

F

Fullerenes and Fullerene Derivatives in Properties and Potential Applications คุณสมบัติและศักยภาพในการประยุกต์ใช้ฟูลเลอรีนและอนุพันธ์ของฟูลเลอรีน

• **Katsiri Laowachirasuwan**

• Full-time Lecturer at General Science Department

• School of Science, University of the Thai Chamber of Commerce

• E-mail: katsiri_lao@utcc.ac.th

บทคัดย่อ

ภายหลังจากการค้นพบฟูลเลอรีน ซึ่งก็คือ โมเลกุลที่ประกอบด้วยคาร์บอน 60 อะตอมมีโครงสร้างเป็นกลุ่มก้อน และเป็นทรงกลมคล้ายกรวย ความสนใจของนักวิทยาศาสตร์และนักวัสดุศาสตร์ได้มุ่งไปที่การคิดค้นเพื่อการสังเคราะห์สารตัวใหม่ๆ ขึ้นมาโดยมีฟูลเลอรีนเป็นองค์ประกอบหลัก คุณสมบัติหลายประการของฟูลเลอรีนนั้นยังคงแปลกใหม่และไม่ธรรมดา เพื่อที่จะเข้าใจคุณสมบัติของฟูลเลอรีนในทางเคมีและทางฟิสิกส์จำเป็นต้องค้นคิดสารใหม่ๆ ขึ้นมา ซึ่งเป็นสิ่งที่ท้าทายโอกาสที่จะเป็นไปได้ในการนำฟูลเลอรีนไปประยุกต์ใช้ในชั้นสูงขึ้นไปอย่างที่เราทราบกันดีว่าฟูลเลอรีนสามารถทำให้เป็นสารอนุพันธ์ต่างๆ ได้โดยง่าย เช่น สามารถเพิ่มสารอื่นเข้าไปในโมเลกุลของฟูลเลอรีนโดยใช้ความรู้ทางเคมีอินทรีย์และเทคนิคในการสังเคราะห์แบบพิเศษ ก็สามารถทำให้เกิดสารใหม่ๆ ที่มีความหลากหลายได้ ด้วยเหตุผลนี้เองทำให้ฟูลเลอรีนสามารถนำไปประยุกต์ใช้ได้อย่างมากมายมหาศาล สำหรับบทความนี้จะกล่าวถึงคุณสมบัติฟูลเลอรีนและอนุพันธ์ของฟูลเลอรีน อะไรคือความน่าทึ่งเกี่ยวกับสารคาร์บอนตัวใหม่นี้ และคุณสมบัติที่ไม่เหมือนใครนี้เองจะสามารถนำไปประยุกต์ใช้ให้เกิดประโยชน์ได้อย่างไร ตัวอย่างการประยุกต์ใช้ฟูลเลอรีนและอนุพันธ์ของฟูลเลอรีนที่จะกล่าวถึงในบทความนี้ เช่น การนำไปใช้เป็นส่วนกึ่งตัวนำ (Semiconductors) สารตัวนำยิ่งยวด (Superconductors) วัสดุเหมือนโพลีเมอร์ (Polymer-like Materials) และใช้เป็นตัวเร่งปฏิกิริยา (Catalysts) ในทางการแพทย์นั้นฟูลเลอรีนและอนุพันธ์ของฟูลเลอรีนถูกนำไปใช้ในการสันนิษฐานหรือทำนายอาการของโรคและนำไปใช้ในการรักษาโรค เช่น นำไปใช้เป็นสารยับยั้งการทำงานของ

ไวรัส HIV-P (Inhibition of HIV-P) สารชีวภาพต้านอนุมูลอิสระ (Biological Antioxidants) สารต้านการเจริญเติบโตของแบคทีเรีย (Antibacterial Activity) และใช้เป็นตัวตัดดีเอ็นเอที่ตำแหน่งจำเพาะโดยใช้แสง (DNA Photocleavage)

คำสำคัญ: ฟูลเลอร์รีน อนุพันธ์ของฟูลเลอร์รีน คุณสมบัติ การประยุกต์ใช้

Abstract

After the discovery of Fullerenes, the 60-atom clusters and large carbon-cage molecules, the attention of scientists and materials scientists has been attracted by the syntheses of new materials based on the family of Fullerene molecules. Many properties of Fullerenes are new and unusual. With a better understanding of their chemical and physical properties, the fabrication of new materials for advanced applications has emerged as a challenging possibility. As we know that Fullerenes are easily modified, using organic chemistry and special synthetic techniques, into other molecular structures, this makes them remarkably versatile. The versatility of Fullerenes gives them enormous applications. This paper will review on Fullerenes and Fullerene derivatives properties, what is interesting about these “new” carbon materials and how their unique properties can be utilized in potential applications. Applications of Fullerenes and Fullerene derivatives in areas such as semiconductors, superconductors, polymer-like materials, catalysts have been reviewed. In the medical field, the potential applications of Fullerenes and Fullerene derivatives include diagnostic or therapeutic agents, inhibition of HIV-P, powerful biological antioxidants, antibacterial activity, and DNA photocleavage.

Keywords: Fullerenes, Fullerene Derivatives, Properties, Applications

Introduction

Carbon is one of the common substances on earth and widely distributed in nature. Natural carbon can exist in several forms. Most people know about graphite and diamond, but there is a fourth allotropic form of carbon, “Fullerenes.” They are new to us. Fullerenes are the 60-atom clusters and large carbon-cage molecules (Pierson, 1993). By

far the most common one is C_{60} , also called a “buckyball” or Buckminsterfullerene. Buckminsterfullerene was named after a noted architect, Richard Buckminster Fuller, who popularized the geodesic dome (Applewhite, 1995). Since Buckminsterfullerene has a similar shape to that of a dome, the name was thought to be widely credited to R. Buckminster Fuller.

Fullerenes were first discovered in 1985 in an apparatus designed by Professor Richard Smalley to produce atomic clusters of the non-volatile element (Kroto, et al., 1985). The experiments that led to the discovery of Fullerenes were aimed at simulating in the laboratory the conditions under which carbon nucleates in the atmosphere of a cool carbon-rich red giant star. The specific goal of the work was to explore the possibility that long carbon chain molecules such as cyanopolynes (HC_nN , $n = 5 \rightarrow 11$) could form when carbon vapor nucleates in the presence of hydrogen and nitrogen. Smalley, Kroto and Curl had developed a powerful technique in which a laser vaporizes atoms of a refractory material (carbon) into a carrier gas (Helium). Smalley, Kroto and Curl's experiments showed convincingly that species such as HC_7N and HC_9N could be produced in the laboratory simulation of conditions in stars. However, even more significant was the unexpected discovery of C_{60} . The discovery of Fullerenes and the insight that led to the interpretation of the magic number featured in the observed mass spectra in terms of hollow carbon molecules led to the award of the Noble Prize in Chemistry to Curl, Kroto, and Smalley in 1996.

The chemistry of Fullerenes is rich and varied, and it allows the properties of basic Fullerenes to be tailored to a given application. Derivatives of all of the basic Fullerenes are

possible such as C_{70} , C_{76} and C_{84} .

This paper will review Fullerenes and Fullerene derivatives, what is interesting about this "new" carbon material, and how their unique properties can be utilized in potential applications.

Properties of Fullerenes

Fullerenes are fascinating because they show unusual properties for carbon material.

Structure and Bonding

Fullerenes are a class of closed-cage carbon molecules, about 7-15 angstroms (\AA) in diameter, consisting of a number of five-membered rings (pentagons) and six-membered rings (hexagons), with a carbon atom at the corners of each hexagon and a bond along each edge. In order to make a closed cage, all Fullerene molecules should have the formula C_{20+m} , where m is an integer number. For example, the proposed structure for C_{60} is a "truncated icosahedron." A truncated icosahedron is derived from an icosahedron by truncating each of the twelve vertices, each vertex being replaced by five-membered rings. The truncating process also converts each of the twenty former triangular faces into six-membered rings which resemble a soccer ball with 12 pentagons and 20 hexagons (Haddon, Brus, and Raghavachari, 1986a). (See Figure 1.)



Figure 1 a) Icosahedron b) Truncated Icosahedron c) Fullerenes, C_{60}

The truncated icosahedron is not the only possible Fullerene-type structure. There are many other hollow cage structures that can be constructed using only pentagons and hexagons. Interestingly, each of these structures contains exactly twelve pentagons while the number of hexagons is arbitrary. The pentagons are necessary for closure. The number of vertices in closed Fullerene-type structure is necessarily even (Kroto, 1987). The smallest possible Fullerenes would be C_{20} , containing twelve pentagons and zero hexagons. Other possible

Fullerenes include C_{28} , C_{32} , C_{50} , C_{70} , C_{80} , and C_{82} . Because the molecular strain tends to be concentrated in the five-membered rings responsible for closure structures that avoid contiguous (edge-sharing), pentagons are particularly stable.

For C_{60} bonding, each vertex of the truncated icosahedron is occupied by a carbon atom. Each carbon is bonded to three other carbons in an infinite two-dimensional array by one double bond and two single bonds (Taylor, 2001). (See Figure 2.)



Figure 2 Dominant Resonance Structure for C_{60}

Carbon atoms with this kind of connectivity are usually referred to as “ sp_2 carbons” because the orbitals used to sigma-bond the three adjacent carbons are hybrids of the 2s orbital and the two 2p orbitals ($2p_x$ and $2p_y$). The remaining 2p orbital ($2p_z$) is responsible for

the pi-bond. The angle between a p axis and a C-C bond vector, θ , is 101.6° . The bowl-shape or concavity at each sp_2 carbon center introduces some strain into the molecule (Haddon, Brus, and Raghavachari, 1986b).

Chemically, Fullerenes are stable, but not totally unreactive; breaking the balls requires temperatures of over 1,000 degrees Celsius (the exact number depends on which particular Fullerenes). Fullerenes are sparingly soluble in many solvents at room temperature. Common solvents for the Fullerenes include toluene and carbon disulfide. At room temperature, the solubility of Fullerenes is about 2.8 mg/mL in toluene. As the size increases, the solubility of Fullerenes decreases. Solutions of pure C_{60} have a deep purple color. Solutions of C_{70} are a reddish brown. The higher Fullerenes C_{76} - C_{84} have a variety of colors (Taylor, 2001).

The HOMO-LUMO gap of Fullerenes is 1.68 eV. (Andreoni, Gygi, and Parrinello, 1992). Due to the low-lying LUMO, Fullerenes are reduced easily, and this is the reason which makes Fullerenes a good oxidizing agent. Fullerenes are unstable at higher temperatures. The process of decomposition is faster in the presence of oxygen. The measurable decomposition can be observed about 830 K (Chen, et al., 1992).

Synthesis of Fullerenes

Fullerenes can be synthesized by evaporating graphite electrodes (rods) via resistive heating in an atmosphere of inert gas, about 100 torr of helium, He (1 atm = 760 torr) being the best (Kratschmer, et al., 1990). This produces a light condensate called Fullerenes soot, which contains only a few percent by weight of C_{60} and a variety of different Fullerenes. C_{60} could be extracted using benzene as solvent. The red-brown benzene solution could be decanted from the black insoluble soot and then dried using gentle heat, leaving a residue of dark brown to black crystalline material yielding Fullerenes.

Species of Fullerenes

(Fullerenes Derivatives)

Can we put something in the cage? The answer is yes. The usual way to combine Fullerenes with other atoms is to put the other atoms inside the balls. Fullerenes with enclosed atoms are called “Endohedral Fullerenes.” Thus, Endohedral Fullerenes are Fullerenes that have additional atoms, ions or clusters enclosed within their inner spheres. (See Figures 3a, 3b.)

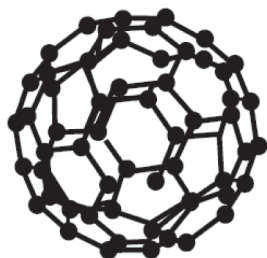


Figure 3a Empty Fullerenes

The first lanthanum Fullerenes complex was synthesized in 1985 called $\text{La}@C_{60}$. The @ sign in the name reflects the notion of a small molecule trapped inside a cage (the first material is inside the second). Two types of Endohedral Fullerenes complexes exist. Firstly, when the atoms trapped inside happen to be metallic, they are called Endohedral Metallofullerenes. Secondly, when the atoms trapped inside are non-metal, they are called non-metal doped Fullerenes (Saunders, et al., 1993). For Endohedral Metallofullerenes, the metals can be transition metals like scandium, yttrium as well as lanthanides, alkaline earth metals like barium and strontium, alkali metals like potassium and tetravalent metals like uranium, zirconium and hafnium. As it is very difficult to open up carbon cage molecules to enclose a foreign atom inside, metals must be synthesized during the formation of the cage itself (Lee, et al., 2002). In 1993, Saunders could prove the existence of the endohedral non-metal doped fullerene complexes $\text{He}@C_{60}$ and $\text{Ne}@C_{60}$ which form when C_{60} is exposed to a pressure of 3 bar of the noble gases (Saunders, et al., 1993). The formation of

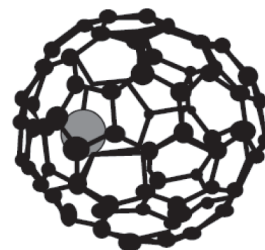


Figure 3b Fullerenes Containing an Encapsulated Metal Atom

endohedral non-metal doped fullerene complexes with helium, neon, argon, krypton and xenon as well as numerous adducts of the $\text{He}@C_{60}$ compound could be proven with operating pressure of 3,000 bars and incorporation of up to 0.1% of the noble gases (Saunders, et al., 1994). Even though C_{60} is the most common Fullerene, few endohedral materials have a C_{60} cage because their structures are small inside. Most of these materials are made out of C_{80} , C_{82} , C_{84} or even higher Fullerenes, such as $\text{Sc}_3\text{C}_2@C_{80}$, $\text{Ce}_2@C_{80}$, $\text{L}@C_{82}$, $\text{Gd}@C_{82}$, etc.

Another significant Fullerene species is Exohedral Fullerenes or Fullerene derivatives which are molecules formed by bonding between fullerenes and other chemical groups, known as functionalized fullerenes. Two main types of primary chemical transformations are possible on the fullerene surface: addition reactions and redox reactions, which lead to covalent exohedral adducts and salts respectively (Schick, et al., 1996). For example, cycloaddition of azomethine yields to Fulleropyrrolidne. (See Figure 4.)

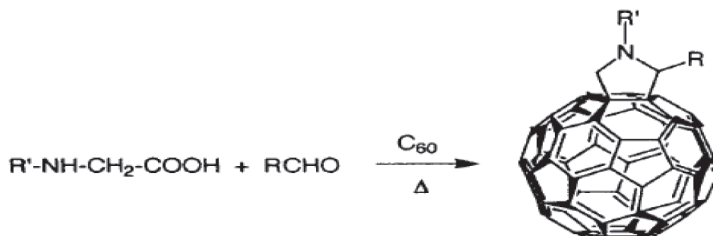


Figure 4 Synthesis of Fulleropyrrolidines

The azomethine ylides are synthesized by condensation of α -amino acids and aldehydes or ketones. Fulleropyrrolidines are obtained with the 5-membered ring fused to a 6,6 bond on the fullerene (Maggini, Scorrano,

and Prato, 1993). This reaction is very useful because it is possible to introduce different substituents on nitrogen and on carbons 2 and 5. (See Figure 5.)

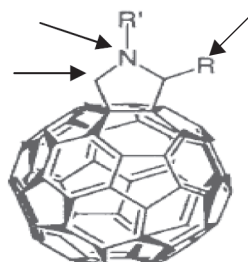


Figure 5 Substituents on Nitrogen and on Carbons 2 and 5

These exohedral Fullerenes retain the main properties of the parent molecule (Fullerenes, C_{60}) and can be made to be more highly lipophilic than basic Fullerenes as well as water soluble and amphiphilic. They include copolymers and derivatives with altered electronic and optical properties (NanoC, 2007).

Potential Applications of Fullerenes and Fullerene Derivatives

After the discovery of Fullerenes, the attention of materials scientist has been

attracted by the synthesis of new materials based on the family of Fullerene molecules. Many properties of Fullerenes are new and unusual, and with a better understanding of their chemical and physical properties, the fabrication of new materials for advanced applications has emerged as a challenging possibility. As we know that Fullerenes are easily modified, using organic chemistry and special synthesis techniques, into other molecular structures, this makes them remarkably versatile. The versatility of Fullerenes gives them enormous applications.

Researchers have shown that solids based on Fullerenes can be insulators, conductors, semiconductors or even superconductors when they are inserted with other atoms or molecules. Pure Fullerene solids form crystal structures, like graphite or diamond that are insulators or semiconductors. Adding 3 alkali atoms per C_{60} resulted in A_3C_{60} compounds (A is one of the alkali metals such as K, Rb, Cs, Na; and these solids can become electricity conducting metals), which turn out to be superconductors at quite a high temperature (19-40 K). They conduct electric current without any resistance at temperature below 19-40 K. For example,

K_3C_{60} , when it is cool, its resistivity begins to drop sharply at about 18 K, indicating the onset of superconductivity (Hebard et al., 1991). As larger alkali-metal cations are incorporated into the lattice and the fcc lattice parameter (a_0) increases, the superconducting transition temperature, T_C , also increases. Therefore, the T_C for Rb_3C_{60} rises to 28 K. This rise in T_C may be related to an increase in the density of states at the Fermi level with increasing lattice constant (Fleming, et al., 1991). The correlation between T_C and lattice constant (a_0) suggests that even higher T_C 's could be obtained by incorporating larger and larger cations, A. (See Figure 6.)

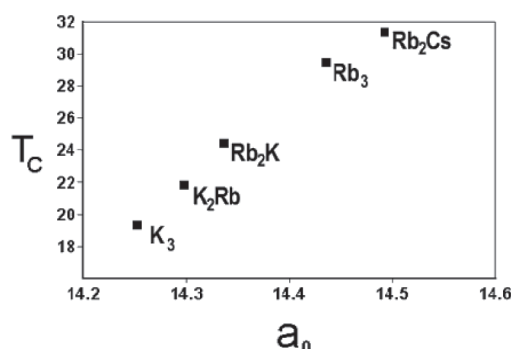


Figure 6 Plot of Superconducting Transition Temperature T_C (K) vs. Lattice Parameter a_0 (angstroms) for Various Compositions of A_3C_{60}

Fullerenes have been known to have excellent n-type organic thin film semiconductor properties (electron acceptor). The high quality thin film of Fullerenes prepared under ultra-high vacuum has been known to show the highest electron mobility. However, the preparation of crystalline thin film of Fullerenes needs

the use of ultra-vacuum equipment which is expensive and hardly controllable. For this reason, to reduce the production costs and to be applicable to the preparation of large-area devices, a new Fullerene derivative, C_{60} -fused pyrrolidine-meta- C_{12} phenyl ($C_{60}MC_{12}$), organic semiconductor materials, has been

synthesized by incorporating an alkyl chain to Fullerenes (C_{60}). $C_{60}MC_{12}$ is soluble in organic solvent, and found to be a good quality crystalline thin film by simple coating where

Fullerene heads self-aggregate to form layered structures (Chikamatsu, et al., 2005). (See Figure 7.)

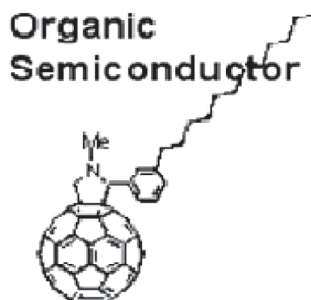


Figure 7 Structure of $C_{60}MC_{12}$

$C_{60}MC_{12}$ is used as an n-type organic thin film transistor. The electron mobility of $C_{60}MC_{12}$ is as high as $0.067\text{cm}^2/\text{Vs}$, which is the highest value for an n-type organic semiconductor prepared through a coating process (Chikamatsu, et al., 2005).

As mentioned before, the LUMO of Fullerenes is relatively low in energy, and it is readily reduced. The interesting electronic properties of Fullerenes have led to the possibility of using units of Fullerenes in the formation of polymers. The Fullerenes polymer-like materials, $C_{60}Pd_n$ or $C_{60}Pt_n$ are formed from C_{60} and $Pd_2(dba)_3 \cdot CHCl_3$ or $Pt(dba)_2$, (dba = dibenzylideneacetone) respectively. These redox-active Fullerene-based polymeric materials can be formed by electrochemical reduction of Fullerenes under specific conditions (Balch, Costa, and Winkler, 1998). These Fullerene polymers have possible applications to adsorb volatile organic

compounds, found in residential environments due to emission from construction materials, paints and glues, at ambient temperature without additional energy sources. A volatile organic compound such as toluene, containing a benzene ring, is hard to remove from the living environment. Fullerenes polymer-like materials, $C_{60}Pd_n$, showed good adsorptivity toward toluene. Even at a low concentration of 1000 ppb, which is close to the actual toluene concentration in the environment, the adsorptivity is retained (Hayashi, et al., 2004). This result should open the route to using Fullerenes polymer-like materials to remove harmful gases from the living environment.

Fullerene materials have also been used as excellent catalysts for H-transfer reaction such as coupling and transalkylation reaction of mesitylene, engaged in transfer hydrogenation with dihydroaromatics, and hydrodealkylations. For example, when mesitylene was heated

under reflux (162°C) in the presence of Fullerenes, it produces dimers and trimers,

as well as transalkylation products under relatively mild conditions. (See Figure 8.)

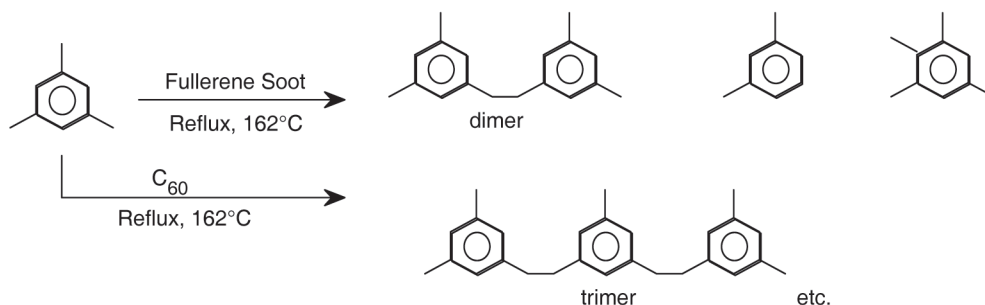


Figure 8 Fullerenes Catalyst Coupling and Transalkylation Reactions

The key structural feature that endows Fullerenes with many of their characteristics is the presence of a pentagon surrounded by hexagons, which endows them with electrophilicity and an ability to stabilize radicals. Fullerenes are also highly effective in promoting the conversion of methane into higher hydrocarbons (higher-value fuels and other chemicals) (Malhotra, et al., 1997). Methane is now burned off rather than transported from distant oil fields. Adding seven carbon atoms to methane (one carbon atom) would convert it to valuable liquid octane (eight carbon atoms). Adding even one carbon atom would convert methane to ethane, which is still a gas but is useful in organic synthesis, as a fuel, and in refrigeration (Trulove, 2007).

Fullerenes and Fullerene derivatives, because their exceptional stability, large size, hydrophobic character and outer surface can be easily manipulated for different

applications, may prove to have value as diagnostic or therapeutic agents in medicine. For diagnostic application, Endohedral metallofullerenes, such as M@C₈₂ (OH)₃₀, are being used as Magnetic Resonance Imaging contrast agents (M = Gd³⁺) (Wharton, et al., 1999), X-ray contrast agents (M = Ho³⁺) and radio pharmaceuticals (M = ¹⁶⁶Ho³⁺ and ¹⁷⁰Tm²⁺) (Ehrhardt, et al., 2000). The radioactive metal is trapped inside the carbon shell, which is non toxic, very stable, and resistant to metabolism by the body. They can stay in the body for approximately one hour, allowing imaging of circulatory system. For therapeutic application, the potential applications of Fullerenes and Fullerene derivatives include inhibitors of the protease enzyme specific to the human immunodeficiency virus 1 (HIV-P). The bis (monosuccinimide) derivative of p,p'-bis(2-aminoethyl)-diphenyl-C₆₀ shown in Figure 9 is an HIV-protease inhibitor (Friedman, et al., 1993).

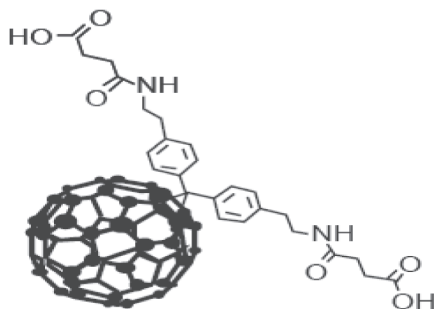


Figure 9 Fullerene Molecule that Inhibits HIV Protease

This molecule has approximately the same radius as the active site of HIV-P and is primarily hydrophobic. An opportunity exists for a strong hydrophobic Van der Waals interaction between the nonpolar active site surface and the C₆₀ surface. Therefore, this

molecule could fit very well inside the HIV-P cavity. (See Figure 10.) This result might prevent the interaction between the catalytic portions of HIV-P and the virus substrates (Marcorin, et al., 2000).

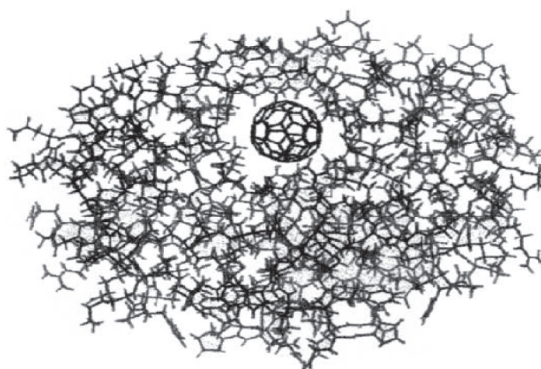


Figure 10 Computer Designed Showing the Accommodation of Synthesized Fullerene Compound Inside the HIV-P Cavity

Recent results indicate that Fullerenes may have potential as powerful biological antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage or death. Because of the large number of conjugated double bonds that are readily attacked by radical

species, Fullerenes are known to behave like a “free radical sponge” and facile addition of up to thirty four methyl radical to C₆₀ has been reported (Wilson, 1999). They can sponge-up and neutralize twenty or more free radicals per Fullerene molecule (100 times more effective than current leading antioxidants

such as Vitamin E) (NanoC, 2007). Fullerenes and Fullerene derivatives are probably the world's most efficient radical scavengers.

Another potential biological application of Fullerene derivatives is antibacterial activity. Fullerene derivatives could produce membrane disruptions by insertion into phospholipidic bilayers. The consequent membrane disorder

could lead to the discharge of metabolites and cell death (Da Ros, Spalluto, and Prato, 2001). Scientists employed different aldehydes (paraformaldehyde or 3,6,9-trioxadecane aldehyde) to synthesize N-mTEG substituted fulleropyrrolidines (mTEG = monomethoxy triethylene glycol) (Bosi, et al., 2000) as shown in Figure 11.

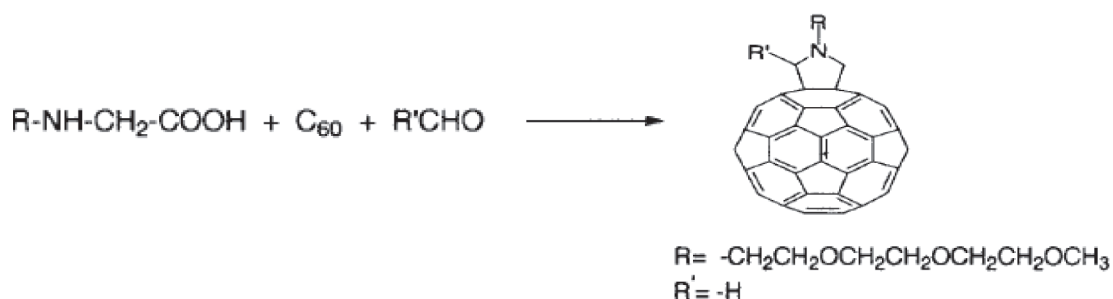


Figure 11 Synthesis of mTEG

Mycobacterium avium is completely inhibited by this synthesized molecule at a dose of 260 mg/mL. The possible explanation could be that presence of the carbon cage destabilizes the tubercular cell wall by intercalation in the hydrophobic part. (Bosi, et al., 2000)

In medicinal chemistry, the potential applications of Fullerenes and Fullerene derivatives include DNA photocleavage. Fullerenes were found to be cytotoxic when exposed to visible light. As shown in Figure 12, they have the following mechanism (Ikeda, et al., 2005).

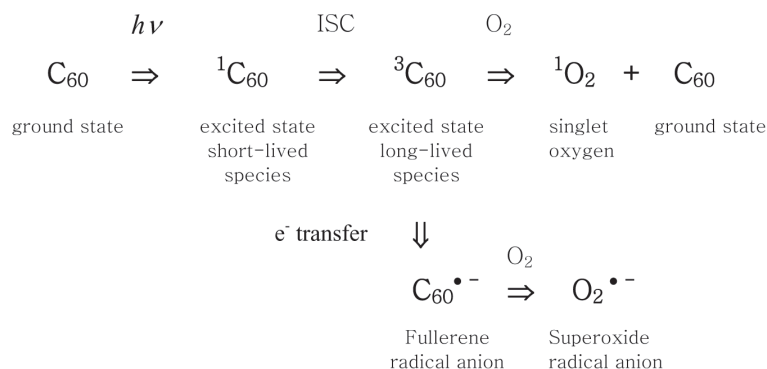


Figure 12 Mechanism of Fullerenes When Exposed to Visible Light

Fullerenes (C_{60}) from ground state were excited by photoirradiation to an excited state and converted to short-lived species, $^1C_{60}$. This $^1C_{60}$ was converted to the long-lived species, $^3C_{60}$ by intersystem crossing (ISC). In the presence of oxygen (O_2), $^3C_{60}$ can transfer its energy to O_2 and return to ground state, generating singlet oxygen, 1O_2 which is known as a highly cytotoxic species or reactive species toward DNA. By electron transfer $^3C_{60}$ can be reduced to Fullerene radical anion, $C_{60}^{\bullet-}$ and $C_{60}^{\bullet-}$ can transfer one electron to produce superoxide radical anion, $O_2^{\bullet-}$ which is known as reactive species toward DNA.

The excited Fullerenes, $^1C_{60}$ and $^3C_{60}$ can be reduced in the presence of the guanosine residue present to DNA (An, et al., 1996). Cytotoxicity of Fullerenes was mediated by its ability to cleave DNA. DNA cleavage was found to occur at guanine residue without any significant sequence selectivity (Tokuyama, et al., 1993). Therefore, Fullerenes are being developed for the treatment of cancer.

Conclusion

The research of Fullerenes has opened a new chapter on the chemistry of carbon. The most important and useful thing that came out of this sort of research is new ideas and paths of investigation. Fullerenes and Fullerene derivatives have been introduced and expected to be very useful with their

unique properties and characteristics showing several potential applications in material science while functionalization chemistry of Fullerenes and Fullerene derivatives have emerged as a key tool to design the material properties as functions of the applications.

References

- An, Y.Z., et al. 1996. "Use of Fullerene Derivatives as DNA Compaction Agent." **Tetrahedron** 52: 5179-5189.
- Andreoni, W., Gygi, F., and Parrinello, M. 1992. "Structure and Electronic Properties of C_{70} -group of 2." **Chemical and Physical Letters** 189: 241-244.
- Applewhite, E.J. 1995. "The Naming of Buckminsterfullerene." **The Chemical Intelligencer** 1: 3.
- Balch, A.L., Costa, D.A., and Winkler, K. 1998. "Formation of Redox-Active, Two-Component Films by Electrochemical Reduction of C_{60} and Transition Metal Complexes." **Journal of American Chemical Society** 120: 9614-9620.
- Bosi, S., et al. 2000. "Antimycobacterial Activity of Ionic Fullerene Derivatives." **Bioorganic Medicinal Chemistry Letters** 10: 1043-1045.
- Chen, H.S., et al. 1992. "Thermodynamic of C_{60} in Pure O_2 , N_2 and Ar." **Journal of Physical Chemistry** 96: 1016-1018.
- Chikamatsu, M. 2005. "*n*-type Organic Thin Film Transistor Prepared by Solution

- Process.” **AIST Today** 5, 12: 21.
- Chikamatsu, M., et al. 2005. “Solution-Processed *n*-Type Organic Thin-Film Transistors with High Field-Effect Mobility.” **Applied Physical Letters** 87: 2035.
- Da Ros, T., Spalluto, G. and Prato, M. 2001. “Biological Applications of Fullerene Derivatives: A Brief Overview.” **Croatica Chemica ACTA** 74, 4: 743-755.
- Ehrhardt, G.J., et al. 2000. **Nuclear and Radiation Chemical Approaches to Fullerene Science**. Dordrecht: Kluwer Academic.
- Fleming, R.M., et al. 1991. “Relation of Structure and Superconducting Transition Temperatures in A_3C_{60} .” **Nature** 352: 787.
- Friedman, S.H., et al. 1993. “Inhibition of the HIV-1 Protease by Fullerene Derivatives : Model Building Studies and Experimental Verification.” **Journal of American Chemical Society** 115: 6506-6509.
- Haddon, R.C., Brus, L.E., and Raghavachari, K. 1986a. “Electronic Structure and bonding in Icosahedral C_{60} .” **Chemical and Physical Letters** 125: 459.
- Haddon, R.C., Brus, L.E., and Raghavachari, K. 1986b. “Rehybridization and p-Orbital Alignment: The key to the Existence of Spheroidal Carbon Clusters.” **Chemical and Physical Letters** 131: 165.
- Hayashi, A., et al. 2004. “The First Application of Fullerene Polymer-Like Materials, $C_{60}Pd_n$, as Gas Adsorbents.” **R&D Review of Toyota CRDL** 40, 1: 15-20.
- Hebard, A.F., et al. 1991. “Superconductivity at 18K in Potassium-Doped C_{60} .” **Nature** 350: 600.
- Ikeda, A., et al. 2005. “Efficient Photocleavage of DNA Utilising Water-Soluble Lipid Membrane-Incorporated [60] Fullerenes Prepared Using a [60] Fullerene Exchange Method.” **Organic and Biomolecular Chemistry** 3: 2907-2909.
- Kratschmer, W., et al. 1990. “Solid C_{60} : A new Form of Carbon.” **Nature** 347: 354.
- Kroto, H.W. 1987. “The Stability of the Fullerenes C_n with $n = 24, 28, 32, 36, 50, 60$ and 70 .” **Nature** 329: 529.
- Kroto, H.W., et al. 1985. “ C_{60} Buckminsterfullerene.” **Nature** 318: 162-163.
- Lee, H.M., et al. 2002. “Crystallographic Characterization of $Kr@C_{60}$ in $(0.09Kr@C_{60}/0.91C_{60}) \cdot \{Ni^{II}(OEP)\} \cdot 2C_6H_6$.” **Chemical Communications**: 1352.
- Maggini, M., Scorrano, G., and Prato, M. 1993. “Addition of Azomethine Ylides to C_{60} : Synthesis, Characterization, and Functionalization of Fullerene Pyrrolidines.” **Journal of American Chemical Society** 115: 9798-9799.
- Malhotra, R., et al. 1997. “Catalytic Properties of Fullerene Materials.” In **Recent Advances in Catalytic Materials : Symposium Held December 2-4, 1997, Boston, Massachusetts, U.S.A.**, pp. 135-136. Warrendale, PA: Materials Research Society.

- Marcorin, G., et al. 2000. "Design and Synthesis of Novel [60] Fullerene Derivatives as Potential HIV Aspartic Protease Inhibitors." **Organic Letters** 2: 3955-3958.
- NanoC. April 15, 2007. **Leading the Development of Nanostructured Carbon Products, Antioxidant & Biopharmaceuticals** [On-Line]. Available: <http://www.nano-c.com/fullerenes/applications.htm>
- Pierson, H.O. 1993. **Handbook of Carbon, Graphite, Diamond and Fullerenes: Properties, Processing, and Applications**. Park Ridge, NJ: Noyes.
- Saunders, M., et al. 1993. "Stable Compounds of Helium and Neon: He@C₆₀ and Ne@C₆₀." **Science** 259, 5100: 1428-1430.
- Saunders, M., et al. 1994. "Incorporation of Helium, Neon, Argon, Krypton, and Xenon into Fullerenes Using High Pressure." **Journal of American Chemical Society** 116, 5: 2193-2194.
- Schick, G., et al. 1996. "Opening and Closure of the Fullerene Cage in cis-1-Bisimino Adducts of C₆₀: The Influence of the Addition Pattern and the Addend G." **Chemistry the European Journal** 2: 935-943.
- Taylor, R. 2001. **Fullerene Chemistry : A Handbook for Chemists**. London: Imperial College Press.
- Tokuyama, H., et al. 1993. "Photo-induced Biological Activity of Fullerene." **Journal of American Chemical Society** 115: 7918-7919.
- Trulove, S. July 15, 2007. "Filled Buckyballs Diamonds from Soot." **Research Magazine Virginia Tech** [On-line serial]. Available : <http://www.research.vt.edu/resmag/2002winter/buckyballs.html>
- Wharton, T., et al. 1999. **Recent Advances in Chemistry and Physics of Fullerenes and Related Materials. Volume 7 : Proceedings of the Twelfth International Symposium**. Pennington, NJ: Electrochemical Society.
- Wilson, L.J. 1999. "Medical Application of Fullerenes and Metallofullerenes." **The Electrochemical Society Interface** Winter: 24-28.



Mrs. Katsiri Laowachirasuwan received her Master of Science in Chemistry (Inorganic Chemistry) from Texas A&M University, Kingsville, USA. She is currently working at the School of Science, the University of the Thai Chamber of Commerce. Her main interest is in material science, inorganic chemistry and analytical chemistry. Her current research includes the characterization of activated carbons.