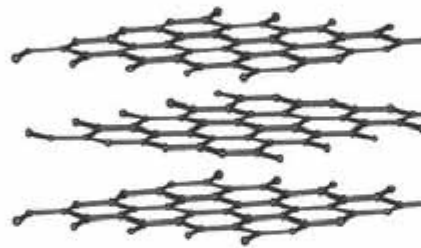# FULLERENES

Forme allotropiche del carbonio

Grafene

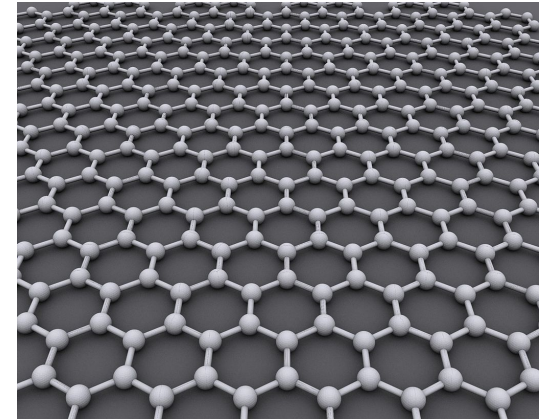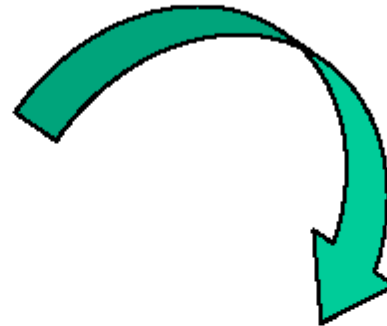**Diamante**

materiale noto per la sua durezza

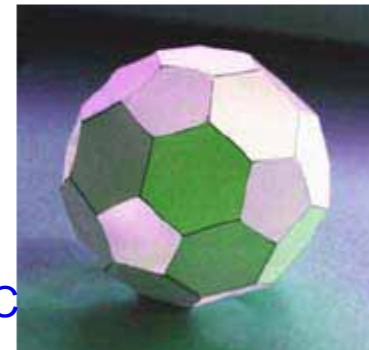si forma atemperature comprese fra i 900 °C ed i 1.200 °C e pressione di circa 50 Kbar

Grafite materiale con elevata conduttività elettrica
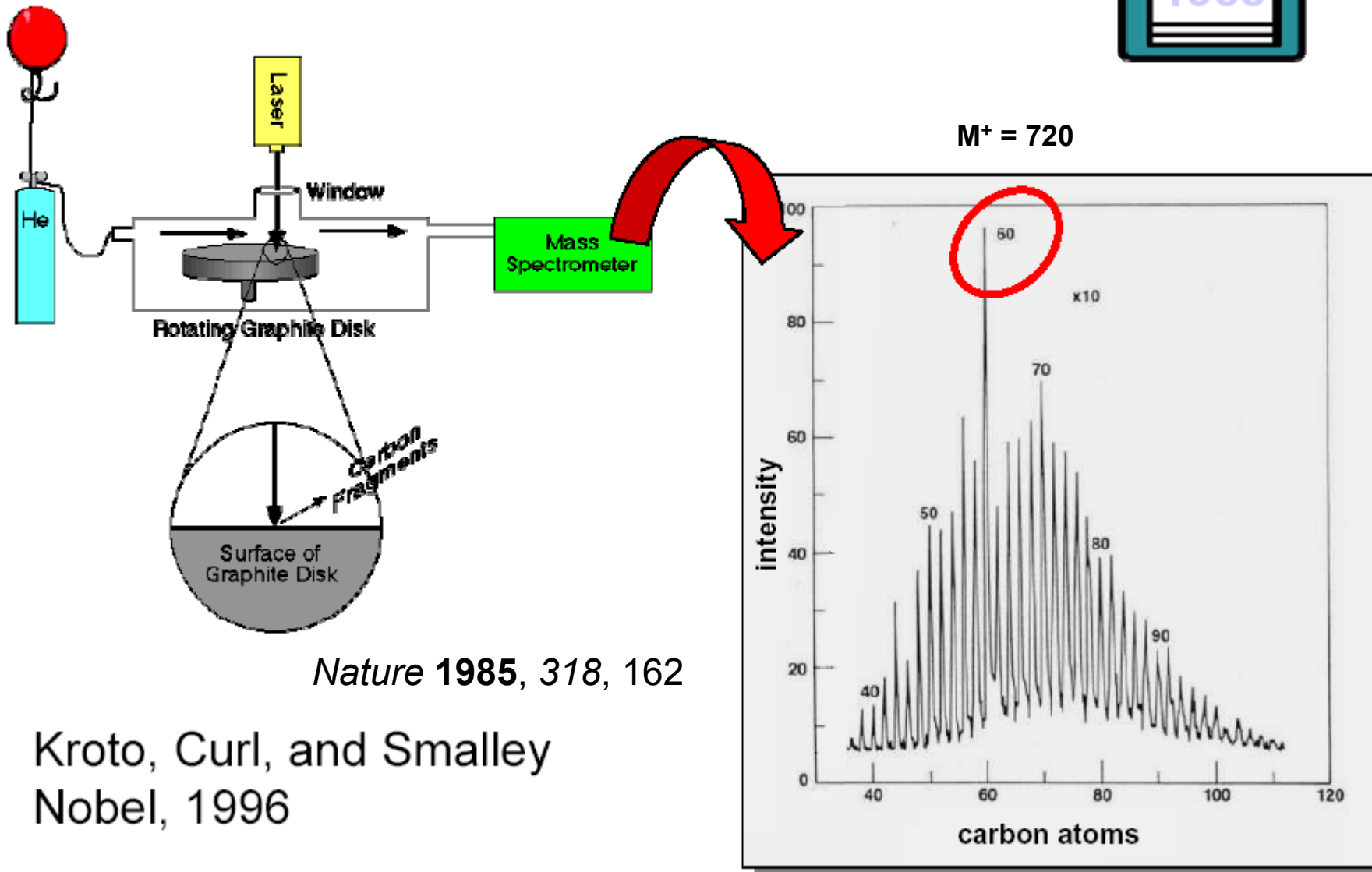
si forma alla temperatura di 1.200 °C

1970 { Eiji Osawa la teorizza
R.W.Henson la propone

Fullerene: la scoperta

1985

M$^+$ = 720

Nature **1985**, *318*, 162

Kroto, Curl, and Smalley
Nobel, 1996

Isolation, Separation and Characterisation of the Fullerenes C_{60} and C_{70}: The Third Form of Carbon

Roger Taylor, Jonathan P. Hare, Ala'a K. Abdul-Sada and Harold W. Kroto

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

Pure samples of the species C_{60} (Buckminsterfullerene) and C_{70} (fullerene-70) have been prepared, and their structures characterised by their mass and ^{13}C NMR spectra; the results indicate the existence of a family of stable fullerenes, thus confirming that carbon possesses a third form in addition to diamond and graphite.
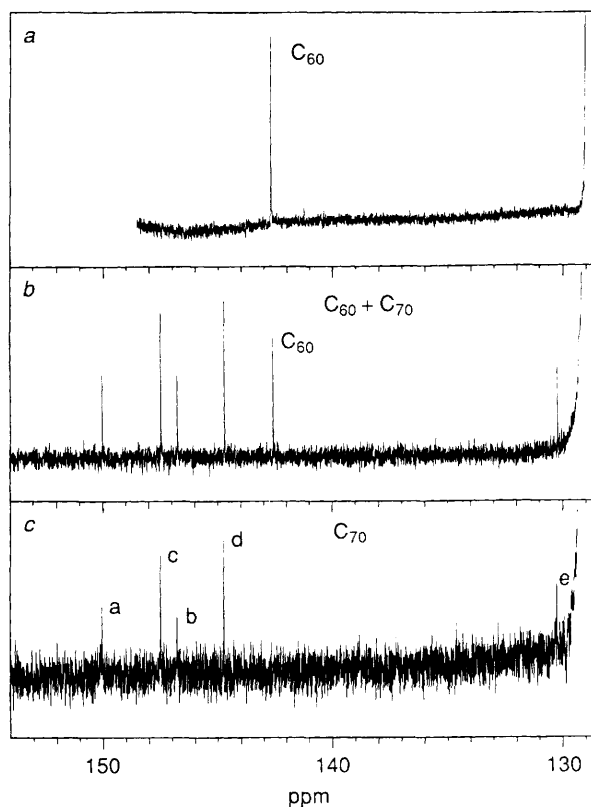
Fig. 3 *a* ^{13}C NMR spectrum of C_{60}, Buckminsterfullerene. *b* ^{13}C NMR spectrum of a mixed sample in which C_{60} is much reduced. *c* ^{13}C NMR spectrum of C_{70}, fullerene-70. The line assignments given are based on the observed intensities and semi-quantitative strain arguments, and are subject to confirmation. The wing of the intense benzene solvent signal lies at the far right hand side
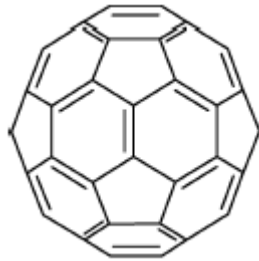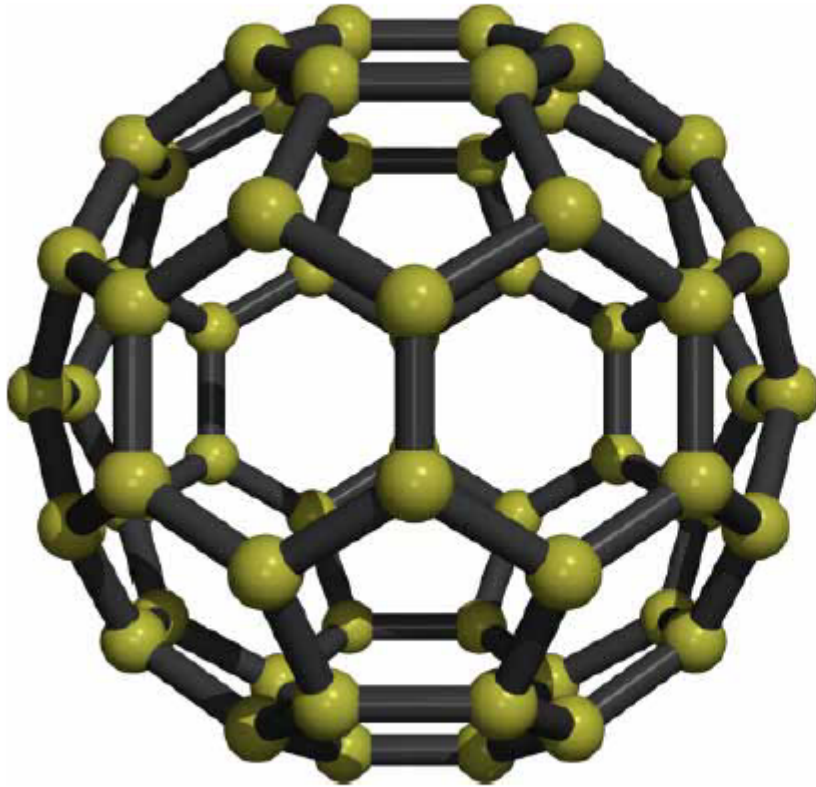
C$_{60}$

scoperto nel 1985 da Kroto, Smalley and Curl, *Nature* **1985**, *318*, 162

1996 Chemistry Nobel Prize

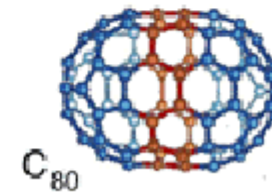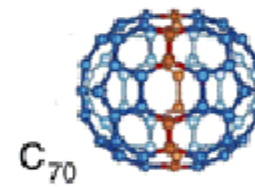**ROBERT F. CURL, Jr.** , **SIR HAROLD W. KROTO** , and **RICHARD E. SMALLEY**

"for their discovery of fullerenes"

Fullereni

Buckminsterfullerene (C_{60})

truncated icosahedron (I_h symmetry)

C_{60}

C_{70}

C_{80}
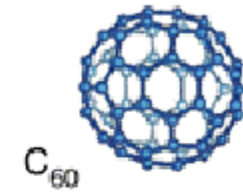
Buckminster Fuller
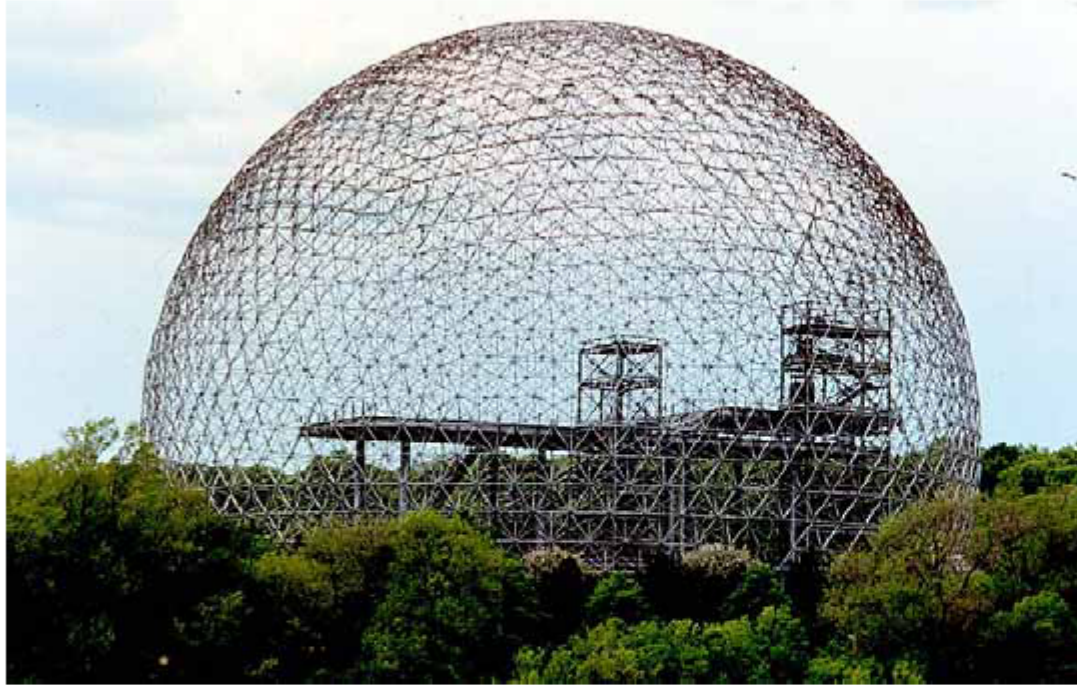
Geodesic Dome

Buckminster Fuller, US Pavilion for the 1967 International and Universal Exposition in Montreal
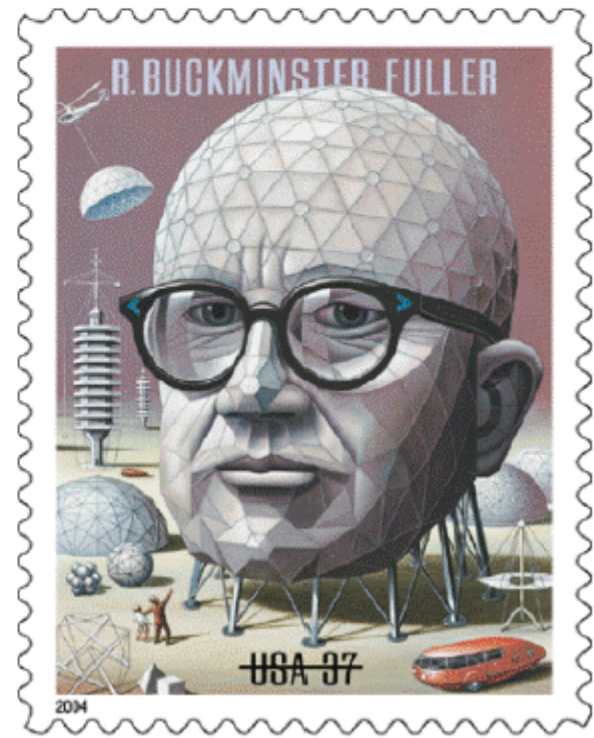
Regola di Eulero

Un fullerene è un poliedro convesso con facce esagonali e pentagonali.

$$F - S + V = 2$$

Se uso solo esagoni $F - S + V = 0$. Affinché la formula di Eulero per i poliedri sia rispettata, occorre che diventi uguale a 2. In breve, occorre sostituire **12** esagoni con altrettanti **pentagoni**

Ci sono esattamente 12 pentagoni in un fullerene. Il più piccolo fullerene è il C_{20}
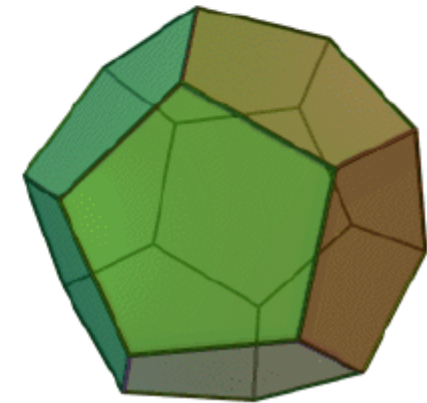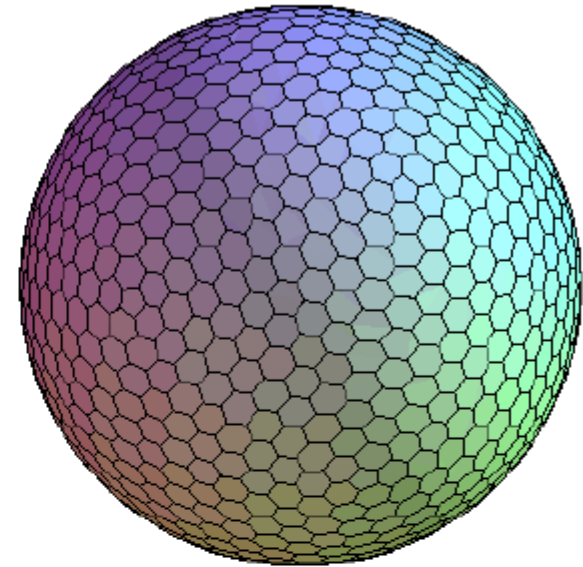
Facce 12

Spigoli 30

Vertici 20

C_{60}

- C_{60} was found to become a superconductor in M_3C_{60} species (M=alkali metal)
- organic soft ferromagnet in $TDAE^+C_{60}^-$ (TDAE=tetrakisdimethylaminoethylene) at 16.1 Kelvin
- a relatively stable hexaanion in cyclic voltammetry
- an interesting material with non-linear optical properties.
  - The C_{60} surface contains 20 hexagons and 12 pentagons. All the rings are fused, all the double bonds are conjugated.

- X-Ray crystal structure determinations on C_{60} and on some of its derivatives have proved the existence of two different types of bonds: 'short bonds' or 6,6 junctions shared by two adjacent hexagons (ca. 1.38 A° long) and 'long bonds', or 5,6 junctions, fusing a pentagon and a hexagon (ca. 1.45 A° long).

Proprietà strutturali del C_{60}

1.45 Å [5,6]

1.38 Å [6,6]
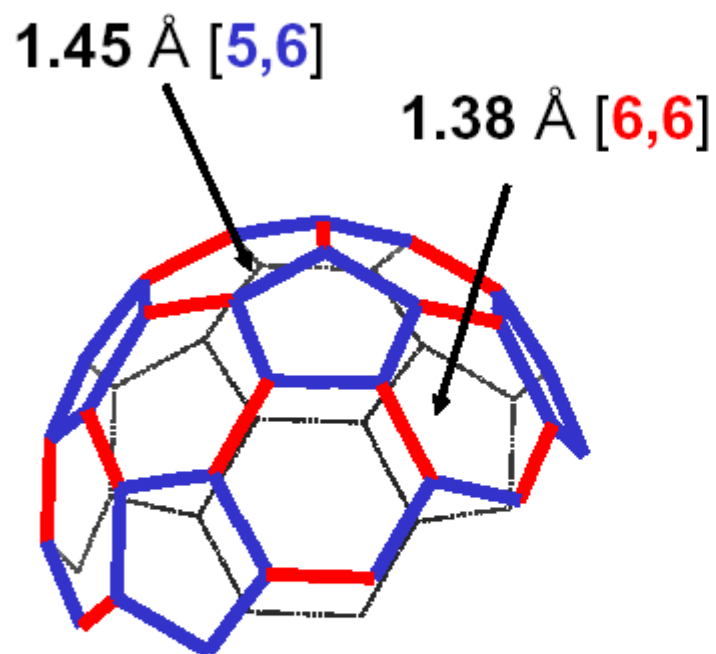
ΔH_f = 10.16 Kcal/mol per C

(ΔH_f)graphite = 0 Kcal/mol

(ΔH_f)diamond = 0.4 Kcal/mol

The six-membered rings are **not aromatic** in that they contain alternating single and double bonds. 6,6-bonds are shorter than 5,6-bonds.

The overall buckyball structure has to be viewed as fused **1,3,5-cyclohaxatrienes** and **[5]radialenes**

spherical geometry causes **pyramidalization** of the unsaturated C-atoms. Strain Energy $\approx$ 80% H_f

- Haddon and Raghavachari, in *buckminsterfullerenes*, VCH, 1993
- H.D. Beckhaus et al. *Angew. Chem.* 1992, 31, 63)

- A. Hirsch, Z. Chen, H. Jiao. *Angew. Chem.* **2000**, *39*, 3915.
- M. Bühl, A. Hirsch *Chem. Rev.* **2001**, *101*, 1119.

Proprietà strutturali del C_{60}
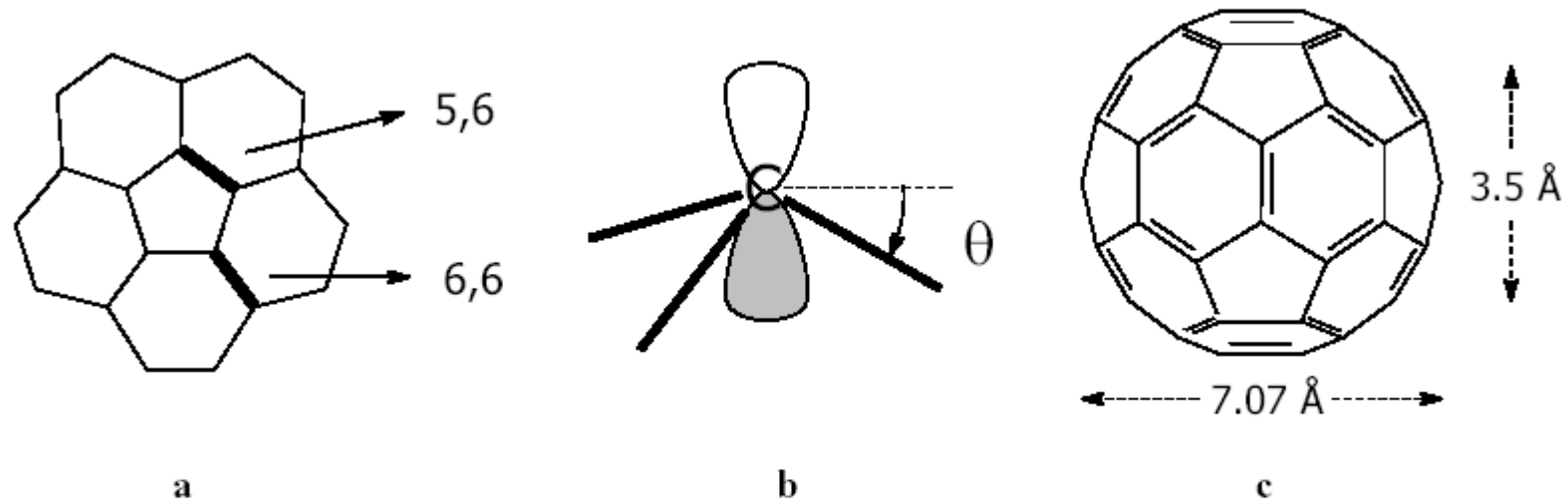
(a) legami 5,6 e 6,6 nel C_{60}; (b) angolo di piramidalizzazione θ; (c) diametro esterno (*edge-to-edge*) e interno del C_{60} (il diametro di Wan der Waals è circa 10.4 Å)

C$_{60}$ solution in toluene
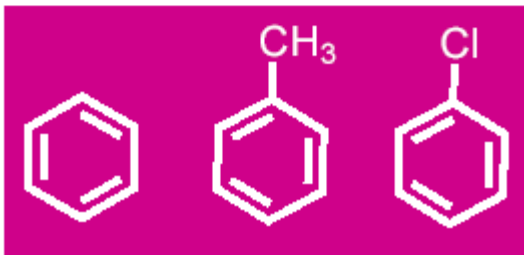
and CS$_2$
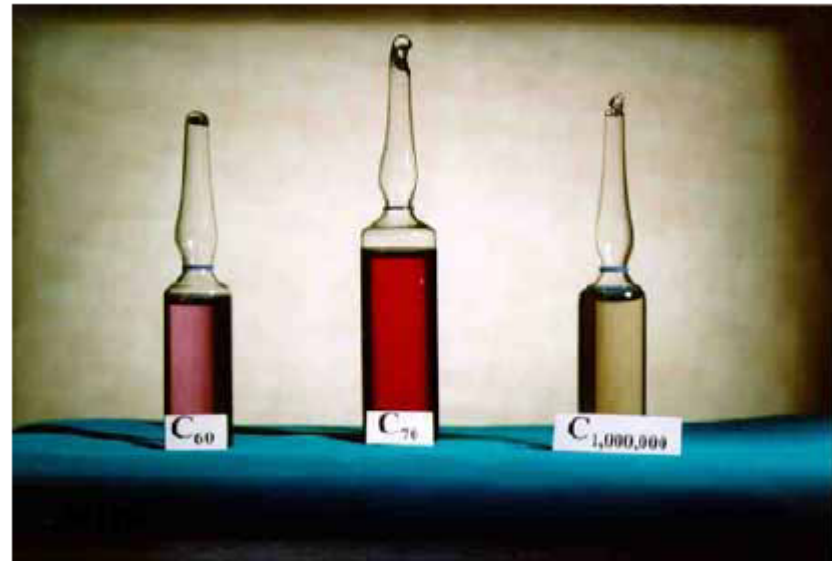
Reattività
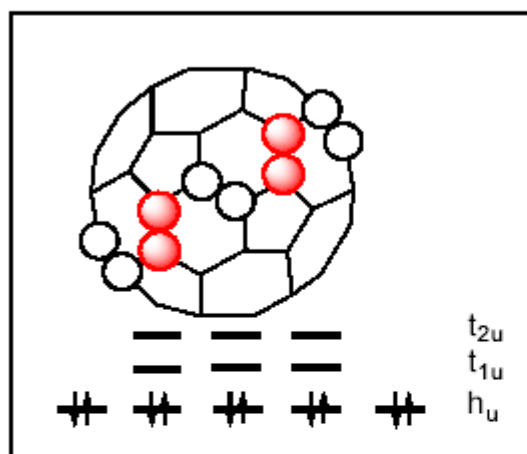
C_{60} behaves essentially as a **strained electron-poor alkene**; addition chemistry is mainly driven by strain relief

fullerenes are very difficult to oxidize but are **readily reduced** (reactivity towards electron-rich reagents)

1,2-additions occur at 6,6-double bonds. In 1,2-adducts the bond-length alternation is totally preserved

the regioselectivity of addition reactions is governed by **avoidance of** products with **5,6 double bonds** in the lowest energy Kekulè structure (price tag of 8.5 kcal mol^{-1})

multiple addition to C_{60} is a complicated process governed by differences in bond order and LUMO coefficients at each site: many possible **regio-isomers**

The **chemical transformations** that are possible with C60 could be classified in five main groups (figure 1.3):

a) *Addition reactions*. Formation of exohedral compounds by addition of nucleophiles or radicals, cycloadditions, complexations with transition metals and others.

b) *Electron transfer reactions*. Chemical reduction of fullerenes can easily be achieved by reaction with electropositive alkali and alkaline earth metals or organic donor molecules.

c) *Heterofullerenes*. Substitution of a carbon atom of the fullerene skeleton for a heteroatom, for example nitrogen or boron.

d) *Ring opening reactions*. Producing a hole in the C60 skeleton while breaking a discrete number of bonds.

e) *Formation of endohedrals*. Introducing and trapping of atoms inside the spherical carbon cage.
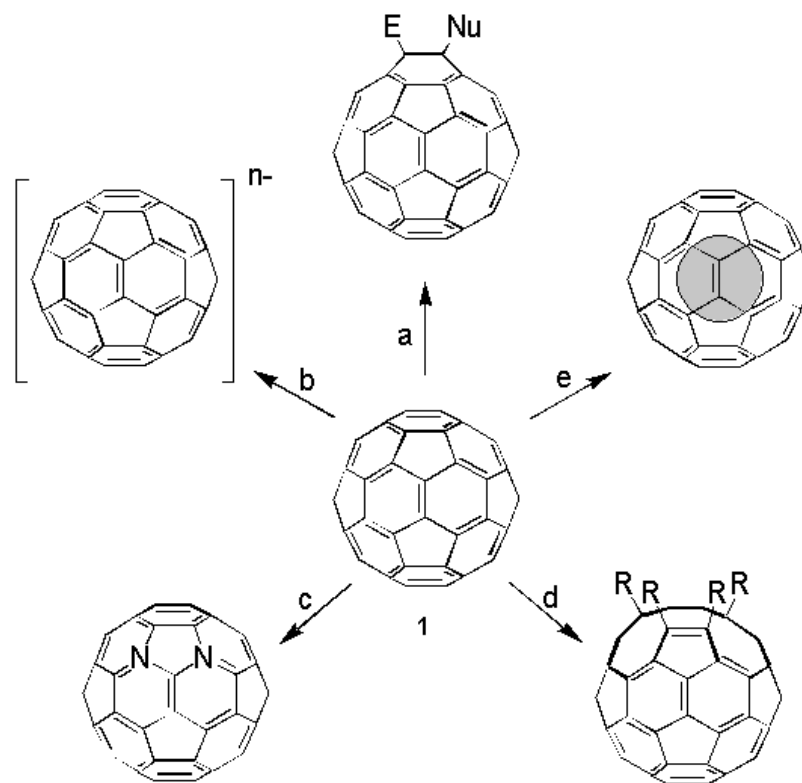
Derivati del C$_{60}$
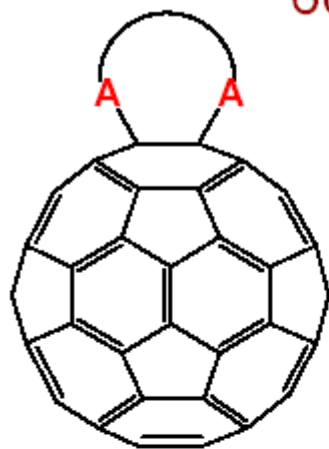
covalent exohedral adducts
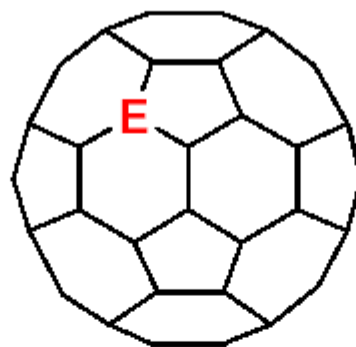
heterofullerenes
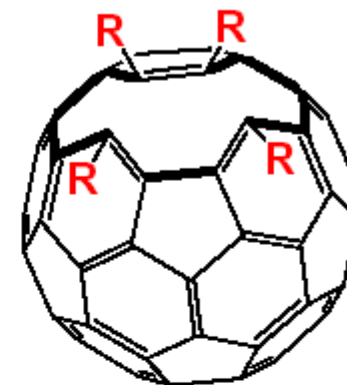
open-cage derivatives
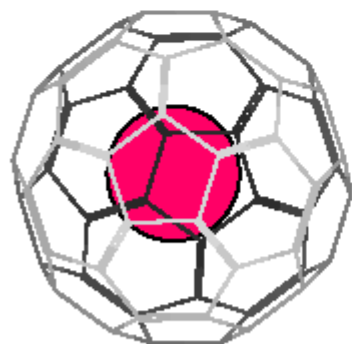
endohedral fullerenes
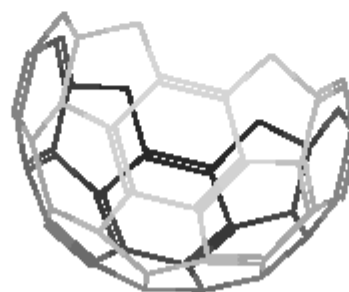
partial structures
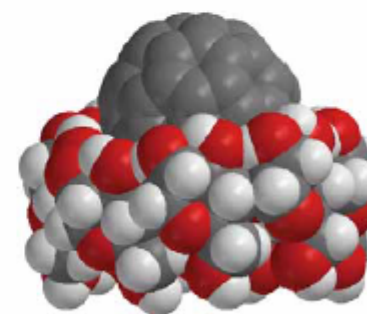
Host-guest assemblies

Addizioni nucleofile al C$_{60}$

A   EtMgBr, H$^+$

B   (malonate structure) , NaH
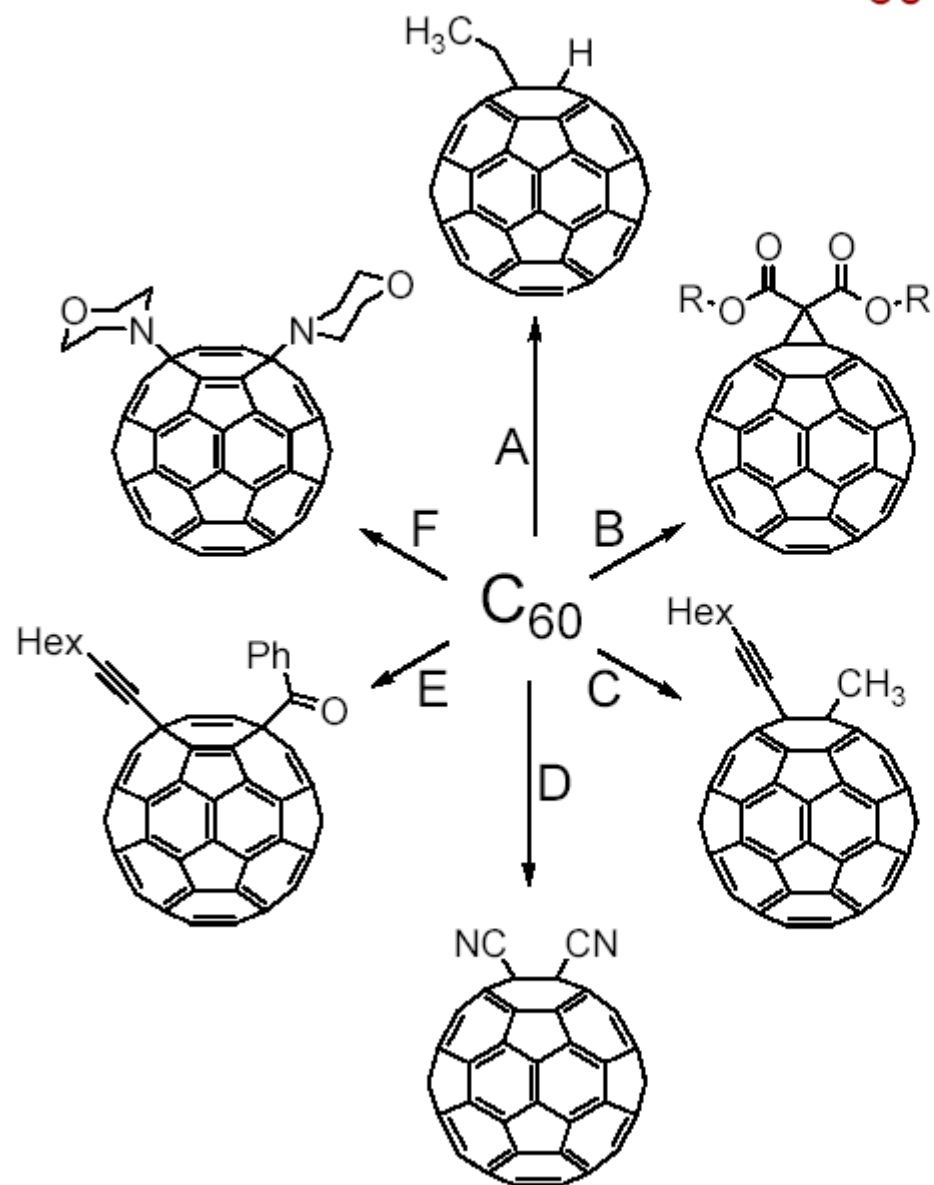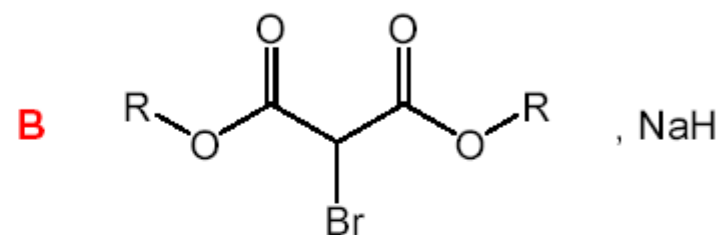
C   Hex━━Li , MeI

D   NaCN, TsCN

E   Hex━━Li , PhCOCl

F   HN morpholine O
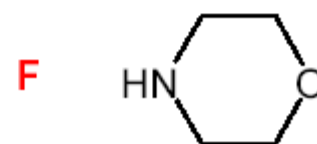
Cicloaddizioni al C$_{60}$
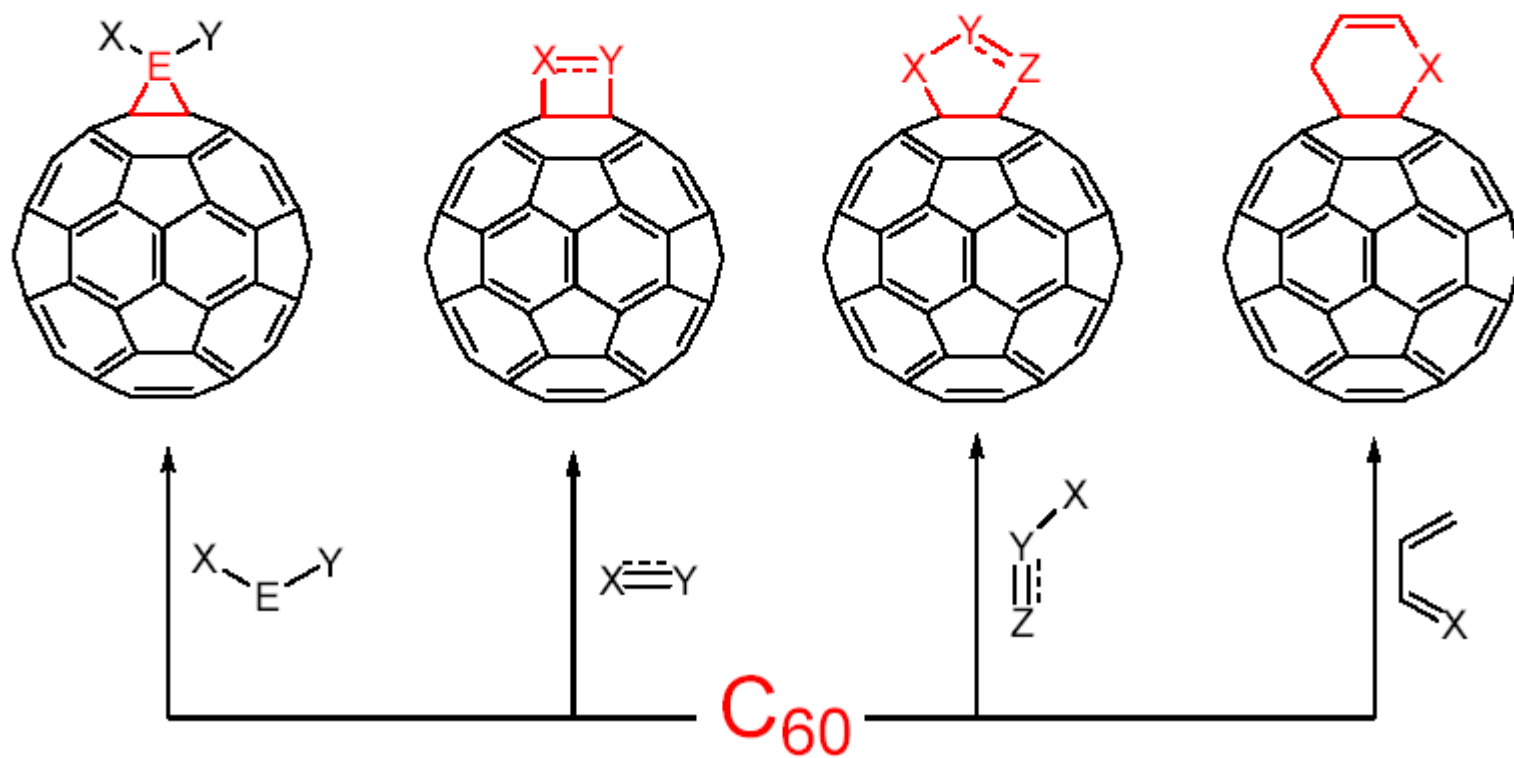
Ciclopropanazione del C$_{60}$
(metanofullereni)
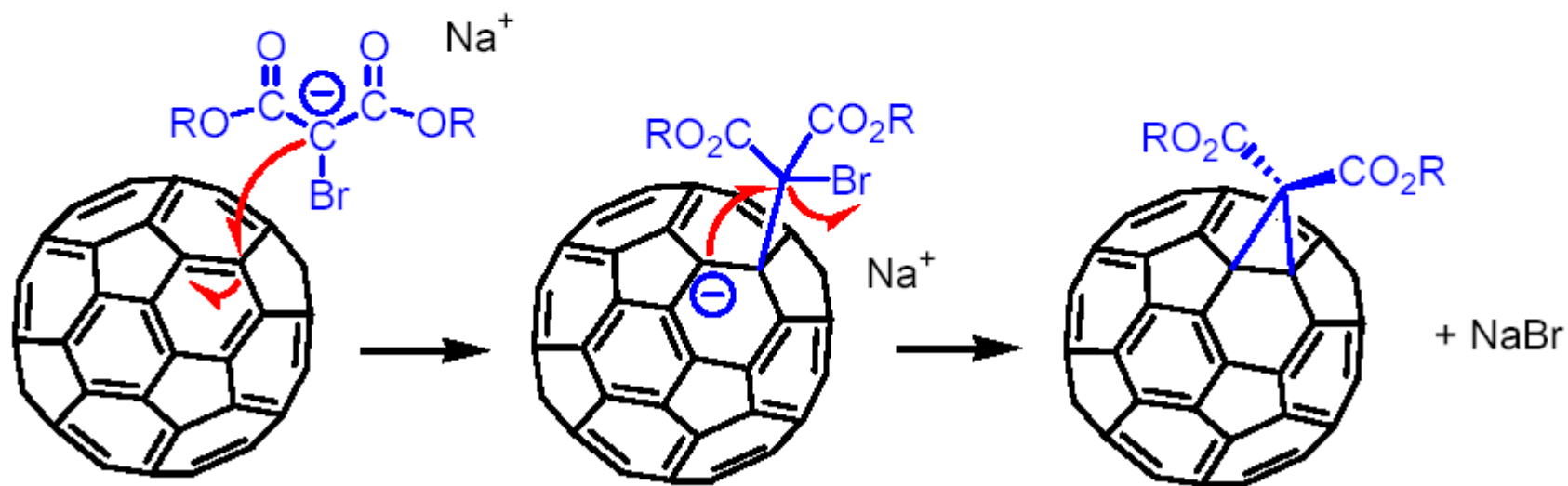
1,3-dipolar cycloaddition of azomethineylides to C60

the Prato's reaction

$$CH_3-NH-CH_2-COOH + CH_2O \xrightarrow[\substack{- CO_2 \\ - H_2O}]{\Delta} \left[\begin{array}{c} CH_3 \\ \overset{|}{N^+} \\ CH_2 \diagdown \diagup CH_2^- \end{array} \right] \xrightarrow{C_{60}}$$

1
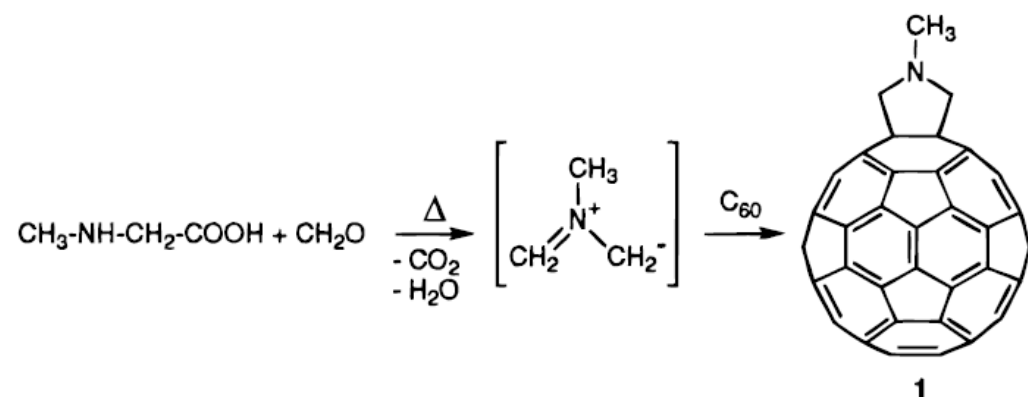
41% yield
82% on the consumed C60

the reaction is site selective in that it affords exclusively the product of cycloaddition across a 6,6 ring junction of the fullerene

Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798−9799.

Cicloaddizione di ilidi azometiniche
(fulleropirrolidine)

$R^1-NH-CHR^2-CO_2H + R^3CHO$
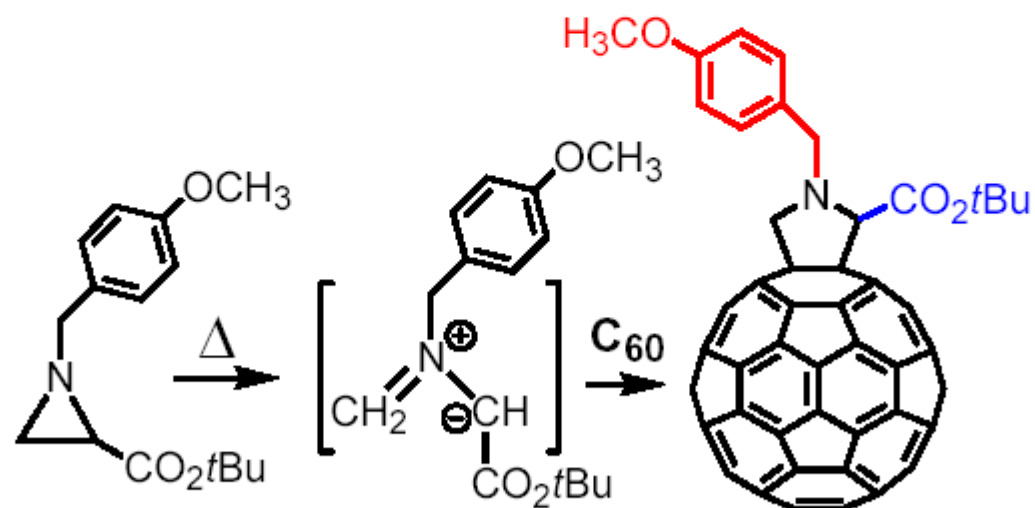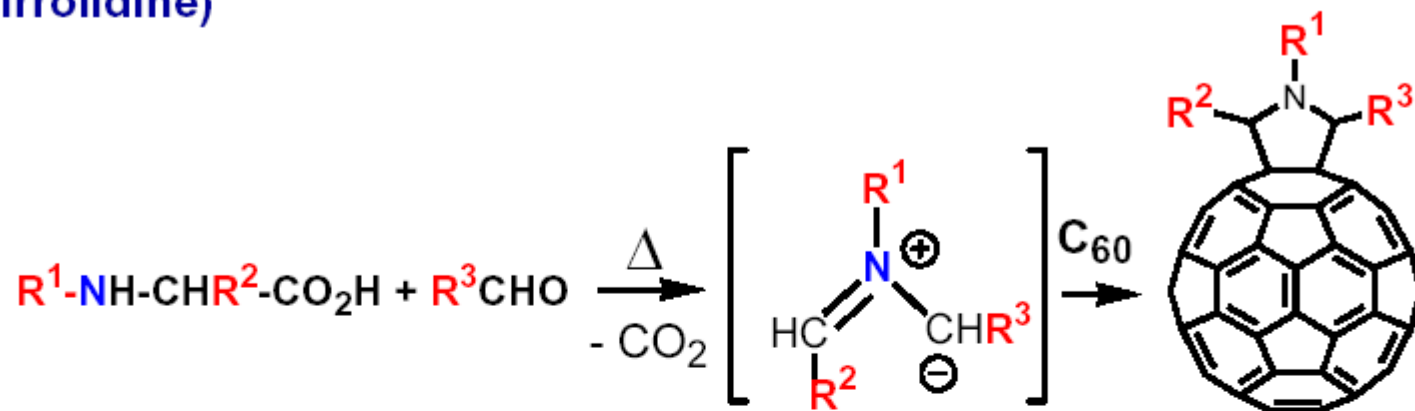
M. Maggini, G. Scorrano, M Prato *J. Am. Chem. Soc.* **1993**, 9798
M. Prato, M. Maggini *Acc. Chem. Res.* **1998**, 519
X. Zhang, M. Willems, C. S. Foote *Tetrahedron Lett.* **1993**, 8187

In the presence of large excesses of reagents, up to nine pyrrolidine rings can be introduced, as detected by MS analysis of the reaction crude.
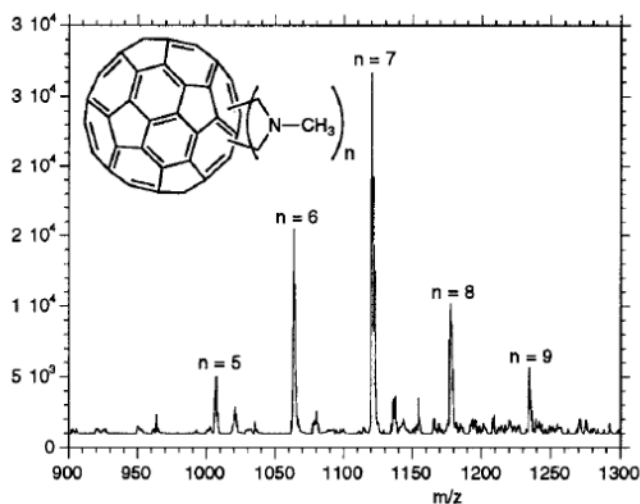
FIGURE 1. APCI-MS spectrum of the crude mixture obtained by heating a toluene solution containing C_{60}, 20 equiv of sarcosine, and 20 equiv of formaldehyde for 8 h.

Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798−9799.

C60 bis-adducts

cis   cis-1 (C_s)   cis-2 (C_s)   cis-3 (C_2)

equatorial   e (C_s)

trans   trans-4 (C_s)   trans-3 (C_2)   trans-2 (C_2)   trans-1 (D_{2h})

C$_{60}$

C sp^2 deviate from planarity

HUCKEL MOLECULAR ORBITALS

11.6°
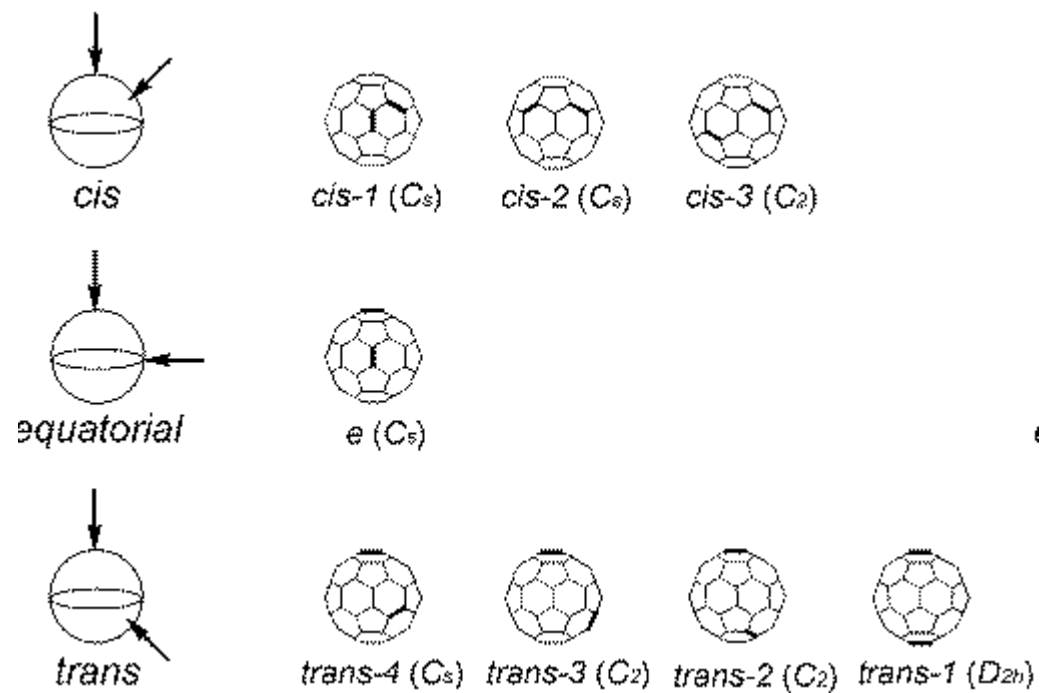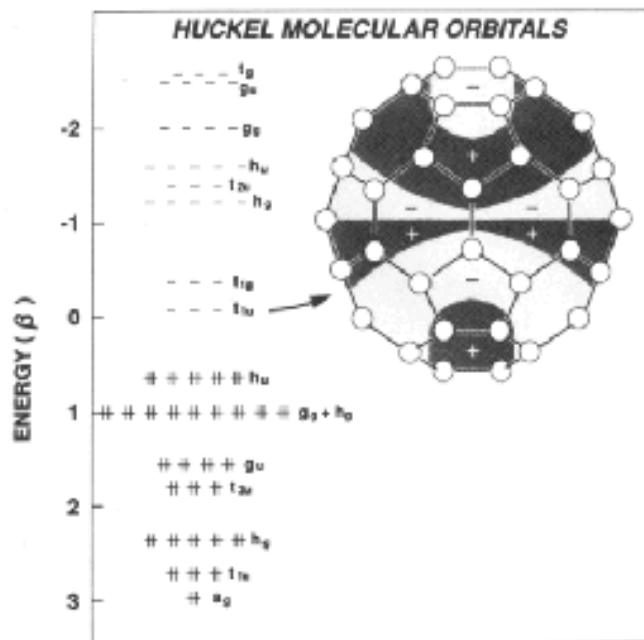
low HOMO-LUMO gap

Huckel energy levels of **C60** together with one component of the triply degenerate t$_{1u}$ set of molecular orbitals which become populated on alkali-metal doping.
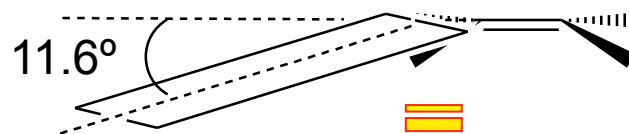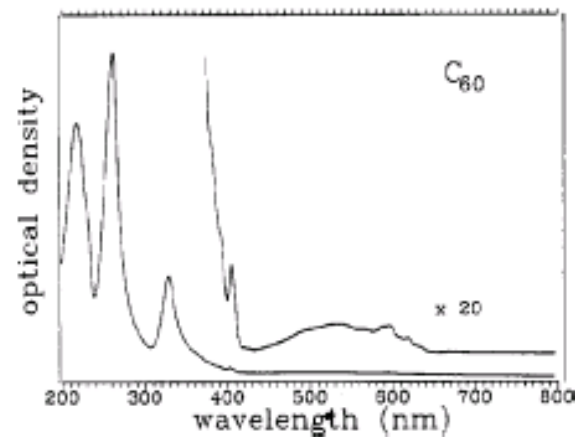
UV-vis spectra of fullerene in hexane solution.

optical HOMO-LUMO gap **2.34 eV**, on the most intense peak, λ 540 nm

ORGANIC ELECTRONICS

C$_{60}$

Cyclic voltammogram (top) and differential pulse voltammogram (bottom) of fullerene in MeCN/

toluene.

Qi. Xie, E. Perez-Cordero, L. Echegoyen J . Am. Chem. Soc. **1992,** *114,* 3978-3980 **C$_{60}$$^{6-}$**

J. Am. Chem. Soc. **2003**, *125*, 15738-15739 C$_{60}$$^{2+}$ e $^{3+}$
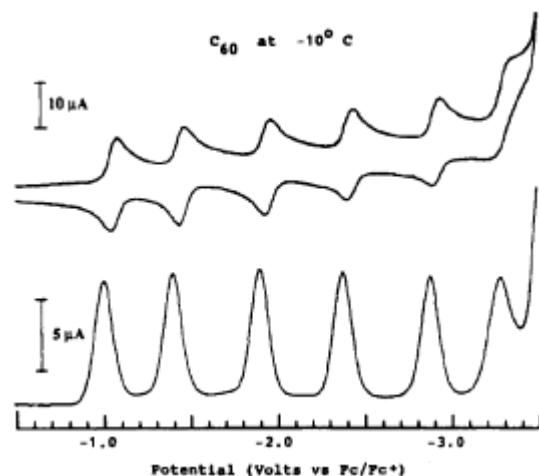
$E°_{1ox} - E°_{1rid}$ = **2.33 eV**

può accettare in modo reversibile fino a 6 elettroni

- **forma deboli complessi a trasferimento di carica con diversi tipici D, come con derivati di TTF (tetrathiafulvalene)**

    in the gas phase
    IP 7.6 eV
    EA 2.7 eV accetta 2e

APPLICATIONS

Fullerene as an acceptor for Donor-Acceptor Diads, Triads and Multiads

D-σ-A

TTF-σ-TCNQ systems (sistemi non coniugati)
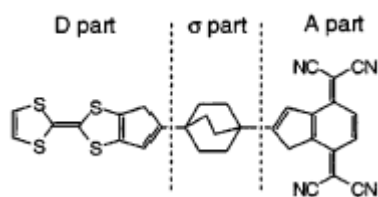
● theoretical proposal

Chemical structure of the Aviram-Ratner (1974)
molecular rectifier TTF-σ-TCNQ
calculated HOMO-LUMO gap of 0.3 eV
A. Aviram, M. Ratner *Chem. Phys. Lett.* **1974**, *29*, 277.

see also: R. M. Metzger *Chem. Rev.* **2003**, *103*, 3803.

la maggior parte dei mono-addotti mantiene le stesse proprietà del fullerene

come donatori sono stati usati: composti aromatici, porfirine, ftalocianine
rotassani, TTF, unità di carotene, Ru-terpy, Ru-bipy, ferrocene, ecc.

C$_{60}$- TTF

HOMO-LUMO gap
~ 1-1.2 eV

non dipende molto dallo
spaziatore

nel TTF da SR a H
riduzione di band gap
di soli ~ 0.1 eV

sostituenti sul C60
diminuiscono le proprietà
elettron-accettore

in queste diadi
weak charge transfer
tra TTF e C60 nello stato
fondamentale

101a, n = 0, R = H
101b, n = 0, R-R = SCH$_2$CH$_2$S
101c, n = 1, R = H,
101d, n = 1, R-R = SCH$_2$CH$_2$S
101e, n = 2, R = H

102

103a, n = 3
103b, n = 10

104

105a, n = 1
105b, n = 10

106a, R = H   106e, R = n-C$_5$H$_{11}$S
106b, R = Me   106f, R = n-C$_8$H$_{17}$S
106c, R = SMe   106g, R = n-C$_{12}$H$_{25}$S
106d, R = CO$_2$Me
106h, R-R = -SCH$_2$CH$_2$S-
106i, R = S(CH$_2$CH$_2$O)$_3$Me
106j, R = S(CH$_2$CH$_2$O)$_4$Me
106k, R-R = -S(CH$_2$CH$_2$O)$_2$CH$_2$CH$_2$S-
106l, R-R = -S(CH$_2$CH$_2$O)$_4$CH$_2$CH$_2$S-

107

108

25
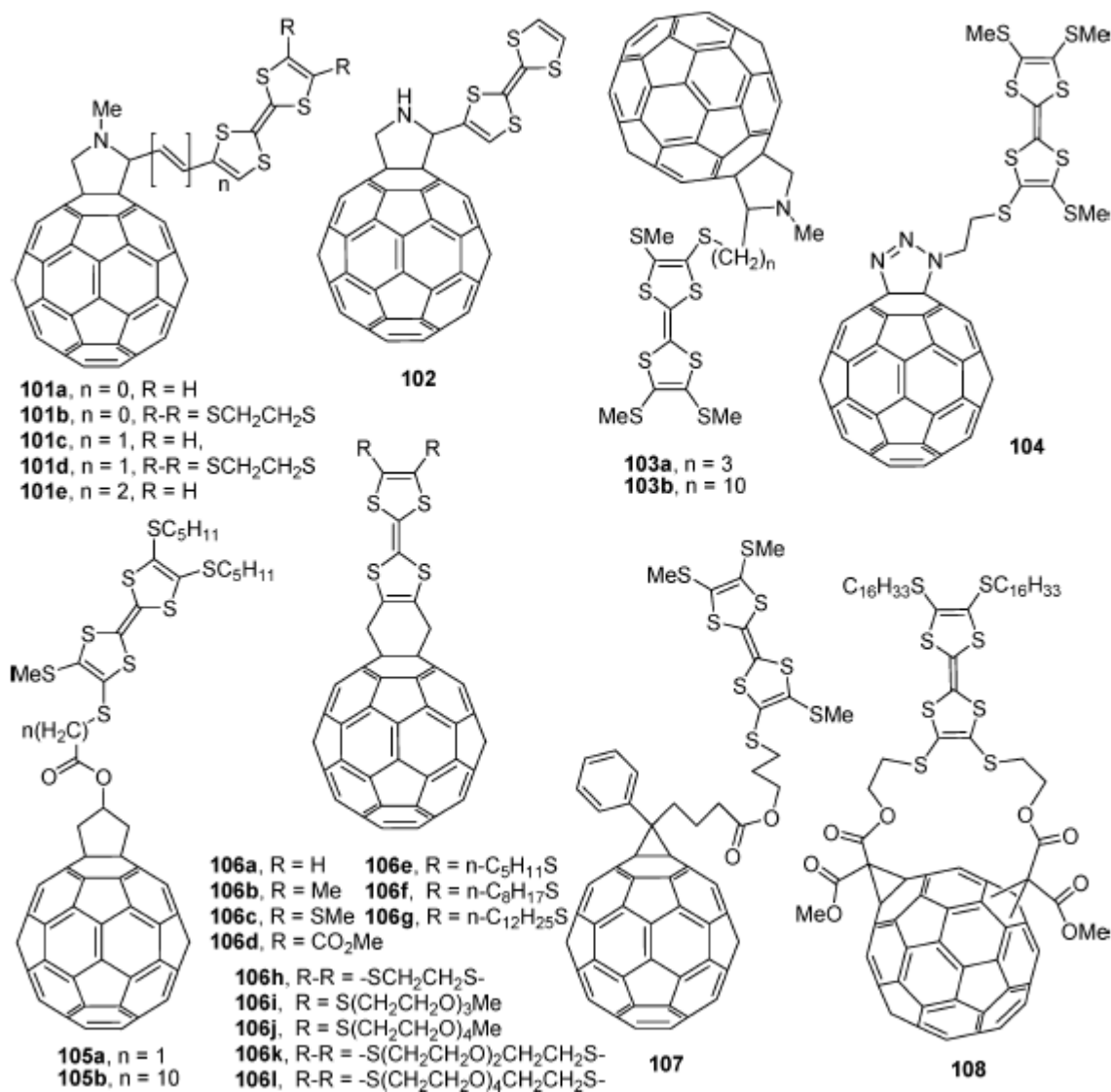
C_{60}- TTF

Triads and Multiads
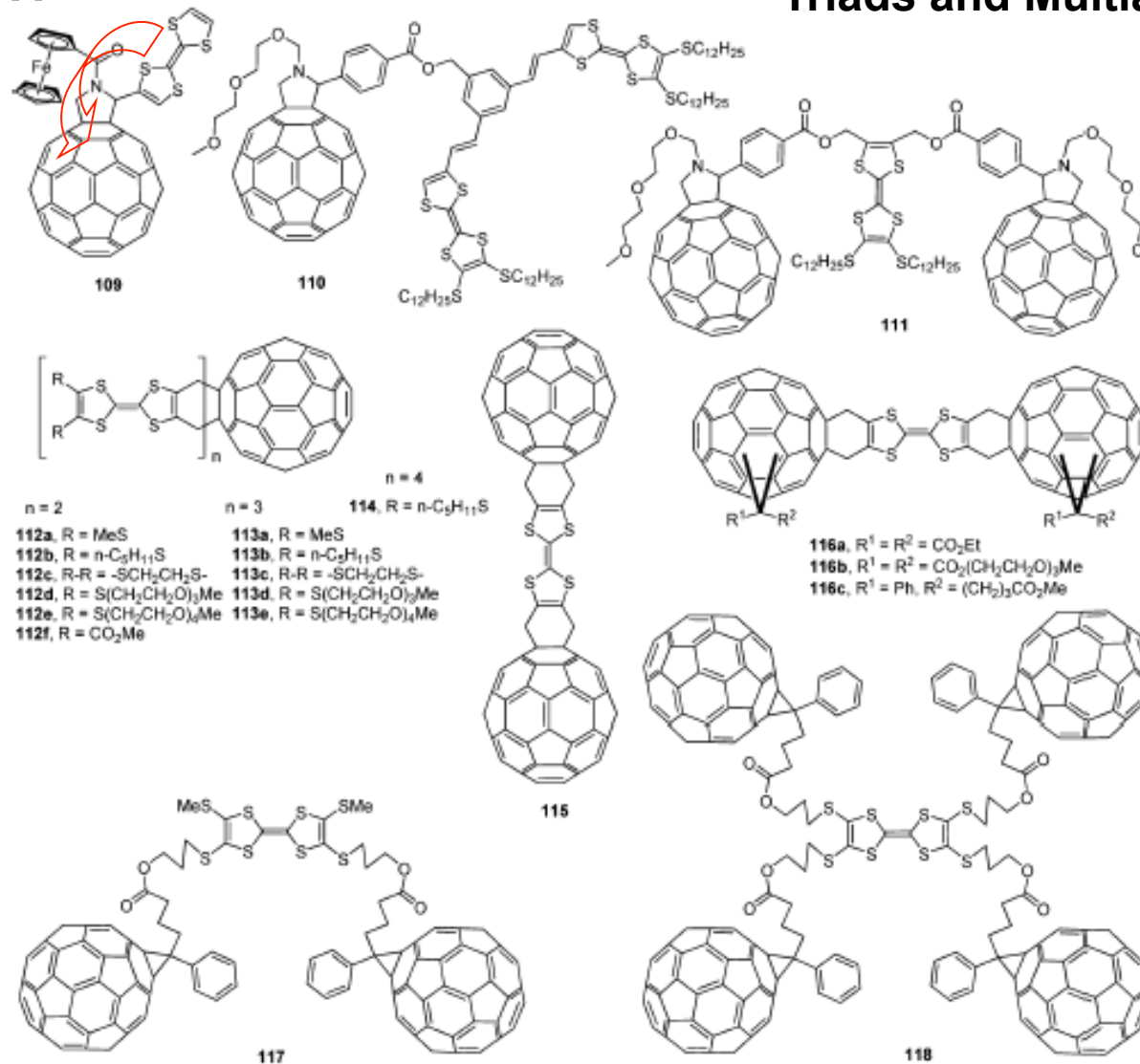
ORGANIC ELECTRONICS

Fluorinated Fullerenes as Ultimate Acceptors for Donor- Acceptor Diads

● Highly fluorinated fullerenes were reported as exceptionally strong electron acceptors (stronger than TCNQ), although this behavior can hardly be attributed simply to the inductive electron-withdrawing effect of fluorine atoms (separated from the π-system by an sp^3 carbon).

EA is increased by ~0.05 eV per each fluorine atom added

Thus, attaching TTF units to fluorinated fullerenes could afford otherwise unavailable donor-acceptor compounds with a very low HOMO-LUMO gap.

E$_g$ ~ 0.5 eV
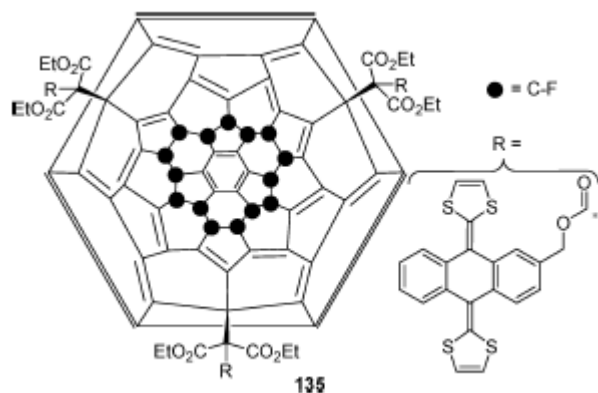
● charge separate state with a long lifetime of 870 ns
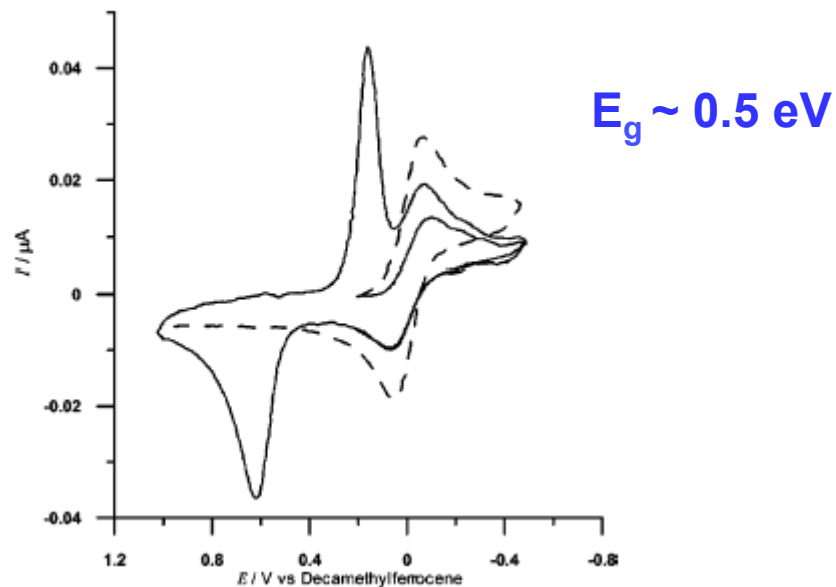
Cyclic voltammogram of the TTFAQ-C60 diad **135** (solid line) and of a related C60 derivative without a TTFAQ fragment (R) C2H5, broken line).

Celle solari di plastica

Alluminio

Matrice attiva

PEDOT/PSS

- +

ITO

Vetro/plastica

miscela

P3HT
(donor)

PCBM
(acceptor)

elevata area di contatto tra accettore e donatore
(*interpenetrating network*)
favorisce generazione e trasporto
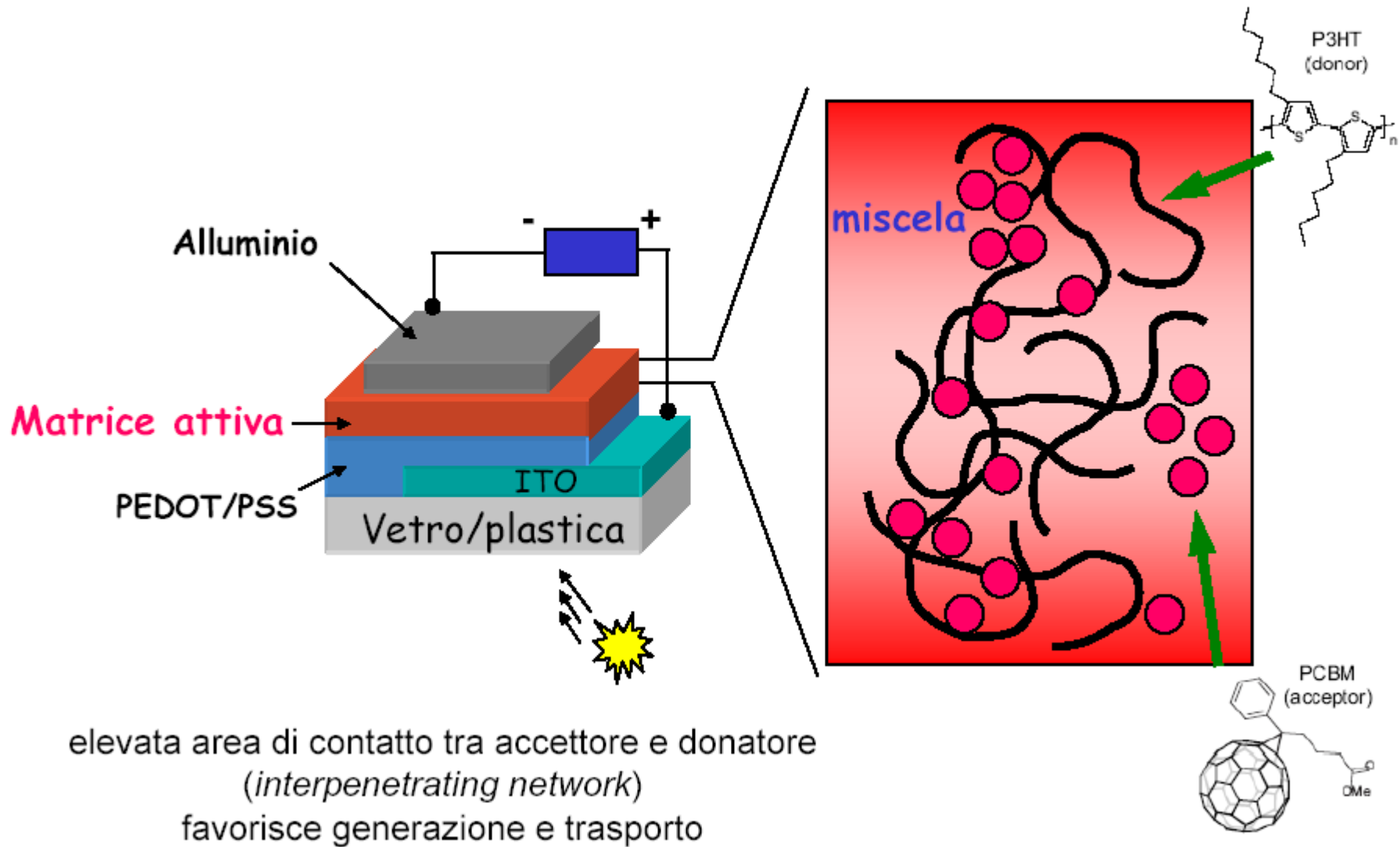
PEDOT:PSS, Poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate)
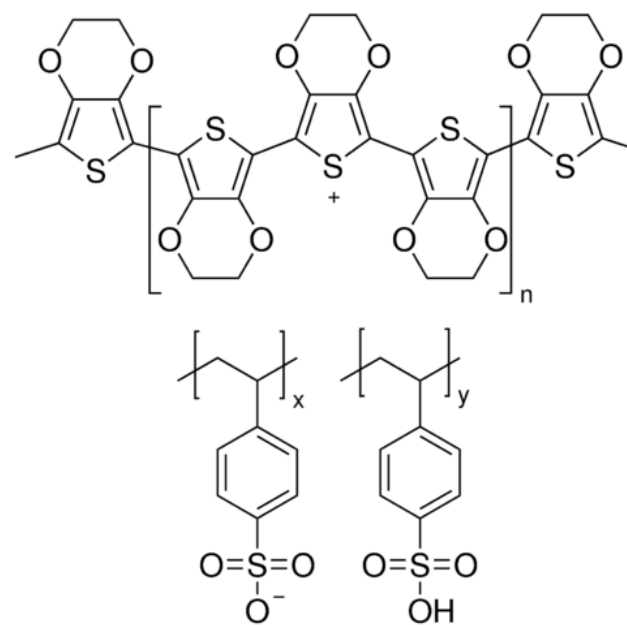
Celle solari di plastica

polimero donatore

fullerene accettore

e⁻

Celle solari di plastica

Organic photovoltaics convert sunlight into electrical power

250 nm

polymer film
transparent conductor
charge transport layer
photo-active layer
charge transport layer
metal electrode

© graphic arts BASF and Bosch

Generazione di ossigeno di singoletto

$$C_{60} \xrightarrow{h\nu} {}^1C_{60} \xrightarrow{ISC} {}^3C_{60} \longrightarrow C_{60}$$

$${}^3O_2$$
substrate

$${}^1O_2 \longrightarrow$$ **oxidized substrate**
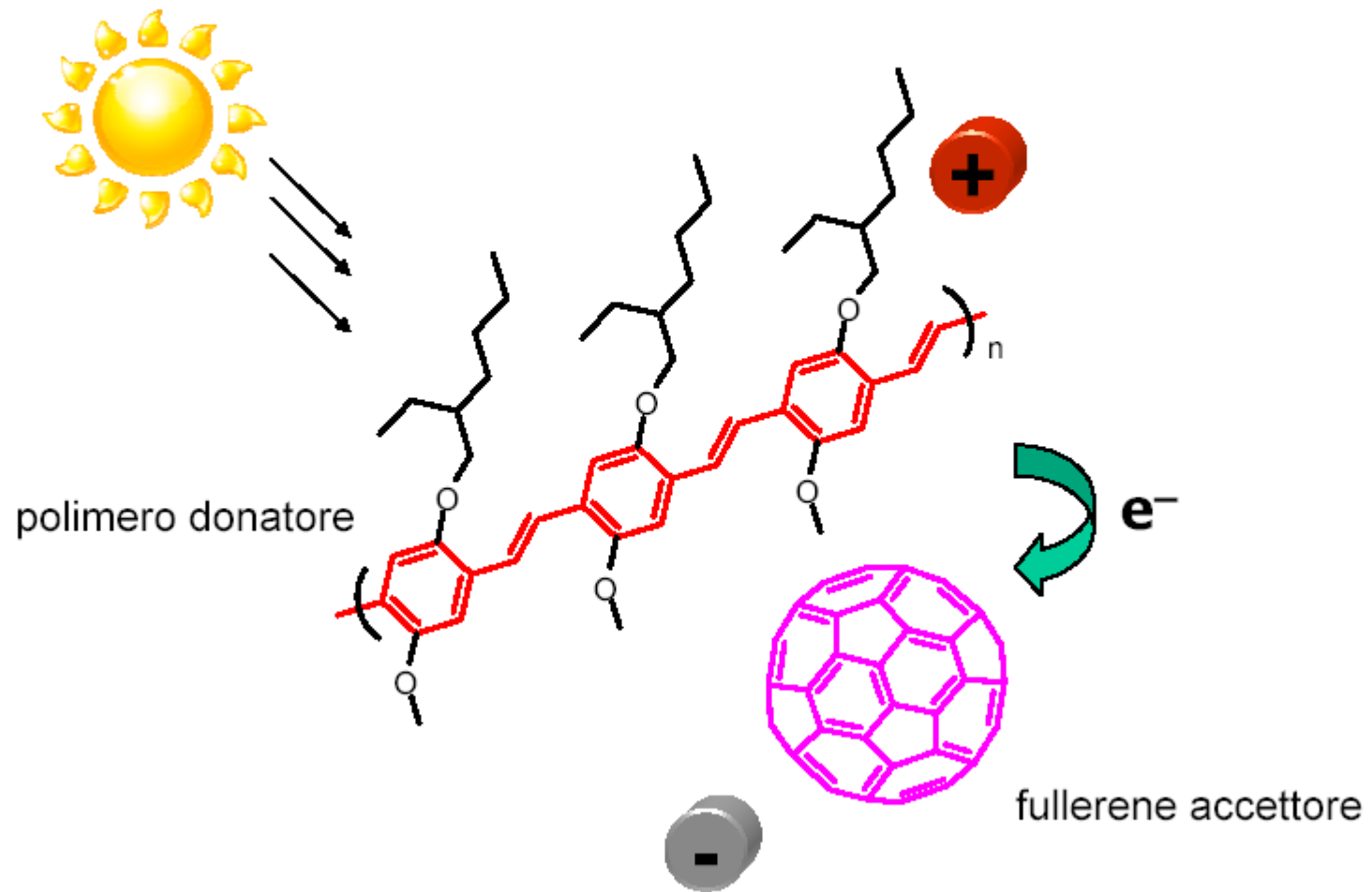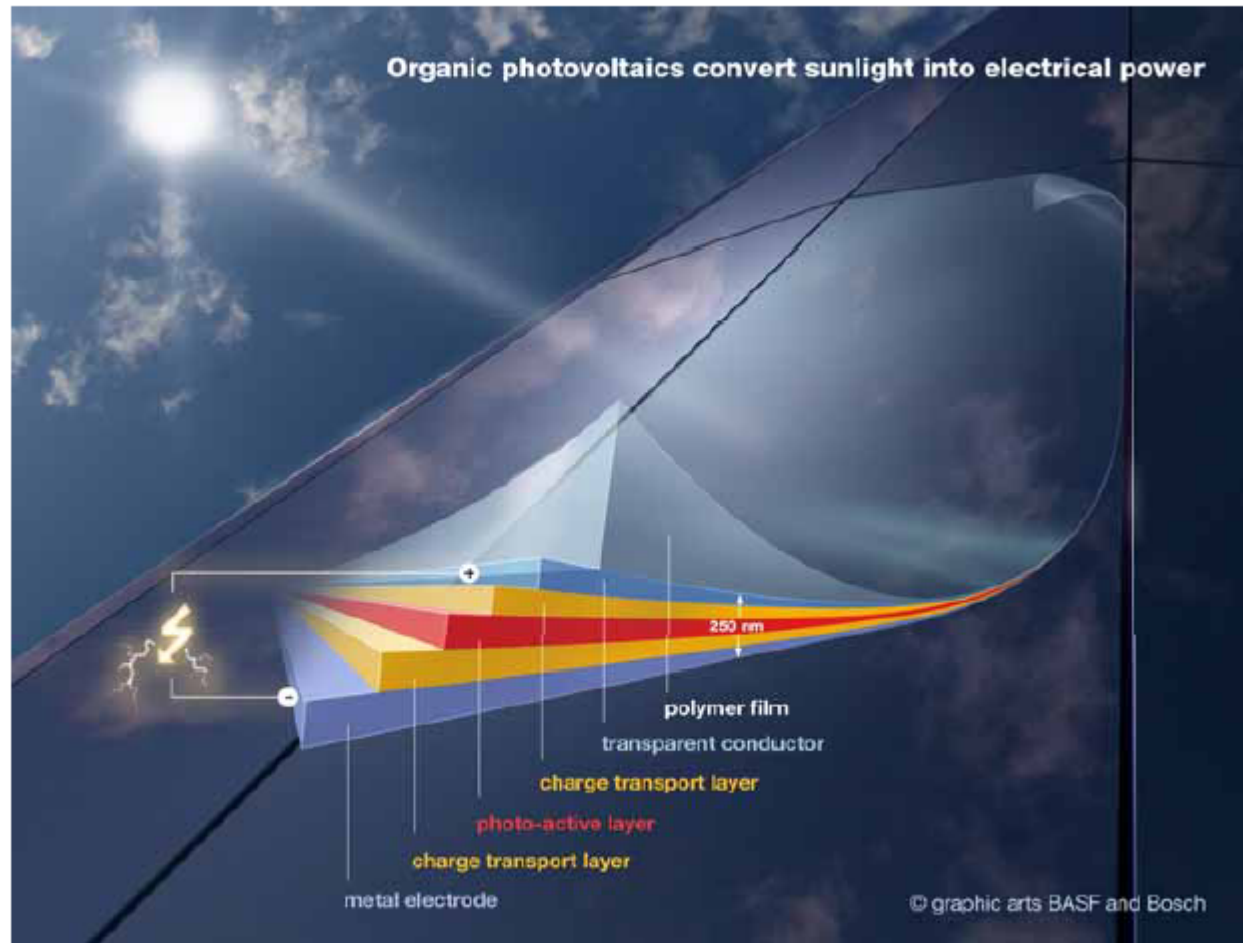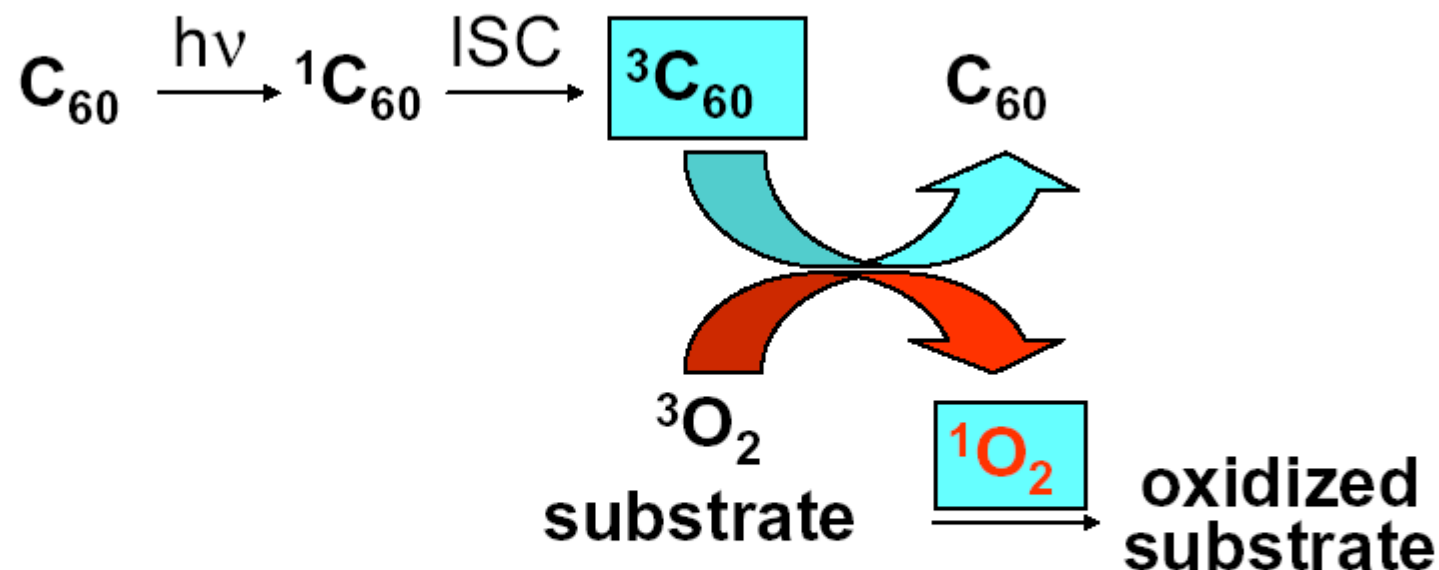
C_{60} **is an excellent singlet oxygen sensitizer**

${}^3C_{60}$ **reacts with oxygen rapidly (k_q=1.9 $\times 10^9$ M^{-1}s^{-1})**

Reactivity of C_{60} with singlet oxygen is very low

C. Foote, Y. Rubin, F. Diederich et al. *J. Phys. Chem.* **1991**, *95*, 11
J. Arbogast, C. Foote *J. Am. Chem. Soc.* **1991**, *113*, 8886

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Generazione di ossigeno di singoletto

Diels-Alder

H. Tokuyama, E. Nakamura, JOC **1994**, *59*, 1135

DNA cleavage photodynamic therapy
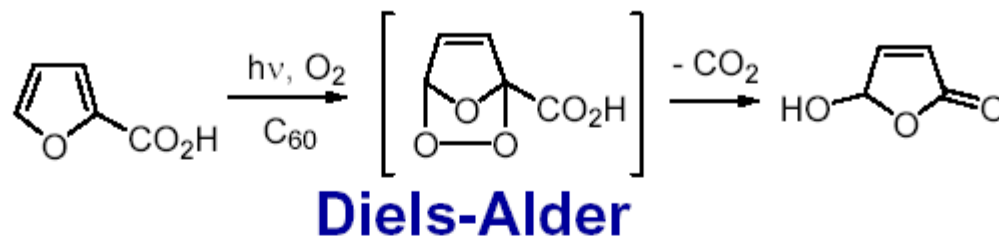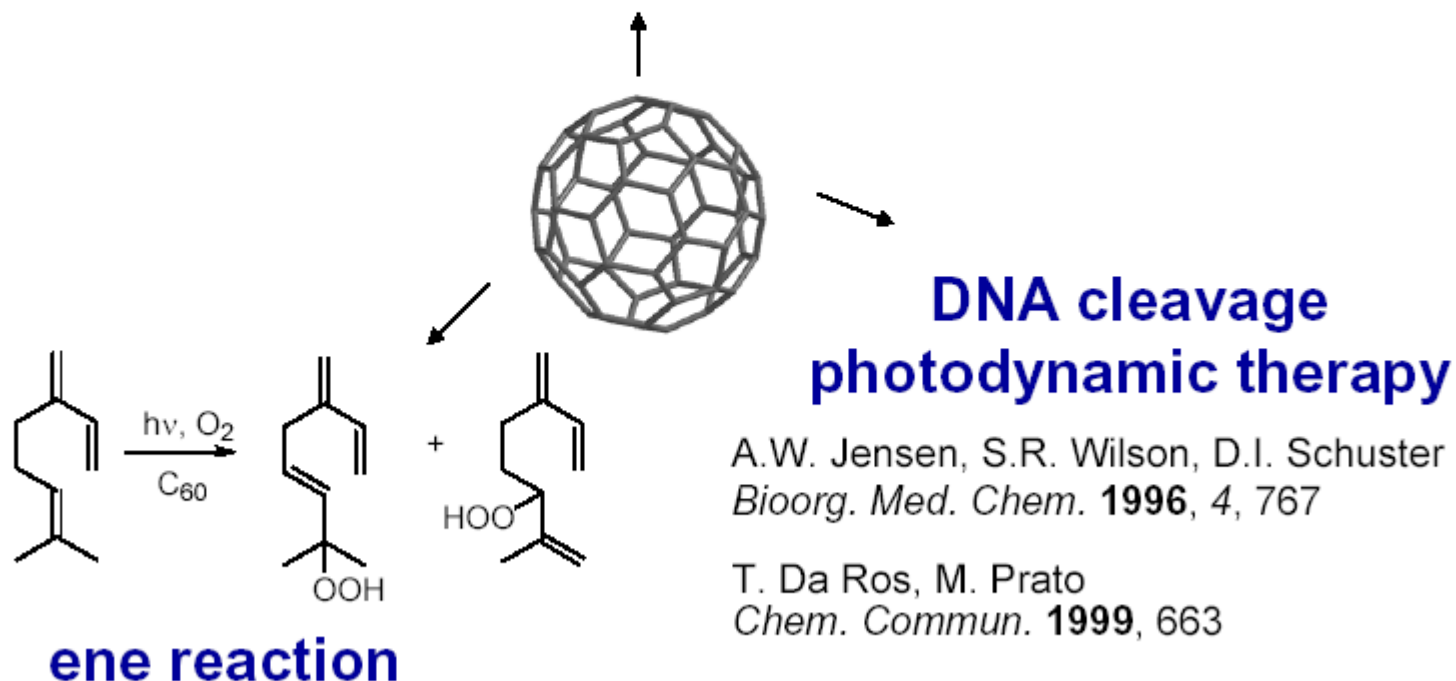
A.W. Jensen, S.R. Wilson, D.I. Schuster
Bioorg. Med. Chem. **1996**, *4*, 767

T. Da Ros, M. Prato
Chem. Commun. **1999**, 663

ene reaction

H. Tokuyama, E. Nakamura, JOC **1994**, *59*, 1135

An efficient approach to chiral fullerene derivatives by catalytic enantioselective 1,3-dipolar cycloadditions

Salvatore Filippone, Enrique E. Maroto, Angel Martin-Domenech, Margarita Suarez, Nazario Martin
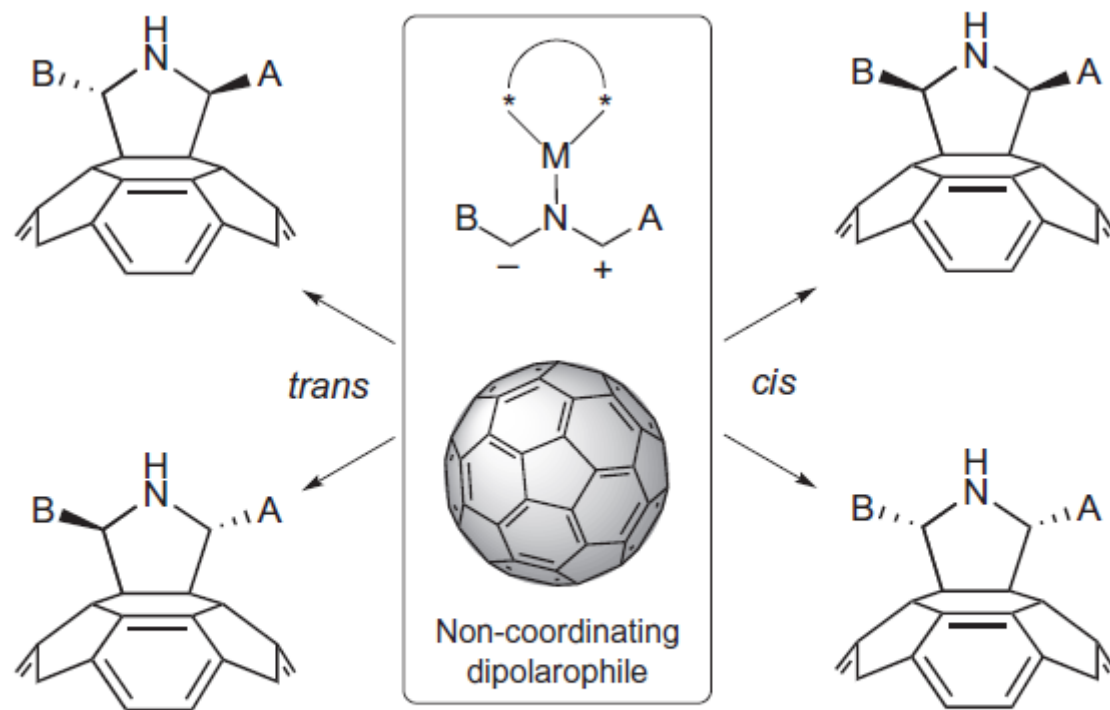
Figure 1 | N-metallated azomethine ylide complexes, prepared from a chiral ligand, a metal salt, an imino-ester and a base, are able to cycloadd to a non-coordinating dipolarophile such as the all-carbon sphere C$_{60}$. Depending on the metal and ligand used in such complexes, it is possible to control the stereochemical outcome in terms of diastereo- and enantioselectivities. Pyrrolidinofullerenes, the most widely used fullerene derivatives, have been easily prepared as *cis* or *trans* stereoisomers with good enantiomeric excesses.

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a: Ar = pMeO-Ph; R^1 = COOMe; R^2 = H
b: Ar = 2-Thienyl; R^1 = COOMe; R^2 = H
c: Ar = pF-Ph; R^1 = COOMe; R^2 = H
d: Ar = pCN-Ph; R^1 = COOMe; R^2 = H
e: Ar = pMeO-Ph; R^1 = COOEt; R^2 = Me
f: Ar = Ph; R^1 = P(O)(OEt)$_2$; R^2 = H
g: Ar = R^1 = 2-Pyridyl; R^2 = H

(2S,5S)-cis-2a–g   (2R,5R)-cis-2a–g   or   trans-2a–g
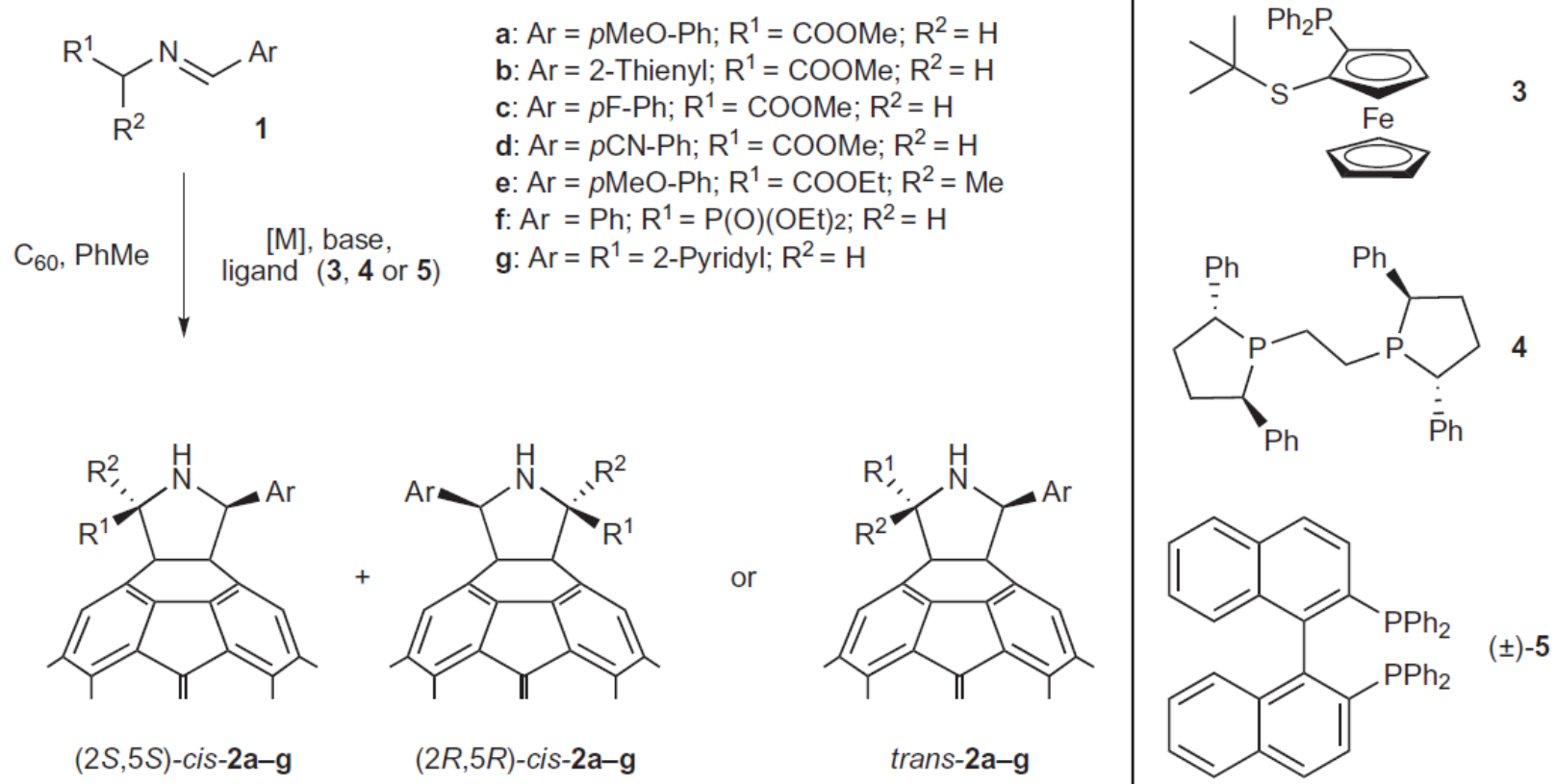
Figure 2 | Catalytic metal–ligand complexes allow the cycloaddidion of the iminoesters 1a–g to C$_{60}$ under mild conditions. Using the chiral catalyst formed by Cu(II) acetate and Fesulphos (3) results in the cis-pyrrolidinofullerenes 2a–g with a 2S,5S configuration. In contrast, the combination of Ag(I) acetate with the BPE ligand 4 induces the formation of the opposite enantiomers (2R,5R)-2a–g. The preparation of trans-pyrrolidinofullerenes has been carried out using Binap 5 and Cu(II)OTf$_2$, for the imines 1a,b.

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Table 1 | Asymmetric Cu(II) and Ag(I)-catalysed 1,3-dipolar cycloadditions of azomethine ylides 1a-g to C_{60} using different chiral ligands.

Entry*	Dipole	Metal salt	Ligand	Time (h)	T (°C)	Yield (%)	Diastereomeric excess (%)	Enantiomeric excess (%)
1	1a	–	–	16	110	30	20	–
2	1a	Cu(OTf)$_2$[†]	dppp[$]	2	r.t.	68	80	–
3	1a	Cu(MeCN)$_4$ClO$_4$[†]	3	4	0	45	94	64 (2S,5S)-2a
4	1a	Cu(MeCN)$_4$PF$_6$[†]	3	4	0	60	98	73 (2S,5S)-2a
5	1a	Cu(AcO)$_2$	3	2	−15	88	>99	90 (2S,5S)-2a
6	1a	Cu(MeCN)$_4$PF$_6$[‡]	3	2	−15	60	>99	92 (2S,5S)-2a
7	1b	Cu(AcO)$_2$	3	2	−15	49	>99	93 (2S,5R)-2b[¶]
8	1c	Cu(AcO)$_2$	3	4	−15	40	>99	90 (2S,5S)-2c
9	1d	Cu(AcO)$_2$	3	2	−15	60	>99	88 (2S,5S)-2d
10	1e	Cu(AcO)$_2$	3	4	−15	40	95	80 (2S,5S)-2e
11	1f	Cu(AcO)$_2$	3	25	r.t.	25	95	65 (2R,5S)-2f[¶]
12	1g	Cu(AcO)$_2$	3	3	r.t.	68	>99	–
13	1a	AgAcO	4	2	−15	60	>99	90 (2R,5R)-2a
14	1b	AgAcO	4	1	−15	45	>99	81 (2R,5S)-2b[¶]
15	1c	AgAcO	4	4	−15	35	>99	85 (2R,5R)-2c
16	1d	AgAcO	4	2	−15	60	>99	86 (2R,5R)-2d
17	1e	AgAcO	4	5	−15	33	80	70 (2R,5R)-2e

The use of copper salts leads to 2S,5S enantiomers, whereas silver salts afford 2R,5R enantiomers. In both cases the acetate anion plays a leading role yielding excellent diasteromeric and enantiomeric excess values.

*Reaction conditions: Ligand: 10% (entry 11: 100%).

[†]Et$_3$N (20%).

[‡]BuN$_4$AcO (20%).

[$]1,3-Bis(diphenylphosphino)propane.

[¶]The different priority of the substituents connected to the stereogenic centre is responsible for the change of configuration in the series.
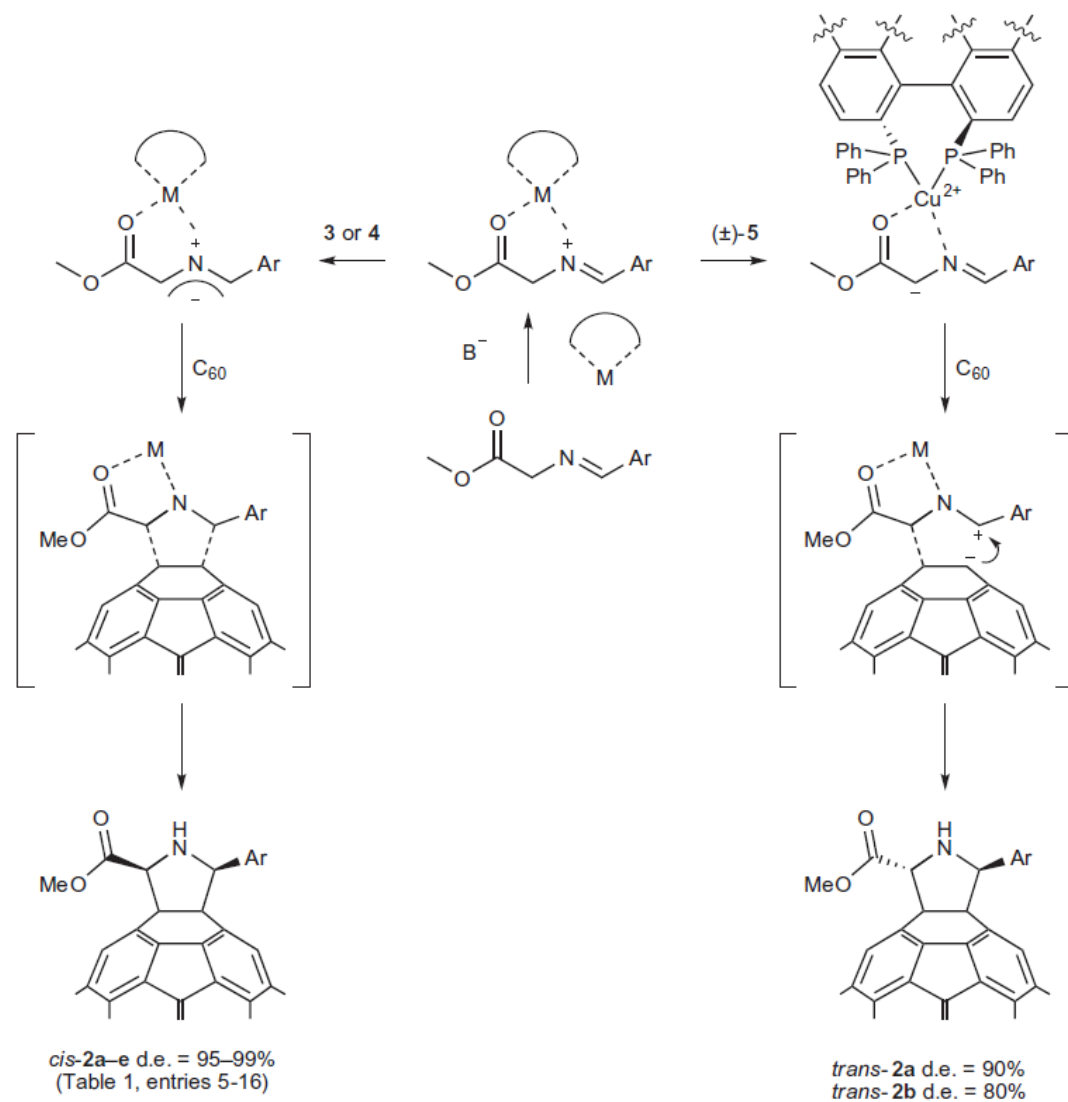
Figure 4 | Proposed concerted versus stepwise mechanism for the stereochemical outcome observed from the metal-ligand-iminoester complex. When the Fesulphos (**3**) or BPE (**4**) ligands are used, the chiral *N*-metallated azomethine ylide—formed after deprotonation by the acetate anion—cycloadds to the C$_{60}$ on a different enantioface, in a concerted *supra-supra* manner (left side). In contrast, the use of Binap (**5**) provokes the formation of an enolate-like species (right side). The addition occurs stepwise, producing a zwitterionic intermediate followed by ring-closing from the opposite face in a *supra-antara* manner, d.e.: diastereomeric excess.

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Groundwork for a Rational Synthesis of C$_{60}$: Cyclodehydrogenation of a C$_{60}$H$_{30}$ Polyarene

Margaret M. Boorum,[1] Yury V. Vasil'ev,[2] Thomas Drewello,[2*]
Lawrence T. Scott[1*]

26 OCTOBER 2001 VOL 294 SCIENCE

Fig. 1. Synthetic route to the C$_{60}$H$_{30}$ PAH **6** and its laser-induced conversion into fullerene-C$_{60}$.
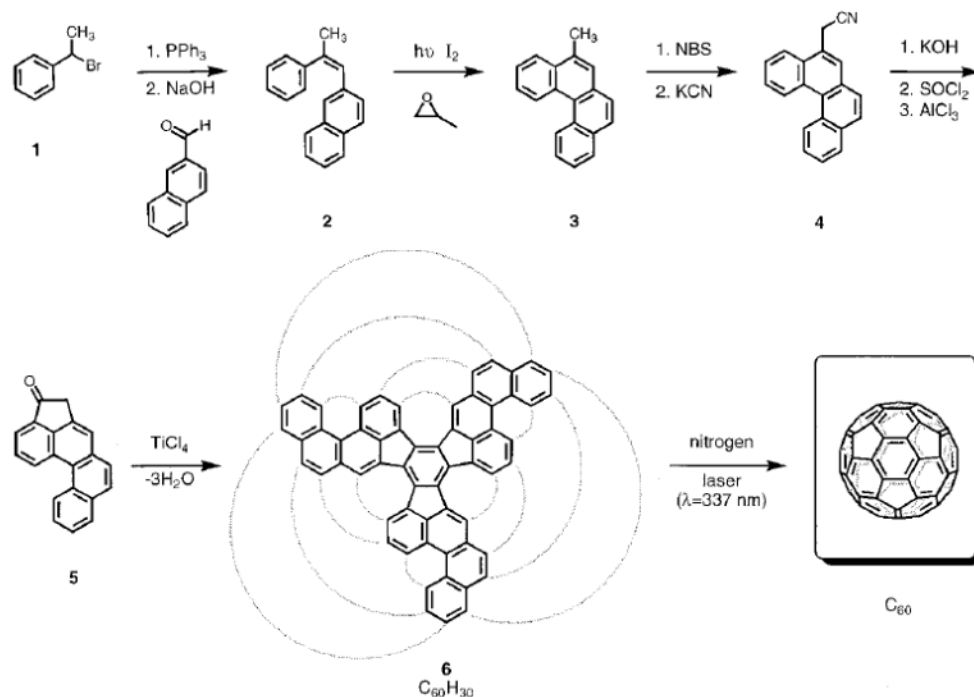
Our previous experience has shown that the strategic incorporation of halogen atoms on PAHs invariably improves the preparative yields of geodesic polyarenes obtained from synthetic precursors, often by more than two orders of magnitude over what can be achieved by direct cyclodehydrogenations of unfunctionalized PAHs

polycyclic aromatic hydrocarbon (PAH)

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A Rational Chemical Synthesis of C$_{60}$

Lawrence T. Scott,[1][*] Margaret M. Boorum,[1]
Brandon J. McMahon,[1] Stefan Hagen,[1] James Mack,[1]
Jarred Blank,[1] Hermann Wegner,[1,2] Armin de Meijere[2]

Isolable quantities of C$_{60}$, the smallest stable fullerene, have been synthesized in 12 steps from commercially available starting materials by rational chemical methods. A molecular polycyclic aromatic precursor bearing chlorine substituents at key positions forms C$_{60}$ when subjected to flash vacuum pyrolysis at 1100°C. No other fullerenes are formed as by-products. The methods we have developed for the target-specific synthesis of fullerenes, applied here to a synthesis of C$_{60}$, should make possible the directed laboratory preparation of other fullerenes as well, including those not accessible by graphite vaporization.

C$_{60}$
Buckminsterfullerene

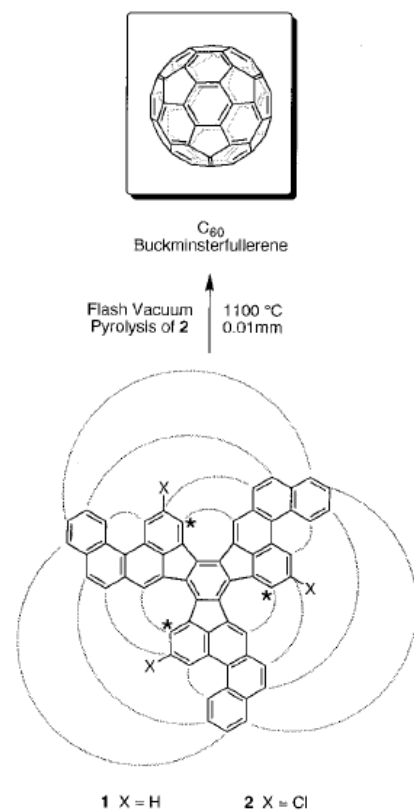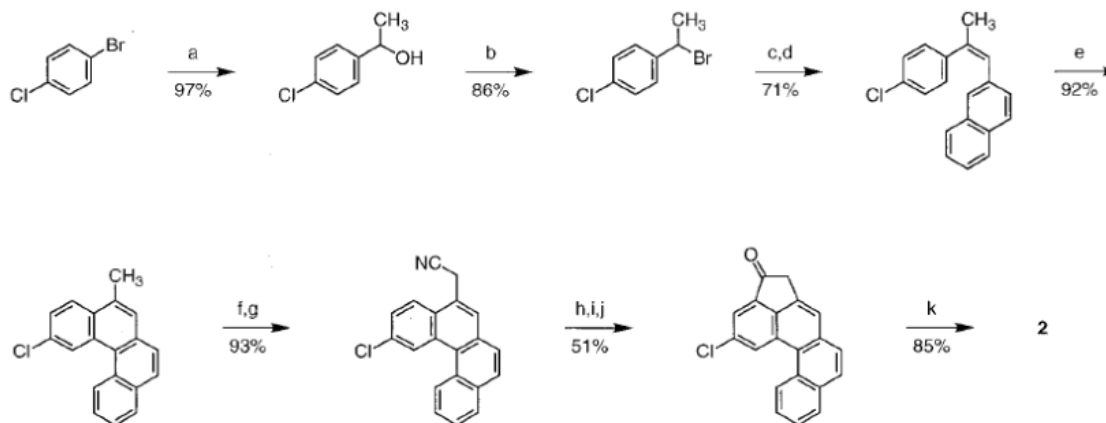Flash Vacuum Pyrolysis of **2**   1100 °C   0.01mm

1 X = H   **2** X = Cl

Fig. 1. Final step in the synthesis of C$_{60}$. Curved lines indicate where the new bonds are formed in the molecular precursor **2** (C$_{60}$H$_{27}$Cl$_3$). The fjord regions mentioned in the text are marked with asterisks. We have previously generated C$_{60}$ in a mass spectrometer by laser-induced cyclodehydrogenation of the corresponding hydrocarbon, **1** (2).

Fig. 2. Synthesis of the C$_{60}$ precursor **2** (C$_{60}$H$_{27}$Cl$_3$). Step a: Treatment with Mg in ether, then acetaldehyde. b: Bromination with PBr$_3$ in benzene. c: Treatment with P(C$_6$H$_5$)$_3$ in toluene. d: Treatment with LiOCH$_2$CH$_3$ and 2-naphthaldehyde in ethanol/dichloromethane. e: Irradiation with UV light (254 nm) in cyclohexane containing iodine and propylene oxide. f: Bromination with N-bromosuccinimide and dibenzoylperoxide in carbon tetrachloride. g: Displacement with KCN and tetrabutylammonium hydrogensulfate in water/dichloromethane. h: Hydrolysis with KOH in ethylene glycol. i: Chlorination with SOCl$_2$. j: Cyclization with AlCl$_3$ in dichloromethane. k: Trimerization with TiCl$_4$ in ortho-dichlorobenzene.

yield: 0.1-1.0%

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FULLERENE

sintesi del C$_{60}$

The first chemical synthesis of C$_{60}$ in isolable quantities:
a) Mg, Et$_2$O, then acetaldehyde; b) PBr$_3$, benzene;
c) P(C$_6$H$_5$)$_3$, toluene; d) LiOCH$_2$CH$_3$, 2-naphthaldehyde,
EtOH, CH$_2$Cl$_2$; e) UV irradiation (254 nm), I$_2$, propylene oxide,
cyclohexane; f) N-BS, dibenzoylperoxide, CCl$_4$; g)
Displacement with KCN, NBu$_4$ HSO$_4$, H$_2$O, CH$_2$Cl$_2$;
h) hydrolysis with KOH, ethylene glycol; i) Chlorination
with SOCl$_2$; j) cyclization with AlCl$_3$, CH$_2$Cl$_2$; k) Trimerization
TiCl$_4$, o-dichlorobenzene; l) FVP, 1100 °C, 0.01 mm Hg.

si sono formati 15 nuovi legami C-C
ogni nuovo legame si è formato con una resa del ~ 60%
[(0.60)^{15} = 0.05%]

40

FULLERENE

Four new principles made this synthesis possible:

1. Curvature can be temporarily induced in polyarenes by flash
    vacuum pyrolysis (FVP).
2. Radical-initiated C(aryl)-C(aryl) coupling reactions can be used to catch
    the distorted conformations.
3. Hydrogen atom 1,2-shifts can be exploited to circumvent onerous
    synthetic challenges.
4. Cyclodehydrogenation cascades can be relied on to stick together
    adjacent arms of a system, once curvature has already been introduced.

M. M. Boorum, Y. V. Vasil'ev, T. Drewello, L. T. Scott *Science*, **2001**, *294*, 828.
L. T. Scott, M. M. Boorum, B. J. McMahon, S. Hagen, J. Mack, J. Blank, H. Wegner, A. de Meijere
Science, **2002**, *295*, 1500.
L. T. Scott *Angew. Chem. Int. Ed.* **2004**, *43*, 4994.