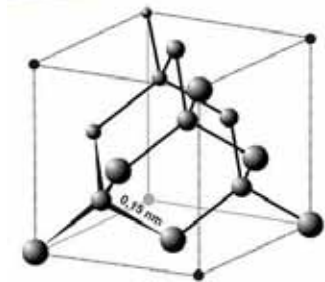
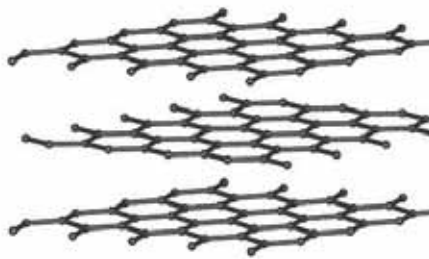


Fullerene: antefatti

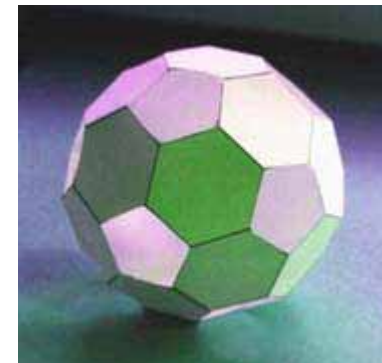
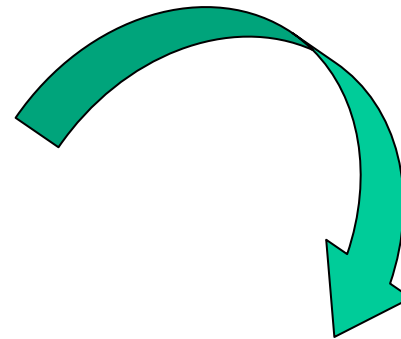
Forme allotropiche del carbonio



Diamante

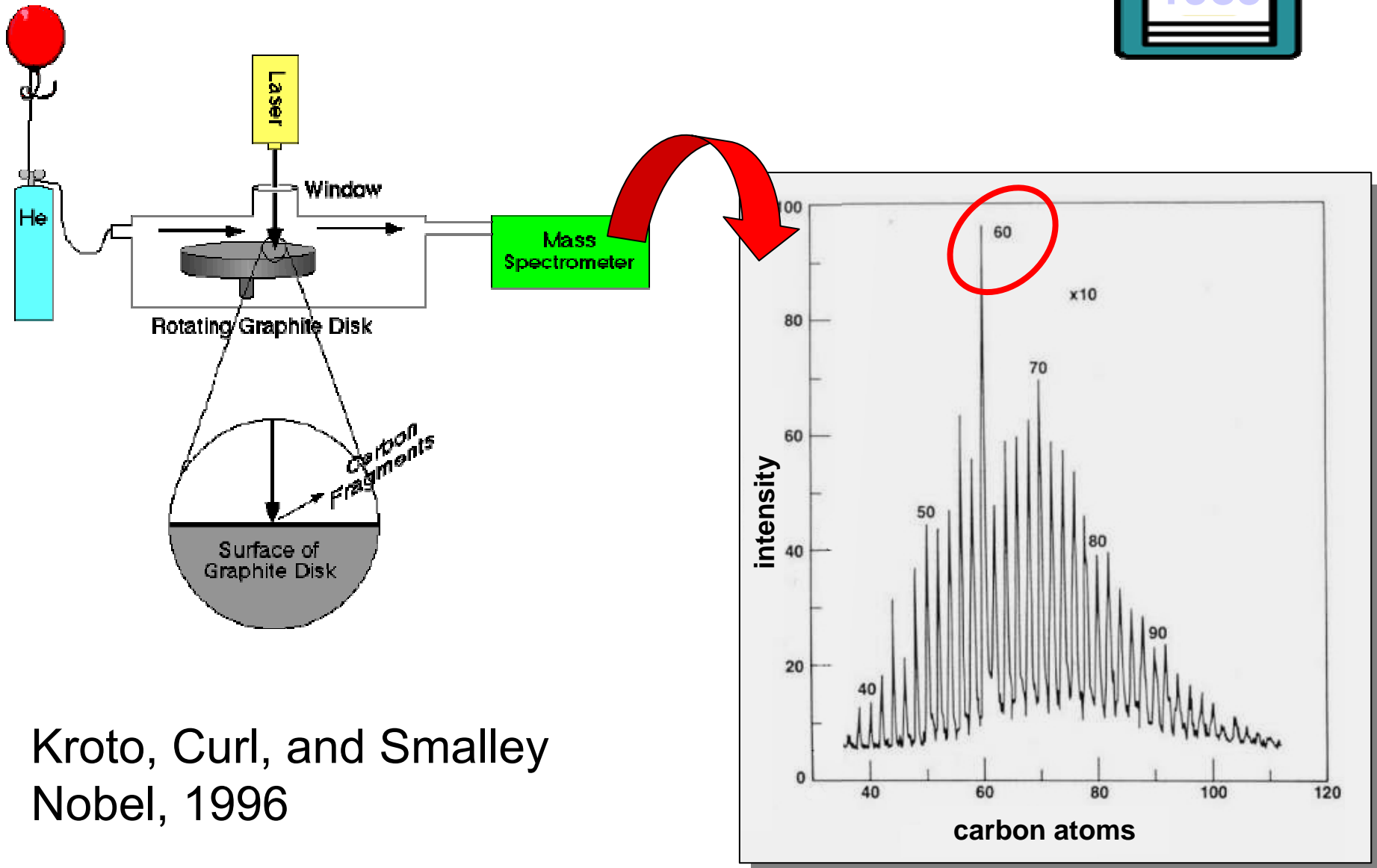


Grafite



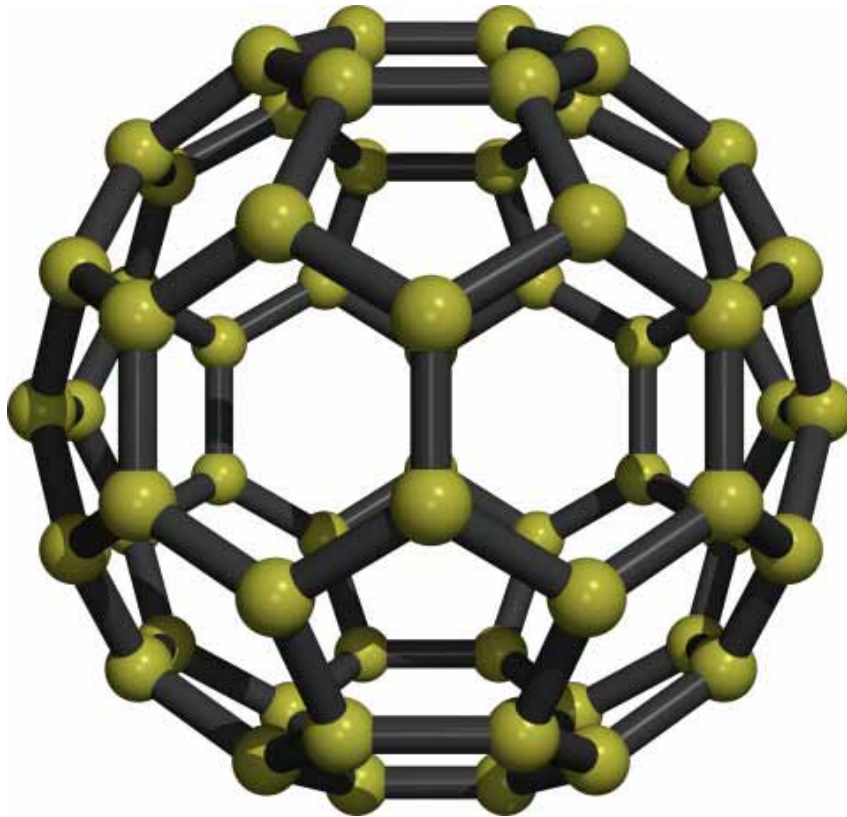
1970 { Eiji Osawa la teorizza
R.W.Henson la propone

Fullerene: la scoperta

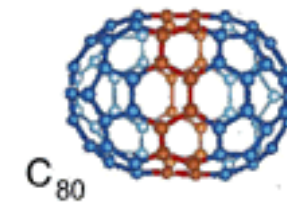
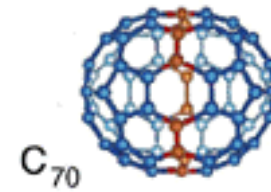
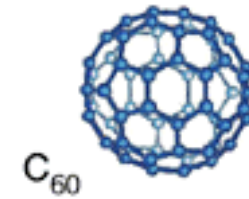


Kroto, Curl, and Smalley
Nobel, 1996

Fullereni



Buckminsterfullerene (C_{60})

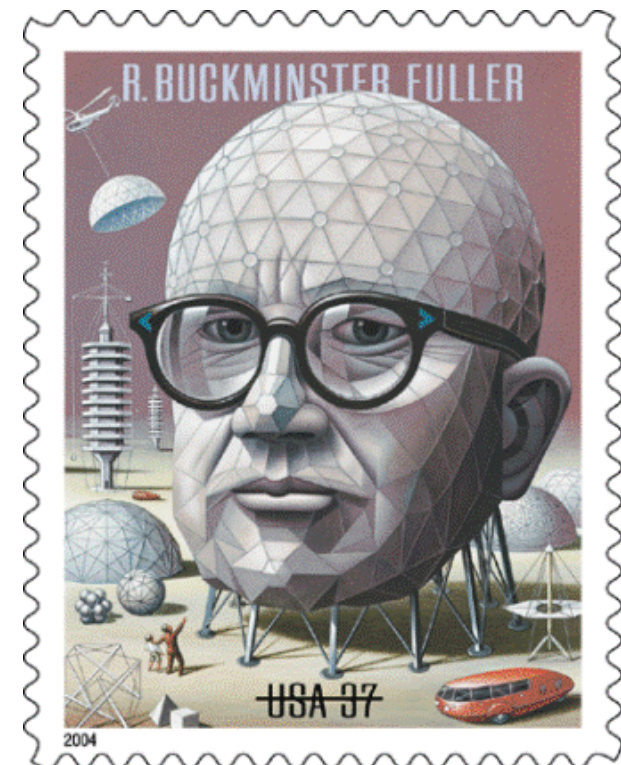


Buckminster Fuller

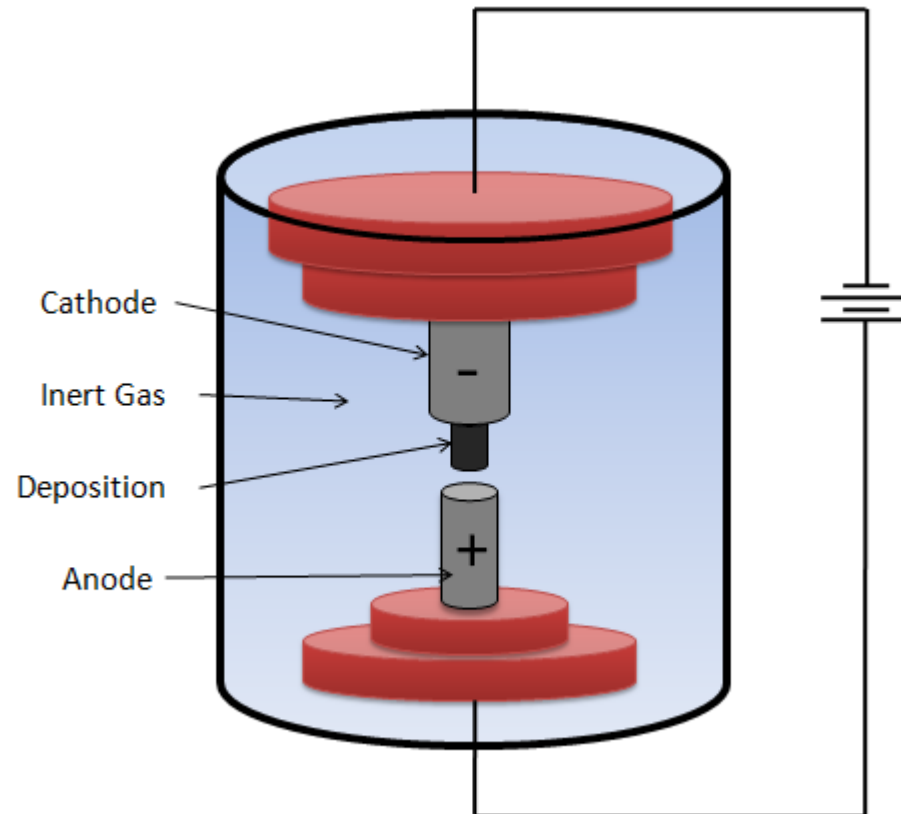


Geodesic Dome

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



Regola di Eulero: sintesi in grammi



Donald Huffman and Wolfgang Krätschmer

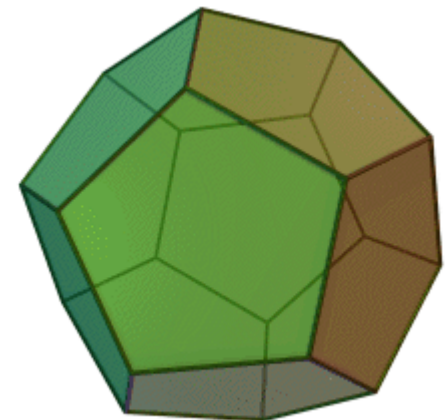
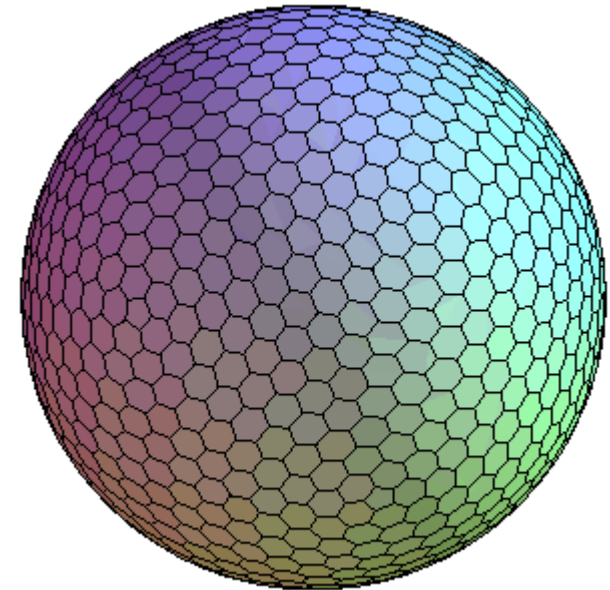
Regola di Eulero

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}

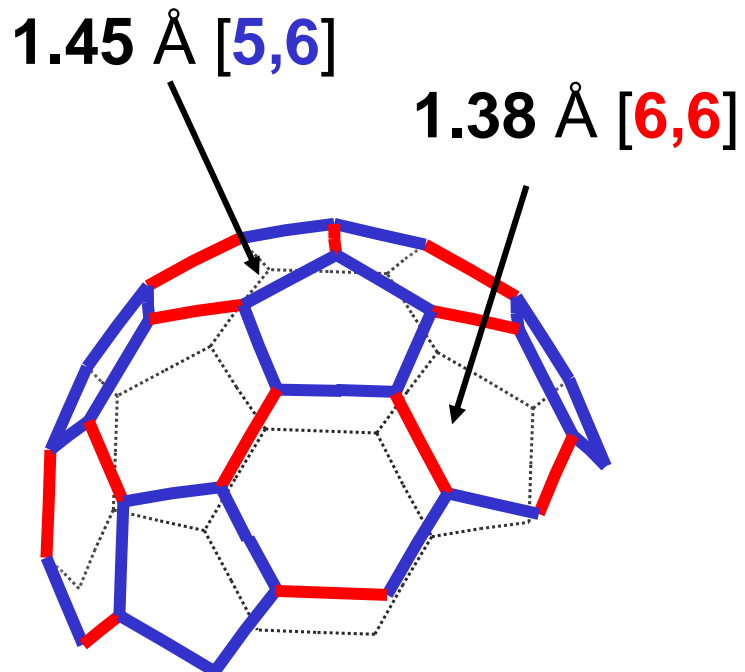


Facce 12

Spigoli 30

Vertici 20

Proprietà strutturali del C₆₀



$$\Delta H_f = 10.16 \text{ Kcal/mol per C}$$

$$(\Delta H_f)_{\text{graphite}} = 0 \text{ Kcal/mol}$$

$$(\Delta H_f)_{\text{diamond}} = 0.4 \text{ Kcal/mol}$$

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.

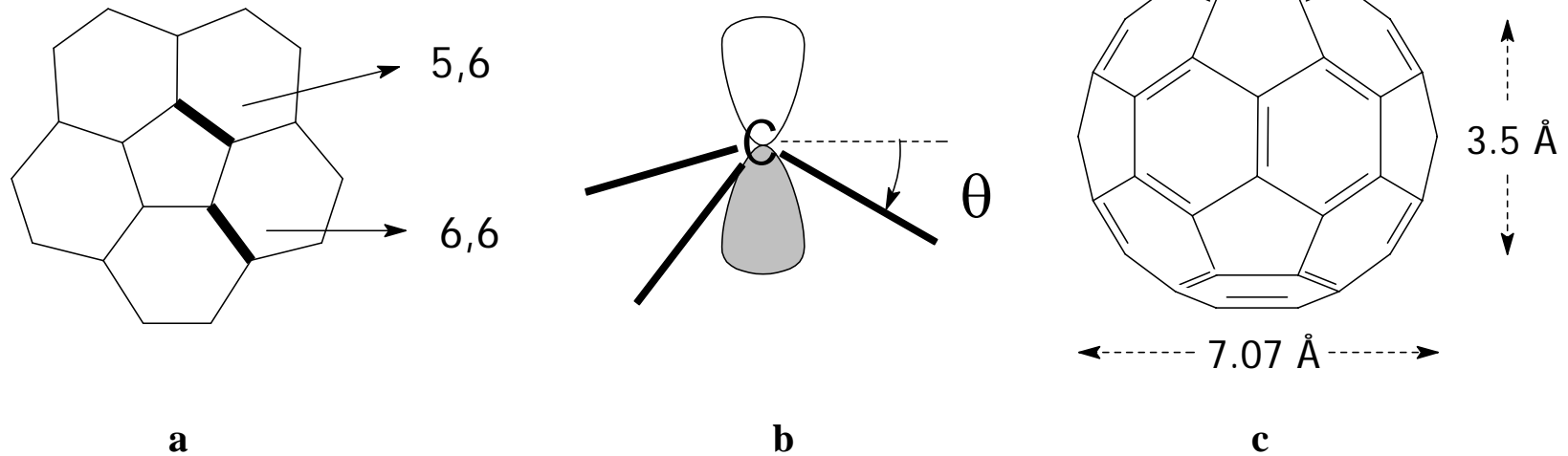
The overall buckyball structure has to be viewed as fused **1,3,5-cyclohexatrienes** and **[5]radialenes**

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)

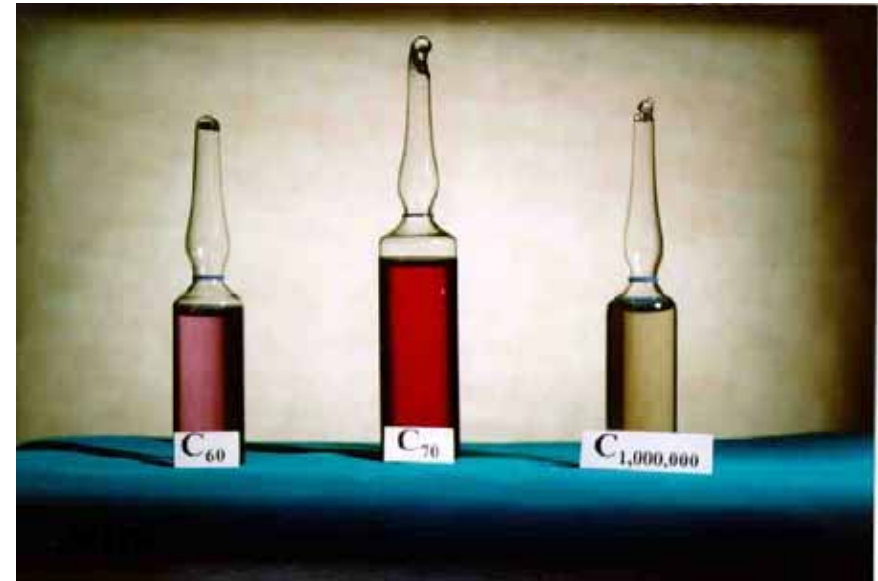
- A. Hirsch, Z. Chen, H. Jiao. *Angew. Chem.* **2000**, 39, 3915.
- M. Bühl, A. Hirsch *Chem. Rev.* **2001**, 101, 1119.

Proprietà strutturali del C_{60}

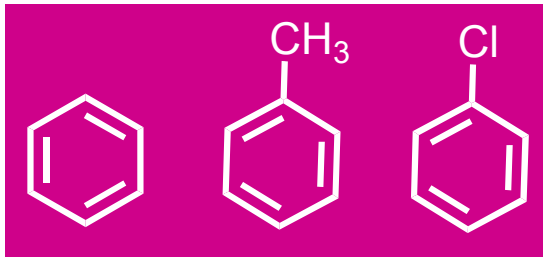


(a) legami 5,6 e 6,6 nel C_{60} ; (b) angolo di piramidizzazione θ ; (c) diametro esterno (*edge-to-edge*) e interno del C_{60} (il diametro di Van der Waals è circa 10.4 \AA)

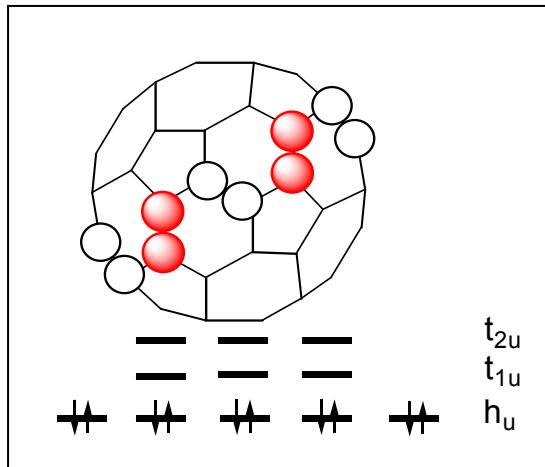
Dendrimeri light-harvesting



C₆₀ solution in toluene



Reattività



C₆₀ behaves essentially as a **strained electron-poor alkene**; addition chemistry is mainly driven by strain relief

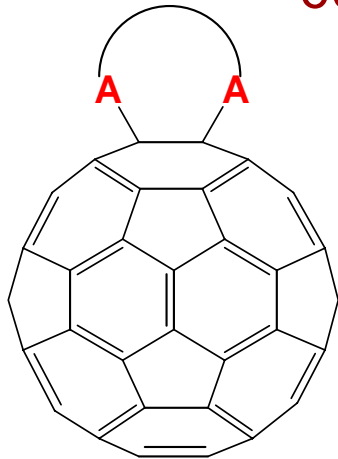
fullerenes are very difficult to oxidize but are **readily reduced** (reactivity towards electron-rich reagents)

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

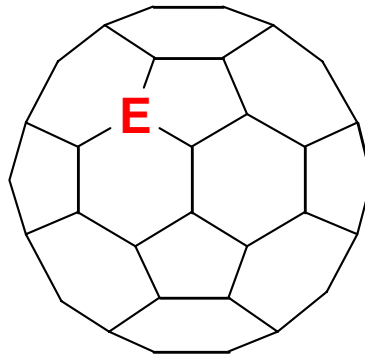
the regioselectivity of addition reactions is governed by **avoidance of products with 5,6 double bonds** in the lowest energy Kekulé structure (price tag of 8.5 kcal mol⁻¹)

multiple addition to C₆₀ is a complicated process governed by differences in bond order and LUMO coefficients at each site: many possible **regio-isomers**

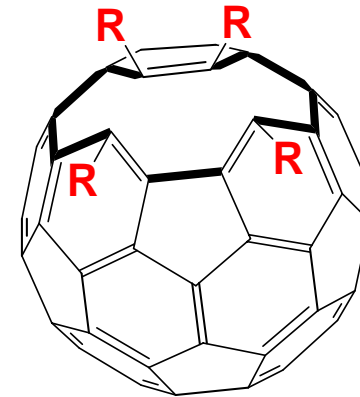
Derivati del C_{60}



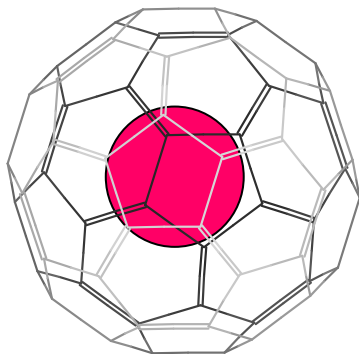
**covalent exohedral
adducts**



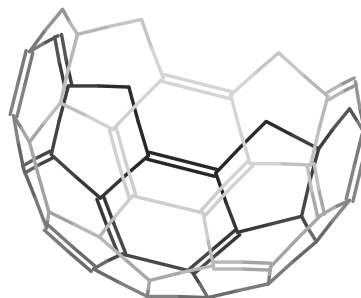
heterofullerenes



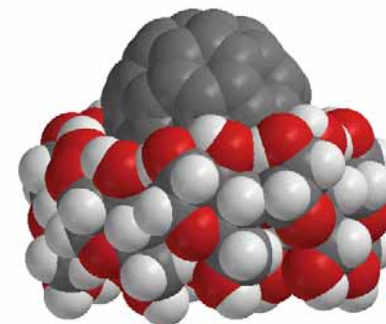
**open-cage
derivatives**



**endohedral
fullerenes**

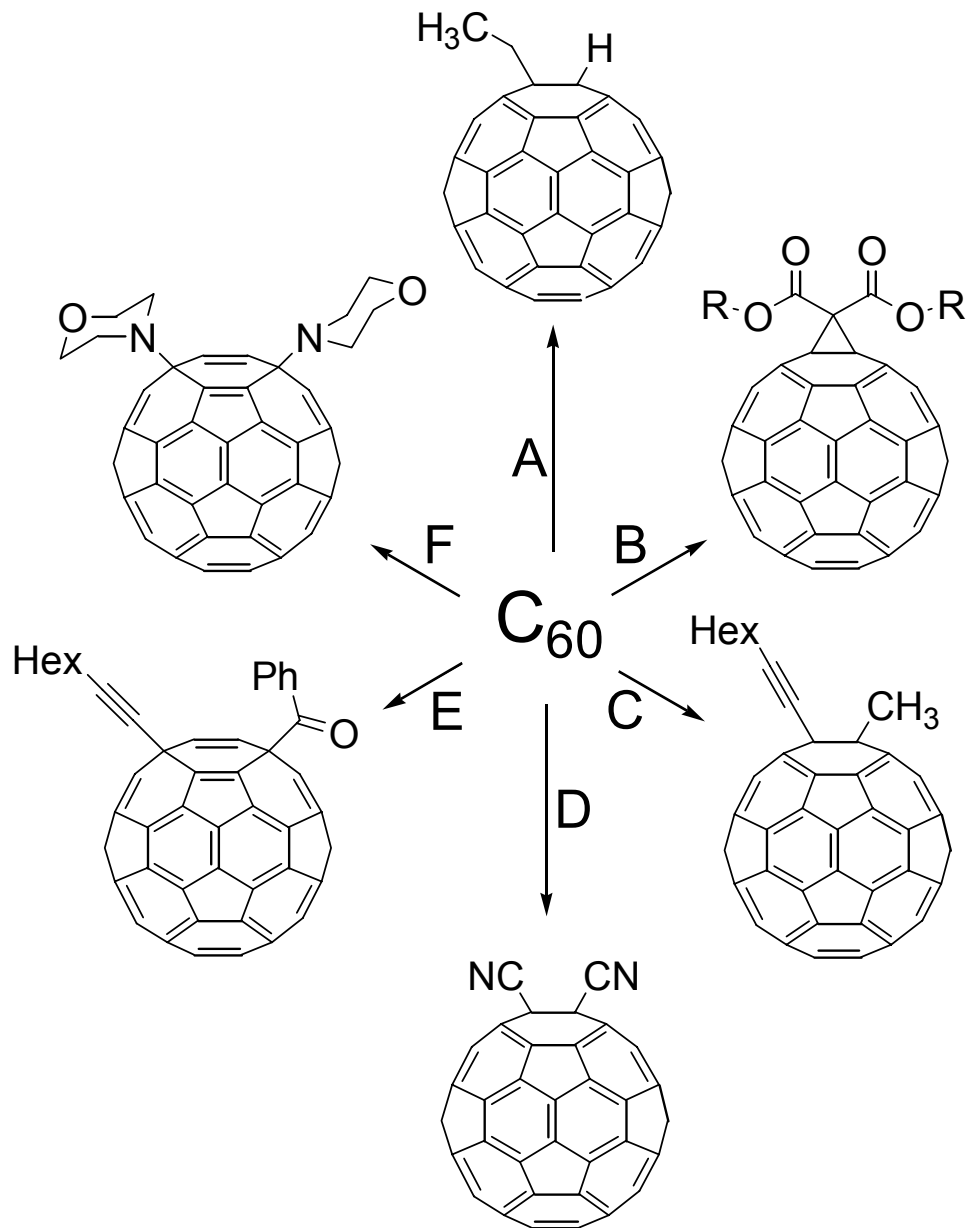


**partial
structures**

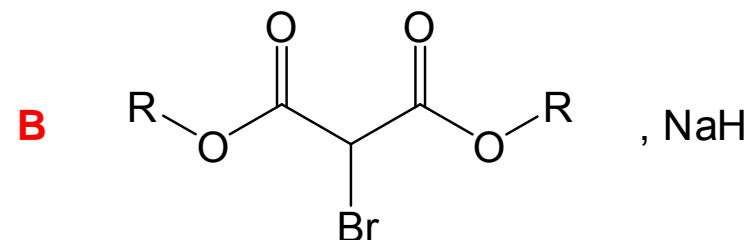


**Host-guest
assemblies**

Addizioni nucleofile al C_{60}



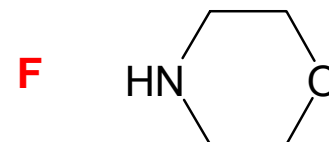
A $EtMgBr, H^+$



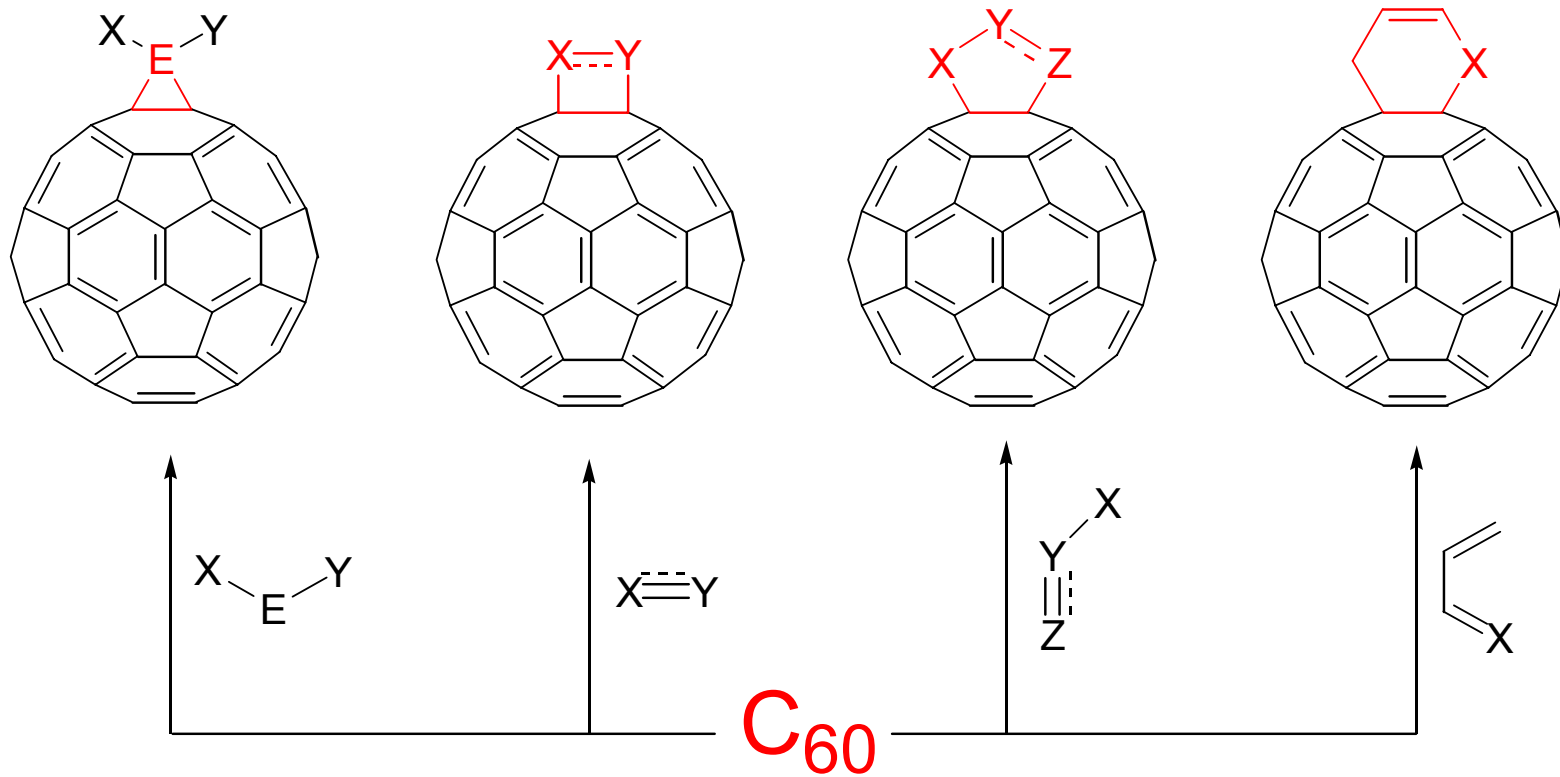
C $Hex-C\equiv C-Li$, MeI

D $NaCN, TsCN$

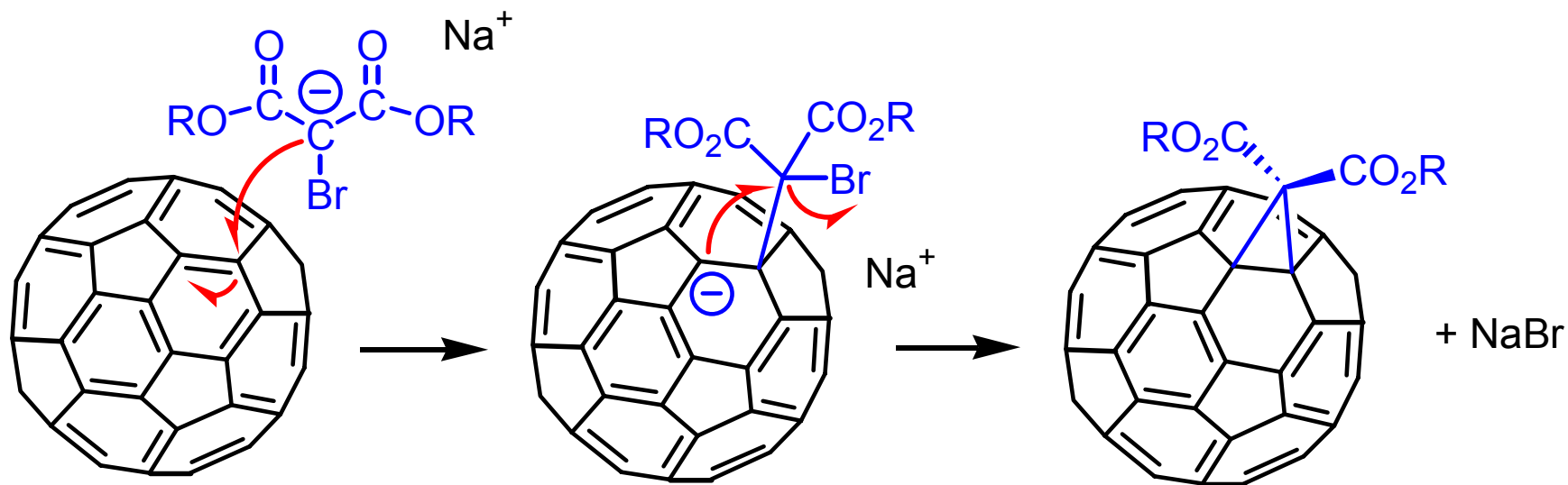
E $Hex-C\equiv C-Li$, $PhCOCl$



Cicloaddizioni al C_{60}

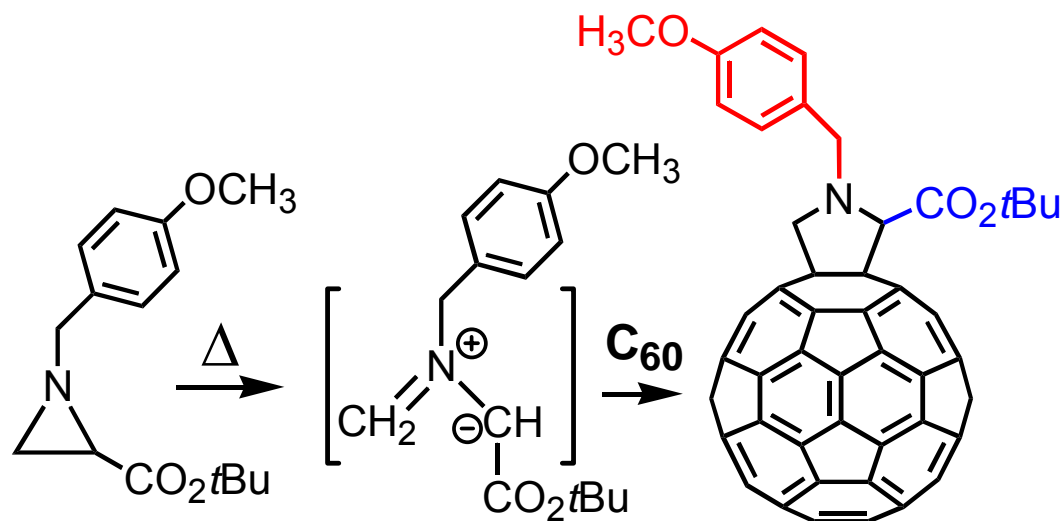
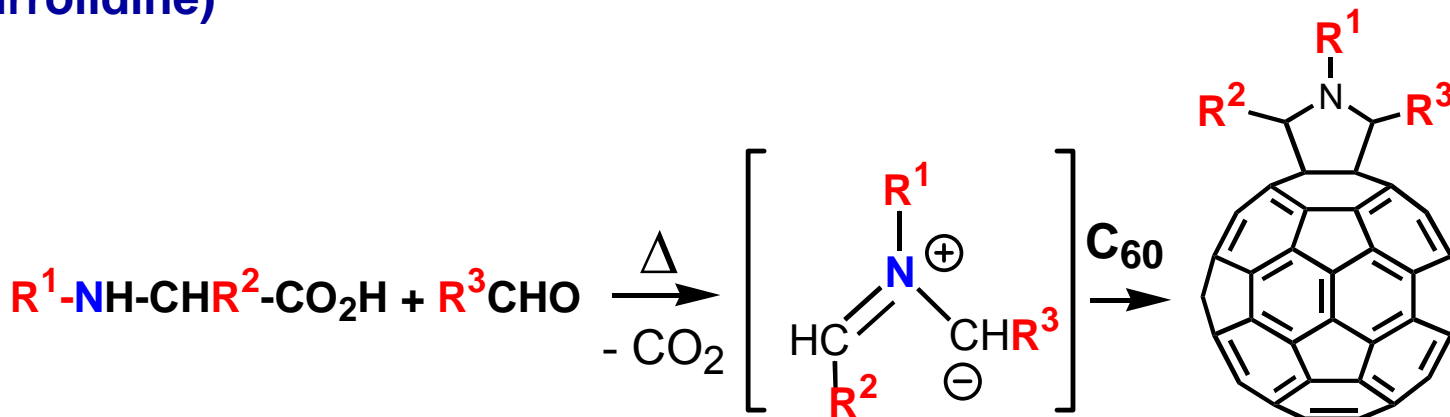


Ciclopropanazione del C_{60} (metanofullereni)



Cicloaddizione di ilidi azometiniche

(fulleropirrolidine)

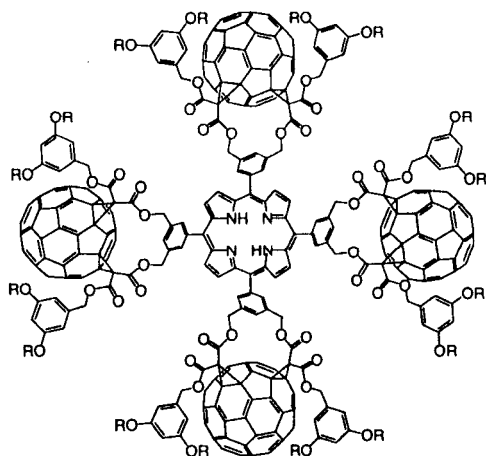
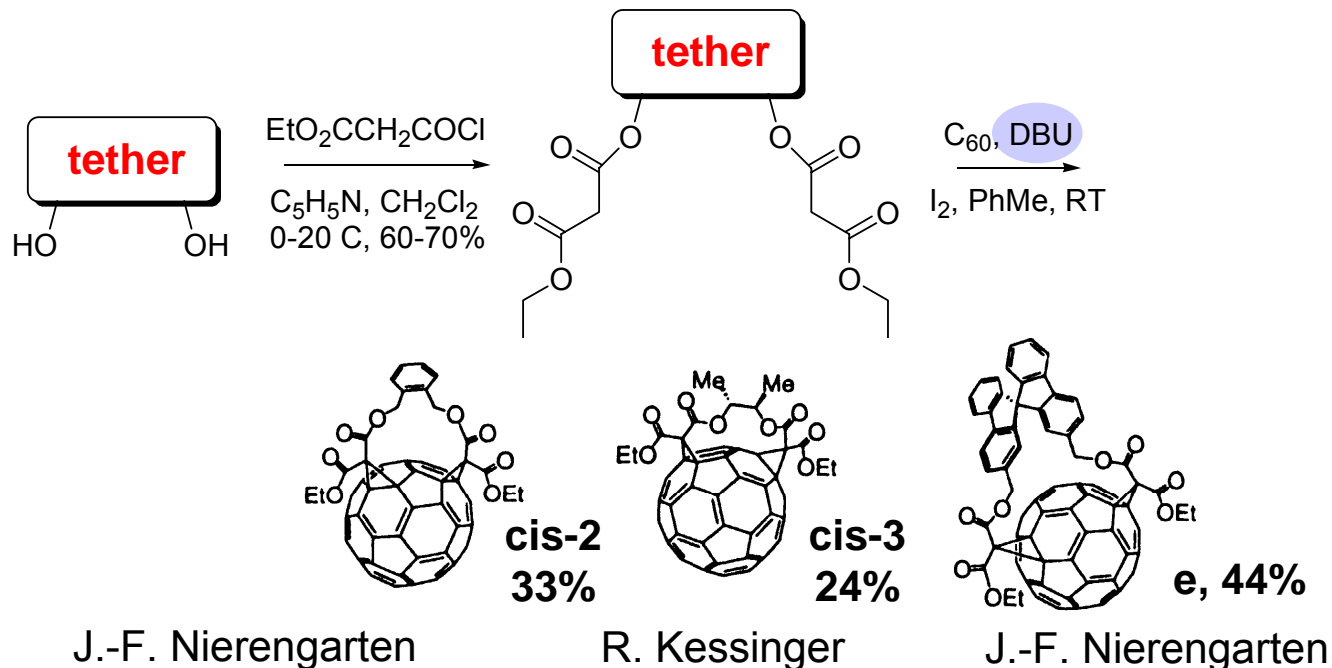
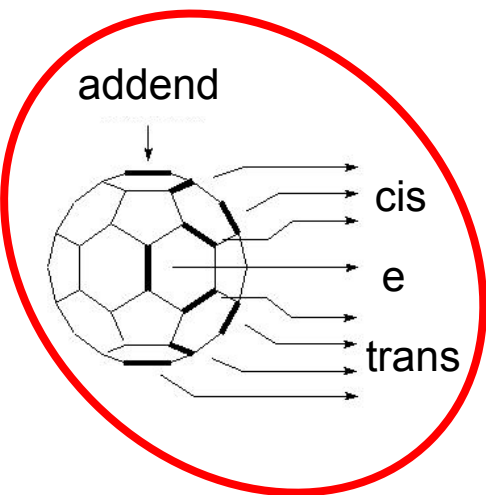


M. Maggini, G. Scorrano, M. Prato *J. Am. Chem. Soc.* **1993**, 9798

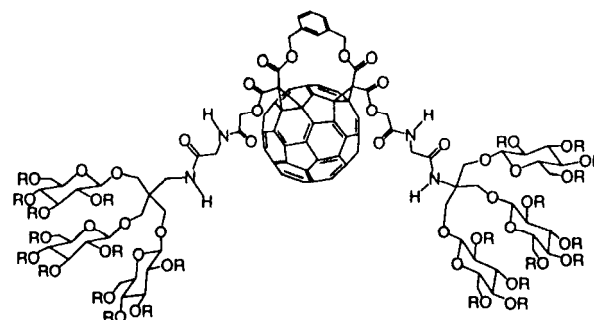
M. Prato, M. Maggini *Acc. Chem. Res.* **1998**, 519

X. Zhang, M. Willems, C. S. Foote *Tetrahedron Lett.* **1993**, 8187

Funzionalizzazione diretta dal linker



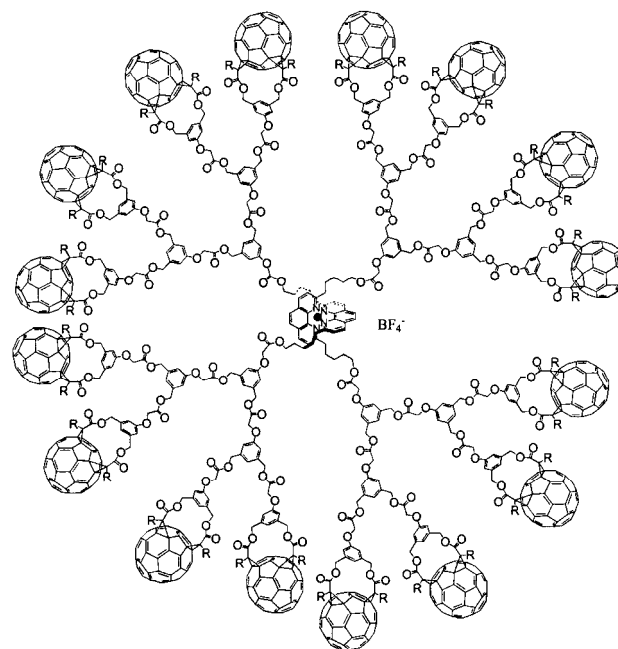
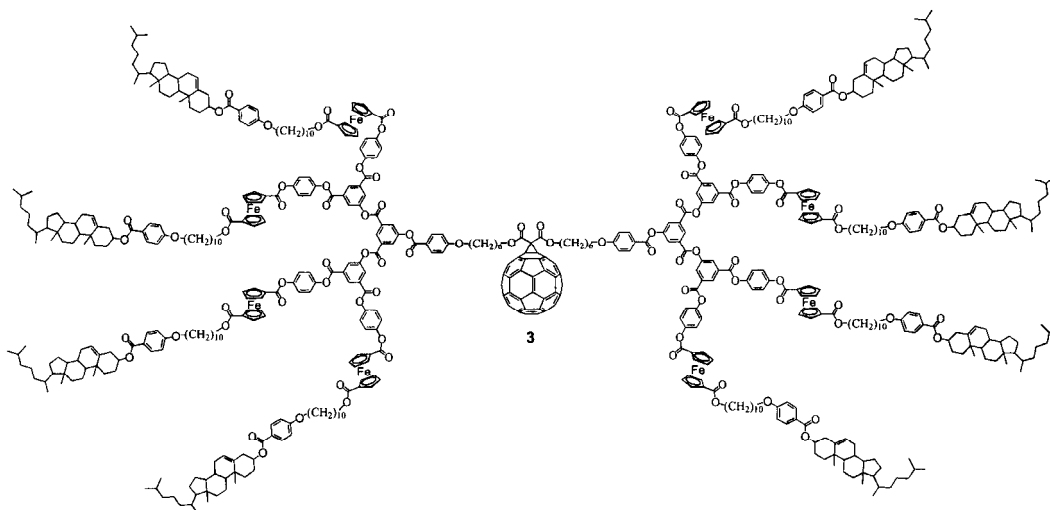
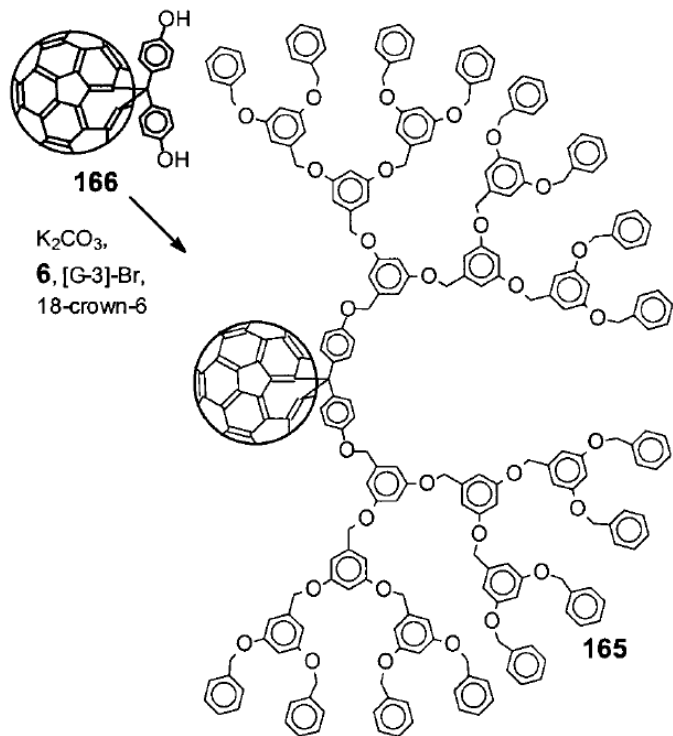
J.-F. Nierengarten



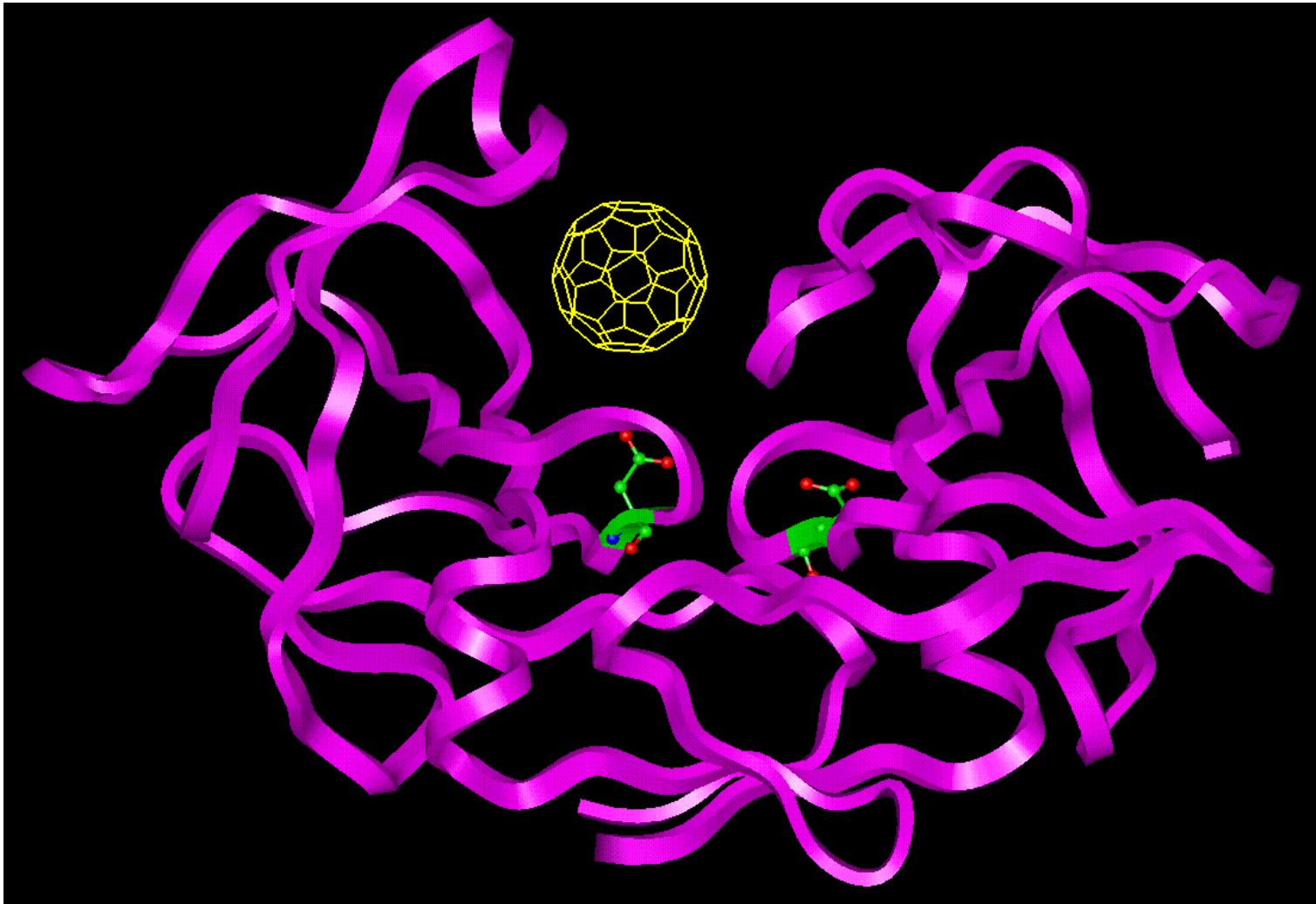
F. Cardullo

F. Diederich, R. Kessinger
Acc. Chem. Res. 1999, 32, 537

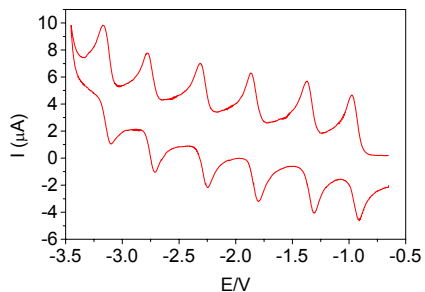
Fullerodendrimeri



Inibitori dell'HIV proteasi



Elettrochimica

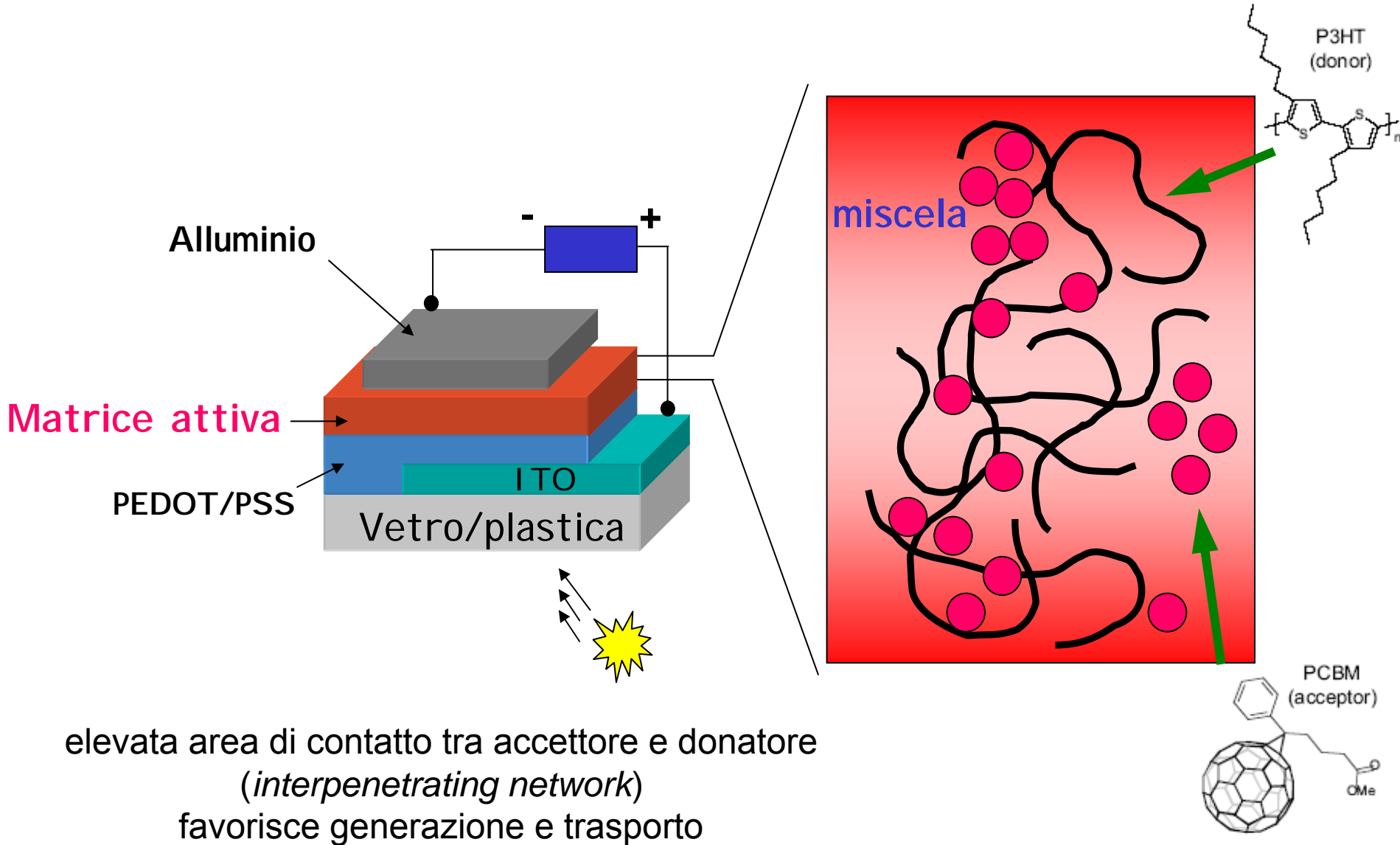


C_{60} : -0.94 -1.33 -1.83 -2.28 -2.74 -3.14

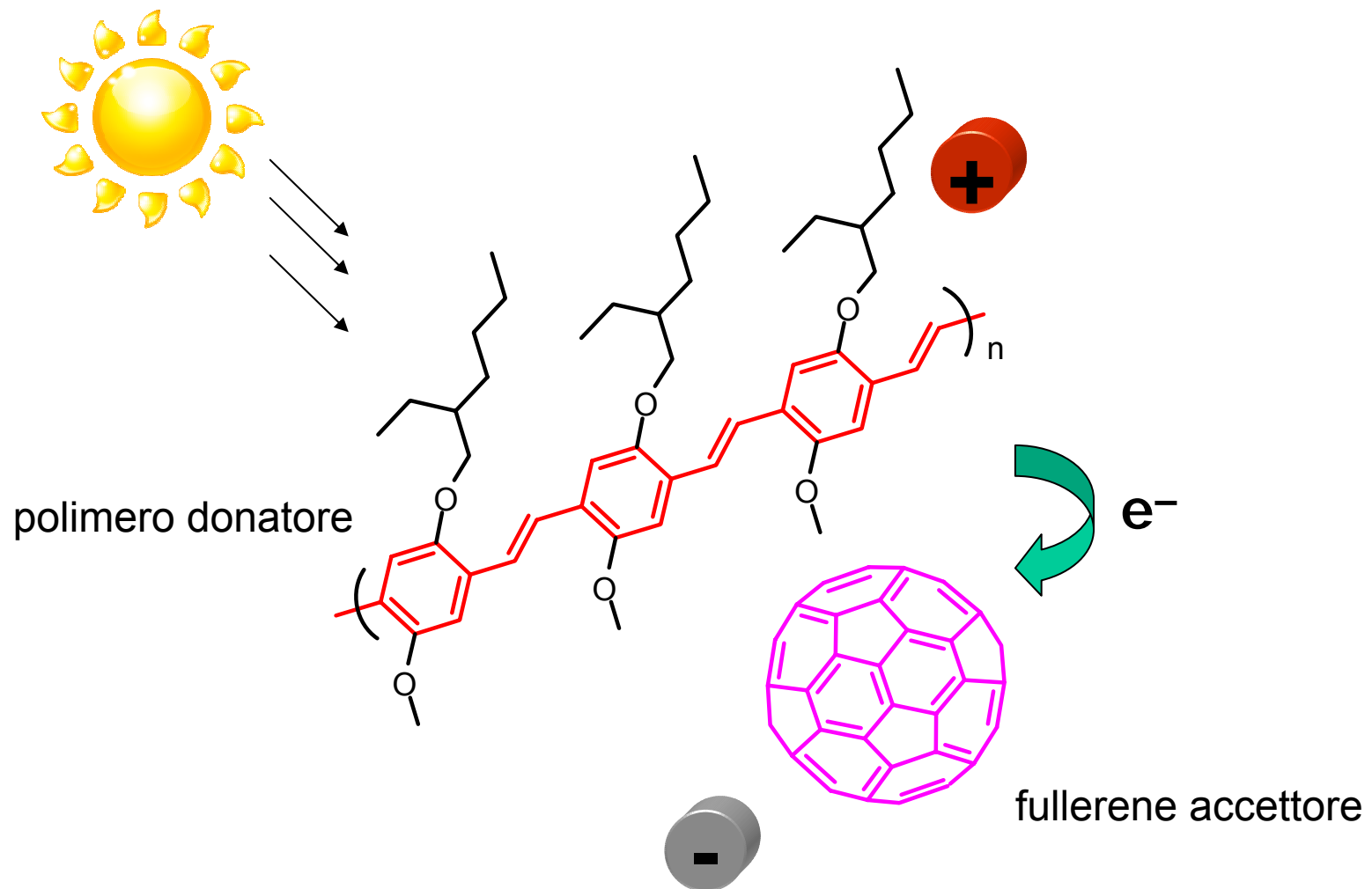
$E_{1/2}$ in V vs Fc^+/Fc

Il fullerene è un ottimo accettore reversibile di elettroni

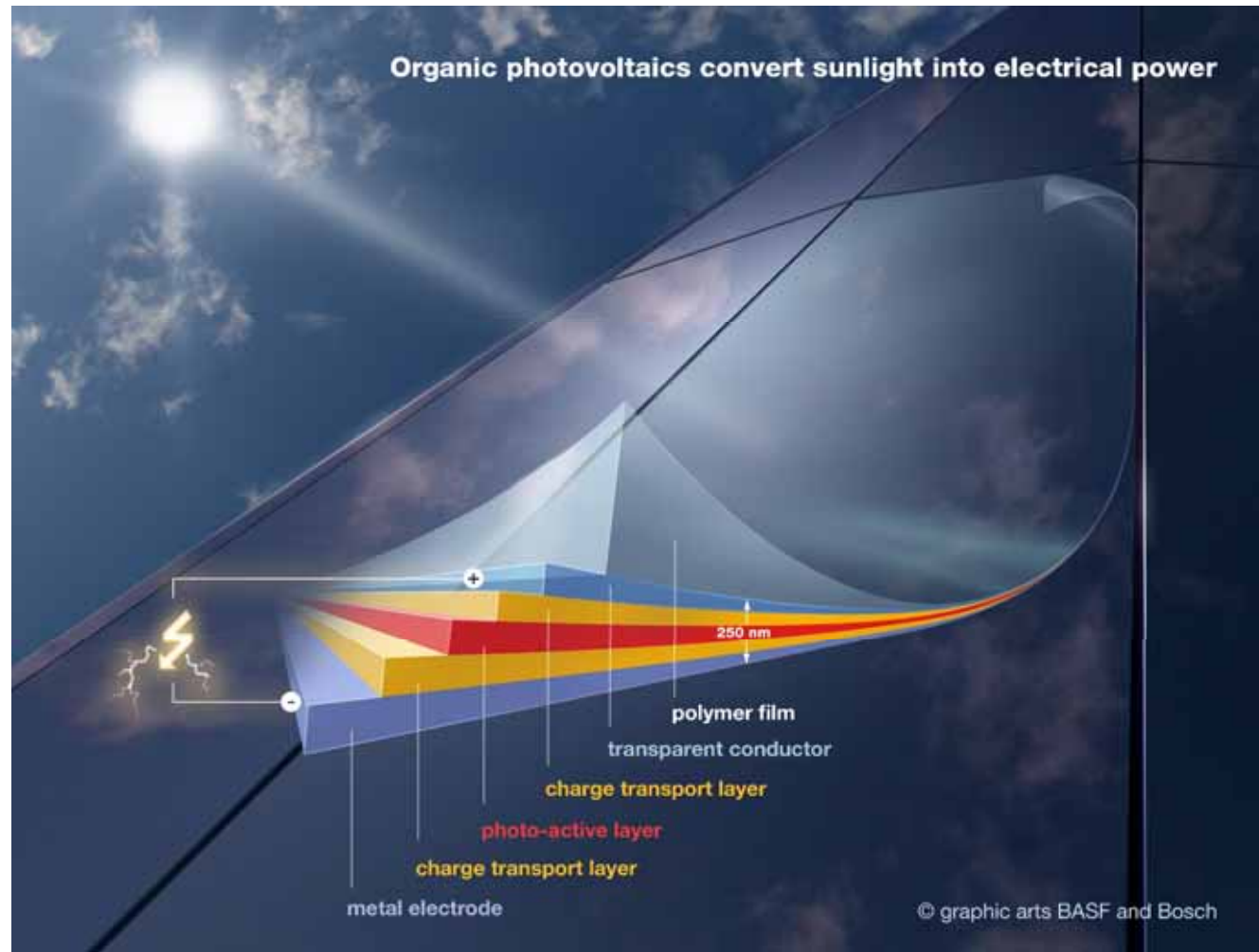
Celle solari di plastica



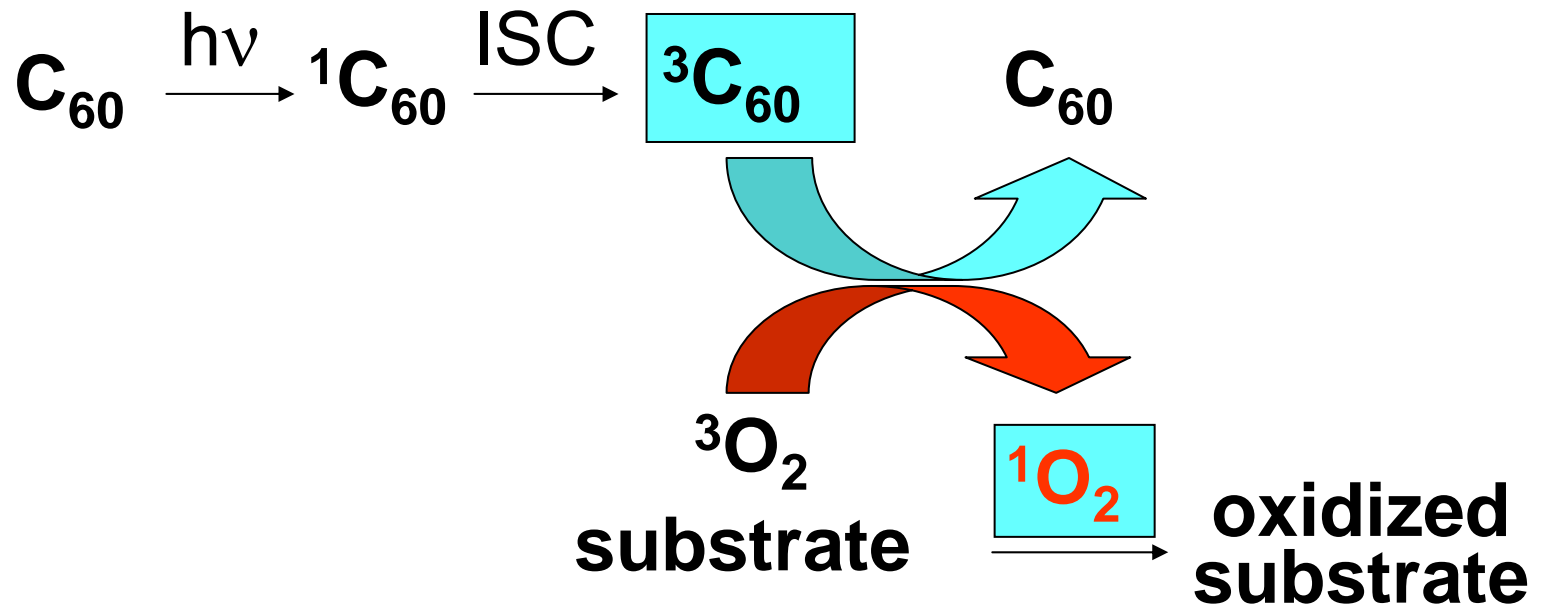
Celle solari di plastica



Celle solari di plastica



Generazione di ossigeno di singoletto

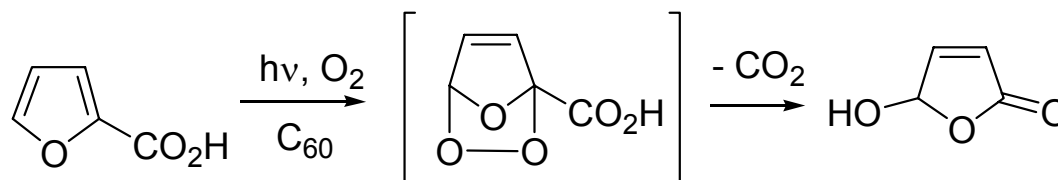


C_{60} is an excellent singlet oxygen sensitizer

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

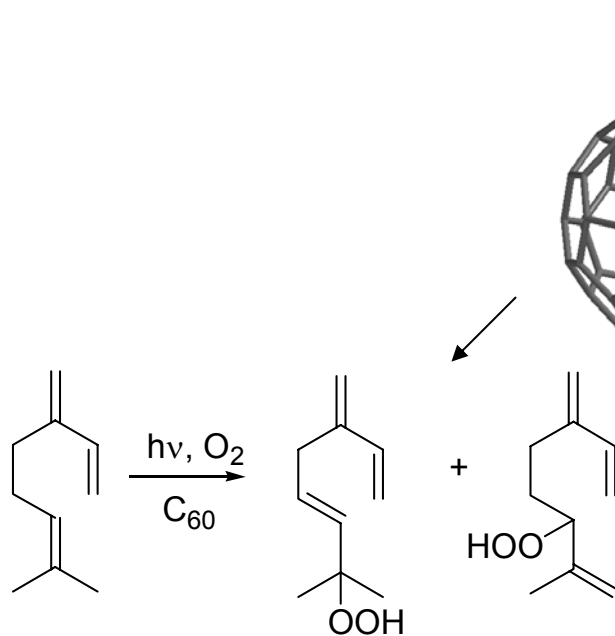
Reactivity of C_{60} with singlet oxygen is very low

Generazione di ossigeno di singoletto



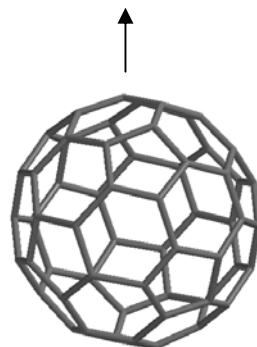
Diels-Alder

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



ene reaction

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