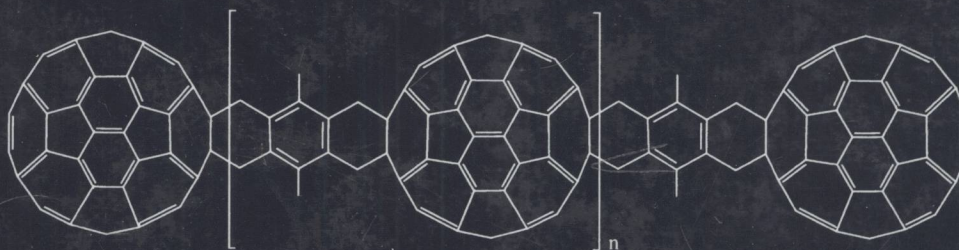


Advanced Functional Molecules and Polymers

Volume 1
Synthesis

Edited by
Hari Singh Nalwa



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Edited by

Hari Singh Nalwa

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Advanced Functional Molecules and Polymers

*To my most honorable Gurus
Professor Satya Vir Arya
and
Professor Padma Vasudevan*

Preface

Organic polymers are the most fascinating materials in the modern industrial era and have emerged as one of the most valued classes of materials in our everyday life. Organic polymers offer widespread applications in many fields of science ranging from solid state technology to biomedical engineering. The applications of polymeric products cover almost every area of consumer products such as telecommunications, the internet, optical fibers, light-emitting devices, displays, aircraft, audio-video systems, television sets, computers, insulators, electronic devices, contact lenses, kitchenware, home appliances, fabrics, sportswear, toys, building materials, automobiles, adhesives, paints, fillers, plastic wall and floor coverings, furniture, pipes, technical instruments, etc. Almost every corporation and institute in the entire world is involved in polymeric materials one way or the other because of their increasing demands. The superiority of polymeric materials is due to the aspects of their tremendous versatility and astonishing degree of tailoring to bring them closer to the novel applications. From a technological point of view, organic polymers offer enormous advantages over traditional materials such as metals, ceramics, glasses, wood, leather, etc. Polymeric materials are light weight, flexible and tough materials, they can be processed in the form of ultrathin films, fibers and even as liquid crystals, they offer low-cost mass production, they manifest good durability and environmental stability, and some are biocompatible.

The polymeric materials discussed in this book are key elements of continued scientific and technological advances in the 21st century and belong to one of the most diverse research fields. The four volume set of *Advanced Functional Molecules and Polymers* consolidates the current knowledge of science and technology of polymers and other low molecular weight organic materials into a single reference source including their synthesis, processing, theory, spectroscopy, and structure–property relationship to device applications. This book aims to bring together all aspects of functional molecular and polymeric materials currently studied in academic and industrial research by covering every single aspect of their science and engineering. The book draws on two decades of pioneering research on functional materials and their technology for the first time, while emphasizing the multidisciplinary nature. This book has 34 chapters presented in four volumes, written by 74 authors coming from 18 countries. The cutting edge state-of-the-art review chapters contain the most up-to-date research in the field of functional polymeric materials.

Volume 1 focuses on different topics related to synthetic aspects that include oligomers and polymeric fullerene derivatives; functional polymers; block and graft copolymers; metal-containing macromolecules; highly cross-linked polymers based on mesogenic monomers; synthesis of block copolymers with combination of different polymerization routes; syntheses and structures of thermotropic liquid crystalline polymers; structure–property relationships in polyurethane ionomers; and novel photoreactions of azadienes and related compounds.

Volume 2 is focused on processing and spectroscopy of polymeric materials covering various spectroscopic techniques. The topics in this volume include surface modification of polymers *via* molecular design; nanostructured polymers *via* microemulsion polymerization; polymer-stabilized metal nanoparticles; monolayers and membranes formed from polymers with surface active head groups; stereochemical and compositional assignments of polymers by NMR spectroscopy; infrared spectroelectrochemistry on conducting polymers and fullerenes; spectroelectrochemistry of intrinsically conducting polymers and fullerenes; structural studies of polymer systems using small angle neutron scattering; and methyl-group dynamics in glassy polymers by neutron scattering.

Volume 3 focuses on electronic and photonic properties of defined chain length oligomers and polymers. The topics include thin film photoconductors; synthesis and properties of electrically conducting polymers such as polythiophenes, polypyrroles, polyacetylenes, polyanilines, poly(*p*-phenylenes) and rigid-rod polymers; electronically conducting ion-exchange polymers; photo-induced non-centrosymmetry in azo-polymers using dual-frequency interferences; second-order nonlinear optical molecules and polymers; poly(*p*-phenylene vinylene) derivatives as photonic materials; and fluorescence probes used in characterization of materials.

Volume 4 focuses on various physical properties and applications of polymeric materials. The topics include photodegradation and stabilization of polymers; properties of immobilized proteins; conduction of heat in polymers; polymer composite propellants; polyimides; ion beam processing and modification of polymers; polymeric membranes for reverse osmosis, ultrafiltration, microfiltration, gas separation, pervaporation and reactor applications; tribology of engineering polymers; use of functional polymers for metal ion complexation and separation; polymer-supported reagents; and the use of polyacetals in biomedical applications.

This book summarizes the current status of the field, covering important scientific and technological developments made over past decades with contributions from internationally recognized experts from all over the world. Fully cross-referenced, the book has clear, precise and wide appeal as an essential reference source long overdue for the scientific community involved in polymer science and engineering. With more than 8,000 bibliographic citations and nearly 1,500 illustrations, tables, chemical structures and equations, this book is an invaluable reference source for graduate and advanced level undergraduate students and scientists working in chemistry; polymer chemistry; polymer engineering; solid-state physics; materials science; electrical, optical and chemical engineering.

I greatly appreciate the tremendous efforts and cooperation of all the contributing authors who devoted their valuable time in preparing state-of-the-art chapters for this book. I would like to thank Professor Seizo

Miyata of the Tokyo University of Agriculture and Technology (Japan), and many colleagues at the Hitachi Research Laboratory, Hitachi Ltd., Japan for their kind support during my stay in Japan. I would like to give my special thanks to my friends Krishni Pal Raghuvanshi, Rakesh Misra, Jagmer Singh, Ranvir Singh Chaudhary, Ashish Kumar and other colleagues who supported my efforts in the compilation of this book. I have great appreciation for my wife Dr Beena Singh Nalwa for her continuous cooperation and patience in enduring this work at home during weekends and late nights, the moral support of my parents Kadam Singh and Sukh Devi and the love of my children, Surya, Ravina and Eric in this exciting enterprise.

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Biographical Note



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Dr Nalwa is the founder and Editor-in-Chief of the *Journal of Nanoscience and Nanotechnology* (from 2001). He was the founder and Editor-in-Chief of the *Journal of Porphyrins and Phthalocyanines* published by John Wiley & Sons (1997–2000) and serves on the editorial boards of the *Journal of Macromolecular Science-Physics* (from 1994), *Applied Organometallic Chemistry* (1993–1999), the *International Journal of Photoenergy* (from 1998) and *Photonics Science News* (from 1995). He also serves as a referee for many international journals, that include the *Journal of the American Chemical Society*, the *Journal of Physical Chemistry*, *Applied Physics Letters*, the *Journal of Applied Physics*, *Chemistry of Materials*, the *Journal of Materials Science*, *Coordination Chemistry Reviews*, *Applied Organometallic Chemistry*, the *Journal of Macromolecular Science-Physics*, *Applied Physics*, *Materials Research Bulletin* and *Optical Communications*.

Dr Nalwa is a member of the American Chemical Society (ACS), American Physical Society (APS), Materials Research Society (MRS), Electrochemical Society (ECS) and the American Association for the Advancement of Science (AAAS). He has been awarded a number of prestigious fellowships that include a National Merit Scholarship, Indian Space Research Organization (ISRO) Fellowship, Council of Scientific and Industrial Research (CSIR) Senior fellowship, NEC fellowship and a Japanese Government Science & Technology Agency (STA) fellowship. He was also an Honorary Visiting Professor at the Indian Institute of Technology in New Delhi. Dr Nalwa has been cited in the Who's Who in Science and Engineering, Who's Who in America, Who's Who in the World and the Dictionary of International Biography.

Dr Nalwa received a B.Sc. degree in biosciences from Meerut University in 1974, a M.Sc. degree in organic chemistry from the University of Roorkee in 1977, and a Ph.D. degree in polymer science from the Indian Institute of Technology in New Delhi in 1983. He was a guest scientist at the Hahn-Meitner Institute in Berlin, Germany (1983), research associate at the University of Southern California in Los Angeles (1984–1987) and the State University of New York at Buffalo (1987–1988). In 1988, he moved to the Tokyo University of Agriculture and Technology, Japan as a lecturer (1988–90) where he was teaching and conducting research on electronic and photonic materials. His research activities include studies of ferroelectric polymers, nonlinear optical materials for integrated optics, low and high dielectric constant materials for microelectronics packaging, electrically con-

conducting polymers, electroluminescent materials, nanocrystalline and nanostructured materials, photocuring polymers, polymer electrets, organic semiconductors,

Langmuir-Blodgett films, high temperature-resistant polymer composites, water-soluble polymers, rapid modeling and stereolithography.

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Contents

Preface	ix
Biographical Note	xi
Contributors	xiii
1 Monomeric, Oligomeric, and Polymeric Fullerene Derivatives..... <i>S. Samal and K.E. Geckeler</i>	1
2 Metal-Containing Macromolecules..... <i>D. Wöhrle and A. Pomogailo</i>	87
3 Highly-Crosslinked Polymers with Ordered Structures Based on Mesogenic Monomers..... <i>V. Strehmel</i>	163
4 Synthesis of Block Copolymers by Combination of Different Polymerization Routes <i>Y. Yagci</i>	233
5 Syntheses and Structures of Thermotropic Liquid Crystalline Polymers..... <i>G. Galli</i>	271
6 Structure–Property Relationships in Polyurethane Ionomers <i>P. Pissis, A. Kyritsis, G. Georgoussis and V. Shilov</i>	317
7 Novel Photoreactions of Azadienes and Related Compounds. Synthetic Applications and Mechanistic Studies..... <i>D. Armesto, M.J. Ortiz and A.R. Agarrabeitia</i>	351
Index	381

Monomeric, Oligomeric, and Polymeric Fullerene Derivatives

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Contents

1	Introduction	2	6	Functionalization <i>via</i> Three-Membered Rings	12
2	Fullerenes as Superalkenes	2	6.1	Carbon Bridging	12
3	Electron Affinity	3	6.1.1	Cyclopropanation Reactions Leading to Donor–Acceptor Molecules	15
4	Exo- and Endohedral Complex Formation	4	6.1.2	Regioselective Synthesis	20
5	Simple Functionalization Reactions	5	6.2	Nitrogen Bridging	24
5.1	Hydrogenation	5	6.2.1	Bisazafullerenes and Fullerides	28
5.2	Halogenation	5	6.3	Oxygen Bridging	29
5.3	Nitration	6	6.4	Metal Bridging	31
5.4	Sulphonation	6	7	Functionalization <i>via</i> Four-Membered Rings	31
5.5	Hydroxylation	6	8	Functionalization <i>via</i> Five-Membered Rings	33
5.6	Alkylation and Arylation	6	8.1	Trimethylene Methane Adducts	33
5.6.1	Nucleophilic Reactions	6	8.2	Substituted Pyrrolidines as Donor–Acceptor Systems	36
5.6.2	Fullerenation of Aromatic Compounds	10	8.3	Attachment of Five-Membered Heterocyclic Rings	38
5.6.3	Radical Addition	10	8.4	Five-Membered Rings with Other Nonmetal and Metal Heteroatoms	39
5.6.4	Ene Reaction	10			
5.6.5	Carbene Addition	11			
5.6.6	Functionalization by Photo- Induced Electron Transfer	11			
5.6.7	Addition of Amines	11			

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9	Functionalization <i>via</i> Six-Membered Rings	40	13	Macromolecular Fullerenes	64
9.1	Diels-Alder Reaction	40	13.1	Fullerene Side-Chain Polymers	65
9.2	Retro-Diels-Alder Reaction	42	13.2	Fullerene Main-Chain Polymers	69
9.3	<i>o</i> -Quinodimethane as Intermediate		13.3	Free Radical Copolymerization	69
	Diene for Diels-Alder Reaction	45	13.4	Fullerene-Initiated Polymerization	72
9.4	Other Functionalization Reactions	46	13.5	Fullerene Ball-and-Chain Polymers	72
9.5	Donor-Acceptor Systems	53	13.6	Fullerene Telechelic Polymers	72
9.6	Attachment of Heterocycles	55	13.7	Fullerene Macrocycles	74
9.7	Direct Attachment of Heterocyclic Rings	57	13.8	Fullerene Dendrimers	77
9.8	[2 + 6] and [2 + 2 + 2] Cycloadditions	58	13.9	Star-Shaped Species with Fullerene Cores	78
10	Azafullerenes	58	14	Conclusions	79
11	Fullerene Dimers	60		Acknowledgements	80
12	Fullerene Tri- and Tetramers	62		References	80

1 Introduction

Carbon clusters were known to exist in carbon arc as early as 1959 [1]. By the laser vaporization technique, C_{60} was first produced from a graphite target by Dietz *et al.* in 1981 [2]. In 1984, larger, even-numbered carbon clusters (C_n , $n = 30-190$) were reported [3]. Kroto *et al.* [4] described the nature and chemical reactivity of C_{60} in 1985. In 1990, Krätschmer *et al.* [5] suggested a method for preparing macroscopic quantities of C_{60} . Since then, the interest on the properties of fullerenes and their derivatives have grown enormously as seen from the avalanche of literature on the subject [6, 7]. In fullerenes, several reactions could be carried out leading to attachment of atoms, molecules, ions, radicals by covalent, ionic and charge-transfer means. These reactions often led to products associated with specific applications. Apparently no other molecule has received so much of attention as is C_{60} in recent times. Looking at a model of C_{60} and realizing that this molecule is made up of only carbon atoms arranged in the form of a soccer ball, and exhibiting a broad range of physical, chemical and biological properties, one would not resist from describing it as 'the most beautiful molecule' [7(d)].

C_{60} was named buckminsterfullerene after Buckminster Fuller, American architect, engineer and constructor of the geodesic dome. C_{60} (buckminsterfullerene) **1** and C_{70} (falmarene) **2** are the most accessible members of the family on which extensive studies have been carried out (Figure 1). Each molecule of fullerene family (C_n) consists of 12 pentagons and m number of hexagons (other than one), conforming to the relation $m = (n - 20)/2$

(Euler's theorem). Therefore C_{60} is composed of 32 faces of which 12 are pentagons and 20 are hexagons and the carbon atoms are arranged at the 60 vertices of a truncated icosahedron. C_{70} consists of 12 pentagons and 25 hexagons and has D_{5h} symmetry. C_{60} has only one type of carbon atoms, however, and two types of C—C bonds, i.e., at the 6,6- and 5,6-ring fusion sites. In contrast, C_{70} consists of 5 types of carbon atoms and eight types of C—C bonds.

2 Fullerenes as Superalkenes

C_{60} is the smallest fullerene in which all the 12 pentagons are isolated from each other. A hexagon containing three π -bonds and fused to two pentagons can be represented in three possible ways, each existing as a resonating pair (Figure 2). Out of the six possible structures (3–8), there is one structure (5) where there is no double bond at the 5,6-ring junction. A double bond in a five-membered ring increases strain and therefore decreases stability.

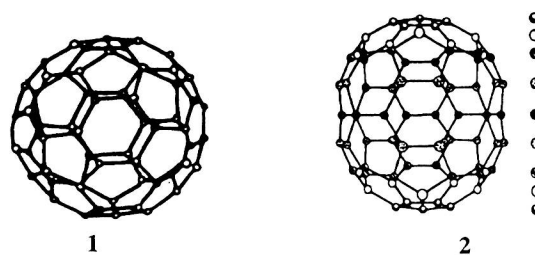


Figure 1 Buckminsterfullerene (**1**) contains one type of carbon atoms whereas falmarene (**2**) has five types.

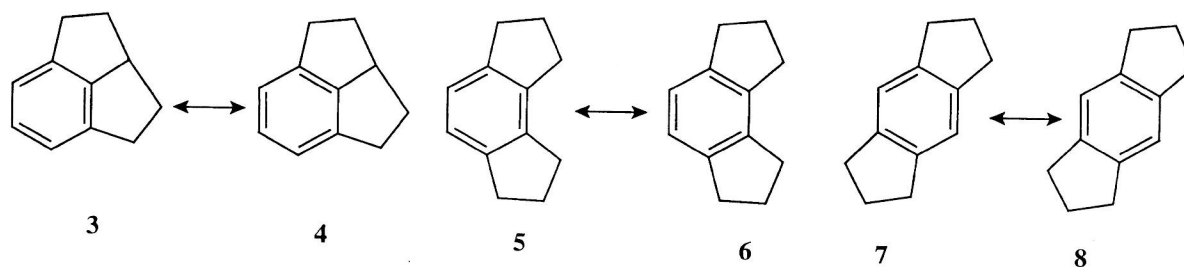


Figure 2 Six possible arrangements of a hexagon fused to two pentagons. In structure 5 there is no double bond in the five-membered rings.

For fullerene to be structurally stable, all the double bonds should be placed in such a manner that there would be no double bonds at the 5,6-ring junctions. Theoretical calculations show that 12,500 resonating structures are possible for C_{60} . Nevertheless, there is only one structure in which the double bonds are localized, no double bonds being present at the 5,6-ring junction making fullerene a reactive molecule containing 30 π -bonds. The $C=C$ bonds of C_{60} react like those of very electron-deficient arenes and alkenes. Therefore C_{60} behaves as an electron-deficient 'superalkene' rather than as a 'superaromatic'.

3 Electron Affinity

The twelve pentagons in C_{60} are arranged in the form of six perylene units (**9**) (Figure 3). Six electrons can be reversibly added to C_{60} across the perylene units. Addition of one electron to each perylene unit creates aromaticity in one of the pentagonal rings (**10**, **11**). This is the driving force for octahedral addition. Electron rich reagents can substitute C_{60} multiple times and a total of at least 12 carbon atoms of the C_{60} framework can participate in bonding. Electron affinity and ionization potential of C_{60} is high. Electron capture produces more sp^3 -character which decreases the strain energy while electron loss increases the sp^2 -character increasing ring strain. Electrochemical reduction of C_{60} to the -6 state can be accomplished in liquid ammonia in the presence of K^+ . A general method capable of generating stable C_{60}^{n-} species where $n = 1-6$ has been developed. Using a

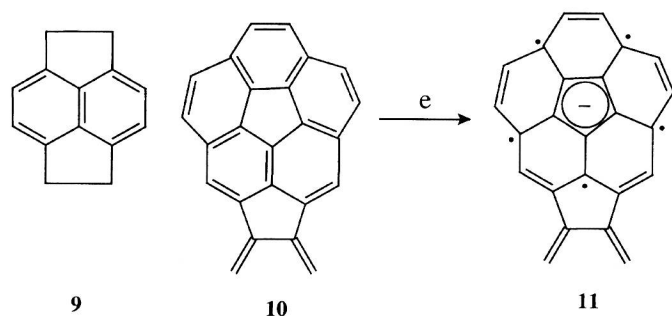


Figure 3 Addition of an electron brings in aromaticity in a perylene unit.

suitably chosen optimal solvent composition, C_{60} and C_{70} could be reduced to C_{60}^{6-} and C_{70}^{6-} .

C_{60} exhibits semiconducting properties in the presence of an electron-donating species. A number of reports exploring the semiconducting properties of metal-doped fullerene are available. Haddon *et al.* [8] reported alkali metal-doped conducting films of C_{60} and C_{70} which was attributed to the formation of energy bands from the π -orbitals of C_{60} and C_{70} , and is partially filled with carriers on doping. The highest conductivities observed in the doped films are 4 S/cm (Cs/C_{60}), 100 (Rb/C_{60}), 500 (K/C_{60}), 20 (Na/C_{60}), 10 (Li/C_{60}), and 2 (K/C_{70}). Yamada *et al.* [9] reported solar cells made from fullerenes. The solar cells of doped- C_{60} as semiconducting material used the *n*- or *p*- layers to form *homo*- or *hetero*-junctions. Haddon [10] reported C_{70} thin film transistors made out of thin films of conductivity 2×10^{-9} S/cm.

Fullerenes, due to their strong electron accepting ability can be hole generators in conducting polymers sensitizing photoinduced charge transfer. Photoconducting films of poly(vinyl carbazole) doped with fullerenes have been reported [11]. The photoconductivity of poly(2,5-dialkoxy-*p*-phenylene-vinylene) is remarkably enhanced by several orders of magnitude upon introduction of several mole% of C_{60} [12]. Positive polarons photogenerated with increased efficiency due to autotization of excitons and/or photopumping from fullerene are considered to be responsible for enhanced photoconductivity. Photoluminescence of polymer is strongly quenched upon C_{60} doping due to dissociations of excitons accompanied by electron transfer to fullerene.

The introduction of 1% of fullerene into a polystyrene (PS) matrix leads to a significant increase in the electrical conductivity of the system [13]. Films of fullerene-containing PS are prepared by mixing toluene solutions of PS and C_{60} and developed on Si, GaAs and glass substrates. The general features of charge-transfer processes in fullerene/conducting polymers (CP) systems, such as energetics of photoinduced charge transfer (PCT) between C_{60} and CP π -electronic states, geometry of π - π overlapping and the role of self-trapping effects to polaronic states on C_{60} and CP chains on the PCT dynamics, were analyzed [14].

4 Exo- and Endohedral Complex Formation

The structure of C_{60} is comprised of rigid spheres of radius 0.498 nm (4.98 Å) with fcc packing, leaving two vacant tetrahedral sites and one octahedral site per C_{60} molecule. These sites are of sufficient size to accommodate spheres of radius 0.112 nm (1.12 Å) and 0.206 nm (2.06 Å), respectively. A number of metal intercalated complexes are known. Fullerenes show a marked tendency to crystallize with solvent molecules trapped in the lattice to form host-guest complexes such as $[C_{60}(\gamma\text{-cyclodextrin})_2]$ and $[C_{60}(1,4\text{-hydroquinone})_3]$. C_{60} also forms charge-transfer complex with a host of molecules such as *bis*(ethylenedithio)tetrathiafulvene.

C_{60} reacts with C^+ over the energy range 2 to 78 eV to give C_{61}^+ , which decays to give C_{60}^+ and C. C_{60}^+ forms exohedral complexes with H and He. C_nHe^+ reacts with D_2 , N_2 , NO, or O_2 (Figure 4). Several other nonmetals like P_4 , S_8 , Si were also incorporated into C_{60} . The metal fullerene complexes were produced by laser vaporization of the metal-graphite mixture under high temperature/argon flow conditions [15]. MC_{60}^+ is found to be very stable and can be fragmented only under extreme activation conditions followed by the sequential loss of C_2 species. Exohedral MC_{60}^+ , $M = \text{Li}-\text{Cs}$, Fe, Co, Ni, Cu, Rh, La, U, and VO was formed by direct attachment of M^+ with C_{60} by charge transfer. C_{60} also forms ternary fullerides, like Ba_2CsC_{60} . The fulleride adopts a novel orientation ordering of the anions in which the Ba cations occupy the tetrahedral sites and Cs the octahedral sites.

A novel synthetic route to the formation of less air-sensitive fullerene superconductors by mixing oxygen-containing alkaline compounds with C_{60} is known [16]. Khairullin *et al.* [17] have systematically studied a new Na-doped C_{60} superconductor prepared from NaN_3 . Hirozawa [18] reported superconductor thin films comprising a C_{60} layer and a group II element layer alternatively grown on plane of a substrate selected from RbI,

RbBr, RbCl, RbF, KI, KBr, KCl, KF, NaBr, NaCl or NaF and containing Na or Li. The superconductive materials have a high superconductive transition temperature.

The synthesis of alkali metal-intercalated fulleride superconductors (M_xC_{60} , $x = 3$) are reported by Fischer *et al.* [19] Wudl *et al.* [20] observed the superconductivity for K_3C_{60} at 18 K and Broderick [21] reported the solution phase synthesis of superconducting M_3C_{60} via soluble alkali metal fulleride precursors. Intercalation of alkali metals by reduction of fullerene to give fullerides M_nC_{60} ($M = \text{Li}-\text{Cs}$ and $n = 0.5-6$) is reported [22]. The synthesis of intercalated compounds of fullerenes by thermal decomposition of azides of K and Na is also reported [23].

Henry *et al.* [24] reported the reaction of face-centered cubic Na_3C_{60} with ammonia at room temperature. The product $(NH_3)_6Na_3C_{60}$, in which both octahedral and tetrahedral interstices in the fulleride array are occupied, despite the similarity in C_{60}^{3-} packing to that in CsC_{60} , shows no superconductivity above 6 K. M_6C_{60} and M_6C_{70} ($M = \text{Cs}, \text{K}, \text{Na}$) exhibit remarkable catalytic activities in H_2-D_2 exchange and olefin hydrogenation at low temperature. The catalytic activities of M_6C_{60} in H_2-D_2 exchange is strongly dependent on metal size, reactivity decreasing in the order $Cs \gg K \gg Na$.

Due to the ~ 0.7 nm (7 Å) diameter of the C_{60} cavity, other elements and small molecules can be encapsulated into the cavity which alters its physical and chemical properties. This field has long attracted attention as new chemical entities with novel properties could be synthesized. The development is summarized in a review on endohedral complexes [25]. Endohedral complexes $M@C_{60}^+$ ($M = \text{La}, \text{K}, \text{Cs}, \text{He}, \text{Ne}, \text{Ar}, \text{Y}, \text{H}_2$) have been formed in the gas phase and $M@C_{70}^+$ can be formed by the reaction of $M@C_{60}^+$ and C_{70} . Cosmic ray interactions may also lead to the formation of endohedral complexes of H, D, and He trapped in fullerene cages. The endohedral metallofullerenes are regarded as a sort of 'super atom'. The charges on the metal is little changed even when $M@C_n$ loses or accepts an electron. This allows the formal view that electron removal or gain takes place on the C_n cage, with the metals acting as a positive core.

Edelmann [26] discussed in a recent review several endohedral metallofullerenes $Ln@C_{2n}$ ($L = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \text{Gd}$; $n = 37-45$), $Ln_2@C_{80}$ ($Ln = \text{Sc}, \text{La}$), $Sc_2@C_{2n}$ ($n = 37, 41, 42$) and $Sc_3@C_{82}$. Scandium preferably forms endohedral fullerene complexes with two atoms trapped inside the fullerene cage ($Sc_2@C_{74}$, $Sc_2@C_{82}$ and $Sc_2@C_{84}$). Other major species that form during the course of reaction are $Sc@C_{82}$ and $Sc_3@C_{84}$. In $Sc_3@C_{82}$, the three Sc atoms form an equatorial triangle. The endohedral metallofullerene $La@C_{82}$ was derivatized yielding an exohedral adduct, and $Gd@C_{82}$ was derivatized with 1,1,2,2-tetramesityl-1,2-disilirane by photoirradiation and thermal reaction. Though the disilirane did not add thermally to empty fullerenes such as C_{60} ,

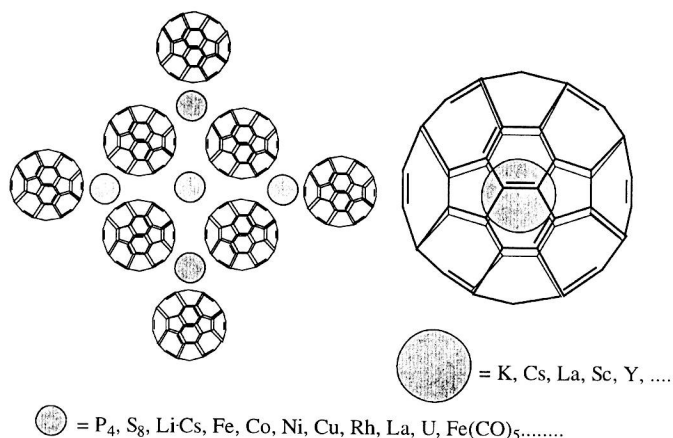


Figure 4 Exo- and endohedral complex formation.

C₇₀ and C₈₂, a facile thermal addition to Gd@C₈₂ took place. This is because Gd@C₈₂ is a stronger electron acceptor than empty fullerenes.

5 Simple Functionalization Reactions

5.1 Hydrogenation

Different routes to hydrogenated fullerenes (called fullerenes, C₆₀H_{2n}) include Birch reduction, hydroboration, hydrozirconation, solution phase and solid phase hydrogenation, hydrogenation by addition of hydrogen atoms, transfer hydrogenation, electrochemical reduction, as well as chemical reduction with diimide, chromous acetate, photoinduced electron transfer, and with hydride reducing agents. Under Birch reduction conditions (Li, liquid NH₃, *t*-BuOH), C₆₀H₃₆, C₆₀H₁₈, and C₆₀H₂ were isolated [27]. Proposed structure of C₆₀H₃₆ consists of only isolated double bonds and non-conjugated or aromatic double bonds. The polyhydrogenated species are unstable towards light and undergo oxidative degradation. In absence of light and oxygen, C₆₀H₃₆ exhibits high thermal stability. Further reduction of C₆₀H₃₄ gives trimethylene adducts.

Treatment of fullerenes with reducing metals and proton sources leads to the formation of C₆₀H_{2n} and C₇₀H_{2n}. Zinc/HCl_{conc} is an excellent and rapid reducing agent for benzene or toluene solutions of fullerenes at room temperature. There are other numerous metals that are useful for the preparation of C₆₀H_{2n} [28]. The reaction of C₆₀ with a variety of metals was investigated, using metals that span a broad range of reducing power, from tin to magnesium, providing useful synthetic route to a number of reduced fullerenes including C₆₀H₂, C₆₀H₄, and C₆₀H₆. It was determined that, despite the huge number of isomers that are possible, a small number are actually formed in these cases. For example, only two isomers of C₆₀H₆ in a 6:1 ratio are obtained with the Zn(Cu) reduction of C₆₀. Three isomers of C₇₀H₁₀ are produced, in ratios that are dependent on reaction time.

The direct solid state synthesis of C₆₀H₂ was carried out by controlling amount of hydrogen [29]. Palladium hydride was used as the source of hydrogen. In addition to C₆₀H₂, small amounts of C₆₀H₄ were obtained. Electrochemical behavior of C₆₀H₂ is very similar to the parent fullerene with C₆₀H₂ being only slightly difficult to reduce [30]. The addition of a single electron is sufficient to induce conversion of C₆₀H₂ to C₆₀. C₆₀H₂ is unstable in presence of C₆₀.

Transfer hydrogenation of C₆₀ with dihydroanthracene produces C₆₀H₁₈ or C₆₀H₃₆ depending on the reaction conditions [31]. The selective two-electron reduction of C₆₀ to 1,2-dihydro[60]fullerene was attained *via* photoinduced electron transfer from 10-methyl-9,10-dihydroacridine to the triplet excited state of C₆₀ in the

presence of trifluoroacetic acid in benzonitrile under irradiation with visible light [32].

5.2 Halogenation

Halogens (fluorine, chlorine, bromine, iodine) can add to the fullerene framework in different proportions giving varieties of products. In the stabilities of the various isomers generated by the addition of halogens to the conjugated double bonds of C₆₀ to form C₆₀X_n have indicated a strong preference for 1,2-addition with X = F and Cl while preference for 1,4 addition with X = Br and I due to their large size. The 1,2-isomers will be clearly destabilized by steric interaction, as X becomes larger.

Bromination of C₆₀ in neat bromine gives evidence for the uptake of 28 bromines to give a quantitative yield of yellow bromine soluble microcrystals which is believed to be C₆₀Br₂₄ along with some C₆₀Br₈ and C₆₀Br₆ [33]. The bromo compound decomposes to C₆₀ on heating and the stability order is fluoro > chloro > bromo and C₆₀Br₂₄ > C₆₀Br₈ > C₆₀Br₆. The instability of C₆₀Br₈ and C₆₀Br₆ may reflect the presence of four and two double bonds in pentagonal rings in their respective structures and C₆₀Br₆ contains an eclipsing steric interaction [34]. The bromine adds to the carbon frame work by 1,4-addition to fused pairs of six-membered rings with the closest Br, Br placement being 1,3.

The treatment of C₆₀ with chlorine in chloroorganic solvents at various temperatures did not result in any detectable reaction but in a hot glass tube under a slow stream of chlorine gas, the reaction takes place readily. On the average 24 chlorine atoms are added to the skeleton [35]. There are reports of addition of ICl to C₆₀ in toluene at room temperature to give a polychloro derivative (C₆₀Cl₆) which is isostructural with C₆₀Br₆. Reaction of iodine monochloride with a benzene solution of C₇₀ produced C₇₀Cl₁₀ [36]. The compound decomposes slowly in air, which was attributed to instability arising from the adjacent and eclipsed chlorines. The proposed structure is unique for a halogenated fullerene in having no double bonds in pentagons. Methoxy groups can replace all chlorine atoms from polychlorinated derivative to give the polymethoxy derivative.

In contrast to the polybrominated and polychlorinated product, addition of sixty fluorines to C₆₀ has been also reported [37]. Stability decreases beyond C₆₀F₄₈ making subsequent addition of fluorine very slow. Fluoro compounds are much more soluble and reactive but their formation is difficult to control. Fluorinated C₇₀ seems to be less stable than fluorinated C₆₀. Fluorinated C₆₀ undergoes nucleophilic substitution by hydroxide ion and the rate of the reaction decreases as the fluorine content becomes reduced. Higher fluoro-fullerenes are strong oxidizing and fluorinating agents. The double charged anions of C₆₀F_x (*x* = 48 and 46) can be generated in the gas phase by sequential electron

capture [38]. The reaction of C_{60} and C_{70} with MnF_3 under vacuum at elevated temperatures resulted in high purity $C_{60}F_{36}$ and $C_{70}F_{36/38/40}$. Fluorination of C_{70} was carried out and the product is a mixture of $C_{70}F_{36/38/40}$ with $C_{70}F_{38}$ as the major component. $C_{60}F_{18}$ has been prepared by reaction between C_{60} and hexafluoroplatinate and the compound is isostructural with $C_{60}H_{18}$ [39]. $C_{60}Cl_6$ reacts with allyltrimethylsilane in the presence of $TiCl_4$ to form a Cs symmetrical, hexaallyl addended[60]fullerene derivative, $C_{60}(CH_2CH=CH_2)_6$ [40]. The use of $FeCl_3$ as the Lewis acid catalyst in the above reaction also produces the same product, but in low yields.

5.3 Nitration

Electrophilic attack of nitronium ion from $RCOO^-NO_2^+$ ($R = C_6H_5$, $p-C_6H_4-Br$) to C_{60} to form an intermediate $C_{60}(NO_2^+)_x$, and nucleophilic 1,3- or 1,5-substitution followed by hydrolysis finally give polyhydroxy organocarboxylate derivative, consisting of average 13–15 hydroxyl substituents and 4–5 *p*-bromobenzoate moieties per C_{60} molecule. This upon hydrolysis gives the corresponding water soluble fullerols consisting of 18–20 hydroxyl groups per C_{60} molecule. Nitro derivatives were also prepared by reacting C_{60} in the inert CCl_4 solution with conc. HNO_3 and NO_2 gas. The product had the composition $C_{60}(NO_2)_x(OH)_y$.

5.4 Sulphonation

C_{60} is sulphonated in fuming sulphuric acid and chlorinated in chlorosulphonic acid. Both reactions involve initial oxidation of C_{60} followed by *in situ*-trapping of the electrophilic C_{60} cation. Reactivity of C_{60} towards oxidative sulphonation reaction, induced by $H_2SO_4-SO_3$, is highly enhanced by P_2O_5 , leading to hexacyclosulphated fullerene intermediates, which are converted to dodecahydroxy fullerenes upon hydrolysis.

5.5 Hydroxylation

Hydroxyl groups can be added to C_{60} by reaction with the BH_3 -THF complex followed by hydrolysis with glacial acetic acid, $NaOH/H_2O_2$, or $NaOH$ giving

water-soluble fullerols. The reaction of C_{60} in toluene with potassium and hydrolysis of the product is a convenient route to fullerols.

5.6 Alkylation and Arylation

5.6.1 Nucleophilic Reactions

Charged nucleophiles can add to C_{60} as alkylation by either Grignard or organolithium reagents followed by reaction with alkyl iodide. In this process, many mono- and polyadducts of C_{60} are formed, e.g., $C_{60}H$ *t*-Bu, $C_{60}HEt$, $C_{60}Me_{10}Ph_{10}$, $C_{60}Me_3Ph_2$, and $C_{60}Me$ *t*-Bu. Nucleophilic reactions led to the synthesis of $C_{60}H(CH_2CMe=CH_2)$, $C_{60}H(CH_2CMe=CH_2)_8$ and $C_{60}H_8(C_9H_7)_8$ by treating C_{60} with 2-methylallyl magnesium chloride and sodium indenide in THF. Controlled addition of organolithium and Grignard reagents to C_{60} demonstrates the formation of monosubstituted fulleride ions (RC_{60}^-) as stable intermediates. In particular, *tert*-butyl and isocynyl fulleride ions were been successfully prepared in solution or isolated as a solid. *tert*-Butyl-1,2-dihydrofullerene (*t*-Bu $C_{60}H$) has a *pK_a* of 5.7 in DMSO, which ranks its conjugate anion, *t*-Bu C_{60}^- as one of the most stable hydrocarbon anions. Aryl-substituted compounds **13** were synthesized by carbocation-carbanion coordination reaction of *t*-Bu C_{60}^- and tropylium ions [41]. A dark-green solution of *t*-Bu $C_{60}^-K^+$ was prepared in THF by treatment of the parent hydrocarbon, *t*-Bu $C_{60}H$, with excess of *t*-BuOK. The addition of BF_4^- or ClO_4^- salt of a tropylium ion (**12**) in the THF- CH_3CN mixed solvent yielded the coordination products (**13**) as dark-brown solids (Figure 5).

Komatsu *et al.* [42] reported the first alkyne C_{60} derivatives, which are versatile precursors to a variety of new molecules. The ethynyl handle was provided by [(trimethylsilyl)-ethynyl]lithium (**14**) and both mono- and bisadducts were isolated (**15**–**17**). The product yields were highly dependent upon the reaction conditions. In order to examine the generality of the methods for ethynylation of C_{60} , addition of phenylethynyllithium was conducted under similar reaction conditions to give the monoadduct $HC_{60}(C\equiv CC_6H_5)$. In order to confirm

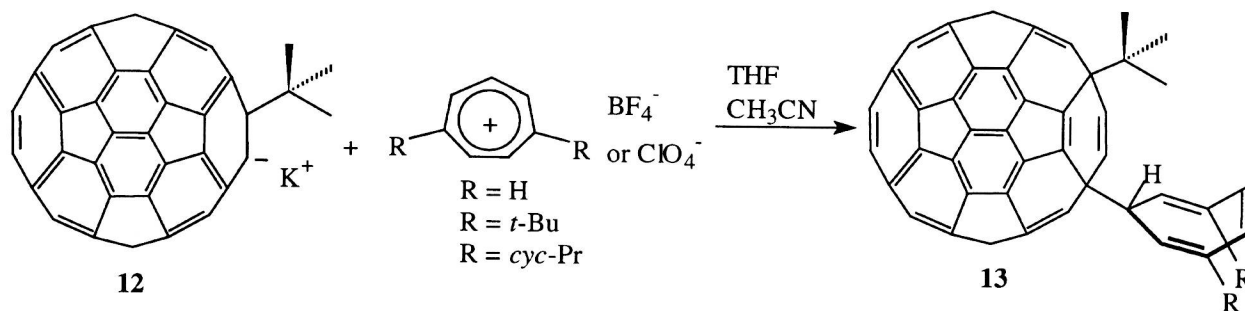


Figure 5 Attachment of tropylium ion to *t*-Bu C_{60}^- .