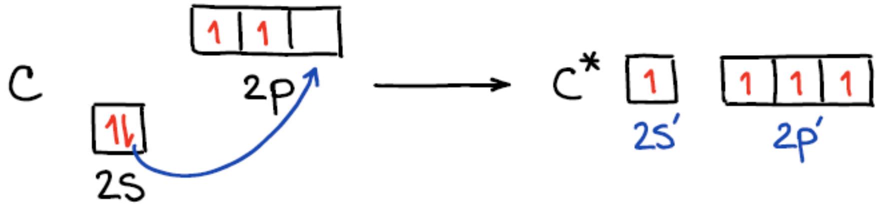
Hybridization and Resonance

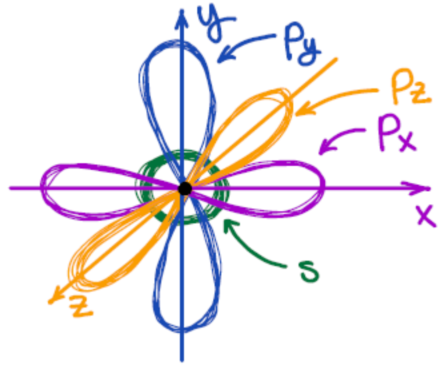
Session 11

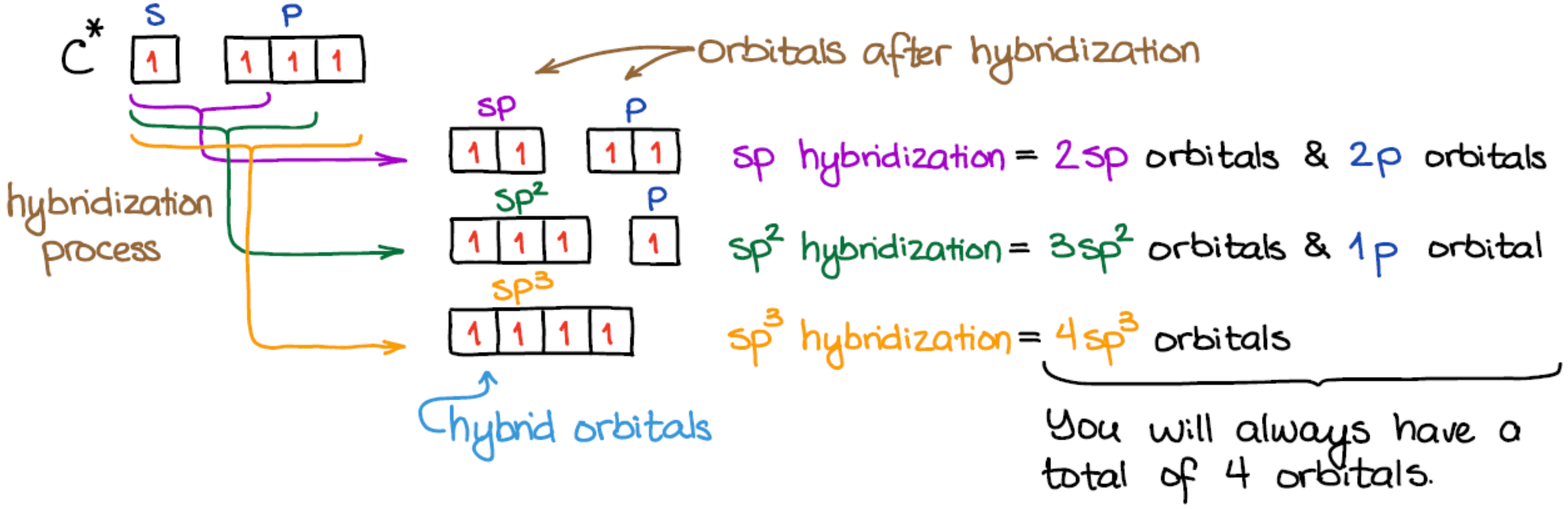
May 18th, 2020

Hybridization

C | 1s2 | 2s2 | 2px | 2py

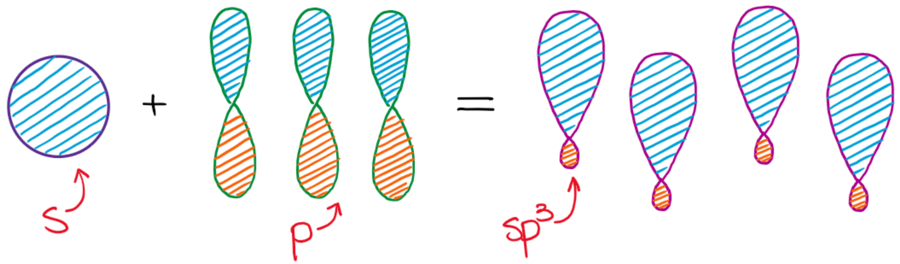


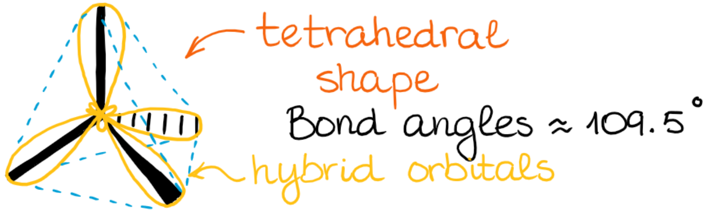


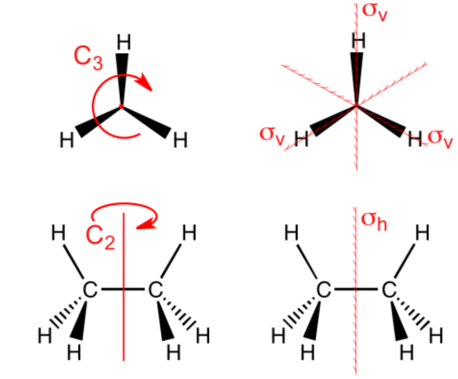


https://www.organicchemistrytutor.com/hybridization/

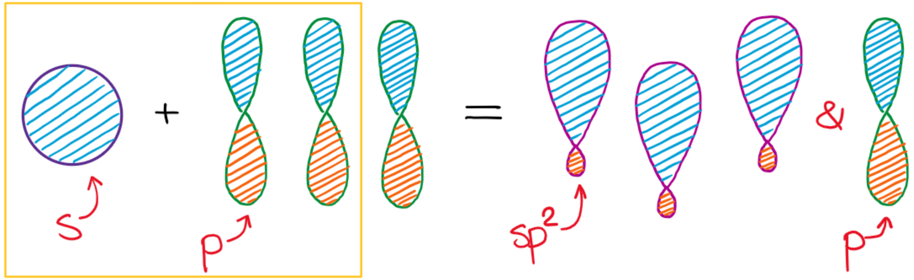
Hybridization

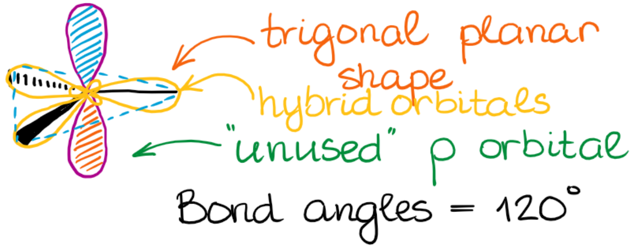


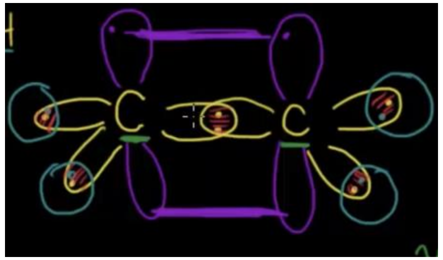


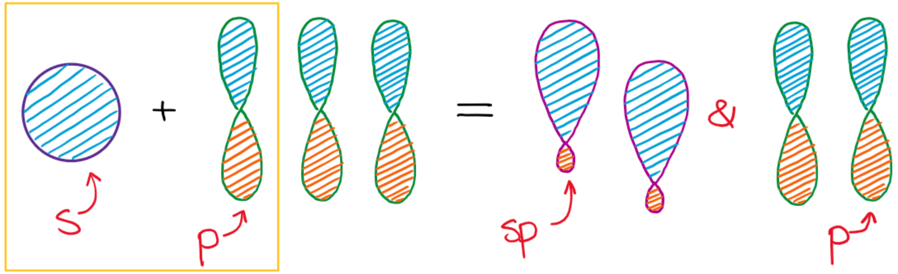


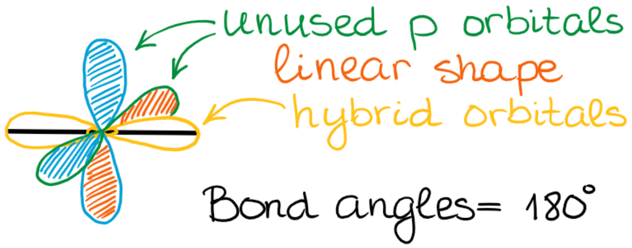
Show all 3 equivalent C_2 axis

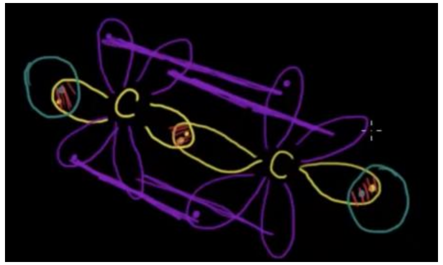








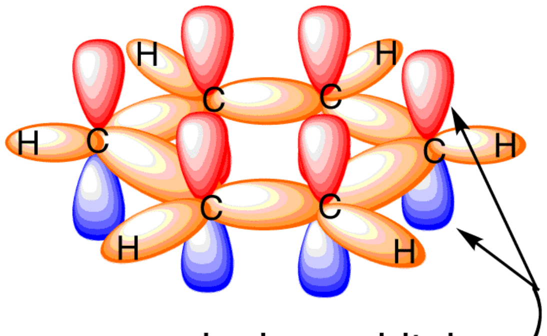




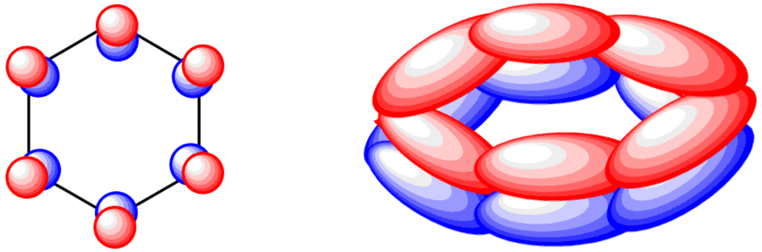
https://www.organicchemistrytutor.com/hybridization/ https://es.khanacademy.org/science/chemistry/chemical-bonds/hybridization-and-hybrid-orbitals-chemistry/v/sp2-hybridization-jay-final

Resonance

σ bonds shown in green



a single p orbital
different phases shown
in red and black



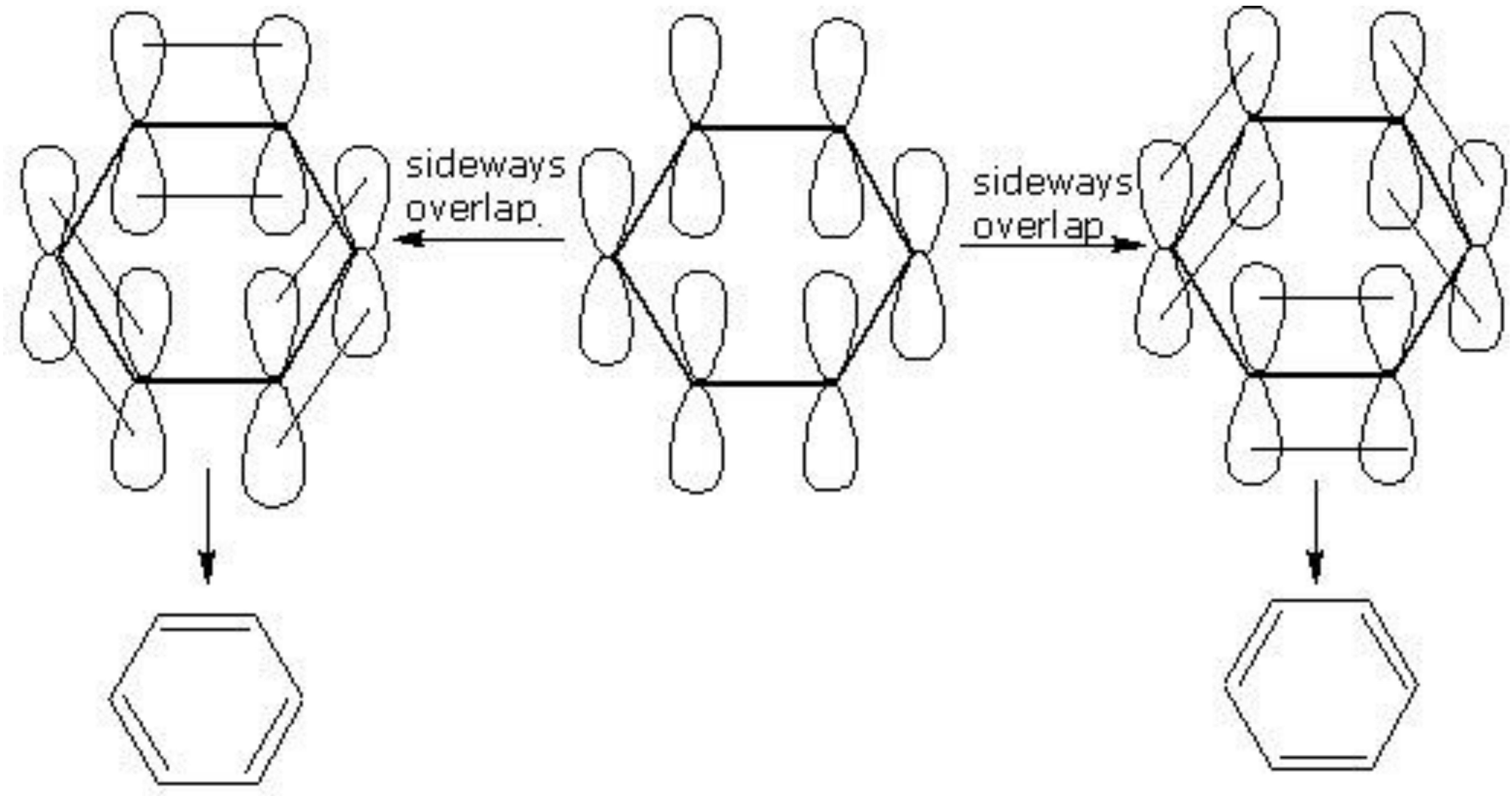
the lowest energy MO for benzene has
all the p orbitals combining in-phase

https://www.chemtube3d.com/orbitalsbenzene/

https://www.chemtube3d.com/vibrationsc6h6/

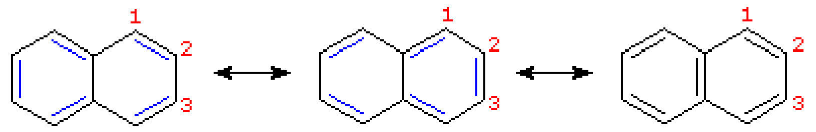
https://www.chemtube3d.com/diamond/

Resonance



Resonance Structures on Aromatic Fused Rings

Napthalene

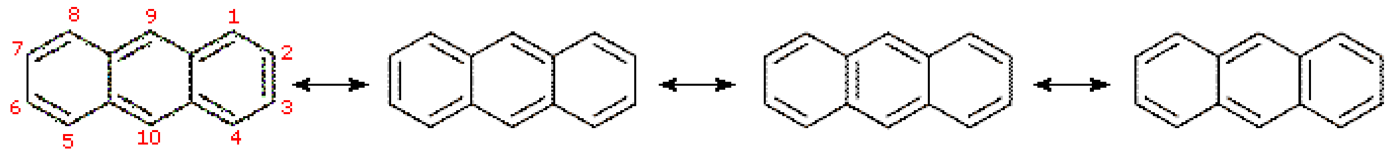


10 π-electron annulenes 2 benzene rings

Resonance Energy = 61 kcal/mole (less than twice benzene)
(30.5 kcal per ring)

The C–C bond lengths in benzene are all 1.40 Å
The C^1–C^2 bond length in naphthalene is 1.36 Å
The C^2–C^3 bond length in naphthalene is 1.42 Å

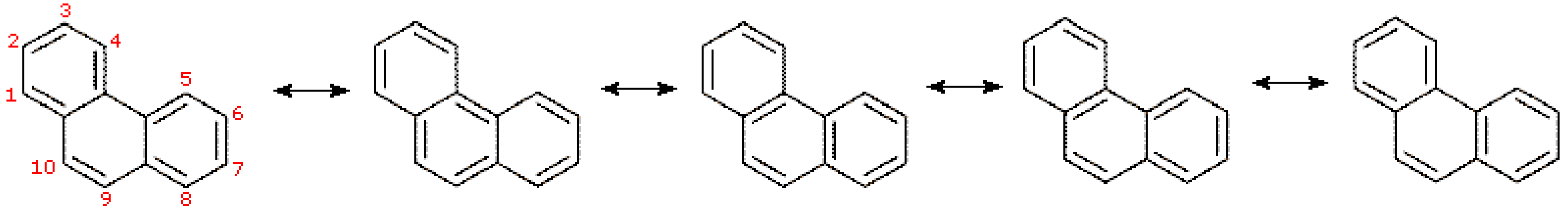
Anthracene



14 π-electron annulenes benzene + 10 π-electron annulene

Resonance Energy = 83 kcal/mole
(27.7 kcal per ring)

Phenanthrene



14 π-electron annulenes 3 benzene rings benzene + 10 π-electron annulene

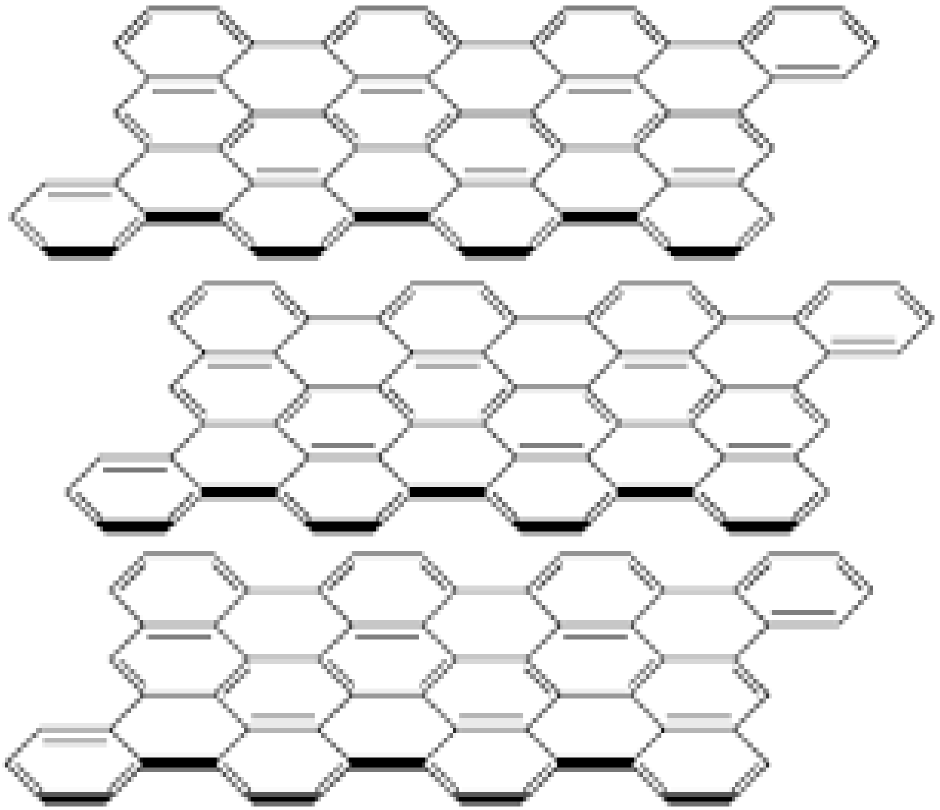
Resonance Energy = 91 kcal/mole
(30.3 kcal per ring)

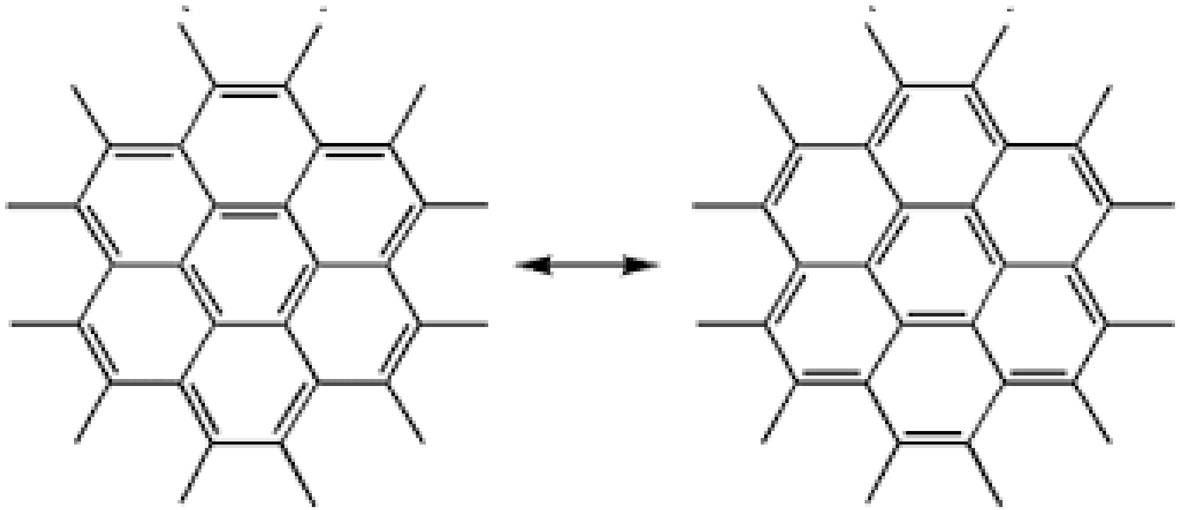
Graphite

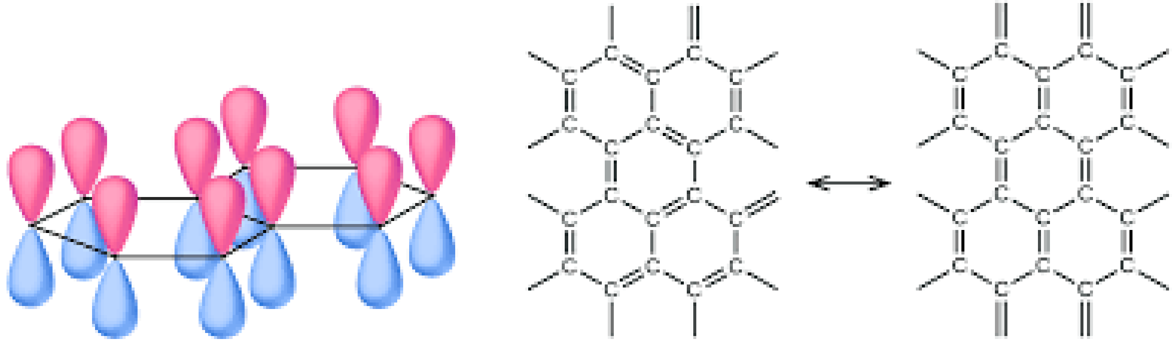
A

B

C



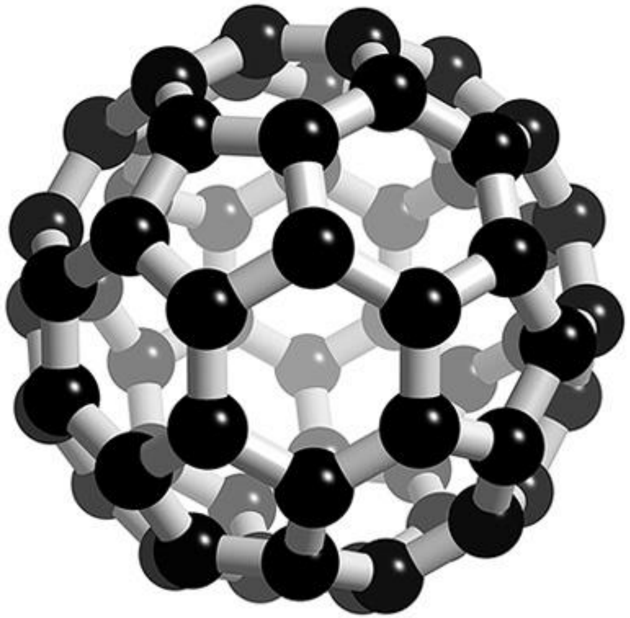




(a) (b)

https://www.google.com/search?q=resonance+graphite&tbm=isch&ved=2ahUKEwiqla7sl77pAhVEfK0KHRpJCDcQ2-cCegQIABAA&oq=resonance+graphite&gs_lcp=CgNpbWcQAzoCCAA6BggAEAUQHlCT5iFY9_YhYOyFlmgAcAB4AIABogGIAawIkgEDMC44mAEAoAEBqgELZ3dzLXdpei1pbWc&sclient=img&ei=R-fCXurVIcT4tQWakqG4Aw&bih=361&biw=559&hl=en-US

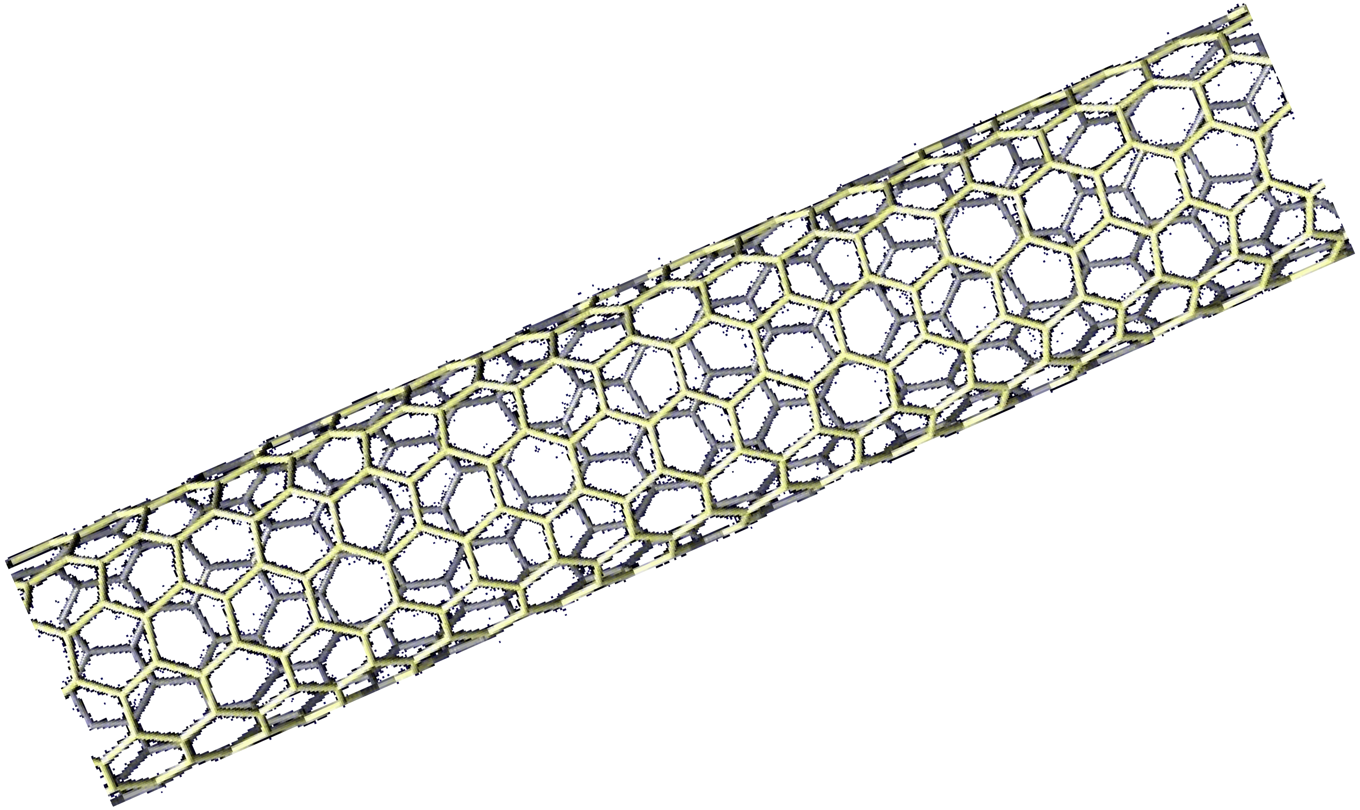
Carbon Fullerene
(an sp2 hybridized material)



https://www.chemtube3d.com/c60/

https://www.chemtube3d.com/ClaydenCarbonAllotropes/

Carbon Nanotube
(an sp2 hybridized material)



Applications

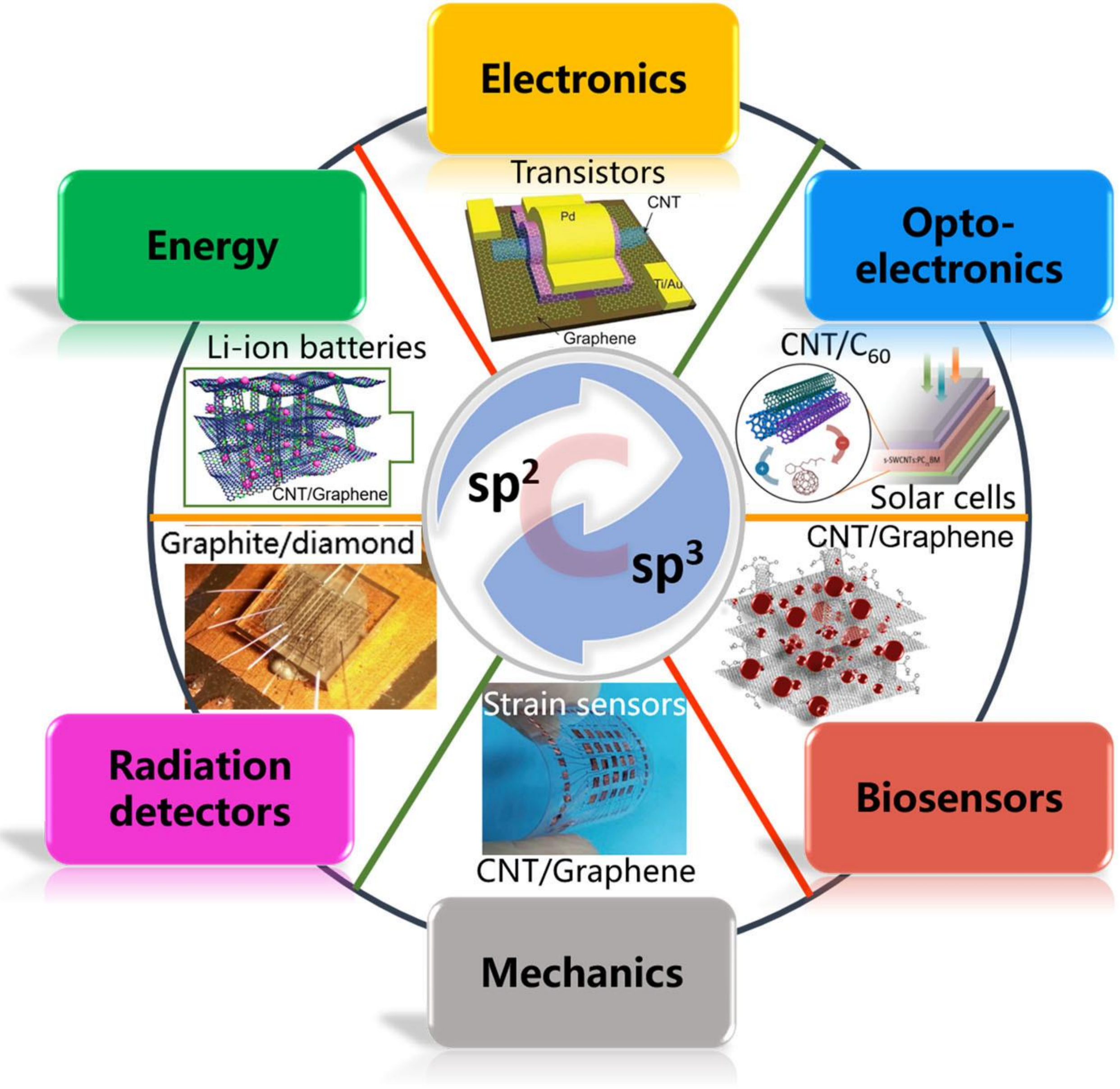


FIG. 2. Various fields of all-carbon device applications.

Published in: Qilong Yuan; Cheng-Te Lin; Kuan W. A. Chee; *APL Materials* **7,** 030901 (2019) DOI: 10.1063/1.5082767.

Thermal Conductivity

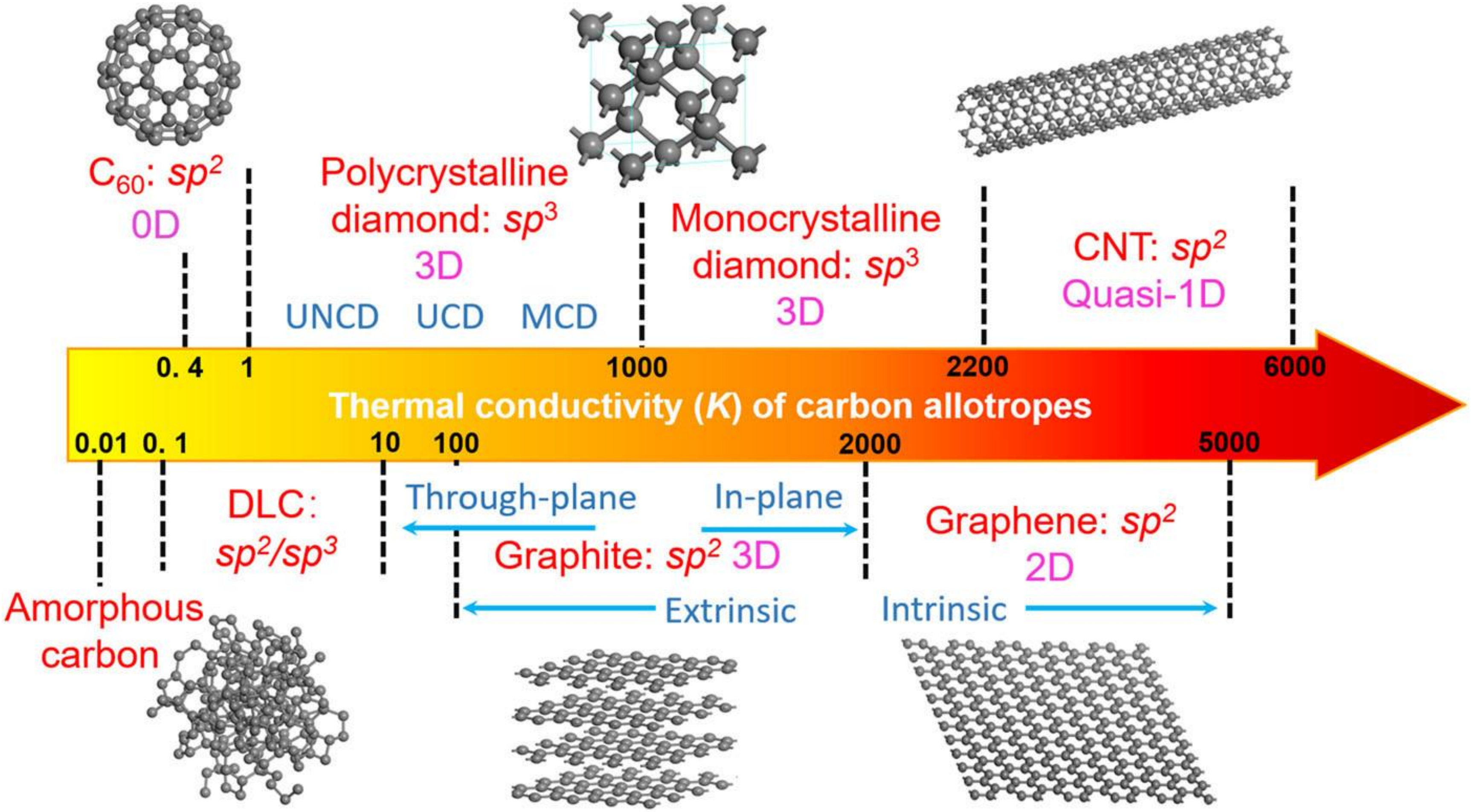


FIG. 1. Thermal conductivities of carbon allotropes (unit: W m^{-1} K^{-1}).

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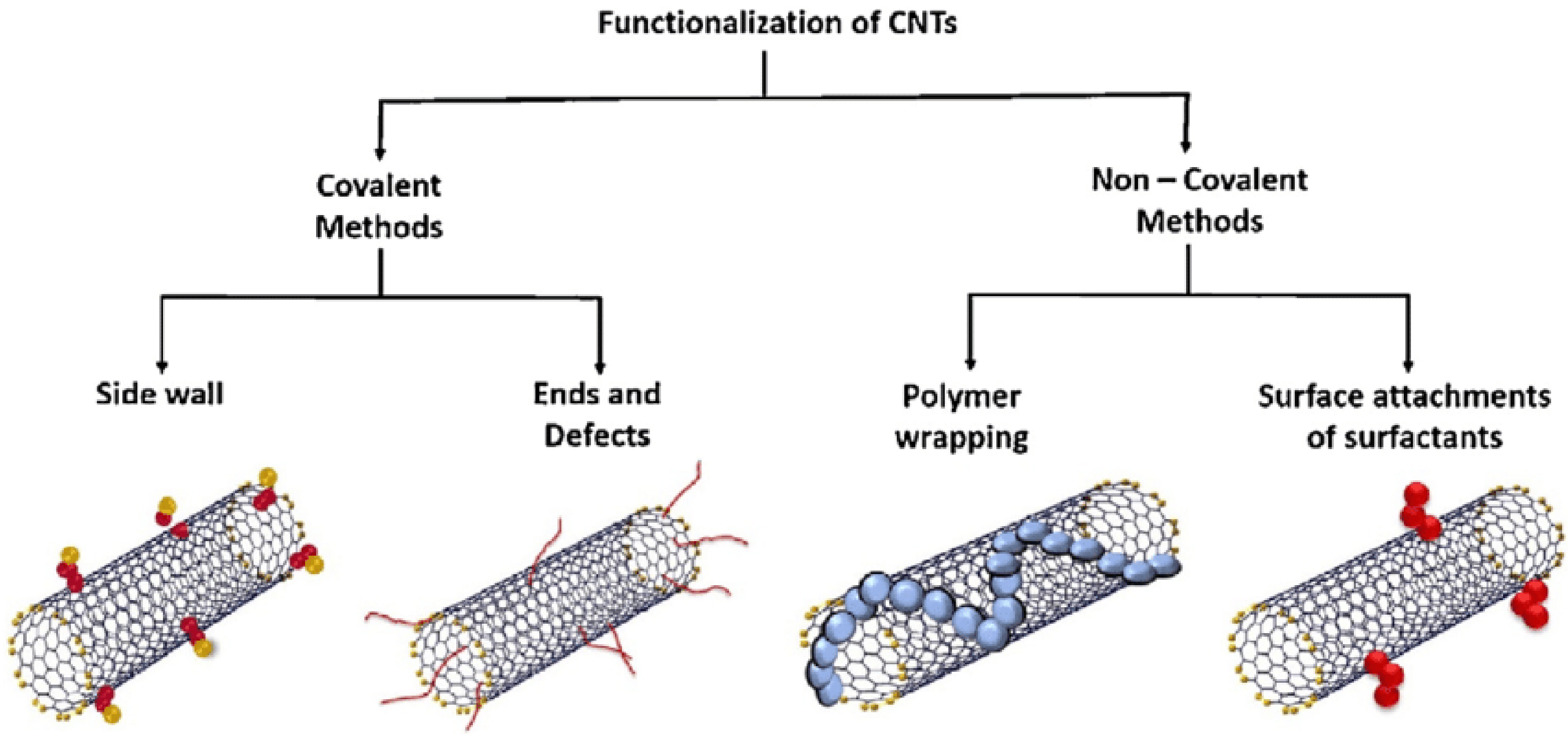
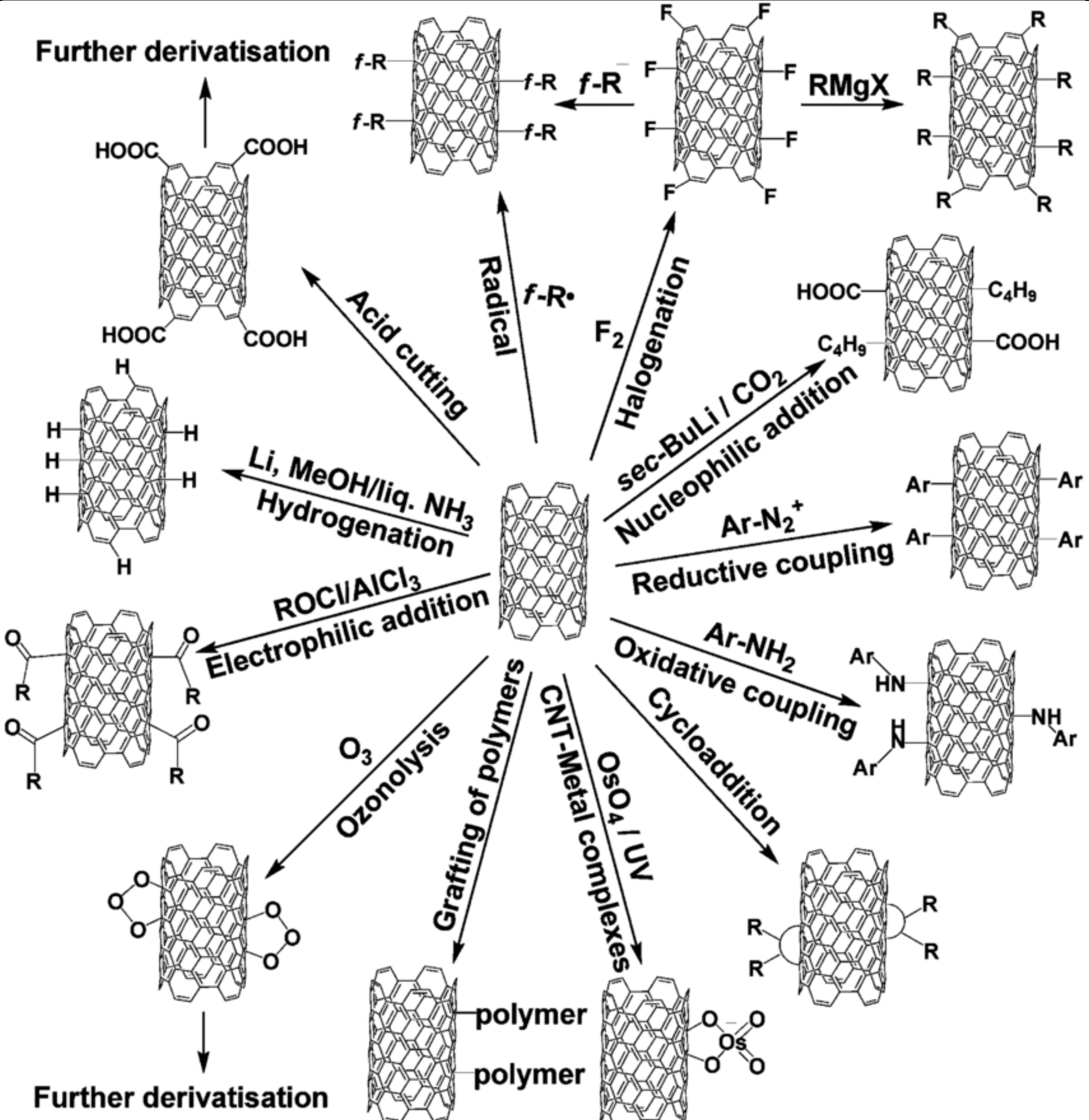

Functionalization of CNTs
Covalent Methods
Non – Covalent Methods
Side wall
Ends and Defects
Polymer wrapping
Surface attachments of surfactants


Further derivatisation
HOOC
COOH
HOOC
COOH
Acid cutting
f-R
f-R
f-R
f-R
f-R⁻
Radical
f-R•
F
F
F
F
F
F
F
F
F₂
Halogenation
RMgX
R
R
R
R
R
R
R
R
HOOC
C₄H₉
C₄H₉
COOH
sec-BuLi / CO₂
Nucleophilic addition
H
H
H
H
H
H
H
Li, MeOH/liq. NH₃
Hydrogenation
Ar
Ar
Ar
Ar
Ar-N₂⁺
Reductive coupling
ROCl/AlCl₃
Electrophilic addition
O
R
O
R
O
R
O
R
Ar-NH₂
Oxidative coupling
Ar
HN
H
N
Ar
NH
Ar
O₃
Ozonolysis
Grafting of polymers
CNT-Metal complexes
OsO₄ / UV
Cycloaddition
R
R
R
R
polymer
polymer
O
O
Os
O
O
Further derivatisation

Effect of Functioalization: An Example

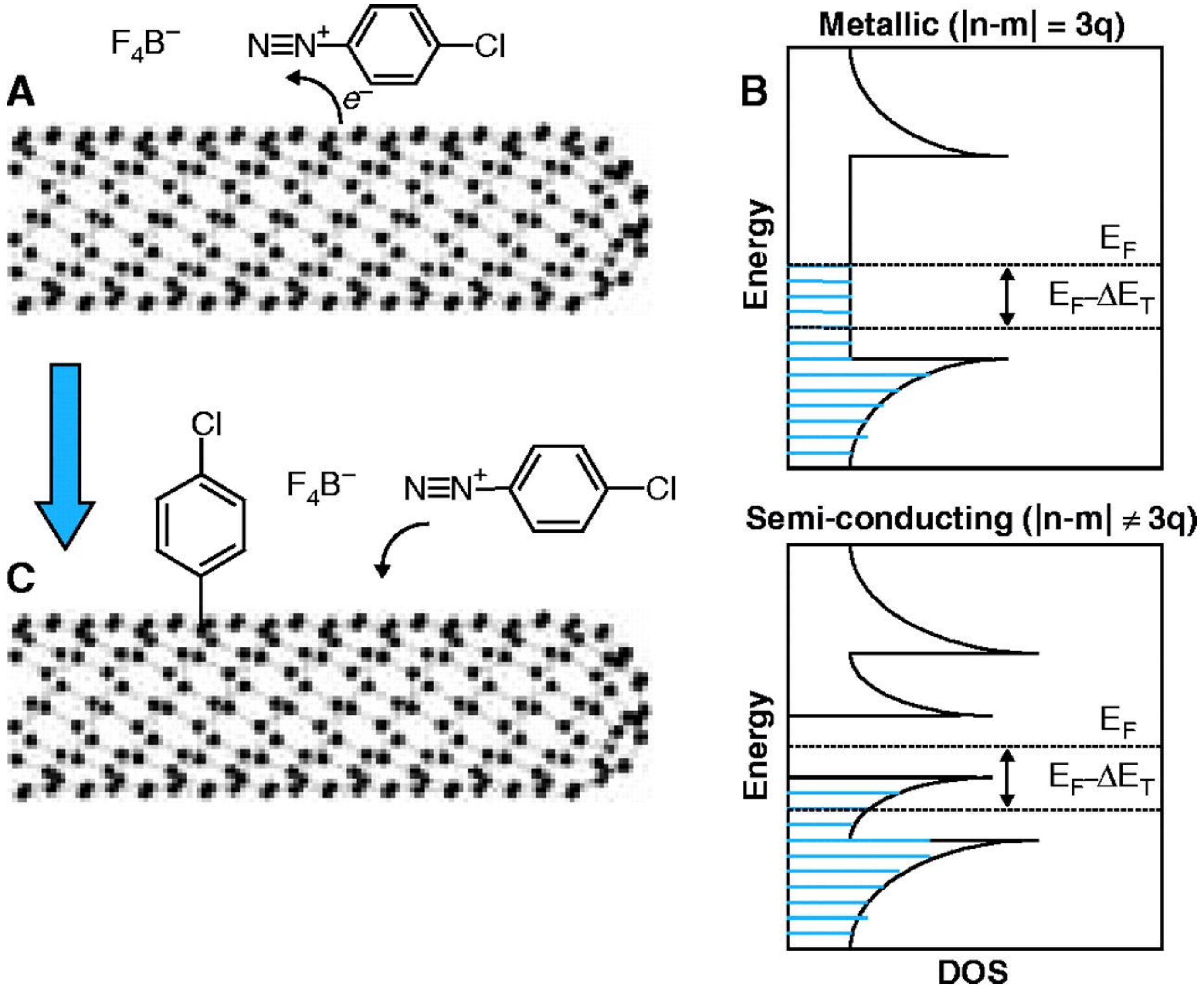


Fig. 1.
(**A**) Diazonium reagents extract electrons, thereby evolving N_2 gas and leaving a stable C -C covalent bond with the nanotube surface. (**B**) The extent of electron transfer is dependent on the density of states in that electron density near E_F leads to higher initial activity for metallic and semimetallic nanotubes. (**C**) The arene-functionalized nanotube may now exist as the delocalized radical cation, which could further receive electrons from neighboring nanotubes or react with fluoride or diazonium salts.

REPORT
Electronic Structure Control of Single-Walled Carbon Nanotube Functionalization
Science 12 Sep 2003:
Vol. 301, Issue 5639, pp. 1519-1522
DOI: 10.1126/science.1087691

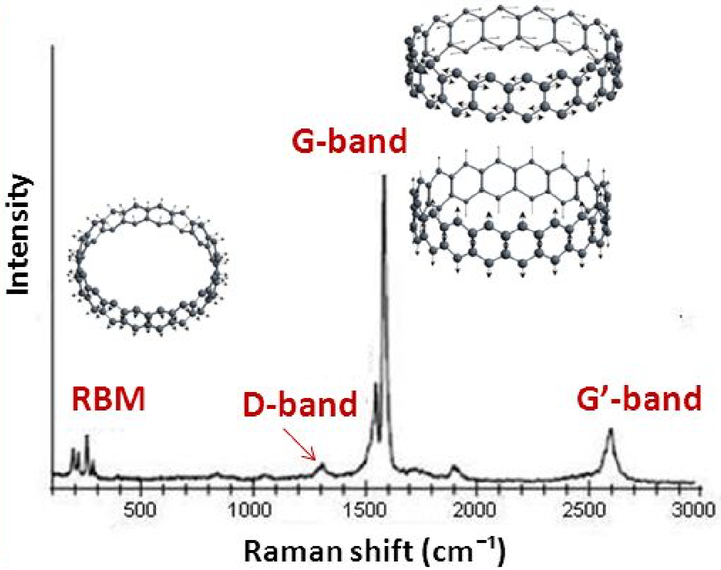
Raman Spectroscopy

Raman spectrum of SWNT

Raman spectrum gives us many information about the vibrational modes of carbon nanotubes.

Principal peaks:

- **RBM**: Radial Breathing Mode ($150 - 350\ cm^{-1}$)
- **D-band**: Disorder induced band ($1350\ cm^{-1}$)
- **G-band**: tangential (derived from the graphite like in-plane) mode ($1560 – 1600\ cm^{-1}$)
- **G'-band**: overtone of D-band



R. Graupner J. Raman Spectrosc. **38**, 673 (2007)

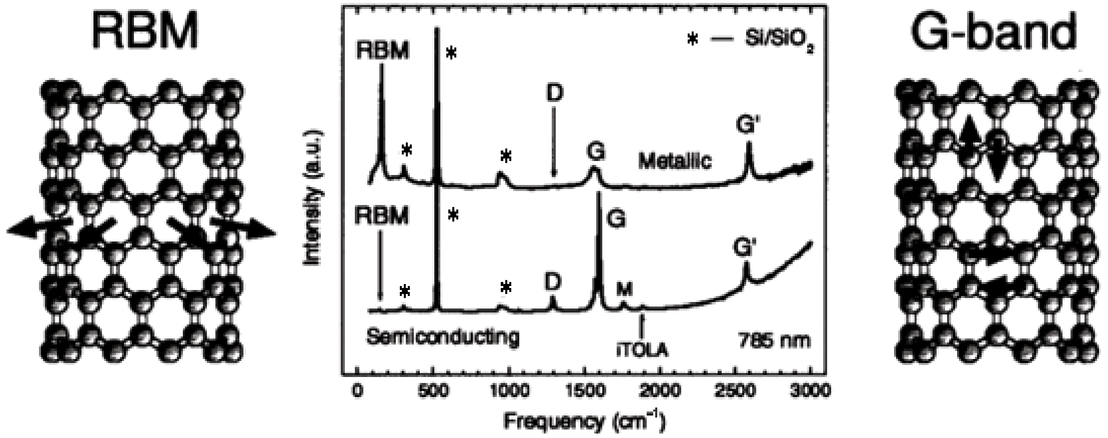


Fig. 2 – Raman spectra from a metallic (top) and a semiconducting (bottom) SWNT at the single nanotube level using 785 nm (1.58 eV) laser excitation, showing the radial breathing mode (RBM), *D*-band, *G*-band, and *G′* band features, in addition to weak double resonance features associated with the M-band and the iTOLA second-order modes. Insets on the left and the right show, respectively, the atomic displacements associated with the RBM and *G*-band normal mode vibrations. The isolated carbon nanotubes are sitting on an oxidized silicon substrate which provides contributions to the Raman spectra denoted by '*' which are used for calibration purposes.

Effect of treatment

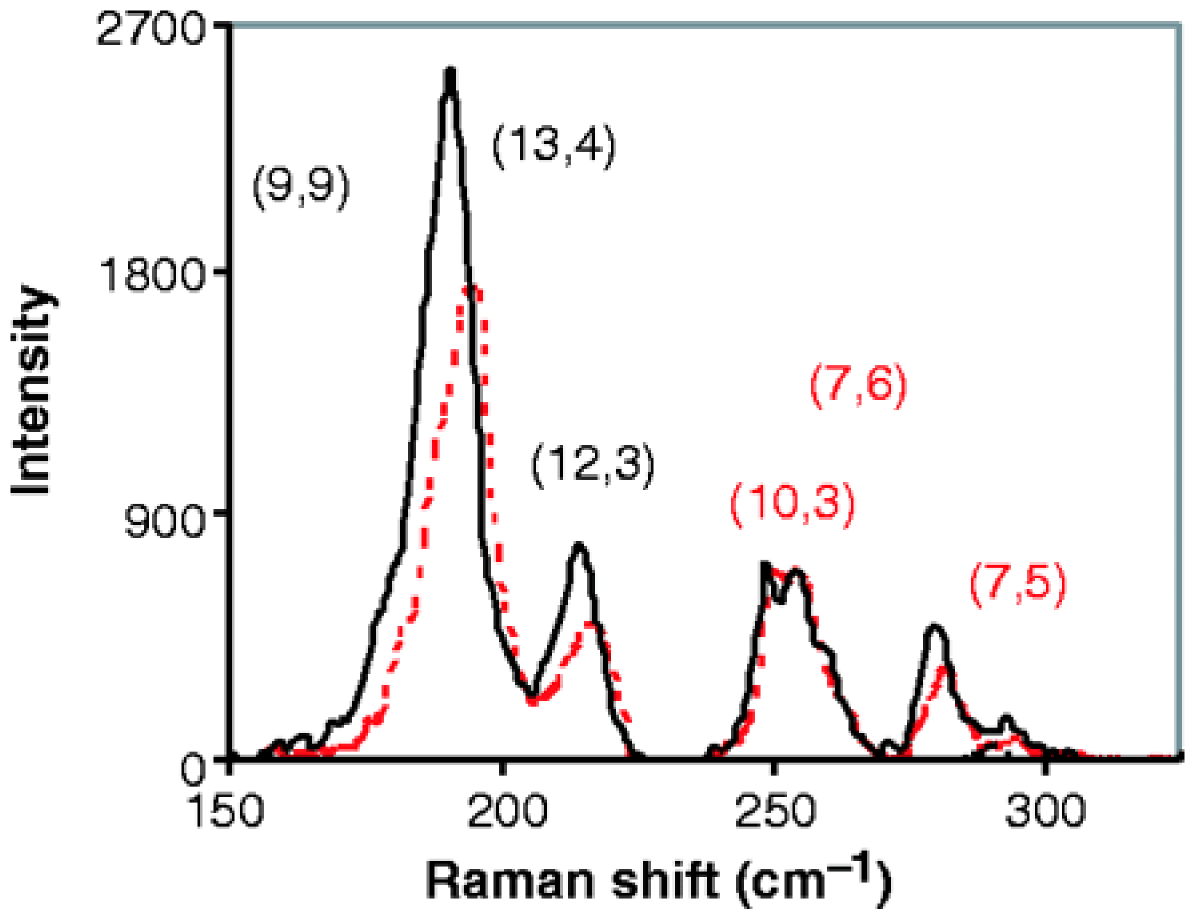


Fig. 5.
Raman spectra at 633 nm probing both metals and semiconducting nanotubes before reaction (solid line) and after recovery and thermal pyrolysis (dotted line). The reversibility of the chemistry implies that intrinsic electronic and optical properties of the pristine nanotubes can be recovered.

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