

## Structure, properties and applications of fullerenes

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### Abstract

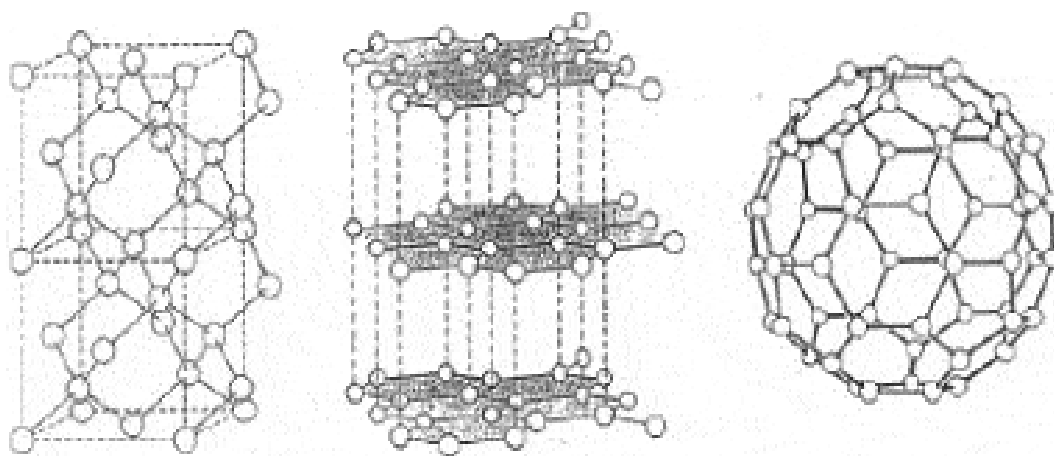
This paper reports about fullerenes, its structure, properties and applications. Fullerenes are the third allotropic form of carbon material after graphite and diamond. These were discovered in 1985 by Harold W. Kroto, Robert F. Curl and Richard E. Smalley. Fullerenes consist of 20 hexagonal and 12 pentagonal rings as the basis of an icosohedral symmetry closed cage structure. Each carbon atom is bonded to three others and is  $sp^2$  hybridized. The  $C_{60}$  molecule has two bond lengths, the 6:6 ring bonds can be considered "double bonds" and are shorter than the 6:5 bonds.  $C_{60}$  is not "superaromatic" as it tends to avoid double bonds in the pentagonal rings, resulting in poor electron delocalisation. As a result,  $C_{60}$  behaves like an electron deficient alkenes and reacts readily with electron rich species. The geodesic and electronic bonding factors in the structure account for the stability of the molecule. Fullerenes can be used as organic photovoltaics(OPV), these are powerful antioxidants, reacting readily and at a high rate with free radicals which are often the cause of cell damage or death. Other uses of  $C_{60}$  like catalysts, in water purification and biohazard protection, portable power, vehicles and medical.

**Keywords:** Fullerenes, carbon nanotubes, electron and bond lengths

### Introduction

The Nobel Prize of the year 1996 for Chemistry has been won by Harold W. Kroto, Robert F. Curl and Richard E. Smalley for their discovery in 1985 of a new allotrope of carbon, in which the atoms are arranged in closed shells. The new form was found to have the structure of truncated icosahedrons and was named Buckminsterfullerene, after the architect Buckminster Fuller who designed geodesic domes in the 1960's.

Formerly, six crystalline forms of the element carbon were known, namely two kinds of graphite, two kinds of diamond, chaoit and carbon (VI). The latter two were discovered in 1968 and 1972. Fullerenes are the third allotropic form of carbon material after graphite and diamond. Figures 1 (a), (b) and (c) show the structure of graphite, diamond and fullerene respectively.



**Figure 1 :** (a) Graphite (b) Diamond (c) Fullerene

When fullerenes were first discovered [1], there was much excitement about practical applications. It was speculated that buckyballs would make great lubricants, rolling like little ball bearings between other molecules. Or perhaps drugs could be trapped inside the cages, and then released slowly by a triggering mechanism that could break open the cages inside the body.

$C_{60}$  is a molecule that consists of 60 carbon atoms, arranged as 12 pentagons and 20 hexagons. The shape is the same as that of a soccer ball: the black pieces of leather are the pentagons, the hexagons are white. There are 60 different points where three of the leather patches meet. Imagine a carbon atom sitting at each of these points, and you have a model of the  $C_{60}$  molecule. That model, however, is vastly out of the scale and if the  $C_{60}$  molecules were the size of a soccer ball, then the soccer ball in turn would be roughly the size of the earth. The most striking property of the  $C_{60}$  molecule is its high symmetry. There are 120 symmetry operations, like rotations around an axis or reflections in a plane, which map the molecule onto itself. This makes  $C_{60}$  the molecule with the largest number of symmetry operations, the *most symmetric molecule*[2].

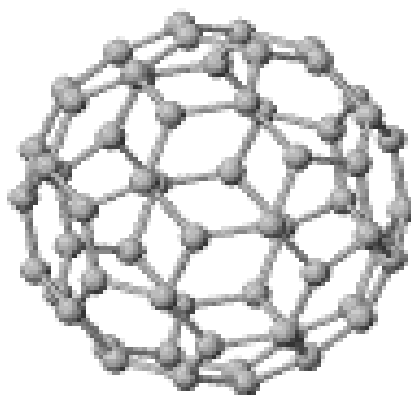
Based on a theorem of the mathematician Leonhard Euler, one can show that a spherical surface entirely built up from pentagons and hexagons must have exactly 12 pentagons. Depending on the number of hexagons, molecules of different sizes are obtained. They are called fullerenes. Fuller was renowned for his geodesic domes, shown in Fig.2, those are based on hexagons and pentagons[3]. Fullerenes are a class of closed-cage carbon molecule,  $C_n$ , characteristically containing 12 pentagons and a variable number of hexagons.

$$\text{Hexagons} = \frac{(\text{carbon atoms}) - 20}{2}$$

Fullerenes composed of less than 300 carbon atoms, or endohedral fullerenes, are commonly known as “buckyballs”, and include the most common fullerene, buckminsterfullerene,  $C_{60}$  (shown in Fig.3). Giant fullerenes, or fullerenes with more than 300 carbon atoms, include single-shelled or multi-shelled carbon structures, onions, and nanotubes.



**Figure 2 :** A geodesic dome shares the same geometric structure as a buckminsterfullerene



**Figure 3 :** The structure of  $C_{60}$  “Buckminsterfullerene”

### Structures and Physical Properties of Some Higher Fullerenes

Fullerenes consist of 20 hexagonal and 12 pentagonal rings as the basis of icosahedral symmetry closed cage structure. Each carbon atom is bonded to three others and is  $sp^2$  hybridized. The  $C_{60}$  molecule has two bond lengths - the 6:6 ring bonds can be considered “double bonds” and are shorter than the 6:5 bonds.  $C_{60}$  is not “superaromatic” as it tends to avoid double bonds in the pentagonal rings, resulting in poor electron delocalisation. As a result,  $C_{60}$  behaves like an electron deficient alkenes and reacts readily with electron rich species. The geodesic and electronic bonding factors in the structure account for the stability of the molecule. In theory, an infinite

number of fullerenes can exist, their structure based on pentagonal and hexagonal rings, constructed according to rules for making icosahedra.

### Fullerenes in Space

As we know that fullerenes tend to form by "rolling up" a graphite sheet and adding pentagons to achieve curvature. If we just roll the sheet like a cylinder, then cap off the ends with pentagon-curved hemispheres. We will have a carbon nanotube. These materials are quite different from the traditional fullerene-type materials (i.e. roundish cages) and so they have rather different properties. Most of the current research centers on nanotubes that have metal atoms incorporated into the carbon structure. These metal-carbon tubes have some really cool properties, such as switching from insulating to metallic depending on the exact shape of the cylindrical region. It is not necessary to roll the tubes "straight," such that the carbon chains make circles around the cylindrical surface. We can roll them with a twist so the carbons spiral up the cylinder looking something like twisted bread sticks. As we twist one additional unit at a time, the tube alternates between metallic and insulating.

There is also the hope that we will be able to put a string of metal atoms down the center of the cylindrical carbon cage. Such a structure is called a "nanowire," and is surely the world's smallest BNC cable. These wires are incredibly strong, if they could be made as thick as a steel cable, they would be able to bear hundreds of times as much weight as steel. The regular fullerenes will probably not turn out to have economical practical applications; research into fullerenes has led to research into carbon nanotubes, in January 2002 which may in fact be practical.

### The size of C<sub>60</sub>

If the C<sub>60</sub> molecule were the size of a soccer ball, then the soccer ball in turn would be about the size of the earth. It is shown in Fig.4.

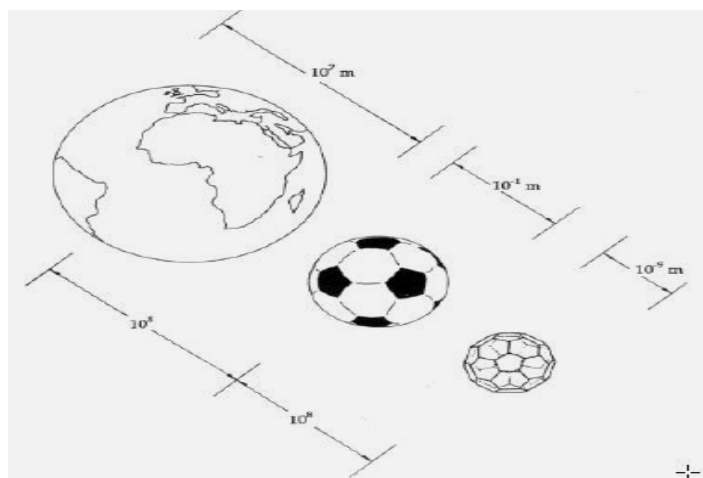


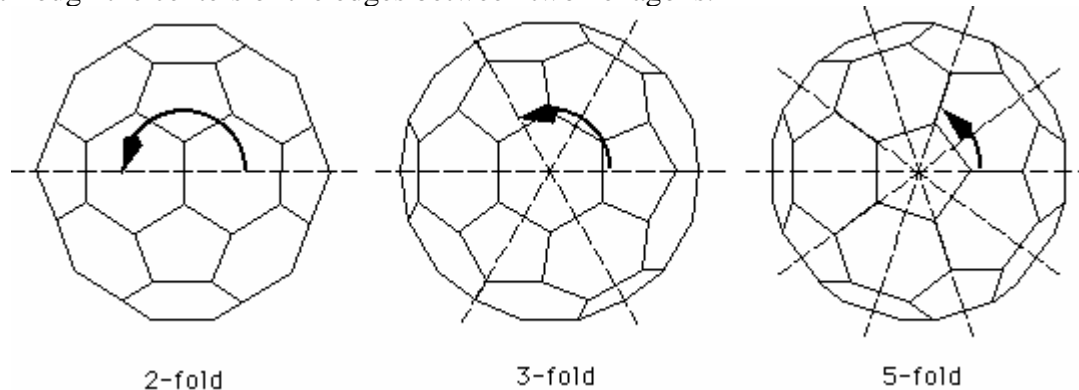
Figure 4 : Comparison of C<sub>60</sub> molecule with size of a soccer ball

Objects	Diameter
Earth	: $12,750 \text{ Km} = 12.75 \times 10^6 \text{ m}$
Soccer ball	: $22 \text{ cm} = 2.2 \times 10^{-1} \text{ m}$
C <sub>60</sub> molecule	: $7 \text{ \AA} = 7.0 \times 10^{-10} \text{ m}$

### Symmetry of the C<sub>60</sub> molecule

The C<sub>60</sub> molecule is highly symmetric, that means one can find many transformations that map the molecule onto itself. All such symmetry operations for a molecule are rotations around an axis, reflections in a plane, and sometimes so called inversions. Clearly all symmetry operations must leave the center of mass of the molecule in place, so all rotation axes and mirror planes must go through that point.

For the C<sub>60</sub> molecule there are three kinds of rotation axes. These are shown in Fig.5. The most obvious ones are the 5-fold axes through the centers of two facing pentagons. Look at one of the pentagons and we find that the molecule is symmetric under rotations of  $360/5 = 72$  degrees. Next there are a rotation axes through the center of two facing hexagons. Observe that these axes are only 3-fold, i.e. it takes a rotation of 120 degrees to map the molecule onto itself. Finally there are 2-fold axes through the centers of the edges between two hexagons.



**Figure 5 :** Rotation axes of the C<sub>60</sub> molecule

Since there are 12 pentagons for three fold axes, therefore, there are 6 different 5-fold axes (remember that each axis passes through *two* pentagons). Likewise, since there are 20 hexagons, there are 10 different threefold axes. To find the number of different two-fold axes, observe that each hexagon is neighbored by three other hexagons. Hence there are 30 edges between two hexagons, i.e. 15 different 2-fold axes. The reflections symmetries are also related to the edges between adjacent hexagons: The mirror planes contain two such edges, hence there are also 15 different mirror planes. Finally, the C<sub>60</sub> molecule is invariant under the inversion with respect to the center of mass. This means that if we replace each point with coordinates (x,y,z) by (-x,-y,-z), the molecule is mapped onto itself. Combining all those transformations, one finds 120 different symmetry operations. They form the *icosahedral group* which is the point group with the largest number of elements.

Hence  $C_{60}$  can be called the most symmetric molecule.

### Physical properties of $C_{60}$ (fullerene)

Density	: 1.65 g cm <sup>-3</sup>
Standard heat of formation	: 9.08 k cal mol <sup>-1</sup>
Index of refraction	: 2.2 (600nm)
Boiling point	: Sublimes at 800K
Resistivity	: 1014 ohms m <sup>-1</sup>
Vapour density	: N/A

### Crystal form Hexagonal cubic

Vapour pressure	: 5 x 10 <sup>-6</sup> torr at room temperature
	: 8 x 10 <sup>-4</sup> torr at 800K

### Organoleptic properties :

#### Appearance

Bucky ball soot	: Very finely divided black powder
Fullerite	: Brown/black powder
$C_{60}$	: Black solid
Odour	: Odourless

The fullerenes are also found to be soluble in common solvents such as benzene, toluene or chloroform. If one shakes up some fullerene soot with toluene and filter the mixture, one obtains a red solution. As the solvent evaporates, crystals of pure carbon appear. An HPLC trace showing fullerenes found in carbon soot:

### Fullerene derivative

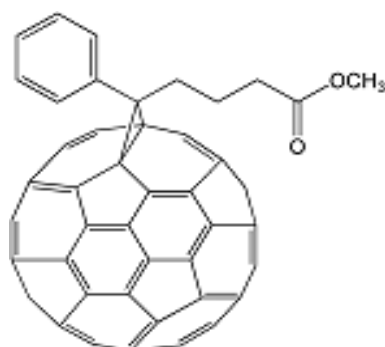


Figure 6 : PCBM

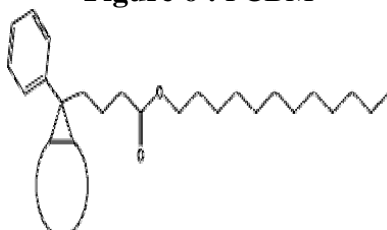
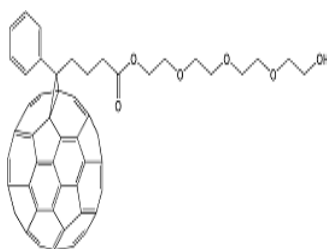


Figure 7 : PCB-C<sub>12</sub> (lipo-soluble for skincare and nutrition)



**Figure 8 : PCB-EO<sub>4</sub>**

The chemistry of fullerenes is rich and varied and allows the properties of basic fullerenes to be tailored to a given application. Derivatives of all of the basic fullerenes are possible; e.g., C<sub>60</sub>, C<sub>70</sub> and C<sub>84</sub>[4]. Derivatives 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.

### PCBM (Phenyl C<sub>n</sub> Butyric Acid Methyl Ester)

The commercialization of the PCBM range of derivatives began in 1994 [5]. PCBM has become today's market standard in polymer electronics and photovoltaics as a result of its flexibility and historic research. We can find a full range of fullerenes with the PCBM chemical modification including C<sub>60</sub>, C<sub>70</sub> and C<sub>84</sub>. The structure of PCBM is shown in Fig.6.

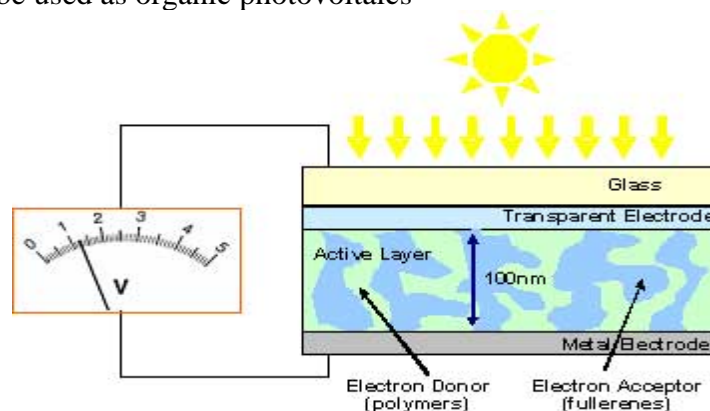
### Other derivative

The structures of other derivatives are shown in Figs.7.& 8. Other range of synthesized fullerene derivatives includes hydroxylated and carboxylated for enhanced water solubility. For enhanced lipid solubility, PCB-C<sub>12</sub> and PCB-C<sub>18</sub> have been synthesized.

## Application of Fullerenes

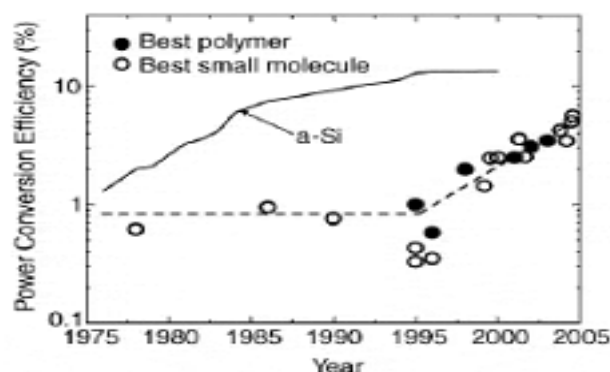
### Organic Photovoltaics(OPV)

Fullerene can be used as organic photovoltaics



**Figure 9 : Source : Janssen, et al, MRS Bulletin 1/2005**

Currently, the record efficiency for a bulk heterojunction polymer solar cell is a fullerene/polymer blend. The fullerene acts as the n-type semiconductor (electron acceptor). The n-type is used in conjunction with a p-type polymer (electron donor), typically a polythiophene. They are blended and cast as the active layer to create what is known as a bulk heterojunction.



**Figure 10** : Source: Forrester, MRS Bulletin 1/2005

Fullerenes are used as is, or they are derivitized to increase their solubility. The most commonly used derivative in photovoltaics is  $C_{60}$ , but  $C_{70}$  has been shown to have a 25% higher power conversion efficiency than  $C_{60}$ . In addition, alternative derivatives such as  $C_{60}$  PCBB have been shown to increase conversion efficiency by over 40% when compared to  $C_{60}$  PCBM in like systems. In November of 2005 a record cell efficiency of 4.4% using a fullerene derivative and illustrating the importance of the characteristics of the active layer on performance was published[6]. As the preferred n-type material, fullerenes can comprise up to 75% of the active layer by weight. Solar cell efficiency continues to increase steadily, placing the potential for commercialization in the not-too-distant future.

The performance of polymer transistors e.g. Organic Field Effect Transistors (OFETS) and photodetectors has also been increasing, in part due to a great deal of synergy between OFETS and OPVs. The leading OFETS use the n-type semiconducting properties of fullerenes based on  $C_{60}$ ,  $C_{70}$  along with  $C_{84}$ . Fullerene OFETS fabricated with  $C_{84}$  show greater mobility than  $C_{60}$  or  $C_{70}$  and exhibit greater stability. While more work is needed, the world of polymer electronics is opening up for both fullerenes and single-walled carbon nanotubes.

### **Antioxidants and Biopharmaceuticals**

Fullerenes are powerful antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage or death. Fullerenes hold great promise in health and personal care applications where prevention of oxidative cell damage or death is desirable, as well as in non-physiological applications where oxidation and radical processes are destructive (food spoilage, plastics deterioration, metal corrosion). Major pharmaceutical companies are exploring the use of fullerenes in controlling the neurological damage of such diseases as Alzheimer's disease and

Lou Gehrig's disease (ALS), which are a result of radical damage. Drugs for atherosclerosis, photodynamic therapy, and anti-viral agents are also in development.

Fullerenes are known to behave like a “radical sponge,” as they can sponge-up and neutralize 20 or more free radicals per fullerene molecule. They have shown performance 100 times more effective than current leading antioxidants such as Vitamin E. Fullerene is highly soluble in almond oil and thus it can be used for screening test for ocular tissue toxicity indicating no adverse effect.

## **Additives & Other**

### **Polymer Additives**

Fullerenes and fullerene black are chemically reactive and can be added to polymer structures to create new copolymers with specific physical and mechanical properties. They can also be added to make composites. Much work has been done on the use of fullerenes as polymer additives to modify physical properties and performance characteristics.

### **Catalysts**

Marked ability to accept and to transfer hydrogen atoms; hydrogenation and hydrodealkylations.  
Highly effective in promoting the conversion of methane into higher hydrocarbons.  
Inhibits coking reactions.

### **Water purification & bio-hazard protection**

Singlet oxygen catalysis of organics with fullerene C<sub>60</sub>

### **Portable power**

Proton exchange membranes for fuel cells

### **Vehicles**

Enhanced durability, lower heat build-up, better fuel economy with use of fullerene black/rubber compounds

### **Medical**

MRI agents

The body of research on fullerene black is small compared to fullerenes and less is known about the physical properties and the potential for application. Certain features however show promise for the use of fullerene black as an improvement over carbon black in various applications. The distinguishing feature of fullerene black compared to typical carbon blacks is that the carbon layer planes of fullerene black are curved and fullerene-like in nature. This curvature is thought to explain the observed higher reactivity of fullerene black compared to conventional carbon black. This feature offers potential for use in various applications, such as catalysts, catalyst supports and rubber additives.

The most common fullerene is the classic “Buckminster Fullerene” with 60 carbon atoms. It is the most abundant form, followed by C<sub>70</sub>, C<sub>76/78</sub>, C<sub>84</sub> and finally the higher fullerenes of C<sub>90</sub> and above. For particularly demanding applications, sublimed

fullerenes with 99.95% purity are available.

### Conclusion

Thus this study gives the basic knowledge of structure of fullerenes and their applications. The fullerenes can be used as organic photovoltaics (OPV). Other uses of C<sub>60</sub> like catalysts, in water purification and biohazard protection, portable power, vehicles and medical.

### Acknowledgement

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### References

- [1] Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F. and Smalley, R. E., 1985, "C<sub>60</sub>: Buckminsterfullerene" *Nature*, **318**, pp.162-163.
- [2] Diwan, Parag, and Bharadwaj, Ashish, 2005, "The nanoscope, Encyclopedia of Nano science and Nanotechnology", Vol. **1**, pp. 250-276.
- [3] Morgan, G. J., 2003 "Historical Review: Viruses, Crystals and Geodesic Domes". *Trends in Bio chemical science* **28**, pp. 86-90.
- [4] Kratshmer, W., Lamb, L. D., Fostiropoulos, K. and Huffman, D. R., 1990, "Solid C<sub>60</sub> : A new form of carbon" *Nature*, **347**, pp. 354-358.
- [5] Hummelen, J. C., Knight, B. W., Lepeq, F., Wudl, F., Yao, J., Wilkins, C. L., 1995 "Preparation and characterization of fullorid", *J. Org. Chem.*, **60**. pp. 532-538.
- [6] Ellis, E. C., Rong, G. L., Lin Z. Y., and Cheng, X. U., 2000, "Nitrogen and the sustainable Village", *Agro-ecosystem Sustainability: Developing Practical strategies* CRC Press, Boca Raton, F. L., Edited by S. R. Gliessman, pp. 95-104.