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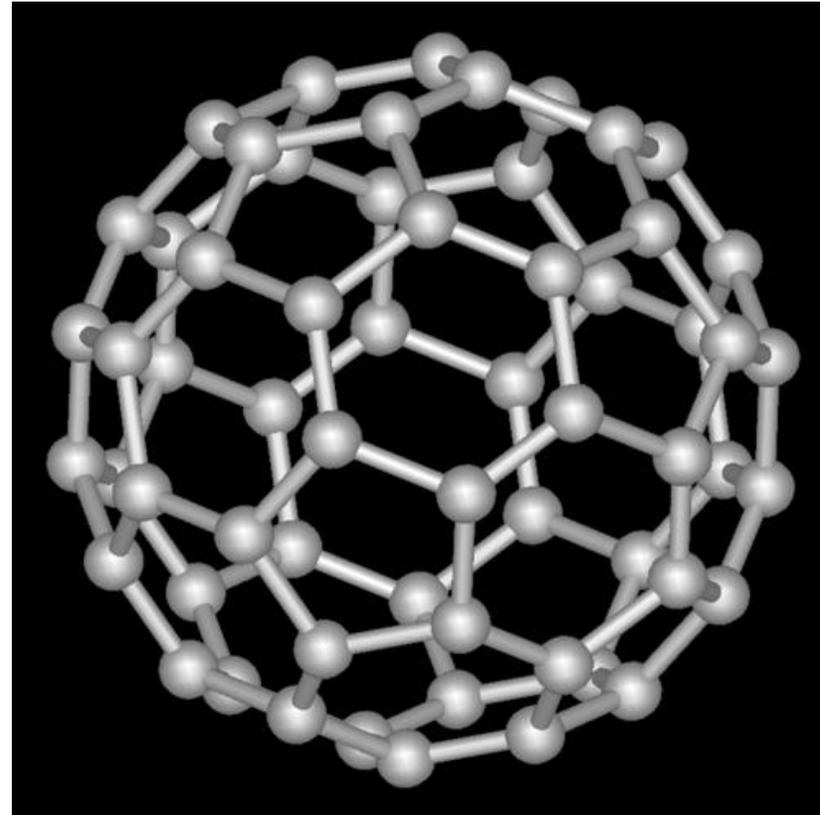
Endohedral & polymeric fullerenes

FRANCESCO BONDI

Metallofullerenes

Always C_{60} cages?

$M@C_{60}$ are unstable in air and solvents.



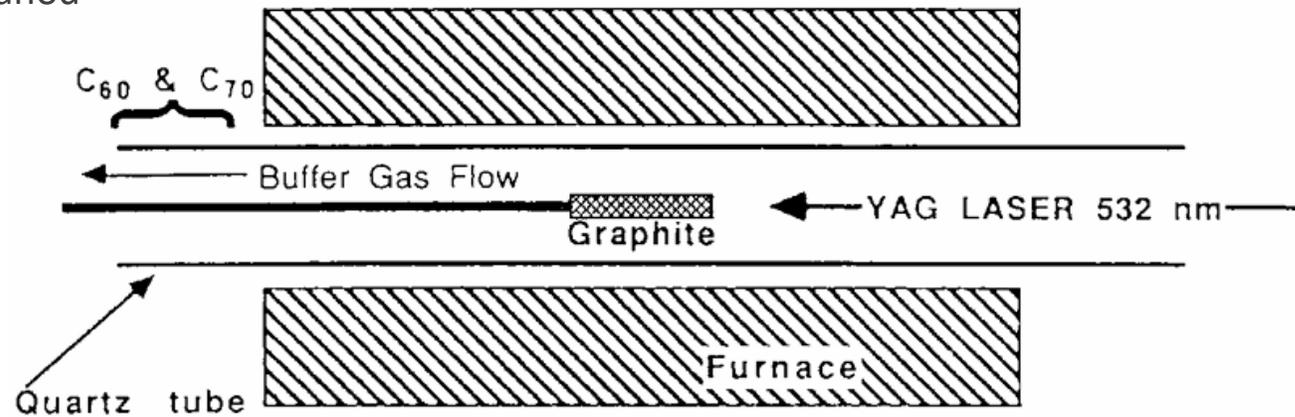
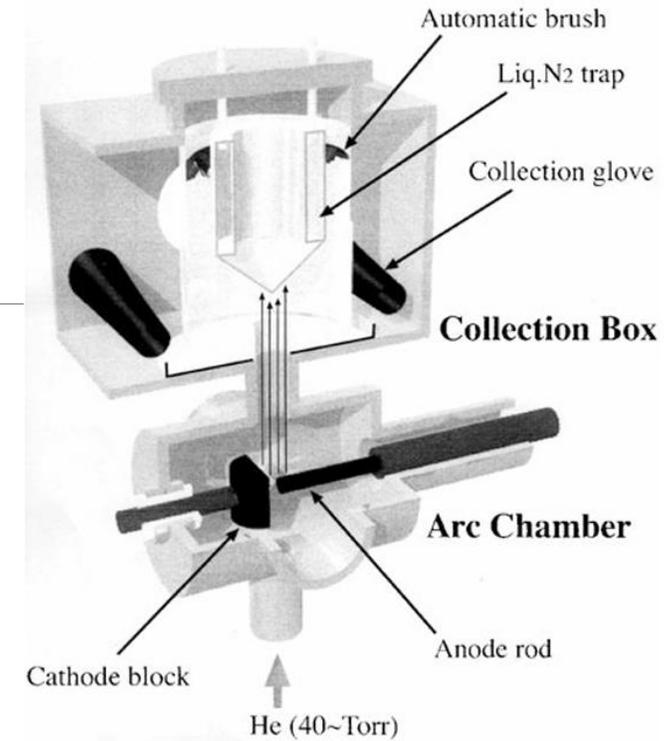
Production

High temperature laser vaporization (or laser furnace):

- Graphite/metal-oxide rod/disc hit by laser beam
- Ar gas flux
- 1200 °C

DC arc discharge:

- Graphite/metal-oxide rod as positive anode
- He gas flux
- 1600 °C



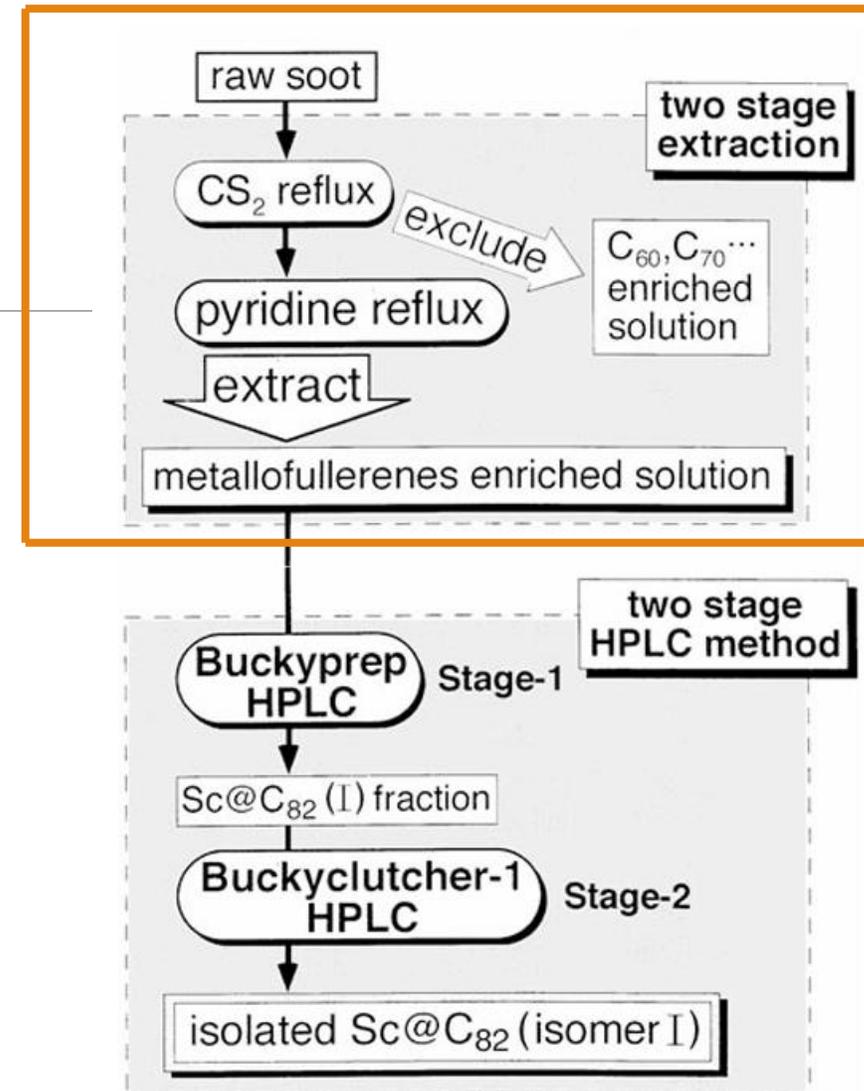
Extraction

Solvent extraction method

- Toluene and CS_2
- But ½ loss → Pyridine and trichlorobenzene

Sublimation method

- Solvent-free
- Heating of soot
- Condensation and trap

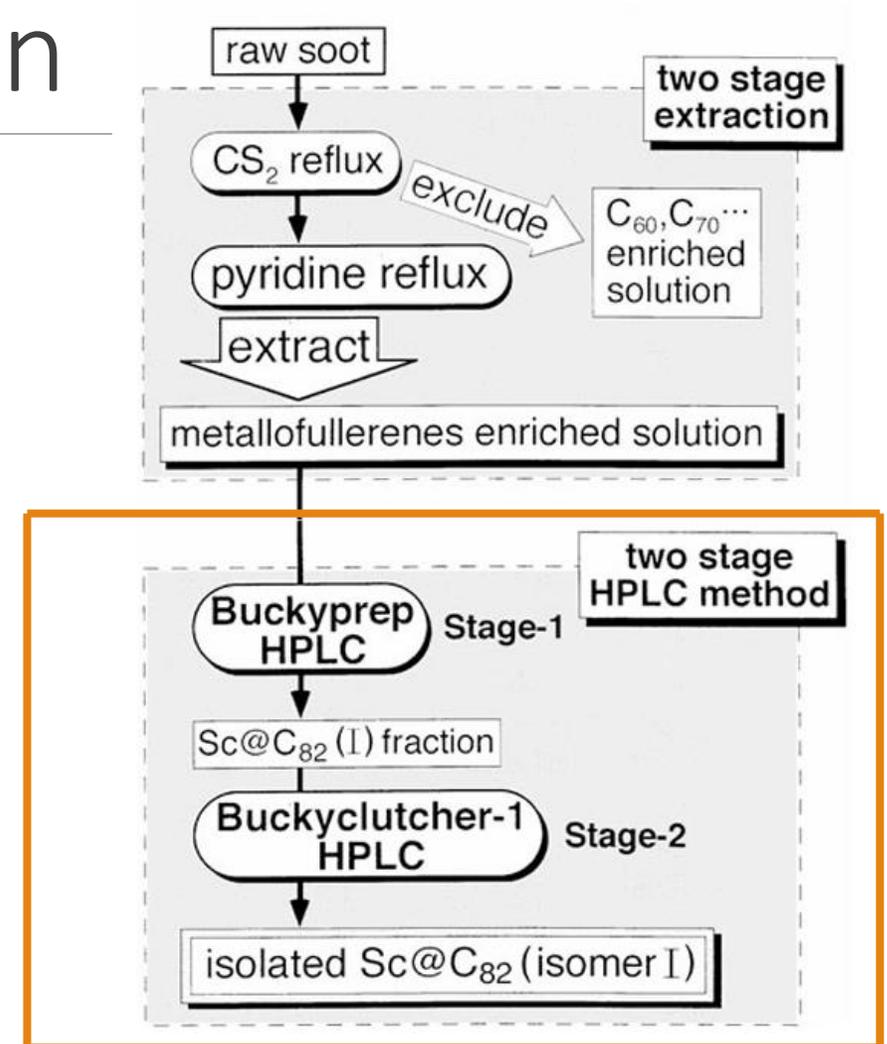


Separation and purification

HPLC (High Performance Liquid Chromatography)

2-stages HPLC:

- Toluene solution separation
- Purification
- Separation of isomers (different retention time)



Structure of metallofullerenes

Endohedral nature demonstrated by:

- Fragmentation experiments
- TEM and STM microscopy
- X-ray diffraction on powder

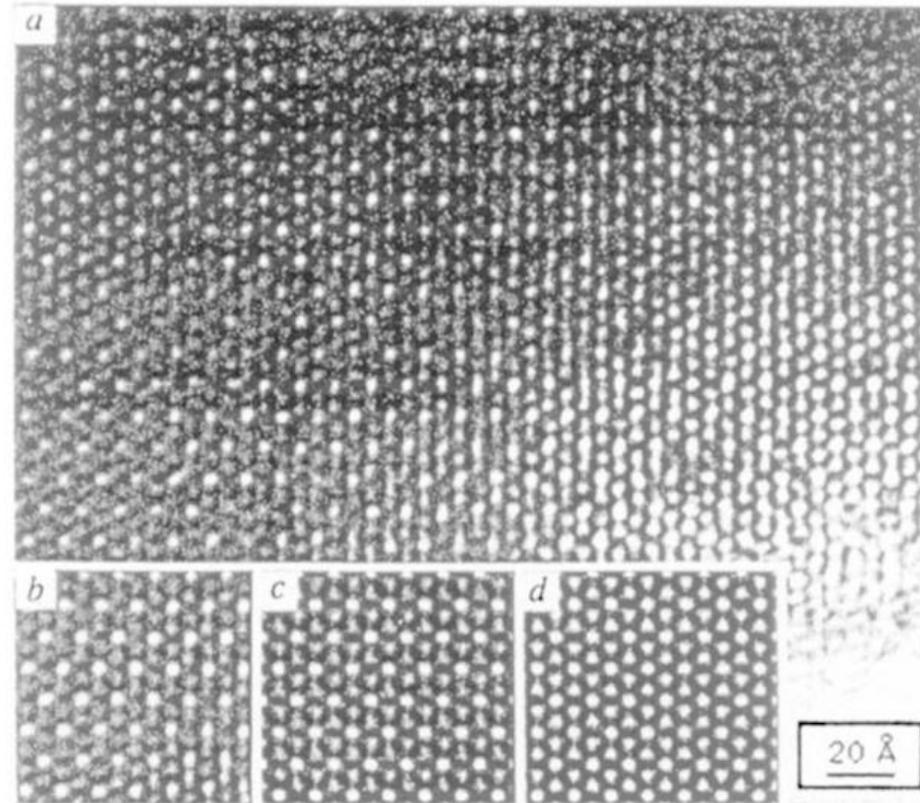


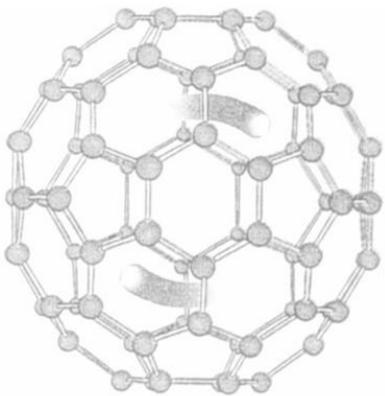
Figure 8. (a) High-resolution TEM image of a $\text{Sc}_2@C_{84}$ crystal, taken along the [0001] direction. Inset (b) is a Fourier-filtered image that brings out the periodicities present in the original image. Insets (c) and (d) are simulated images of 67 Å thick $\text{Sc}_2@C_{84}$ and C_{84} crystals, respectively.

Structure

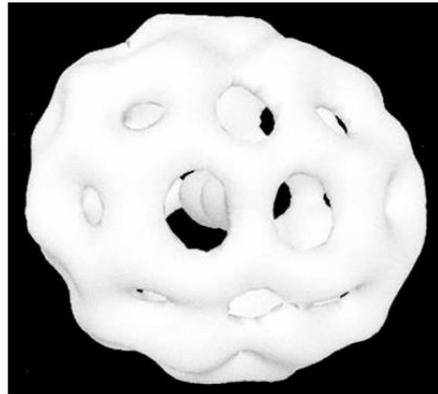
X-ray diffraction:

- electronic density distribution $Y@C_{82}$, $Sc@C_{82}$, $La@C_{82}$
- dynamics insight the cage: $La_2@C_{80}$, $Sc_2@C_{84}$
- charge state: $(Sc_2)^{2+}@C_{84}^{2-}$; $(Sc_3)^{3+}@C_{82}^{3-}$

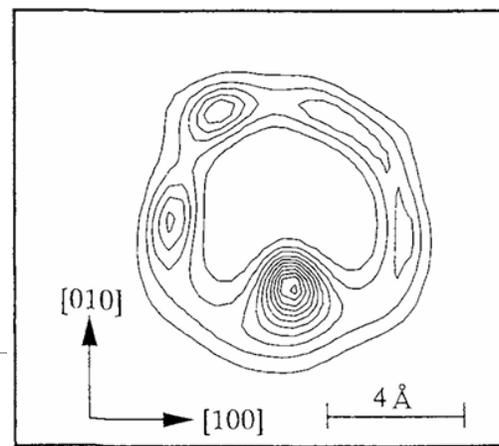
Crystal structures



$La_2@C_{80}$

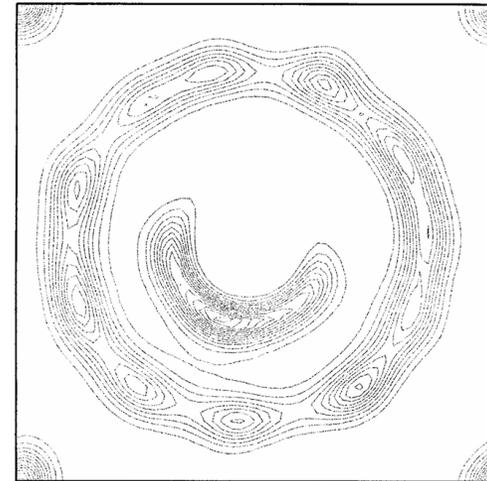


$Sc_2@C_{80}$

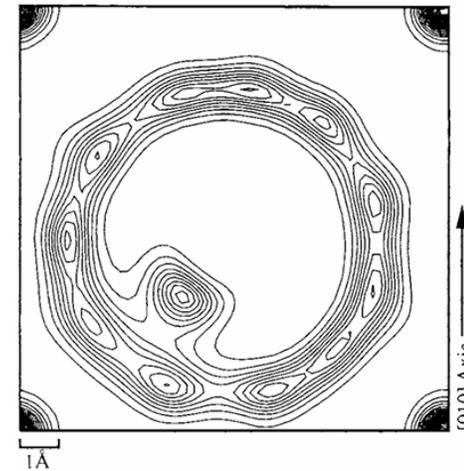


$Y@C_{82}$

(100) PLANE, SECTION = 22, SINGLE UNIT CELL



$La@C_{82}$



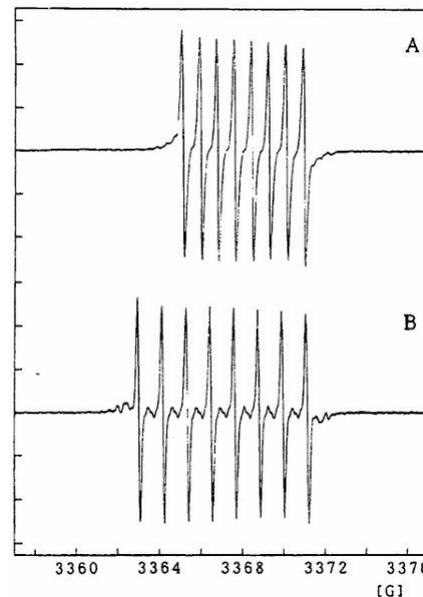
$Sc@C_{82}$

Charge state

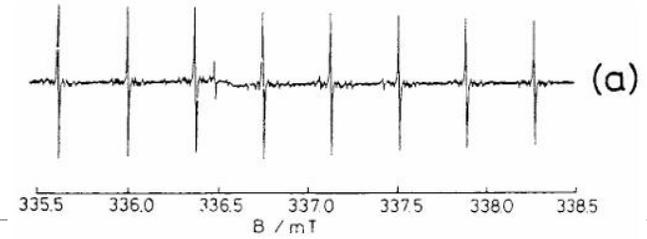
ESR studies: hyperfine spectra

- $La^{3+}@C_{82}^{3-}$, $Y^{3+}@C_{82}^{3-}$, $Sc^{2+}@C_{82}^{2-}$
- Di-metallo fullerenes with Y, Sc, La are silent to ESR (diamagnetic)
- Broadening of linewidth \propto temperature

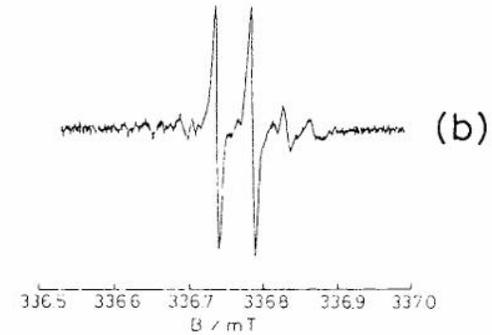
ESR on structural isomers: different hfs



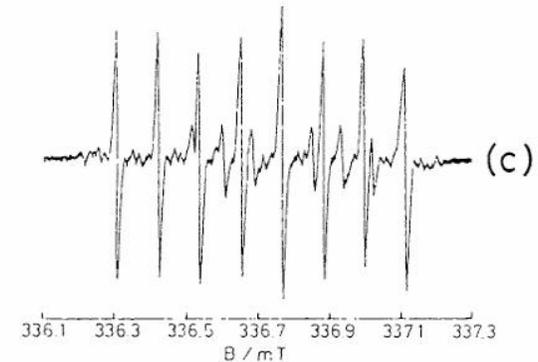
$La@C_{82}$



$Sc@C_{82}$



$Y@C_{82}$



$La@C_{82}$

Electronic properties

Electrochemistry: cyclic voltammetry → reduction/oxidation properties

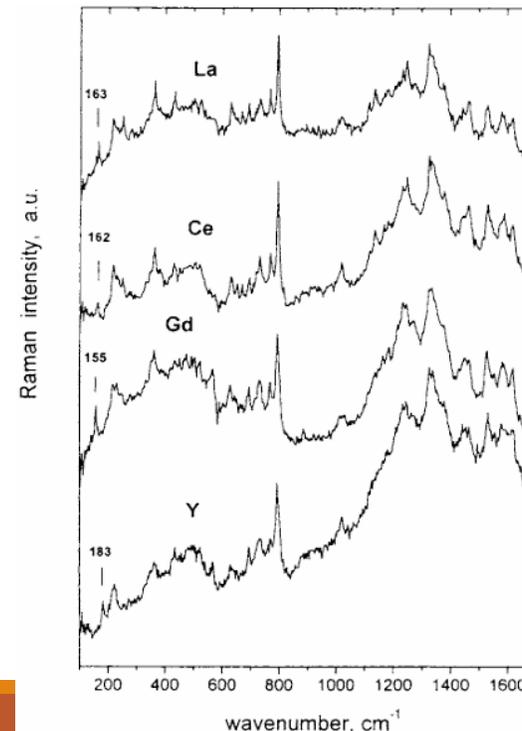
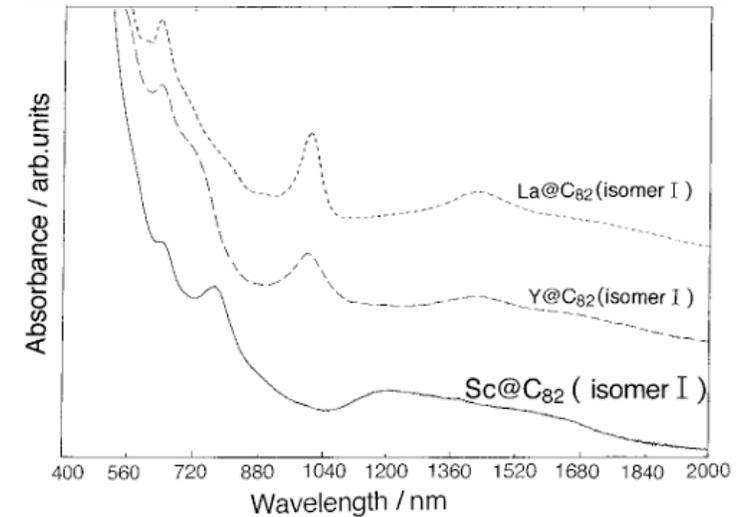
- $La@C_{82}$ both donor and acceptor

UV-VIS-NIR absorption spectra → differences due to

- divalent/trivalent charge state
- Isomers structure
- Similar spectra of $M@C_{82}$ irrespective of the kind of encaged metal

Vibrational (IR and Raman) spectra → differences due to:

- Metal insight
- Charge state

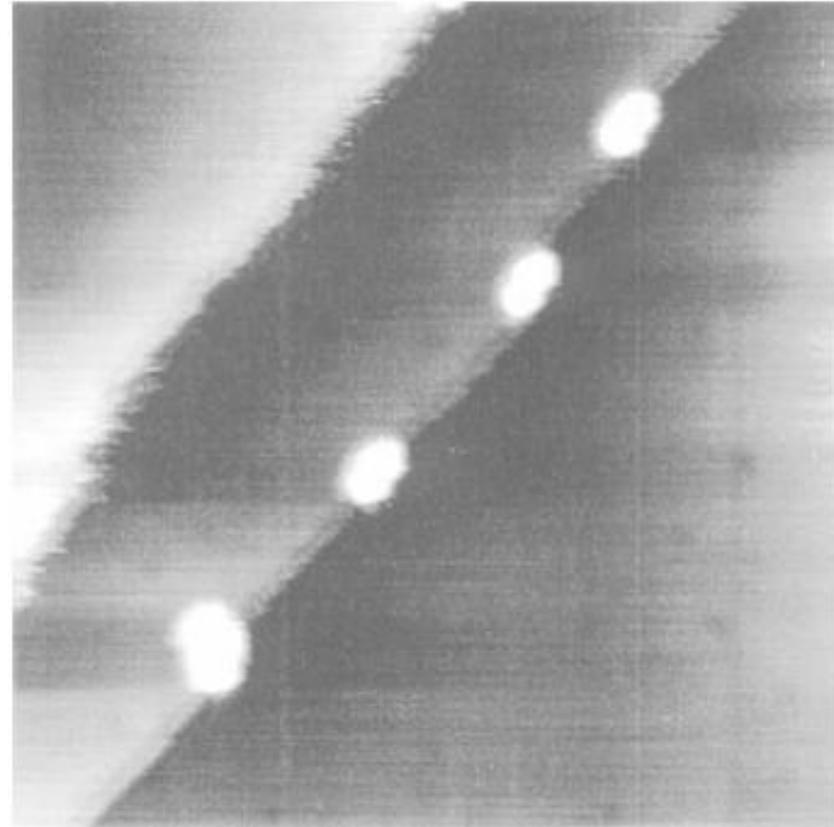


Imaging on surfaces

STM microscopy

Superatom character:

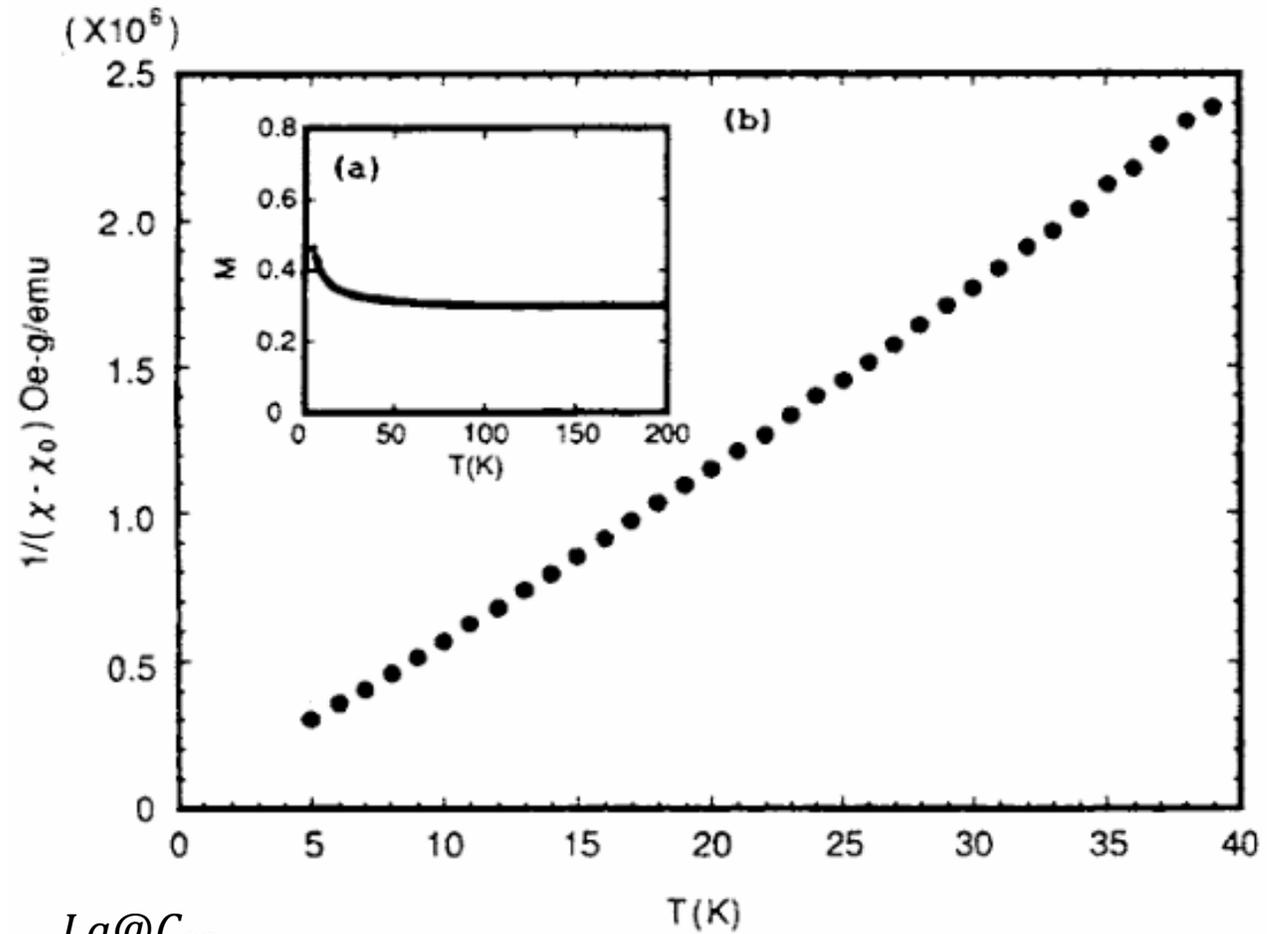
- $Y@C_{82}$ on Cu surface forms dimers
- $Y^{3+}@C_{82}^{3-}$ → positive core and negative cage



Magnetic properties

SQUID measurements

$La@C_{82}$, $Gd@C_{82}$ are paramagnetic



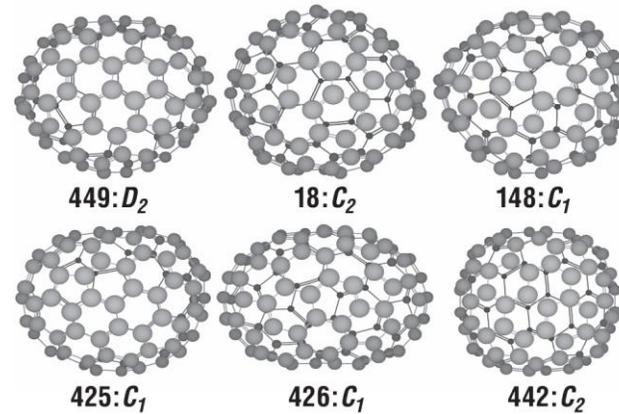
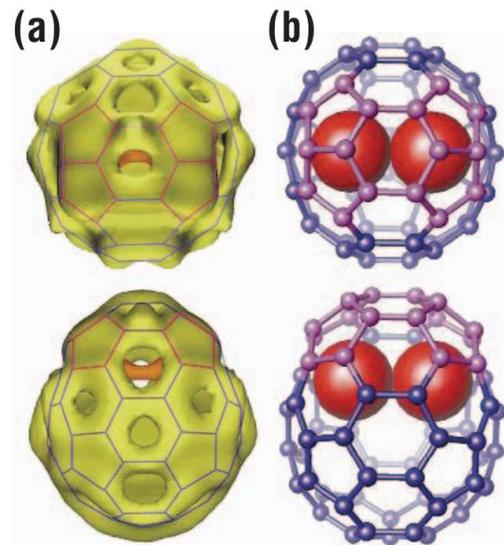
Interesting metallofullerenes

IPR form to minimize of steric strain and dangling bonds

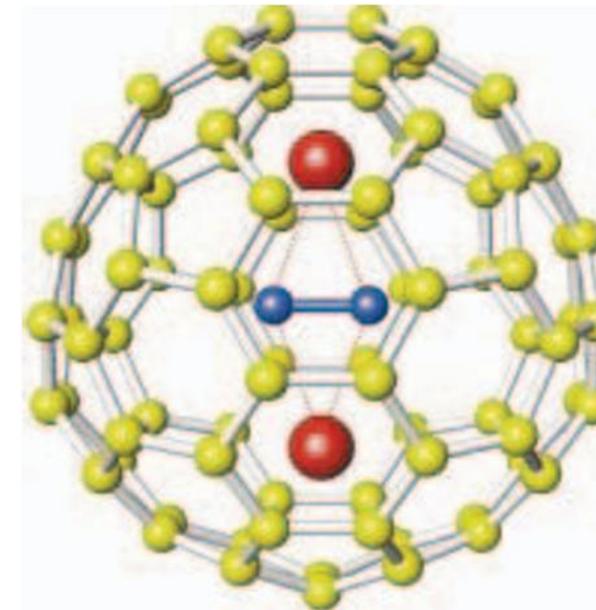
Non IPR stabilized by di-metallo structures: $Sc_2@C_{66}$, $La_2@C_{72}$

Carbide structure: $Sc_2C_2@C_{84}$

Di-/tri-metallofullerenes \rightarrow higher fullerene cages: $Dy_2@C_{100}$



$Dy_2@C_{100}$



$Sc_2C_2@C_{84}$

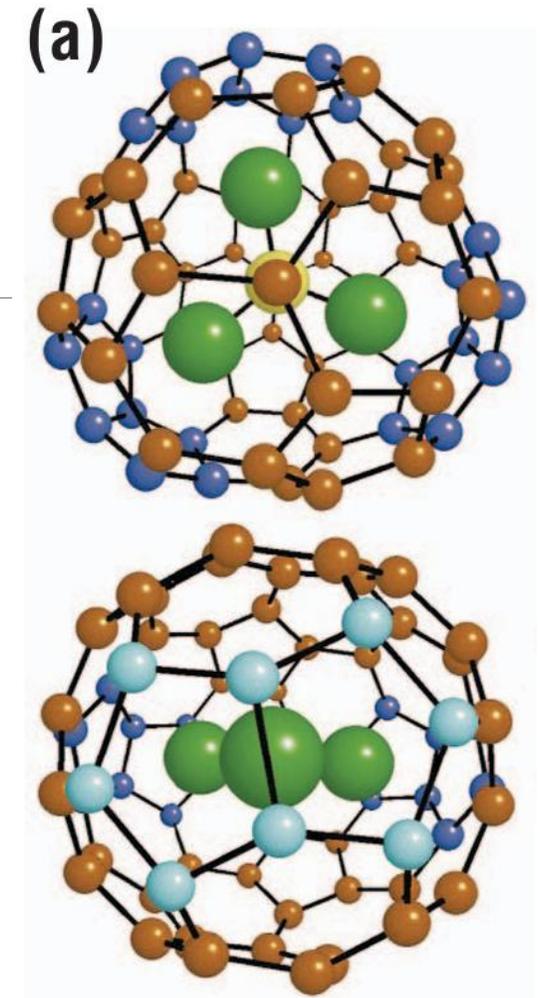
L. Dunsch, S. Yang, *The Electrochem. Society Interface* (2006)

Fig. 1. (a) X-ray structure of the IPR-violating $Sc_2@C_{66}$ (C_{2v}) fullerene, showing a top view along the C_2 axis and a side view. (b) Calculated $Sc_2@C_{66}$ structures. (Adapted from Ref. 3.)

Nitride cluster fullerenes:

- $Sc_3N@C_{80}$: trimetal nitride cluster and C_{80} cage isolated aren't stable
- Structure (of cage and cluster encaged) by: XRD, NMR, vibrational spectroscopy, UV-VIS-NIR
→ electronic properties
- C=C bond → reaction between fullerenes
- Magnetic properties:
 - ✓ M=Tb, Ho: moments of M coupled to field of M_3N cluster
 - ✓ $Dy_3N@C_{80}$: Ising-like anisotropy

Metallofullerenes inside carbon nanotubes: peculiar conduction properties



$Sc_3N@C_{80}$

L. Dunsch, S. Yang, *The Electrochem. Society Interface* (2006)

Nano peapods for quantum computing

Peapods: single walled nanotubes containing fullerenes → spin chains

Endohedral fullerenes → hybridized orbitals: unpaired electron delocalized across the cage: qbit

Chains controlled globally

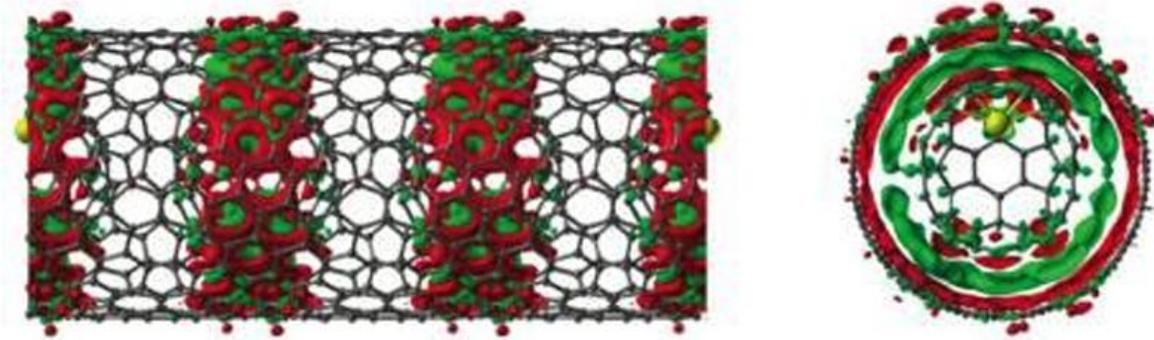
Problems to be understood:

- Charge arrangement within the peapods
- Electron spin distribution
- Coupling between spin qbits
- Spin interaction fullerene-nanotube

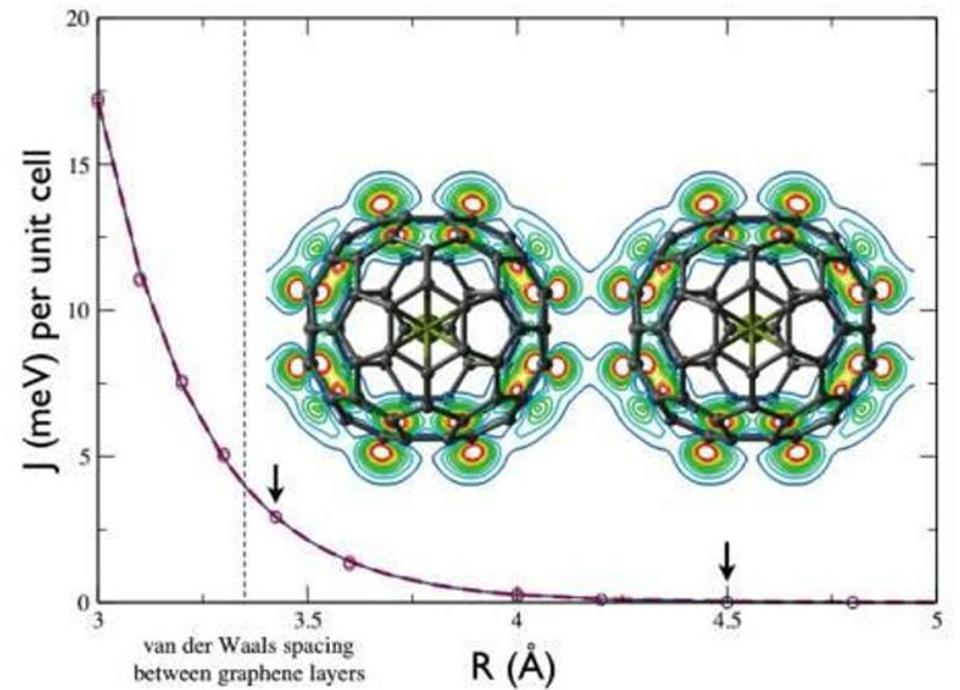
$Sc@C_{82}$: e^- in the HOMO. $\frac{1}{2}$ spin state

Electron transfer from Sc and from nanotube to cage

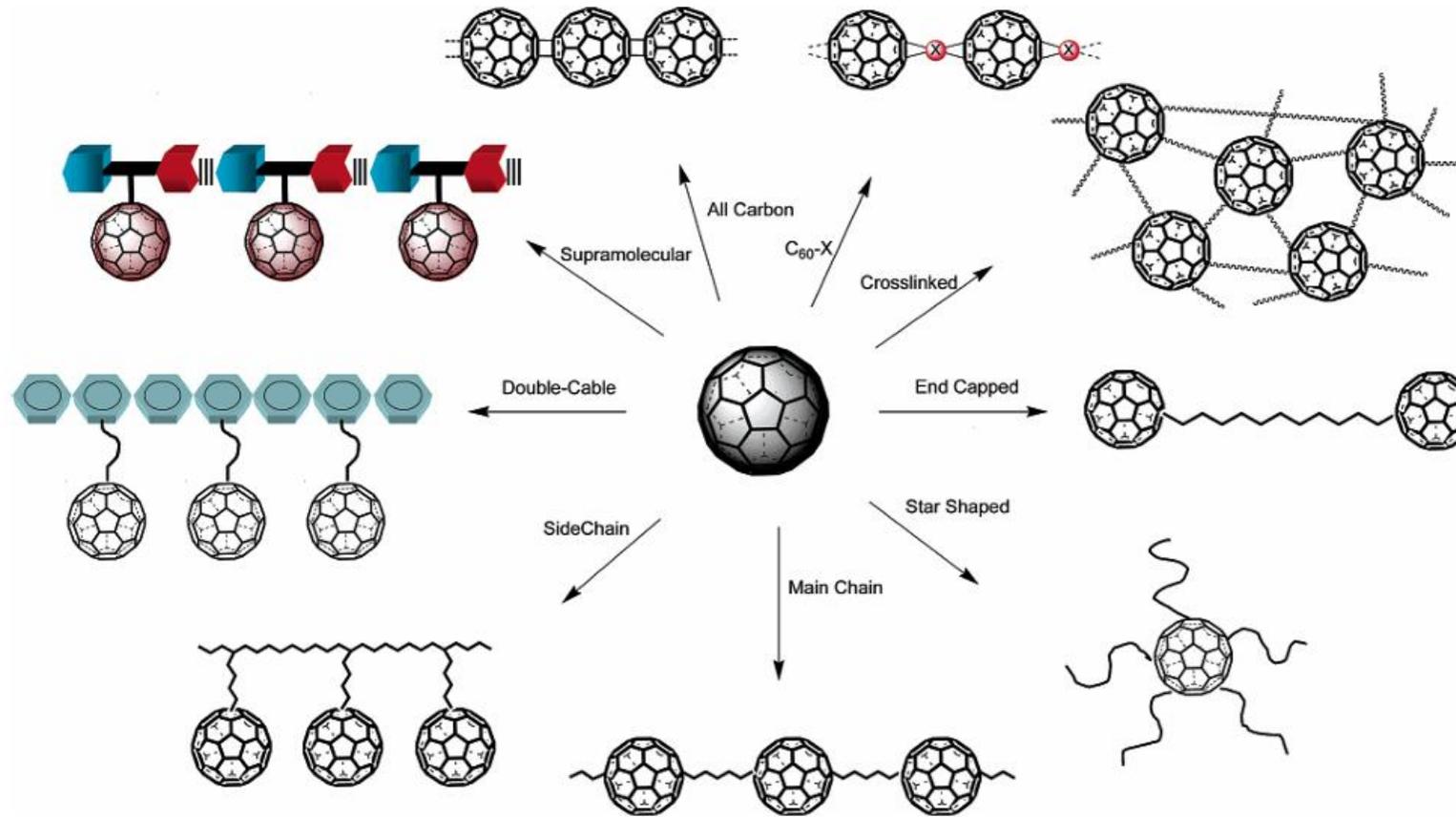
Spin coupling: antiferromagnetic



L. Ge, *St Anne's Research, Modelling Nano Peapods for Quantum Computing STAAR* (2009)



Fullerene polymers



All- C_{60}

Synthesis:

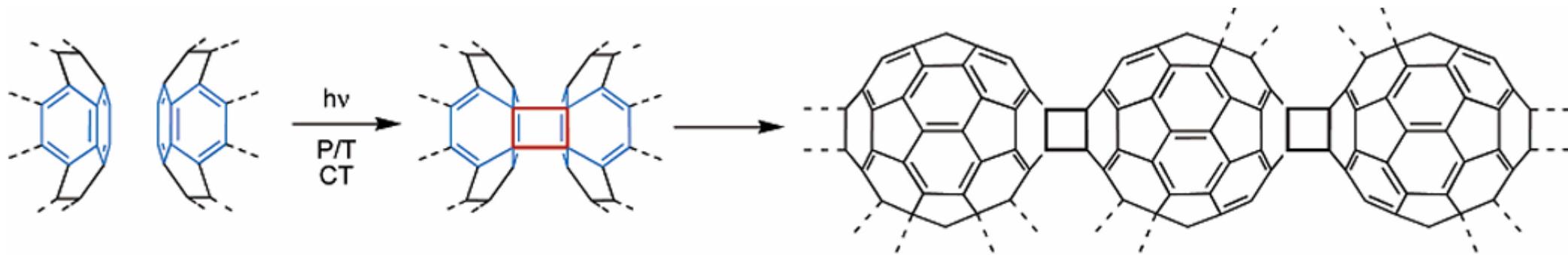
Pressure, photo- and charge transfer polymerization

[2+2] cycloaddition

Mass spectrometry, photophysical, absorption, optical limiting properties (photopolymerization)

C_{60} /Pd films \rightarrow n-doping, cation transport to the film; $C_{60}Pd_n$ polymers \rightarrow gas absorbent (toxic compounds)

$(C_{60}O_n)$ \rightarrow 8 electrons on C_{60} : energy storage



F. Giacalone, N. Martin, Vol. 106, No. 12 (2006) **5136-5190**

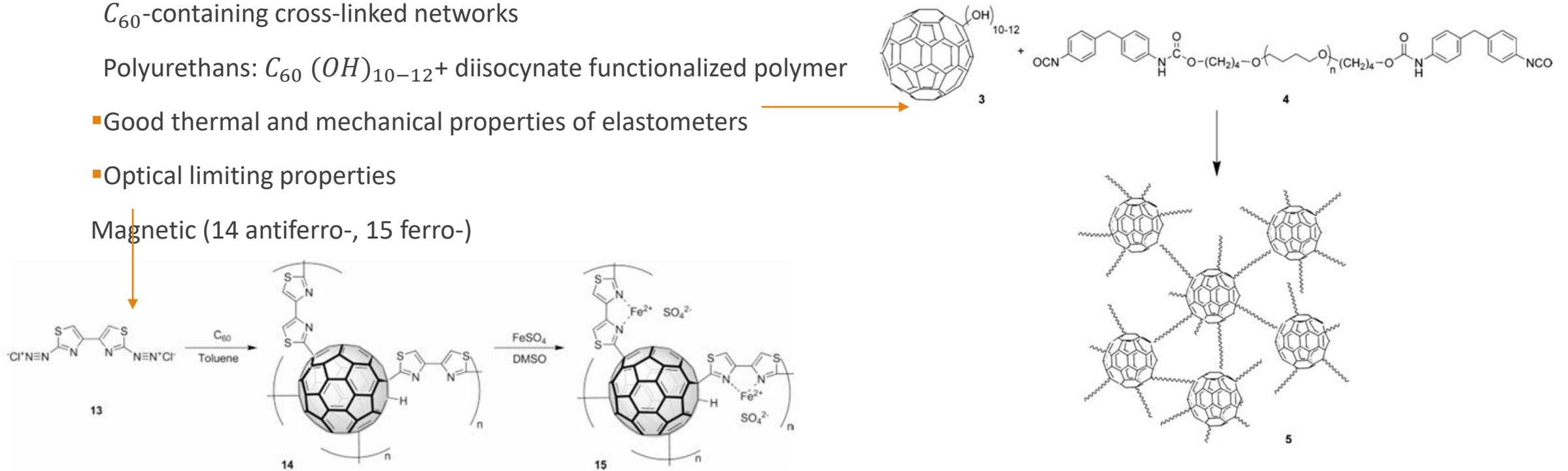
Cross-linked

C_{60} -containing cross-linked networks

Polyurethans: C_{60} $(OH)_{10-12}$ + diisocyanate functionalized polymer

- Good thermal and mechanical properties of elastometers
- Optical limiting properties

Magnetic (14 antiferro-, 15 ferro-)

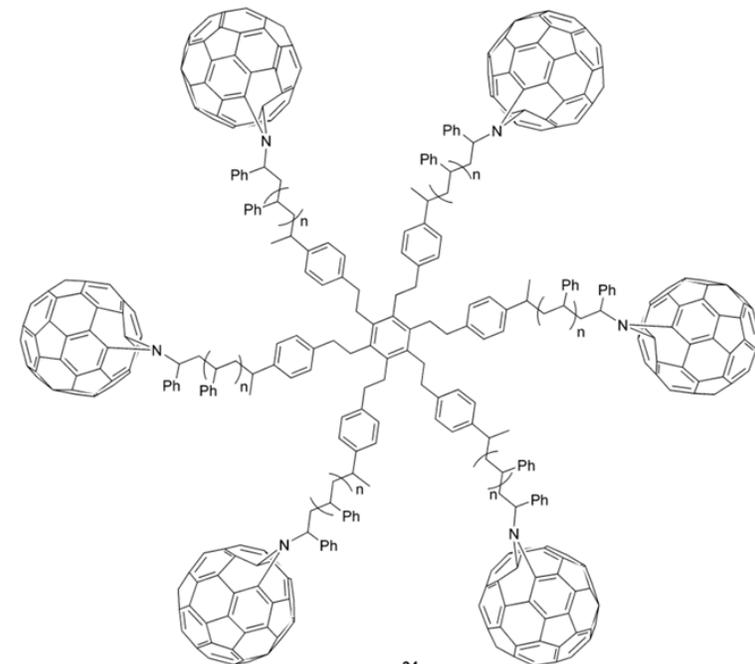
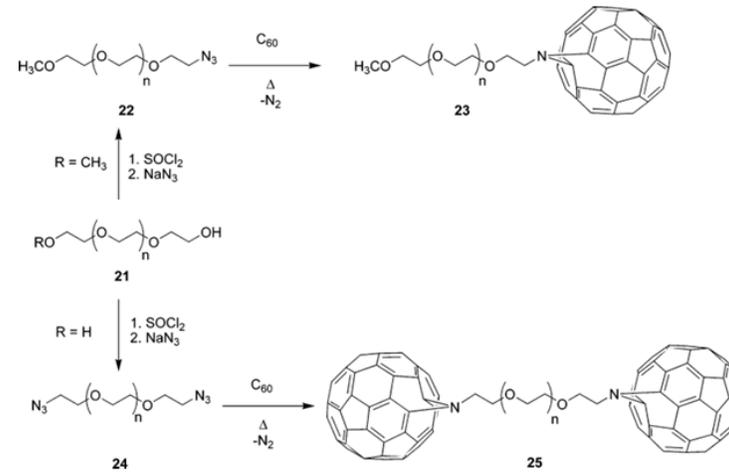


End-capped

C_{60} at terminal positions of the polymer chain

Poly(ethylene glycol) (PEG)

- Hydrogen bonding with other polymers
 - Films: good mechanical properties
- Polystyrene (PS):
- Mono-end-capped PS: good conductivity
 - Hexafullerene: polyelectronic reservoir
 - Solubility in organic solvents
 - Polymeric LED



Poly(methyl methacrylate) (PMMA):

- Quenching of fluorescence
- Water-soluble

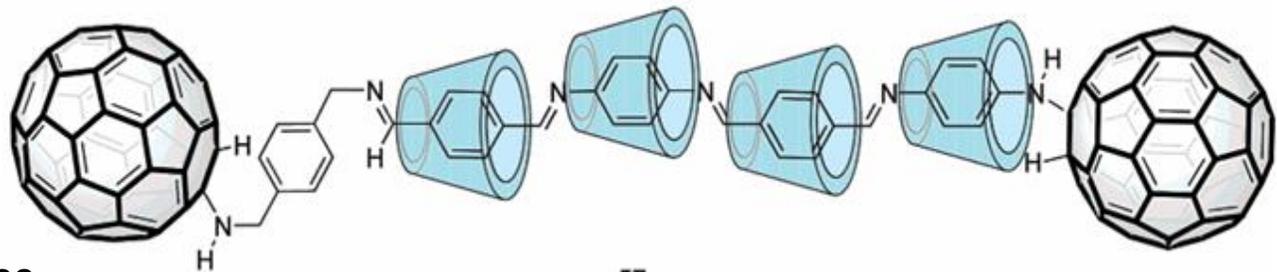
Poly(tert-butylacrylate) (PtBA):

- photoconductivity $\propto C_{60}$ content

Other polymers:

Micelle-shaped aggregates \rightarrow drug/gene carriers

C_{60} as a stopper (β -cyclodextrin)



Star-Shaped

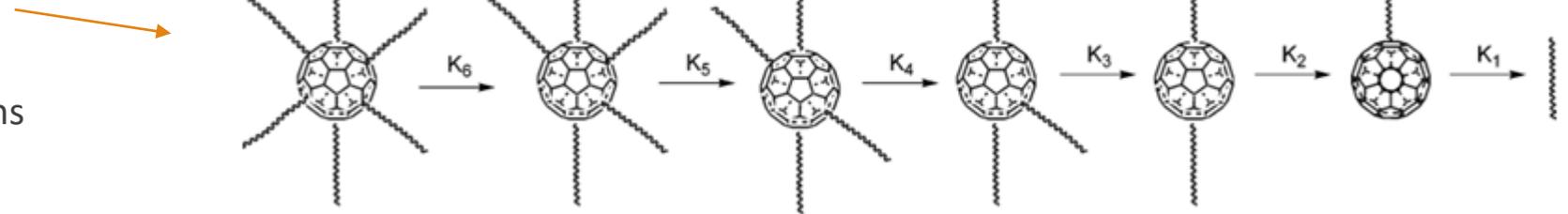
2-10 polymer chains covalently linked to a C_{60}

$C_{60}(PS)_x$:

- Highly soluble
- Melt processable: spin-coating, extrusion
- Thermal degradation

Polyaniline- C_{60} :

- Photoexcitation of electrons



Main-Chain

Bi-anthracene derivative + C_{60} :

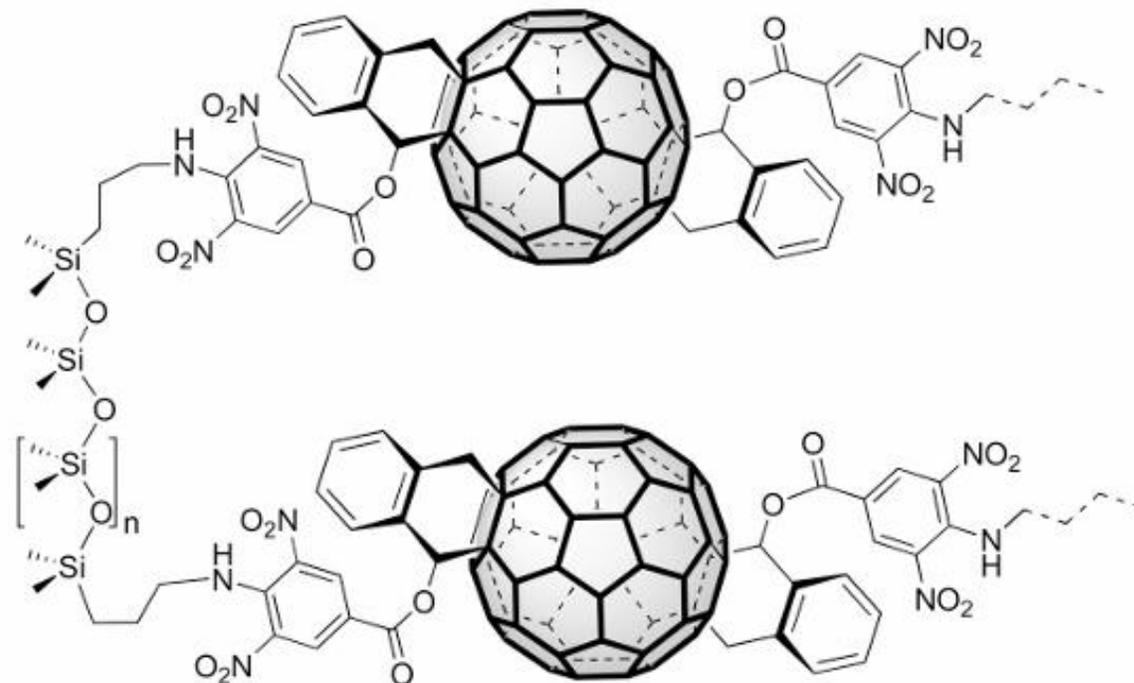
- Thermoreversible

Poly(dimethylsiloxane) (PDMS):

- Good solubility, thermal stability

CD-BPE (CD-bis-(p-aminophenyl) ether complex):

- DNA cleavage under VIS light condiction → photodynamic cancer therapy



Side-chain

C_{60} as pendants of the polymeric chain

Poly(vinylcarbazole) (PVK): electron transfer C_{60} -polymer

Styrene/acrylamide:

- photoconductivity

Inorganic polymers:

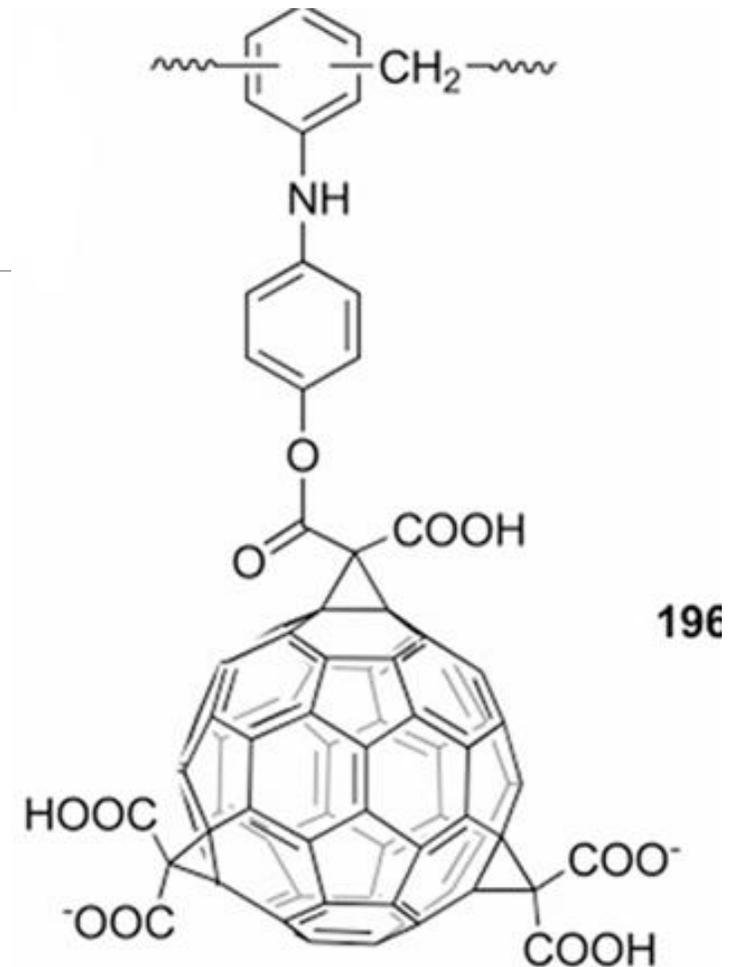
- flame-retarding, liquid crystals, photoconductors, nonlinear optical materials

C_{60} -tricarboxylic acid + diazoresin: ultrathinfilms:

- Stable toward polar solvents; load-bearing capacity

General properties of Side-chain

- Water- solubility (for organic polymers)
- Donor-acceptor materials → photovoltaic devices



Doble-Cable

Porpouse: electron donor/acceptor molecules

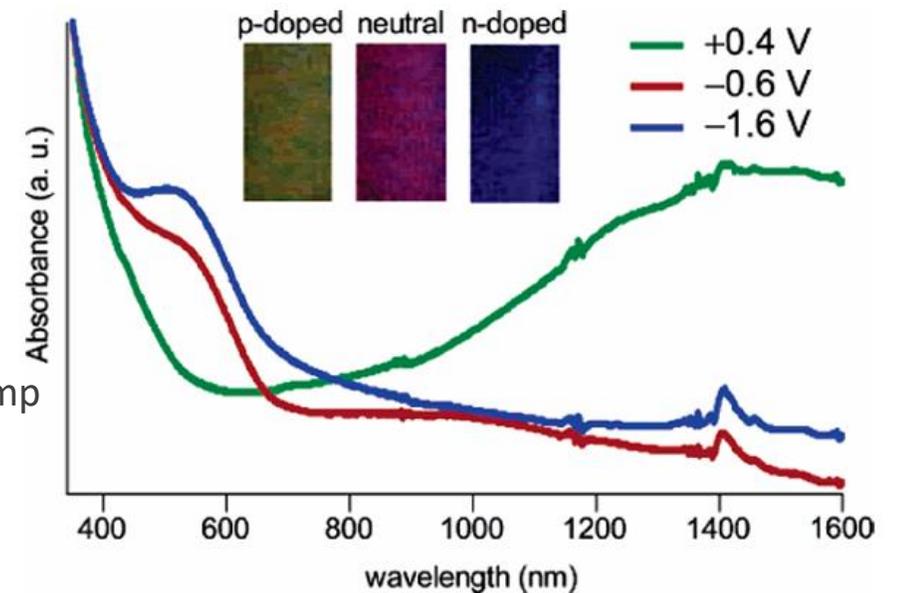
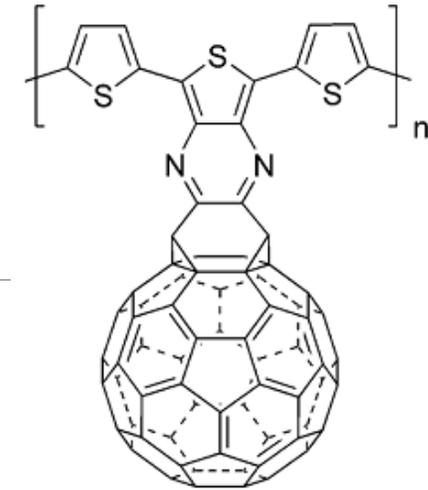
Drowback: compatibility polymers-fullerenes (C_{60} clusters)

⇒P-type backbones (donor cable) & n-type fullerenes (acceptor cable):

- Larger interfacial area
- Tunable electronic interaction
- Easy processability & low cost
- Compatibility with other organic materials

Alkyl chain or proton incorporated in fullerene: balance solubility- electronic jump

Applications: LED optoelectronics, solar cells



Supra-Molecular

Secondary and tertiary structure of many macromolecules

Additional order in solid state

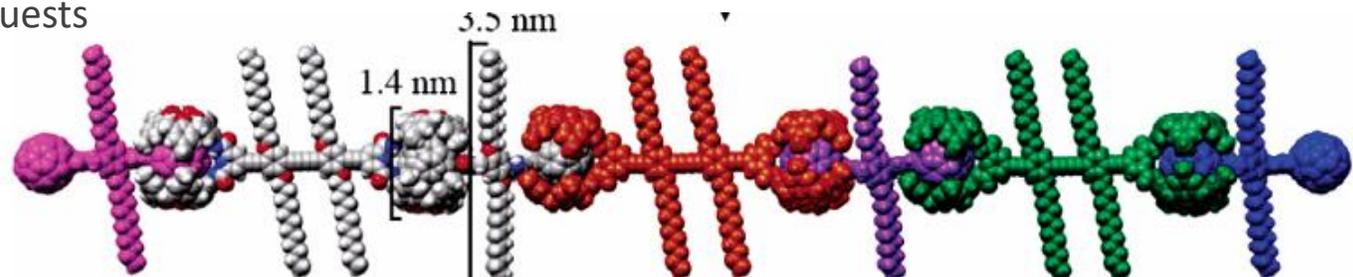
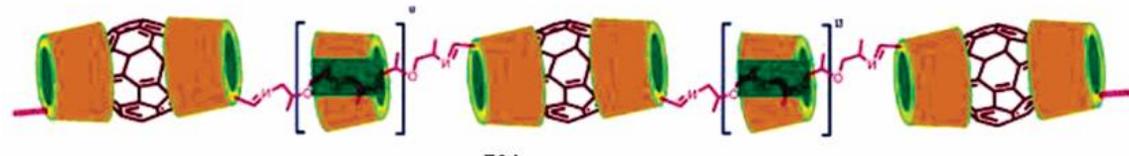
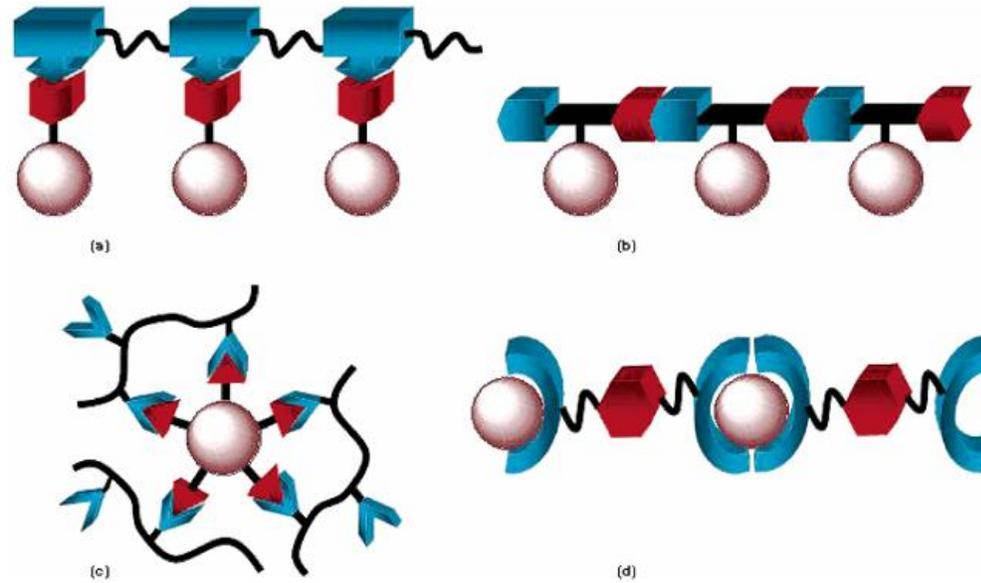
Four classes → interactions between:

- a) functionalized polymers and C_{60} derivatives
- b) self-assembly of C_{60} derivatives
- c) multifunctionalized C_{60} and polymeric backbones
- d) pristine C_{60} and ditopic concave guests

Thermal & mechanical properties

Dielectric & photovoltaic properties

Applications in medical chemistry



Metals or insulators?

Coming back to *All- C₆₀*...

Cross linking by:

- [2+2] cycloaddition four membered rings
- Seven or eight membered rings (peanut shape)

Band gap depending on spatial dimensionality

[2+2] cycloaddictional four membered rings

1D:

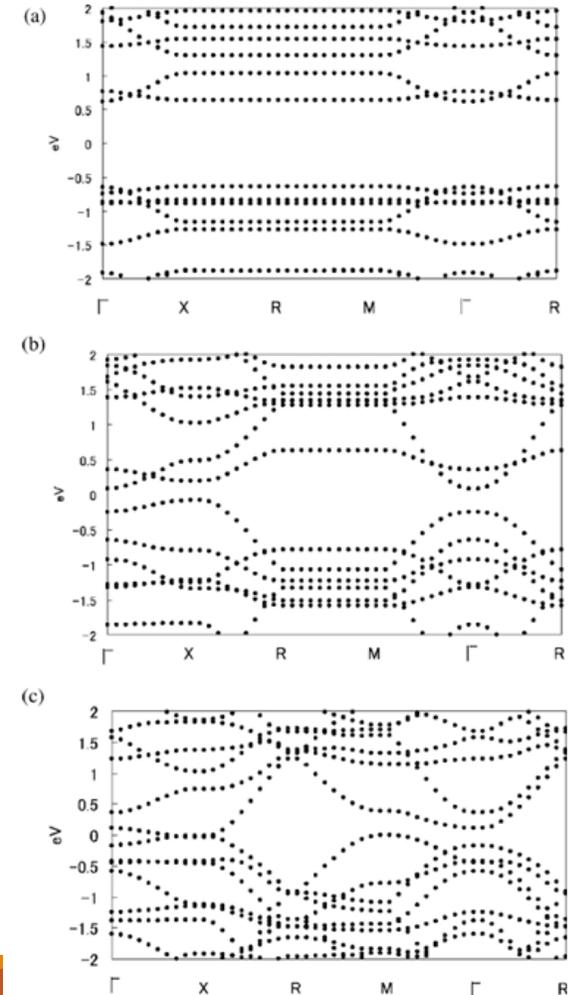
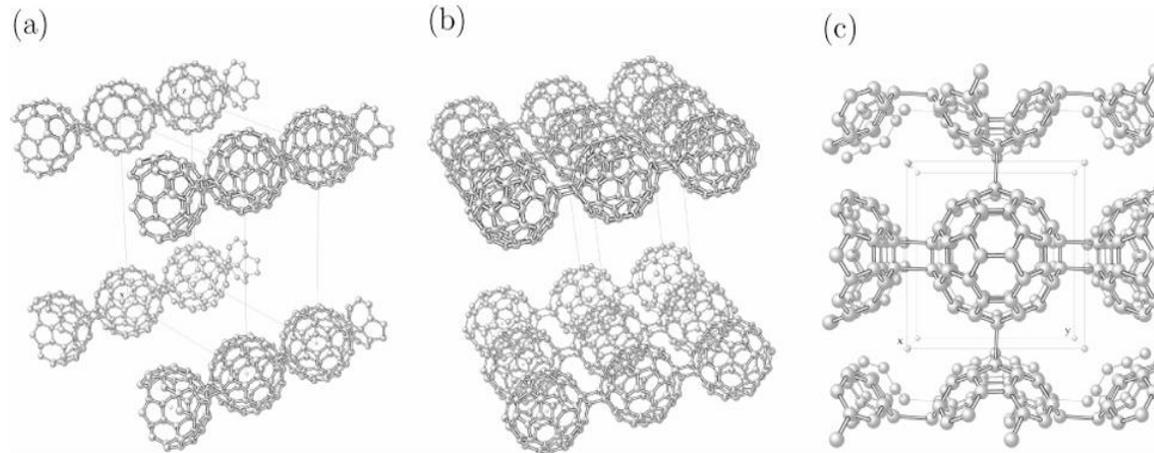
- tetragonal cell
- Energy gap 1.25 eV

2D:

- tetragonal cell;
- Energy gap 0.16 eV

3D:

- cubic cell
- Bands overlap: semimetal
- Larger bands than in C_{60} crystal



S. Ueda et al., J. Phys. Chem. B, Vol. 10, No. 45 (2006) **22374-22381**

Peanut shaped: seven membered rings

1D:

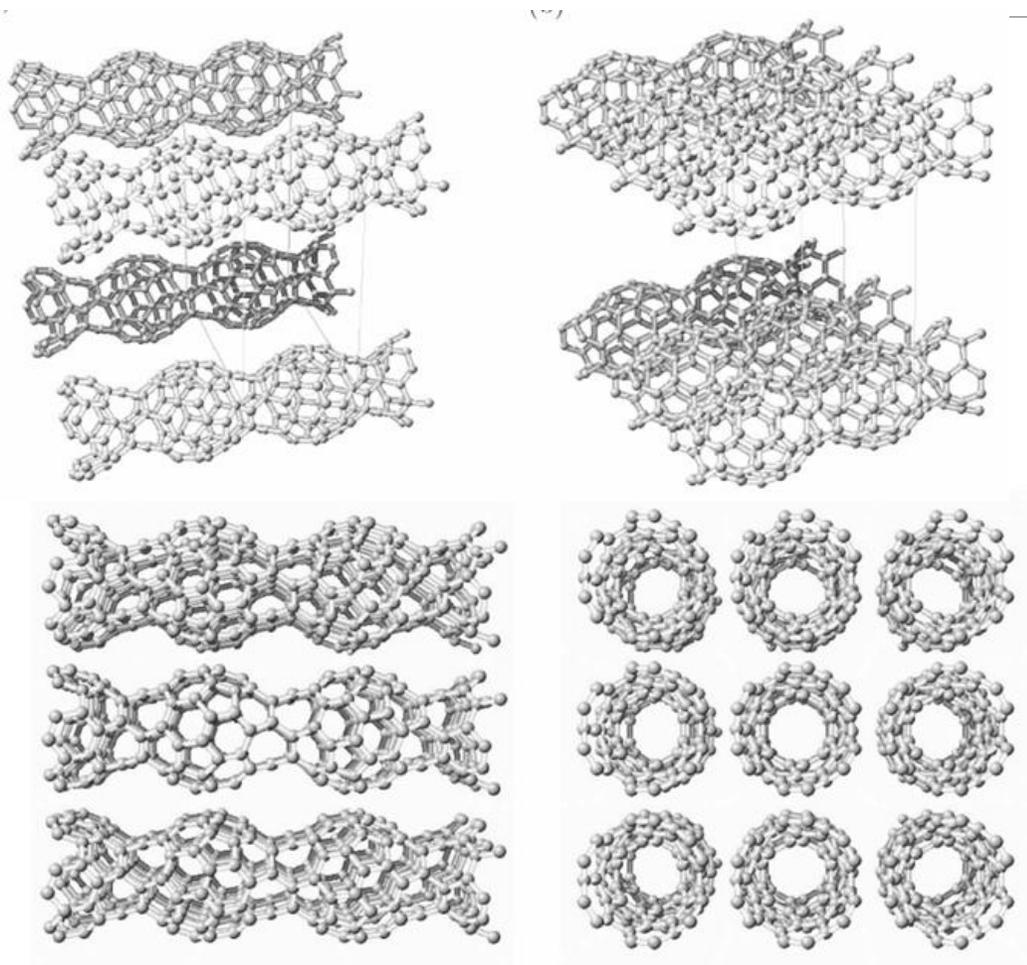
- tetragonal cell
- Energy gap 1.23 eV

2D:

- tetragonal cell;
- Energy gap 0.27 eV

3D:

- cubic cell
- Energy gap 0.22 eV



Peanut shaped: eight membered rings

1D:

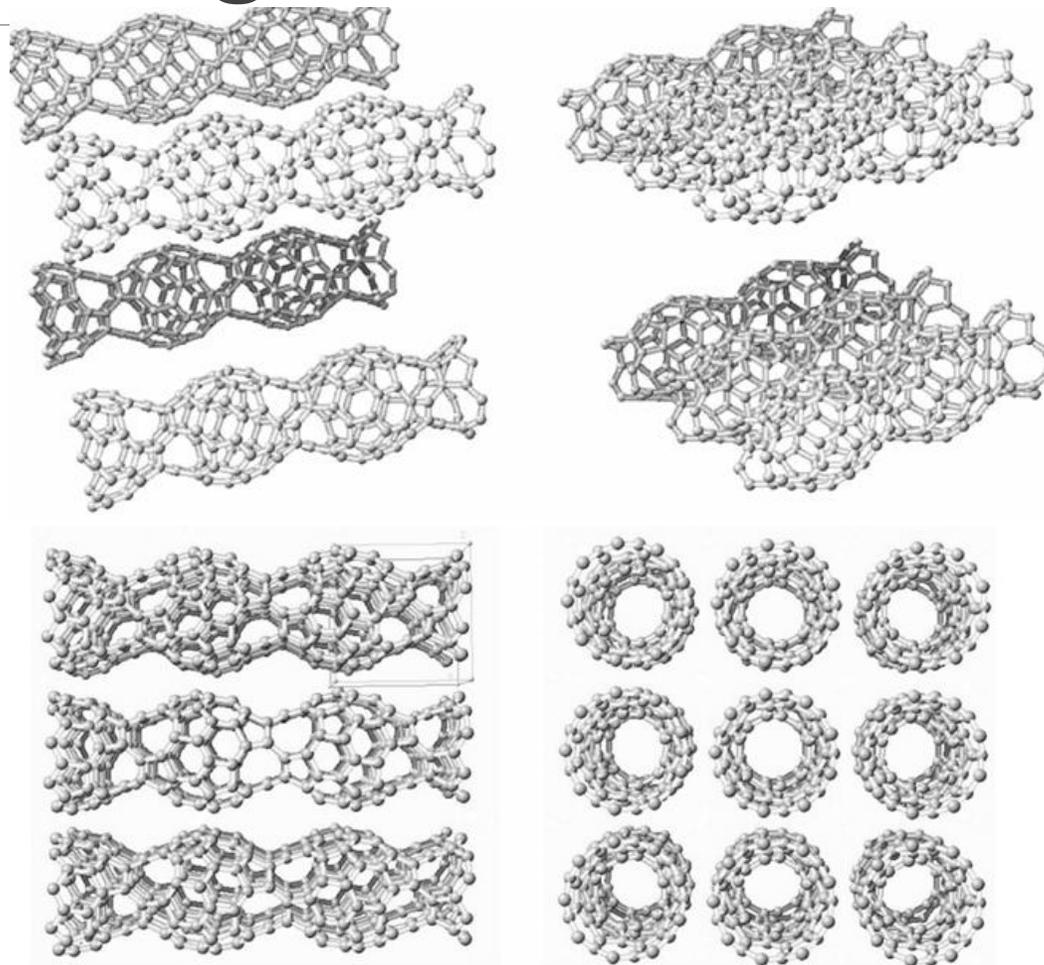
- tetragonal cell
- Energy gap 1.00 eV

2D:

- tetragonal cell;
- Energy gap 0.54 eV

3D:

- cubic cell
- Bands overlap: semimetal



Underestimation of band gaps by a $2/3$ factor

Energy gap decreases as spatial dimensionality increases

2D and 3D peanut-shaped interact with weak [2+2] cycloaddition four-membered rings