CHAPTER 1

INTRODUCTION
Introduction

Supramolecular chemistry [1], as a new line of research has evolved and has developed intensively in the past few years. This interdisciplinary science encompasses the chemistry of noncovalent interactions, molecular physics and molecular biology. Its main attention is focused on the systems, which are capable of self-organization, i.e., spontaneous production of definite structures by self-assembly of constituents into supramolecular assemblies. The synthesis of such structures is based on the molecular recognition principle and is affected by the cooperation of various non-covalent bonding etc.

Chemists usually pursue the imitation of nature, which constructs large and complex systems with high degree of efficiency. One of the vehicles used for this research are the rotaxanes, one of the interlock molecule (from the Latin words rota, wheel and axis, axle) [2].

Mechanically interlocked molecules [3] are composed of two or more components between which there are no covalent bonds; only noncovalent bonds usually and at least one mechanical bond are present.

Recently, interlocked molecules such as – (a). Rotaxanes (b). Catenanes and (c). Knots (Fig.1) have become popular playgrounds for preparative chemists; out of which with these species topologies considerations additionally come into play.
Rotaxanes are composed of one (or more) macrocycle(s) encircling a single dumbbell component that bears two large building groups or stoppers at both ends of the linear thread. These stoppers serve to prevent the macrocycle(s) from slipping off the ends.

While, in chemical terms, insertion of an acyclic molecule ‘A’ inside the cavity of a macrocyclic one ‘B’ affords (Fig. 2) a supramolecular complex ‘C’. Dissociation of ‘C’ into its components ‘A’ and ‘B’ can occur and the equilibrium between the species in solution is controlled by the free energy of complexation. Attachment of two bulky
stoppers to the ends of the acyclic component of the Supramolecular complex 'C' affords a molecular compound 'D' which cannot dissociate into its constituent components. A molecule, such as 'D' is termed as a rotaxane.

![Diagram of reversible formation of a pseudo-rotaxane C from its components (A and B) and its irreversible conversion into a rotaxane D.]

**Fig. 3. Reversible Formation of a Psuedorotaxane 'C' from its Components ('A' and 'B') and its Irreversible Conversion into a Rotaxane 'D'.**

A rotaxane containing a single ring is called [2] rotaxane and one containing 'n' rings is named [n] rotaxane.

At first glance, rotaxanes might be less intriguing since they are not topologically isomeric to the set of their constituent components - the ring(s) and the axle(s). The reason is that in the imaginary transition from one arrangement to break or from the mechanical bond, which is consequently not a topological one and owes its stability to the lack of flexibility of the molecular entities. Thus one could consider "mechanical isomerism" here.

One of the most striking features of rotaxane architecture is that their mechanically interlocked components can, in principle, move relative to one another without covalent
bonds. Such dynamic processes are currently attracting considerable attention from chemists, physicists and materials scientists because they combine the possibility of precisely positioning the individual components of a molecule with that of changing their relative separation and orientation to order, possibly through the influence of external stimuli.

Semirotaxanes and pseudorotaxanes (Fig. 4) are analogues to conventional inclusion complexes that are not restrained mechanically from dissociation since the axles carry either one stopper or no stopper at all respectively. Semirotaxanes and pseudorotaxanes (Fig. 3) act as precursors in rotaxane synthesis are called prerotaxanes [4].

When size complimentarily between the stoppers and the macrocyclic component is achieved, certain “rotaxanes” behave as pseudorotaxanes and can dissociate into their constituent components under appropriate conditions [5]. Thus, a species, which is a rotaxane at ambient temperature, might well be a pseudorotaxane at elevated temperatures. Even a solvent change can turn a rotaxane into a pseudorotaxane at the same temperature.

Rotaxane, semirotaxane and pseudorotaxane are conveniently represented by formula given as axle@wheel, semiaxle@wheel and pseudcaxle@wheel respectively.

![Fig. 4 Schematic Representation of (a) Semirotaxane (b) Pseudorotaxane](image-url)
Homorotaxanes are composed of cyclic and linear species that are chemically identical or nearly same, e.g. hydrocarbon linear and hydrocarbon cyclic, while in the case of heterorotaxanes cyclic and linear species are chemically distinct e.g. hydrocarbon linear and polyether cyclic [6]. The threading in homorotaxanes is driven by the entropic term and is therefore temperature independent. As in any equilibrium, the ration of cyclic and linear components is important, as are their absolute concentrations. Geometrical factor of importance are the size and rigidity of the two components.

Recently, O.Lukin et al. [7] coined the name “Knotaxanes” for a challenging, hypothetical type of compound: a rotaxane in which the stoppers are molecular knots. They report the first successful synthesis of two members of this new topological family and their chiral resolution. Interest in this species comes on the one hand from their topological chirality, since unlike having just a stereocenter, as in classical stereochemistry, the whole nano-sized molecular skeleton is chiral (“nanochiral”). Their chirality, therefore, should be quite pronounced, and strong chirotopic effects and chiral inductions are expected. The use of the rotaxane platform, on the other hand, makes such an assembly a particularly attractive architecture with a option to control the direction of rotation or the shutting of mechanically linked constituent parts.

Such unusual architecture of rotaxanes also presents the possibility of synthesizing polymeric materials with unique mechanical properties suitable for advanced application. An example of such a class of molecules that has stimulated considerable recent interest is rotaxanes and their polymeric analogues, polyrotaxanes [8], consisting of linear polymers threaded through macrocyclic molecules without the formation of any covalent
bonds. Polyrotaxanes exhibit a diverse range of chemical and mechanical properties characteristic of free "Physical polymers".

The possibility of introducing multiple linear and macrocyclic element types further augments the scope of important industrial applications [9] wherein polyrotaxanes may find further significant uses.

Polyrotaxanes are polymers with a novel molecular architecture where cyclic molecules are threaded onto the polymer chain. There are in principle many subclasses of polyrotaxanes, which differ in the nature and location of the covalent and physical linkages. Since polyrotaxanes are a novel class of polymer molecular topology it is anticipated that their properties are distinct from other polymeric architectures. The distinguishing feature of polyrotaxanes is the potential for lateral and translational motion of the cyclic molecules relative to the linear chain that penetrates it. This in turn raises intriguing fundamental questions that test our knowledge and theoretical concepts of the molecular basis of the behaviour of polymeric materials.

Polyrotaxanes are roughly categorized into two types: 1). Main-chain-type polyrotaxane and 2). Side-chain-type polyrotaxane. Since they have completely different topologies, they have expected to display different physical behaviors. Among the various side-chain-type polyrotaxanes, polymer with one wheel per side-chain are among the most simple and versatile. Since various molecular devices have been proposed using interlocked compounds, such side-chain-type polyrotaxanes make the molecular devices arrays of polymer chain possible [10]. However, reports on side chain polyrotaxanes have been limited, compared with a larger number of studies on main chain polyrotaxanes.
Two main types of such complexes are distinguished, viz., 'linear polyrotaxanes' where, the macrocycles are threaded onto the main chain (Fig. 5a) and 'comb-like polyrotaxanes' (Fig 5b).

![Diagram of polyrotaxanes](image)

**Fig 5. A Schematic Representation of Polyrotaxanes: (a) Linear (b) Comb-like**

The conceptual transition from [2] rotaxane into a polyrotaxanes can be achieved by a number of different strategies, which are available in literature. By encircling a polymeric dumbbell-shaped component with (n-1) macrocycles, 'main-chain' polyrotaxanes namely, an [n] rotaxane (d) is obtained. Alternatively, a [2] rotaxane can be transformed into a main-chain polyrotaxane by incorporating either its dumbbell-shaped (e) or embedding its macrocyclic (f) component into a polymeric backbone. When the macrocyclic and the dumbbell-shaped components are both part of the polymeric backbone, another main-chain polyrotaxane (g) a so-called 'daisy-chain' polymer is generated.

While, in a 'side-chain' polyrotaxane, either the dumbbell-shaped (h) or the macrocyclic (i) components of rotaxane subunits are attached covalently to a polymeric backbone. Interestingly, while in the polyrotaxanes d-g, h and i the polymeric backbones are held by covalent bonds, covalent and mechanical bonds alternate along the main axis of a daisy-chain polymer (g).
The fundamental difference between interlocked macromolecules and conventional polymers is the nature of the bonding interactions, which hold them together. In pseudorotaxanes, polyrotaxanes covalent bonds are supplemented by mechanical links, robust and otherwise, and in many instances, by noncovalent bonds.

**Properties of Rotaxanes and Polyrotaxanes**

The main driving-force for research on interlocked molecules today, however, is perhaps not the synthetic challenges but the interesting properties and potential applications of the molecules themselves.

The properties of these interlocked macromolecules are just starting to be investigated and understood. Preliminary studies have already revealed that the fundamental differences, which exist between conventional covalent polymers, which exist between...
conventional covalent polymers and unconventional interlocked macromolecules, are reflected dramatically in their physical properties. Indeed, mechanical interlocking influences solubilities, phase-transition behaviour, hydrodynamic volumes and stabilities, offering the opportunity to the synthetic chemist of being able to construct a new generation of exotic polymeric materials.

The properties of rotaxanes (where a macrocycle is mechanically locked onto a linear threaded by bulky stoppers, Fig. 7) have thus far largely focused on (i). Translational isomerism (changing the distance or orientation between parts of the interlocked components with a view to developing "molecular machinery") and (ii). The isolation of sections of the thread from the outside world (leading to dramatic changes in properties such as solubility, aggregation, biocompatibility, crystallinity, fluorescence, electrochemistry and stability) [11].

Apart from synthetic aspects, rotaxanes are very interesting molecular species from the viewpoint of spectroscopic and electrochemical investigations. In the rotaxanes and in their "free" dumbbell-shaped and macrocyclic components, one can single out several chromophoric and electroactive units and study their interactions which often lead to charge-transfer processes and to very unusual redox patterns. Because of these interactions, rotaxanes and related systems are interesting for the design of chemically, photochemically and electrochemically-active molecular devices [12].

Interlocked molecules often exhibit markedly different properties to their non-interlocked analogues. This can include, for example, differences in spectroscopic responses, chemical reactivity or mechanical properties. These differences are a direct result of the interlocked architecture, yet perhaps the most exciting consequence of the mechanical
bond, is the unique way in which different parts of the molecule can move with respect to
the rest of the system (Fig. 7). Controlling these submolecular motions is a very active
area of research in many groups across the world.

![Diagram](image)

(i). Changing separation of pendent functionality

(ii). Changing shape through thread-macrocycle interactions

(iii). Changing interaction of 'thread' with outside world (protection by encapsulation, solubility changes etc)

**Fig 7. Properties of Rotaxane Architectures**

Rotaxanes have properties that differ from those of their components or a mixture
thereof. When proper ionization modes are used, they produce patent ions in a mass
spectrometer. They have distinct melting points, NMR and IR spectra may or may not
vary from the mixture of components. Perhaps most interesting is the fact that colligative
properties, which are generally considered to reflect the total number of "particles" in
solution, when measured for rotaxanes comprising large macrocycles and relatively long
linear molecules, lead to molecular weight estimates which are the average of the two
components rather than their sum. This has been rationalized on the basis of the size and
flexibility of the species involved, leading to a situation in which the two species in
solution behave to a large independently [4].
Polyrotaxanes are believed to have extraordinary thermal, electrical, photochemical, mechanical and rheological properties [13,14].

Recently, applications of polyrotaxanes to a novel molecular electronics devices [15] and a novel drug releasing system [16] have been examined.

The incorporation of macrocycles into polymers causes significant changes in the physicochemical properties (e.g., solubility, thermal and mechanical characteristics) of the rotaxanes formed in comparison with the starting materials. For example, poly(ethylene glycol)s, as well as α-CD, are soluble in water. However, the pseudopolyrotaxane, which was obtained by threading α-CD rings onto poly(ethylene glycol)s, is insoluble in water. Exactly the opposite behavior has been observed [17] for the poly(acrylonitrile) based pseudorotaxane.

Some authors [18-20] consider crown-ether-based polyrotaxanes as specific copolymers of the cyclic and linear components. The solubilities of polyurethane [21] and polyester-based [22] rotaxanes depend on their composition as well as on the nature and size of the macrocycle. For example, the incorporation of 60-crown-20 [23] increases the polarities of polyurethane-based rotaxanes so that these compounds, contrary to the original polymer, become soluble in polar solvents. In some cases, synthetic polyrotaxanes were water-soluble producing micellar structures. Treatment of polyurethane-based rotaxanes with solvents, which are selective with respect to the incorporation polymer, was accompanied by the aggregation and even crystallization of the cyclic component, which was attributed to the free migration of the crown ethers along the rod molecule.

According to Gibson et al., [18-20] the properties of polyrotaxanes formed by polymerization of monomers can be changed directionally by varying their compositions.
The feasibility of incorporation of crown ethers into polymers as plasticisers was also considered [24].

The formation of micelles and gels has been noted after the threading of crown ethers onto polyurethane and of α-CD rings onto poly (ethylene glycol)s. When phase mixing of the interlocked components occurs, significant changes of the glass transition temperature (Tg) can result. For example, the Tgs of some polyurethane-based pseudorotaxanes correspond [25] to a weighted average of those of the separate components. By contrast, the Tgs of side-chain polyrotaxanes are often higher than those of the separate components [26].

Studies of the thermal characteristics of polyrotaxanes by DSC revealed that phase-transition temperature strongly depend on the nature of the interacting components and the composition of the supermolecules formed. For example, the polymer based on poly (butane-1, 4-diyl sebacate) and 60-crown-20 produced two endothermal peaks at 40 and 60 °C, which correspond to the melting of the cyclic and linear components, respectively. These values are several degrees lower that those for the corresponding individual crown ethers and the polyester, which suggests a decrease in the crystallinity of each of the polyrotaxanes components. The glass transition of polyurethane-based rotaxane is also observed at a lower temperature range in comparison with the glass transition temperatures for the original components [27].

Melting points of polymeric materials are also affected by interlocking. In pseudorotaxane, where the macrocyclic components have sufficiently high mobilities, aggregation, nucleation and crystallization have been observed. Thus, two distinct
melting points, both slightly lower than those of the separate components, are often associated with pseudopolyrotaxane.

It is interesting to note that the X-ray diffraction patterns of threaded macrocyclic components are remarkably similar to those obtained by analyzing the same macrocycles in their free form in the solid state [28].

In pseudopolyrotaxane, gel permeation chromatographic analyses have revealed [29] that the hydrodynamic volumes increase on threading relative to those associated with the parent components. As a result, intrinsic viscosities also increase. This effect has been exploited [30] in order to follow pseudopolyrotaxane formation by monitoring viscosity changes with time.

In polyester-based polyrotaxanes, the threaded macrocycles inhibit the entanglement of the polymeric backbones in the melt. As a consequence, the melt viscosity is reduced significantly.

Comparison of the melt viscosities of a series of polyester-based polyrotaxanes with those of their parent polymers revealed [31] that the melt viscosities are substantially lower for the polyrotaxanes. Thus, the threading of macrocycles onto polymeric backbones is expected to enhance the pseudorotaxane.

In general, pseudorotaxanes dissociate rapidly into their separate components under equilibrium conditions. By contrast, random coiling of the polymeric backbone in pseudopolyrotaxane makes their dethreading a much more difficult process, thus increasing their stability considerably.

Characteristics, physicochemical properties of rotazane-like structures are determined by both the unusual topology and the nature of their constituents.
General Approaches for the Synthesis of Rotaxanes and Polyrotaxanes

With the continued expansion and sophistication of synthetic chemistry, fascinating, intricate yet highly ordered mechanically interlocked molecular arrays like rotaxanes are no longer considered synthetically challenged exotic species of scientific curiosity, but have steadily moved into the more practical world of supramolecular chemistry and are increasingly being synthesized in impressive yields and efficiencies by template directed mechanisms. The application of templates not only raises the yield but also often enables the preparation of otherwise unobtainable products.

The synthesis of such structures is based on the molecular recognition and is affected by the co-operation of various non-covalent bonding etc. The principle of molecular recognition can be exemplified in the formation of complexes of the ‘host – guest’ type. The role of ‘hosts’, i.e., receptors, is played by cyclic molecules, e.g., cryptands [32], crown-ethers [33], cyclodextrins [34], calixarenes [35] and calix-crown [36]. The chemical nature of ‘guests’ is extremely diverse; they include both small particles (e.g., inert gas atoms, metal ions, etc.) and complex bulky molecules of the fullerene type. In the past few years, supramolecular chemistry has been enriched by systems with polymers as the ‘guest’ molecules, which underlines the supramolecular chemistry of polymers.

This approach has made it possible to obtain mechanically interlocked compounds such as rotaxanes, catenanes and knots and also ‘molecular necklaces’, dendrimers, etc., which possess novel, previously unknown structure and remarkable properties.
In recent times, the supramolecular chemist has adopted the concepts such as self-assembly, self-replication and self-organization that are prolific in biology and applied them successfully into the artificial world of synthetic chemistry. However, it has been possible to design and synthesize well-defined compatible and complementary molecular components with illustrate the potential of the self-assemblies by employing noncovalent interactions \[37\].

The synthetic challenges associated with the intriguing structure of rotaxanes have prompted numerous efforts to develop efficient synthetic methodologies to afford them. The first molecules with "mechanical bonding" were already reported in the 1960s they were regarded as exotic compounds that could only be obtained in low yields and by a difficult multistep synthetic pathway.

The first union of a linear molecule threaded through a cyclic one was synthesized in 1961 \[38\].

Steifer and Lihotzky worked out the synthesis of rotaxanes cursorily in 1962 \[38\]. However the results were not published till 1967; the first experimental report was made by Schill and co-workers and the name was given \[40\].

Three different principles known as "Threading", "Slipping", "Clipping" were envisioned (Fig. 8a-c).
From the Fig. 8a-c, we can say that in the case of slipping, a presynthesized size complementary ring and a dumbbell are assembled under the influence of an appropriate amount of thermal energy. In the threading principle, a preformed macrocycle is threaded onto the molecular axle at first, followed by the covalent attachment of the stoppers to the ends of the thread. Finally, in the case of clipping principle the macrocyclization of the ring-component is preformed in the presence of the preformed dumbbell-component [2]. The threading of a string through a ring is a difficult task on the molecular scale because there are no mechanical instruments to grasp, fix, or maneuver the components. Indeed threading has to be programmed by giving the molecules appropriate chemical and physical properties. Not least because of the seemingly impossible task to synthesize preparative amounts, mechanically interlocked molecules were mere laboratory curiosities until about the late 1980s and did not get the attention of a larger scientific audience undeservedly so [41].
Early pioneers in the field were Schill and Lurtringhaus who relied on a multistep directed strategy via di- and triansa prerotaxanes and precatenanes [42]. However elegant, it was an extremely tedious approach considering the rather primitive-from today’s viewpoint—analytical and chromatographic techniques of the late 1960s.

Three synthetic methods, statistical, directed and template have been developed to construct rotaxane according to the previous principle (Fig. 8).

Fig 9. The Three Synthetic Methods Based on the Threading/Stoppering Principle

The synthetic methodology of rotaxanes based on co-ordination chemistry, in a broad sense, involves the existence of non-covalent interactions between the components of the rotaxane to be assembled. The early examples of rotaxane were made by statistical threading producing what referred to as homorotaxanes, in which the chemical structures of cyclic and linear species are identical or nearly the same.
In the statistical synthesis, a certain portion of the linear species in inserted through the ring-component as a result of statistical threading. This portion is very minor under normal condition but it can be more significant if the ring itself is used as solvent.

The pioneer work of Harrison has been reported. Harrison’s statistical preparation of rotaxane by temperature-controlled slipping onto dumbbell-component. In order to force the threading process, the solvent used was the macrocyclic component itself.

The first attempts to synthesize rotaxanes were based on statistical threading of a cyclic component onto linear molecules. The first report on a successful synthesis of such complexes, which consisted of random threading of a macrocyclic acyloin onto decane-1, 10-diol using bulky trityl groups as stoppers was published in 1967 [43].

Via statistical threading, i.e. equilibrium of the linear and cyclic species, Harrison found that rings with less than 22 methylene units cannot be threaded while rings with more than 33 methylene units cannot be retained by tritylcapped chains. Using the statistical threading method, Schill et al. prepared rotaxanes whose yields increased as a function of ring size (n = 21-29) and chain length (n = 10-38) [44].

The directed method relies on the synthesis of a prerotaxanes in which linear and cyclic subunits are linked covalently to each other. Once rotaxane backbone is built, the covalent bonds are cleaved. This alternative method to the construction of rotaxanes was developed by Schill and coworkers [45].

The template method requires the components to interact through non-covalent bonds (e.g. van der Walls, hydrogen-bonding, π-π stacking or metal-ligand interactions) leading of the assembled prerotaxanes. Since mid 1980s, the use of template effects boosted the preparation and examination of interlocked molecules. Quite varieties of different
templated syntheses have been developed during the last 15 years. Most prominent among them are those that utilize metal co-ordination, \( \pi \)-donor-\( \pi \)-acceptor complexes or hydrogen bonding to ammonium cation, amides or phenolate anions. However, despite much better understanding of non-covalent interactions, it is still difficult to design and predict the formation of host-guest complexes suitable for interlocking one molecule within the order.

In this way the different strategies and methods can be combined according to their particular features. Thus, the statistical synthesis relies on the threading or slipping one. The template method is more general, since it can make use of all the strategies.

The early syntheses of rotaxanes were mainly based on the statistical or directed methods, whose drawbacks are very particular reaction conditions for the former, numerous chemical steps for the latter. The high degree of control imposed by the use of template upon these synthetic methods raised the possibility of assembling efficiently and precisely rotaxane incorporating a wide diversity of chemical modifications.

The rotaxane synthesis is based on the use of the fundamental principle of supramolecular chemistry, namely, the self-organization of molecules due to specific non-covalent interactions. In this approach (template) the process is directed by molecular recognition between two or more complementary fragments of the interacting molecules. Depending on the type of bonding, the following main routes to the rotaxane synthesis may be distinguished: (1) the formation of metal-ligand co-ordination bonds: (2) donor-acceptor interactions: (3) combined interactions, which are observed in the formation of inclusion complexes, based on cyclodextrins [46].
Anderson et al. [47] reported conjugated [2] and [3] rotaxanes by using hydrophobic self-assembly in aqueous solution, by Glaser coupling a water-soluble alkyne in the presence of a cyclophane. No rotaxanes were formed when cyclodextrins were used instead of the cyclophane. The water-soluble rotaxanes are fully characterized by electrospray mass spectrometry, NMR and UV-VIS emission/absorption.

Yuji et al. [48] reported an efficient method for preparation of rotaxanes involving H-bonding guided self-assembly and diaryldiazoalkane ester forming end capping of pseudorotaxanes. The self assembly of rotaxanes, pseudorotaxanes and pseudopolyrotaxanes having the \( \pi \)-electron deficient cyclobis (paraquat-p-phenylene), as threads and \( \pi \)-electron rich hydroquinone ring incorporated symmetrical polyether chains, as dumbbell components have been reported [49].

Lin et al. [50] have prepared three novel hetero [3] rotaxanes which comprise one neutral tetraamide cyclophane, one tetracationic cyclophane and one linear component, which have been assembled by utilizing H-bonding and donor acceptor interactions through three neutral [2] rotaxanes as intermediate.

Nobuhiro et al. [51] reported [3] and [5] rotaxanes consisting of a crown ether and sec ammonium salts in which [5] rotaxanes is the first that has no steric barrier to suppress the shuttling of the wheel on the axle. The synthesis and characterization of photoactive rotaxanes were shown by Benniston et al. [52] These rotaxanes have an anthracenyl stopper at each end of a flexible polyether thread, which folds to facilitate \( \pi \)-stacking between the centralized cyclophane and the anthracene moieties, forming a 5-membered \( \pi \)-stacking. Smukste et al. [53] have synthesized aminoacid [2] rotaxanes, which is based on dibenzo [24] crown-8 derivatized with either N-acetyl algininyl or a carboxylic group
as the ring and using phenylalanine and 3,5-di-tert-butyl benzene moieties blocking groups.

The thermodynamic synthesis of rotaxanes comprising of cyclobis (paraquat-p-phenylene) with its $\pi$ - electron deficient bipyridinium units as the ring, $\pi$-electron rich 1,5-dioxynapthalene or 1,4-dioxybenzene ring system as the dumbbell component and aromatic imine containing stoppers, have been described [54]. The synthesis of asymmetric and chiral [2]-pseudorotaxane by the combination of $\pi$-electron deficient cavity; tetracationic cyclophane cyclobis (paraquat-p-phenylene) tetrakis (hexa fluoro phosphate) and linear noncentrosymmetric acyclic polyethers have been accomplished [55]. Artuno et al. [56] described the oriental pseudorotaxane synthesis in which triphenyl ureidocalix [6] arene was used as wheel Grubert et al [57] synthesized novel [2]-rotaxanes containing tetracationic cyclophane cyclobis (paraquat4, 4'-biphenylene) linked mechanically to a dumbbell shaped molecular thread incorporating a pair of diarylcycloheptatriene units in 35 % yield, by the acylative end capping method. Charge transfer interaction between the two components can also provide an enthalpic attractive interaction and helps drive the threading by hydrogen bonding and dipole-dipole interaction as is seen in the rotaxanes derived from paraquat, a $\pi$-electron deficient cavity and bis (p-phenylene)-[34]-crown-10, a $\pi$-electron rich molecule, wherein the paraquat resided within the cavity of bis (p-phenylene)-[34]-crown-10. The threading of dibenzoyl ammonium filament through the cavity of the macrocyclic polyether dibenzo [24]-crown-8 and cyclodextrins earned hetero rotaxanes [58-64].

A novel energy transfer rotaxane with naphthalene modified $\alpha$-cyclodextrin penetrated by dansyl and terminated by poly (ethylene glycol), was given by Tamura et al [65]. In
this rotaxane, singlet energy transfer occurs from the naphthalene moiety to the terminal
dansyl units. Substituted naphthalene and benzene–spaced tweezer molecules have been
found to form stable complex with N, N-bis (3,5-di-tert-butyl benzyl)-4,4-bipyridinium, a
substituted viologen dication, and exhibits the structure of a clipped rotaxane with a
wheel opened on one side [66].

Yoshio et al [67] reported sulfide-type [2] rotaxane in high yield by tritylative end
capping of an in situ formed pseudorotaxane consisting of dibenzo- [24]-crown-8 and
axle having group at the end by treatment with trityl hexafluorophosphate at room
temperature. Molecular-necklaces are formed from rotaxanes during an attempt to
synthesized polyrotaxanes by Witting step-growth polymerization between a dibenzyl bis
(triphenylphosphonium)-stoppered [2] rotaxane, with an NH₂⁺ recognition site encircled
by a DB24C8 ring, and appropriate derivatives of terephthaldehyde carrying groups [68].
The preparative synthesis of new nano-sized rotaxane assemblies was described by
Duennwald et al [69]. The synthesis of tris [2]-rotaxane and the bis [2]-rotaxane were
made by the directed incorporation of sulfonamide group into the amide linked rotaxane
building blocks. The sulfonamide moiety can be used as a functional group in alkylation
reactions thus showing the synthetic potential of this sulfonamide strategy in the
preparation of multirotaxane and dendritic rotaxane [70-72]

Affeld et al. [73] achieved three series of rotaxanes by slipping synthesis, in which axis
and wheel are melted in admixture, by recognition of amide groups inside the
macrocyclic wheel or by an anionic template method, in which the stoppering phenolate
are hydrogen bonded with a semi-axle 3,5-di-tert- butyl phenyl stoppers were used for
most of these rotaxanes.

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Belaissaoui et al. [73] reported the mechanically linked oligo[2]rotaxane by polycondensation of bifunctional [2] rotaxane bearing two free functional groups each in the ring and axial parts, with methylene diphenyl disocyanate. A novel methodology to make rotaxanes via covalent formation has been developed. Rotaxanes composed of crownphanes having two phenolic hydroxy groups as a molecular rotor and an axle having diamide moieties were synthesized in moderate yields via three step processes: tandem Claisen rearrangement, intramolecular diesterification, and aminolysis [75].

A novel [2] rotaxane was synthesized when an aniline-bearing [2] pseudorotaxane generated by the hydrogen bond-driven threading of a dibenzylammonium filament through the cavity of the macrocyclic polyether dibenzo [24] crown-8 was stoppered via reaction with a bulky isocyanate, which was characterized by NMR spectroscopy, mass spectrometry and X-ray crystallography [76]. Xi He et al. [77] reported a metallo-rotaxane, which was formed in the aqueous solution through the self-assembly of pseudorotaxane of cucurbituril/spermine and alkylcobaloxime, it was characterized by $^1$H NMR, ESI-MS, and UV/Vis analysis.

Philip et al. [78] reported the first rotaxane involving a bound ferrocenyl moiety and β-cyclodextrin and the product rotaxane, isolated in 11% yield, has been characterized by NMR. The template-directed synthesis of porphyrin stoppered [2]-rotaxanes were investigated by Ashton et al. [79]. Coumans et al. [80] have presented a novel procedure to synthesize porphyrin containing [3] rotaxanes starting from [2] pseudorotaxanes through a self metathesis reaction using Grubb’s catalyst.

The strategies of rotaxane synthesis can also be applied to the development of procedures for the preparation of structurally more elaborate compounds, viz., polyrotaxanes that represent supramolecular assemblies where multiple macrocycles are non-covalently bound with the polymeric chains.

There are several approaches for the synthesis of polyrotaxanes.

[1]. The formation of polymer in the presence of a macrocycle.

[2]. The formation of a ring in the presence of a macromolecule.

[3]. Polymerization or polycondensation of a stable pseudorotaxane.

[4]. Self-organization of a pseudorotaxanes due to specific non-covalent interactions.

[5]. Temperature induced slipping of the macrocycle onto the stopper, viz., and terminal groups or those pertaining to the main chain.

It should be noted that cyclization is usually performed in dilute solutions. However, if polyrotaxanes are synthesized by the second approach, the Le Chatelier principle requires that the polymer was used as a solvent or was taken excess. This results in a significant
increase in the viscosity of the reaction mixture and, correspondingly, in a decrease in the rate of the reaction. For this reason, second approach is virtually inapplicable to the synthesis of polyrotaxanes. The role of macrocycles is usually played by synthetic or natural cyclic molecules, e.g., crown ethers or cyclodextrins [27].

Mainly there are three steps for the synthesis of polyrotaxanes (Fig 10).

The three key steps are: (1). **Threading**: The monomer unit, which will form the conjugated backbone, threads inside the insulating molecular bead, to form a pseudorotaxane. (2). **Coupling**: The threaded monomer units are coupled to yield a pseudorotaxane. (3). **Capping**: The insulating beads are prevented from falling off by bulky stopper units, thus forming a polyrotaxane.

![Diagram of the synthesis of polyrotaxanes](image)

**Fig. 10 Three Key Steps for the Synthesis of Polyrotaxanes by Radical Polymerization**
One cannot rely only on statistical threading because most insulating macrocycles cannot be used, as solvent, so molecular recognition and non-covalent binding are needed in the first step. The hydrophobic effect is an appealing way to promote threading because it does not require a special recognition site to be built into the monomer; it will suffice that the monomer is hydrophobic, which is generally true of all monomers used to make conjugated polymers. The insulating unit needs a hydrophobic interior, to accommodate the guest, and a hydrophobic exterior to render it water-soluble. There are several well-documented amphiphilic macrocycles such as cyclophane and the cyclodextrins, which bind hydrophobic guests in water. The hydrophobic effect has already been employed to promote rotaxane formation. If we use the hydrophobic effect to drive threading, then coupling and capping must also be carried out in water. Several reactions can be used to form a conjugated backbone under aqueous conditions; these include Suzuki coupling, Glaser coupling, Heck coupling and Azo-coupling [47]. More recently Ritter [86-88] and Takata et al [89] have independently reported the preparation of side-chain-type polyrotaxanes by the polymerization of pseudorotaxanes bearing polymerizable functional groups (Fig. 11 a-c) Thus, when an axle monomer with an attractive interaction site is mixed with a complementary ring molecule, the corresponding pseudorotaxanes monomer results in the corresponding side-chain-type polyrotaxane.
Most of the already reported side chain polyrotaxanes were prepared by side chain reactions. As depicted in Fig 11, the side chain rotaxane group was usually constructed according to method (a), which involves the side chain reaction in the presence of macrocyclic species such as cyclodextrins. Recently radical polymerization of vinyl compounds having the side chain rotaxane group has also been reported (method (b) in Fig. 11) [90]. Radical polymerization was also used for the synthesis of pseudorotaxanes based on polyacrylonitriles. Polystyrene-based polyrotaxanes were synthesized by anionic polymerization of styrene in the presence of 36-crown-12 and 42-crown-14.
Pseudorotaxanes and polyrotaxanes based on various polyesters and polyurethanes were obtained by polycondensation and polyesterification [27].

Recently Kamimura et al. [91] and Yui et al. [92] groups reported the polyrotaxanes, which can be used in pharmacology and medicine as drug carriers and drug permeation enhancers. The interaction of these polyrotaxanes with blood cells was studied in detail; it was found that hydroxypropylated polyrotaxanes increase the fluidity of membranes and control the level of calcium by inhibiting platelet-induced elevation of Ca\(^{2+}\). The same group of investigators proposed to use this principle in the design of drug conjugates on the basis of polyrotaxanes and were the first to attempt to prepare such conjugates with insulin and theophylline, which are covalently linked to CD molecules.

Synthesis and dynamic mechanical properties of an aliphatic polyurethane rotaxane have been reported. These were prepared by polymerization of ethylene glycol, hexamethylene diamine, vinylidene chloride and β-cyclodextrin, in the presence of [30]-crown-10 [93-97].

A comblike side chain polyrotaxane, containing rotaxane units in the side chain was synthesized via the self-assembly process. Using 2,6-dimethyl β-cyclodextrin and the monofunctional blocking group N-(p-diphenyl methyl) phenyl) butadiene, a semirotaxane was made. The amino–functionalized semirotaxane was then reacted with a poly (methyl methacrylate) copolymer having reactive carboxylic acid sites along the chain to build a polyrotaxane [98]. Later on monomeric and polymeric rotaxanes based on polyester, polyamide, polystyrene, polyacrylomide system as the linear chain and cyclic polyethers as cyclic components have been synthesized [99]. The synthesis of new side chain
polyrotaxanes containing 2,6-dimethyl α-cyclodextrin rings with side groups attached via amide a function at an aromatic polyether-polysulfone was reported. W. Kamimura et al. [100] reported the biodegradable polyrotaxane consisting of α-CDs and PEG capped with benzyloxycarbonyl-L-phenylalanine and the interaction with skin stratum corneum was examined by means of a differential scanning calorimetry. It was found that the hydroxypropylated polyrotaxane enhanced the interaction with lipid components in the stratum corneum. Obtained results suggest the feasibility of such polymeric supramolecular assemblies as novel candidates for penetration enhancers.

The synthesis and characterization of a new polythiophene based pseudorotaxanes and a new amphiphilic approach for preparing homopolyrotaxanes that lack an enthalpic driving force for dethreading have been synthesized [101].

The preparation of main chain polyrotaxane by threading crown ethers onto preformed polyrotaxanes [102] and aliphatically bridged [n]-rotaxanes with chiroptical properties have been reported [103]. The donor-acceptor rotaxanes with cyclic acceptor, cyclobis (paraquat - p - phenylene) and α-cyclodextrin and poly (ethylene oxide) based polyrotaxanes have been synthesized [104]. A network system which trapped macrocycles by threading them onto linear chains between two cross linking points, threading efficiency variation with ring size of dibenzo crown ethers (15-, 30-, 44-, and 58- membered rings) and chain length of linear ethylene glycols and polyrotaxanes comprised of polyurethane back bone and crown ether via statistical threading method has been reported [105].

Recently crown-ethers, cyclodextrins (CD), cyclophanes and cucurbituril have been used as ring components of rotaxanes, symmetric and asymmetric [2] rotaxanes containing α-
CD and methylated β-CD have been prepared and characterized. However, all the rotaxanes are ionic and in some cases their stoppers are metal complexes, which are in equilibrium with dissociation states, so rings may come off. To obtain non-ionic rotaxanes, it is necessary to design a dumbbell part, which consists of neutral stoppers and a neutral axle.

A systematic investigation of the kinetics of these self-assembly processes, performed while varying the size of both the macrocycle and the stoppers has demonstrated that the size complementary between the components is the major requirement for success in the slippage approach to rotaxanes. Indeed, only when the macrocyclic component possesses a cavity large enough for it to slip over the bulky stoppers covalently attached at the ends of the dumbbell-shaped compound is rotaxane formation observed. Furthermore the kinetic investigation of slippage, performed over a range of temperature and in various solvents has demonstrated that the enthalpic and entropic constrictions to the free energy of activation associated with the second order slipp ing on-process namely the self - assembly of the rotaxane are approximately the same, while the opposite slipping off process namely the dismembering of the rotaxane is mainly enthalpically demanding. Also, the polarity of the solvent is reflected in the rates of both slipping-on and slipping-off processes suggesting that solvation of the components have a significant effect on the kinetics of these processes.

It should be noted that threading of cyclic molecules onto linear components, which forms the basis for all the strategies of the rotaxane synthesis, is a reversible which is described by the equilibrium constant $K_{eq} = [Rt] / [L][C]$. 
Therefore, the creation of conditions where the equilibrium of the reaction is shifted towards complex formation is the key event in the assembly of rotaxane molecules. Quantitatively, this process can be described by standard thermodynamic equations:

\[ RT \ln K_{eq} = -\Delta G = -(\Delta H - T\Delta S), \quad (1) \]

\[ \ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (2) \]

As can be seen from Eqn (2), two extreme cases are thermodynamically possible. First, the so-called statistical threading, i.e., a random collision and interaction of molecules of different nature (e.g., L and C). The enthalpy of such a reaction, \( \Delta H \), is close to zero or is positive, i.e., the threading is determined by the entropy factor. Second, template-directed threading, which is based on the principle of molecular self-assembly where the reaction is energetically favourable due to the existence of specific non-covalent interactions between the particles L and C (\( \Delta H < 0 \)) [27].
Supramolecular Devices and Analytical Applications of Rotaxanes
And Polyrotaxanes.

The incessant demand for increasingly sophisticated technologies is encouraging scientists to think more intently on the nanometer scale in the quest for more efficient ways of writing, storing, processing, reading and transferring information than they can boast presently. The scientific community is growing increasingly conscious of the fact that the lithographic techniques used in today’s production of miniaturized silicon-based transistors may be reaching their limit, and that a fundamentally new approach is needed for the rapid handling of vast amounts of information on the nanometer scale. By proposing a ‘bottom-up’ approach, starting from atoms and molecules, to meet this challenge, Richard Feyman was first person who dared to think so small back in the 1960s [106].

Supramolecular chemistry had revealed advanced from more or less simple beginning of molecular recognition (host-guest systems) to the second generation of systems with inbuilt functionality to address and stimulate the assemblies to perform useful chemistry, and further still to arrays which can emulate meso-scale processes. Molecular machines, nanotechnology, synthetic enzymes, artificial photosynthesis, molecular scale electronic devices - wires, switches, diodes, relays, etc. are just some of the applications that derived from the controlled and rational development of new-age mechanically interlocked supramolecules [107].

In the recent years, rotaxanes as molecular assemblies are considered as promising candidates for the construction of supramolecular devices which represent functional,
structurally organized systems [108]. The feasibility of using rotaxanes in this area is due primarily to the ease of control over molecular directionality, which determines the specific spatial configuration of their constituents. The introduction of photoelectron or ion-active groups into as well as the transmission of signals and the storage of information.

The design of photonic, electronic and ionic supramolecular devices based on molecular components and their incorporation into well-organized assemblies is the next step in the development of functional materials on a nanoscale. Further studies in this field will inevitably culminate in the construction on their basis of multifunctional chemical ‘machines’ as the basis for the development of chemical informatics and an analysis of functioning of these devices in close conjunction with related biological processes.

In biology, molecular machines and motors play an essential role. Many examples are known for proteins, which undergo important shape changes, such as folding–defolding, after a signal has been sent to the molecules. Molecular motors consist of several components, among which some parts will be considered as motionless and some others will move continuously while energy is consumed. Biological motors can be classified as rotary or linear motors, ATP synthase being certainly the most important and best understood rotary motor [109].

Artificial molecular machines and motors have appeared as one of the emerging fields of chemistry in the last decades. Molecules or molecular assemblies for which a certain part can be set into motion deliberately have triggered great interest as ‘machines’ in the course of the last 7-8 years. Several such systems have been designed and elaborated recently, many of them being based on electroactive compounds whose shape will be
modified at will by a redox process. Threading or interlocking rings are ideally suited to the construction of machines can be envisaged with such architectures, without the risk of damaging the chemical structure of the system. If a ring is threaded onto a rod, it can either spin around the axle or undergo a translation movement. In a similar way, a ring can glide and spin within another ring in interlocking ring systems (catenanes). [110]

Artificial molecular machines, which can be defined as assemblies of a distinct number of molecular components designed to performed machinelike motions in response to appropriate external stimuli, such as light, electrons, or pH changes, are of great interest because of their potential applications in the creations of nanometer-scale molecular devices.

Rotaxanes can now be obtained efficiently using template-directed protocols that rely upon supramolecular assistance to covalent synthesis, there are still a limited number of recognition motifs that can be exploited for the preparation of these interlocked molecular compounds which hold out so much promise for the fabrication of actuators, amplifies, motors, sensors, and switches at the nanoscale level.

Yet another promising line of investigations is the preparation of controlled ‘molecular switches’ (or ‘shuttles’ according to Stoddart). Molecular switches-on/off processes represent reversible transitions of one of the components between the two positions, which differ either in structure or in conformation. The recently synthesized [2]-rotaxane (Fig. 12) can serve as an example of an electrochemical (or chemical) ‘molecular shuttle’. In this case, the migration of the macrocycle occurs as result of a redox reaction or protonation-deprotonation.
Pseudorotaxanes, rotaxanes and catenanes are appealing examples of such entities, particularly since the relative positions of their component parts can be induced to change.
as a result of some external stimulus. Hence, they may be considered as particular types of molecular level switches. In most cases mechanical movements occur between two different well-defined states (Fig. 13) and are accompanied by on/off switching of some observable property expressed in their NMR or electronic absorption spectra or by luminescence. Chemical or electrical energy and light have been used to induce the mechanical movements, opening up the way to process information at the molecular level.

*(Fig 13. Schematic Representation of the Mechanical Movements Relating to (A and A') in (a) Pseudorotaxanes (b) Rotaxanes)*

Studies with polyrotaxanes based on β-CD and the PEO-PPO-PEO triblock copolymers also manifest the properties of ‘molecular switches’[111]. The transition of polyrotaxanes from the insoluble into the soluble state can occur either upon a rise in the temperature or
upon an increase in pH above 12 due to the destruction of the hydrogen bonds between the CD molecules. As a result, the macrocycles migrate along the rod molecule.

Recently, mechanically interlocked molecules such as catenanes and rotaxanes have received a great deal of attention in the design of supramolecular devices because of their ability to switch between two or more states as a result of induced relative movement of their non covalently interacting components on application of external stimuli. A number of prototype molecular machines based on rotaxanes, pseudorotaxanes, and catenanes, which exploit shuttling, threading/dethreading, and circumrotational motions, respectively, have been reported over the past decade.

Cucurbituril, a macrocycle comprised six glycoluril units, has been employed in the construction of a wide variety of interlocked molecules and more recently, rotaxane-based molecular machines and switches as well.

Organic molecules with long conjugated π-systems can be regarded as “molecular wires” [112] because they have mobile electrons. These conjugated polymers have many potential applications; in non-linear optics, in organic electroluminescent display devices, and as organic semiconductors [113], but the small HOMO-LUMO energy gaps responsible for their special electronic properties often lead to chemical reactivity and instability, which can limit their neighbors and from the external environment.

Others in a variety of ways have explored this idea, for example, molecular wires have been insulated by threading them through zeolite frameworks, and using ligand shells [114].

The insulation of molecular wires is to thread a series of insulating molecular beads onto a conjugated backbone to form a molecular necklace. The addition of large bulky end-
groups, or stoppers, to prevent the insulators from unthreading, yields a polyrotaxanes. Sung Im Jun et al. [115] reported reversible molecular switch, in which a pseudorotaxane containing cucurbituril (as a molecular ‘bead’) threaded on fluorenyltriamine (as a ‘string’) behaves as a fluorescent, molecular switch and switching of the molecular bead from one site to the other site on the ‘string’ induced by pH change is easily detected by change in colour and fluorescence.

**Complexation Studies of Rotaxanes and Polyrotaxanes**

Complexation studies involving rotaxanes with metal ions has generally been carried out by using a metal complex in the form of a metallated porphyrin, either as a stopper, or by exploring the template effect of some metal ions in bringing together the cyclic and the linear component for threading.

Ogino [116,117] was the first who used the dimeric cobalt (III) complex, as a linear component and α or β-cyclodextrin chiral ring as the cyclic moiety for the synthesis of rotaxanes. Similar rotaxanes with polymethylene bridged dinuclear Co (III) complexes have also been reported [118].

An attempt was made by Ashton et al. [119] in synthesizing template-directed metallated (Zn) tetraaryl porphyrin stoppered [2]-rotaxanes, employing aromatic π - π stacking interaction as the major source of molecular recognition by the clipping approach.

Sauvage et al. [120,121] studied photoinduced intermolecular electron transfer between Zn (II) and Au (III) porphyrin stoppers in some transition metals. Such transition metal directed threading of molecular fragments, containing a central chelate and an end-
attached gold (III) porphyrin afforded a rotaxane precursor, while the second porphyrin acted as an efficient stopper and afforded a copper complexed [2]-rotaxane as well as a novel compartmented [3]-rotaxane. These bis-porphyrin rotaxanes represent a modular system in which the electronic properties of the groups, or of the medium through which the electron is supposed to travel, can be tuned by demetallating the tetrahedral site or recomplexing it by a selected metal. The principle of the strategy is indicated in Fig. 14.

Fig. 14 (I) The Macrocycle (A) Incorporating a Co-ordinating Fragment (thick line) Interact with a Metal Centre (Bulky Axle) and an Asymmetrical Open Chain Chelate (B) Bearing One Porphyrin and a Precursor Function to Form the Threaded Intermediate (C). (II) The Second Porphyrin Ring is then Constructed, Affording the Transition Metal Complex-Rotaxane (D).
The template effect for the synthesis of a very stable rotaxane using the tetrahedral geometry of Cu (I) complex is described in the claw shaped phenanthroline bisphenol threaded by a cyclic phenanthroline compound [122].

Porphyrin stoppered rotaxanes were synthesized having central copper (I) bis (1,10-phenanthroline) complex while gold (III) and zinc (II) porphyrin acting as terminal stoppers. Upon selective excitation of either porphyrin, rapid electron transfer occurred from the zinc porphyrin to the appended gold porphyrin [123].

A successful synthesis of a novel copper (I) co-complexed rotaxane with two fullerene stoppers was given by Dietrich et al. [124] that consisted of a co-ordinating ring, a copper (I) centre and a difunctionalized fragment.

Multiporphyrin [2]-rotaxanes via copper (I) templated synthesis was reported by Chambron et al. [125]. Condensation of dipyrylmethane units onto a diphenylphenanthroline bearing copper (I) complex, afforded a copper (I) complexed bis-porphyrin-stoppered [2]-rotaxane.

A directed self-assembly of chiral, optically active tetranuclear molecular squares was attempted by Stang et al. [126]. The reaction of the chiral, square-planer (around the metal), R (+)-[binap palladium (III) and platinum (II) bis (triflate) complexes (binap = 1,1-binapthyl-2, 2'-dyl) bis (diphenyl phosphate)] with 2,6-diazaanthracene in acetone at room temperature gave an excellent yield of the self assembled single, diastereomeric, stable product as assessed by NMR techniques.

Kimura et al. [127] showed intra-complex electron transfer in pthalocyanine [2]-pseudorotaxane, which was formed from a Zn (I) - phthalocyanine complex, electron
rich hydroquinone containing polyether sub units segments and electron deficient
cyclobis (paraquat - p - phenylene) tetracation units.

Baxter et al. [128] reported the self-assembly of rigid rack multimetallic Cu (I)
complexes of rotaxane displaying a high degree of spatial organization. The design of
such a system was made by use of rigid linear ligands on 2,2'-bipyridine sub units and
1,10-phenanthroline containing macrocycle. The X-ray structure revealed that the two
macrocycles are threaded onto a linear quartepyridine ligand to form a dimetallic
rotaxane.

Whang et al. [129] for the first time, synthesized metal mediated polyrotaxanes, with
high structure regularity in the solid state, based on a co-ordination polymerization.
The strategy to synthesize a pseudorotaxane by threading a molecular bead of
eucurbiturl molecules with a string of N, N-bis (4-pyridylmethyl)-1,4- dianinobutane
dihydrochloride and then coordinating the end functional groups of the pseudorotaxanes
with metal centers (Cu(NO₃)₂) to form a coordination polymer was reported /130/. A
similar type of two-dimensional polyrotaxane, having the structure [Zn (1,4 bis -
(imidazol-1-ylmethyl) benzene)₂] 4.5H₂O, was also reported.

Markis et al. [131] reported the X-ray structure of an organometallic rotaxane formed by
complexation of di-p-tolyl magnesium with [18]-crown-6 and [15]-crown-5, where Mg
showed an unusual type of hexacoordination.

Raehm et al. [132] reported transition metal containing rotaxane. In this work they
described a rotaxane in which a new type of motion (pirouetting of the wheel around its
axle) could be electrochemically triggered. It was synthesized by using the three-
dimensional effect of copper (I).
The synthesis and characterization of porphyrin stoppered [3]- and [5]-rotaxanes were shown by Solladie et al. [133]. A dicopper (I)-complexed [3]-rotaxane was prepared in 34% yield by the transition metal template strategy involving a bis-chelating molecular thread, chelating unit-incorporating macrocycles and porphyrin stoppers as key components. A tetra copper (I)-complexed [5]-rotaxane was obtained as a by-product in 8% yield. Coordination chemistry was performed either at the 2,9-diphenyl-1,10-phenanthroline chelates or at the porphyrin stoppers. The latter were metallated by Zn (II), Au (III), or Zn (II) and Au (III).

Shukla et al. [134] reported a [2]-rotaxane with a crown ether as wheel component. The synthesized [2]-rotaxane was shown to bind (K⁺) which alters the rotaxanes dynamic properties.

It was shown by Chichak et al. [135] that coordination to the axial position of the metalloporphyrin Ru (TTP) (Co), is an effective means to end-cap the 1,2-bis (4,4'-dipyridinium) ethane dication of dibenzo [24]-crown-8 [2]-pseudorotaxane and generate the stable porphyrin [2]-rotaxane.

Chang et al. [136] showed the self-assembly and dynamics of [2]- and [3]-rotaxanes with a dinuclear macrocycle containing reversible Os-N coordinate bonds.

A novel supramolecular assembly, bis (molecular tubes composed of complexes of organo selenium-bridged β-cyclodextrins and platinum (IV) ion, have been fabricated via the pseudorotaxane with poly (propylene glycol) by Liu et al. [137]

The transition metal complex rotaxanes as molecular machines, motors and self-assemblhes have been discussed [138-140].
Agrawal et al. [141] reported a rapid and sensitive method for the extraction and spectrometric determination of Se (IV) with [2] rotaxane.

The selective self-assembly of a thread-like tetracation, containing two dialkylammonium (NH$_2$ $(1+)$) centers and a 4,4'‐bipyridinium unit, with an assortment of macrocyclic polyethers was investigated by Ashton et al. [142].

Dipyrido [24]-crown-8 has been shown to form [2]-pseudorotaxanes spontaneously with dibenzyl ammonium ions. That the complexation is faster and stronger as compared to dibenzo [24]-crown-8 counterpart was reported by Chang et al. [143].

**Future Directions**

Supramolecular chemistry has already advanced from more or less simple beginning of molecular recognition (host-guest systems) to the second generation of systems with inbuilt functionality to address and stimulate the assemblies to perform useful chemistry, and further still to arrays, which can emulate meso-scale processes.

Clearly, the first steps have been taken along the pathway toward constructing simple supramolecular devices. The next generation of supramolecular molecular devices will need to be congregated on surfaces or allowed to organize themselves at air-water interfaces such that the molecules behave coherently, either in parallel or in series. These challenges are considerable ones; yet, we can start to meet them in the knowledge that nature has been “there” before and has managed to come up with some exceedingly elegant solutions to a multitude of problems, relating to machines that operate on the molecular level, in the course of an evolutionary process that has spanned many billions
of years. The time scale in the laboratory will be a lot less, but no one knows at this time how much less. Supramolecular devices are the forerunners of molecular computers—still an emotive term among chemists.

Since these early days, more and more functionality has been introduced into the molecules, either in relation to electron and energy processes or with regard to controlled molecular motions. The use of transition metals as templates and of their complexes as electroactive and mobile components turned out to be particularly useful in the construction of electromechanical molecular devices based on coordination compounds.

It would of course be unwise to predict that nanoscopic motors and related machines will have any practical application in the future as molecular information storage devices or as nanoscale components in electronics, but the search for such molecules or molecular assemblies is important in itself.

The variety of impulse to be used is immense: redox (as in present examples), photonic, pressure change, magnetic field variation, pH change, chemical signal, electric field etc. The effect obtained is also multifarious and could lead to dramatic modifications of the bulk properties of the system. Since a simple signal can change the shape and the volume of a compound and of its assemblies, fascinating features related to devices could be imagined, reminiscent of biological systems such as muscles or other biological molecular machines.

There are those who dismiss as far-fetched the idea of man-made molecular scale computers. Only a few decades ago, however, these same individuals might have classified as science fiction a proposal that somebody there would be a man on the Moon, that fertility could be controlled by taking a pill, or that we could learn the structure of
DNA. But since we know that molecular computers are routine accessories of all animals from ants to zebras, it would be prudent to change the question from whether there will be man-made counterparts to questions concerning when they will come into existence and who will be leading in their development. The when question will be answered on the basis of fundamental research in chemistry: the who question will depend on which countries commit the required resource and creativity to the search.

Molecular-based computers, an as yet-unrealized dream, would use molecules of chemical compounds, rather than silicon-based transistors, as switches. They would be smaller and more powerful and have other advantages over silicon-based computers. A group of chemists and other researchers at the University of California, Los Angeles (UCLA), and Hewlett-Packard Laboratories, Palo Alto, California, reported a major step toward such devices with development of the first molecular-based logic gate. The researchers used a class of molecules termed rotaxanes as molecular switches.

The researcher group linked rotaxanes and molecular wires into a configuration of logic gates and showed that the switches operate. Although many challenges remained, J.R. Health of UCLA, who led the team, predicted that a chemical computer would be in operation within 10 years.

Although the use of the rotaxane system as components of potential molecular electronics devices has been extensively reported and discussed, fabricating them into real nanometer scale devices creates a new dimension to the problem. Many such artificial supramolecular devices have been shown to operate efficiently in solution but in an incoherent manner. For the next generation of mechanically interlocked systems to operate at a macroscopic level, they need to be organized at interfaces, on solid supports,
or at surfaces, so that they can operate in unison. There are at least several approaches being adopted in attaching these systems to solid surfaces in order to optimize their ability to work in practical sense. However, it is often difficult to study such systems in their solid form.

**Aim and Scope of the Thesis**

The review of literature survey reveals that rotaxane is fastest growing area of the experimental chemists. Many of the most impressive discoveries and inventions of this century in supramolecular science have drawn their inspiration from disciplines outside chemistry, as well as from disciples who were not chemists. Supramolecular chemistry—the chemistry of the noncovalent bond is practiced and exemplified by biochemical systems. The awe-inspiring efficiency of natural systems alerts us to the fact that the concepts of self-organization, self-assembly and self-replication are necessary to tame the chemical synthesis of large, well defined and functioning molecular structures and superstructures. One of the vehicles used for this research is rotaxane. The introduction of chelating group, such as hydroxamic acid may further enhance the complexing ability towards metal ions.

With this in view, the new [2] rotaxane with functionality of hydroxamic acid has been synthesized and used for the speciation, complexation, separation and preconcentration of vanadium(V), indium(III), gallium(III) and thallium(III).
Present Investigation

The research described in this thesis deals with different aspects of rotaxane discussed in previous section. Chapter 2 describes a synthetic approach namely slippage to self-assembling functionalized hydroxamic acid linked [2] rotaxane incorporating dumbbell-shaped component and polyether macrocycle has been developed. In particular, the so-called slippage methodology relies upon the size complementarily of preformed macrocyclic and dumbbell-shaped components. From this point of view, functionalized hydroxamic acid linked [2] rotaxane has been synthesized by reacting sebacoyl chloride with hydroxylamine of nitro calix [6] arene, which is resulting in formation of dumbbell-shaped component. By slipping approach, preformed 42-crown-14 has been inserted into the dumbbell-shaped component under the suitable condition. The spontaneous self-assembly of this complementary component into rotaxane in solution can be achieved under the influence of an appropriate amount of thermal energy. This newly synthesized rotaxane has well been characterized and interpreted by IR, \(^1\)H NMR and \(^{13}\)C NMR.

In chapter 3 a new reagent [2] rotaxane hydroxamic acid is reported for extraction and trace determination of vanadium (V) in nutritional and biological substrates. The extraction mechanism of vanadium from 6 M HCl media is investigated. The influence of reagent, diverse ions on distribution constant of vanadium examined. The overall stability constant (log\(\beta_2K_\alpha\)) and extraction constant (K_\alpha) are 2.50 ± 0.02 and 4 0 ± 0.02 x 10^{-8} respectively in chloroform. The system obeys Beer’s law in the range of 0.815-3.26 \(\mu\)g mL^{-1} of vanadium(V). The molar absorptivity is 6.66 x 10^3 L mol^{-1} cm^{-1} at 525 nm. The vanadium complex chloroform extract was directly inserted into plasma for ICP-AES.
measurements, which increases the sensitivity by 50 folds. The method is applied for determination of vanadium in real standard samples and environment samples.

Chapter 4 describes a novel method for liquid-liquid extraction, speciation, sequential separation and trace determinations of indium, gallium and thallium with the synthesized [2] rotaxane hydroxamic acid is reported. Indium(III), gallium(III) and thallium(III) are extracted at pH 5.5, 3.5 and 7.0, respectively in chloroform and recovered them in presence of large number of cations and anions. The extraction mechanism is investigated. The influence of the reagent concentration, PAR and xylenol orange concentrations, pH, shaking time, diverse ions and stoichiometry is discussed. Indium and gallium are quantitatively extracted from aqueous phase at pH 5.5 and 3.5, respectively into chloroform with [2] rotaxane hydroxamic acid and determined spectrophotometrically using PAR and xylenol orange, respectively while that of thallium is quantitative extracted at pH 7.0 into chloroform with [2] rotaxane hydroxamic acid. Indium gives red coloured complex at \( \lambda_{\text{max}} \) 525 nm having molar absorptivity \( 5.5 \times 10^4 \) L mol\(^{-1}\) cm\(^{-1}\), gallium gives reddish violet coloured complex at \( \lambda_{\text{max}} \) 545 nm having molar absorptivity \( 3.79 \times 10^4 \) L mol\(^{-1}\) cm\(^{-1}\) and thallium gives yellow coloured complex at \( \lambda_{\text{max}} \) 370 nm having molar absorptivity \( 4.5 \times 10^5 \) L mol\(^{-1}\) cm\(^{-1}\). For the trace determination, the extracts were directly inserted into plasma for ICP-AES measurements, which enhances the sensitivity by 60 folds and obeys Beer’s Law for In(III) 0.306 – 1.83, for Ga(III) 0.33 – 1.83 µg mL\(^{-1}\) and for Tl(III) 2.44 – 613.11 ng mL\(^{-1}\). The method is applied for the determination of In, Ga and Tl in alloys, environmental, minerals, water and biological samples.
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