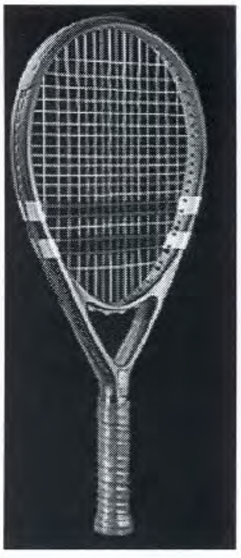
Examples of Nanotube Applications

RETAIL & CONSUMER GOODS

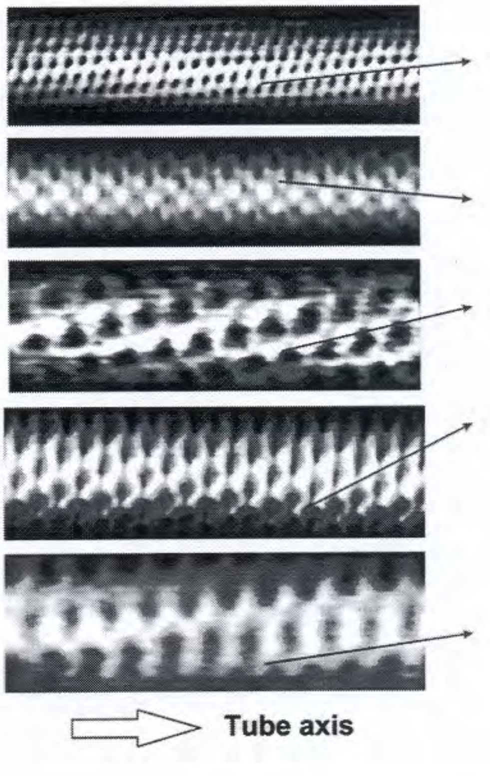


CARBON NANOTUBE™ The material of the future

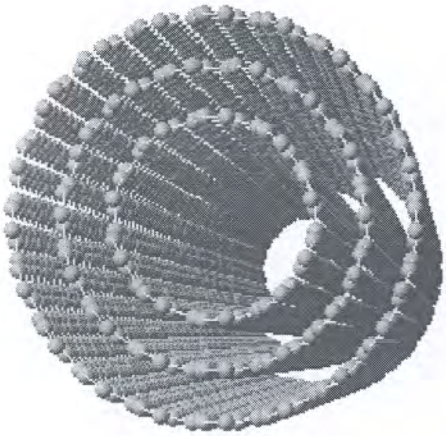
Designed to meet the growing demand for light rackets with oversized heads, VS Nanotube™ brings unparalleled performance to passionate players looking for power and comfort.
One hundred times more rigid than steel (and six times lighter!), 10 times stiffer than conventional graphite, Carbon Nanotube™ is the ideal material.
Extremely resistant and highly reactive, it provides power to the racket through rigidity and playing sensations never before experienced. The use of Carbon Nanotube™ is a major break through in the world of sports.

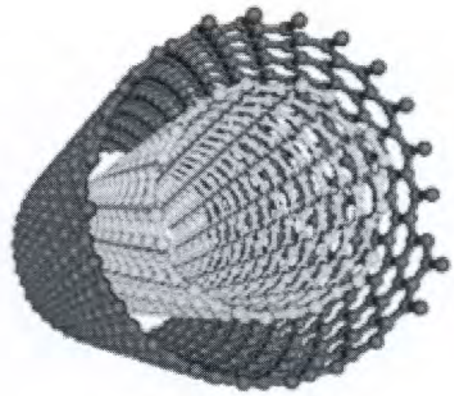
Atomic resolution STM

Large variety of helicities



Taken from Cees Dekker website U Delft)





Multiwall nanotubes Double wall nanotubes

Physico-Chemical Properties of Carbon Nanotubes

CNT possess an ordered structure

Diameter 1 - 20 nm, Length few tens of nm - several μm

A nanotube of 300 nm length is made of 50000 carbon atoms, 25000 aromatic rings, 600000 Da

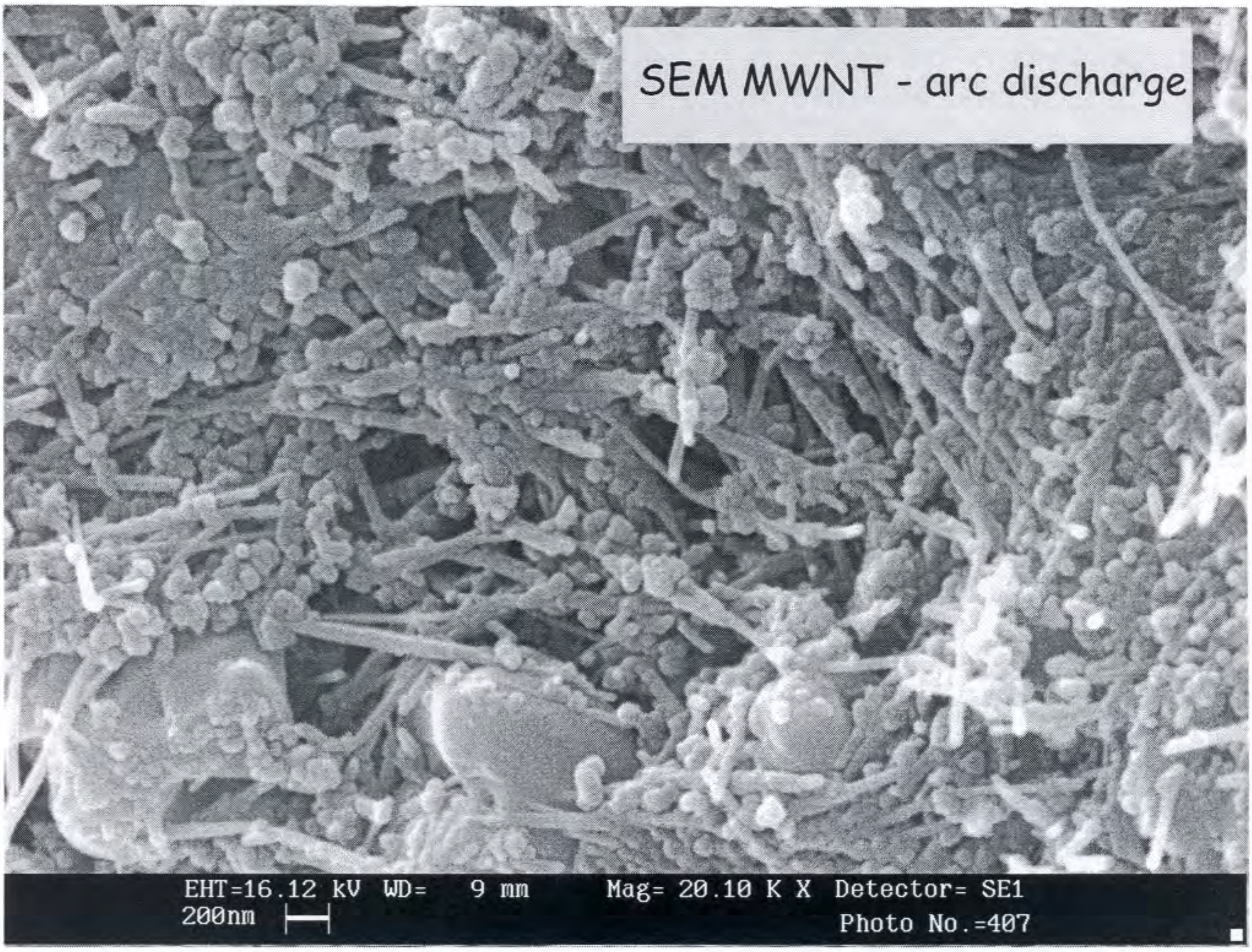
CNT exhibit extraordinary mechanical properties

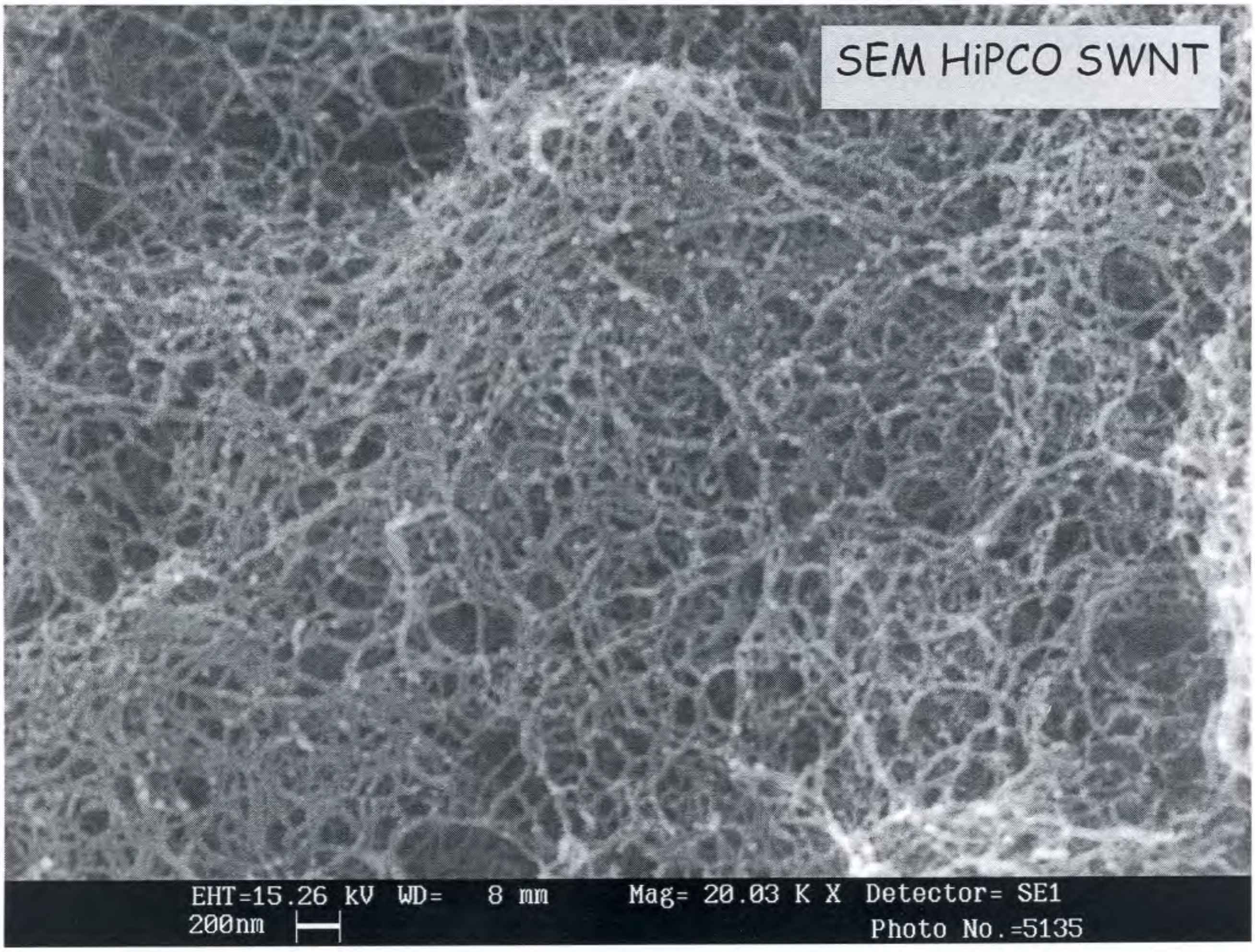
- High strain resistance

CNT exhibit interesting electronic properties

- Metallic
- Semiconducting-Insulating

CNT are insoluble in any organic solvent or aqueous solution


SEM MWNT - arc discharge
EHT=16.12 kV WD= 9 mm Mag= 20.10 K X Detector= SE1
200nm
Photo No.=407


SEM HiPCO SWNT
EHT=15.26 kV WD= 8 mm Mag= 20.03 K X Detector= SE1
200nm
Photo No.=5135

Nanotubes from an organic chemist point of view

Nanotubes should be easier to handle than they are:

1) Purification would be easier if NT were soluble
2) Preparation of composites (e.g. with plastics) would give more homogeneous materials
3) Solution properties of NT could be investigated

↓

Need to be chemically functionalized to increase solubility and processibility

IMPORTANT DATES IN FULLERENE HISTORY

1985: C_{60} is first seen in mass spectrometry by Kroto, Smalley et. al.

1990: C_{60} is first isolated and characterized by Krätchmer and coll.

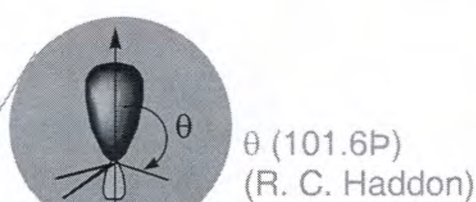
1996: Kroto, Smalley and Curl are awarded the Nobel Prize in Chemistry

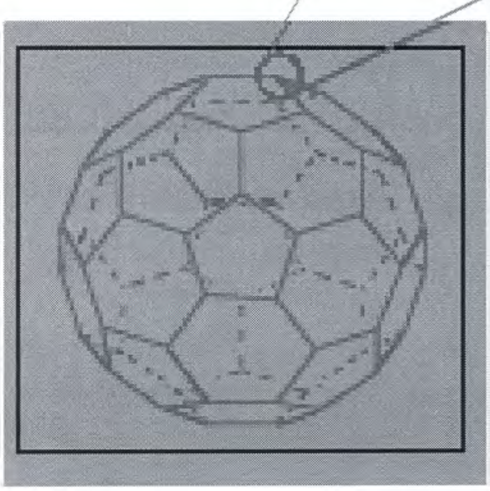
Potential Applications of Fullerenes

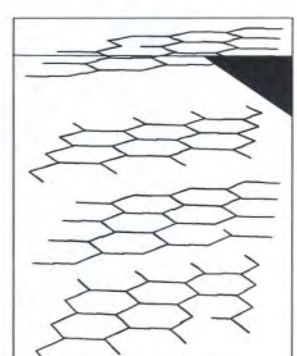
catalyst
lubricant
superconductor
organic magnet
production of:
- batteries
- diamond
- nanotubes
- electro- and photoluminescent materials
- electronic and optical devices
- toner for fotocopier
- photochromic glasses

PHARMACO-BIOLOGICAL

[60]Fullerene is soluble curved graphite

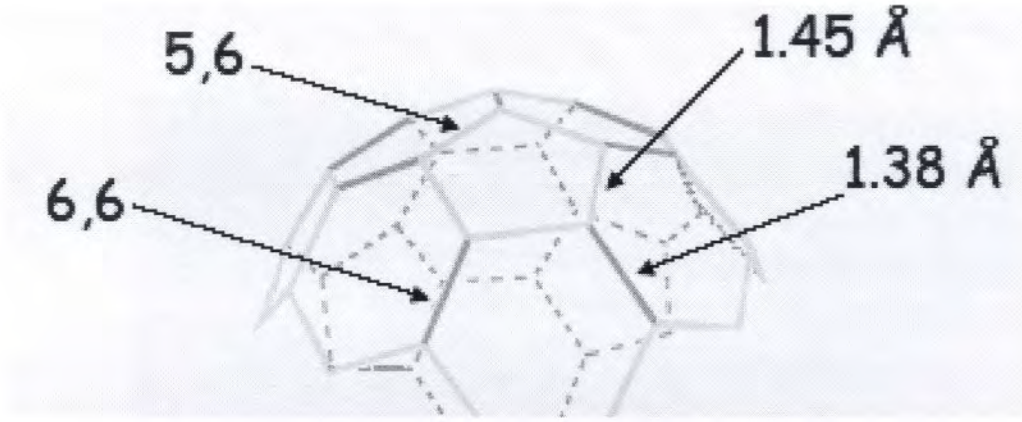






60 atoms of C
20 hexagons
12 pentagons

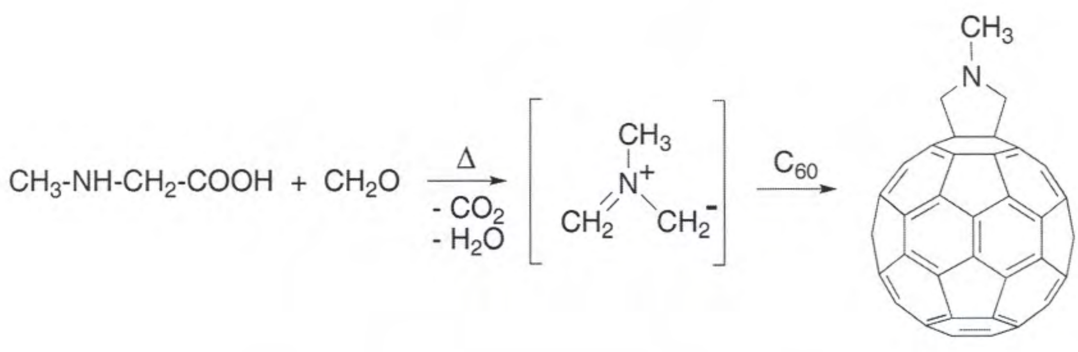
Strain Energy = ca 8 Kcal/mol
per C atom (ca 80% H_f)



90 *C-C* bonds
30 "conjugated" double bonds

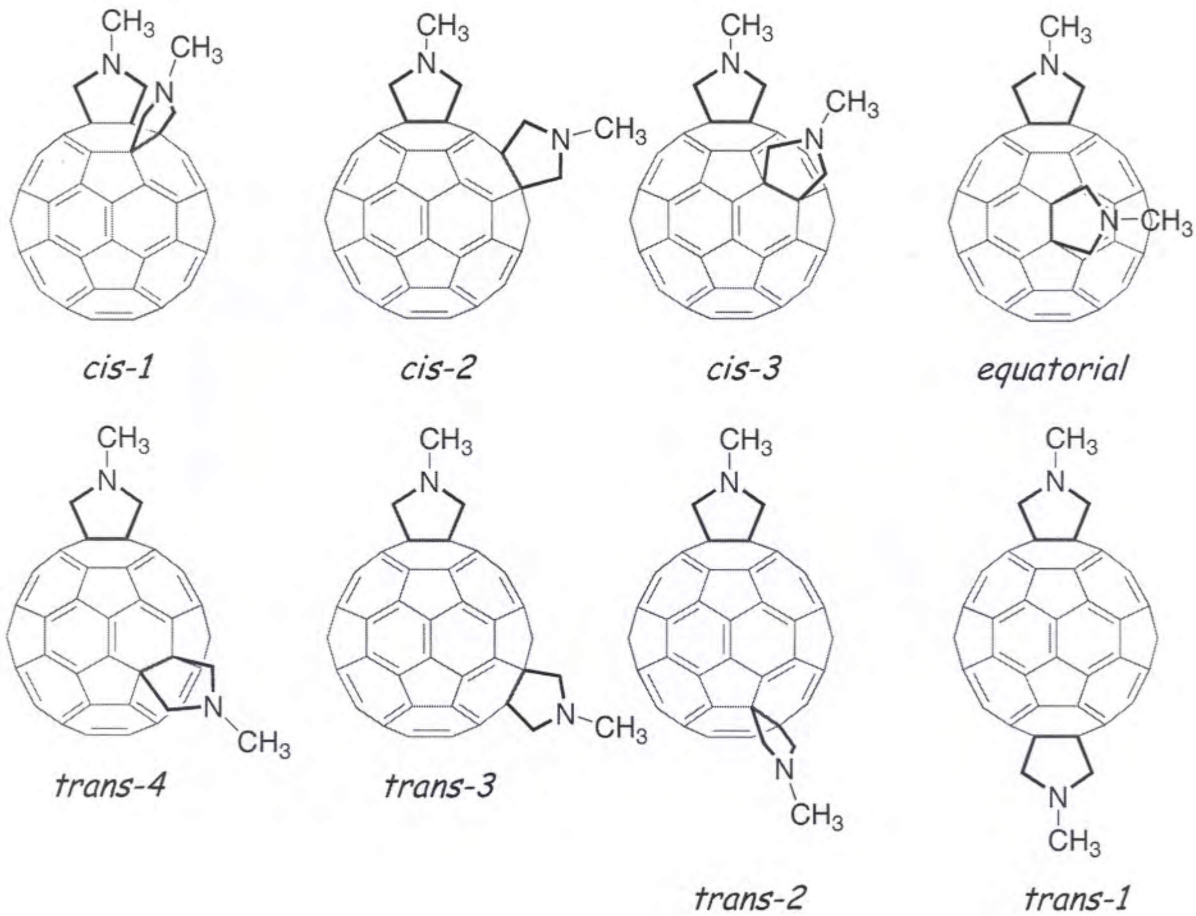
12,500 possible resonance structures
no delocalization ⟹ only 1 polyenic structure

Azomethine Ylide Cycloaddition to C_{60}

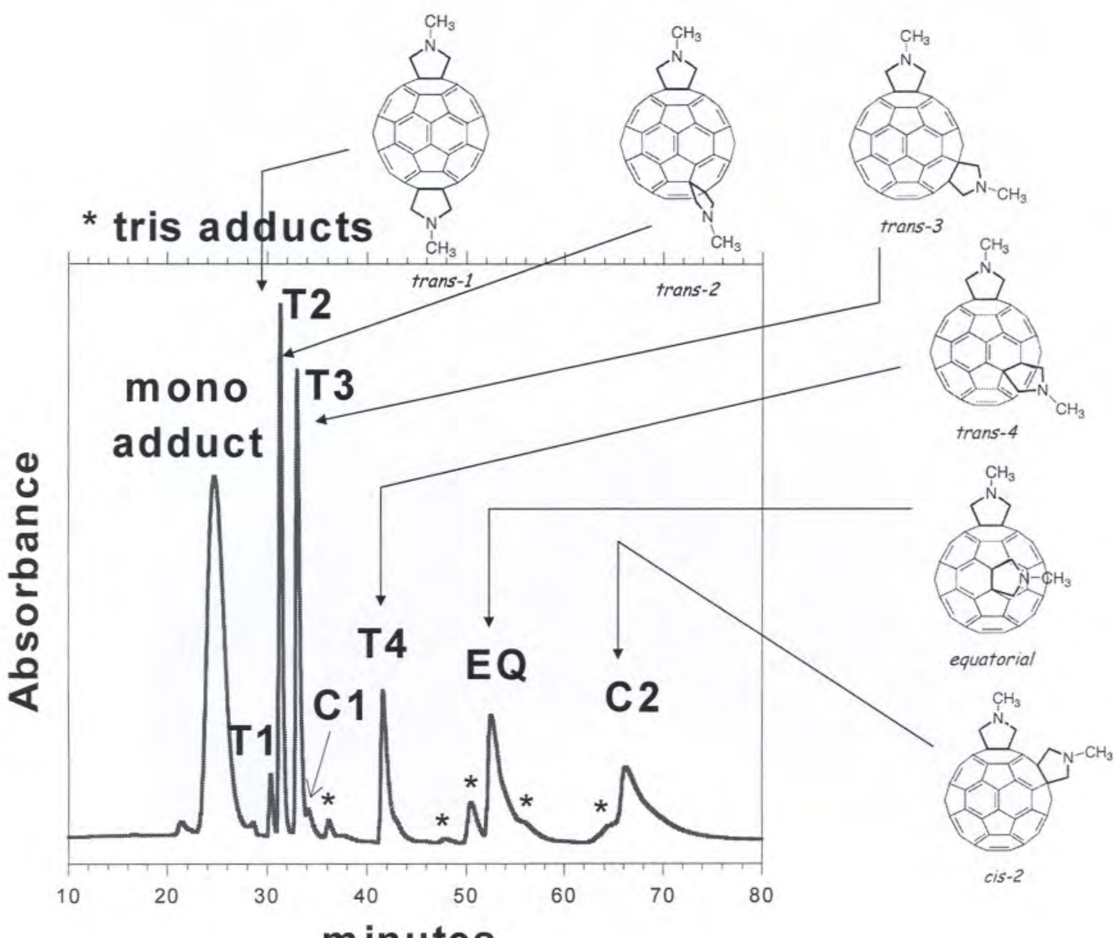


(41 % yield, 82 % based on C_{60} recovery)

Maggini, Scorrano, Prato *JACS* **1993** *115* 9798

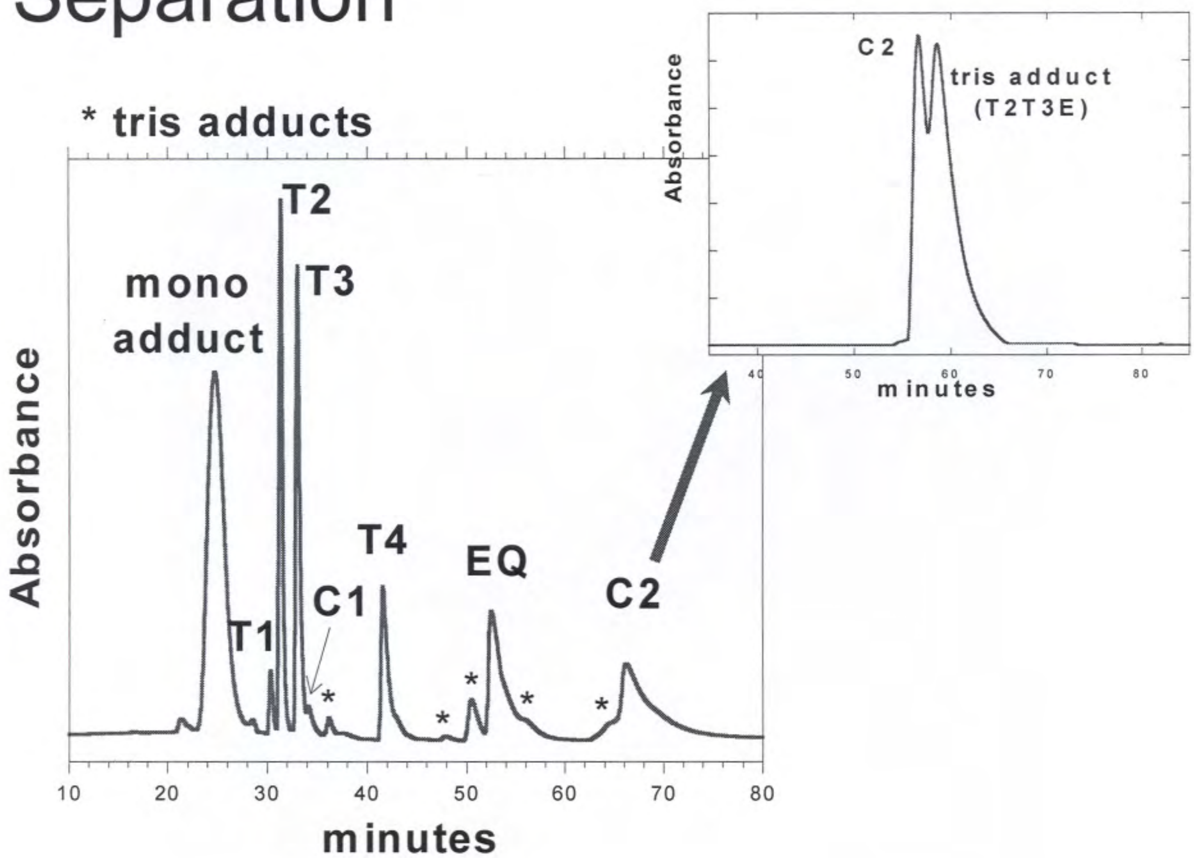


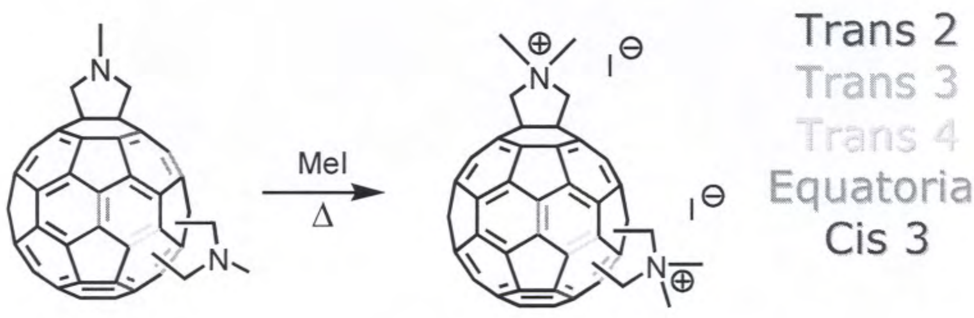
cis-1
cis-2
cis-3
equatorial
trans-4
trans-3
trans-2
trans-1



* tris adducts
trans-1
trans-2
trans-3
trans-4
equatorial
cis-2
T2
T3
mono adduct
T4
EQ
C1
C2
T1
Absorbance
minutes
10
20
30
40
50
60
70
80

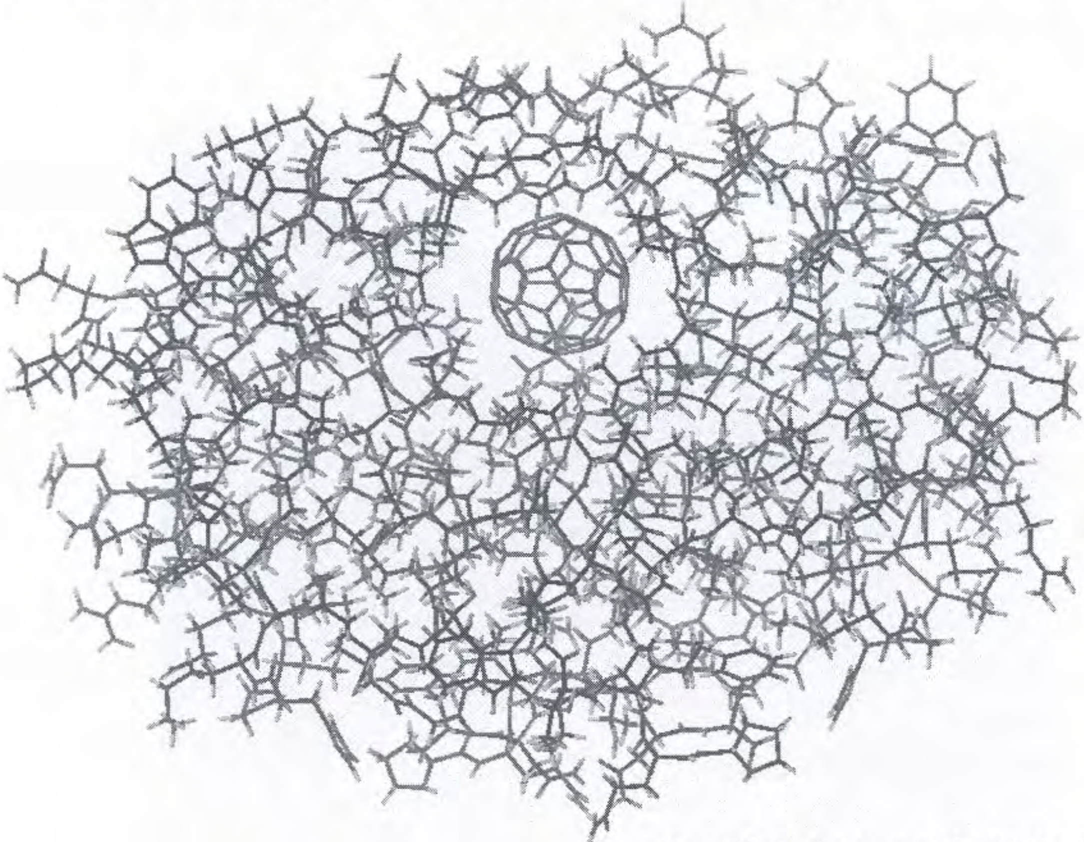
Separation





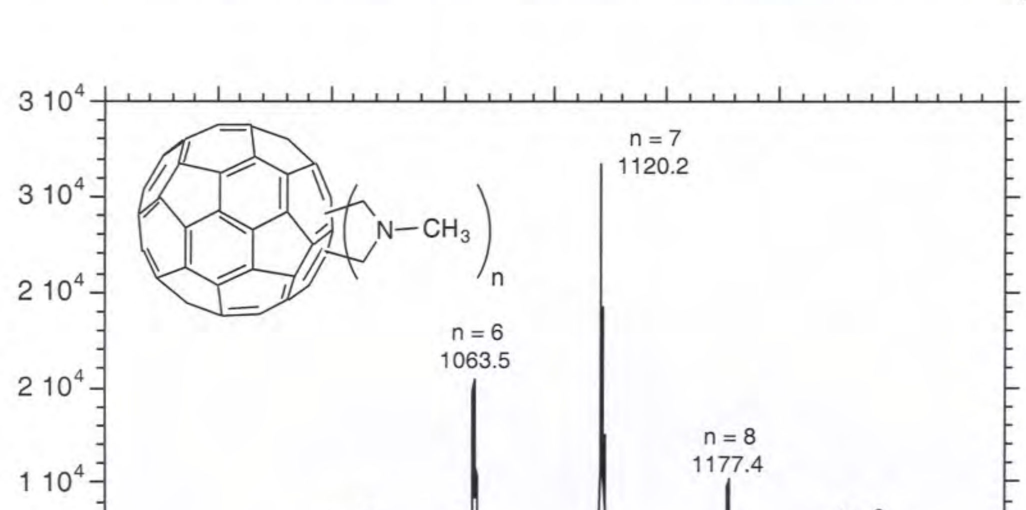
Partially soluble in water

Molecular modeling: HIV Protease-C60 complex

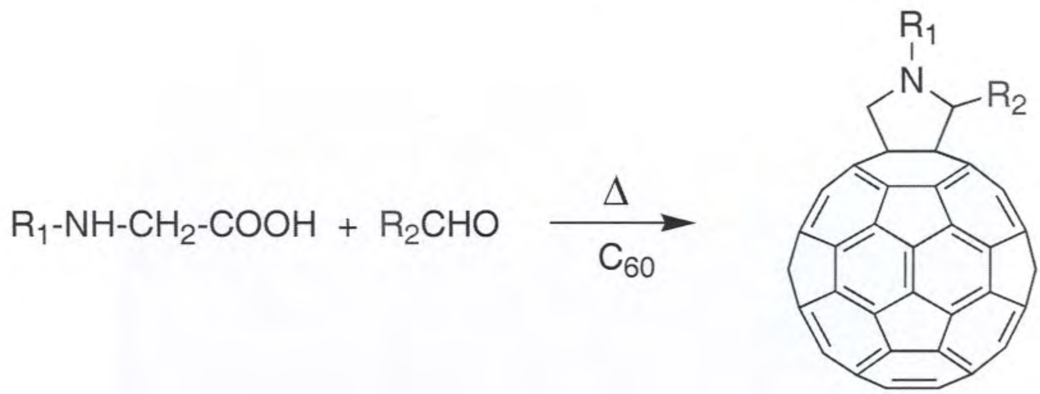


S. H. Friedman et al, JACS 1993

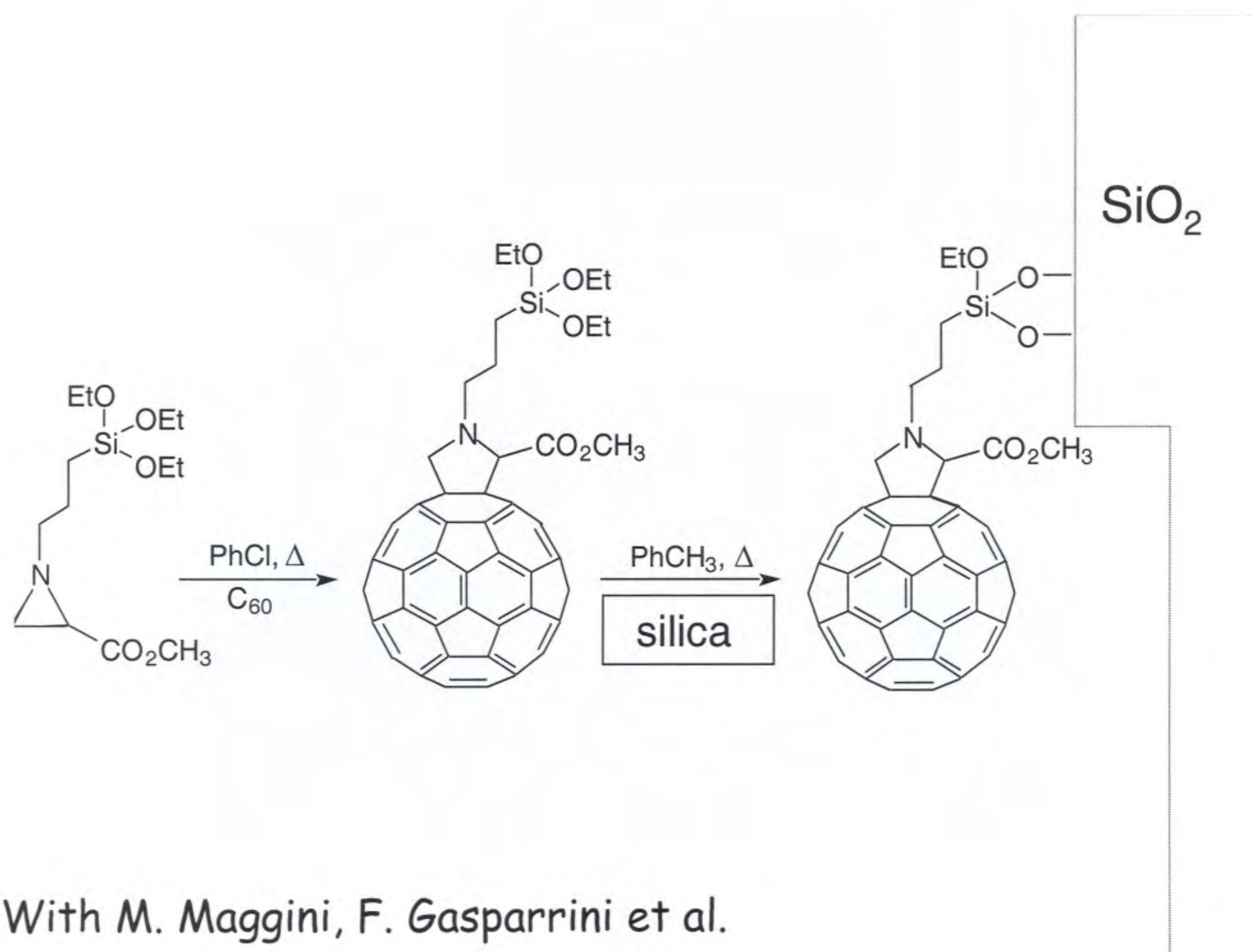
$$CH_3\text{-NH-}CH_2\text{-COOH (20 eq) + HCHO (20 eq) + } C_{60} \xrightarrow[\text{8h}]{\text{toluene, } \Delta}$$



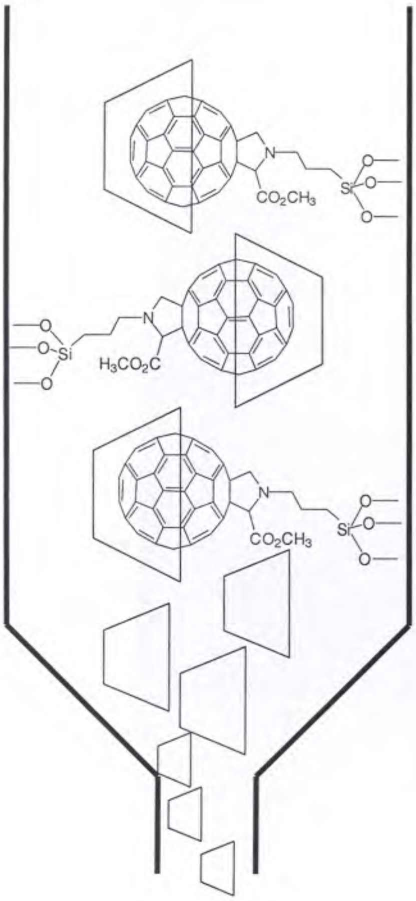
General Approach to Functionalized Fulleropyrrolidines



Maggini, Scorrano and Prato, *JACS*, **1993**, *115*, 9798
Prato and Maggini, *Acc. Chem. Res.*, **1998**, *31*, 519
Tagmatarchis and Prato, *Synlett* **2003**, *6*, 768



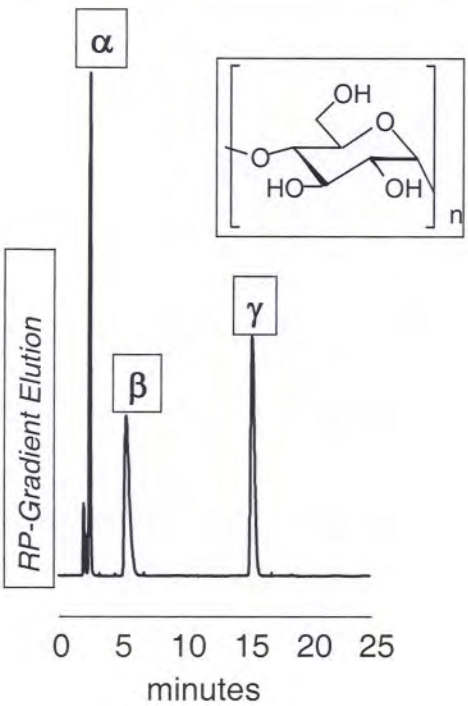
With M. Maggini, F. Gasparrini et al.



Size- and Shape-Selective Chromatography

color: dark brown
Loading: 72 mg/g silica (0.4 mmol/m²)
efficiency: 5 x 104 N/M
media: organic and aqueous
expectations: high selectivity with more complex solutes

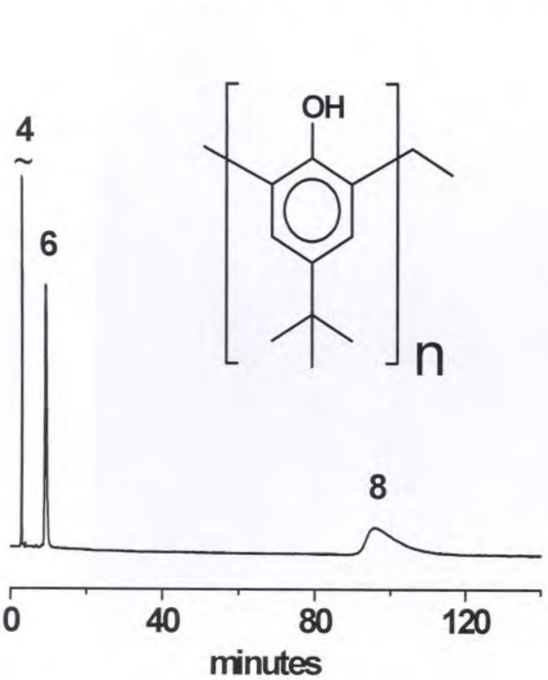
Reverse Phase HPLC on Fullerene-Modified Stationary Phase Separation of α-, β- and γ-Cyclodextrins



Column: Silica-Bound Fullerene
250 x 2 mm ID
Eluent: CH_3CN/H_2O 70/30
Flow Rate: 0.3 ml/min
Detector: Light Scattering

J. Amer. Chem. Soc. **1997**,*119*, 7550

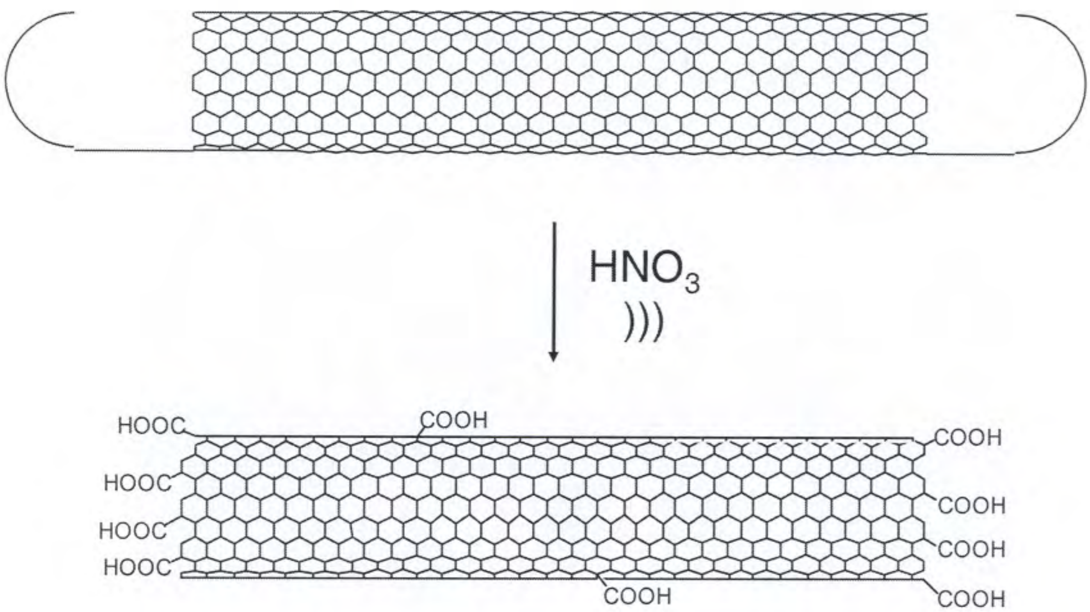
Direct Phase HPLC on Fullerene-Modified Stationary Phase
Separation of ᵗButyl-Calix-n-Arenes

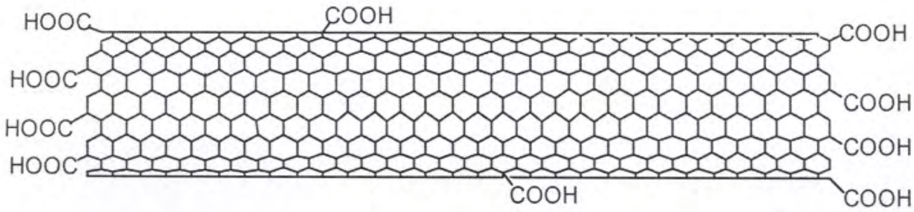


Column: Silica-Bound Fullerene
250 x 2 mm ID
Eluent: 0.5% 2-propanol in CH_2Cl_2
Flow Rate: 0.5 ml/min
Detector: UV @ 280 nm

J. Amer. Chem. Soc. **1997**, *119*, 7550

Most common way to purify SWNT



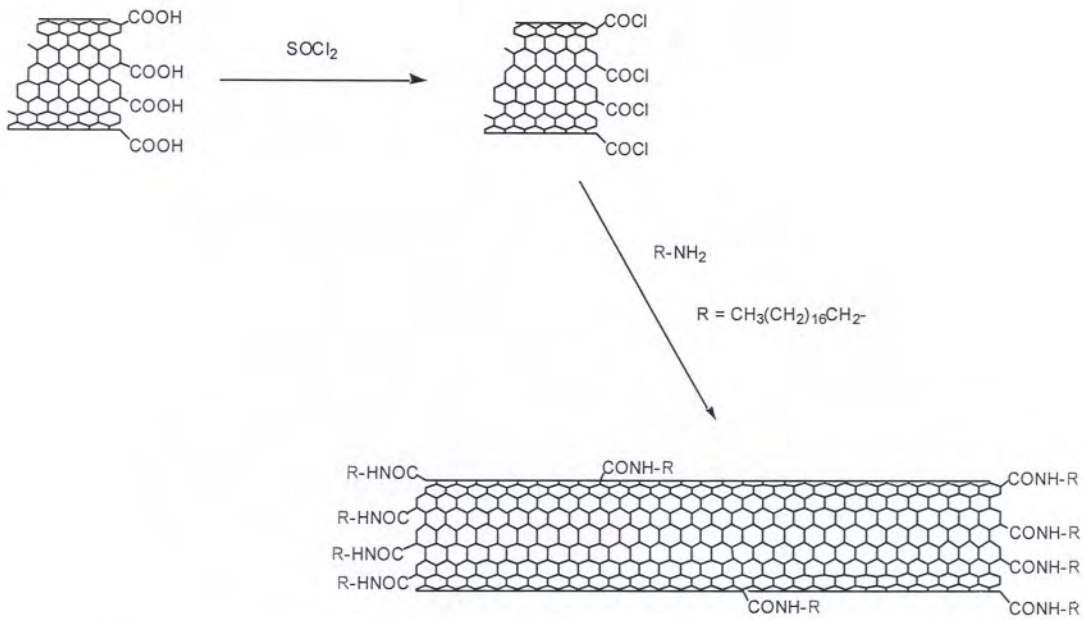


Disadvantages:

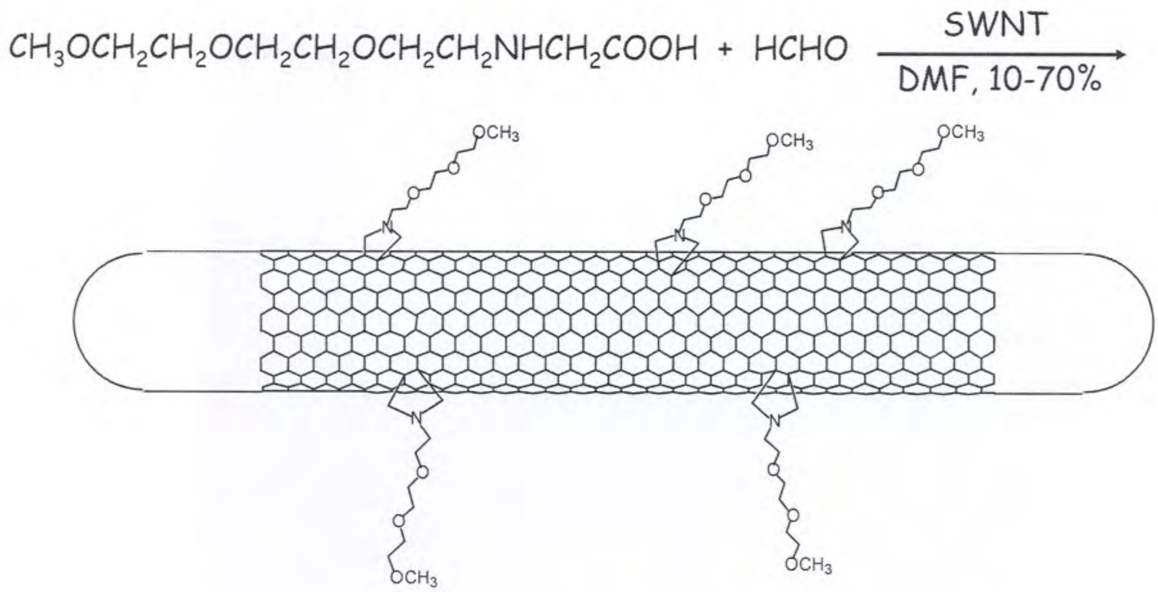
partial loss of structure
loss of material
increased number of defects

Advantages:

cleaner materials
carboxylic groups allow for further functionalization

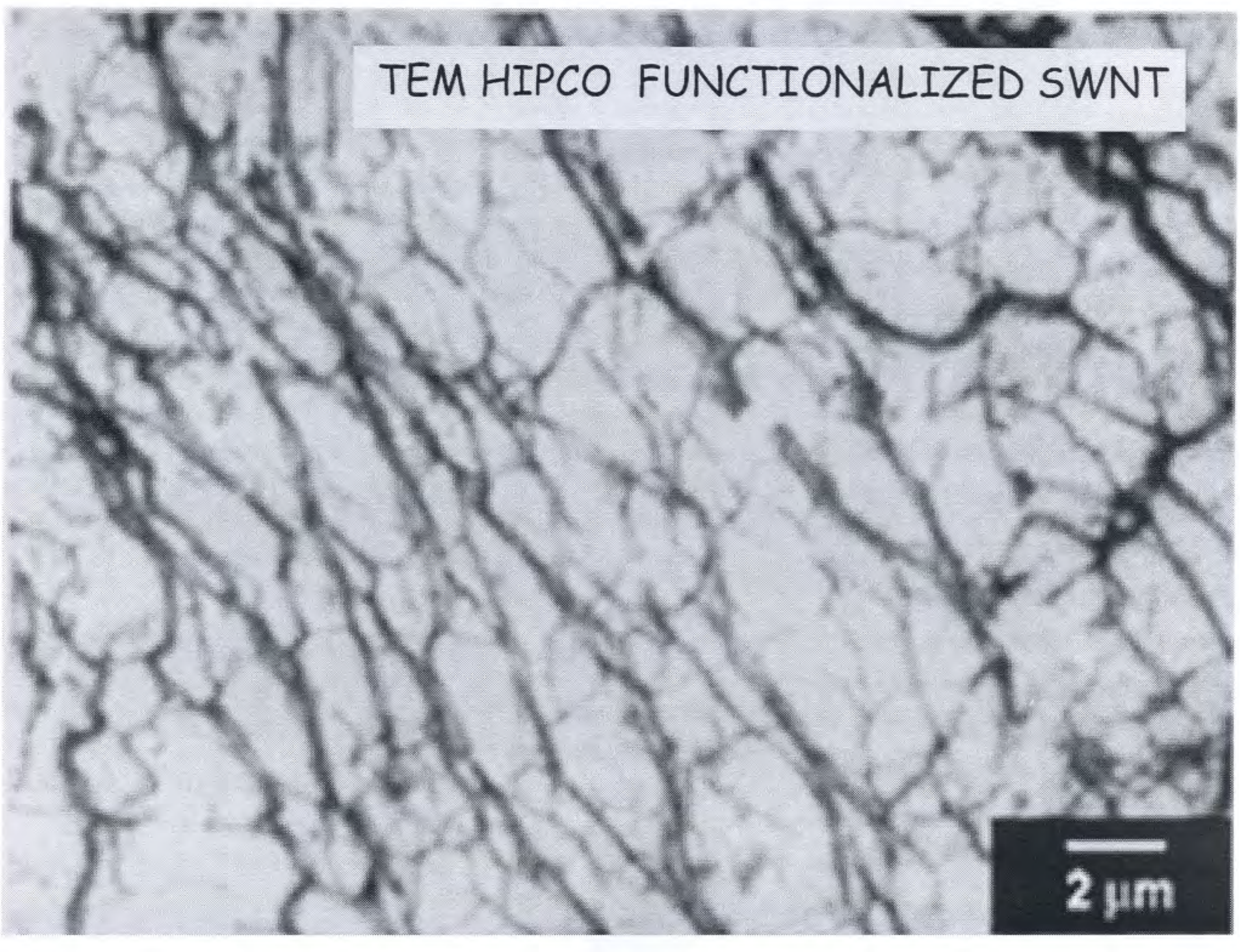


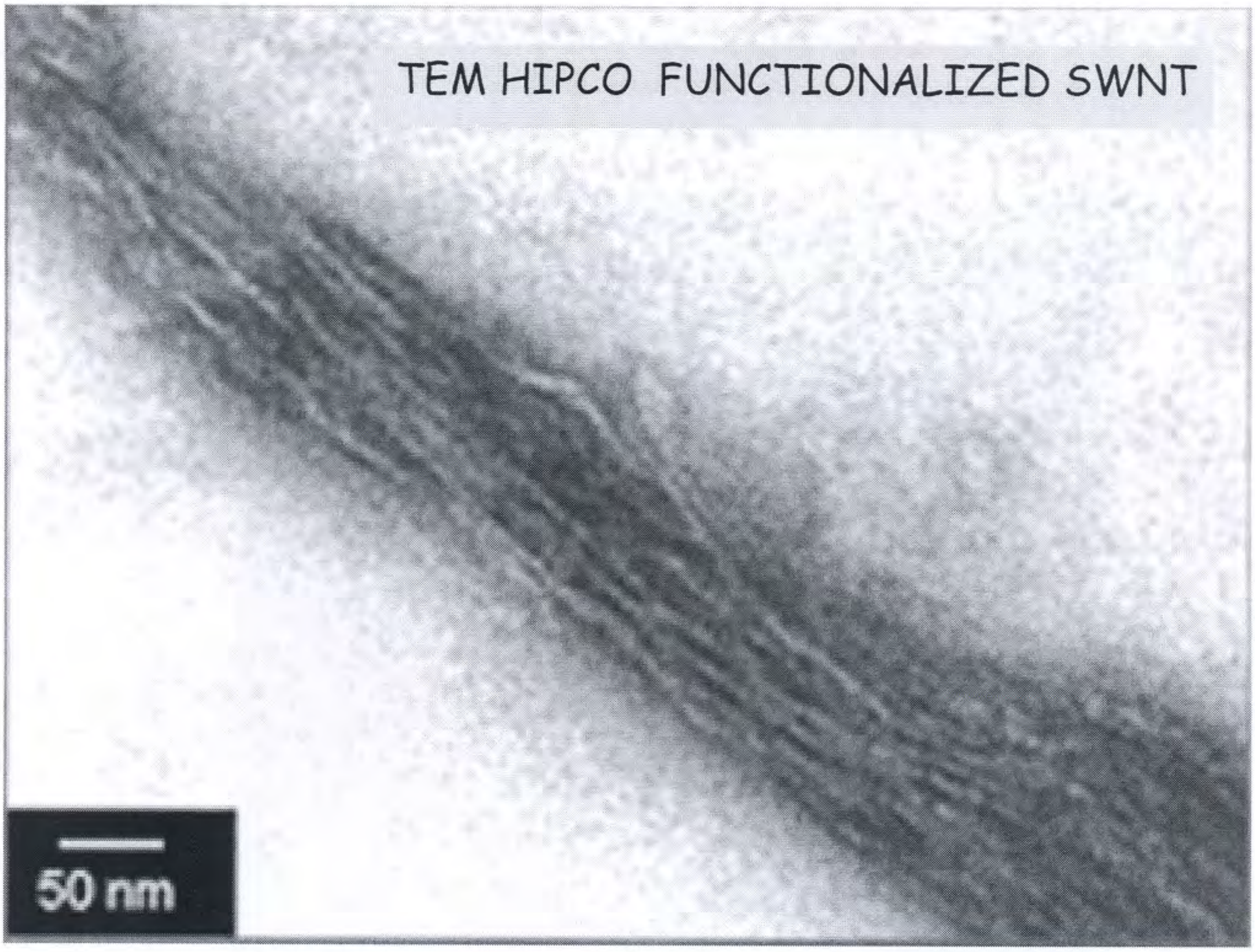
R.C. Haddon et al, *Science,* **1998,** *282,* 95-98.



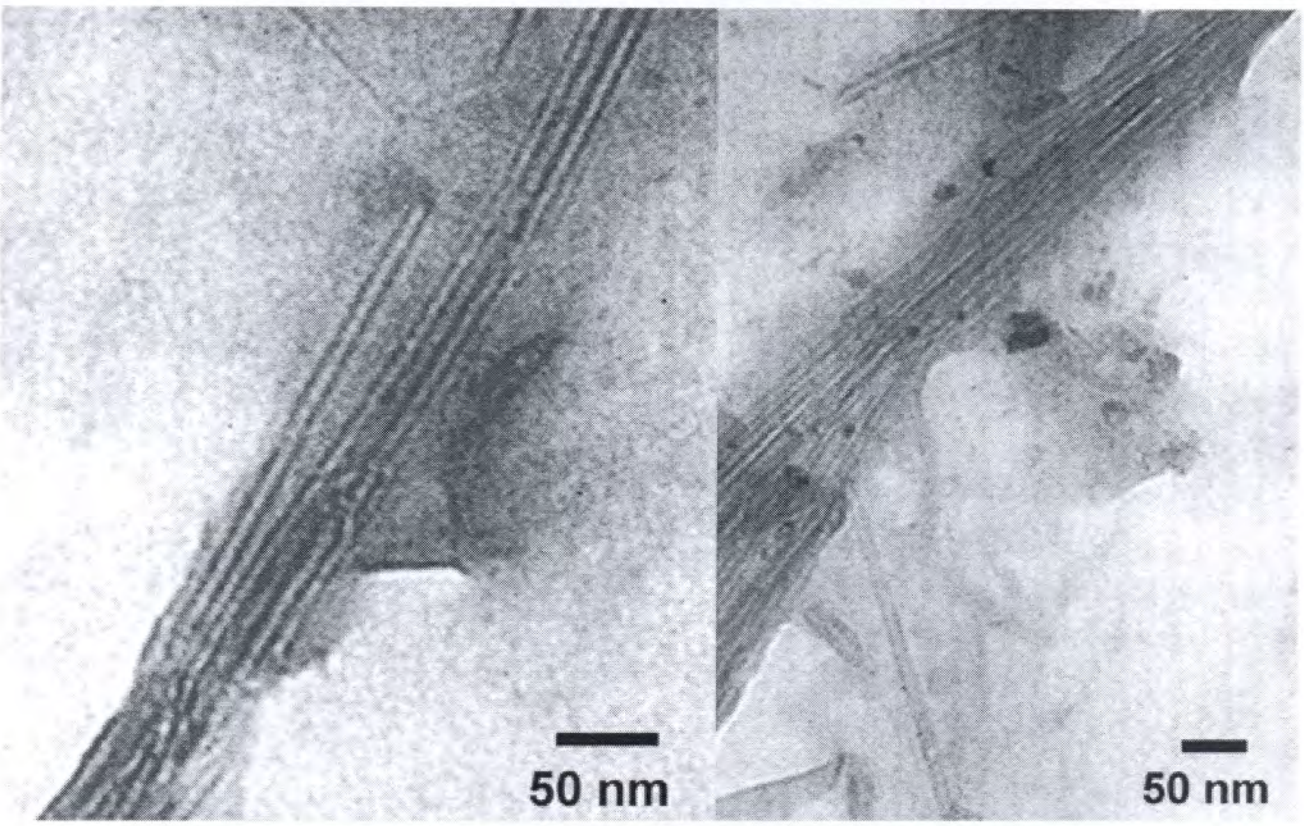
Degree of functionalization: 1 pyrrolidine group every 100 carbon atoms

Georgakilas et al. JACS 2002, **124**, 760



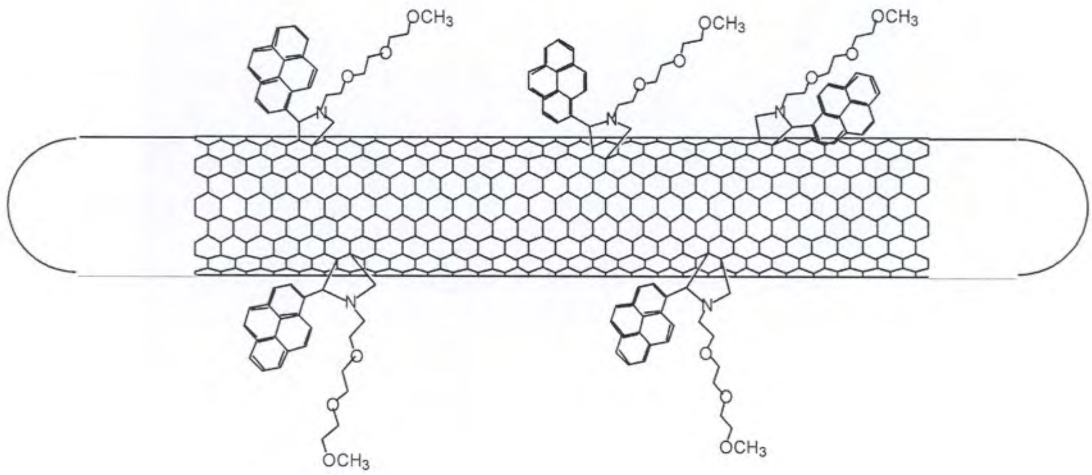


TEM HIPCO FUNCTIONALIZED SWNT

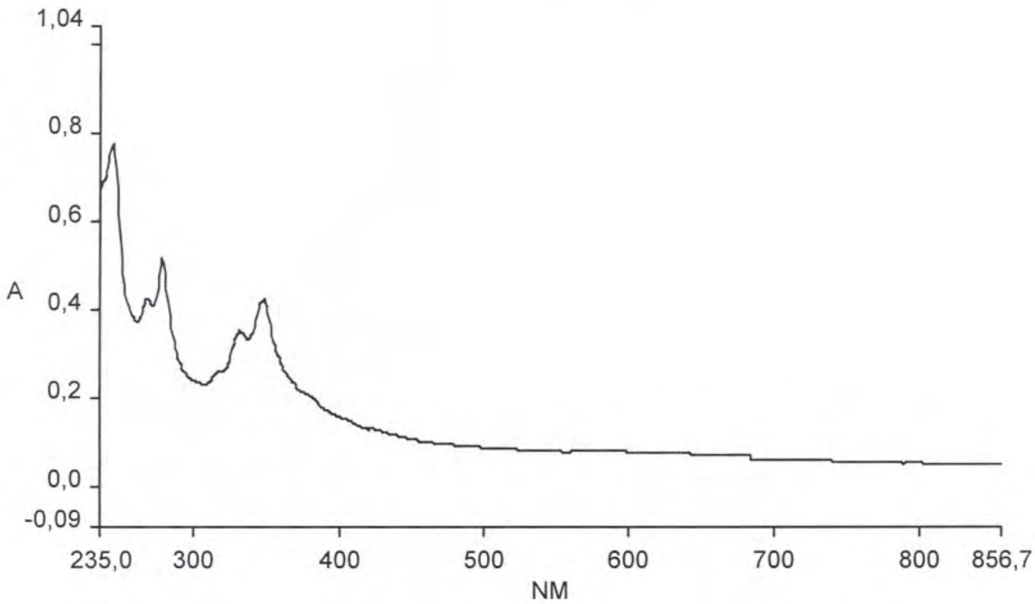


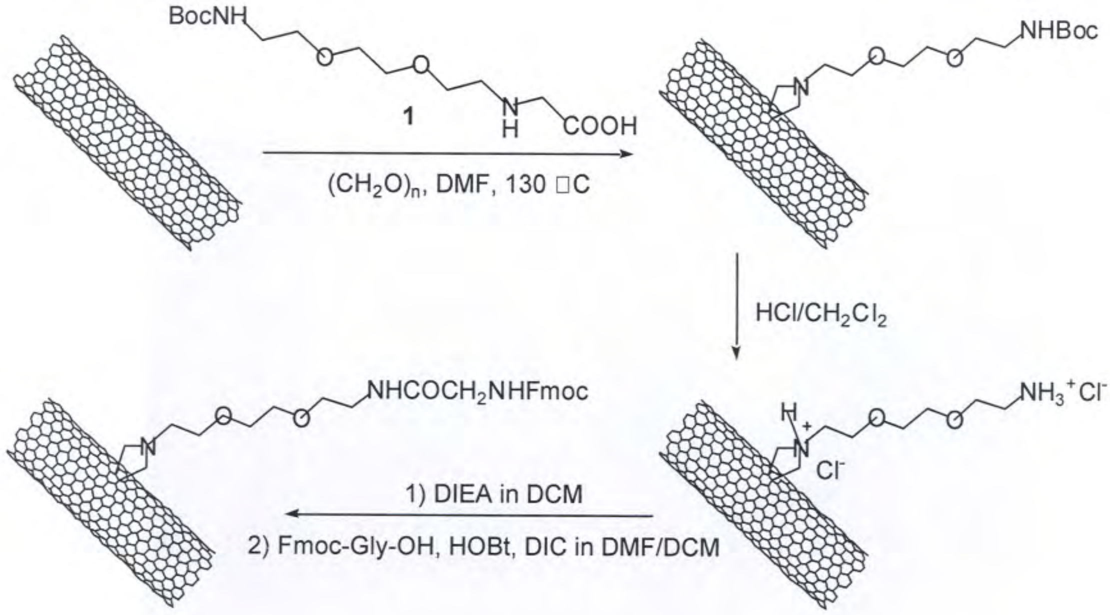
TEM ARC DISCHARGE FUNCTIONALIZED MWNT

$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2NHCH_2COOH + \text{Pyrene-CHO} \xrightarrow{\text{SWNT}}$$



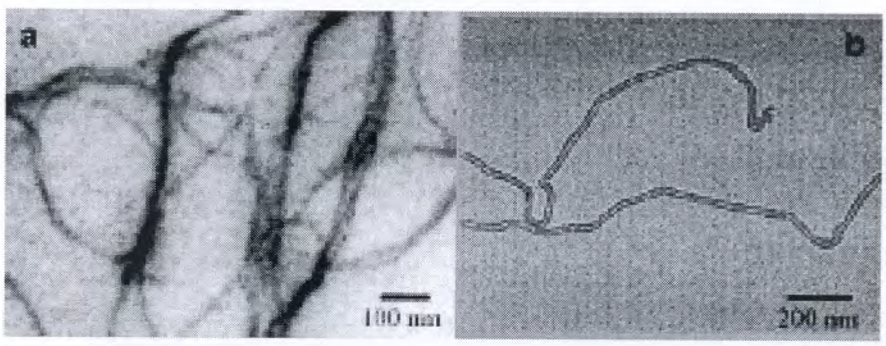
UV-VIS ARC DISCHARGE PYRENE- FUNCTIONALIZED SWNT

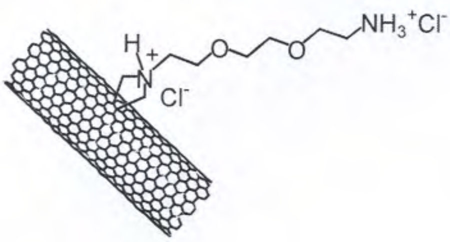




Chem. Commun. **2002**, 3050-3051

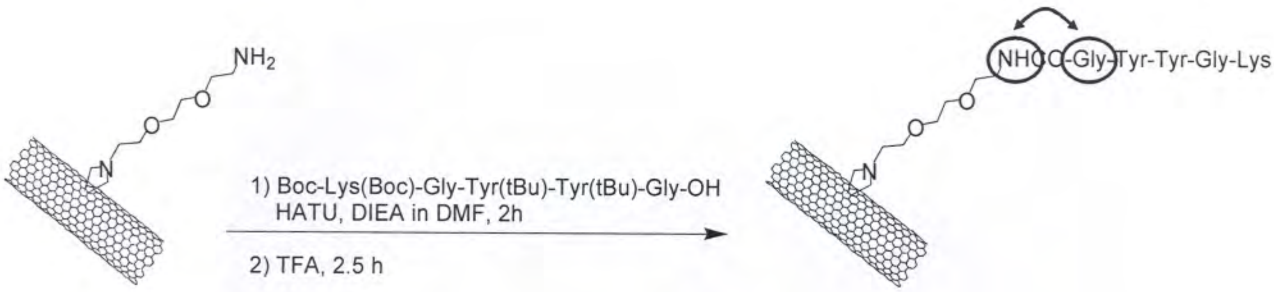
TEM OF WATER SOLUBLE SWNT AND MWNT





Chem. Commun. **2002**, 3050-3051

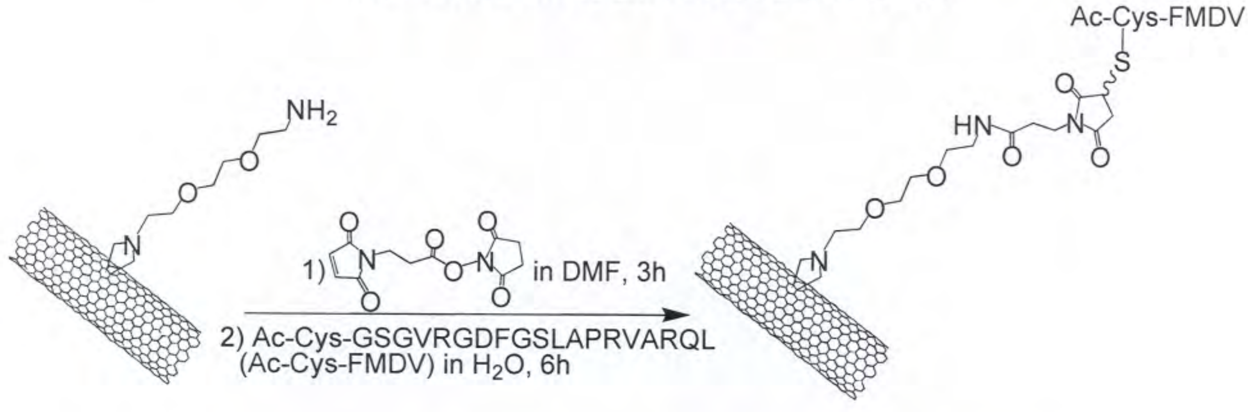
SYNTHESIS OF A WATER SOLUBLE SWNT PENTAPEPTIDE BY FRAGMENT CONDENSATION



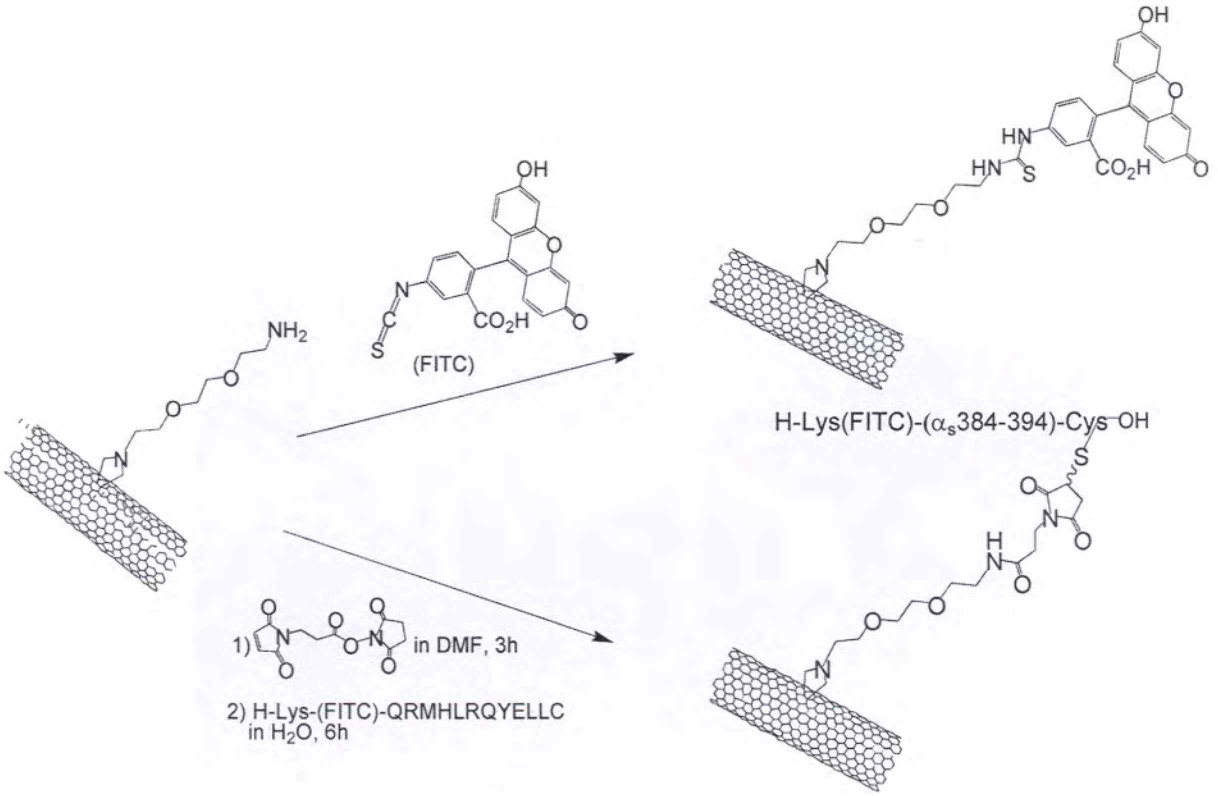
1) All the diagnostic signals were identified by (2D) NMR spectra
2) A spatial correlation between the αH of glycine and NH-glycol confirmed the covalent bonding of the peptide to the SWNT

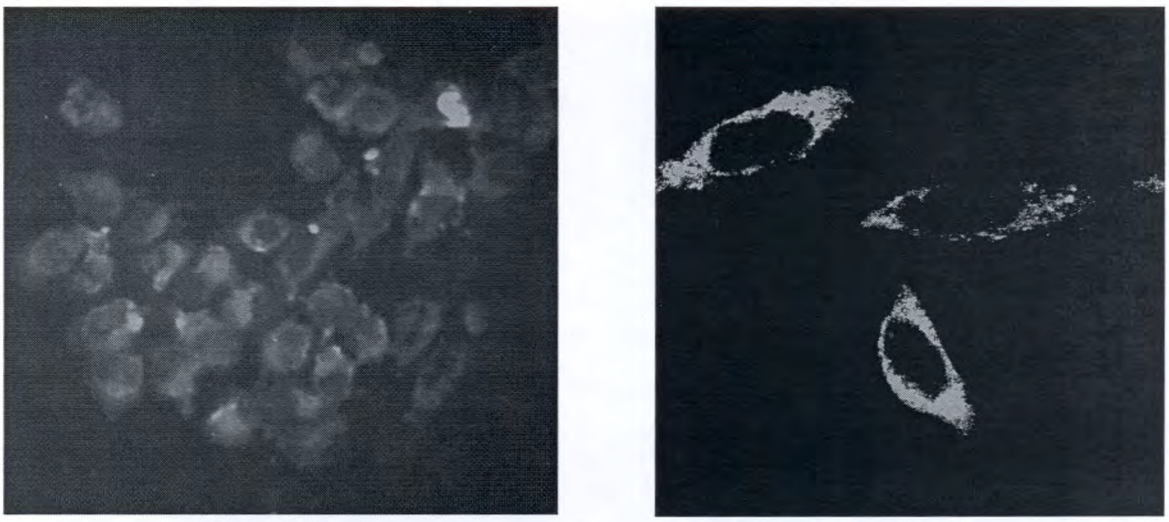
With Dr A. Bianco, CNRS Strasbourg

SYNTHESIS OF A BIOACTIVE SWNT EICOSAPEPTIDE BY CHEMOSELECTIVE LIGATION



1) B-cell epitope from the foot-and-mouth disease virus (FMDV);
2) This peptide elicits neutralizing antibody response for protection;
3) On SWNT, this peptide keeps the same conformational behavior;
4) Antibodies recognize the FMDV peptide attached to SWNT;
5) No anti-SWNT antibodies are induced;
6) In vivo experiments demonstrate that peptide-nanotube conjugates are immunogenic, eliciting antibody responses of the right specificity.





Epifluorescence Microscopy   Confocal Microscopy

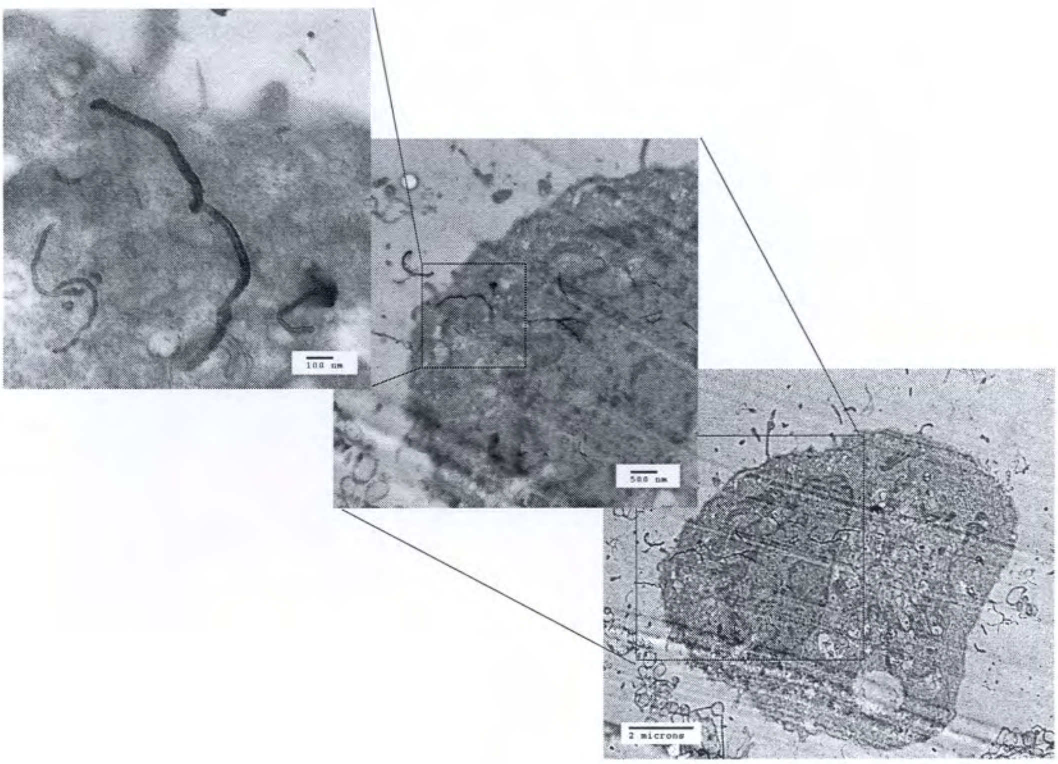
FITC-SWNT accumulate mainly in the cytoplasm

Epifluorescence Microscopy

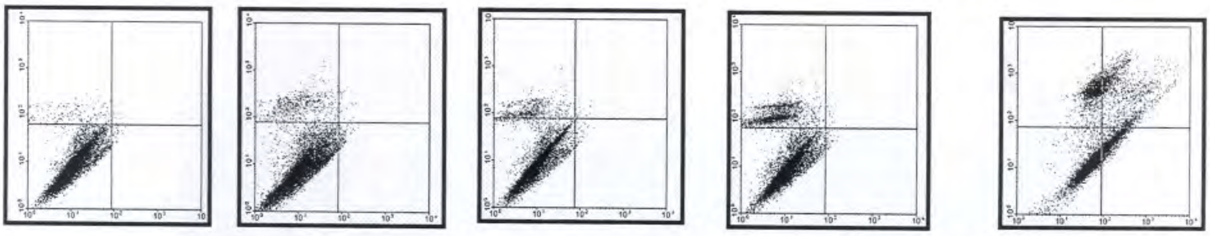
+ DAPI

Peptide-SWNT accumulate mainly in the nuclei

HeLa cells incubated with 10μM MWNT-$NH_3^+Cl^-$ washed, fixed, stained, embedded, sectioned and analysed by TEM (75 kV).



Cell Viability of Functionalized Carbon Nanotubes



Control 0.01 mg/ml 0.1 mg/ml 1 mg/ml 10 mg/ml

Cell viability was studied using flow cytometry by treating HeLa cell cultures with increasing doses of *f*-SWNT and *f*-MWNT and for long incubation times. Only 50% of the cells died after a 6-hour incubation period with 5-10 mg/ml of nanotube solution, a concentration considered excessively high

D. Pantarotto et al, 2004, Angew. Chem. in press

Conclusions and Perspectives

CNT can be made water soluble by organic functionalization and can be derivatized with peptides

CNT present peptides with the right conformation for antibody recognition

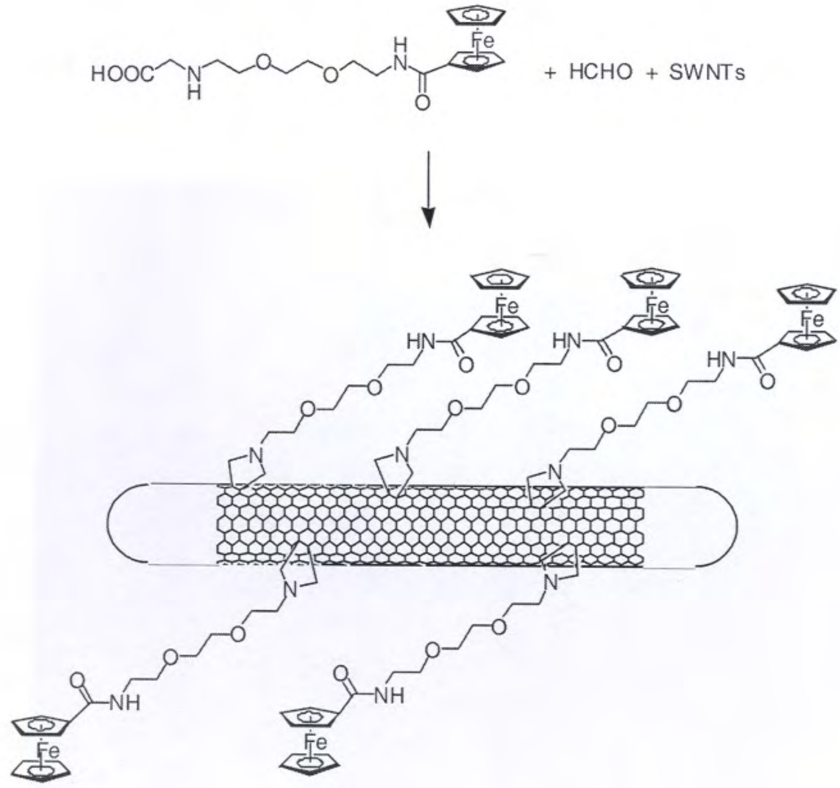
Peptide-CNT conjugates are immunogenic

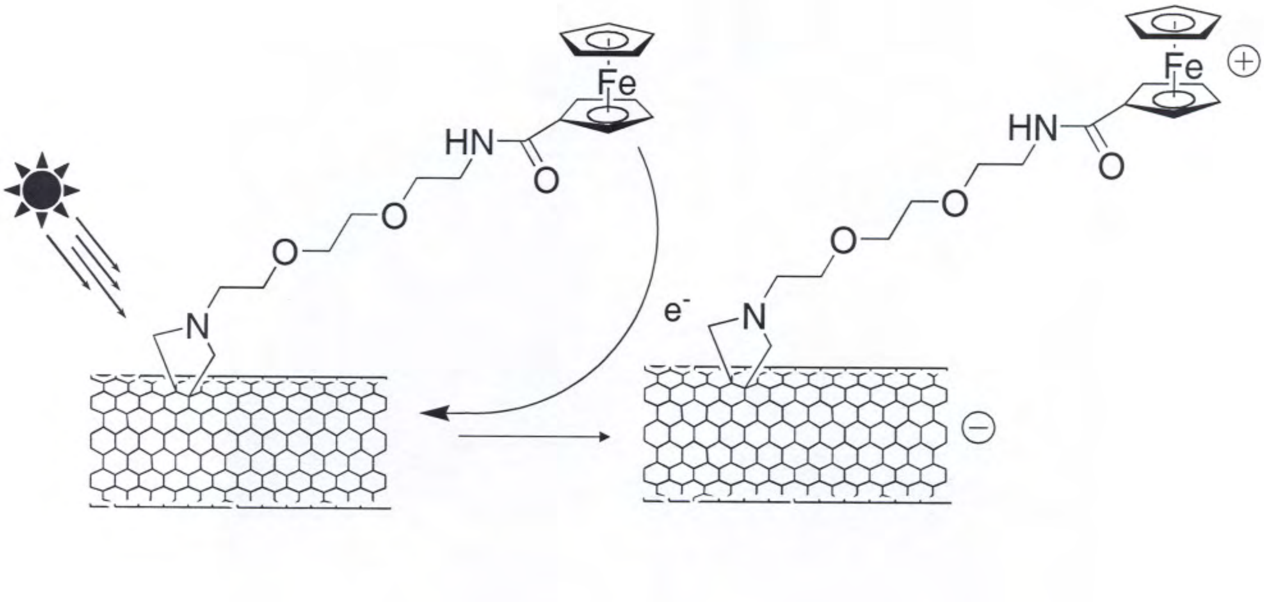
CNT devoid of peptide moiety are not immunogenic

CNT present peptides to the immune system in an efficient way and could have potential applications for future vaccine delivery

CNT are able to penetrate the cell membrane and can have potential applications in drug delivery

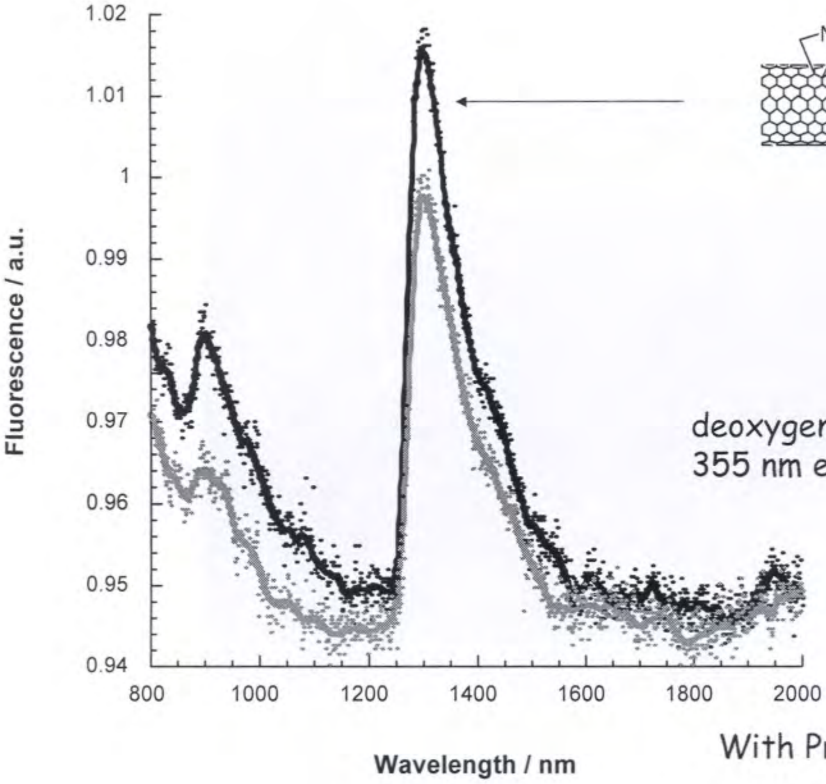
JACS & Chem. Biol., 2003

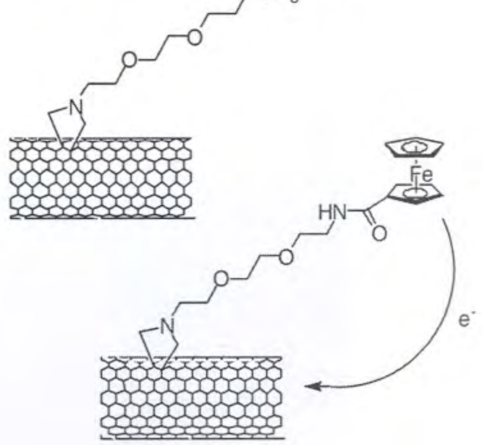




Angew Chem 2003

Fluorescence Spectra of Functionalized SWNT

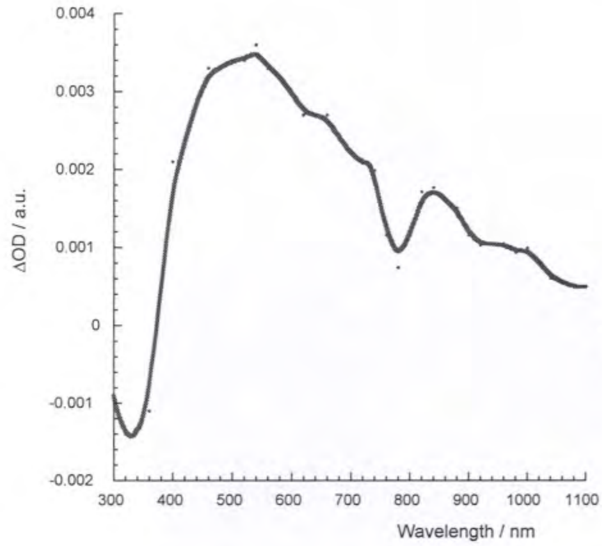


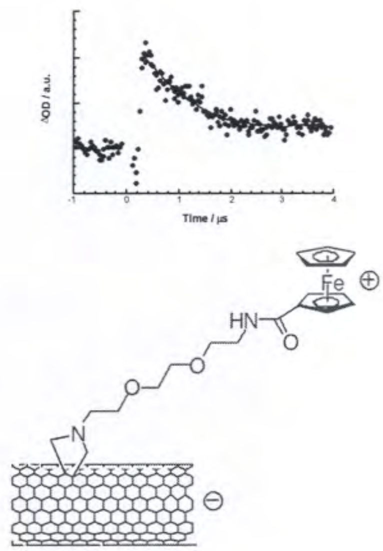


deoxygenated dichloromethane
355 nm excitation (OD_{355nm} = 0.5)

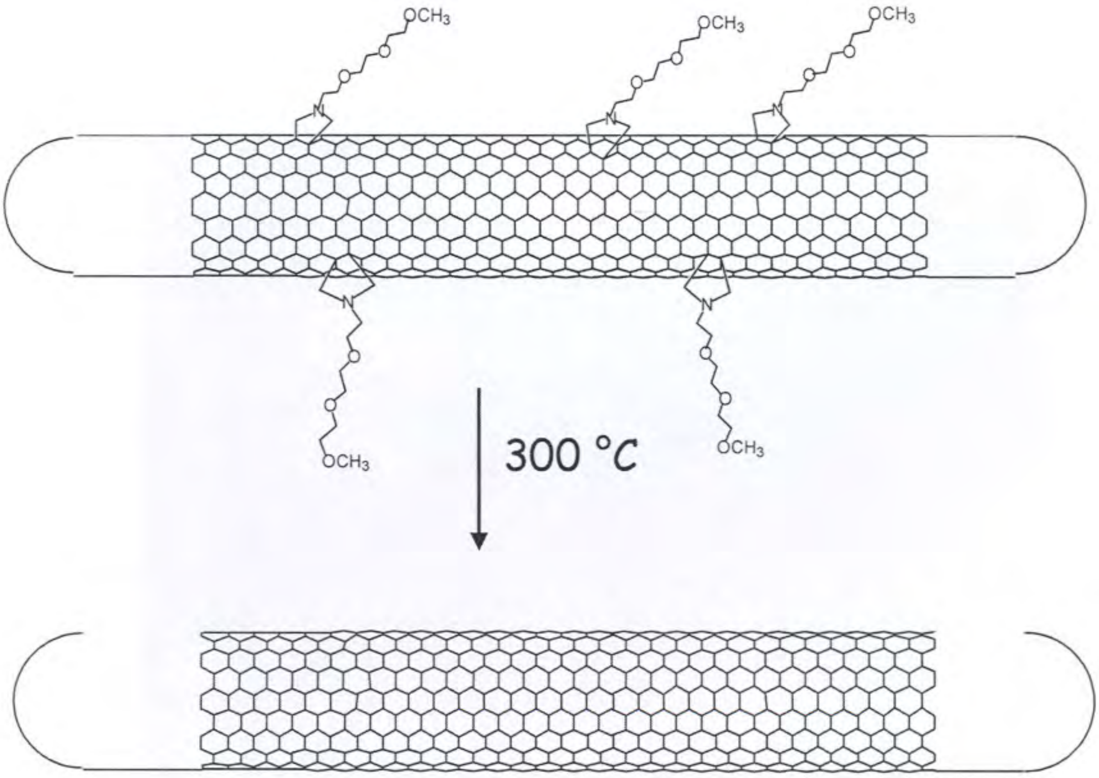
With Prof. D. Guldi, U Notre Dame

Photoinduced Transient Absorption Spectra

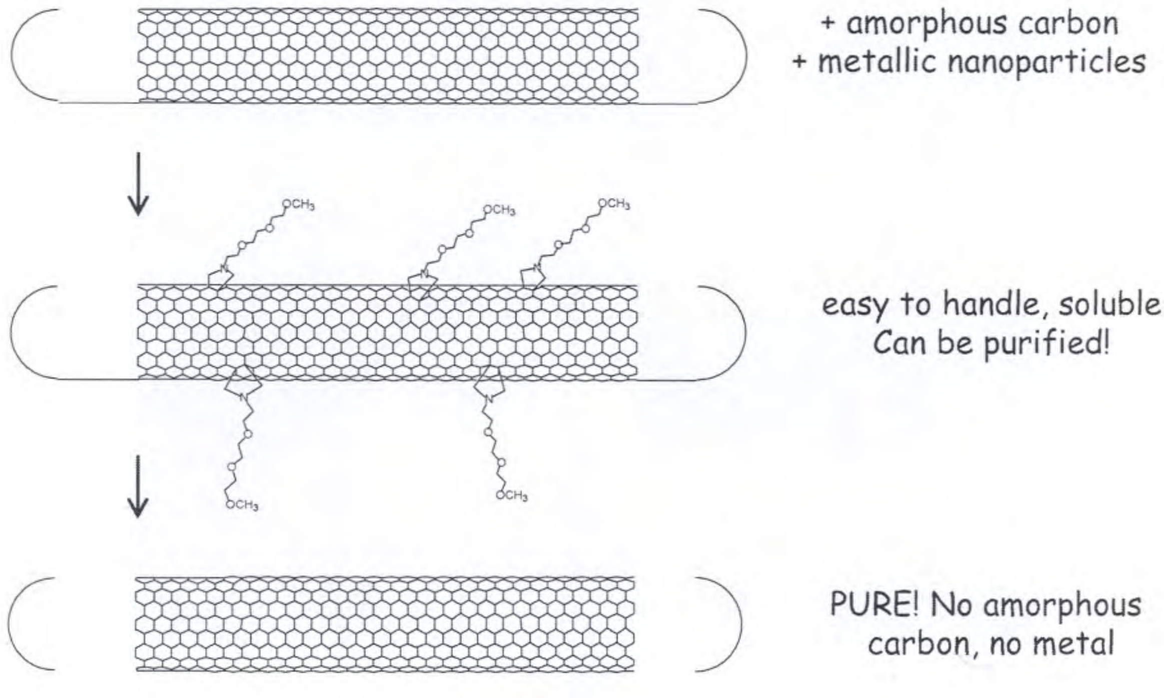




deoxygenated dichloromethane
50 ns following an 8 ns 355 nm laser pulse

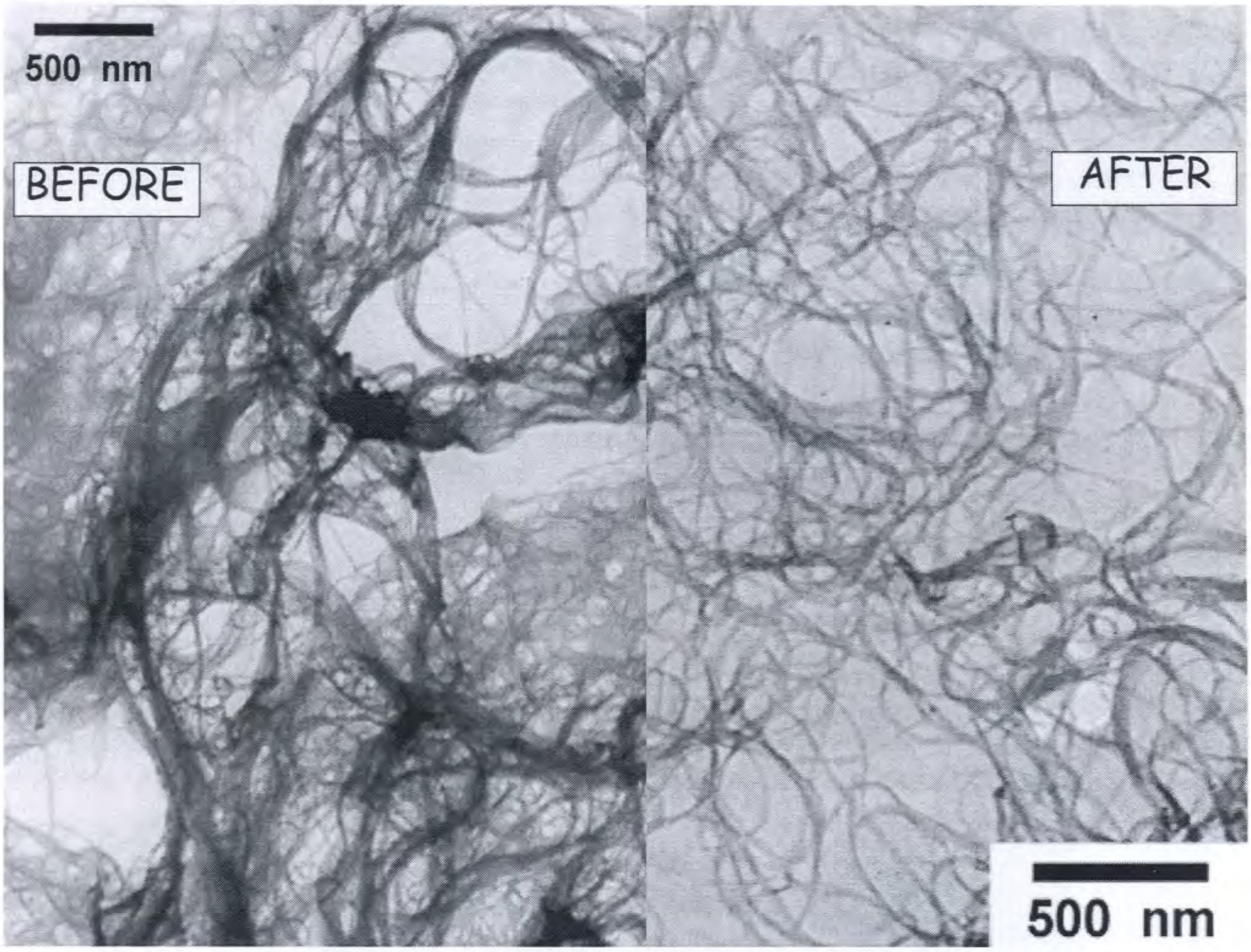


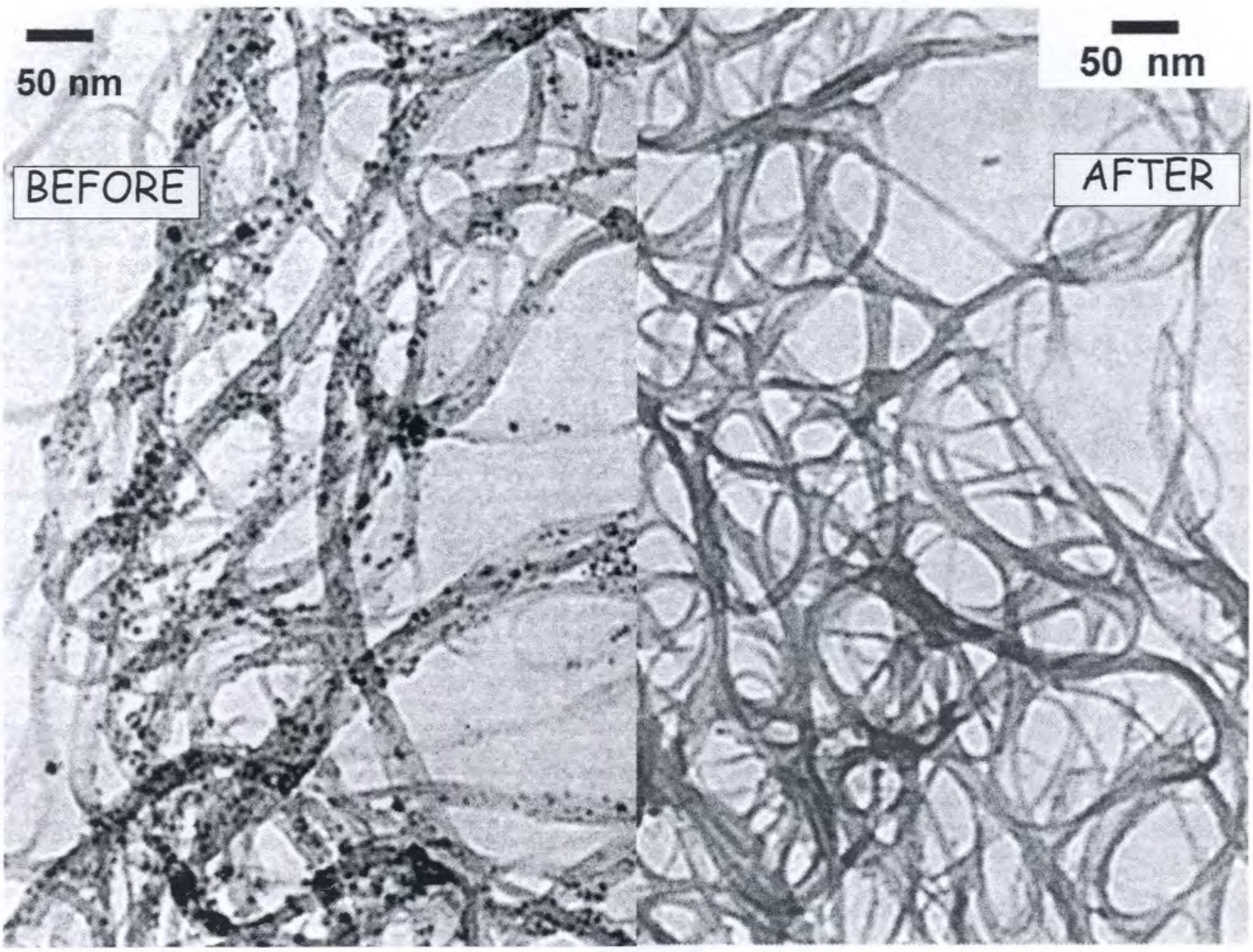
A New Methodology for the Purification of SWNTs



J. Am. Chem. Soc. **2002**, *124*, 14318-14319

PCT/EP03/08350


500 nm
BEFORE
AFTER
500 nm


50 nm
BEFORE
50 nm
AFTER