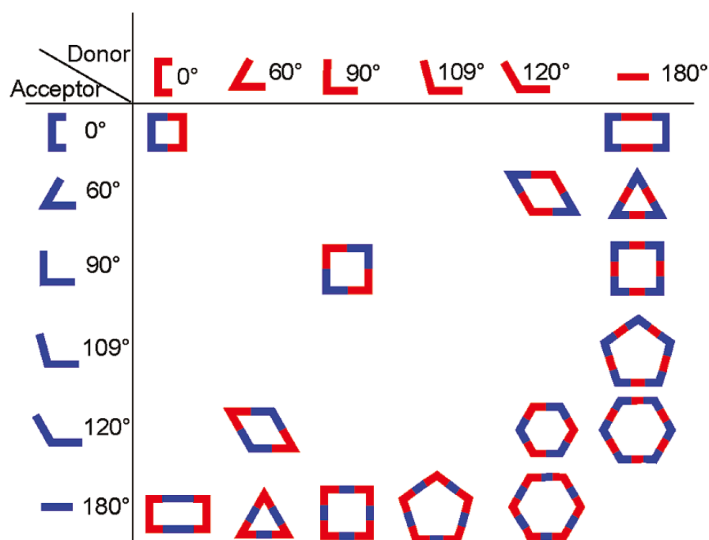
## INTRODUCTION

Self-assembly that is one of the important organizing principles of biological systems is a widely applied strategy in supramolecular chemistry as the driving forces are used to assemble various artificial structures from simple building blocks. The design and synthesis of self-assembled metallacycles has matured as

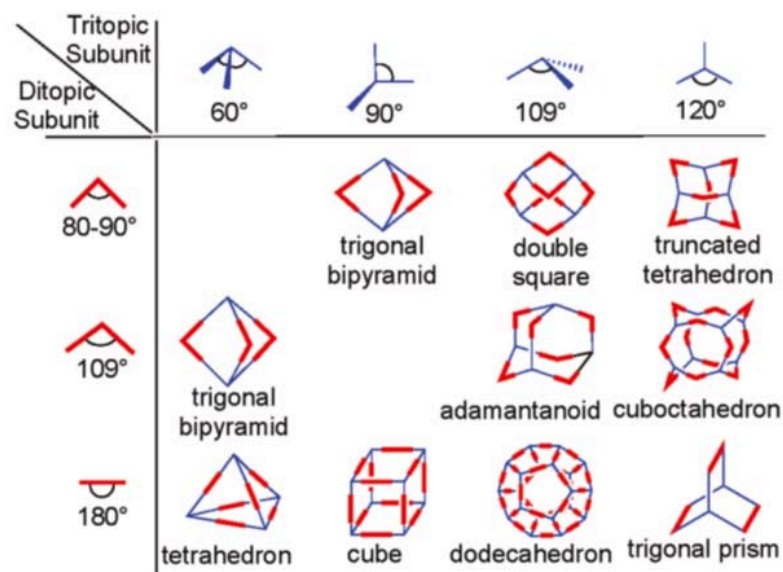
---

\* Corresponding author Murugesan Velayudham and Pounraj Thanasekaran: Department of Chemistry, Thiagarajar College of Engineering, Madurai – 625015, Tamilnadu, India and Department of Chemistry, Pondicherry University, Kalapet, Puducherry -605 014, India; Tel: +917708446619; E-mails: velayudham@gmail.com, ptsekaran@gmail.com

an intensely active area of research in supramolecular chemistry owing to their internal cavities with well-defined shape and size and promising potential applications (Figs. 1 - 2) [1 - 10]. Several synthetic approaches such as directional bonding [1, 11, 12], symmetry interaction [13], and a weak-link approach [14] permit the formation of a single thermodynamic product in high yield with reducing synthetic costs. Thanks to the diversity of coordination-driven self-assembly, a large number of intriguing molecular assemblies, such as molecular triangles, squares, rectangles, cages, prisms, *etc.* have been synthesized *via* a self-assembly route using suitable organic ligands and various metal ions. For instance, the Fujita [11] and Stang [1, 15] groups used a multicomponent self-assembly method for designing large structures based on specific information set within the individual components. Raymond *et al.* significantly extended the investigations towards the dynamic behaviour, chirality and catalysis in supramolecular coordination complexes (SCCs) [16 - 18]. Nitschke *et al.* introduced the concept of 'sub-component self-assembly' [19] according to which the actual linker is formed *in situ* to allow covalent post-assembly modifications of the SCCs [20]. Therefore, metallosupramolecular architectures *via* coordination-driven self-assembly are at the forefront of supramolecular chemistry and will continue to attract focused research.



**Fig. (1).** Combination of various building units for accessing convex polygons and canonical polyhedra. Reproduced with permission from ref. 15. Copyright (2011) American Chemical Society.



**Fig. (2).** Three-dimensional architectures formed by the combination of ditopic and tritopic subunits by the directional bonding approach. Reproduced with permission from ref. 15. Copyright (2011) American Chemical Society.

A majority of these designed metallacycles possess attractive properties such as Lewis acidity, magnetism, redox activity, absorption or luminescence properties, which allow them for use in potential applications in various areas like sensing and catalysis [21]. Especially, the inspiration for using metallacycles in host-guest applications originates from their characteristic properties, such as the ease of fine-tuning the structures, the judicious choice of metal ions and ligands with specific sizes, their coordination geometry, and the simple incorporation of essential functional group modifications [15, 22 - 27]. The photophysical properties from the UV through the visible to the near IR can be tuned by varying the structure of the ligands used, as well as the metal ions present in the metal-organic architectures, which is more favorable for biological studies. Compared with conventional compounds with covalent interactions, the host-guest system based on metallacycles and guests can provide greater flexibility [17]. These compounds offer interesting opportunities for incorporating different cavity sizes that can act as hosts for aromatic guests through  $\pi$ - $\pi$ , hydrophobic interactions or producing a cavity with functional groups that can act as a hydrogen-bond donor or acceptor and would be expected to allow the selective uptake of hydrogen-bonding guests in addition to photochemical reactions and molecular devices [3, 15, 28]. In addition, by taking advantages of the improvement in photoluminescent properties and cavity size of these host

## CHAPTER 7

## Recent Developments in the Dynamics of Fluorescently Labelled Macromolecules

Kandhasamy Durai Murugan<sup>1,\*</sup>, Pandi Muthirulan<sup>2</sup> and Vijayanand Chandrasekaran<sup>3</sup>

<sup>1</sup> Department of Bioelectronics and Biosensors, Alagappa University, Karaikudi-630003, Tamilnadu, India

<sup>2</sup> Department of Chemistry, Lekshmipuram College of Arts and Science, (Affiliated to MS University, Tirunelveli) Neyyoor-629802, Tamilnadu, India

<sup>3</sup> Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore-632014, Tamilnadu, India

**Abstract:** There is considerable interest in the photophysics and photochemistry of water-soluble macromolecules functionalized as pendant or copolymerized on the macromolecular backbone itself. A promising feature of functionalized macromolecules is that a large variety of chemical modifications based on molecular design is possible as compared to conventional organized assemblies such as micelles and vesicles. Photoactive macromolecules have important applications in photoresists, xerography, photocuring of paints and resins, and solar energy conversion systems. These macromolecular systems are broadly classified into two categories: (1) in which chromophores are directly attached to the backbone of the macromolecule as a pendant and (2) in which the macromolecule acts as a host to the photosensitizing molecules. Various aspects of photochemical and photophysical processes in polymers are discussed earlier in detail. Time resolved fluorescence techniques have been extensively used to study the dynamics of natural and synthetic macromolecules. This book chapter covers the investigations on the dynamics polymers in solution using a variety of time resolved techniques ranging from a few femtoseconds to several seconds.

**Keywords:** Dynamics, Macromolecule, Photochemistry, Time Resolved, Timescale of motion.

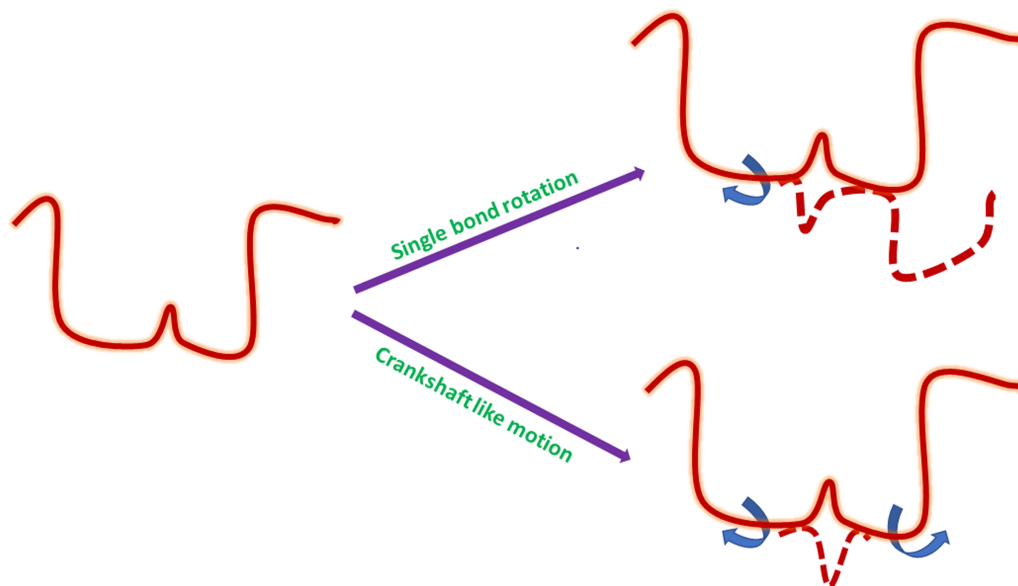
### INTRODUCTION

Enumerable applications of macromolecular self-assemblies in several fields force us to understand their properties not only in solution but also in various forms of matter [1 - 7]. The properties of macromolecular systems, in general, includes

---

\* Corresponding author **Kandhasamy Durai Murugan:** Department of Bioelectronics and Biosensors, Alagappa University, Karaikudi-630003, Tamilnadu, India; Tel: +917708446619; E-mail: kdmurugan@gmail.com

their conformations and dynamics which are governed by various factors like pH of the solution, concentration, molecular weight, temperature and the presence of smaller molecular weight additives [8]. Polymers, especially polyelectrolytes, undergo several conformations in solution and films. Two postulates concerning the mechanism of the conformational transition of polymers in solution are proposed as shown in Fig. (1) [9].



**Fig. (1).** Schematic representation of the conformational transition in a polymer chain.

Rotation around one bond, with the rest of the molecules remaining conformationally unchanged, is one way that requires a large portion of the chain to swing through the viscous medium with a prohibitive expenditure of energy. To avoid this difficulty, Kuhn and Kuhn proposed a theory more than 60 years ago. Accordingly, two temporally correlated rotations would take place so that only a small loop would move which is later described as a “crankshaft-like motion [10]. However, this mechanism, in which two energy barriers have to be surmounted simultaneously implies that the activation energy for the conformational transition in the center of a long-chain molecule is substantially higher (and the transition much slower) than in an analogous small molecule [11]. Later it is shown that a single hindered rotation is required for a conformational transition of a polymer [12]. It is conjectured that the stress introduced into the chain molecule by a hindered rotation is relieved by small distortions of the internal angle of rotation, which requires a very small expenditure of energy [13]. Later, Winnik and co-workers studied the kinetics of conformational transition of poly(styrene) in



toluene and estimated the activation energy of the cyclization [14]. The calculated activation energy coincides with that required for a single bond rotation.

Naturally, the dynamics are related to the structure of the polyelectrolytes and the studies on the structural properties of the polyelectrolytes to some extent provide information on the dynamical properties of the polyelectrolytes at different length scales [15]. However, detailed investigations at different time regions are required to understand the dynamics of polyelectrolytes. The dynamics of macromolecules span several time domains depending upon the nature of the motion of the molecular systems as shown in Table 1. In the shorter time region, the vibrational motion and the bending of the bonds takes place on the atomic scale while at a longer time scale the entire molecular motions and the folding are the prominent processes occurring in the polymers [16].

**Table 1. Time scale and molecular motion.**

Time Scale	Amplitude	Description
$10^{-15}$ – $10^{-12}$ s	0.001 – 0.1 Å	– bond stretching, angle bending – constraint dihedral motion
$10^{-12}$ – $10^{-9}$ s	0.1 – 10 Å	– unhindered surface side chain motion – loop motion
$10^{-9}$ – $10^{-6}$ s	1 – 100 Å	– folding in small peptides – helix coil transition
$10^{-6}$ – $10^{-1}$ s	10 – 100 Å	– protein folding – domain motion

In the case of macromolecules such as polypeptides and synthetic polymers, the dynamical processes involving the motions of the side chains and loops take place in the sub-picosecond to nanosecond time scale. The coil transitions occur in a few nanoseconds to microseconds in solution [17].

### **POLY(ACRYLIC ACIDS) – STRUCTURAL TRANSITION AND DYNAMICS**

The conformations and dynamics of poly(acrylic acids) are subjects of intense investigation over several decades. The ionization of these polymers in solution is a function of the pH of the solution. Hence, these polymers show different conformations regulated by electrostatic interactions, hydrogen bonding, hydrophobic and other weak interactions, which are dependent upon the pH of the solution [18]. Poly(acrylic acid), PAA, is gradually expanded to a linear chain by increasing the pH of the solution [19]. On the other hand, poly(methacrylic acid), PMAA, which has a methyl substituent at the  $\alpha$ -carbon, shows a different

## SUBJECT INDEX

### A

- Absorption spectra 153, 169, 197, 198  
 triplet-triplet 198
- Acid 14, 22, 23, 32, 66, 82, 83, 126, 144, 145,  
 148, 162, 183, 189, 193, 197, 200, 201
- acrylamidoglycolic 193
- carboxylic 200, 201
- carminic 14
- chloranilic 148, 162
- gallic 32
- gastric 126
- lewis 82, 83
- methacrylic 183, 189, 193, 201
- oxalic 66
- perfluorooctanoic 22, 23
- picric (PA) 144, 145
- polyacrylic 197
- polymethacrylic 197
- sulfuric 83
- trifluoroacetic 83
- trifluoromethanesulfonic 83
- Aggregation 6, 94, 96, 98, 99, 103, 140  
 induced emission (AIE) 6, 94, 96, 98, 99,  
 103  
 process 98, 140
- AIEgen 94  
 behaviour 94  
 luminescence 94
- AIE turn-on fluorescence behaviours 94
- Alkyl chain, dinitrobenzene-containing 96
- Alzheimer's disease 146
- Amide-functionalized metallacycles 167
- Amines 122, 154, 155
- Amino acid 18, 123, 124  
 chemosensor 123  
 enantiomers 18  
 residue in peptide sequences 124  
 transportation 18
- Analysis 116, 149, 162, 163, 166, 171  
 absorption titration 163  
 emission titration 171
- fluorescence spectroscopic 116
- fluorescence titration 149, 166
- single-crystal X-ray diffraction 162, 163
- Analytes 14, 17, 111, 112, 113, 115, 116, 117,  
 118, 119, 121, 132
- aliphatic alcohol 14
- amine-based 118
- steroid 17
- Angle neutron scattering measurements 201
- Anion sensors 43
- Anthracene 15, 66, 96, 100, 101, 141, 142,  
 149, 164, 165, 166, 193  
 bearing Pillar 96  
 fluorescent 96
- Antibacterial 58, 60, 65, 70, 71  
 activity 60, 70  
 and antioxidant activity 58, 65, 71
- Anticancer activity 42
- Antioxidant 58, 65, 70, 71  
 activity 58, 65, 70, 71  
 agents 58
- Anti-tumour agents 70
- Applications 58, 60, 65, 70, 71, 84, 86, 100,  
 102, 175, 199  
 antibacterial 70, 71  
 biochemical 175  
 catalysis 58  
 catalytic 60  
 diverse 84, 86, 100, 102  
 environmental 60  
 industrial 199  
 of resorcinarene crowns 65
- Architecture 47, 78, 88, 168, 172, 173  
 distorted trigonal prismatic 172  
 fabricating luminescent 47  
 hammock-shaped 168  
 novel macrocyclic 78  
 rectangular prismatic 173
- Arene 42, 46, 68  
 metalloporphyrin 68  
 oxacyclophane architectures 42  
 system 46

## **Subject Index**

Aromatic 60, 66, 141, 142, 163, 166, 167, 172  
  alcohols 172  
  aldehydes 60  
  guest molecules 163, 166, 167  
  hydrocarbons 66, 141, 142  
Aromatic rings 87  
Artificial light harvesting systems 187  
Assay 124, 172  
  emission profile 172  
Associative binding assay (ABA) 116, 117,  
  118, 119, 122, 127, 128  
Atomic force microscopy 184

## **B**

Behaviour 33, 44, 87, 89, 90, 101, 138, 184  
  dynamic 138  
  fluorescent 101  
  inducing luminescence 33  
Benesi-Hildebrand equation 142, 156  
Benzene derivatives 66, 71  
Benzimidazole scaffold 46  
Benzophenanthridine alkaloid sanguinarine 5  
Bi-functional calix 46  
Binding 5, 38, 44, 59, 60, 111, 112, 115, 123,  
  142, 143, 147, 149, 151, 156, 157, 159,  
  160, 161, 164, 169, 172, 173, 174  
  affinities 5, 44, 59, 111, 112, 115, 123  
  constants 142, 143, 147, 149, 151, 156,  
  157, 159, 160, 161, 164, 169, 172, 173,  
  174  
  properties 38, 59, 60  
  stoichiometry 147  
Binding interaction 5, 123, 167  
  carbohydrate-protein 5  
Bioimaging applications 41  
Biological 15, 19, 78, 120, 121, 124, 126, 130,  
  132, 137, 200  
  applications 19, 124, 132  
  assays 15  
  imaging applications 120  
  process, life-sustaining 78  
  systems 121, 126, 130, 137, 200  
Biomimetic nanochannel 18

## **Photophysics of Supramolecular Architectures 215**

Biomolecule adenosine diphosphate 46  
Buffered biological media 126  
Building blocks, glycoluril 113

## **C**

Calix 33, 34, 35, 36, 37, 40, 41, 42, 43, 44, 45,  
  46, 47  
  anthraquinone-modified 37  
  fluorescent 37, 40, 44  
  fluorescent amino thiadiazole 42  
  fluorescent guanidinium 45  
  triazole-modified 33, 44  
Calixarenes 31, 32, 33, 38, 39, 44, 46, 47, 48,  
  58, 60, 78, 79, 81, 112, 114, 165  
  developing luminescent 47  
  fluorescent 33, 44  
  lanthanoid 47  
  luminescent 47  
  organometallic 165  
Capillary electrophoresis 11  
Cetyltrimethylammonium bromide 33  
Chains 47, 182, 185, 192  
  arene coordination 47  
Change, luminescence intensity 147  
Charge distribution 190, 193  
  electronic 193  
Charge interactions in polyelectrolyte  
  solutions 185  
Charge transfer (CT) 78, 118, 119, 141, 142,  
  151, 193, 199  
  interactions 199  
  singlet metal-to-ligand 141  
  triplet metal-to-ligand 141  
Chelation 42, 164  
  displayed 42  
Chemical 66, 67, 70  
  amplification resistance 70  
  sensors 67  
  separations 66  
Chemiluminescence 188  
  activity 188  
  of polymer materials 188  
Chemistry 137, 194

inorganic 137  
liquid phase 194  
Chemosensing 23, 118  
Chemosensor(s) 1, 31, 33, 37, 41, 65, 71, 98, 112, 119, 123, 125, 126  
  application 37  
  simple molecule-based 98  
Chloride 83, 92, 95  
  ferric 83  
  tetrabutylammonium 92  
Chloroform 88, 96, 103  
Commercial antioxidants 188  
Competitive binding assay 121  
Complexe(s) 9, 10, 23, 123, 138, 141, 142, 143, 146, 156, 157, 175, 193, 199, 200  
  DNA structure 193  
  dye-doped 10  
  formation host-guest 9  
  insoluble 200  
  polyelectrolyte 199  
  stable ternary 123  
  supramolecular coordination 138  
  tricarbonyl 175  
Concentrations, low chromophoric 188  
Condensation 69, 79, 82, 83  
  acid-catalyzed 82  
Condensation reaction 60, 61, 62, 63, 65, 82, 113  
  acid-catalyzed 60  
  catalyzed 60, 63  
Conformational dynamics of 188  
  polyelectrolytes 188  
Conformations 33, 43, 59, 118, 182, 183, 185, 201  
  coiled 185  
  isoenergetic 118  
Conglomeration 46  
Constants 142, 143  
  diffusion-controlled rate 143  
  emission quenching rate 142  
Constraint dihedral motion 183  
Copillar 83, 84, 93, 97, 98, 99  
  rhodamine-appended 97  
  thymine-appended 98, 99  
Copolymerization 102, 103

Cordycepin 120  
Coumarin 122  
  derivatives 122  
  dye 122  
Crown ethers, cloverleaf resorcinarene 63  
Crystals 33, 60, 62, 167  
  elongated nanoporous micro 33  
  liquid 60  
CTAB complexes 33  
Cyclic polysaccharide 1  
Cyclocondensation reaction 61  
  catalyzed 62  
Cyclodextrin-based intra-nanogap particles 4  
Cyclodextrins 1, 20, 78, 79, 86, 112, 114, 117  
  amphiphilic 20  
Cyclooligomerization 82  
  acid-catalyzed 82  
Cyclopentamer 79  
Cyclopentanone 128  
Cyclotrimerization 149  
Cytoplasmic protein-powered fluorescence  
  cascade amplifier 18, 19  
  based 19  
Cytotoxic agents 175

## D

Delivery 16, 45, 60  
  gene 60  
  genetic material 45  
Density 43, 85, 115, 143  
  functional theory (DFT) 43, 143  
  high  $\pi$ -electron 85  
  residual electron 115  
Derivatives 2, 11, 41, 45, 71, 77, 86, 91, 115, 116, 117, 118  
  arene-hexaamide 45  
  peptide 118  
  resorcinarene crown 71  
Detection 11, 13, 14, 15, 46, 94, 95, 111, 112, 113, 115, 116, 122, 123, 143, 144, 145, 146  
  amplified fluorescence 46  
  colorimetric 119

## **Subject Index**

fluorescence-based 122  
laser-induced fluorescence 11  
ultra-trace 15  
Development of supramolecular chemistry 77,  
78  
Dibutylloxamidato bridges 158  
Dimethoate 67  
  electron-deficient 67  
Direct-binding assays (DBAs) 117, 118  
Dissymmetry factor 10  
DLS studies and electron 101  
Drug 1, 2, 23, 31, 60, 112, 129  
  anticancer 129  
  delivery vehicles 23  
DSA 100, 124  
  guest binding 100  
  linked pillararene derivatives 100  
DSQ fluorescence 124  
Dye(s) 12, 33, 122, 185, 196  
  encapsulation 12  
  molecule, fluorescent 185  
  phenosafranine 196  
  phthalocyanine 122  
  ruthenium 33  
Dynamical processes 183  
Dynamic(s) 89, 94, 101, 181, 182, 183, 185,  
188, 189, 193, 194, 196, 197  
  light scattering (DLS) 89, 94, 101, 185  
  polymers 181  
  rotational relaxation 193  
  segmental 193

## **E**

Effect, superamplified quenching 145  
Electroanalytical techniques 127  
Electron 86, 101, 115, 119, 144, 145, 171,  
191, 199  
  donor hydroquinone 86  
  pairs pointing 115  
  process 191  
  transmission 144  
Electron transfer 7, 99, 119, 149, 189, 190,  
191, 192

## **Photophysics of Supramolecular Architectures 217**

  induced ground-state 7  
Electronic energy transfer 190  
Electrospray ionization mass spectroscopy 87  
Electrostatic potential (EP) 115, 116  
Emission 1, 4, 7, 12, 31, 43, 97, 100, 119, 123,  
126, 143, 144, 149, 150, 153, 159, 160,  
164, 166, 169, 171, 173  
  aggression 123  
  assembly-induced enhanced 100  
  enhancement 153, 164, 173  
  ligand-based 149  
  quenching 126, 143, 144, 166, 169  
  spectroscopy 87  
  techniques 159, 160  
  tunable light 12  
  wavelength 119, 144, 171  
Emission properties 11, 102, 143  
  aggregation-induced 143  
  assembly-induced 11  
Emission spectra 125, 145  
  of nanoaggregates 145  
  of tryptophan 125  
Emitting gold nanoclusters 15  
Enantiomers 11, 81, 82  
Enantioselectivities 6  
Encapsulated lipase nanoparticle 46  
Encapsulation 7, 69, 86, 124  
  thiabendazole 7  
Energy 48, 99, 119, 182, 187, 188, 190  
  absorbed light 187  
  conversion efficiency 188  
  devices 48  
  migration 187  
Energy transfer 43, 89, 141, 157, 187, 190,  
191  
  efficiencies 89  
  fluorescence resonance 43  
  pathway 141  
Environment 2, 111, 115, 126, 132, 194, 196,  
197, 202  
  coiled polymer 197  
  hydrophilic 202  
  microheterogeneous 194  
Environmental contaminants polyaromatic  
  hydrocarbons 141

Epoxidation 68

  catalytic 68  
  reactions 68

Ester functionality 172

Ethylene 31, 200, 201

  bridge 31  
  oxide 200, 201

## F

FITC molecule 101

Fluorescence 1, 10, 14, 21, 31, 33, 34, 35, 37,  
  40, 43, 83, 90, 92, 93, 96, 98, 100, 101,  
  102, 111, 112, 116, 117, 118, 119, 122,  
  123, 130 132, 164, 191, 193

  anisotropy 193

  assay 164

  displayed chelation-enhanced 33

  dynamic 193

  energy transfer technique 191

  guided photothermal cancer therapy 21

  intracellular green 130

  intensity 33, 40, 90, 92, 93, 100, 101, 102,  
  122, 123, 124, 130, 132

  microscopy 20

  naphthalene 118

  properties 33, 116

  quantum 86, 93

  quenched 96

  resonance energy transfer (FRET) 10, 33,  
  43, 100, 117

  sensitization 14

  spectroscopic measurements 185

  spectroscopy 3, 34, 47, 124, 127, 201

  techniques 1, 111, 113

  titration data 151

  turn-on probe 17

Fluorescence emission 86, 95, 100, 101, 123,  
  126

  intensities 101, 126

  spectroscopy 95

Fluorescence quenching 13, 15, 39, 40, 42, 43,  
  46, 117, 119, 149, 151, 189

  isomer-induced 15

  nature 43

Fluorescent 9, 14, 34, 35, 39, 40, 93, 99, 101,  
  117, 118, 124, 131, 164, 190

  chemosensor 34, 35, 39, 40

  data 164

  dyes 9, 117, 118, 124, 131

  enhancement 93

  imprintable hydrogels 9

  materials 99

  quenching 14

  uranyl acetate 190

  vesicles 101

Fluorescent sensor 13, 14, 15, 37, 38, 39, 41,  
  45, 93, 99, 101, 102

  ion-induced 37

  sensitive 41

  temperature-dependent 101

  thermo-responsive 102

  system 14

Fluorophore rhodamine 17

FRET-capable supramolecular polymer 88

FT-IR spectroscopy 140

Function 111, 137, 140, 153, 160, 183, 193,  
  197, 198

  exponential frequency 153

## G

Gas chromatography (GC) 58, 65, 71

GC capillary column 66

Geometric metallacyclic structures ranging  
  174

Geometry 119, 168

  distorted octahedral 168

Glutathione 13, 16

  coated gold nanoclusters 13

Graphitic carbon nitride (GCN) 12

Growth 70, 91, 129, 188

  bacterial 70, 129

  seeding 91

Guest 21, 87, 92, 121, 139, 157, 161

  displacement assay (GDA) 121

  hydrogen-bonding 139

  molecules fluorescence behaviour 87

## **Subject Index**

polymer 21  
triphenylene 157, 161  
viologen molecules 92

## **H**

Heating-cooling cycles 102  
High performance liquid chromatography (HPLC) 58, 65, 66, 71  
Homocysteine 16  
Host 64, 67, 68, 86, 111, 115, 117, 123, 124, 139, 142, 143, 151, 159, 161, 169  
  bis-crown resorcinarene 64  
  concentration 103  
Host-guest 6, 77, 79, 86, 87, 96, 100, 112, 114, 137, 140  
  assembly 6, 100  
  binding behaviours 86  
  binding properties 79, 86  
  chemistry 77, 87, 96, 112, 114, 137, 140  
Host-guest complexation 85, 86, 88, 92, 100, 102, 104, 132, 172  
  arene-based photoresponsive 88  
  behaviour 85, 92  
Host-guest inclusion 2, 20, 21, 99  
  complexation interactions 21  
  interaction 20  
Host-guest interaction 3, 5, 18, 20, 87, 89, 93, 96, 131, 140, 141, 151, 152, 159, 161, 169  
  high-affinity 131  
Host molecule 111, 113, 131  
  synthetic 111, 131  
  synthetic macrocyclic 113  
HPLC separation column 66  
Human 17, 22  
  growth hormone 17  
  serum albumin 22  
Hydration 194, 184  
  dynamics of proteins 194  
  process 184  
Hydrogen 200  
  bonded interpolymer complexes 200

## **Photophysics of Supramolecular Architectures 219**

Hydrogen bonding 7, 111, 115, 119, 123, 159, 175, 183, 184, 189, 197, 198, 200, 201, 202  
  interactions 115, 159  
  intermolecular 111  
  properties 175  
Hydrolysis 1, 197  
  enzymatic 1  
Hydrophobic 1, 7, 86, 112, 115, 126, 144, 183  
  analytes 112  
  biomolecules 126  
  microenvironment 7  
Hydrophobicity 66, 115, 119, 154, 175, 200  
Hydrostatic pressure 15

## **I**

Imaging Wilson's disease copper trafficking 38  
Imidazolium derivatives 89  
Imino nitrogens 35  
Indicator 124  
  fluorescent 124  
Indicator displacement assays (IDA) 116, 117, 118, 119, 120, 121, 127, 128  
  for molecular recognition 120  
Inflammatory bowel disease 18  
Interactions 1, 2, 4, 31, 32, 67, 111, 119, 142, 143, 152, 159, 160, 161, 162, 163, 166, 183, 185, 190  
  coulombic 198  
  donor-acceptor 161  
  electrostatic 67, 111, 119, 183, 190  
Internal filter effect (IFE) 42  
Interpolymer 199, 197, 200, 201, 202  
  adduct formation 202  
  complexes 199, 200, 201  
Intracellular alkaline phosphatase activity 18  
Intramolecular 35, 82, 189  
  charge transfer (ICT) 35, 189  
  H-bonding interactions 82  
Ion 33, 58, 65, 71  
  chromatography 58, 65, 71  
  sensing applications 33

Isomers 15, 23, 82, 172  
conformational 82  
constitutional 82

## L

Lewis 61, 79, 85, 139  
acid catalyst 61, 79, 85  
acidity 139  
Ligands 40, 66, 167  
functionalized flexible ditopic 167  
macrocyclic 40, 66  
Light 23, 129, 185, 187, 191  
absorption 185  
energy conversion 191  
Light-harvesting 89, 137  
capability 89  
Light scattering technique 185  
Lower 35, 36, 64, 66  
rim modification 66  
rim proximal triazolylpyrenes 35, 36  
rim resorcinarene crown derivatives 64  
Luminescence 1, 10, 11, 31, 47, 93, 94, 137, 139, 143, 154, 174  
lanthanide 11  
polarized 10  
intensity 93  
properties 47, 139, 174  
quenching 154  
sensor 143  
Luminescent 2, 5, 31, 32, 46, 174  
dye molecules 2  
guest molecules 2, 32  
guests 31  
host-guest systems 32  
lanthanoid calixarene complexes 46  
lanthanoids 46  
properties 5, 32, 174  
Luminous transmittance 11

## M

Macrocycles 1, 31, 77, 113, 115, 116, 117, 127

synthetic 77  
Macrocyclic 58, 78, 91, 94, 111  
pillararene 94  
supramolecular hosts molecule 60  
Macrocyclic systems 78  
novel synthetic 78  
Macromolecules 181, 199  
synthetic 181, 199  
water-soluble 181  
MCR-HPS column 66  
Mechanically interlocked molecules (MIMs) 96  
Mechanism 33, 38, 45, 94, 97, 117, 119, 126, 182, 184, 187  
click reaction 38  
dye exchange 126  
of hydration of PMAA film 184  
traditional sensing 119  
turn off-on 45  
Metal 5, 11, 36, 98, 116, 122  
detoxification 36  
ion recognition 5, 116, 122  
ion removal procedure 98  
organic frameworks (MOF) 11  
Metallacycles 137, 139, 140, 141, 143, 145, 147, 149, 151, 153, 163, 164, 165, 167, 175  
ionic 140  
multicavity 175  
rhenium-based 137  
Metallacyclophanes 167, 169, 175  
bridged tetrarhenium 167  
dimeric 175  
Metalloporphyrin 68, 71  
Methanol guest molecules 164  
Methods 5, 98, 111, 184  
calorimetric 184  
fluorescence detection 98  
label-free fluorescence-based 5  
spectrofluorometric 111  
spectroscopic 5, 184  
Methyl 118, 119, 199  
methacrylate 199  
viologen (MV) 118, 119  
Microcantilever array 45



## Subject Index

Microheterogeneity 190  
MnRCP-catalyzed epoxidation reactions 69  
Molecular 2, 6, 33, 117, 120, 129, 139, 151  
  devices 139  
  docking 2  
  interactions 6  
  oxygen 129  
  recognition systems 117, 120  
  rectangles, thiolato-bridged 151  
  taekwondo processes 33  
Molecularly imprinted polymer (MIP) 44  
Monomer 33  
  fluorescence 33  
  phosphorescence 33  
Morphology 11, 95, 188  
  possessed spherical-like 11  
  transformation 95

**N**

Nanoparticles, synthesized iron magnetic 46  
Naphthalene fluorophores 117  
Nitroaromatic reagents 47  
Nitrophenol isomers 15  
NMR 86, 87, 88, 96, 143  
  proton 87, 88  
NMR 167, 184  
  analysis 167  
  spectroscopy 184  
Non 2, 7, 100  
  luminescent nature 2  
  radiative process 100  
Nonradiative relaxation 7  
Nuclear magnetic resonance spectroscopy 86

**O**

Organic 175  
  macrocyclic architectures 175  
Organic molecules 87, 126, 127, 185, 186  
  absorbing 185

## Photophysics of Supramolecular Architectures 221

## P

Pathway 38, 47, 77, 86, 100, 185, 189  
  copper trafficking 38  
  radiative decay 100  
  rotational diffusion 189  
Peptides 16, 67, 112, 118, 123  
  fluorescent 16  
Pesticides 16, 67  
  toxic organic 16  
Phase transfer catalyst (PTC) 63  
Phosphorescence 7, 186  
  efficient room-temperature 7  
Photochemical processes 202  
Photodynamic 111, 113, 128, 129, 132, 175  
  cancer therapy 132  
  therapies 128  
  therapy 111, 113, 128, 129, 175  
Photoerasable red-luminescent ink 8  
Photoinduced electron transfer (PET) 17, 37,  
  39, 42, 118, 188, 191  
  mechanisms 17  
Photoluminescence efficiency 140  
Photoluminescent properties 139  
Photophysical properties 1, 47, 77, 104, 116,  
  139, 140, 150, 193  
Photophysical techniques 185, 188  
Photopolymerization and photocuring science  
  and technologies 187  
Photoresists 181, 186  
Photoresponsive 88  
Photosynthetic systems 187  
Phototherapeutic action 20  
Pillararenes 87, 103  
  photophysical behaviour of 87  
  reactive synthetic supramolecular host 103  
Polyanions 199  
Polyelectrolytes 182, 183, 184, 185, 188, 189,  
  190, 192, 193, 194, 196, 197, 199, 202  
  anionic 190  
  dynamics of 183, 202  
  natural 194  
Polyelectrolyte transition 191  
Polymer 7, 99, 193, 195, 196, 200

acts, linear supramolecular ternary 99  
concentration 195, 196, 200  
conformation 193  
dynamics 193  
free electrospinning 7  
Polymeric 6, 187  
  electrolytes 187  
  ionic liquid (PIL) 6  
Polymerization process 189  
Polymer(s) 15, 92, 93, 96, 181, 182, 183, 185,  
  186, 187, 188, 189, 190, 191, 192, 193,  
  197, 199, 200, 201, 202  
  complementary 199, 201, 202  
  conjugated 92, 93  
  crossed linked 96  
  cross-linked 15  
  electron donating 199  
  photoactive 186  
  photophysics 190  
  proton donating 200  
  synthetic 183, 200  
Porphyrins 11, 20, 68, 192  
  adamantane-conjugated 20  
  conjugate 68  
Prisms 137, 138, 171, 172  
  supramolecular hexarhenium 171  
Probe 5, 15, 17, 40, 42, 91, 117, 137, 146,  
  185, 189, 193, 194  
  based CHEF-PET fluorescence 42  
  based fluorescence 15  
  luminescent 137  
Processes 101, 102, 111, 174, 175, 183, 185,  
  186, 187, 188, 190, 193, 194  
Prodrug-conjugate adamantane 130  
Progesterone quenching 120  
Properties 71, 35, 46, 85, 89, 96, 100, 114,  
  116, 137, 139, 140, 141, 181, 183, 188,  
  193, 199  
  antibacterial 71  
  chemical 137  
  dynamical 183  
  electronic 35  
  light-switching 140  
  magnetic 46  
  photoluminescence 100

  reversible fluorescence quenching 96  
  rheological 199  
Proteins 32, 45, 116, 125, 145, 147, 191, 194,  
  200  
  red fluorescent 45  
Proximity-induced interactions 14  
Pseudorotaxanes 93, 100, 123  
Pyrene 36, 152, 161, 166, 174  
  guest molecules 152, 161, 166, 174  
  monomer emission 36  
Pyrene-appended calix 37, 40  
  triazole-bridged 40

## Q

Quantum dots (QDs) 11, 13  
Quartz crystal microbalance 67  
Quaternary ammonium guest acetylcholine 64  
Quenching 7, 111, 118, 119, 122, 123, 137,  
  142, 143, 197  
  dynamic 7, 142

## R

Radiationless deactivation processes 86  
Reaction 63, 96, 112, 139, 148, 149, 151, 155,  
  158, 159, 160, 165, 167, 169, 170, 173,  
  191, 193  
  biochemical 193  
  enzymatic 112  
  ion-induced 96  
  nucleophilic substitution 63  
  photochemical 139  
Reactive oxygen 128  
Receptors 35, 38, 91, 111, 117, 118, 119, 124,  
  126  
  metal ion 38  
  synthetic 91  
Recognition 41, 43  
  fluorescent 41, 43  
  sensitive fluorescence 42  
Resorcinarene derivatives 65, 66, 68  
Resorcinarenes synthesis 60, 62, 63

## ***Subject Index***

Response 37, 117  
  distinct colorimetric 37  
  spectroscopic 117  
Reversible addition-fragmentation chain  
  transfer polymerization 6  
Room-temperature phosphorescence (RTP) 7  
Rotaxane sensor 96, 97  
  interlocked molecular 36  
  self-immolative 96  
RTP emission 7

**S**

Scanning electron micrographs 70  
Selective 39, 64  
  fluorescent chemodosimeters 39  
  functionalization of resorcinarene 64  
Sensing aromatic 143, 160  
  compounds 160  
  hydrocarbons 143  
Sensitized fluorescence technique 14  
Sensors 33, 58, 60, 89, 93, 112, 116, 117, 119,  
  124, 131, 137, 141, 144, 145, 160, 164  
  double fluorescence 89  
  efficient anion-responsive fluorescence 93  
  electrochemical 131  
  luminescent 137  
  luminescent calixarene 33  
Separation, ion chromatography 66  
SERS technique 91  
Silver nanoparticles 37, 45, 68  
  reduced 45  
  synthesizing 37  
Singlet oxygen 129, 130, 140  
  photosensitization, effective 140  
Spectral techniques 141  
Spectroscopic technique 86  
Spectrum, electronic 97  
Static light scattering (SLS) 185  
Stern-Volmer 142, 151  
  analyses 151  
  equation 142  
Supramolecular 11, 77, 91, 92, 98, 99, 100

## ***Photophysics of Supramolecular Architectures 223***

assemblies 11, 16, 60, 88, 98, 100, 111, 112,  
  125, 138, 140  
  chemosensors 112  
  coordination complexes (SCCs) 138, 140  
  synthesized 88  
Supramolecular gel 102, 103  
  arene-based fluorescent 102  
  cross-linked 102  
  pillarenes-based stimuli-responsive 103  
Supramolecular nanoparticles 8, 11  
  red-luminescent quaternary 8  
Supramolecular polymer 7, 21, 96, 98, 99, 103  
  blue fluorescent 103  
  prepared pillarenes 99  
Supramolecular systems 77, 78, 85, 87, 98,  
  103  
  novel photoemitted 87  
Surface enhanced Raman spectroscopy  
  (SERS) 91  
Systems 7, 20, 21, 31, 38, 44, 58, 65, 71, 78,  
  88, 96, 99, 104, 112, 116, 119, 122, 124,  
  132, 140, 175, 181, 186, 189  
  artificial light-harvesting 88, 104  
  biomimetic 78  
  catalytic 58, 65, 71  
  columnar structural macrocyclic 78  
  electron-rich aromatic host 99  
  enzyme-triggered 20  
  fluorescent recognition 44  
  light-harvesting mimicking 88  
  luminescent sensor 31  
  microheterogeneous 189  
  polymeric 78, 186  
  porphyrin 7  
  solar energy conversion 181, 186

**T**

Thermal 157, 158, 168, 186  
  ellipsoids 157, 158, 168  
  energy 186  
Thermodynamic equilibrium 112  
Thermo-responsive fluorescent vesicle 101  
Thiacalixphenyl, modified 41

Time-resolved fluorescent measurements 100  
TMR 118  
    chemosensors 118  
    conjugate 118  
Toxic 98, 175  
    anticancer agents 175  
    heavy metal ion removal applications 98  
Transition 46, 148, 153, 163, 164, 166, 182,  
    183, 184, 189  
    conformational 182, 184, 189  
    electronic 46  
    helix coil 183  
    intraligand 148, 163, 164, 166  
    metal-to-ligand charge transfer 153  
Transmission electron microscope 91  
Triphenylene guest molecules 156, 161  
Tryptophan fluorescence 118  
TTET technique 191  
Tubular polymeric structure 33  
Twisted internal charge transfer (TICT) 124

## U

UV 2, 87, 93, 102, 139  
    initiated polymerization 102  
    light illumination 93

## V

Vinyl propyl ether (VPE) 201

## W

Waals interactions 33, 38, 111  
Wilson's disease 38

## X

Xerography 181, 186



**Paulpandian Muthu Mareeswaran**

---

Dr. Paulpandian Muthu Mareeswaran received Ph. D. from Madurai Kamaraj University, Madurai, Tamilnadu, India in the field of supramolecular photochemistry. After Ph.D., he spent two years at Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea. He received Brain Pool Korea (BK21 Plus) Fellowship in 2013. In 2014, he joined as DST INSPIRE Faculty at Department of Industrial Chemistry, Alagappa University, Karaikudi, Tamilnadu, India. Three Ph. D. students are graduated under his guidance. He published fifty-two publications in reputed journals. He has membership in academic bodies like Indian society for radiation and photochemistry (ISRPS). His current research activities include supramolecular photochemistry, carbon dioxide mitigation, sustainable energy resources and environmental science.



**Palaniswamy Suresh**

---

Dr Palaniswamy Suresh has revied his PhD degree from Madurai Kamaraj University, India, in organic supramolecular Chemistry under the supervision of Prof. K. Pitchumani. After that, he worked as a post-Doctoral fellow at the University of Puerto Rico, USA, under the supervision of Prof. Raphael G. Raptis. Then, he returned to India and joined as an Assistant Professor in August 2010 at the School of Chemistry, Madurai Kamaraj University, Madurai, India. He is the recipient of the UGC-Raman fellowship to carry out collaborative research work at Florida International University, Miami for twelve months in 2016-2017 and SERB international travel grant to visit China in 2019. His research interest includes catalysis, C-H bond activation, metal-organic framework, graphene materials (both catalysis and sensors development), synthesis and application of modified cyclodextrin and asymmetric catalysis.



**Seenivasan Rajagopal**

---

Prof. Seenivasan Rajagopal served as senior professor in the Department of Physical Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai, India. He had 43 years of teaching experience and 39 years of research experience. He served as Chairperson of School of Chemistry and Head of the Department of Physical Chemistry at Madurai Kamaraj University, Madurai, Tamilnadu, India. Forty students have earned Ph. D. under his guidance and he published more than 120 papers in reputed journals. He spent one year as UNESCO Fellow at Tokyo Institute of Technology, Japan. He was a Visiting Professor for one year at Institute of Chemistry, Academia Sinica, Taiwan and as Visiting Scientist via Indo-Taiwan Exchange program in the period 2010-2012. He operated more than ten projects. His research work has been widely cited particularly in fundamental text books like Advanced Organic Chemistry by J. March, 4th Edition, Wiley, 1992, New York and Advanced Physical Chemistry by P. W. Atkins and Juilo de Paula, Oxford University Press, 2006, London.