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6. Supramolecular Chemistry, Types of Supramolecular Systems and Its Applications

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6.1 Supramolecular Chemistry:

Supramolecular chemistry, also known as “chemistry beyond the molecule”, is a fast-expanding discipline concerned with the chemical interactions of molecules. Recent years have seen a substantial increase in interest in this topic as a result of the possibility of developing novel materials and systems with distinct functions. In this chapter, we will discuss the fundamental concepts of supramolecular chemistry, recent trends and advancements in the field, and potential future applications. Supramolecular chemistry is fundamentally concerned with the interactions between molecules that take place via non-covalent interactions [1], such as hydrogen bonding, metal coordination, hydrophobic interactions, etc., [2]. Through their interactions, molecules can create intricate structures known as supramolecular assemblies, which can exhibit their unique properties. And behavior is different from those of the individual molecules.

One of the main goals of supramolecular chemistry is to design and synthesize molecules that can self-assemble into well-defined structures. These structures can have a wide range of functions, such as the ability to store and release energy, conduct electricity, or act as catalysts. [3] Supramolecular chemistry has several important applications in various fields such as medicine, materials science, nanotechnology, etc.

In medicine, supramolecular systems can be used for targeted drug delivery, as the self-assembling nature of these systems allows for specific targeting of diseased cells. In materials science, supramolecular systems can be used to create new materials with improved mechanical and thermal properties. In nanotechnology, supramolecular systems can be used to create nanoscale devices with a range of applications. [4]

In recent days, supramolecular chemistry is focused on the development of new materials and devices with improved properties and also the development of new synthetic methods and characterization of supramolecular systems. In addition, the development of new theories and models can easily understand their behaviour in the application of these systems in real-world problems, due to the numerous applications and the potential for further discovery, supramolecular chemistry remains a rapidly growing and exciting field.

6.2 Mechanically Interlocked Molecules (Mims):

Mechanically interlocked molecules (MIMs) are a class of supramolecular compounds that are held together by non-covalent interactions, such as hydrogen bonding, electrostatic interactions, and van der Waals forces [5]. There are several different types of MIMs, each with its own unique properties and potential applications. Some of the most well-known types of MIMs are discussed in this chapter.

A. Rotaxanes:

Rotaxanes are a class of molecular structures that consist of a macrocycle, or large ring, that surrounds a smaller and linear component called an axle. The axle is able to move within the macrocycle but it is prevented from completely escaping from the macrocycle due to the presence of one or more stoppers, like bulky groups, that are attached to the axle. This unique mechanical bond between the macrocycle and the axle makes rotaxanes an attractive subject for research in the field of supramolecular chemistry. The structure of rotaxanes resembles A dumbbell-shaped molecule with a ring trapped between its two ends.

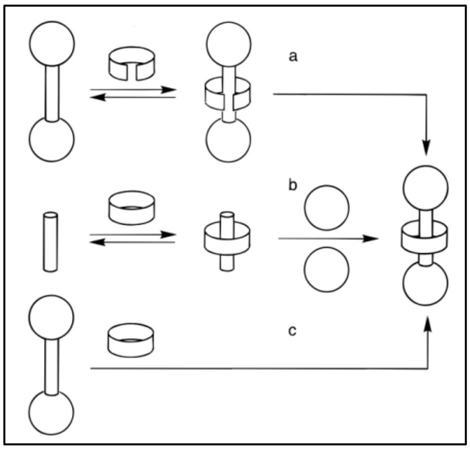

Figure 6.1: Three different approaches to the construction of rotaxanes: (a) "clipping"; (b) "threading"; (c) "slippage" [5].

Rotaxanes have been shown to have potential applications such as drug delivery [6], chemical and biological sensors [7], and data storage [8] due to their ability to undergo dynamic changes in conformation and responsive behavior to external triggers. Furthermore, rotaxanes also have the potential for use in molecular machines and devices as their mechanical bond allows for rotational motion and/or translation of the axle [9].

B. Catenanes:

Catenanes are a class of molecular structures in which two or more interlocked macrocycles are connected in a "chain" formation. They are similar to rotaxanes, but with multiple macrocycles linked together. Catenanes are named based on the number of interlocked rings, e.g. a [2] catenane consists of two interlocked rings (Figure 6.2). The "ane" ending of the term is a reference to alkanes, and catenanes are typically considered to be organic compounds, although they may not always consist of hydrocarbon groups. In situations where the interlocked ring system can act as a ligand for a metal centre, the terms [n] catenand and [n] catenate may also be used, in analogy with the terms cryptand and cryptate. The term "catenand" refers to the free ligand that forms a catenate complex in the presence of metal ions [10].

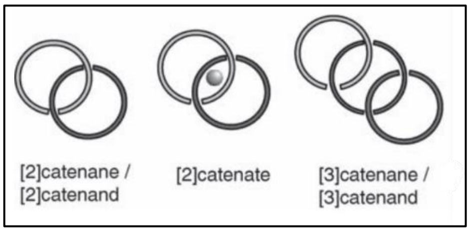

Figure 6.2: Nomenclature and schematic representation of Catenanes [10].

The synthesis of catenanes can be challenging, but various methods have been developed, including template-directed synthesis, mechanically interlocked synthesis, and chemical synthesis [11]. Catenanes have potential applications in fields such as molecular electronics, drug delivery, and as molecular machines. Their unique properties, including their ability to perform mechanical movements in response to external inputs, can be utilized for switching and sensing purposes. They have also been explored as molecular shuttles, molecular switches, and artificial muscles [12].

C. Clathrates:

Clathrates are a class of molecular structures in which a host molecule encapsulates or "traps" a guest molecule inside a cage-like structure. The host molecule forms the walls of the cage, and the guest molecule is held inside by non-covalent interactions such as hydrogen bonding or van der Waals forces.

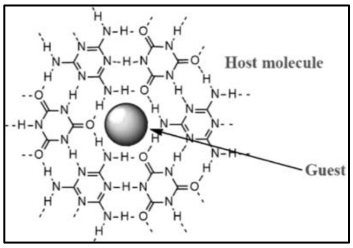

Figure 6.3: Schematic representation of Clathrates

Clathrates have been found in various forms of matter such as gases, liquids, and solids. In the field of chemistry, clathrate hydrates are known for their ability to trap gases such as methane and carbon dioxide, making them of interest for natural gas storage and carbon capture [13]. They also have potential applications in various fields such as drug delivery, catalysis [14], storage of gases like natural gas, hydrogen, and others in solid form, treatment of wastewater and concentration of organic mixtures, as well as separations and storage of gas mixtures. Clathrates are a topic of ongoing research, and the full potential of these structures is yet to be fully understood and harnessed. Further research is needed to develop new synthetic methods and to better understand the properties of these complex structures.

D. Cavitands:

Cavitands are a class of molecular structures that are characterized by a "cavity" or a hollow interior space. These cavities are formed by the arrangement of atoms or chemical groups in a specific way, and they can be either hydrophobic or hydrophilic in nature, which has potential applications in various fields like molecular sensors [15], catalysis, drug delivery, and separation science. In separation and purification, cavitands can be used to sort and isolate specific molecules, such as proteins and enzymes, based on their size and shape. They have also been explored as scaffolds for the formation of supramolecular assemblies, and in the field of host-guest chemistry as receptors for specific molecules [16].

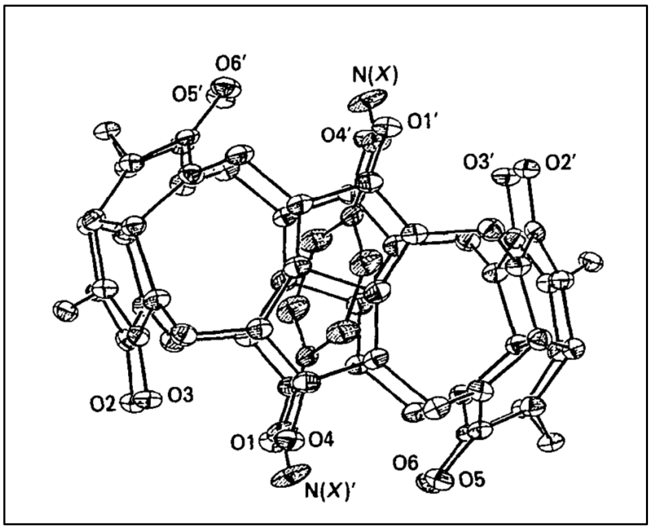

Figure 6.4: A cavitand (cucurbituril) bound with a guest p-xylylenediammonium [16].

F. Cryptands:

Cryptands are a class of molecular structures that have found significant application in the field of supramolecular chemistry. They are characterized by a "crypt" or a hollow cavity that can selectively bind or "capture" specific guest molecules within it. The structure of cryptands is composed of a macrocyclic ring with a number of binding sites that can interact with specific guest molecules via non-covalent interactions viz., hydrogen bonding or electrostatic interactions. In supramolecular chemistry, cryptands have been used to form various types of assemblies, including host-guest complexes, supramolecular polymers, and supramolecular gels. They have also been explored as receptors for specific molecules, such as small ions or metal ions [17].

Cryptands have numerous applications in a variety of fields such as chemistry, biochemistry, materials science, etc. Their ability to selectively bind specific guest molecules makes them attractive for use in chemical separations, and the formation of supramolecular assemblies can be used to create new materials with specific properties. These molecules are valued for their high selectivity and specificity in recognizing cations, anions, neutral molecules, and even isotopes. They play a crucial role in ion transportation studies and are used as stationary phases in column chromatography for separating cations, anions, and isotopes. In addition, they are utilized in the study of redox systems, photo physical properties, non-linear optics, amphiphiles, sol-gel materials doping, and as structural directing agents in synthesis [18].

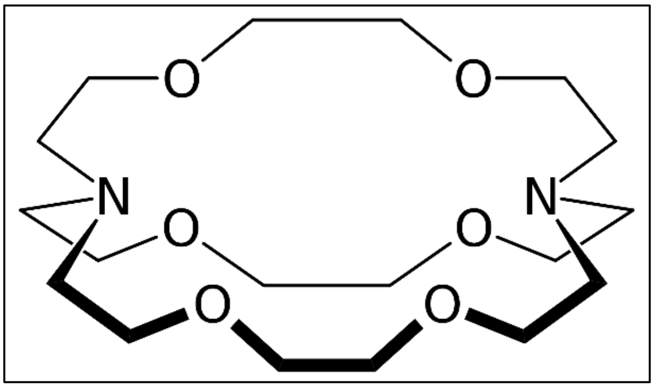

Figure 6.5: Structure of [2.2.2] Cryptand

6.3 Molecular Self-Assembly:

Molecular self-assembly is a fundamental concept in supramolecular chemistry that refers to the process by which individual molecules come together to form ordered structures without any external inputs. This process is driven by non-covalent interactions such as hydrogen bonding, electrostatic interactions, and van der Waals forces. Self-assembly has been used to create a wide range of structures including, but not limited to, vesicles, fibers, gels, and even more complex supramolecular systems [19]. The ability to manipulate and control the self-assembly process is of great interest in supramolecular chemistry, as it allows the creation of new materials with specific properties [20]. Self-assembly can be directed by various strategies such as the use of pre-designed templates or by controlling the chemical composition and stoichiometry of the system. The utilization of self-assembling peptides, small molecules, and lipids is also gaining recognition as a flexible approach to creating new materials with specific characteristics [21]. Molecular self-assembly is an active area of research in supramolecular chemistry and has potential applications in fields such as materials science, nanotechnology, biotechnology, etc.

A. Micelles:

Micelles are a form of supramolecular structures that are composed of a core of hydrophobic units surrounded by a shell of hydrophilic groups. They form spontaneously in water-based solutions and are stabilized by non-covalent interactions such as hydrogen bonding and van der Waals forces. Micelles are of great interest in supramolecular chemistry due to their ability to encapsulate hydrophobic molecules and act as a carrier for drugs and other hydrophobic molecules, allowing for targeted drug delivery and improved bioavailability [22].

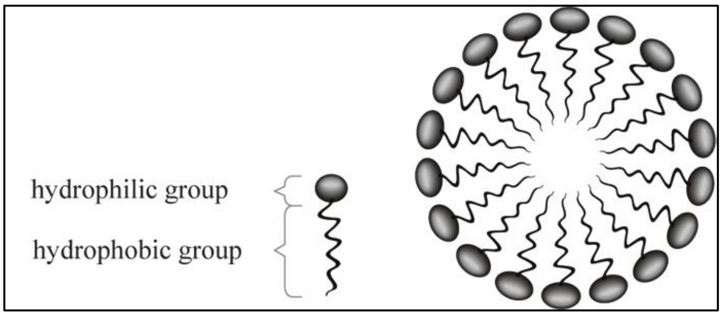

Figure 6.6: Schematic Structure of Micelle

Micelles have a wide range of applications due to their unique properties. Including, drug delivery, biomedical imaging, environmental remediation, cosmetics, etc [23].

B. Lipids:

Lipids are a class of biomolecules that play an important role in supramolecular chemistry. They are composed of a hydrophobic tail and a hydrophilic head, which allows them to spontaneously form structures such as vesicles, bilayers, and micelles in aqueous environments. These structures, known as lipid assemblies, have unique properties that make them of great interest in various fields, including cosmetic and food industries, and in nanotechnology [24]. Lipid assemblies have been used as a model for cell membranes and have been explored as a carrier for drugs and other hydrophobic molecules in targeted drug delivery [25].

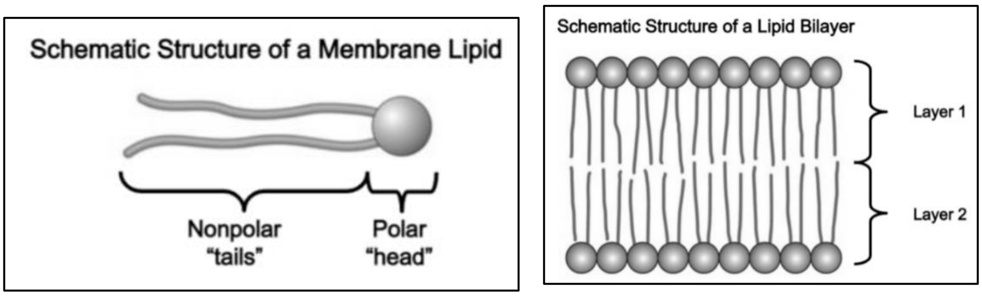

Figure 6.7: Schematic Structure of Lipids

Lipid assemblies have also been explored as a scaffold for the formation of supramolecular assemblies, and as a tool to understand the principles of self-assembly.

C. Liposomes:

Liposomes are a type of supramolecular structure that is composed of a phospholipid bilayer enclosing an aqueous compartment [26]. They are stabilized by non-covalent interactions such as hydrogen bonding and van der Waals forces. Liposomes have been used as a carrier for drugs, allowing for targeted drug delivery and improved bioavailability. Additionally, they have been explored as a means of gene therapy and as a tool for delivering drugs to specific cells or tissues [27].

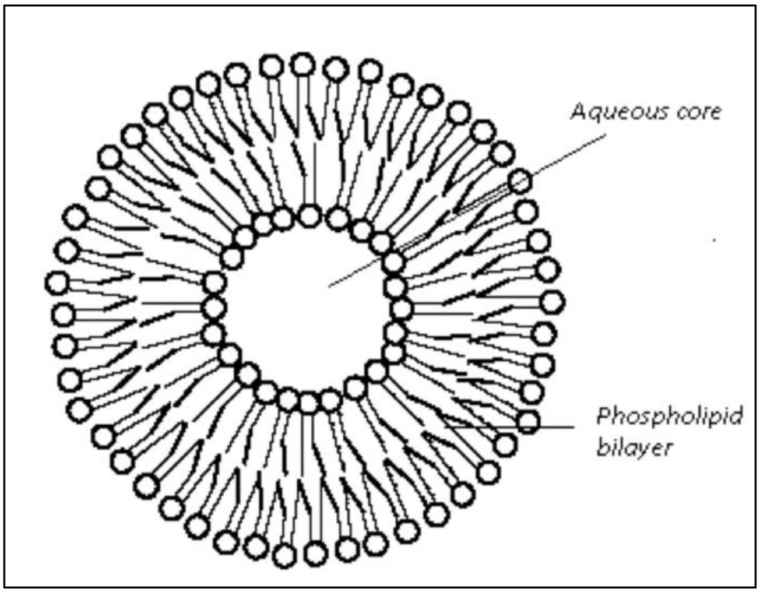

Figure 6.8: Schematic Representation of A Liposome

Liposomes have been used to create new materials with specific properties, such as liposome-based membranes for separation and filtration. Liposomes have also been found to be useful in the field of ‘sensing’, as they are able to encapsulate and detect specific molecules [28]. In addition, it is also useful in various fields like healthcare, cosmetics, medical imaging techniques, and the agricultural industry.

6.4 Molecular Recognition (Host-Guest Chemistry):

Molecular recognition is the specific interaction between more than two molecules via non-covalent interactions such as hydrogen bonding, metal coordination, hydrophobic forces, Van der Waals forces, pi-pi interactions, electrostatic, and electromagnetic effects. The molecule that receives an incoming entity is referred to as a host molecule, while the incoming entity itself is known as a guest molecule. The main concept of molecular recognition is lock and key. In this model, the host molecule makes interaction with a guest molecule or ion.

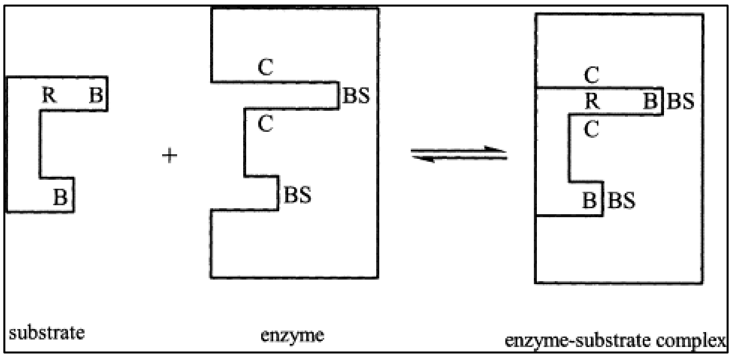

Figure 6.9: Lock and Key Model

Host + Guest= Host Guest Complex; Host = Enzyme; Guest = Substrate

In this complex, the host molecule is bigger in size and also has hollow nature than the guest molecule. Such kinds of interactions are mainly known as the bio-recognition process. Eg., enzyme–inhibitor, antigen-antibody, and DNA- protein interaction.

A. Crown ether:

Crown ethers are the first class of artificial host cyclic compounds which consist of ring groups containing ether (R-O-R). The most common crown ethers are oligomers and ethylene oxide. E.g.; 18-crown-6

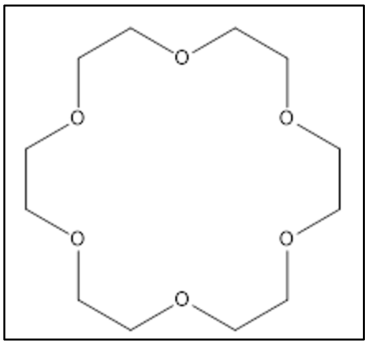

Figure 6.10: Structure Of 18-Crown-6

In the crown ether, the number used in the first is referred to as the number of atoms in the system and the last one says the number of oxygen atoms present in that system. Crown ethers are strongly bound to form complexes with metal ions based on the size of the atom. Crown ethers are soluble in nonpolar solvents because of their hydrophobic character which is mainly useful in phase transfer catalysis [29].

The modification of crown ethers, based on their number of the atom to giving various crown ethers by attaching some functional groups to the edges of the crown ethers, which enrich them with some interesting properties and made them ideal candidates for the fabrication of supramolecular polymers [30].

B. Cyclodextrin:

Cyclodextrin is a naturally occurring cyclic host molecule, which is a family of oligosaccharides of a macrocyclic ring of the glucose subunits joined by 1,4 glycidic bonds constituted by 6-8 glucopyranoside units. Which is prepared by the treatment of starch materials with enzymes. The CD has the molecular recognition capacity, and also enhanced their properties through chemical modification by introducing the –OH groups on the exterior rims. β-CD derivatives are widely used as greener textile auxiliaries for potential applications in the textile industry [31]. E.g.; β cyclodextrin

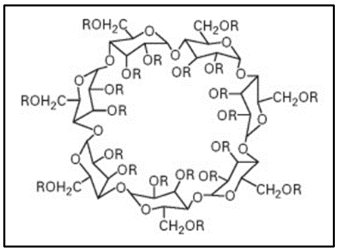

Figure 6.11: Structure Of Β Cyclodextrin.

Cyclodextrin sponges are a microporous newly cross-linked 3D network of cyclodextrin that was designed as novel delivery for the lipophilic or hydrophilic active agents. Cyclodextrin's hydrophobic outer cavity and hydrophilic inner cavity enable their ability of novel delivery. Cyclodextrin possesses various applications like they are versatile absorbent for volatile organic compounds abatement [32].

C. Polyamine:

Replacing an oxygen atom in the crown ethers by nitrogen atom-induced cyclic hosts are called macrocyclic polyamines, many synthetic polyamines feature NCH_2CH_2N linkages which contain more than two amino groups most of the alkyl polyamines are natural and some of them are synthesized by the laboratory. Several synthetic polyamines are used in the chemical industry and the research laboratory. They are mainly used as additives to motor oil and as co-reactants (cold hardeners) with epoxy resins. E.g.; Cyclen

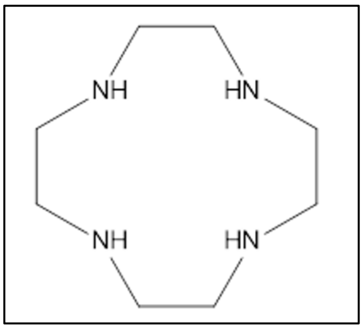

Figure 6.12: Structure Of Cyclen

Polyamines are possible therapeutic agents in biological disorders such as cancer and parasite diseases. They also act as ion–exchange blockers or vectors in gene delivery.

D. Calixarene:

Calixarenes are made from phenol units, which are attached by methylene bridges known as calixarene, and can have different cavity sizes. Each of these has conformation isomers, and the phenolic hydroxyl group is constantly modified. This type of character possesses to made calixarene derivatives with various structural modifications.

This isomeric host has different selectivity in metal ion inclusion in the upper cavity and the lower cavity. The number of phenol inclusion in the calixarene alters the guest molecule size appropriate for effective inclusion.

Calixarenes has attention in the treatment of cancer, it is mainly useful in delivery systems because of its biocompatibility and non-cytotoxicity [33]. And also used in the field of host-guest chemistry and sensing of metal ions.

E. Cyclophane:

Cyclophanes are three-dimensional cyclic hosts made from the linking of aromatic rings between aliphatic units. Cyclophanes are classified as follows, [n] orthocyclophane,[n] metacyclophane,[n] paracyclophane.

The aromatic ring in the cyclophane system is maybe either heterocyclic or carbocyclic. Cyclophane core unit is in many biologically active molecules and is also used in pharmaceutical catalysis [34]. Figure; [6.12**]** paracyclophane

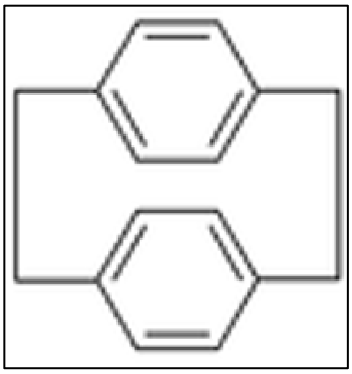

Figure 6.13: Structure of Paracyclophane

The small cyclophanes are the model for the fundamental studies of strain and aromaticity. The short bridges in cyclophanes give free rotations of the ring, and this takes place to thermodynamically disfavoured rotation to each other. This is not in open-chain molecules. This cyclic core was twisted because of the strain on the whole system. This kind of strain only acquires natural cyclophanes, not artificial ones [35].

6.5 Molecular Tree:

A. Dendrimers:

Dendrimers are tree-like macromolecules, which consist of core, branching, and surface units. It is in nanometres to tens of nanometers in size, which is larger than a typically closed molecule (diameter,0.7nm) and smaller than a microsphere(diamatere0.1-10μm). In dendrimers, if we increase the branching units, which will increase the dendrimer generation from zeroth to first, second, and so on.

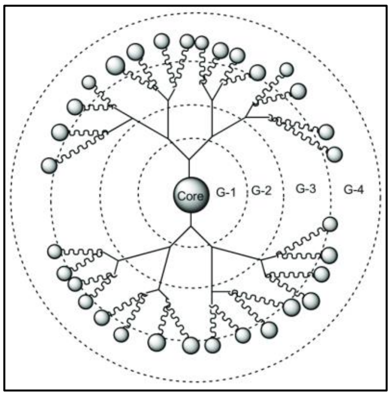

Figure 6.14: Schematic Representation of A Dendrimer Structure [36].

Dendrimers have been widely studied for their potential applications in drug delivery [63], where they can be utilized to transport therapeutic agents directly to diseased cells or tissues. In addition, they have been investigated for their use as imaging agents for diagnosing diseases, as well as in tissue engineering and regenerative medicine, where they can be utilized to deliver growth factors to promote tissue regeneration. Dendrimers have also shown promise as carriers for gene therapy, where they can be used to deliver genes to specific cells, thereby modifying their functions. These and other applications highlight the versatility and potential of dendrimers in the fields of medicine and biology [37].

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