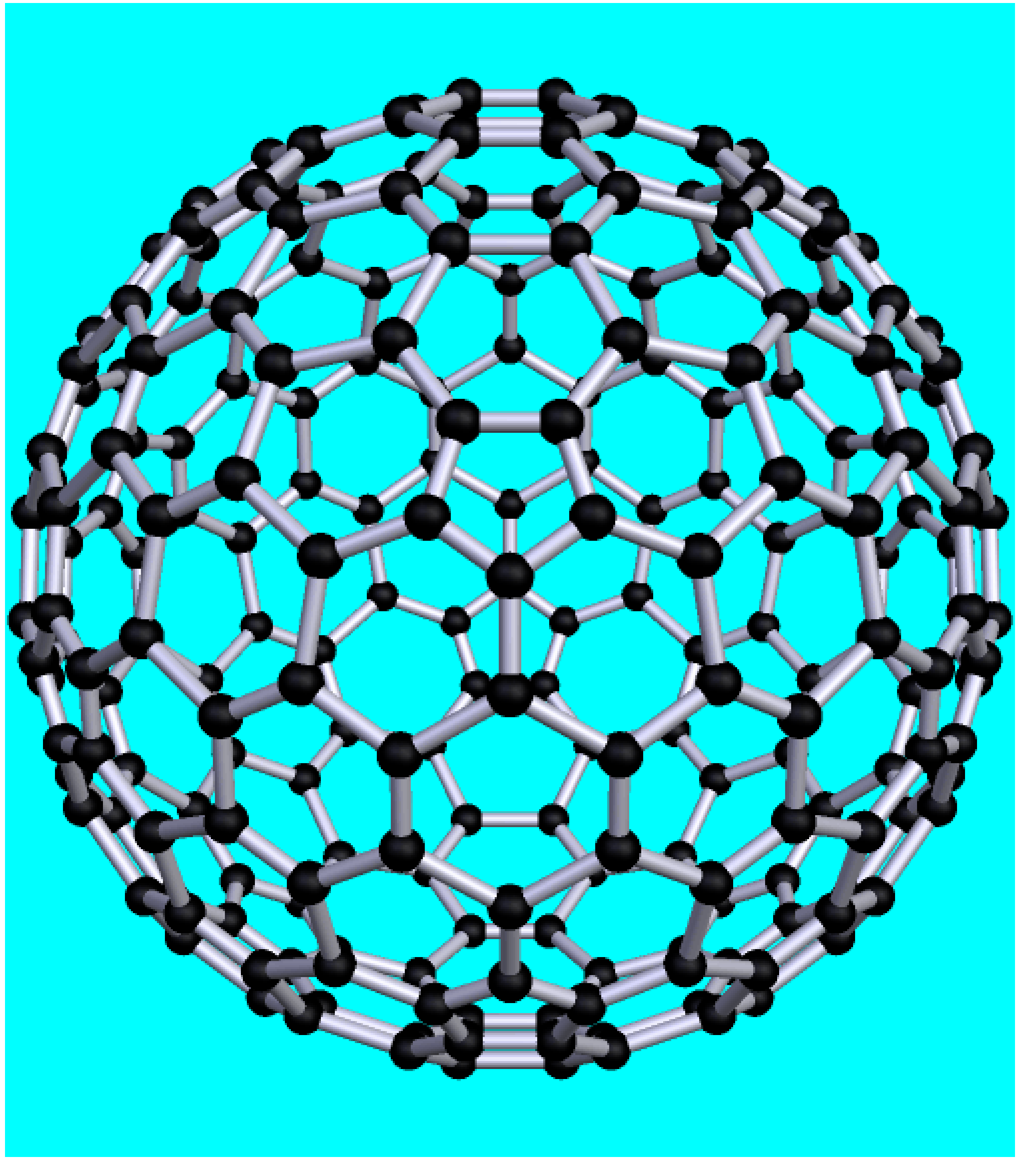
Module VII: Fullerene, carbon nanotubes, and graphene

Course: CSO203
Instructor: Dr. Prakash Chandra Mondal
Department of Chemistry, IIT Kanpur

C_{60} – FULLERENE



Discovery of C_{60}

- The C_{60} was discovered in 1985 by a team of sicentists including Harold Kroto, Robert Curl, and Richard Smalley at Rice University.
- They were awarded the Nobel Prize in Chemistry in 1996 for their discovery.

The discovery of carbon atoms bound in the form of a ball is rewarded

KUNGL.
VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

9 October 1996

The Royal Swedish Academy of Sciences has decided to award the 1996 Nobel Prize in Chemistry to

Professor **Robert F. Curl, Jr.**, Rice University, Houston, USA,

Professor **Sir Harold W. Kroto**, University of Sussex, Brighton, U.K., and

Professor **Richard E. Smalley**, Rice University, Houston, USA,

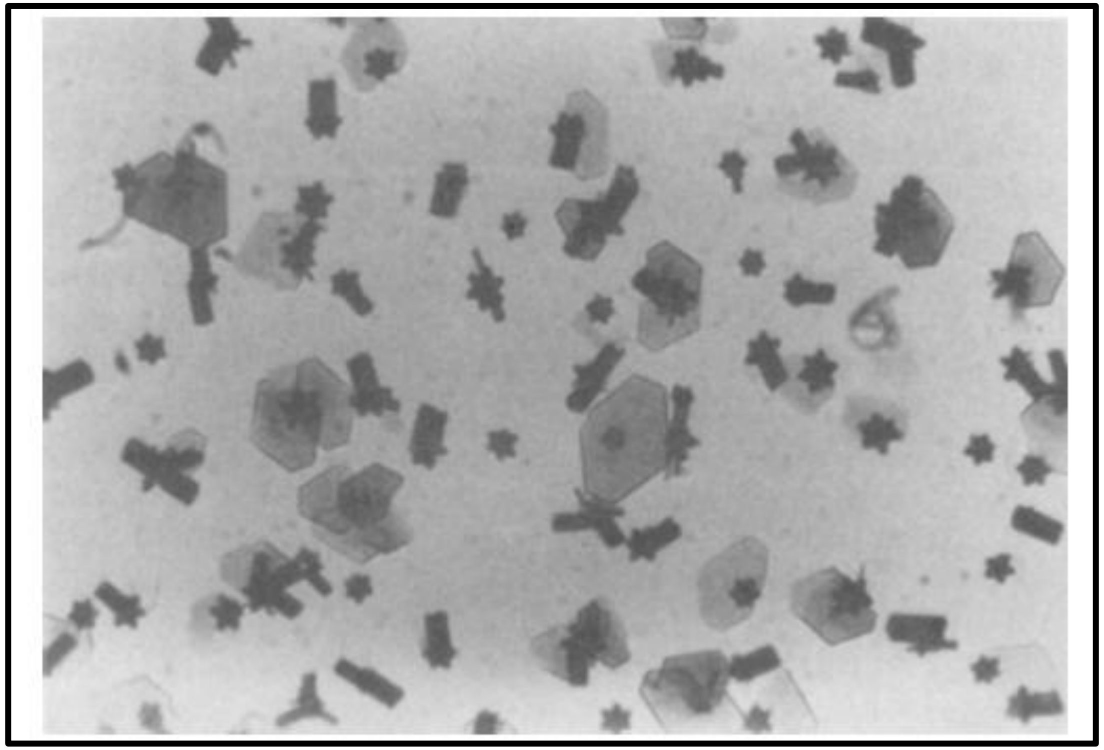
for their discovery of fullerenes.

Preparation of C_{60}

Experiment Setup:

- The researchers used a laser to vaporize graphite. This produced clusters of carbon atoms which were then cooled rapidly

- The resulting carbon clusters were analyzed using mass spectrometry



Transmission micrograph of a typical crystal of C_{60} showing thin platelets, rods, and stars of hexagonal symmetry

Salient features of C_{60}

<u>Observations:</u>

- **Among the various carbon clusters, one particular cluster containing 60 carbon atoms (C_{60}) was unusually stable and abundant**

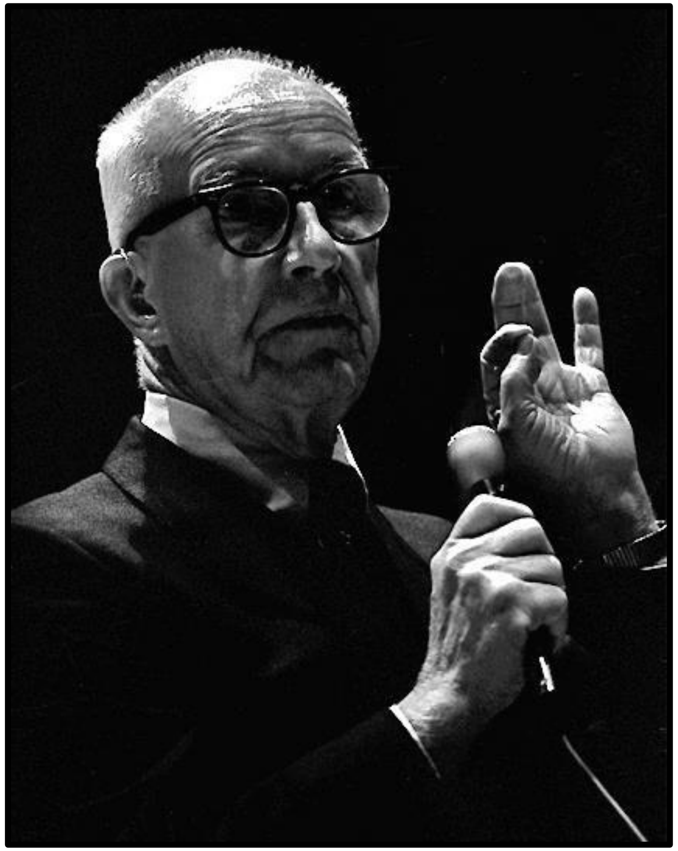
- **This suggested a unique and highly symmetrical structure, different from the known forms of carbon**

- **They deduced that C_{60} must have a spherical structure for its stability. Hence, proposing that the 60 carbon atoms were arranged in a pattern similar to a soccer ball, consisting of 12 pentagons and 20 hexagons**

The history of C_{60}

Curl, Kroto and Smalley performed this experiment together with graduate students J.R. Heath and S.C. OBrien during a period of eleven days in 1985. By fine-tuning the experiment they were able in particular to produce clusters with 60 carbon atoms and clusters with 70. Clusters of 60 carbon atoms, C_{60}, were the most abundant. They found high stability in C_{60}, which suggested a molecular structure of great symmetry. It was suggested that C_{60} could be a "truncated icosahedron cage", a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5-angled) surfaces. The pattern of a European football has exactly this structure, as does the geodesic dome designed by the American architect R. Buckminster Fuller for the 1967 Montreal World Exhibition. The researchers named the newly-discovered structure *buckminsterfullerene* after him.

Buckminster Fuller, who coined the term "geodesic"



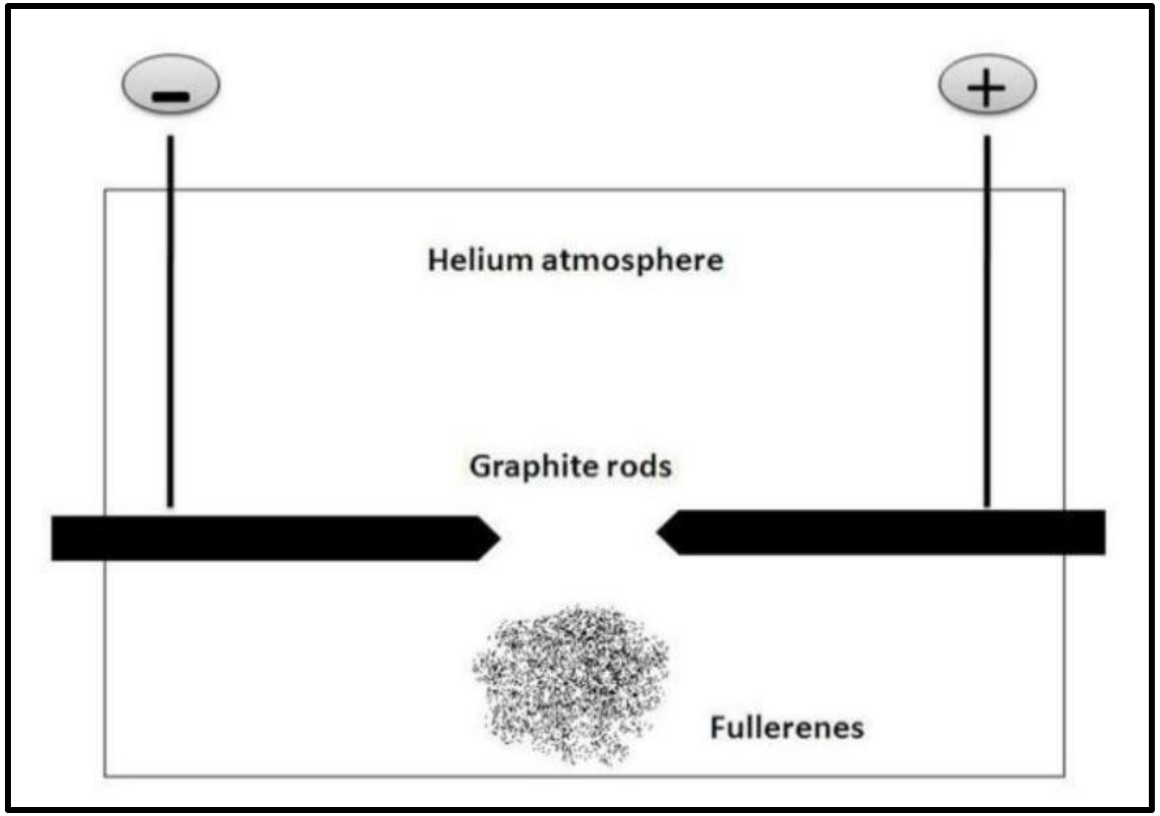
The structure resembled the geodesic domes designed by American architect Buckminster Fuller, leading to the molecule being named Buckminsterfullerene

Preparation of C_{60}

Starting Material:

- **The process begins with pure graphitic carbon soot produced by evaporating graphite electrodes in an atmosphere of ~100 torr of helium (inert conditions)**

- **The inert gas prevents oxidation and other unwanted reactions**



Preparation of C_{60}

- **Collection and Dispersion:**

The resulting black soot is gently scraped from the collecting surfaces inside the evaporation chamber and dispersed in benzene, producing a wine-red to brown liquid depending on the concentration of C_{60}

- **Separation and Drying:**

The liquid is separated from the soot and dried gently, leaving dark brown to black crystalline material.

Purification of C_{60}

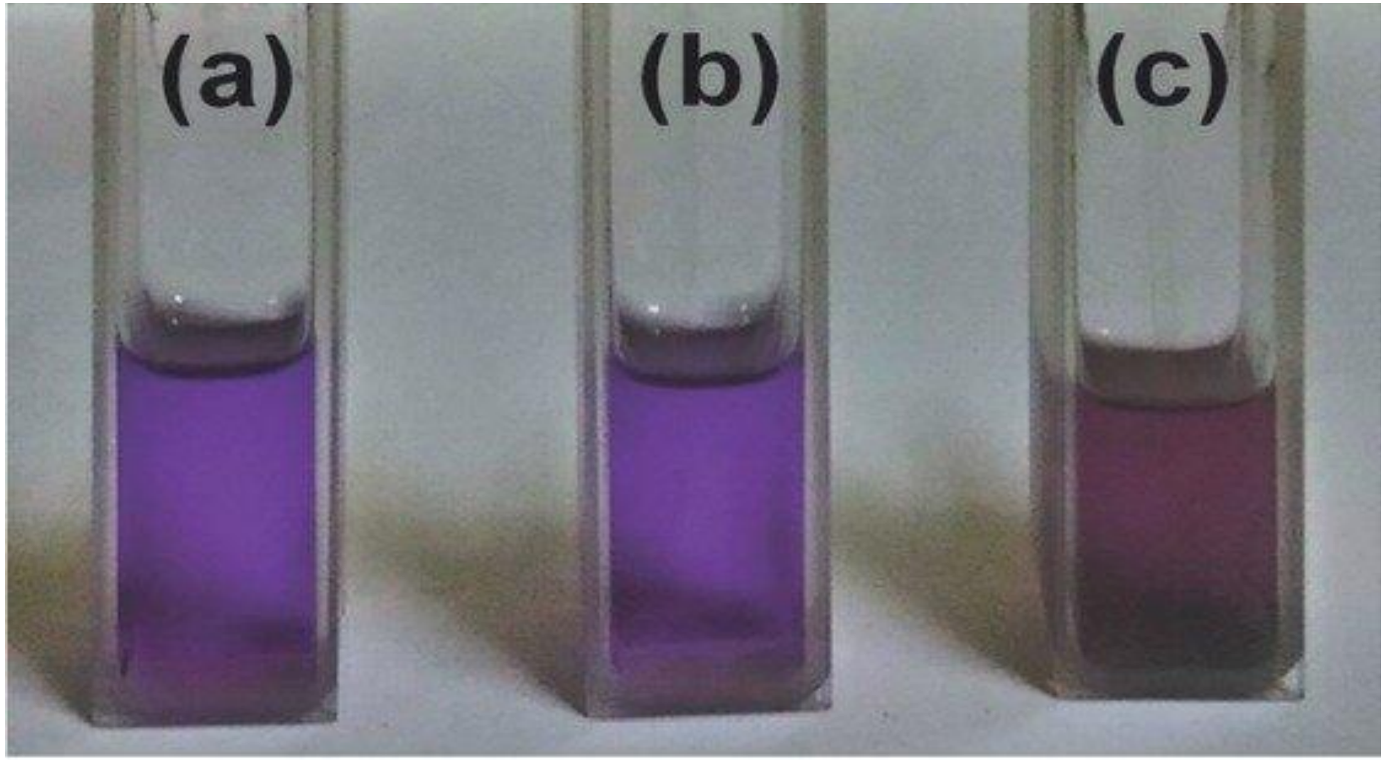
- **Purification:**

To purify C_{60}, it is needed to remove hydrocarbons by washing the initial soot with ether before the concentration procedure. The material can be sublimed repeatedly without decomposition

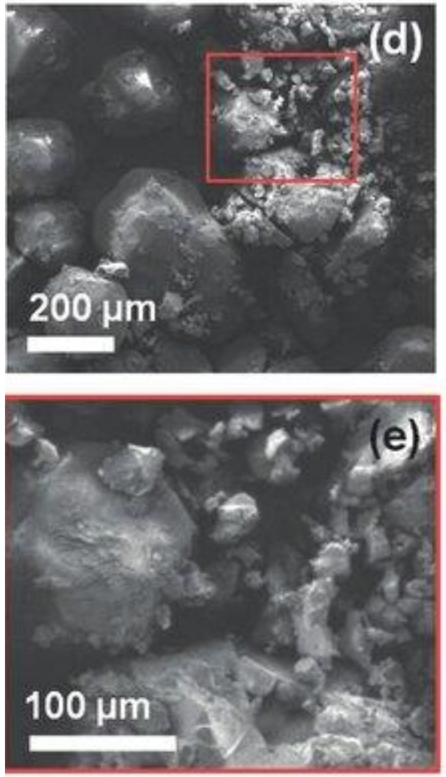
- **Crystallography:**

Optical microscopy reveals crystals (rods, platelets, star-like flakes) with six-fold symmetry. They appear red-brown in color

Color of C_{60}



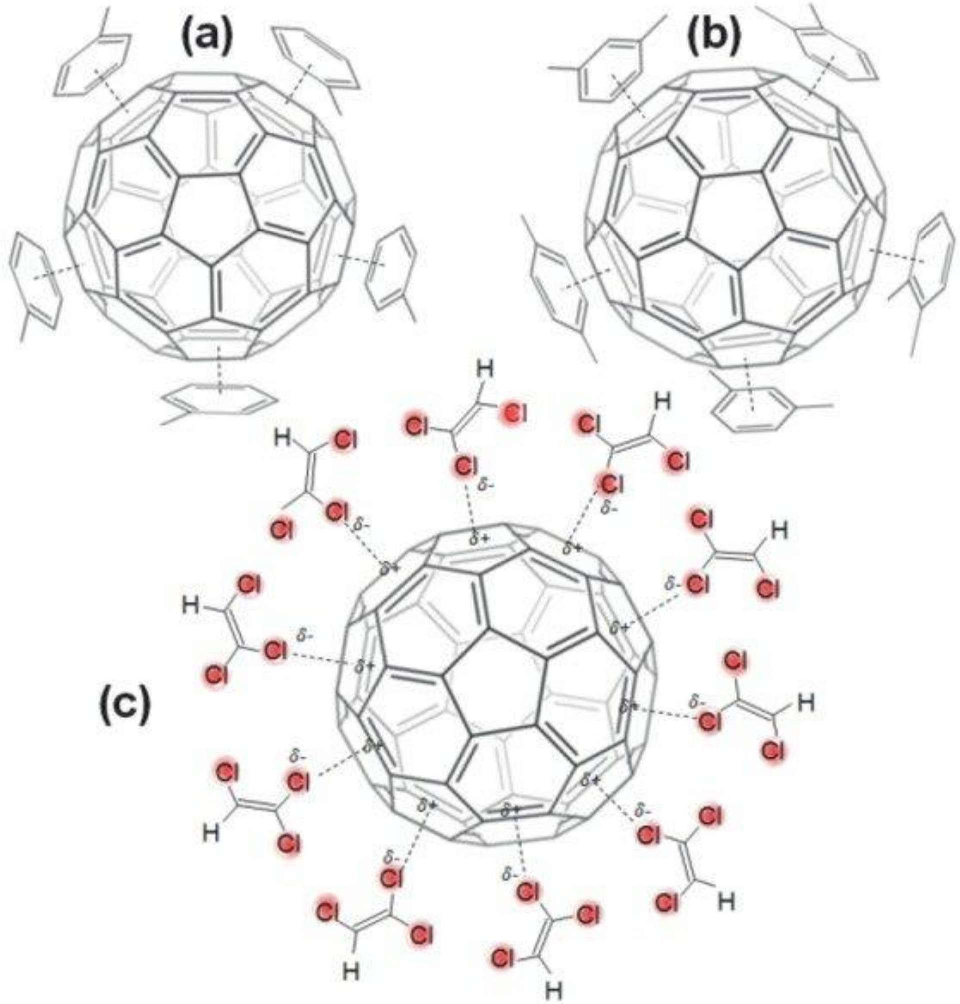
The C_{60} solution in different organic solvents: (a) toluene, (b) xylene, and (c) TCE.



The SEM imaging of solid C_{60} at a different magnification.

Open Chem., 2019; 17: 1198–1212

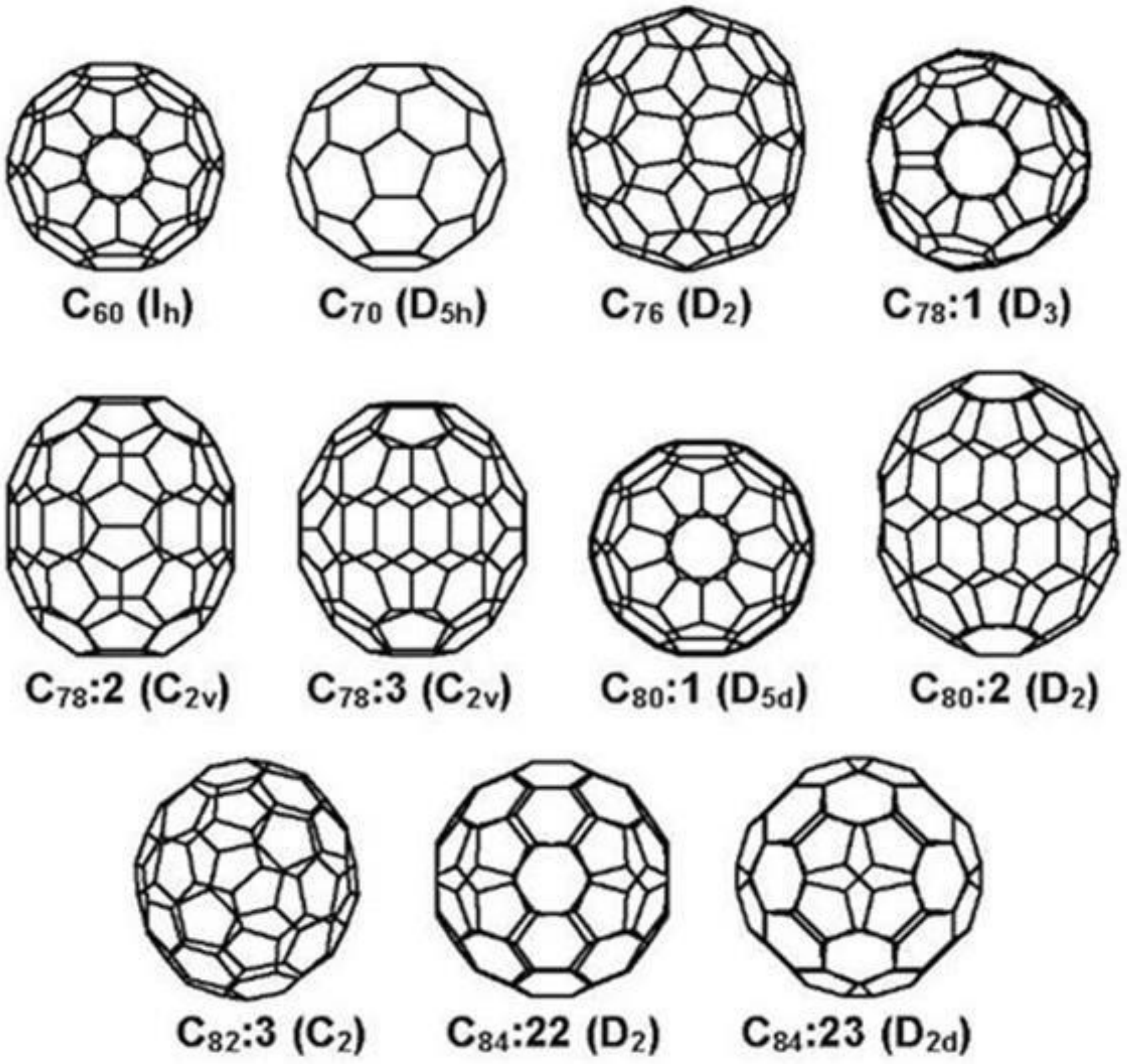
Interactions of C_{60} with the different solvents



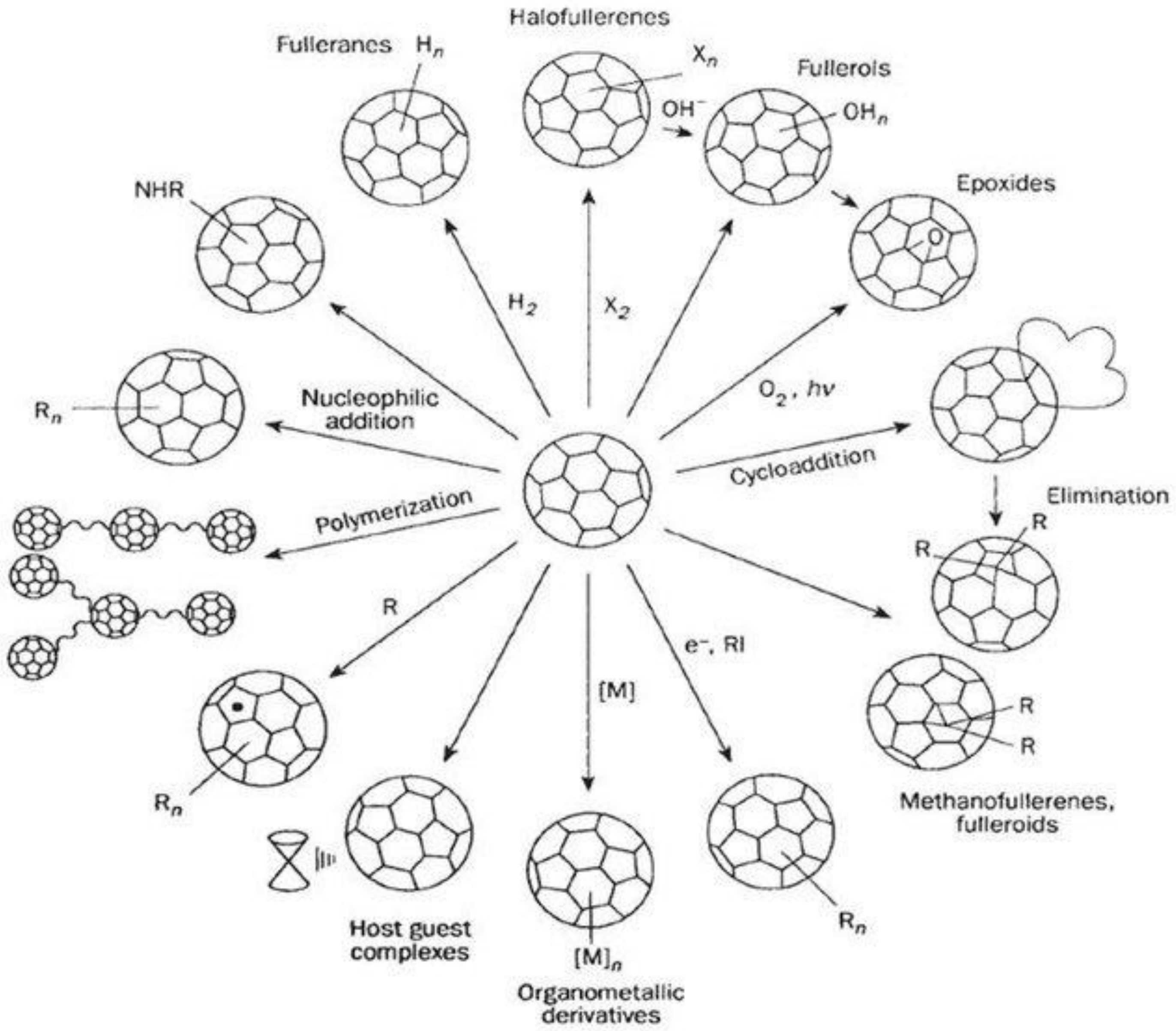
The C_{60} solution in different organic solvents: (a) toluene, (b) xylene, and (c) TCE.

Open Chem., 2019; 17: 1198–1212

The major isomers of C_{60}



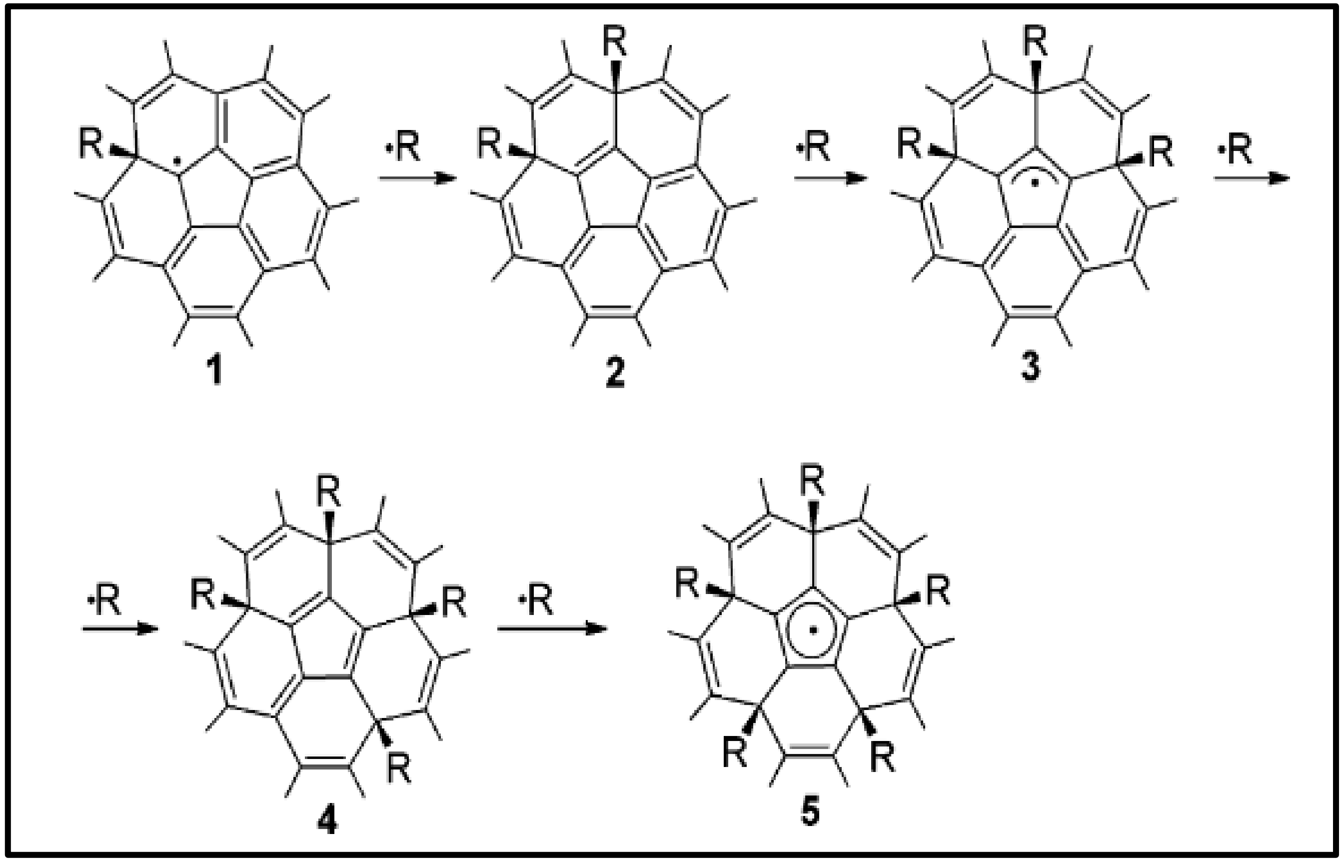
Generic reactions C_{60}



Radical reactions C_{60}

- **Prolonged irradiation of C_{60} solutions in the presence of excess radical precursors leads to multiple radical additions**

- **Photochemically generated benzyl radicals react with C_{60}, producing radical and non-radical adducts R_nC_{60} ($R = C_6H_5CH_2$) with n = 1-15 and in case of methyl, n =1-34**

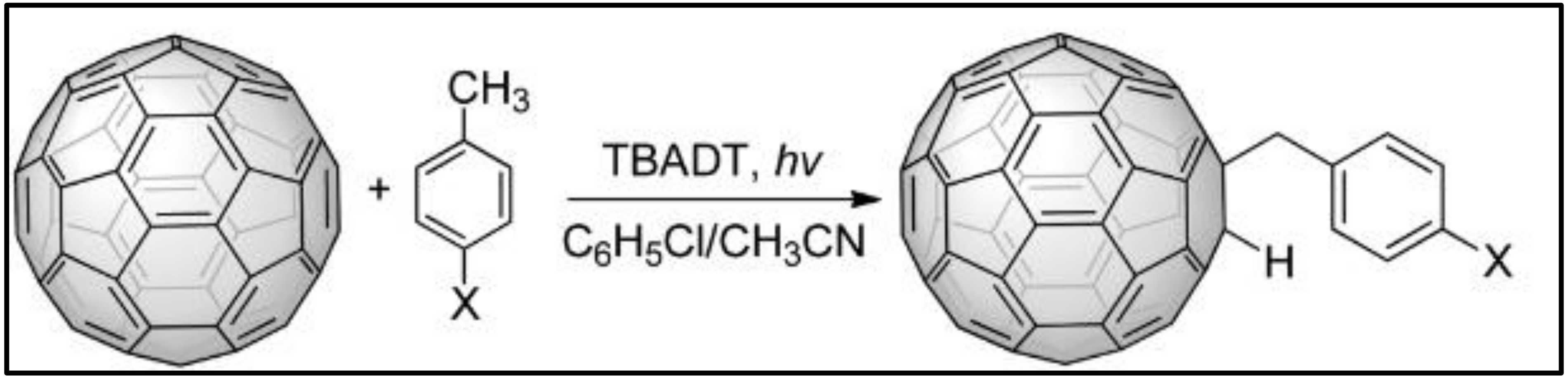


- **(3) and (5) were found to be highly localized on the C_{60} surface due to the steric protection lent by the three or five benzyl substituents that shelter the surface's radical sites**

Radical reactions of C_{60}

- **The use of tetrabutylammonium decatungstate [TBADT, $(n\text{-}Bu_4N)_4W_{10}O_{32}$] catalysis can be regarded as a general and highly efficient strategy for C−C bond formation in fullerenes**

- **This method has enabled the otherwise inaccessible chemical modification of fullerene C_{60} with several classes of organic compounds, including toluene, anisole, thioanisole, aldehydes, ethers, sulfides, and alcohols**



Reduction of C_{60}

- If traces of CS_2 used for extracting fullerene soot are not completely removed, passing down an alumina column (containing traces of water) becomes converted into H_2S, COS, CO, and CO_2.

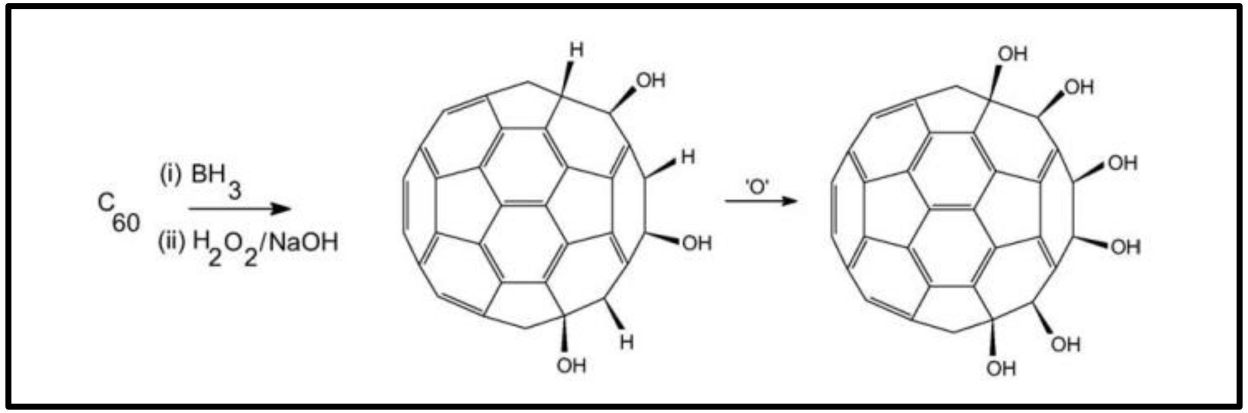
- The H_2S then reduces the fullerene and is converted into Sulphur. Separate experiments showed that C60 converts H_2S into Sulphur

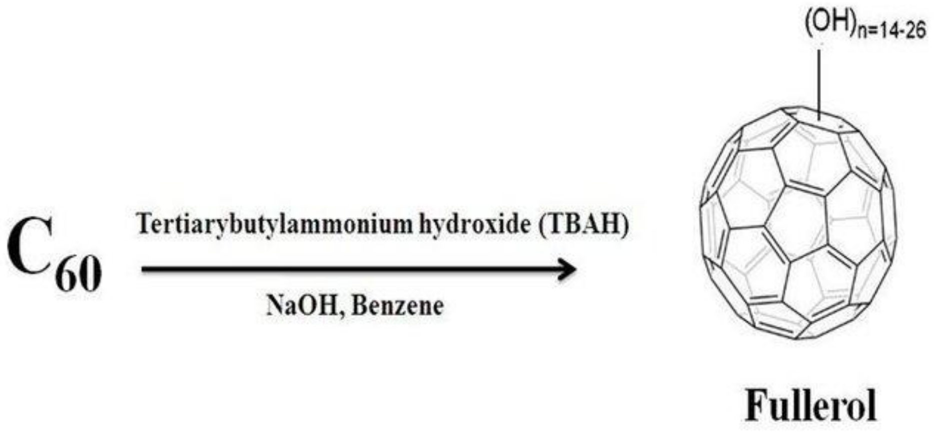
$$CS_2 \xrightarrow{Al_2O_3/H_2O} H_2S \xrightarrow{C_{60}} S \quad (+C_{60}H_2)$$

Hydroboration of C_{60}

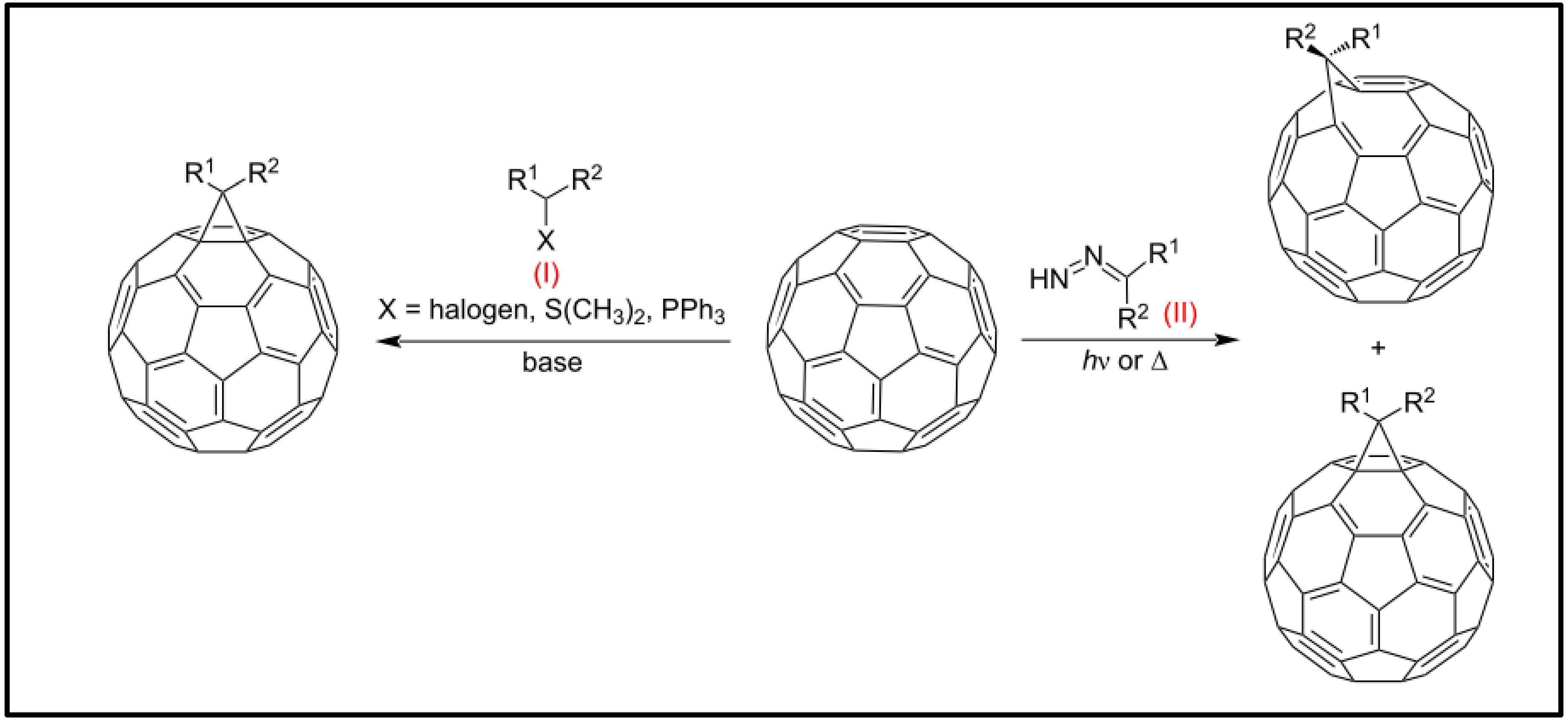
- Hydroxyfullerenes are water-soluble and can be converted into a variety of polymers with very strong cross-linking

- The ready occurrence of allylic oxidation means that multiple additions of H and OH pairs in the latter reaction can only be achieved if the reaction is performed under N_2





[2+1] cycloaddition reactions of C_{60}



Major developing methods for C_{60} functionalization prefer [2 + 1] cycloaddition processes in which reactions leading to methanofullerenes are widely used