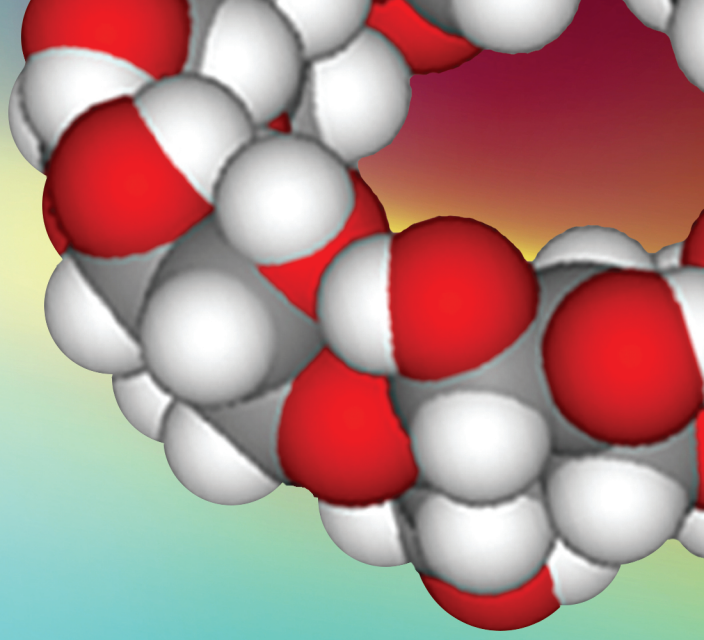

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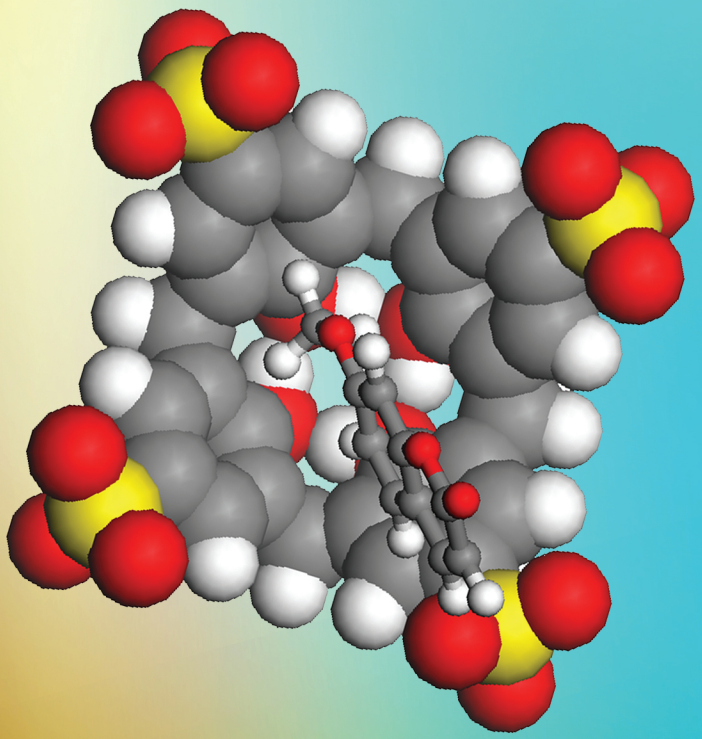

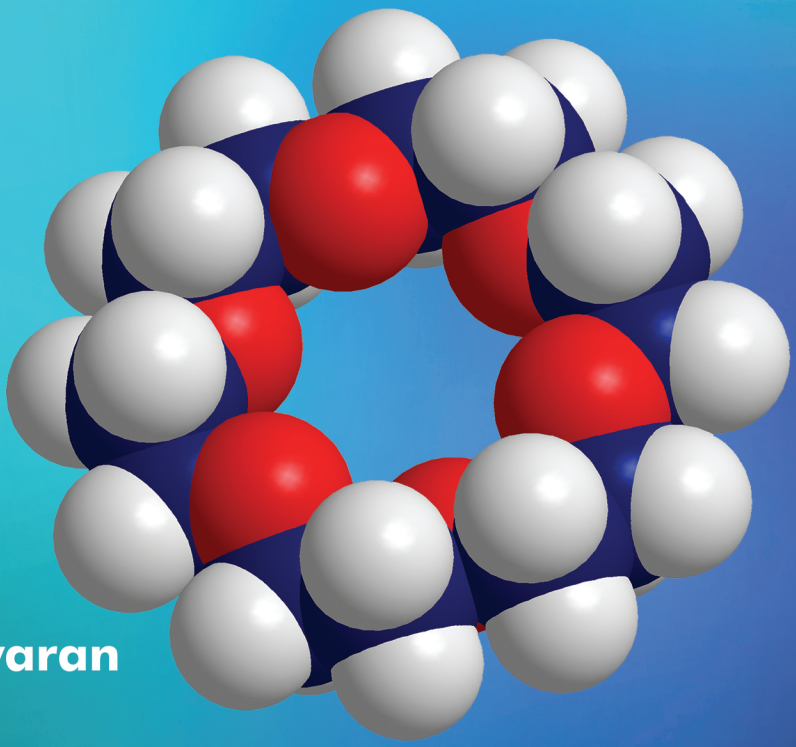

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Photophysics of Supramolecular Architectures

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CONTENTS

FOREWORD

The introduction of surfactants and micelles to study the photophysics and photochemistry of molecules opened up a new approach to mimick 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.

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PREFACE

Supramolecular architectures, the prevalent architectures in nature, are designed through a variety of non-bonding interactions like hydrogen bonding, π-π 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 cavitand. 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 cavitands like cylclodextrin, 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 coordinations 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 cavitand molecular system, reported only in 2008. This chapter focuses on the host-guest chemistry of pillararenes with fluorescent guest molecules. The self-assembly of pillarene 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.

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CHAPTER 1

Luminescent Cyclodextrin Systems and Their Applications

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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, Macrocycle, Recognition, Nanocarrier, Nanoparticles.

INTRODUCTION

Cyclodextrin (CD) is a cyclic polysaccharide derived from enzymatic hydrolysis of starch [1]. CD has three native forms, α-CD, β-CD and γ-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 α, β, and γ-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

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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 β-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 β-CD. Roy *et al.* [8] explored the umbelliferone, a drug with α-CD inclusion complex. The complex (Fig. **1**) has been optimized by molecular docking and increased bioavailability with minimal dosage in the human body.

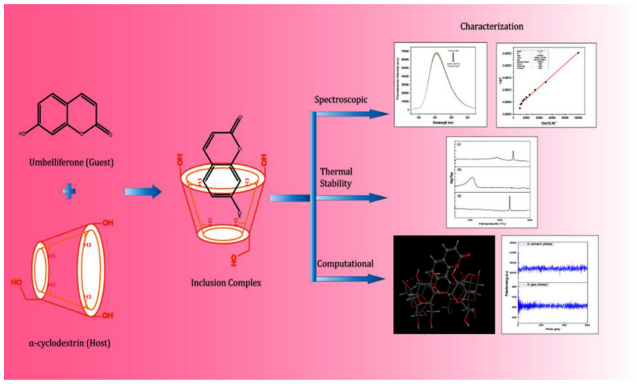

Fig. (1). Schematic representation of the studies of umbelliferone and α-CD inclusion complex [8].

Periasamy *et al.* [9] studied the host-guest inclusion complex of β-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: β-CD complex formation and the molecular docking studies also support this. A detailed spectroscopic investigation of the binding of pyrene with β-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 α-CD, β-CD and γ-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 β-CD dimer and tetra-orth--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].

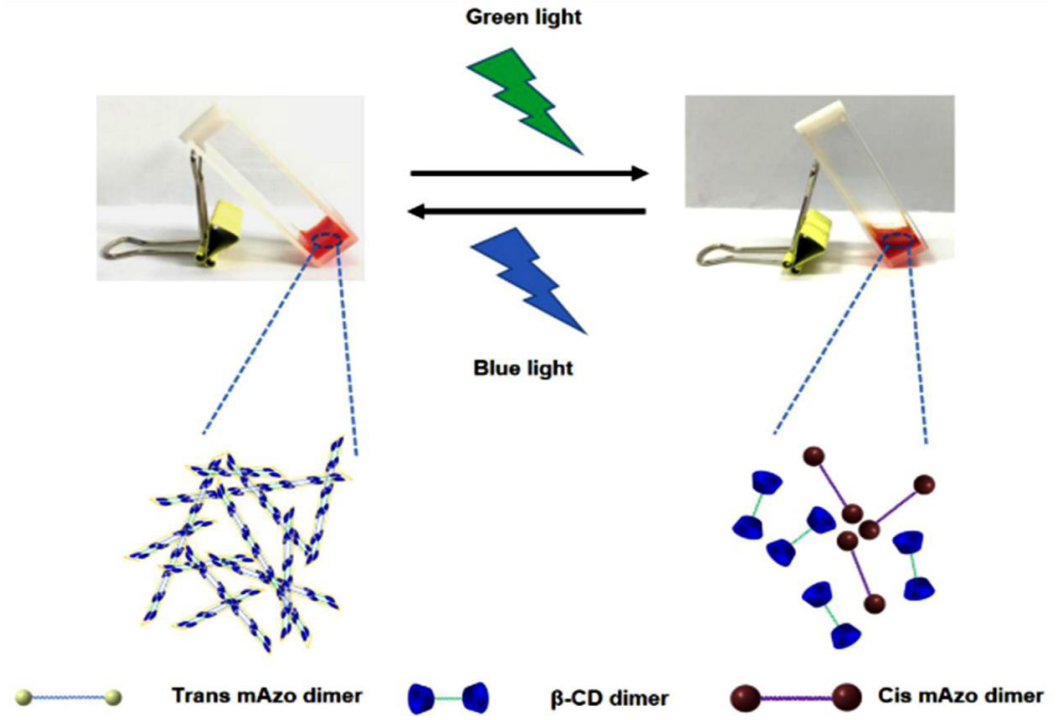

Fig. (2). Schematic representation of visible-light responsive β-CD dimer host-guest supramolecular gels [12].

Kim *et al.* [13] reported a synthetic strategy to form high yield CD based intra-nanogap particles (Fig. **3**) with a well-defined ~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

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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-π interactions [8, 9]. The upper and lower rims can be synthetically tuned to target the specific guest molecules by

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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.

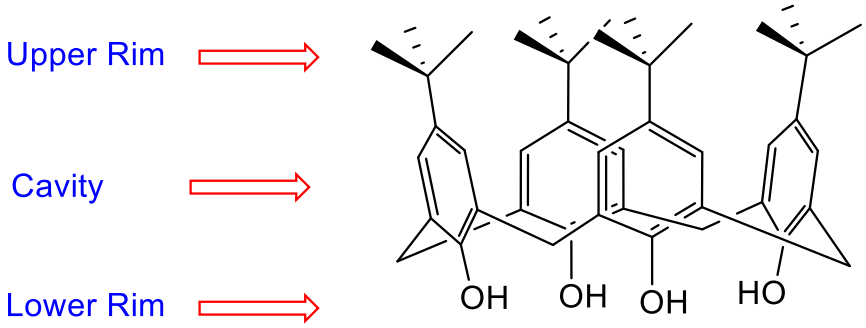

Fig. (1). Structure of t-butyl calix [4]arene and their parts are represented. Most of the fluorophore guests were accommodated within the cavity.

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^+, Rb^+ and K^+ 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-tetr--sulfonate-25,26,27,28-tetra-carboxymethoxycalix [4]arene with a lanthanoid ion (Tb^{3+}) complexation has been studied in gelation medium. The calix [4]arene derivative formed an efficient energy transfer complex with Tb^{3+} 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.

CHAPTER 3

Resorcinarene Crowns as Versatile Host Molecules and Their Potential Applications

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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 chromatrography (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.

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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]-octacosa-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**)).

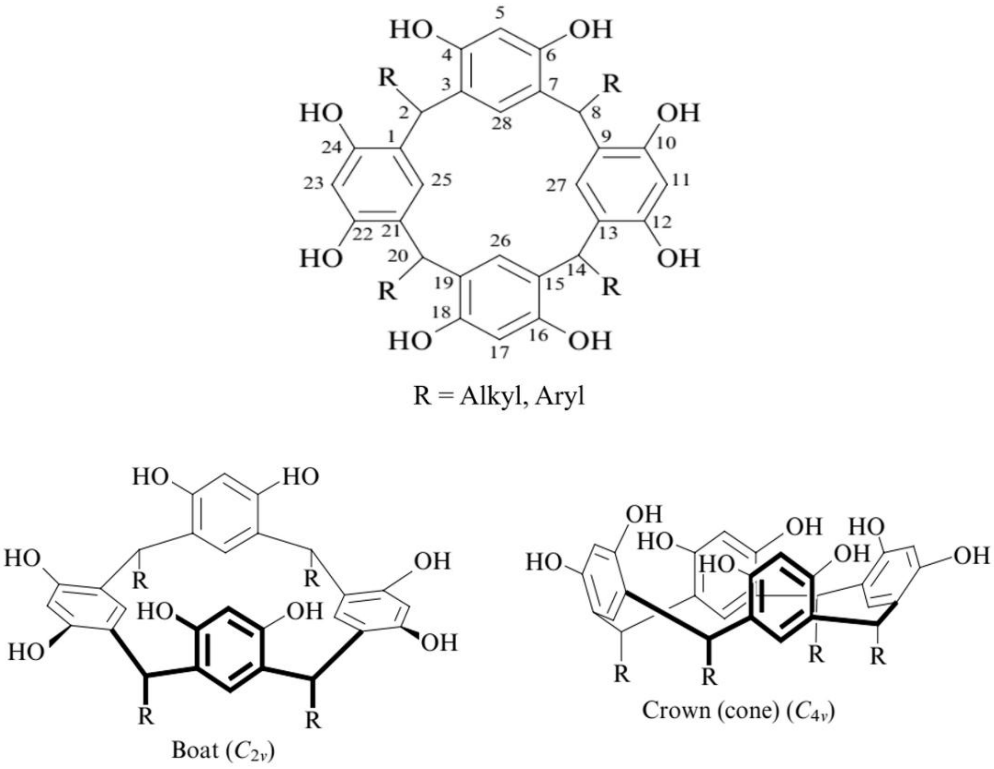

Fig. (1). Conformations of resorcinarenes.

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.

CHAPTER 4

Pillararenes: Younger Luminescent Supramolecular Systems

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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 π-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

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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 π-π 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 architectured 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 pillarenes 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-dimethoxybenze (DMB) with paraformaldehyde in the presence of an appropriate Lewis acid catalyst.

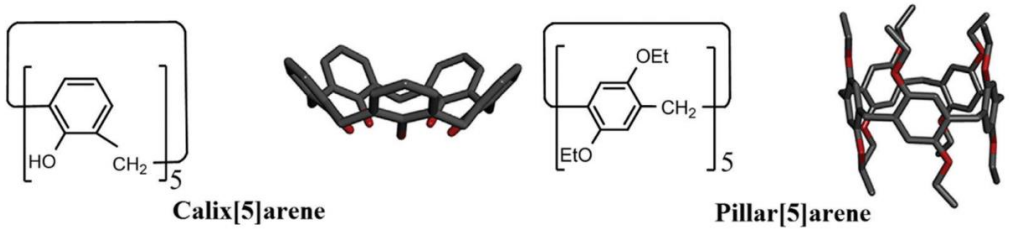

Fig. (1). Comparison of chemical structures of pillar [5]arene [P5A] and calix [5]arene. (Adopted with permission from ref. 8).

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 pillarenes 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^{o}, which is very close to the normal bond angle of the sp^{3} carbon atom, 109^{o}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 ~4.7 Å (Table **1**), which is close to that of curcubit [6]uril (~5.8 A) [12] and α-cyclodextrin (~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 ~6.7 Å, analogous to cucurbit [7]uril (~7.3 Å) [12] and β-cyclodextrin (~6.0 Å) (Fig. **3**)

CHAPTER 5

Cucurbit[n]urils Based Molecular Recognition with Fluorescence Signalling

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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, π-π 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.

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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 sexist 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)> 10^3M^{-1} is commonly preferred. The calixarene or cyclodextrin based macrocycles rarely provide K_a values beyond 10^3M^{-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 crystalized 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 3.9Å and 5.8Å 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, whereas the inner cavity volume of CB [10] is 870 $Å^3$, 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 hemicucurbitruil or twisted/inverted CB[n] [16].

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

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

CHAPTER 6

Rhenium(I)-Based Metallacycles for Sensing Applications

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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

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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.

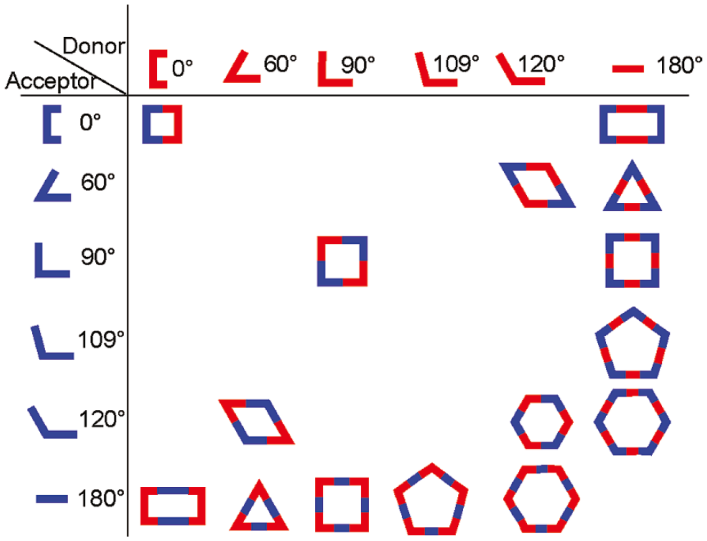

Fig. (1). Combination of various building units for accessing convex polygons and canonical polyhedra. Reproduced with permission from ref. 15. Copyright (2011) American Chemical Society.

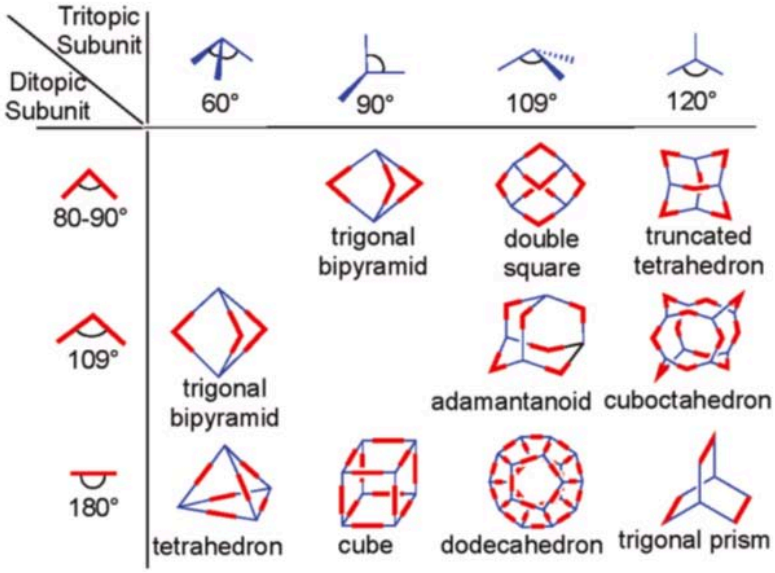

Fig. (2). Three-dimensional architectures formed by the combination of ditopic and tritopic subunits by the directional bonding approach. Reproduced with permission from ref. 15. Copyright (2011) American Chemical Society.

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 π-π, 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

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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

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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].

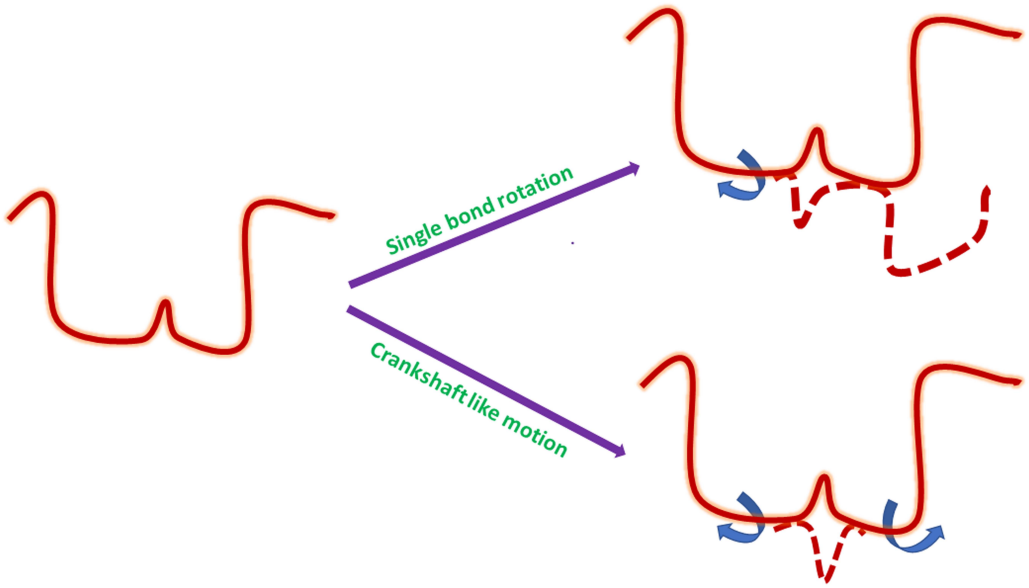

Fig. (1). Schematic representation of the conformational transition in a polymer chain.

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 α–carbon, shows a different

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Paulpandian Muthu Mareeswaran

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