

Functionalization: Tailoring nanocarbons through attached molecules and particles

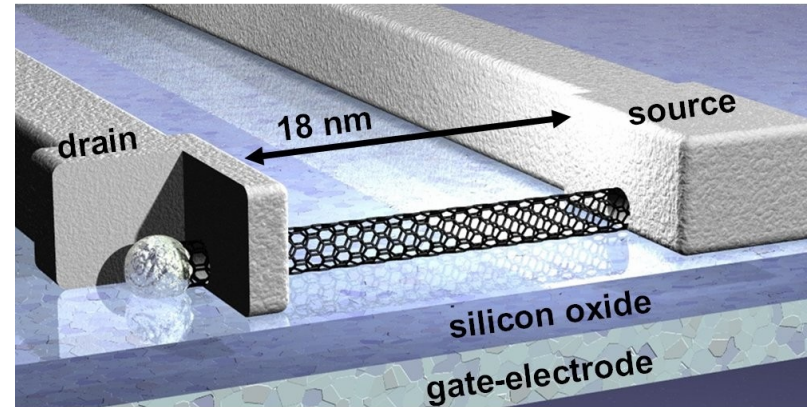
Gabriel Kabbe

Supervisor: Pascal Blümmel

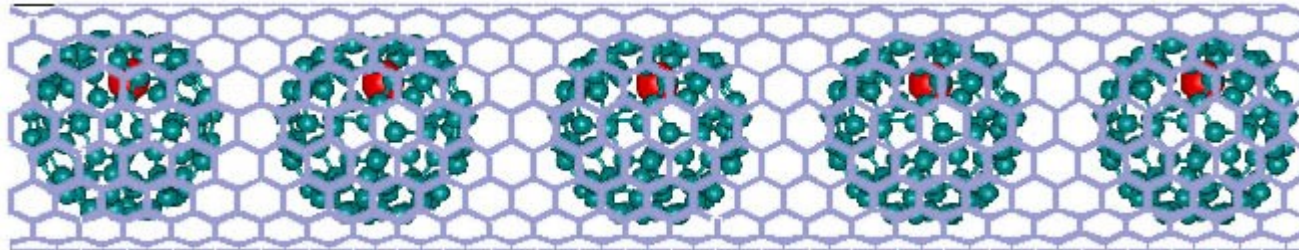
Why functionalizing nanotubes?



<http://www.cen-der-blog.de/wordpress/wp-content/uploads/2009/08/Wassertropfen.jpg>

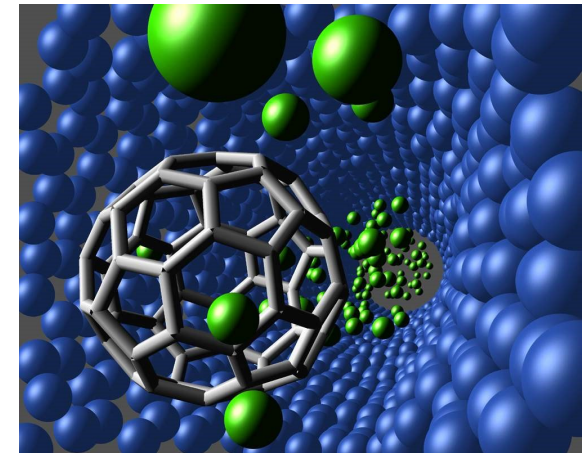
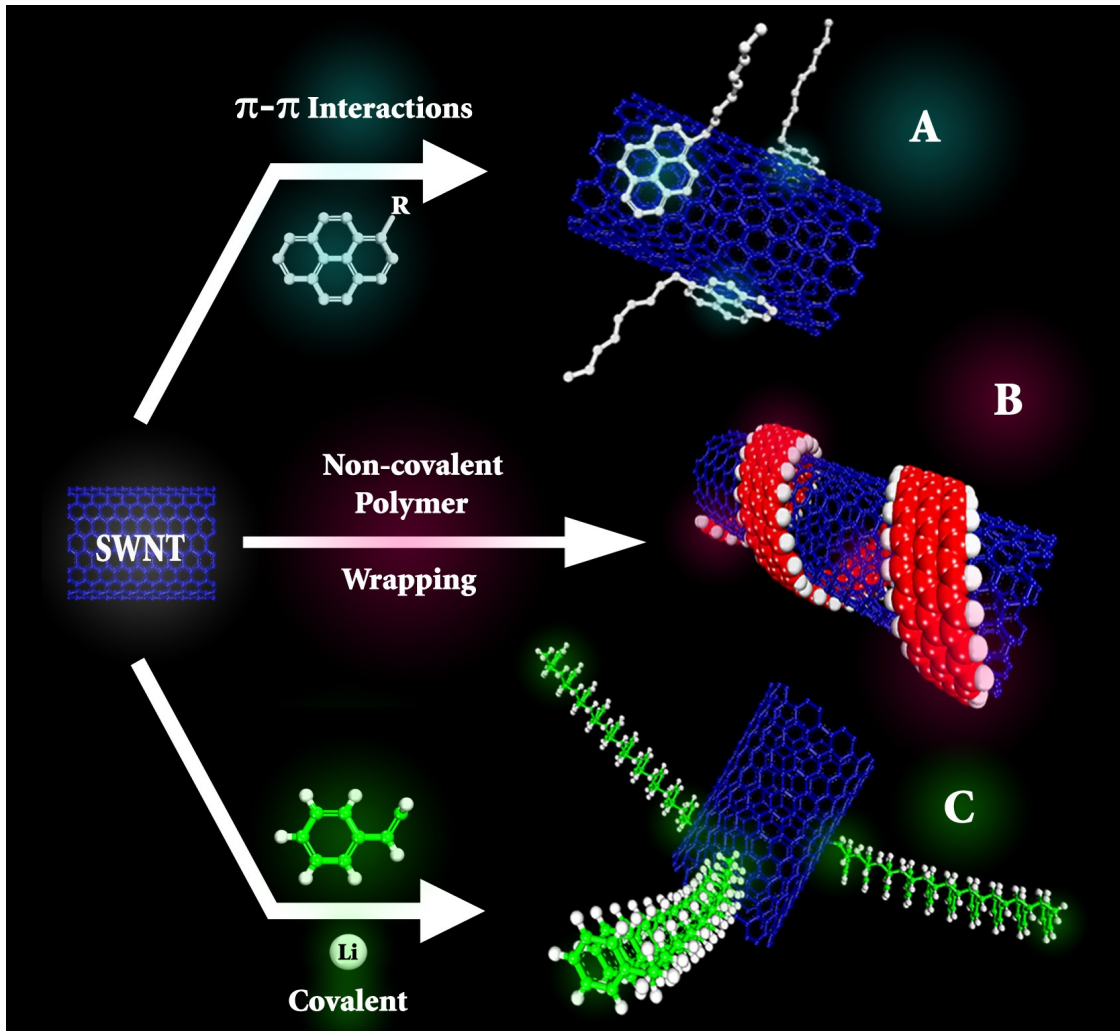


<http://www.nanotech-now.com/images/Infineon-nanotube.jpg>



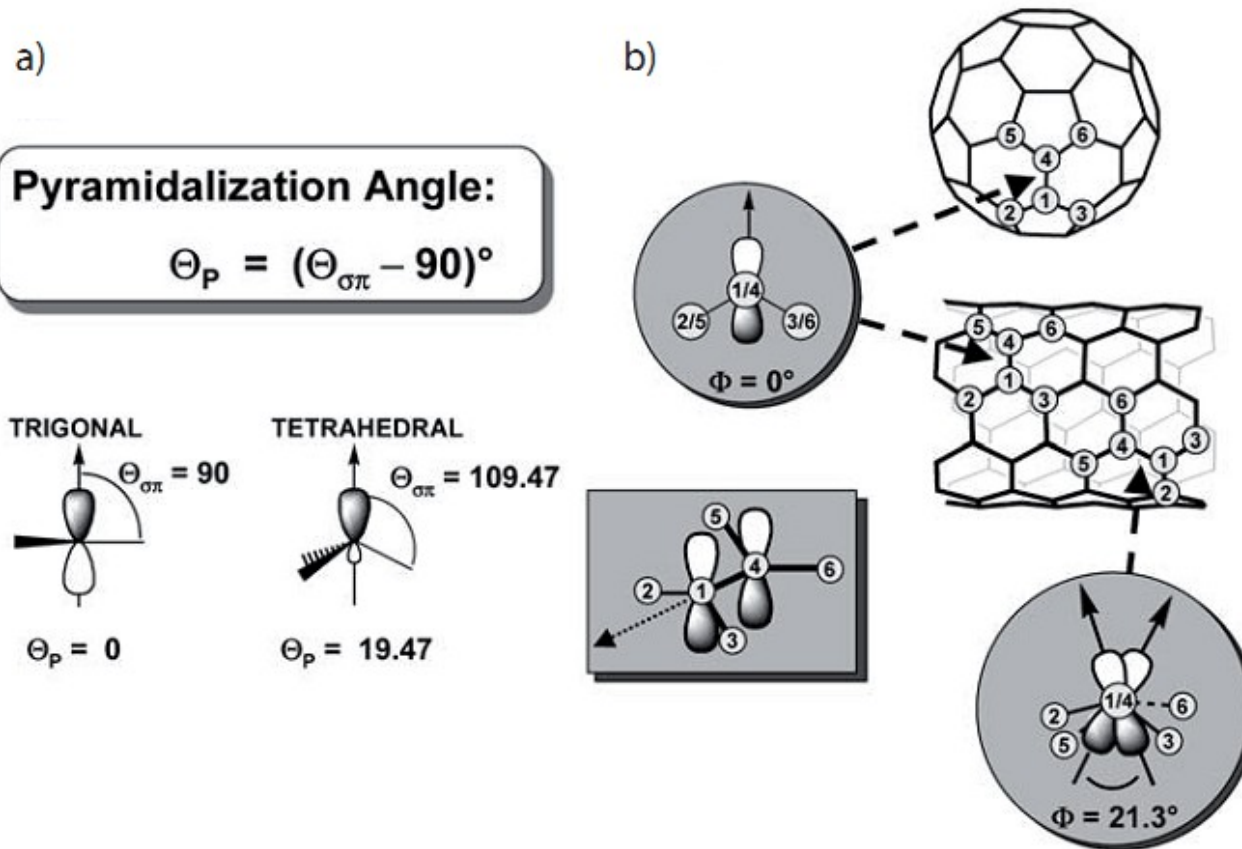
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Different forms of functionalization

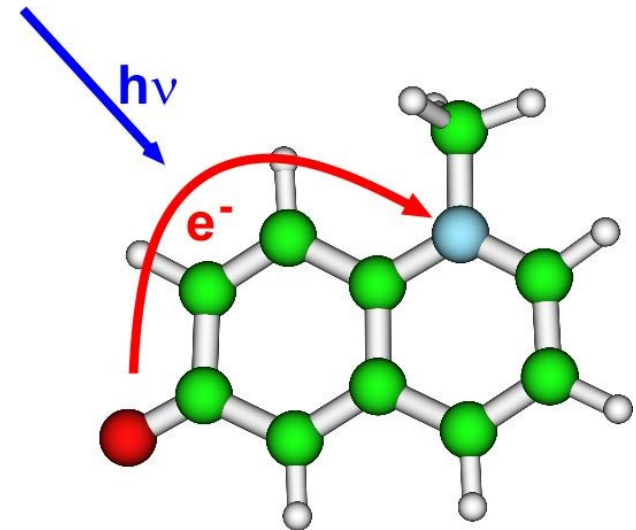
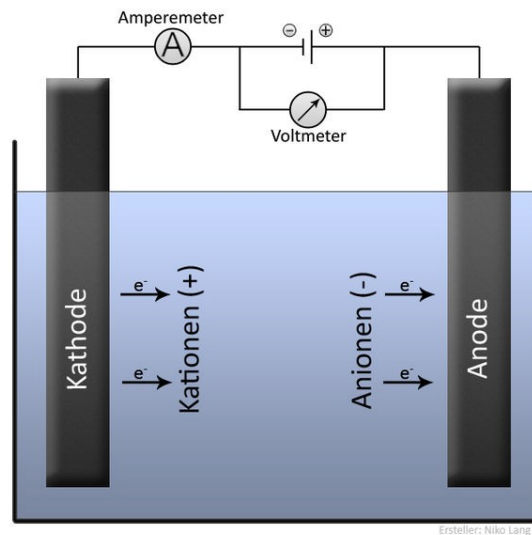


Endohedral functionalization

Covalent functionalization



Covalent functionalization



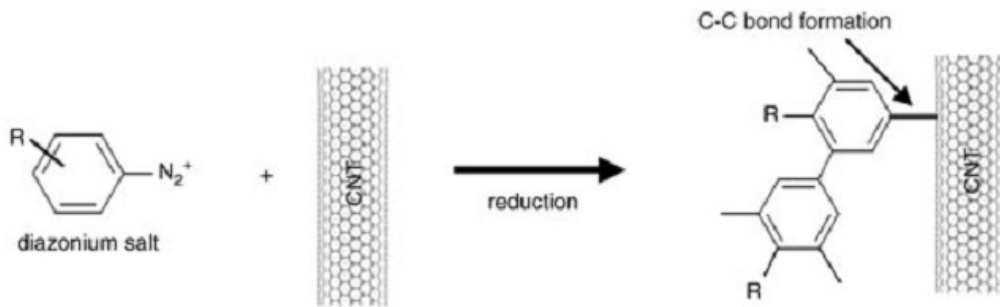
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http://upload.wikimedia.org/wikipedia/commons/thumb/4/4b/Elektrolyse_Allgemein.jpg/621px-Elektrolyse_Allgemein.jpg

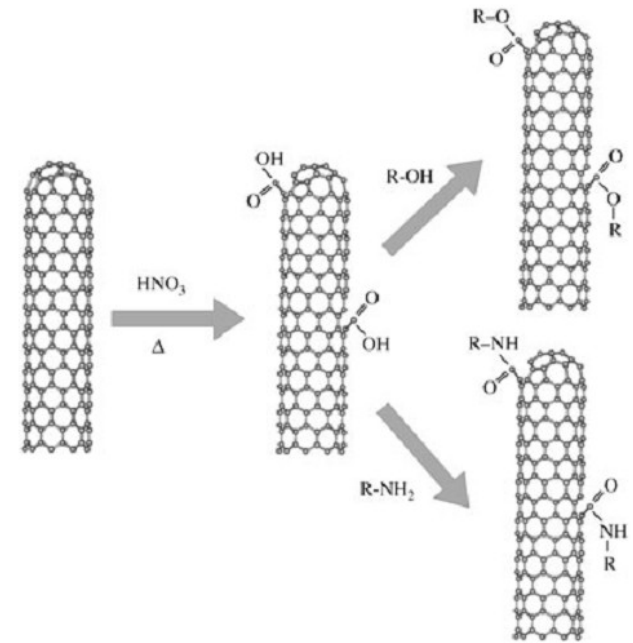
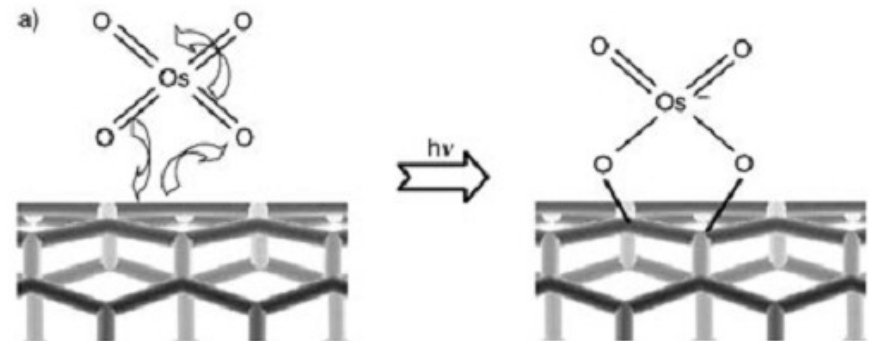
Covalent functionalization

- CNT oxidation and Carboxyl-based couplings

- Electro Chemical Modification



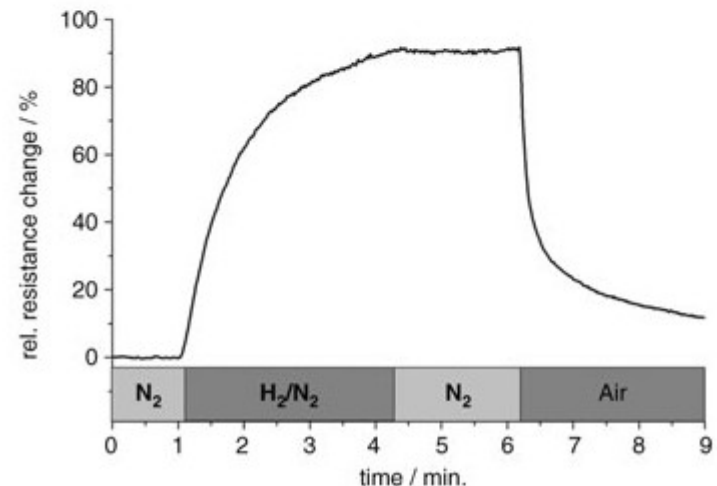
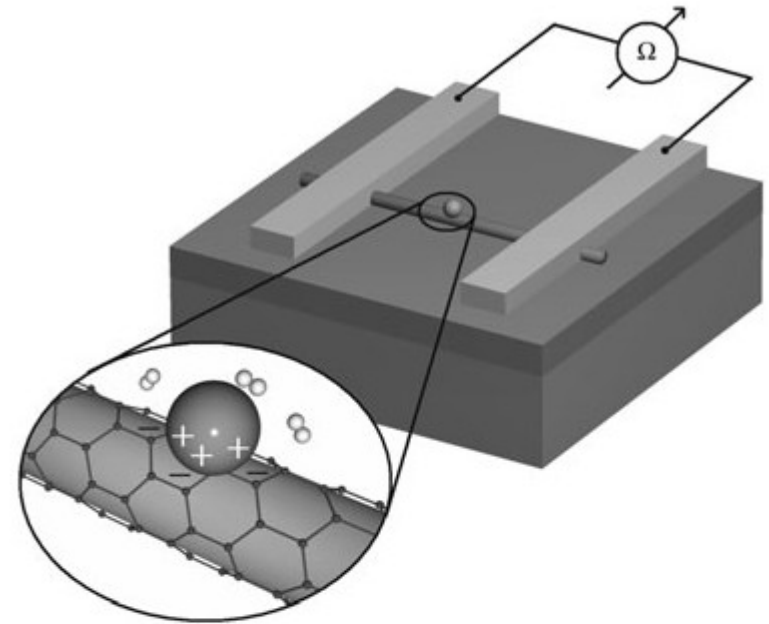
- Photochemical functionalization



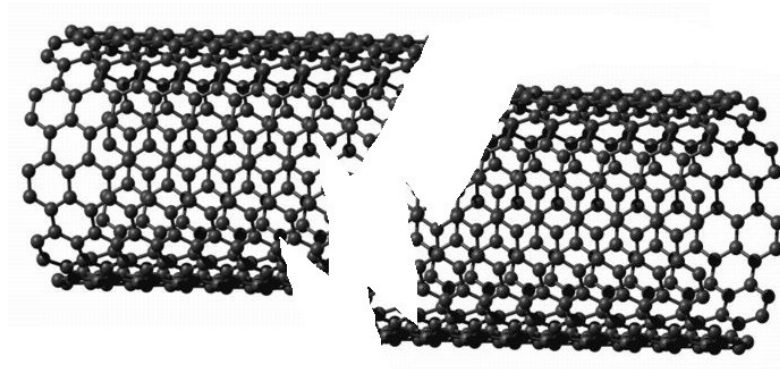
Covalent functionalization

Applications:

- hydrogen sensor
 - semiconducting nanotube is covered with Pd layer
 - H₂ is split into H⁺ by Pd
 - charge-carrier concentration of SWCNT is changed
 - electrical resistance changes



Covalent bonding



Disadvantage:

→ mechanical and electronic properties are changed!!

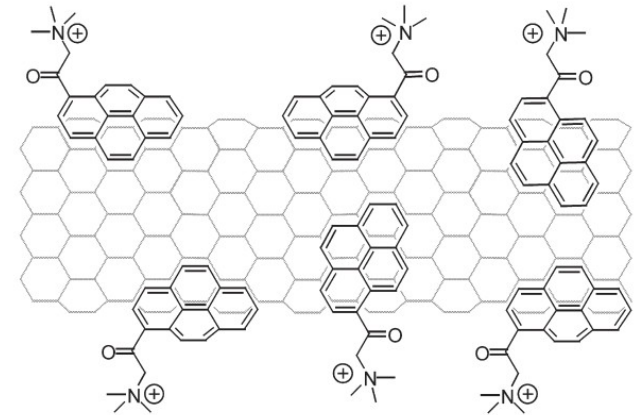
http://homepage.mac.com/jhgowen/research/nanotube_page/nanotube.jpg

Non-covalent bonding

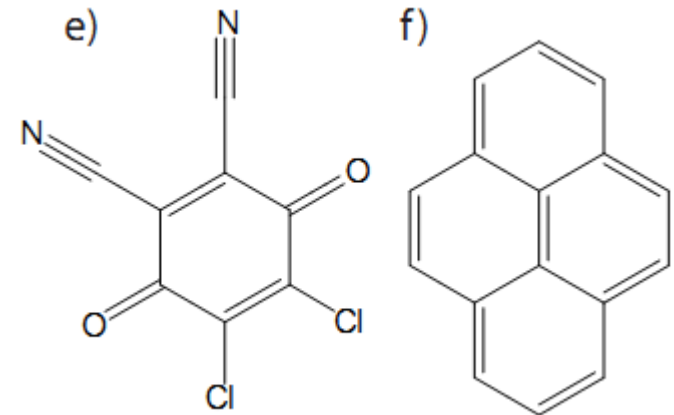
- non-destructive
- π - π -interaction and/or van-der Waals interaction
- examples:

e) DDQ (2,3,-dichloro-5,6-dicyano-1,4-benzoquinone)

f) Pyrene



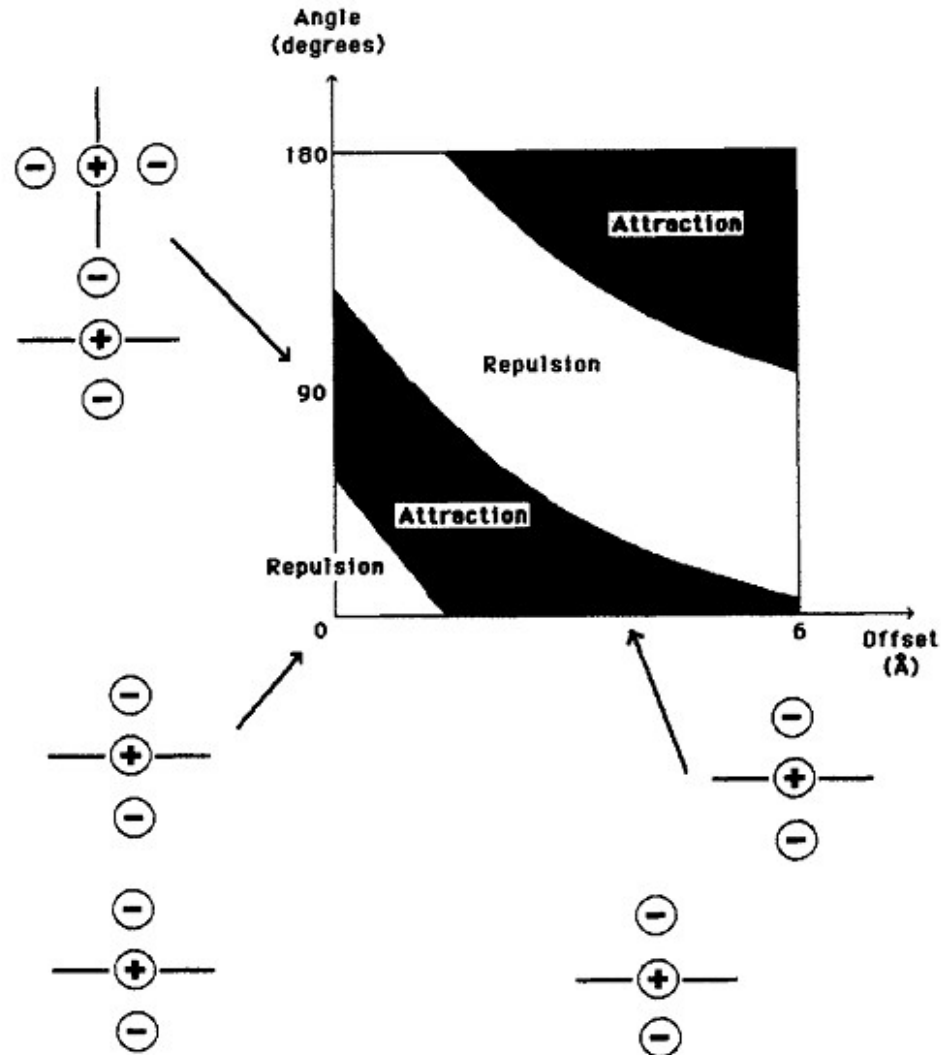
Picture:Hirsch, Vostrowsky Functionalization of Carbon Nanotubes Springer-Verlag 2005



Picture: P.Blümmel: Solubilization and Individualization of Carbon Nanotubes by Noncovalent Functionalization with Switchable Molecules

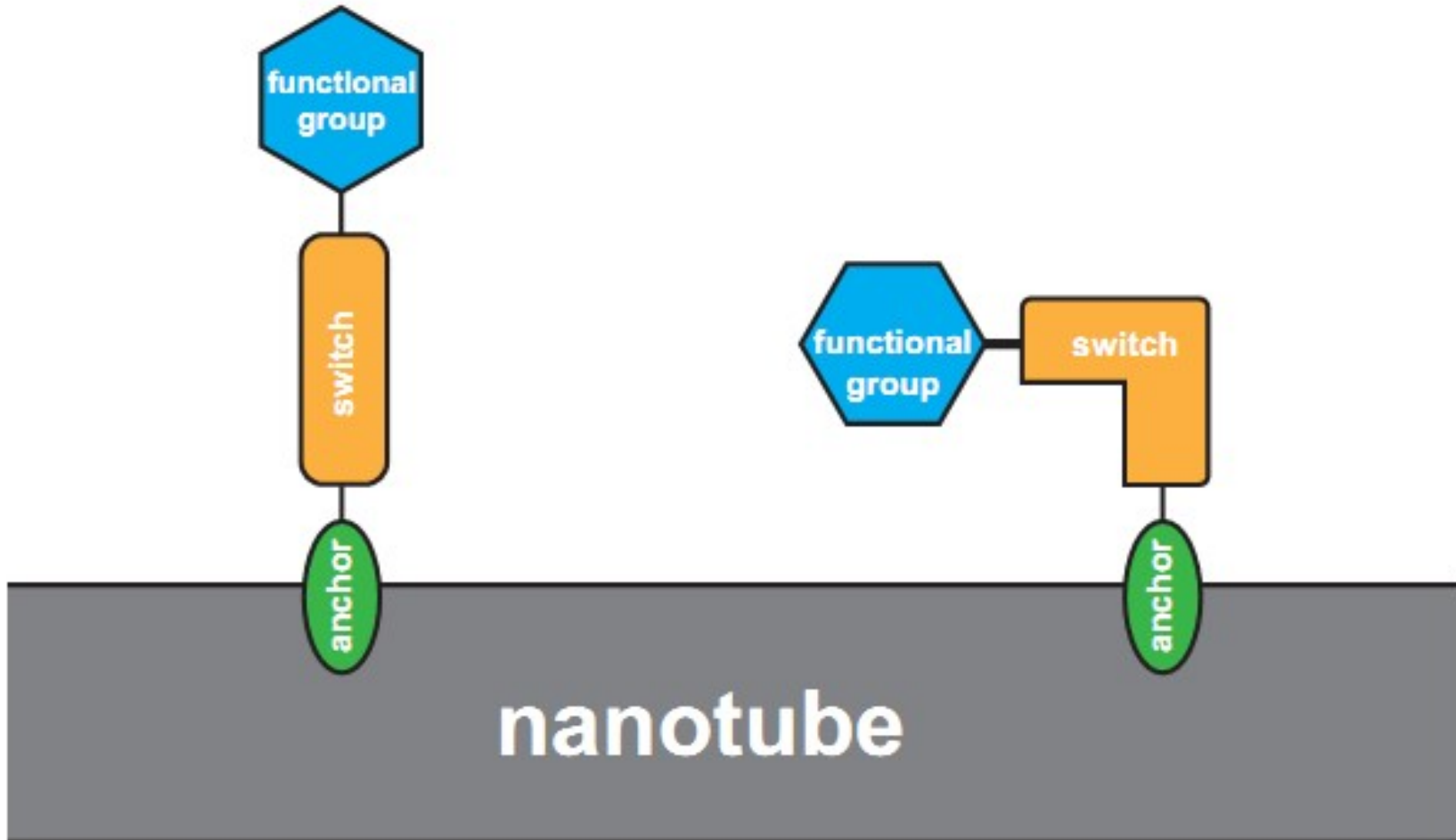
π - π -interaction (Hunter-Sanders-Model)

- a) group charges of an atom into π - electrons (negative charge) and core plus σ -electrons (positive charge)
- b) attraction/repulsion depends on relative angle and offset between two atoms



Christopher A. Hunter, Jeremy K. M. Sanders
The Nature of π - π Interactions

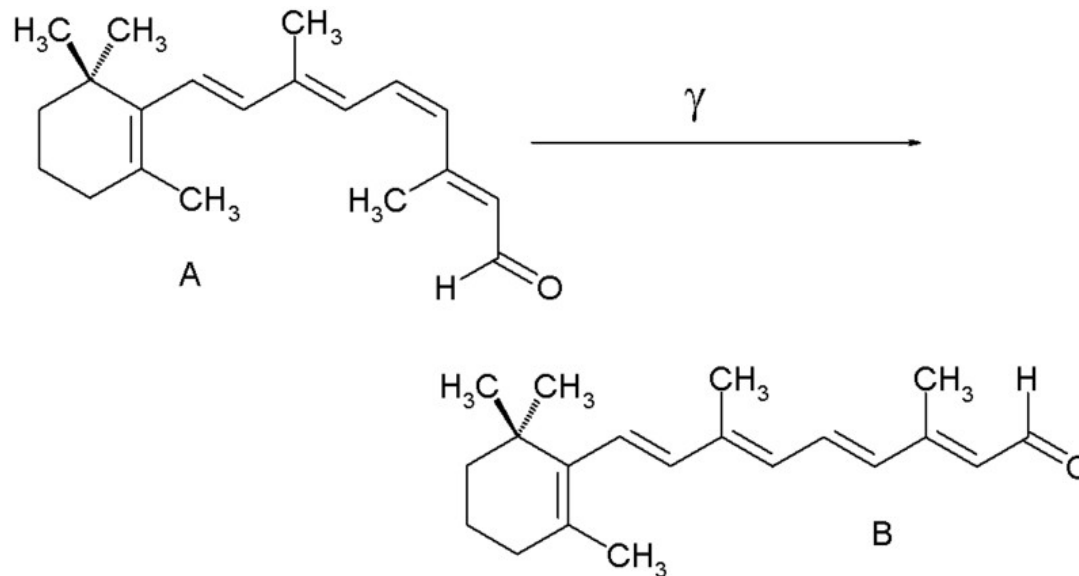
Functionalization with switches



Picture: P.Blümmel: Solubilization and Individualization of
• Carbon Nanotubes by Noncovalent Functionalization
with Switchable Molecules

Functionalization with switches

Retinal (11-cis and all-trans)



<http://upload.wikimedia.org/wikipedia/commons/thumb/1/11/RetinalCisandTrans.png/800px-RetinalCisandTrans.png>

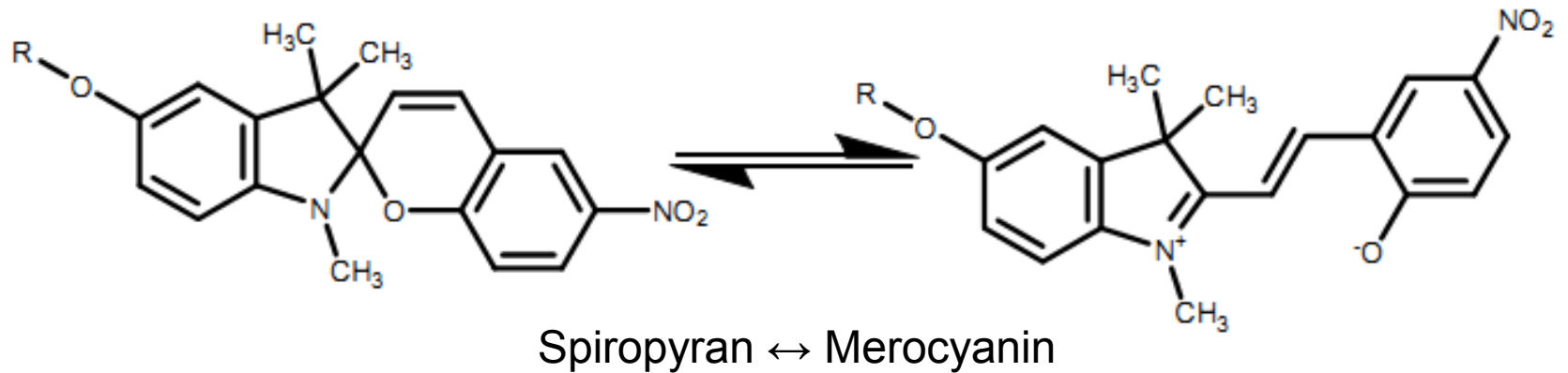
Functionalization with switches



nanotube

Picture: P.Blümmel: Solubilization and Individualization of
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with Switchable Molecules

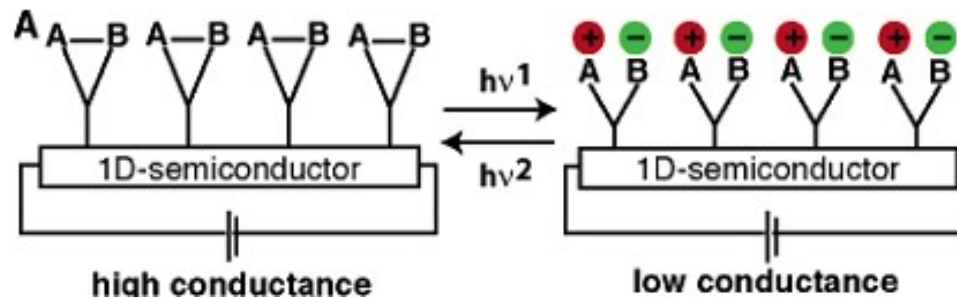
Functionalization with switches



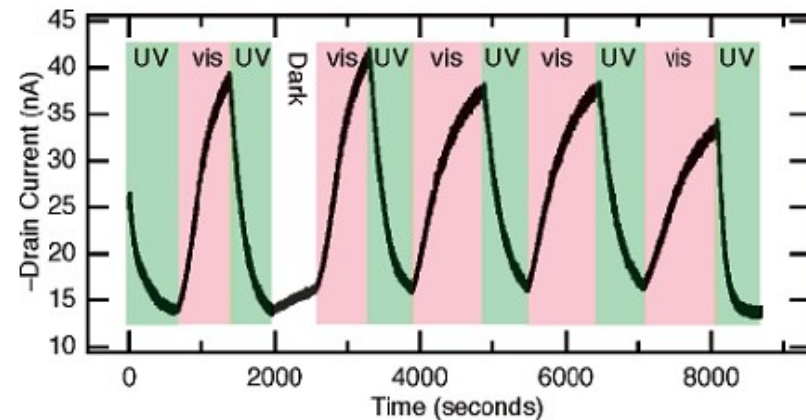
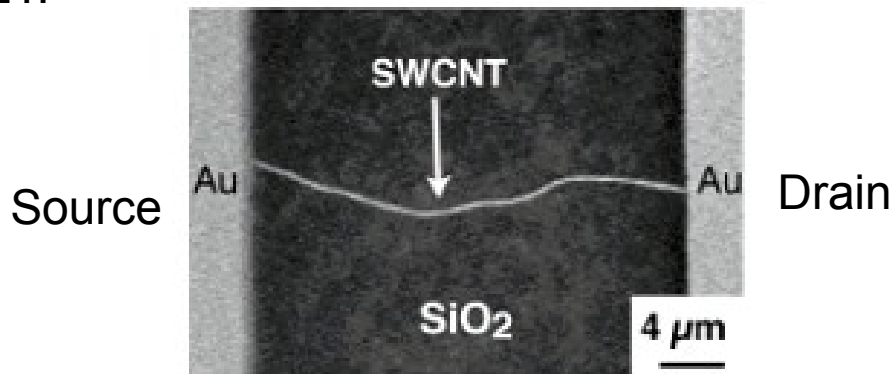
Picture: P.Blümel: Solubilization and Individualization of
 • Carbon Nanotubes by Noncovalent Functionalization
 with Switchable Molecules

Functionalization with switches

Example: Spiropyran non-covalently connected to semiconducting nanotubes

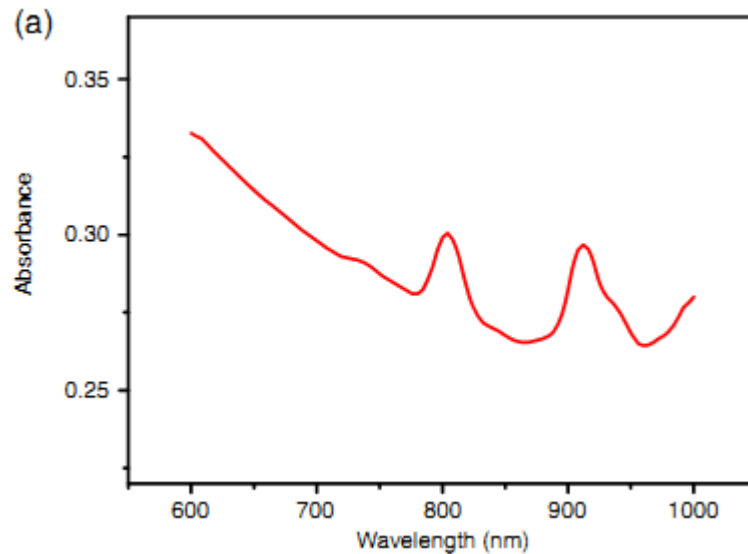
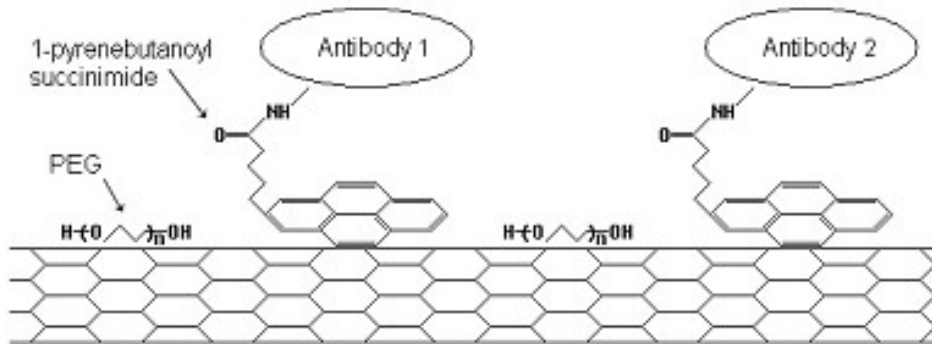


FET:

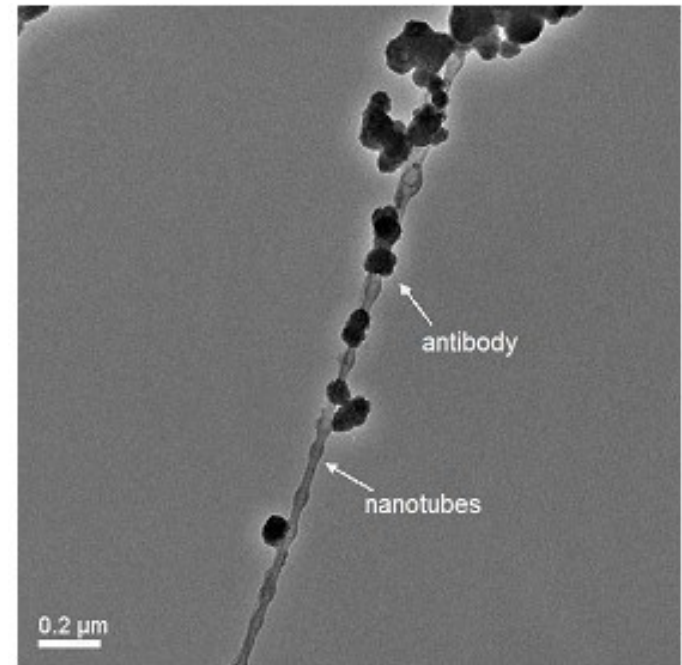


Directing and Sensing Changes in Molecular Conformation on Individual Carbon Nanotube Field Effect Transistors
 Xuefeng Guo, Limin Huang, Stephen O'Brien, Philip Kim,* and Colin Nuckolls

Functionalization with antibodies

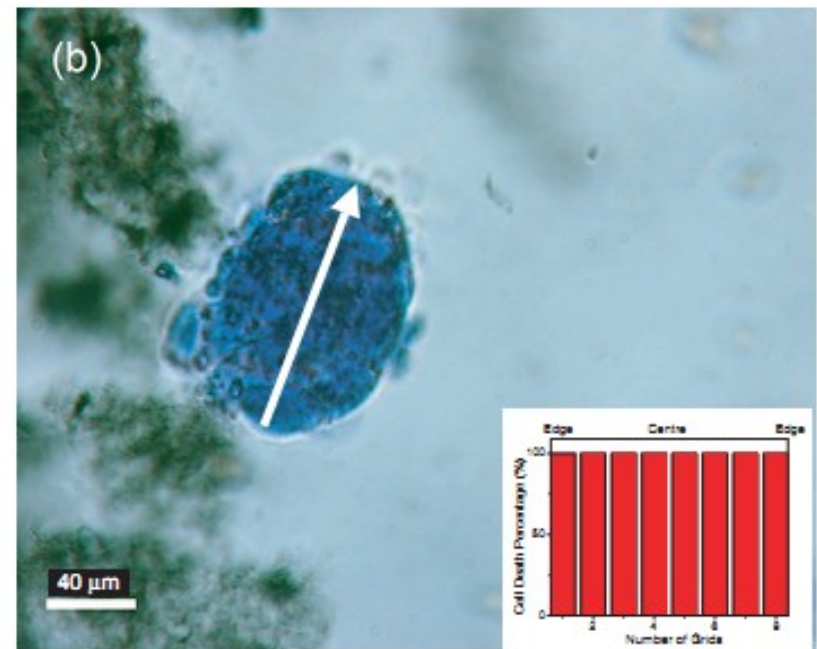
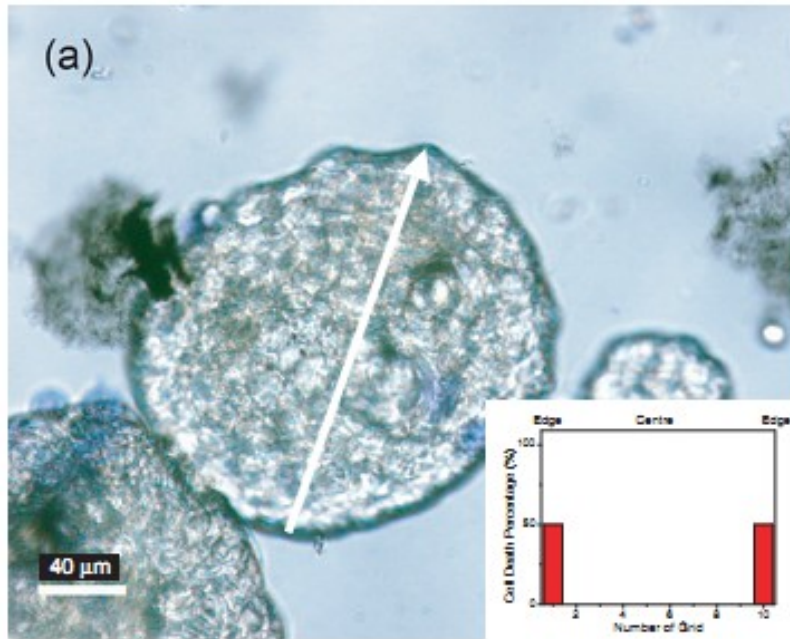


absorbance spectrum



Integrated molecular targeting of IGF1R and HER2 surface receptors and destruction of breast cancer cells using single wall carbon nanotubes
 Ning Shao, Shaoxin Lu, Eric Wickstrom2 and Balaji Panchapakesan1

Functionalization with antibodies

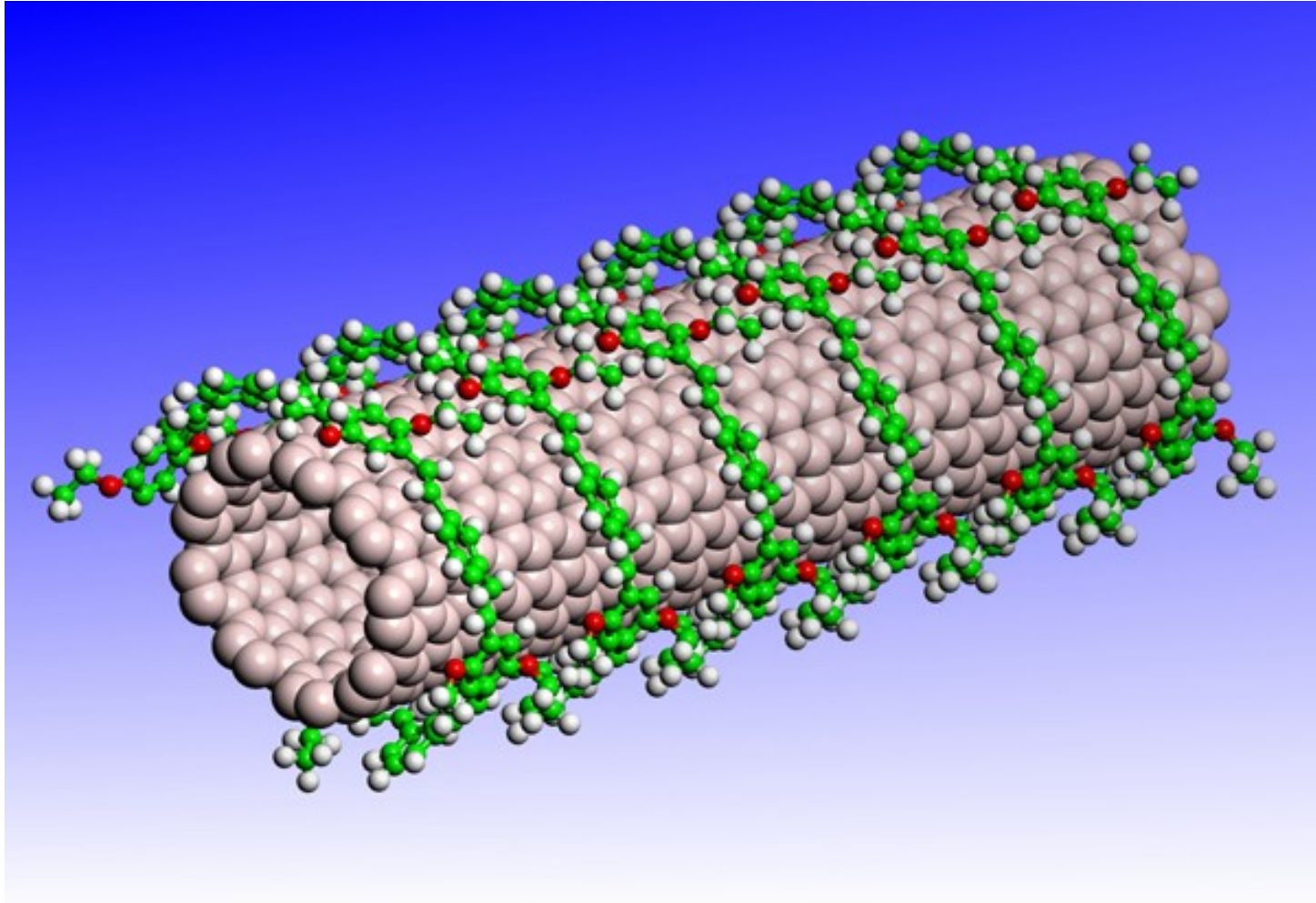


NIR (near-infrared) without nanotube + antibody

NIR with nanotube + antibody

Integrated molecular targeting of IGF1R and HER2 surface receptors and destruction of breast cancer cells using single wall carbon nanotubes
 Ning Shao, Shaoxin Lu, Eric Wickstrom2 and Balaji Panchapakesan1

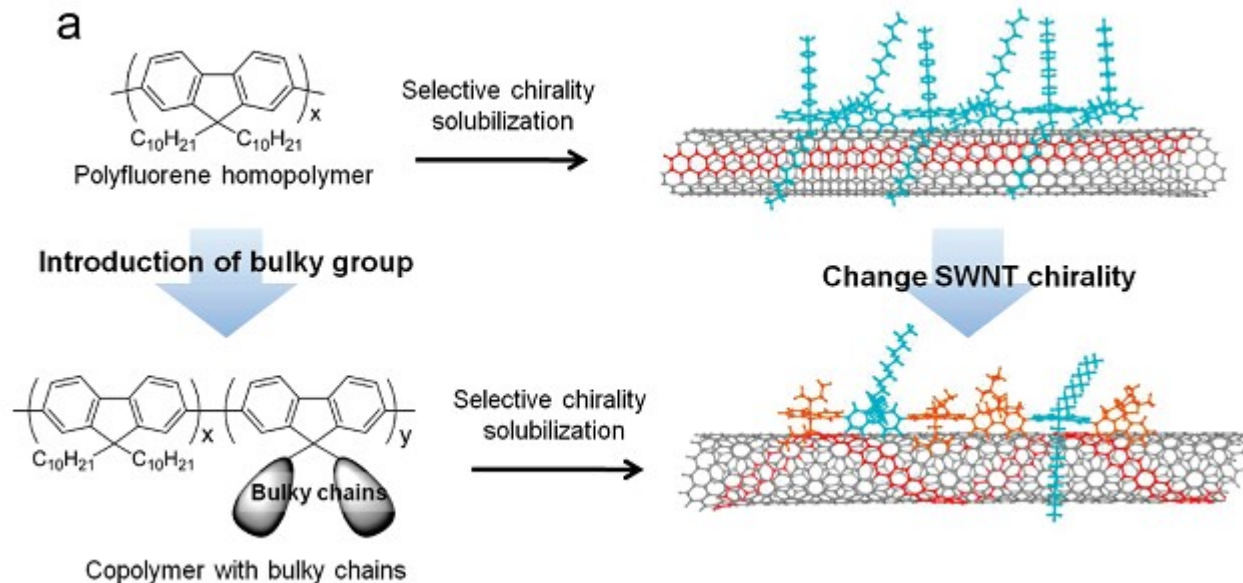
Polymer wrapping



http://www.nanotech-now.com/images/Art_Gallery/Accelrys-helical-wrap-large.jpg

Polymer wrapping

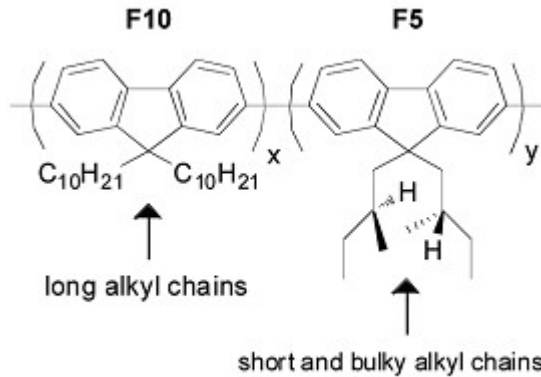
Application: Chirality enrichment



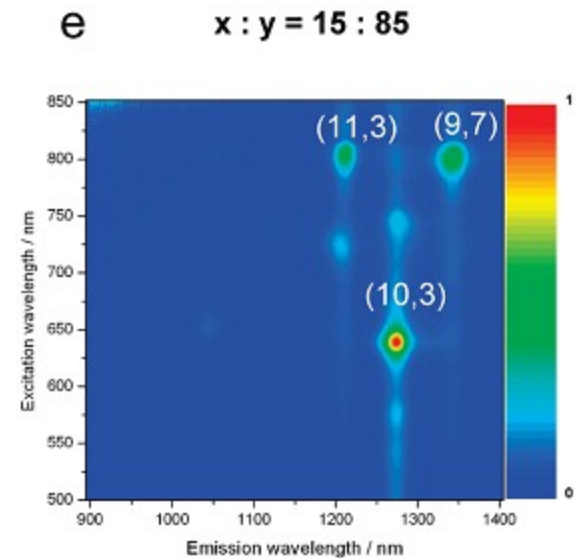
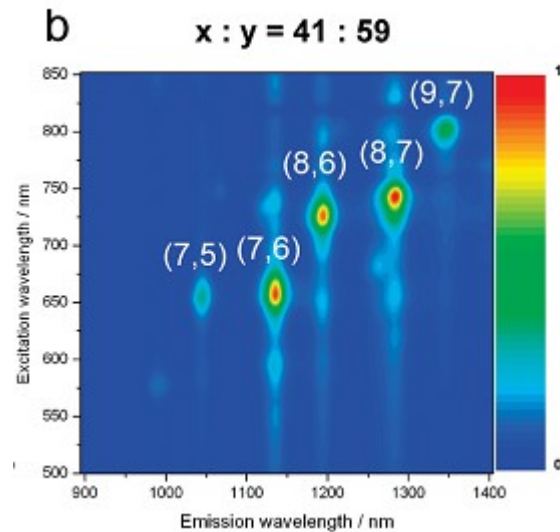
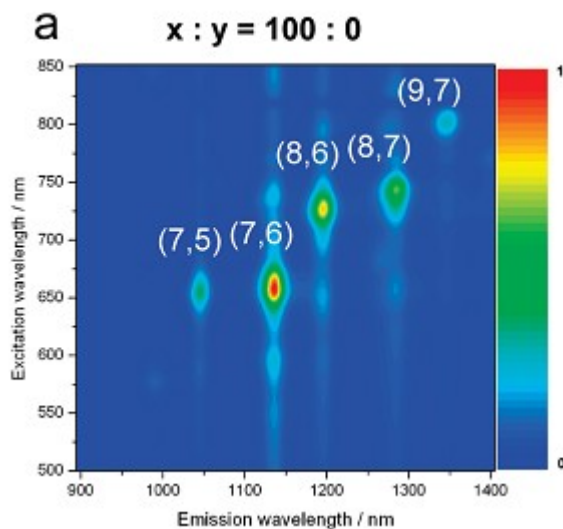
Rational Concept To Recognize/Extract Single-Walled Carbon Nanotubes with a Specific Chirality
 Hiroaki Ozawa, Tsuyohiko Fujigaya

Polymer wrapping

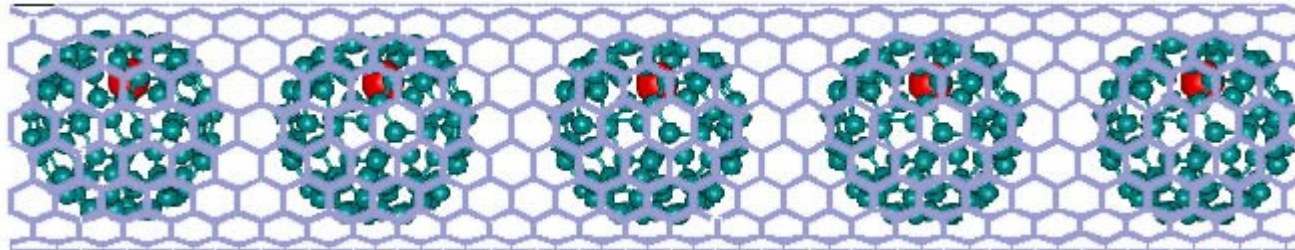
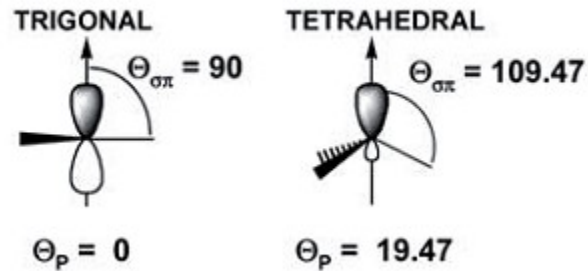
copolymer:



Rational Concept To Recognize/Extract Single-Walled Carbon Nanotubes with a Specific Chirality
Hiroaki Ozawa, Tsuyohiko Fujigaya



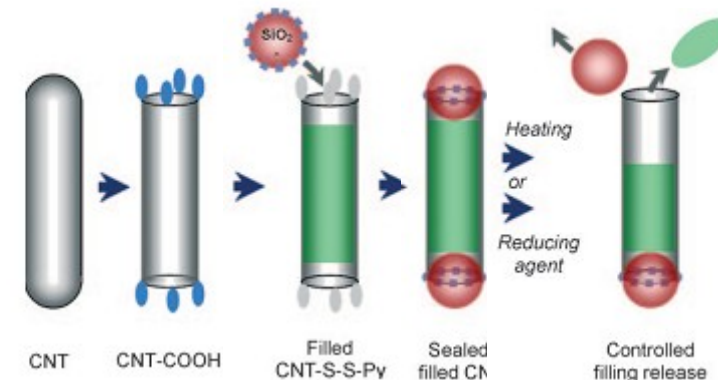
Endohedral functionalization



Endohedral functionalization

„Filling“ a tube:

- heat/oxidation process → open tube ends and introduce carboxyl groups at the openings



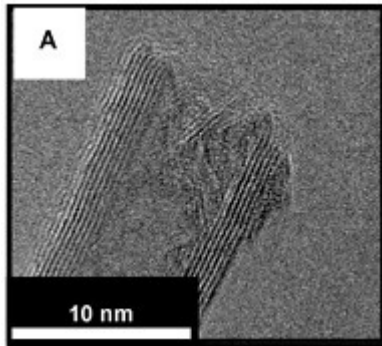
- $\text{S-(2-aminoethylthio)-2-thiopyridine} + \text{CNT-COOH} \rightarrow \text{CNT-S-S-Py}$
- Tubes are filled with fluorescein
- Thiol-silica nanospheres close the tubes
- Reopen by heating or via reducing agents

Chen et al. Carbon-Nanotube-Based Stimuli-Responsive Controlled-Release System

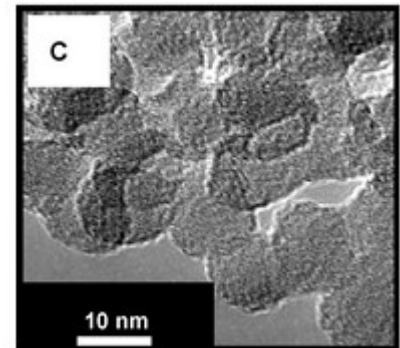
Endohedral functionalization

TEM images:

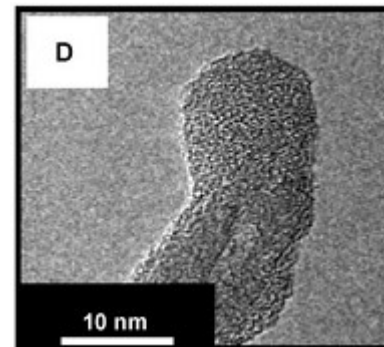
Opened CNT



Silica sphere



Closed CNT



Summary

Covalent

- Destroys Carbon framework
- Irreversible

Non-covalent

- Leaves CNT intact
- Reversible

Endohedral

- Uses CNT's weak reactivity inside

Polymer wrapping

- Chirality selection

Thank you!!!

References

- P.Blümmel: Solubilization and Individualization of Carbon Nanotubes by Noncovalent Functionalization with Switchable Molecules
- Balasubramanian, Burghard: Functionalization of Carbon Nanotubes
- Tasis, Chemistry of Carbon Nanotubes (Chem.Rev.2006)
- Hirsch, Vostrowsky Functionalization of Carbon Nanotubes Springer-Verlag 2005
- Christopher A. Hunter, Jeremy K. M. Sanders The Nature of π - π Interactions
- Guo et al. Directing and Sensing Changes in Molecular Conformation on Individual Carbon Nanotube Field Effect Transistors (2005)
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