International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2013): 4.438

Supramolecular Chemistry-Concepts and Applications

Ajay Kumar Manna

Ramananda College, Department of Chemistry, Bishnupur, Bankura, West Bengal, 722122, INDIA

Abstract: ***In this review paper the chronological development of concepts of supramolecular chemistry have been discussed in details with relevant references. The topic discussed molecular self-assembly, molecular recognition, complexation, template directed synthesis, mechanically interlocked molecular architectures, Dynamic Covalent Chemistry, Molecular Imprinting Techniques, concepts of molecular machines and biomimetics. Applications of these concepts in the field of materials technology, efficient catalysis, controlled drug delivery, data storage, processing devices, green chemistry and high-tech devices.***

Keywords: Supramolecular chemistry, molecular self-assembly, molecular recognition, template directed synthesis, dynamic covalence, molecular imprinting, molecular machines and biomemetics.

1. Introduction

Supramolecular chemistryis one of the new areas of chemistrywhich deals with secondary interactions rather than covalent bonds in molecules and focuses on the chemical systems made up of a discrete number of assembled molecular subunits or components. The forces responsible for the spatial organization may vary from weak intermolecular forcesto strong covalent bonding.The weak intermolecular forces arehydrogen bonding,metal coordination,hydrophobic forces,van der Waals forces, pi-pi interactions and electrostatic effects.

The existence of intermolecular forces was first postulated byJohannes Diderik van der Waals in 1873. Later in 1894, Nobel laureate Hermann Emil Fischer introduced the philosophical roots of supramolecular chemistry by suggesting "lock and key" mechanism for enzyme-substrate interactions, which is the fundamental principle of molecular recognitionand ‘host-guest’ chemistry. In the early twentieth century non-covalent bonds were understood in gradually more detail, with the hydrogen bond being described by Latimer and Rodebush in 1920.

The use of these principles led to the better understanding ofprotein structureas well as other biological processes. For instance, elucidation of the double helical structureof DNA(by Watson and Crick) occurred when it was realized that there are two separate strands of nucleotides connected through hydrogen bonds. The use of non-covalent bonds is essential to replication because they allow the strands to be separated and used to template new double stranded DNA.

The importance of supramolecular chemistry was established by the research work of Nobel laureates Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen in 1987 for Chemistry[1].The development of selective "host-guest" complexes [2, 3] particularly, in which a host molecule recognizes and selectively binds a certain guest, was cited as an important contribution.Supramolecular chemistry enrichedby the research works of James Fraser Stoddart[4-6] with the development of concepts ofhighly complex self-assembledstructuresandmolecular machinery [7-8]. Again, Itamar Willner developed concepts of bio-sensors and methods of electronic and biological interfacing. Simultaneous development of nanotechnologyalso had a strong influence on this subject, with building blocks such asfullerenes [9-12],nanoparticles [13-15], anddendrimers[16-20] becoming involved in synthetic systems.

The subject gradually develops by the research works onmolecular self-assembly[21,22],folding[23-28] molecular recognition [29-31],mechanically-interlocked, molecular architectures[32]anddynamic covalent chemistry [33,34]The study of non-covalent interactionsis crucial to understanding many biological processes from cell structure to vision that rely on these forces for structure and function. Biological systemsare often the best inspiration for researches in supramolecular chemistry.

2. Basic Concepts and Literatures ofSupramolecular Chemistry

Followings are the important concepts developed during last decades which play important role in the understanding and developing several areas of applications.

2.1 Molecular self-assembly

Molecular self-assembly is the process by which molecules adopt a defined arrangement without external influences. There are two types of self-assembly─ intermolecularself-assemblyandintra-molecularself-assembly. Commonly, the term molecular self-assembly refers to intermolecular self-assembly, while the intramolecular analog is more commonly called folding.

Perhaps the best known intermolecular self-assembling structure in biological systems is naturally occurring DNA, which exists in a double helical form [35-37]. The two single strands are held together by a number of hydrogen bonds, involving acidic hydrogen atoms (hydrogen bonding donor), oxygen (hydrogen bonding acceptor), and nitrogen atoms (hydrogen bonding acceptor) of the purine and pyrimidine bases in order to maintain the double helical structure **(Figure-1a)** In this double helix guanine (G) forms triple hydrogen bonds with cytosine (C) and adenine (A) forms double hydrogen bonds with thymine (T).

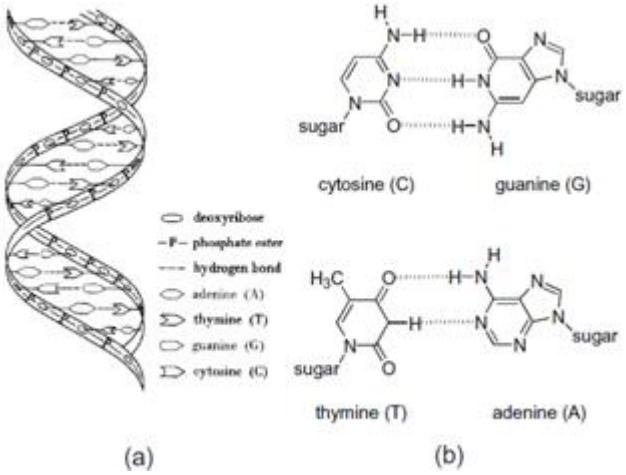

Figure 1: a) Complementary base pairing in DNA helical structure and b) base pairing in DNA (guanine and cytosine form triple hydrogen bonds; adenine and thymine form double hydrogen bonds).

Guanine selectively interacts with cytosine because the G-C complex is much more stable than G-T complex which would form only one hydrogen bond **(Fig-1b)**. Similarly, adenine exclusively forms complex with thymine because adenine would form no hydrogen bonds with cytosine. The X-ray diffraction studies revealed that the hydrogen bonds holding G-C and A-T complexes are about the same length (2.9 ± 0.1 Å).

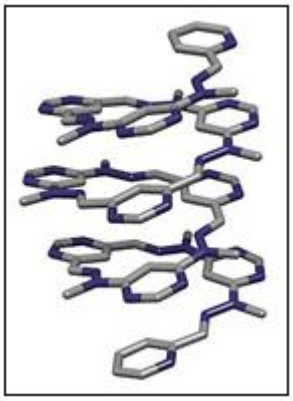

Figure 2: Crystal structure of a foldamer reported by Lehn and coworkers [Helv.Chim.Acta., 2003, 86, 1598-1624].

Intra-molecular self-assembly or folding occurs infoldamers and polypeptides. A foldamer is a discrete chain molecule oroligomerthat folds into a conformationally ordered state in solution. They are artificial molecules that mimic the ability ofproteins,nucleic acids, andpolysaccharidestofoldinto well-defined conformations, such ashelicesandβ-sheets. The structure of a foldamer is stabilized bynon-covalent interactionsbetween nonadjacent monomers [38, -40]. Foldamers are studied with the main goal of designing large molecules with predictable structures. The study of foldamers is related to the themes of molecular self-assembly, molecular recognition and host-guest chemistry.

Molecular self-assembly also allows the construction of larger structures such as micelles,membranes,vesicles,liquid crystals, and is important tocrystal engineering. Micelle is an aggregate ofsurfactantmolecules dispersed in a liquidcolloid. A typical micelle in aqueous solutionforms an aggregate with thehydrophilic"head" regions in contact with surroundingsolvent, sequestering thehydrophobicsingle-tail regions in the micelle centre. This phase is caused by thepacking behaviorof single-taillipidsin abi-layer. The difficulty filling all the volume of the interior of a bi-layer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group, leads to the formation of the micelle. This type of micelle is known as a normal-phase micelle (oil-in-water micelle).Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Otherphases, including shapes such as ellipsoids, cylinders, andbi-layers, are also possible [41]. The shape and size of a micelle are a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration,temperature,pH, andionic strength. The process of forming micelles is known as micellisation and forms part of thephase behaviorof many lipids according to their polymorphism.[42,43].

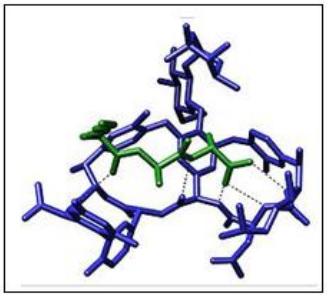

Figure 3: Crystal structure of a short peptide L-Lys-D-Ala-D-Ala (bacterial cell wall precursor) bound to the antibiotic vancomyc in through hydrogen bonds[Knox, James R.; Pratt, R. F. (1990)].

Liquid crystals (LCs)are the state of matter that has properties between those of conventionalliquid and those of solidcrystal. For instance, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way. There are many different types of liquid-crystal phases, which can be distinguished by their differentopticalproperties (such asbirefringence). When viewed under amicroscopeusing apolarizedlight source, different liquid crystal phases will appear to have distincttextures. The contrasting areas in the textures correspond to domains where the liquid-crystal molecules are oriented in different directions. Within a domain, however, the molecules are well ordered. LC materials may not always be in a liquid-crystal phase [44-46].

Liquid crystals can be divided into thermotropic, lyotropicand metallotropic phases. Thermotropic and lyotropic liquid crystals consist oforganic molecules. Thermotropic LCs exhibit a phase transitioninto the liquid-crystal phase as temperature is changed. Lyotropic LCs exhibit phase transitions as a function of both temperature andconcentrationof the liquid-crystal molecules in a solvent (typically water). Metallotropic LCs are composed of both organic and inorganic molecules; their liquid-crystal transition depends not only on temperature and

concentration, but also on the inorganic-organic composition ratio [47-49].

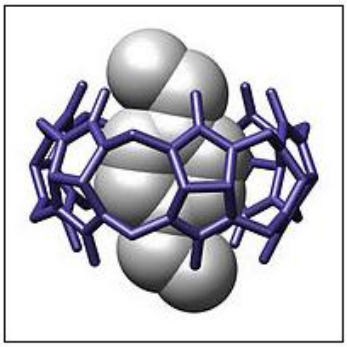

Figure 4: Crystal structure of Host-Guest Complex with a p-xylylenediammonium bound within a cucurbit[6]uril[By Freeman in ActaCrystallogr B, 1984]

Examples of liquid crystals can be found both in the natural world and in technological applications. Most contemporaryelectronic displaysuse liquid crystals. Lyotropic liquid-crystalline phases are abundant in living systems. For example, many proteins and cell membranes are liquid crystals. Other well-known examples of liquid crystals are solutions ofsoapand various relateddetergents. [50-51].

2.2Molecular Recognition and Complexation

Molecular recognition is the specific binding of a guest molecule to a complementary host molecule to form ahost-guest complex. Often, the definition of which species is the "host" and which is the "guest" is arbitrary. The molecules are able to identify each other using non-covalent interactions. Key applications of this field are the construction ofmolecular sensors andcatalysis [52-54]. The specific interaction between host and guest moleculesoccurs through non-covalent bondingsuch as hydrogen bonding,metal coordination,hydrophobic forces,van der Waals forces,π-π interactions,halogen bonding, electrostatic and/or electromagnetic [55]effects. In addition to these *direct* interactions as well solvent can play a dominant *indirect*role in driving molecular recognition in solution [56]. Thehost and guestinvolved in molecular recognition exhibit molecular complementarity [57].

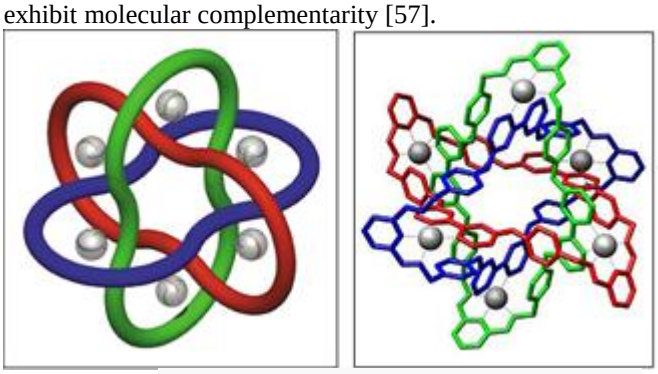

Figure 5: a) Schematic of a molecular Borromean ring, b) Crystal structure reported byStoddart JF et. al (2002).

Molecular recognition plays an important role in biologicalsystems and is observed in between receptor-ligand,antigen-antibody,DNA-protein,sugar-lectin,RNA-ribosome, etc. An important example of molecular recognition is the antibiotic vancomyc in that selectively binds with the peptides with terminal D-alanyl-D-alanine in bacterial cells through five hydrogen bonds. The vancomyc in is lethal to the bacteria since once it has bound to these particular peptides they are unable to be used to construct the bacteria'scell wall. Recent work suggests that molecular recognition elements can be synthetically produced at the nano-scale, [58] circumventing the need for naturally-occurring molecular recognition elements for the development of sensing tools for small molecules.

2.3 Template-directed synthesis

Molecular recognition and self-assembly may be used with reactive species in order to pre-organize a system for a chemical reaction (to form one or more covalent bonds). It may be considered a special case of supramolecularcatalysis. Non-covalent bonds between the reactants and a "template" hold the reactive sites of the reactants close together, facilitating the desired chemistry. This technique is particularly useful for situations where the desired reaction conformation is thermodynamically or kinetically unlikely, e.g., in the preparation of large macrocycles. This pre-organization also serves purposes such as minimizing side reactions, lowering theactivation energyof the reaction, and producing desiredstereochemistry. After the reaction has taken place, the template may remain in place, be forcibly removed, or may be "automatically" decomplexed on account of the different recognition properties of the reaction product. The template may be as simple as a single metal ion or may be extremely complex. Template directed synthesis of a genetic polymer in a model protocell is shown by Bravo J. A., et. al, and Mansy SS et. al[59, 60]. Lot of literatures available on template directed synthesis of specific compounds.

2.4Mechanically-interlocked molecular architectures

Mechanically-interlocked molecular architectures consist of molecules that are linked only as a consequence of their topology. Some non-covalent interactions may exist between the different components but covalent bonds do not. Supramolecular chemistry and template-directed synthesis in particular, is key to the efficient synthesis of the compounds. Examples of mechanically-interlocked molecular architectures include catenanes, rotaxanes, molecular knots, molecular Borromean rings and ravels [61].

Molecular Borromean rings are an example of a mechanically-interlocked molecular architecture in which three macro cycles are interlocked in such a way that breaking any macrocycle allows the others to disassociate. They are the smallest examples of Borromean rings. The synthesis of molecular Borromean rings was reported in 2004 by J. Fraser Stoddartet. al.[62]. The so-called Borromeate is made up of three interpenetrated macro cycles formed from the reaction between 2,6-diformylpyridine and diamine compounds, complexed with zinc.

2.5 Dynamic Covalent Chemistry

Dynamic covalent chemistry deals with the synthesis of large complex molecules from simple one. Here only one product is captured from areversible reactionunderthermodynamic reaction controland out of many products. The concept of dynamic covalent chemistry was further demonstrated in the development of specific molecular Borromean rings [63-65].

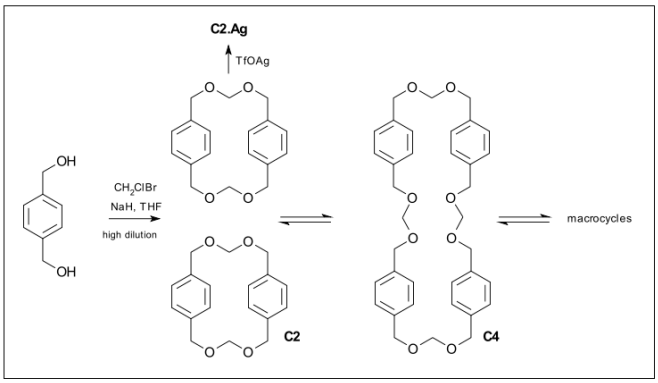

Figure 6: Formation tetramer of cyclic ether

The idea of rapid equilibration allows the coexistence of a huge variety of different species among which one can select molecules with desiredchemical,pharmaceuticalandbiologicalproperties. The concept is demonstrated in an illustrative example involving cyclophane having C_2can be prepared by the irreversible highly diluted reaction of a diol withch lorobromo methane in the presence of sodium hydride.

The dimer however is part of series of equilibria between polyacetal macro cycles of different size brought about by acid catalyzed (triflic acid)trans-acetalization [66].Regardless of the starting material,C_2, C_4or a highmolar massproduct, the equilibrium will eventually produce an identical product distribution. In this system it is also possible to*amplify*the presence ofC_2in the mixture when the catalyst is silver triflate because the silver ion fits ideally and irreversibly in itscavity.

2.6 MolecularImprinting Techniques

Molecular imprintingis a method by which a host is constructed from small molecules using a suitable molecular species as a template. Molecularly imprinted materials are prepared using a template molecule and functionalmonomersthat assemble around the template and subsequently get crosslinked to each other. The functional monomers, which areself-assembledaround the template molecule by interaction betweenfunctional groupson both the template and monomers, are polymerized to form an imprinted matrix (commonly known in the scientific community as amolecular imprinted polymeri.e. MIP). Then the template molecule is removed from the matrix under certain conditions, leaving behind a cavity complementary in size and shape to the template. The obtained cavity can work as a selective binding site for a specific template molecule.Molecular imprintingis a technique to create template-shaped cavities inpolymermatrices with memory of the template moleculesto be used inmolecular recognition.The technique is demonstrated in the following diagram[67,68].

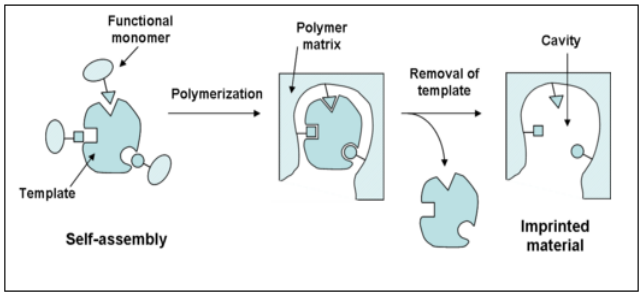

Figure 7: A Model work on molecular imprinting technique

Figure-7 shows a method of synthesizing molecularly imprinted polymers by copolymerization of template and functional monomers followed by template removal. This technique is based on the system used by enzymes for substrate recognition, which is called the "lock and key" model. The active binding site of an enzyme has a unique geometric structure that is particularly suitable for a substrate. A substrate that has a corresponding shape to the site is recognized by selectively binding to the enzyme, while an incorrectly shaped molecule that does not fit the binding site is not recognized.

2.7 Concepts of Molecular Machines

The idea of molecular machine (also called nanomachine) has biological applications.It is defined as any discrete number of molecular components that produce quasi-mechanical movements (output) in response to specific stimuli (input) [69, 70].The expression is often more generally applied to molecules that simply mimic functions that occur at the macroscopic level. The term is also common in nanotechnology where a number of highly complex molecular machines have been proposed that are aimed at the goal of constructing amolecular assembler. Molecular machines can be divided into two broad categories; synthetic and biological.

Molecular systems capable of shifting a chemical or mechanical process away from equilibrium represent a potentially important branch ofchemistryandnanotechnology. As the gradient generated from this process is able to perform useful work these types of systems, by definition, are examples of molecular machinery.

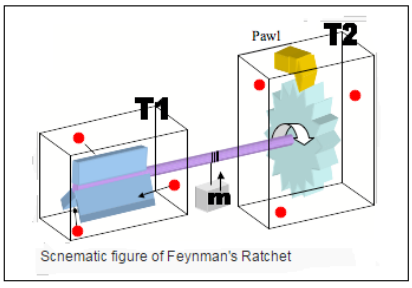

Figure 8: Model for molecular machinery.

Molecular machinesare molecules or molecular assemblies that can perform functions such as linear or rotational movement, switching, and entrapment. These devices exist

at the boundary between supramolecular chemistry andnanotechnology, and prototypes have been demonstrated using supramolecular concepts [71].

2.8 Biomimetics

Biomimetics or biomimicryis the knowledge borrowed from natural models or systems to solve real life or scientific problems.The terms biomimetics and biomimicry come fromAncient Greek: *bios* (life), and *mīmēsis*(imitation). Living organisms haveevolvedwell-adaptedstructures and materials over geological time throughnatural selection. Biomimetics has given rise to new technologies inspired bybiologicalsolutions at macro and nanoscales. Humans have looked at nature for answers to problems throughout our existence. Nature has solved engineering problems such as self-healing abilities, environmental exposure tolerance and resistance,hydrophobicity, self-assembly, and harnessing solar energy. Many synthetic supramolecular systems are designed to copy functions of biological systems. Examples include photo-electrochemical systems, catalytic systems,protein designandself-replication [72].

Biomimetics could in principle be applied in many fields like aviation technology (following birds and bats), nanosurface (following shark skin), tread design of tires (following toe pads of tree frogs), thermal collectors and clothing (following polar bear), solar power collection (mimicking the arrangements of leaves) etc. Some examples of biomimetic applications at various stages of development from prototypes to technologies that might become commercially usable have been described by Bharat Bhushan [73].

3. Applications

3.1 Development of New Materials

In the development of new materials supramolecular chemistry andmolecular self-assemblyprocesses been applied very much. Large structures can be readily accessed usingbottom-upsynthesis as they are composed of small molecules requiring fewer steps to synthesize. Thus most of the bottom-up approaches tonanotechnologyare based on supramolecular chemistry [74, 75].

3.2 Efficient Catalysis

A major application of supramolecular chemistry is the design and understanding ofcatalystsandcatalysis [76-78]. Non-covalent interactions are extremely important in catalysis, binding reactants into conformations suitable for reaction and lowering thetransition stateenergy of reaction. Template-directed synthesis is a special case of supramolecular catalysis. Encapsulation systems such as micelles and dendrimers [79]are also used in catalysis to create microenvironments suitable for reactions (or steps in reactions) to progress that is not possible to use on a macroscopic scale.

3.3 Medicinal

Supramolecular chemistry is also important to the development of new pharmaceutical therapies by understanding the interactions at a drug binding site. The area ofdrug deliveryhas also made critical advances as a result of supramolecular chemistry providing encapsulationand targeted release mechanisms [80,81]. In addition, supramolecular systems have been designed to disruptprotein-protein interactions [82,83] that are important to cellular function [84]

3.4 Processing and Data Storage

Supramolecular chemistry has been used to demonstrate computation functions on a molecular scale. In many cases, photonic or chemical signals have been used in these components, but electrical interfacing of these units has also been shown by supramolecularsignal transductiondevices[85,86].Data storagehas been accomplished by the use ofmolecular switcheswithphotochromic [87,88]andphotoisomerizableunits [89,90], byelectrochromicandredox-switchable units [91,92], and even by molecular motion. Syntheticmolecular logic gateshave been demonstrated on a conceptual level. Even full-scale computations have been achieved by semi-syntheticDNA computers. [93]

3.5 Green Chemistry

Research in supramolecular chemistry also has application ingreen chemistrywhere reactions have been developed which proceeds in the solid state directed by non-covalent bonding. Such procedures are highly desirable since they reduce the need for solvents during the production of chemicals [94,95].

3.6 High-Tech Devices

Supramolecular chemistry is often pursued to develop new functions that cannot appear from a single molecule. These functions also include magnetic properties, light responsiveness, self-healing polymers, synthetic ion channels,molecular sensors, etc. Supramolecular research has been applied to develophigh-tech sensors, processes to treat radioactive waste and contrast agents for CAT-scans[96,98].

4. Conclusions

Intensive researches in supramolecular chemistry enable us to synthesize materials with very specific properties for specific applications. It opens up the new era of most effective catalyst synthesis for the catalytic reactions.It enable us template directed drugs synthesis which reduces the side products; molecular encapsulation as well as drug delivery to specific organs. High-tech devices as well as data storagecan be developed by usingmolecular switcheswith photochromic and photoisomerizable units, by electrochromic and redox-switchable units and even by molecular motion are one step ahead to automation. Researches in supramolecular chemistry also enable us

green synthesis of several materials avoiding the uses of several hazardous chemicals.

References

[1] "Chemistry and Physics Nobels Hail Discoveries on Life and Superconductors; Three Share Prize for Synthesis of Vital Enzymes"Harold M. Schmeck Jr.*New York Times*October 15, 1987.
[2] Crystal structure of ahost-guest complexwith a p-xylenediammonium bound within a cucurbit[6]uril reported by Freeman in*Acta Crystallography B*, 1984, 382-387.
[3] Witlicki, Edward H. et al. (2009). "Determination of Binding Strengths of a Host–Guest Complex Using Resonance Raman Scattering".*J. Phys. Chem. A***113** (34): 9450–9457.
[4] "Nanotechnology Star Fraser Stoddart to Join Northwestern".*NewsCenter*. Northwestern University. 2007-08-16. Retrieved2009-01-19.
[5] Coskun, M. Banaszak, R. D. Astumian, J. F. Stoddart, B. A. Grzybowski,*Chem. Soc. Rev.*, 2012, 41, 19-30.
[6] Coskun, J. M. Spruell, G. Barin, W. R. Dichtel, A. H. Flood, Y. Y. Botros, J. F. Stoddart, [http://dx.doi.org/10.1039/C2CS35053J *Chem. Soc. Rev.*, 2012, 41, 4827—4859
[7] Ballardini R, Balzani V, Credi A, Gandolfi MT, Venturi M. (2001). "Artificial Molecular-Level Machines: Which Energy To Make Them Work?". *Acc. Chem. Res.* **34** (6): 445–455.
[8] V. Balzani, M. Gomez-Lopez and J. F. Stoddart (1998) "Molecular Machine", Accounts of Chemical Research, 31 (7): 405-414.
[9] Gonzalez Szwacki, N.; Sadrzadeh, A.; Yakobson, B. (2007). "B_{80} Fullerene: An Ab Initio Prediction of Geometry, Stability, and Electronic Structure". *Physical Review Letters* **98** (16): 166 804. Bibcode:2007.
[10] De, S.; Willand, A.; Amsler, M.; Pochet, P.; Genovese, L.; Goedecker, S. (2011). "Energy Landscape of Fullerene Materials: A Comparison of Boron to Boron Nitride and Carbon". *Physical Review Letters* **106** (22).
[11] Prasad, D.; Jemmis, E. (2008). "Stuffing Improves the Stability of Fullerenelike Boron Clusters".*Physical Review Letters***100**(16): 165504.Bibcode:2008PhRvL.100p5504P.
[12] Tegos, G. P.; Demidova, T. N.; Arcila-Lopez, D.; Lee, H.; Wharton, T.; Gali, H.; Hamblin, M. R. (2005). "Cationic Fullerenes Are Effective and Selective Antimicrobial Photosensitizers". *Chemistry & Biology* **12** (10): 1127.
[13] Taylor, Robert; Coulombe, Sylvain; Otanicar, Todd; Phelan, Patrick; Gunawan, Andrey; Lv, Wei; Rosengarten, Gary; Prasher, Ravi; Tyagi, Himanshu (2013). "Small particles, big impacts: A review of the diverse applications of nanofluids". *Journal of Applied Physics*, Volume 113, Issue 1, pp. 011301-19.
[14] Taylor, Robert A; Otanicar, Todd; Rosengarten, Gary (2012)."Nanofluid-based optical filter optimization for PV/T systems".*Light: Science & Applications***1**(10): e34.
[15] Supramolecular Chemistry: From Molecules to Nanomaterials, P. A. Gale and J. W. Steed (Eds). Wiley (2012), ISBN 978-0-470-74640-0.
[16] Quintana, E. Raczka, L. Piehler, I. Lee, A. Myc, I. Majoros, A.K. Patri, T. Thomas, J. Mule, J.R. Baker Jr. (2002). "Design and Function of a Dendrimer-Based Therapeutic nanodevice targeted to tumor cells through the folate receptor". *Synthesis***19**: 1310–1316.
[17] Tekade, Rakesh Kumar; TathagataDutta, VirendraGajbhiye and Narendra Kumar Jain (2009). "Exploring dendrimer towards dual drug delivery". *Journal of Microencapsulation* (Pharmaceutics Research Laboratory, Department of Pharmaceutical Sciences, DrHari Singh Gour University,) **26** (4): 287–296.
[18] Twyman, L. J.; Ellis, A.; Gittins, P. J. (2012). "Pyridine encapsulated hyperbranched polymers as mimetic models of haeme containing proteins, that also provide interesting and unusual porphyrin-ligand geometries". *Chemical Communications* (Royal Society of Chemistry) **48** (1): 154–156.
[19] TathagataDutta, MinakshiGarg, and N.K.Jain. "Poly(propyleneimine) dendrimer and dendrosome based genetic immunization against Hepatitis B". *Vaccine*. 2008. 26(27-28): 3389-3394.
[20] Crooks, Richard; Scott, Wilson (September 2005). "Synthesis, Characterization, and Applications of Dendrimer-Encapsulated Nanoparticles". *American Chemical Society* (109): 692–704.
[21] Hasenknopf, Bernold; Lehn, Jean-Marie; Kneisel, Boris O.; Baum, Gerhard; Fenske, Dieter (1996). "Self-Assembly of a Circular Double Helicate".*AngewandteChemie International Edition in English***35**(16): 1838.
[22] H. Yan, S. H. Park, G. Finkelstein, J. H. Reif& T. H. Labean (2003). "DNA-Templated Self-Assembly of Protein Arrays and Highly Conductive Nanowires". *Science***301** (5641): 1882–1884.
[23] Hill DJ, Mio MJ, Prince RB, Hughes TS, Moore JS (2001). "A field guide to foldamers". *Chem. Rev.* **101** (12): 3893–4012.
[24] vanGunsteren, Wilfred F. (2007).*Foldamers: Structure, Properties, and Applications; Simulation of Folding Equilibria*. Wiley-VCH Verlag GmbH & Co. KGaA. pp. 173–192.
[25] Foldamers: Structure, Properties, and Applications" Stefan Hecht, Ivan Huc Eds. Wiley-VCH, Weinheim, 2007. ISBN 9783527315635.
[26] vanGunsteren, Wilfred F. (2007). *Foldamers: Structure, Properties, and Applications; Simulation of Folding Equilibria*. Wiley-VCH Verlag GmbH & Co. KGaA. pp. 173–192.*b*
[27] Martinek, T.A.; Fulop, F. (2012). "Peptidic foldamers: ramping up diversity". *Chem. Soc. Rev.* **41**: 687–702.
[28] Juwarker, H.; Jeong, K-S. (2010). "Anion-controlled foldamers". *Chem. Soc. Rev.* **39**: 3664–3674. .
[29] Gellman, Samuel H. (1997). "Introduction: Molecular Recognition". *Chemical reviews* **97** (5): 1231–1232.
[30] Lehn, Jean-Marie(1995). *Supramolecular Chemistry*. Weinheim: Wiley-VCH.ISBN-978-3-527-29312-4.
[31] Baron, Riccardo; McCammon, J. Andrew (2013). "Molecular Recognition and Ligand Binding". *Annual Review in Physical Chemistry* **64**: 151–175.
[32] G. A. Breault, C. A. Hunter and P. C. Mayers (1999). "Supramolecular topology".*Tetrahedron***55**(17): 5265–5293.

[33] Rowan SJ; Cantrill SJ; Cousins GR; Sanders JK; Stoddart JF (March 2002). "Dynamic covalent chemistry". *Angew. Chem. Int. Ed. Engl.* 41 (6): 898–952.
[34] Cacciapaglia R, Di Stefano S, Mandolini L (October 2005). "Metathesis reaction of formaldehyde acetals: an easy entry into the dynamic covalent chemistry of cyclophane formation". *J. Am. Chem. Soc.* 127 (39): 13666–71.
[35] Stryer, L. *Biochemistry*; Fourth Edition edn.; W. H. Freeman and Company: New York, 1995.
[36] F. H. Beijer, H. Kooijman, A. L. Spek, R. P. Sijbesma& E. W. Meijer (1998). "Self-Complementarity Achieved through Quadruple Hydrogen Bonding". *Angew. Chem. Int. Ed.***37** (1-2): 75–78
[37] Kauzmann W (1959). "Some factors in the interpretation of protein denaturation". *Advances in Protein Chemistry* **14**: 1–63.
[38] Lodish, Berk, Zipursky, Matsudaira, Baltimore, Darnell (2000),.*Noncovalent bonds– Molecular Cell Biology (textbook)*, 4thEdn. W. H. Freeman and Company
[39] Anslyn, Eric (2004).*Modern Physical Organic Chemistry*. Sausalito, CA: University Science.ISBN978-1-891389-31-3.
[40] Eisler, Matthew (2010).*Encyclopedia of nanoscience and society*. Thousand Oaks, Calif.: Sage.ISBN978-1-4129-7209-3
[41] W. Rawicz, K. C. Olbrich, T. McIntosh, D. Needham and E. Evans."Effect of chain length and unsaturation on elasticity of lipid bilayers." Biophysical Journal. 79. (2000) 328-39.
[42] David Dunmur; David A. Dunmur; Tim Sluckin (2010-11-04).*Soap, Science, and Flat-Screen TVs: A History of Liquid Crystals*. Oxford University Press. pp.259,260.ISBN978-0-19-954940-5
[43] E. Corvera, O. G. Mouritsen, M. A. Singer and M. J. Zuckermann."The permeability and the effect of acyl chain length for phospholipid bilayers containing cholesterol." BiochimicaetBiophysicaActa. 1107. (1992) 261-270.
[44] M.A. Wahab (2005).Solid State Physics: Structure and Properties of Materials. Alpha Science. pp.1–3.ISBN1-84265-218-4.
[45] F. White (2003).*Fluid Mechanics*.McGraw-Hill. p. 4.ISBN0-07-240217-2.
[46] D.L. Goodstein (1985).*States of Matter*.Dover Phoenix.ISBN978-0-486-49506-4.
[47] L. Valigra (2005)."MIT physicists create new form of matter".MIT News. Retrieved23 February 2010.
[48] V. Bendkowsky*et al*. (2009). "Observation of Ultralong-Range Rydberg Molecules".*Nature***458**(7241): 1005–8.
[49] V. Gill (23 April 2009)."World First for Strange Molecule".BBC News. Retrieved 23 February2010.
[50] Shao, Y.; Zerda, T. W. (1998). "Phase Transitions of Liquid Crystal PAA in Confined Geometries".*Journal of Physical Chemistry B***102**(18): 3387–3394.
[51] G. Murthy *et al*. (1997). "Superfluids and Supersolids on Frustrated Two-Dimensional Lattices".*Physical Review B***55**(5): 3104.
[52] G Kurth, Dirk (2008). "Metallo-supramolecular modules as a paradigm for materials science".*Science and Technology of Advanced Materials*(free-download review)**9**: 014103.
[53] Bureekaew, Sareeya; Shimomura, Satoru; Kitagawa, Susumu (2008). "Chemistry and application of flexible porous coordination polymers". *Science and Technology of Advanced Materials*(free-download review)**9**: 014108.
[54] J. M. Lehn, (1990). "Perspectives in supramolecular chemistry - from molecular recognition towards molecular information-processing and self-organization".*AngewandteChemie-International Edition in English***29**(11): 1304–1319.
[55] Cosic, I (1994). "Macromolecular bioactivity: is it resonant interaction between macromolecules?—theory and applications".*IEEE transactions on bio-medical engineering***1**(12): 1101–14.
[56] Baron, Riccardo; Setny, Piotr; McCammon, J. Andrew (2010)."Water in Cavity-Ligand Recognition".*Journal of the American Chemical Society***132** (34): 12091–12097.
[57] Supramolecular Chemistry, J.-M. Lehn, Wiley-VCH (1995), ISBN 978-3-527-29311-7.
[58] Zhang, Landry, Strano et al. Nature Nanotechnology 2013 http://www.nature.com/nnano/journal/v8/n12/full/nnano.2013.236.html
[59] Bravo, J. A. et al. (1998). "High Yielding Template-Directed Syntheses of [2]Rotaxanes".*Eur. J. Org. Chem.***1998**(11): 2565–2571
[60] Mansy SS[1],Schrum JP ,Krishnamurthy M,Tobé S,Treco DA,Szostak JW (2008) Template-directed synthesis of a genetic polymer in a model protocell. Nature.454 (7200):122-5.
[61] Ikeda, Taichi; Stoddart, James Fraser (2008). "Electrochromic materials using mechanically interlocked molecules".*Science and Technology of Advanced Materials*(free-download review)**9**: 014104.
[62] K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart,*Science*, 2004, 304, 1308-1312.
[63] *Molecular Borromean Rings*Kelly S. Chichak, Stuart J. Cantrill, Anthony R. Pease, Sheng-Hsien Chiu, Gareth W. V. Cave, Jerry L. Atwood,J. Fraser StoddartScience, Vol 304, Issue 5675, 1308-1312 , 28 May**2004.**
[64] *NanoscaleBorromean links for real*Andrea J. Peters, Kelly S. Chichak, Stuart J. Cantrill andJ. Fraser StoddartChemical Communications,**2005**, (27), 3394 – 3396.
[65] *Making Molecular Borromean Rings. A Gram-Scale Synthetic Procedure for the Undergraduate Organic Lab*Cari D. Pentecost, Nicholas Tangchaivang, Stuart J. Cantrill, Kelly S. Chichak, Andrea J. Peters, and J. Fraser Stoddart Vol. 84 No. 5 May**2007**Journal of Chemical Education855.
[66] Astruc D. (2005). "The metathesis reactions: from a historical perspective to recent developments" -*New J. Chem.***29**(1): 42–56.
[67] Alexander C, Andersson HS, Andersson LI, Ansell RJ, Kirsch N, Nicholls IA, O'Mahony J, Whitcombe MJ J. Mol. Recognit. 2006; 19: 106–180, *molecular imprinting science and technology.*
[68] Whitcombe MJ, Kirsch N, Nicholls IA J. Mol. Recognit. 2014; 27: 297-401 *Molecular Imprinting Science and Technology.*

[69] Satir, Peter; Soren T. Christensen (2008-03-26) 'Structure and Function of mammalian cilia' Histochemistry and Cell Biology, 129 (6) 688.
[70] Ballardini R, Balzani V, Credi A, Gandolfi MT, Venturi M. (2001)."Artificial Molecular-Level Machines: Which Energy To Make Them Work?".*Acc. Chem. Res.***34**(6): 445–455.
[71] V. Balzani, M. Gomez-Lopez and J. F. Stoddart (1998), 'Molecular Machines' Accounts of Chemical Research**, 31** (7) 405-414.
[72] Vincent, Julian F.V.; Bogatyreva, Olga A., Bogatyrev, Nikolaj R., Bowyer, Adrian, Pahl, Anja-Karina (21 August 2006). "Biomimetics: its practice and theory".*Journal of The Royal Society Interface***3**(9): 471–482.
[73] Bharat Bhushan (15 March 2009) Biomimetics: lessons from nature–an overview http://rsta.royalsocietypublishing.org/content/367/1893/14.
[74] Supramolecular Chemistry: From Molecules to Nanomaterials, P. A. Gale and J. W. Steed (Eds) Wiley (2012) ISBN-978-0-470-74640-0.
[75] G Kurth, Dirk (2008). "Metallo-supramolecular modules as a paradigm for materials science".*Science and Technology of Advanced Materials*(free-download review)**9**: 014103.
[76] Helmut Knözinger, Karl Kochloefl "Heterogeneous Catalysis and Solid Catalysts" in Ullmann's*Encyclopedia of Industrial Chemistry*2002, Wiley-VCH, Weinheim.
[77] "Recognizing the Best in Innovation: Breakthrough Catalyst".*R&D Magazine*, September 2005, p. 20.
[78] BårdLindström and Lars J. Petterson (2003) "A brief history of catalysis,"*Cattech*,**7**(4): 130-138. Available on-line at:ScienceNet.
[79] D. Astruc, E. Boisselier, C. Ornelas (2010). "Dendrimers Designed for Functions: From Physical, Photophysical, and Supramolecular Properties to Applications in Sensing, Catalysis, Molecular Electronics, and Nanomedicine".*Chem. Rev.***110**(4): 1857–1959.
[80] Silverman, Richard B. (2004).*The organic chemistry of drug design and drug action*(2nded.). Amsterdam [u.a.]: Elsevier.ISBN978-0-12-643732-4.
[81] Crooks, Richard; Scott, Wilson (September 2005). "Synthesis, Characterization, and Applications of Dendrimer-Encapsulated Nanoparticles". *American Chemical Society* (109): 692–704.
[82] Phizicky, E. M.; Fields, S. (1995)."Protein-protein interactions: Methods for detection and analysis".*Microbiological reviews***59**(1): 94–123.
[83] Terentiev, A.A.; Moldogazieva, N.T.; Shaitan, K.V. (2009). "Dynamic proteomics in modeling of the living cell. Protein–protein interactions.".*Biochemistry. Biokhimiia***74**(13): 1586–607.
[84] Bertrand, N, Gauthier, M.A, Bouvet, C, P., Petitjean, A, Leroux, J. C., Leblond, J. (2011), New Pharmaceutical Applications for molecular binders, Journal of Controlled Release, **155** (2), 200-210 and Proceedings of the 15thInternational Symposium on Recent Advances in Drug Delivery System.
[85] Krauss, Gerhard (2008).*Biochemistry of Signal Transduction and Regulation*. Wiley-VCH. p.15.ISBN - 978-3527313976.
[86] Gilcrease MZ. (2006). "Integrin signaling in epithelial cells".*Cancer Lett.***247** (1): 1–25.
[87] Irie, M. (2000). "Photochromism: Memories and Switches – Introduction".*Chemical Reviews***100**(5): 1683–1684.
[88] Such, Georgina K.; Evans, Richard A.; Davis, Thomas P. (2006). "Rapid Photochromic Switching in a Rigid Polymer Matrix Using Living Radical Polymerization".*Macromolecules***39**(4): 1391.
[89] Mammana, A. et al. (2011). "A ChiropticalPhotoswitchable DNA Complex".*Journal of Physical Chemistry B***115**(40): 11581–11587
[90] Vachon, J. et al. (2014). "An ultrafast surface-bound photo-active molecular motor".*Photochemical and Photobiological Sciences***13**(2): 241–246.
[91] Rodgers, Glen (2012).*Descriptive Inorganic, Coordination, and Solid-State Chemistry*. Brooks/Cole, Cengage Learning. p. 330.ISBN978-0-8400-6846-0.
[92] Tratnyek, Paul G.; Grundl, Timothy J.; Haderlein, Stefan B., eds. (2011).*Aquatic Redox Chemistry*. ACS Symposium Series**1071**
[93] Nayebi, Aran (2009). "Fast matrix multiplication techniques based on the Adleman-Lipton model".*arXiv: 0912.0750*: 1–13.
[94] ichel Baron (2012). "Towards a greener pharmacy by more eco design".*Waste and Biomass Valorization* .**3**: 395–407.
[95] J.A. Linthorst (2010). "An Overview: Origins and Development of Green Chemistry".*Foundations of Chemistry***12** (1): 55–68.
[96] Herman, G. T., Fundamentals of computerized tomography: Image reconstruction from projection, 2nd edition, Springer, 2009
[97] Poston, edited by Michael T. Ryan, John W. (2005).*A half century of health physics*. Baltimore, Md.: Lippincott Williams & Wilkins. p. 164.ISBN9780781769341.
[98] Hill B, Venning AJ, Baldock C, 2005. A preliminary study of the novel application of normoxic polymer gel dosimeters for the measurement of CTDI on diagnostic X-ray CT scanners. Medical Physics. 32 1589-1597