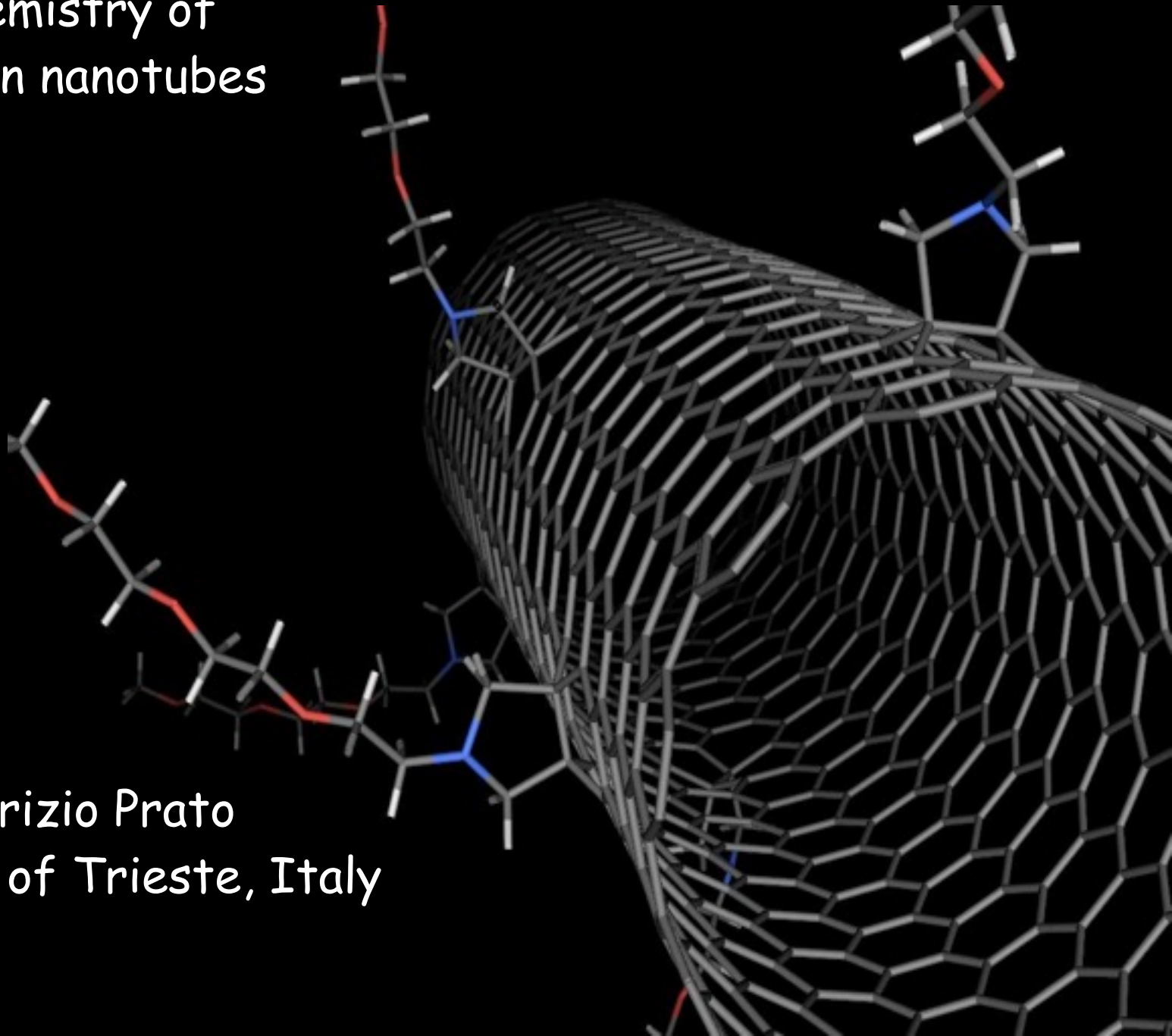
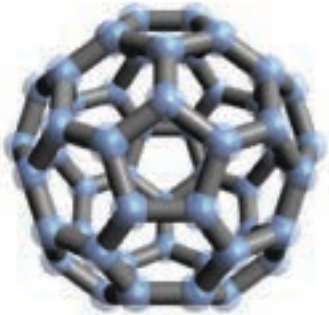
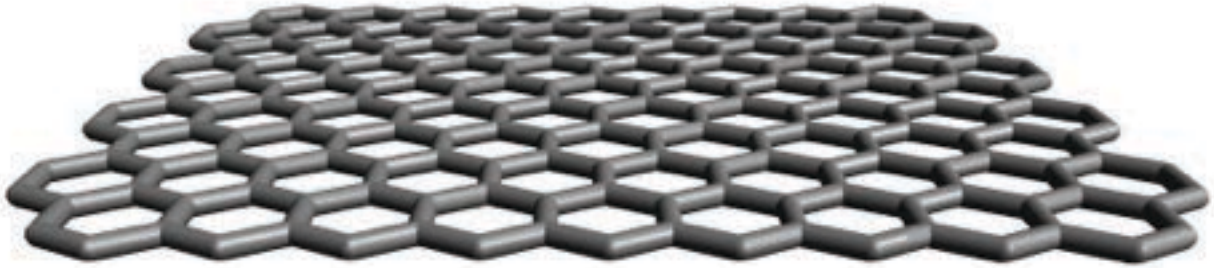
Chemistry of carbon nanotubes



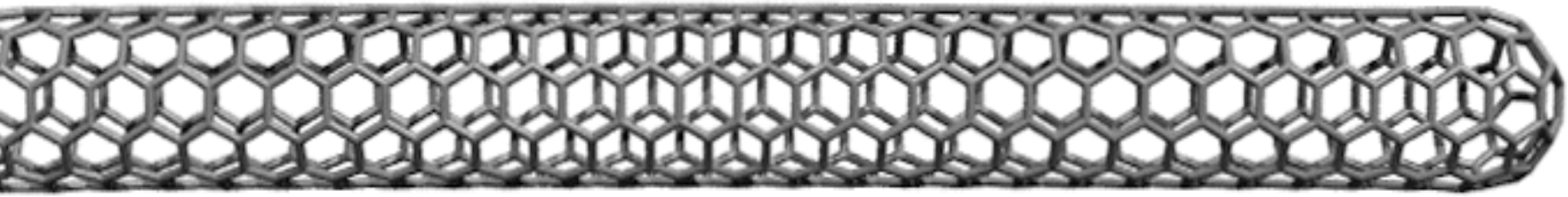
Maurizio Prato
University of Trieste, Italy



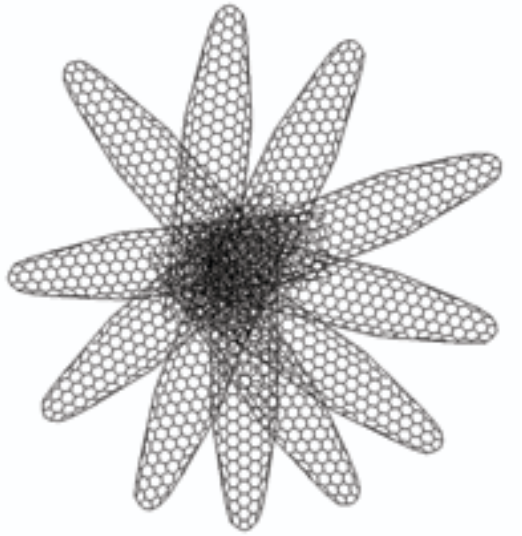
fullerene



graphene

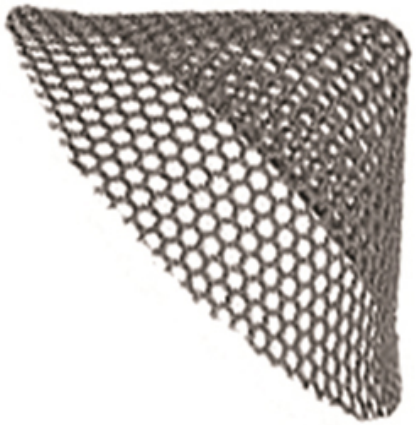


nanotube



carbon nanohorns

electron transduction

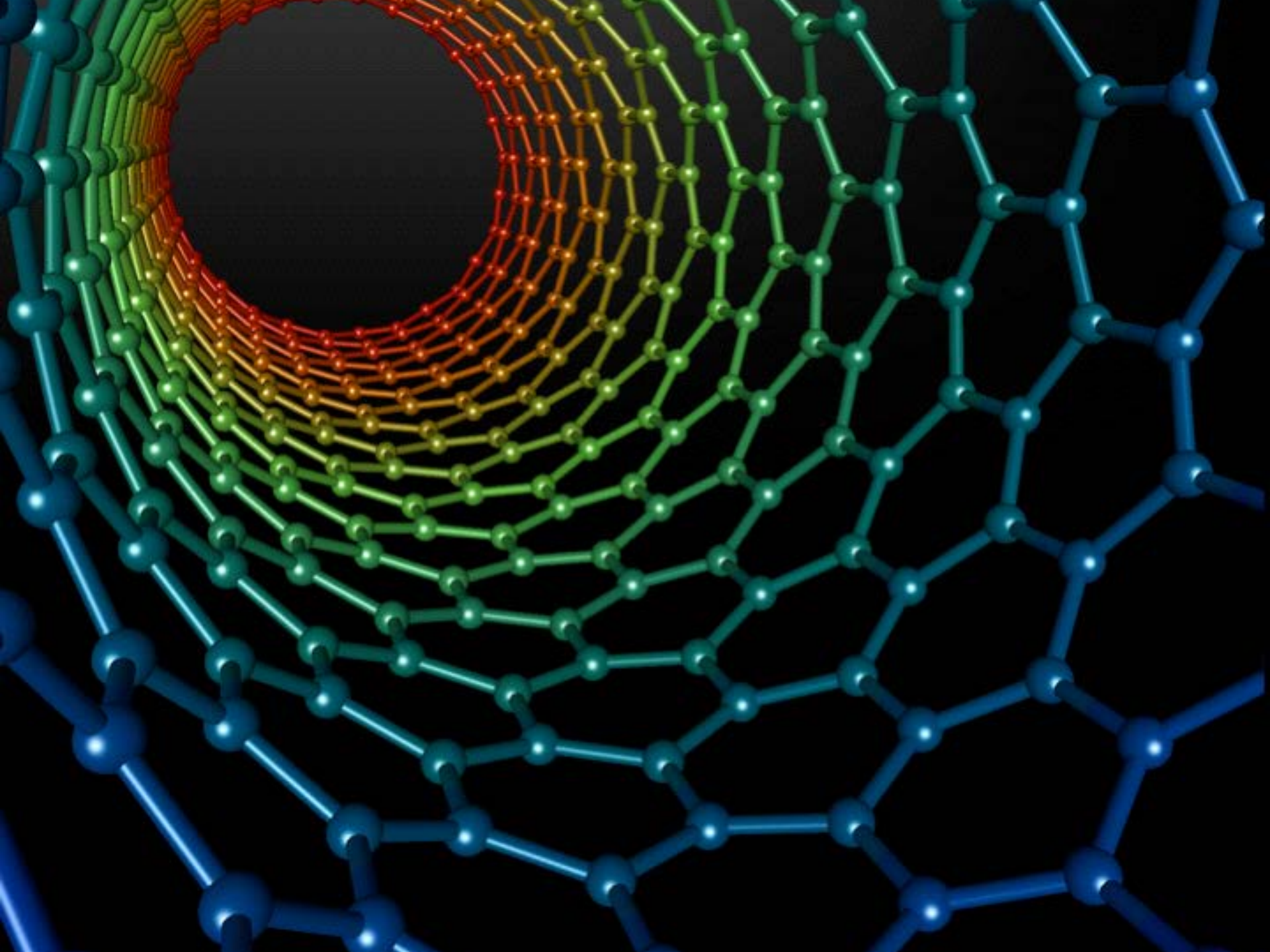


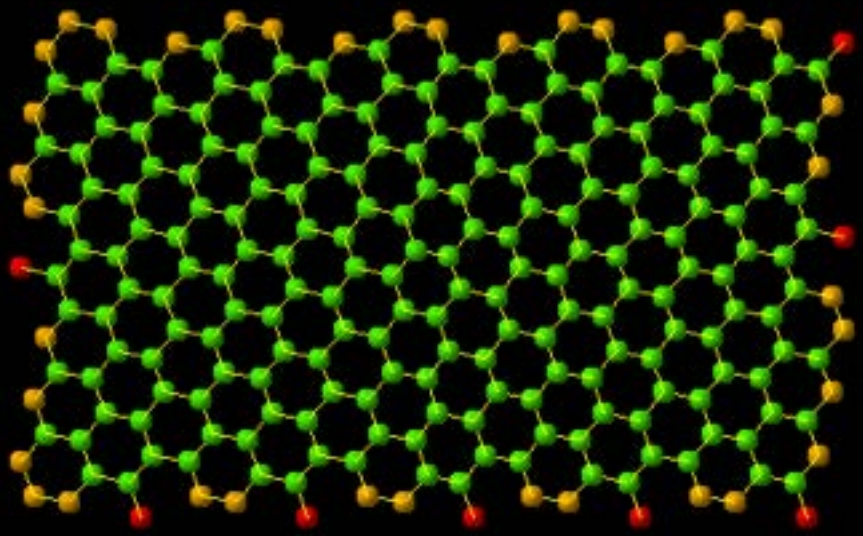
carbon nanocones

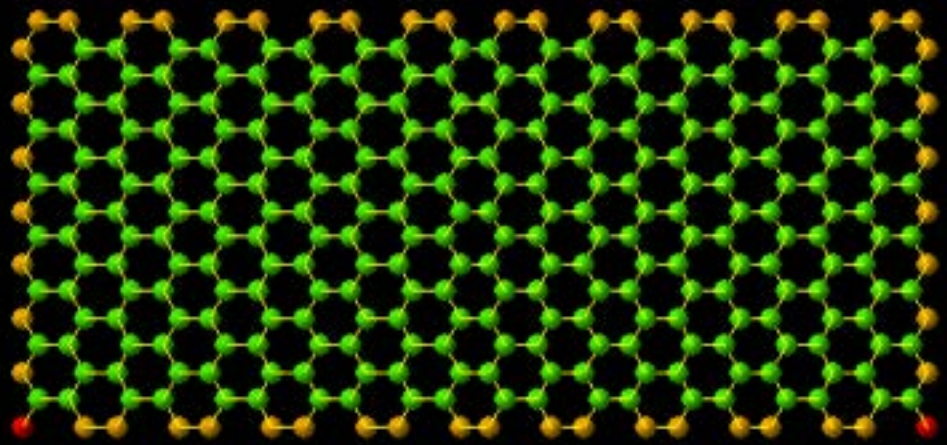
Just one Material, so much Potential (NASA)

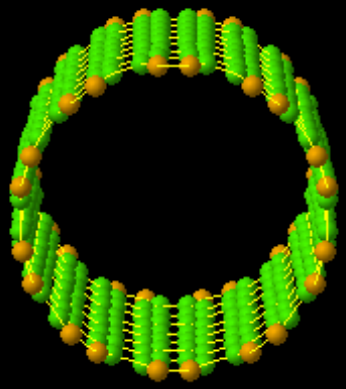
http://www.ipt.arc.nasa.gov/spacetransport.html

Floyd Landis

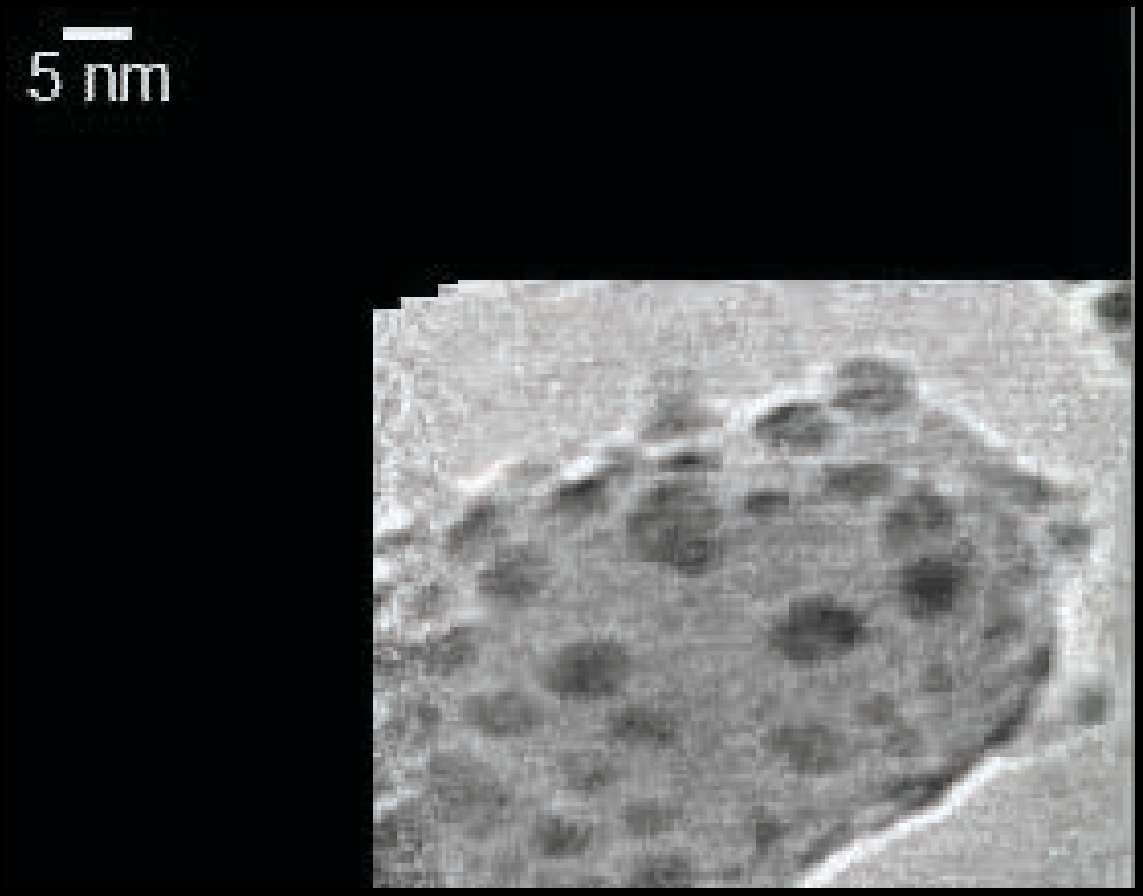




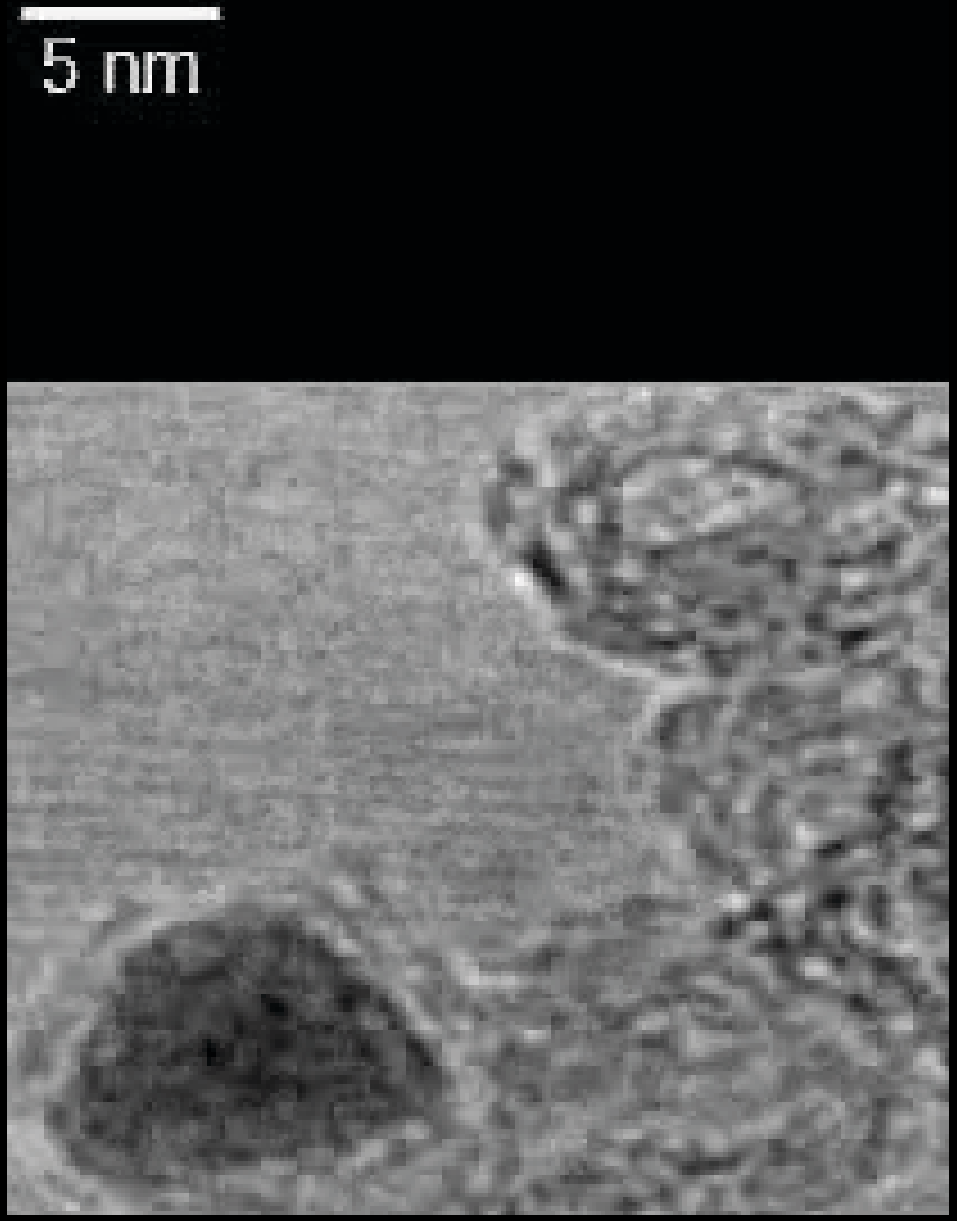




Movies from: http://www.photon.t.u-tokyo.ac.jp/~maruyama/nanotube.html

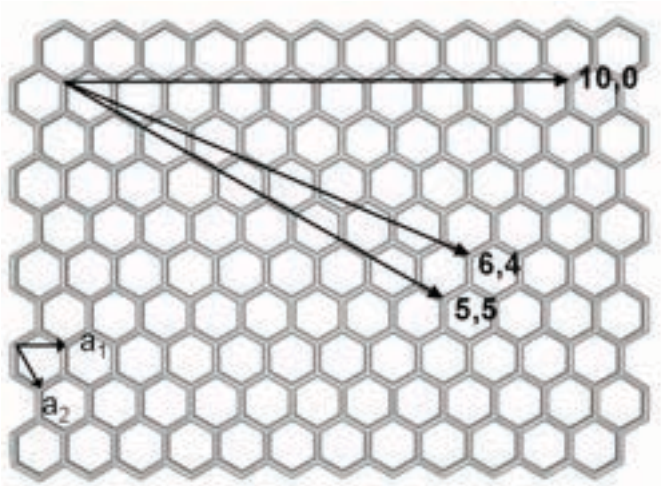


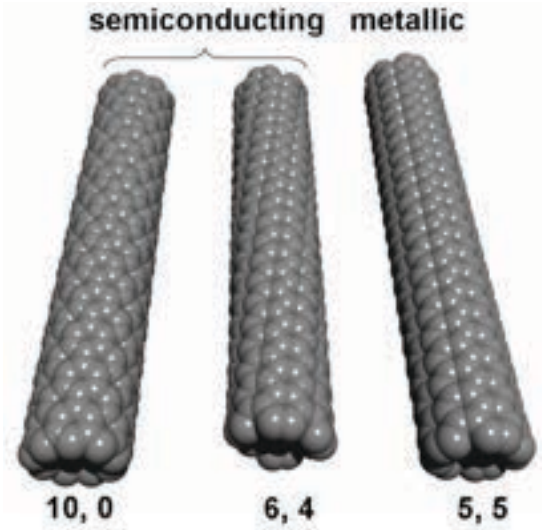
Courtesy of S. Hofmann, U Cambridge



Courtesy of S. Hofmann, U Cambridge

Atomic resolution STM



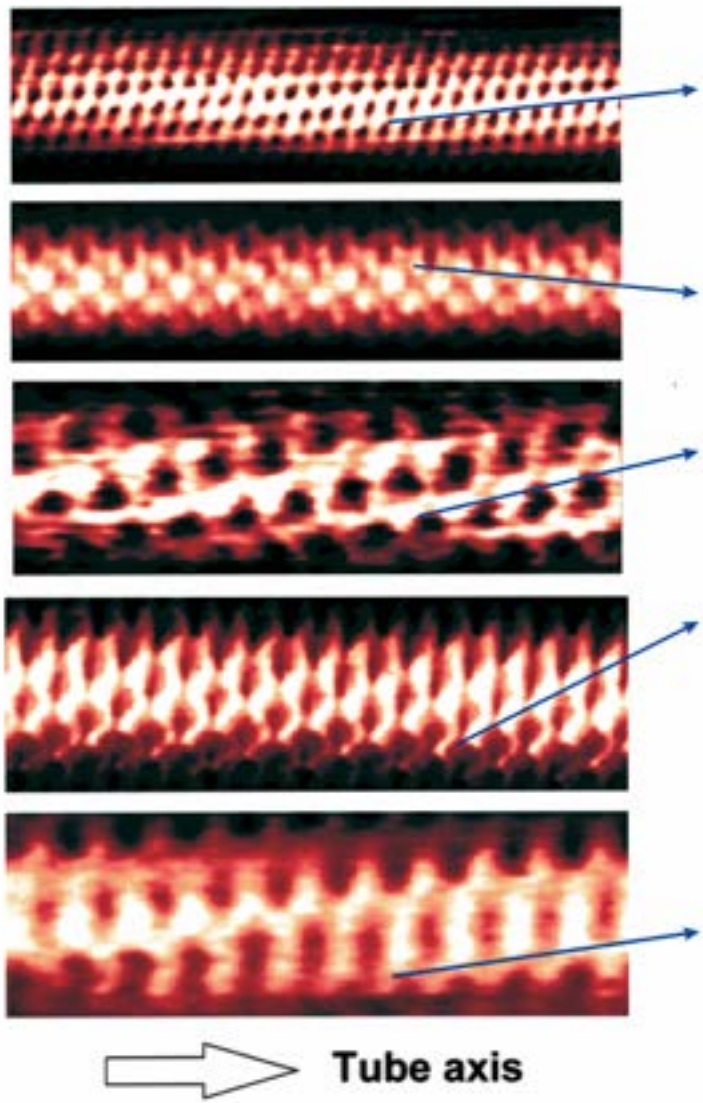


Zigzag

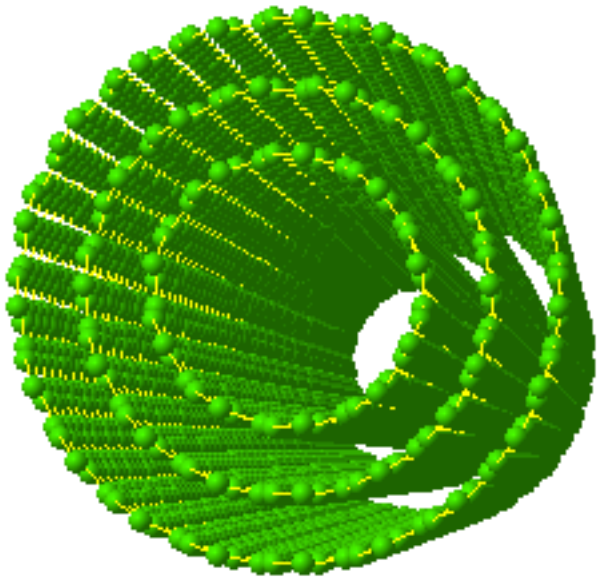
Armchair

chiral index (n, m):. nanotubes in which n = m are metallic and quasi-metallic (with tiny band gap) if n-m is divisible by 3. All other tubes are semiconducting with band gaps of the order of 0.5 eV

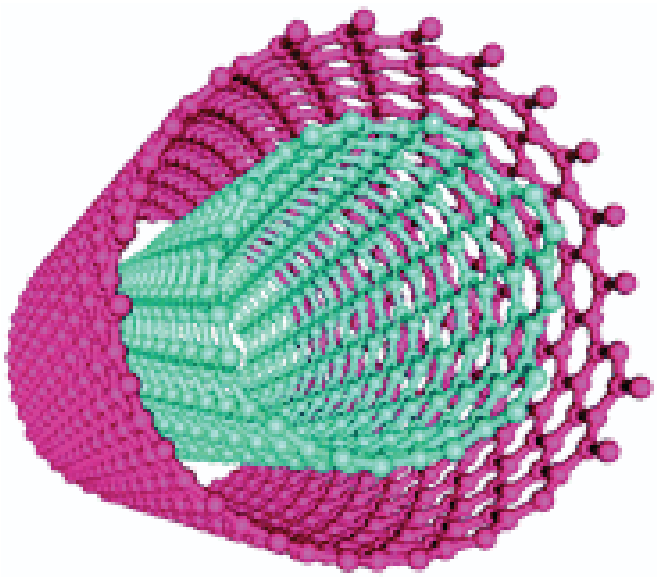
Large variety of helicities



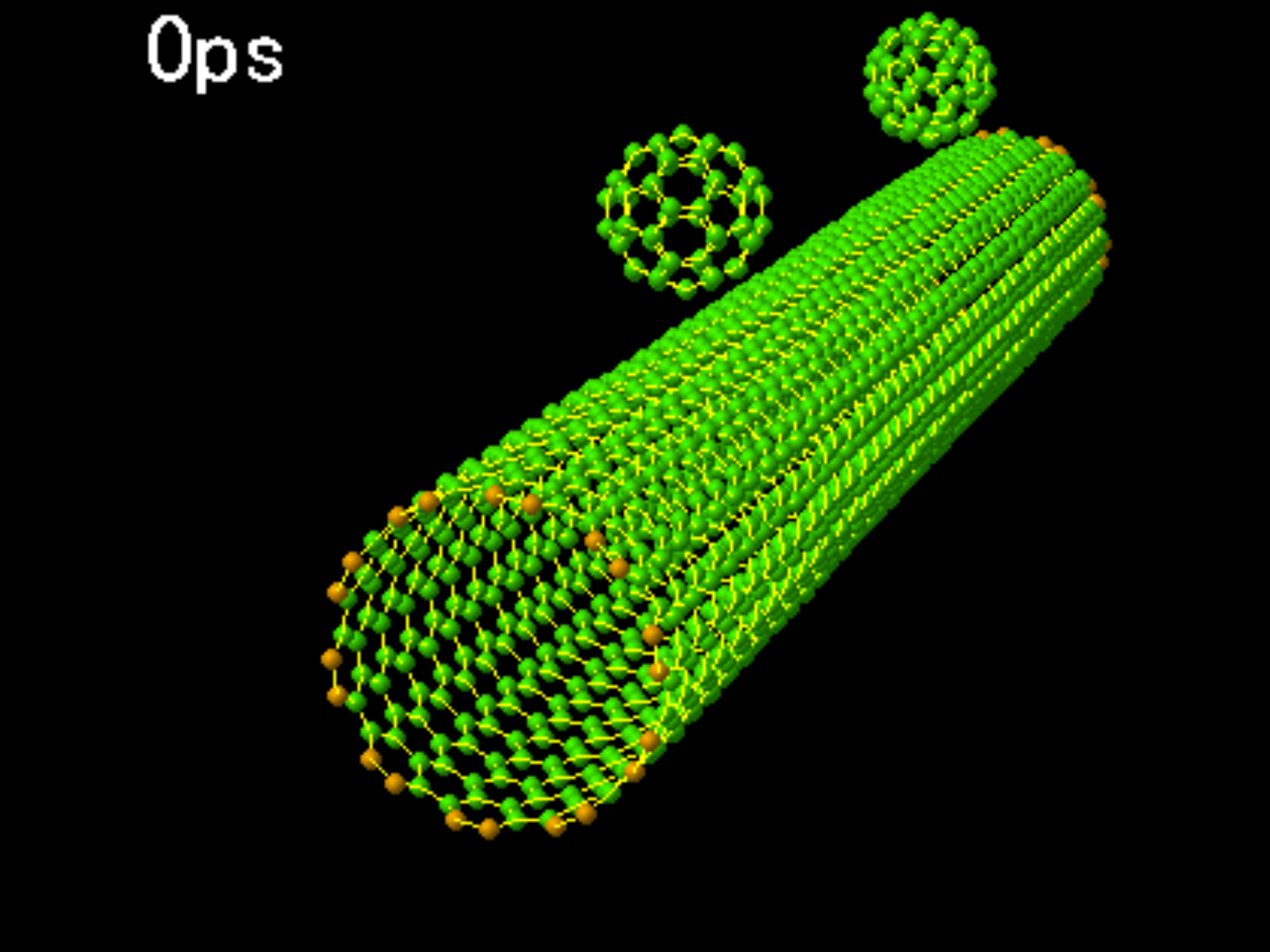
Taken from Cees Dekker (Delft, NL) website

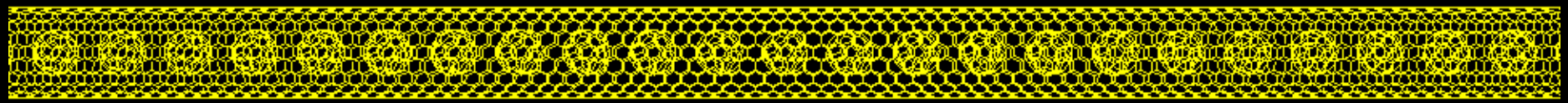


Multiwall nanotubes

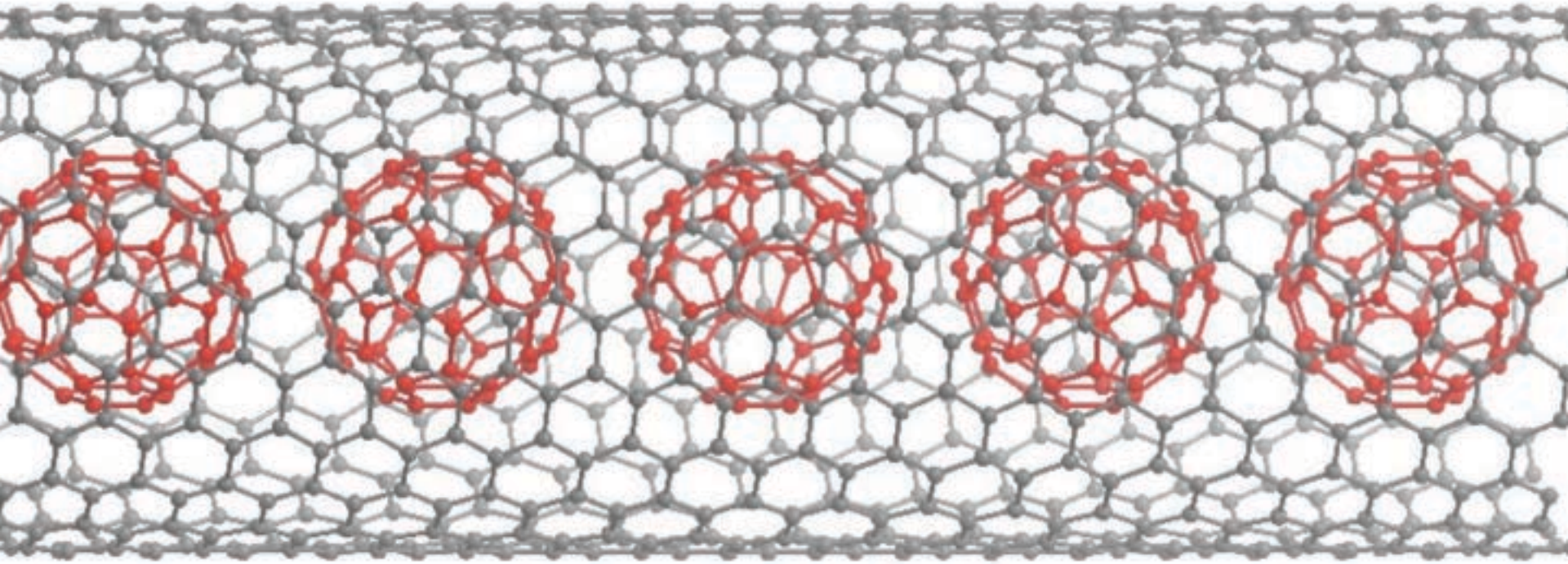


Double wall nanotubes

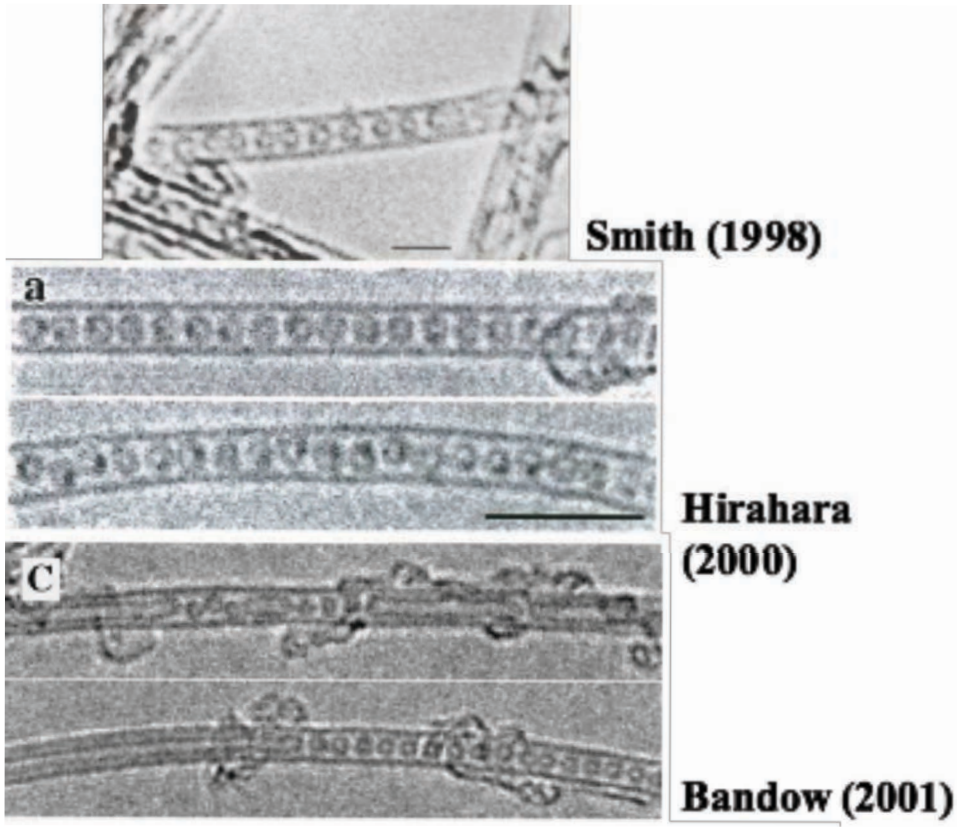

0ps

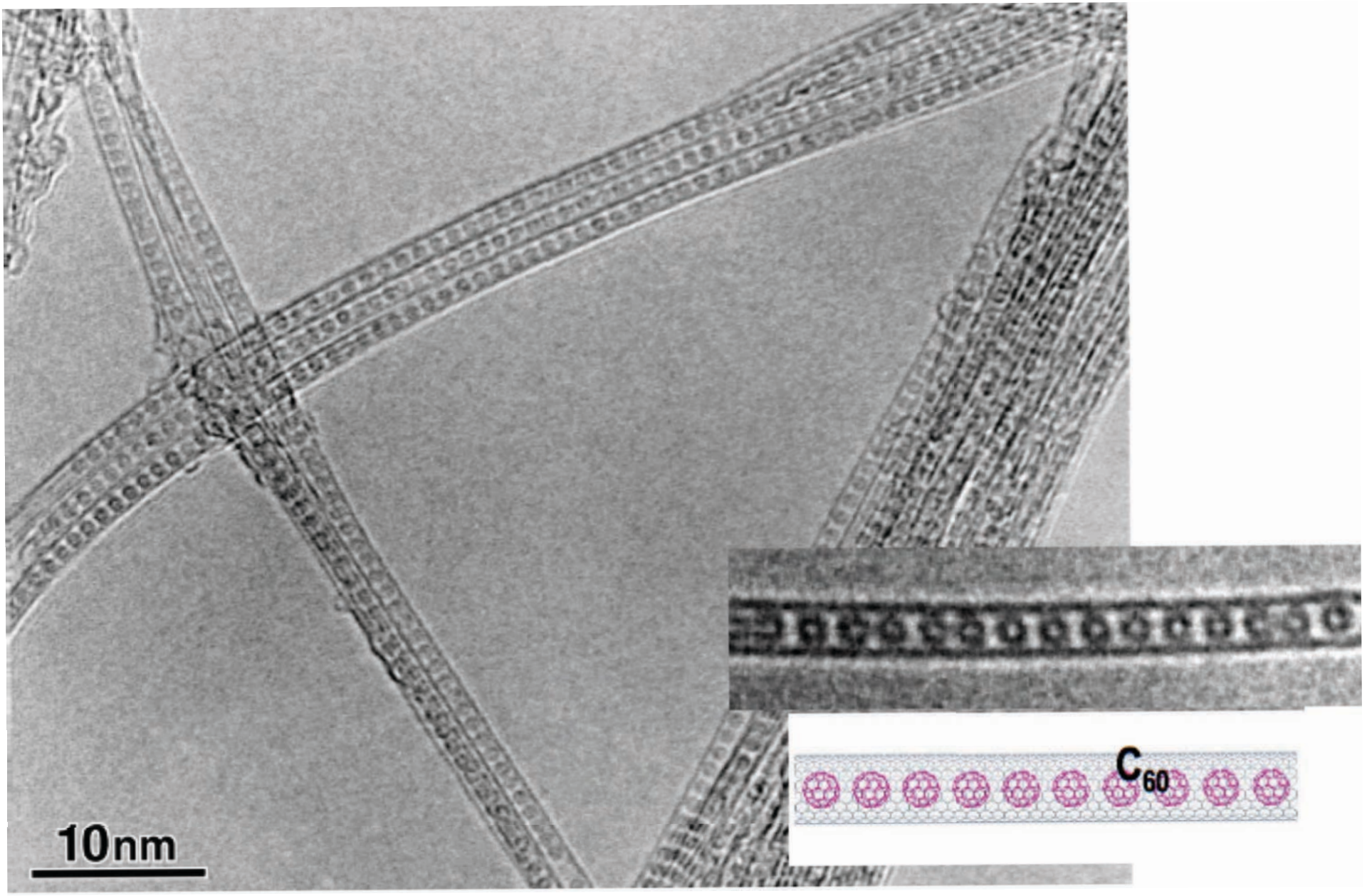


Peapods

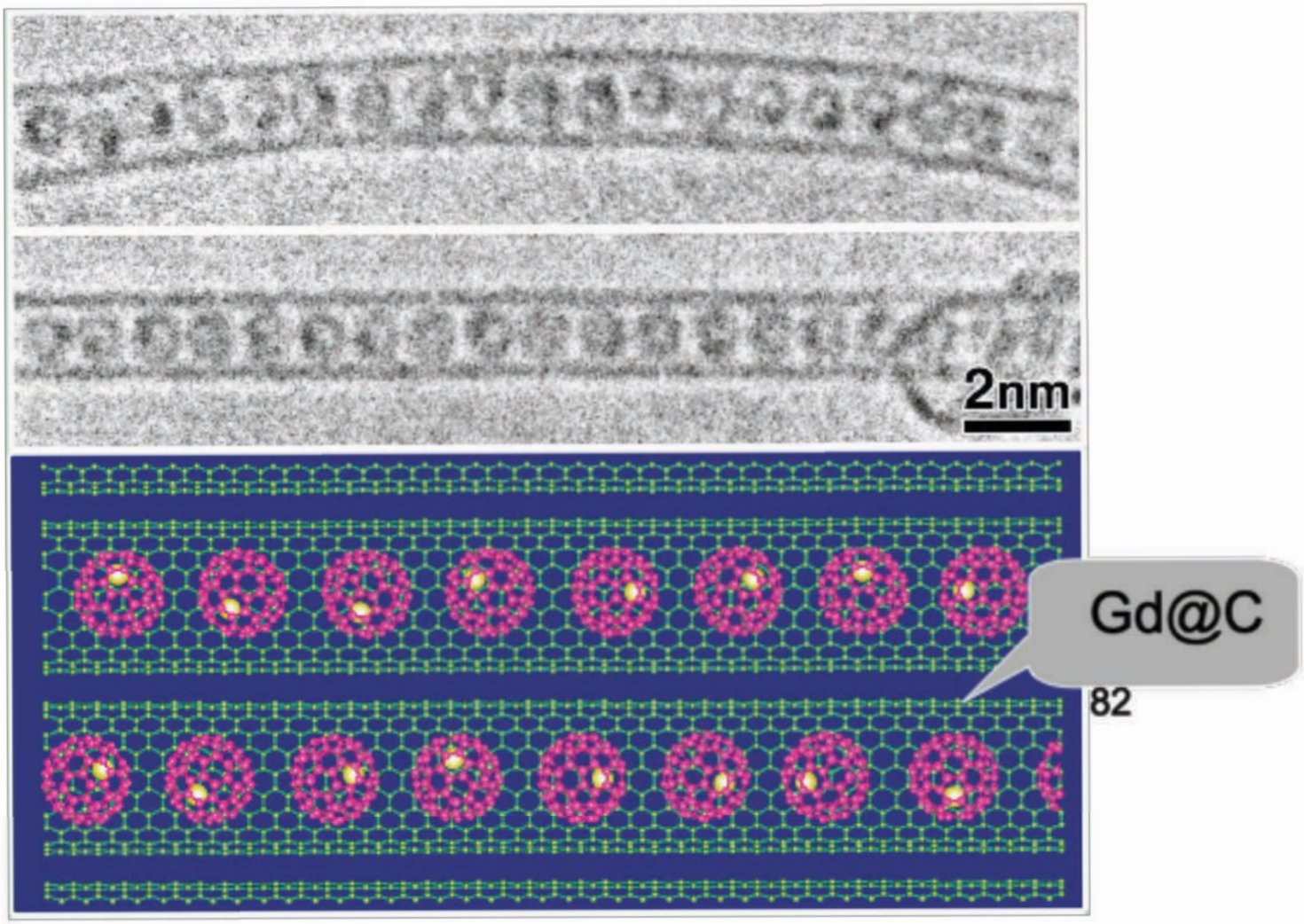


Peapods

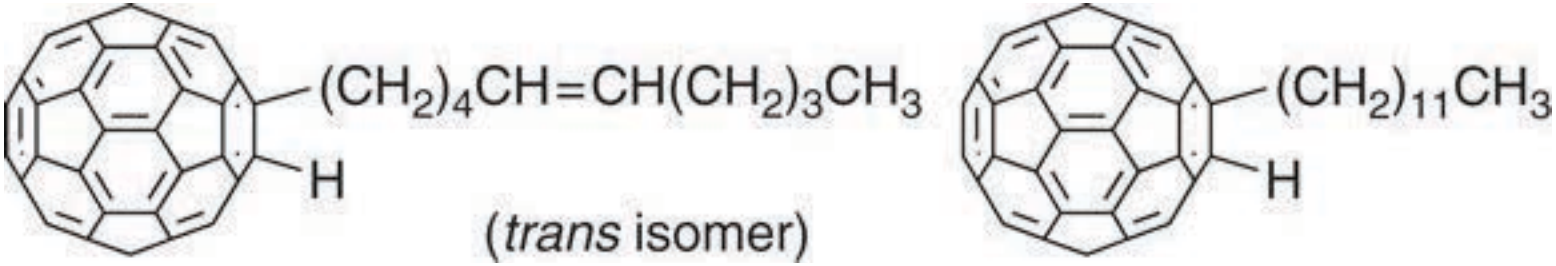


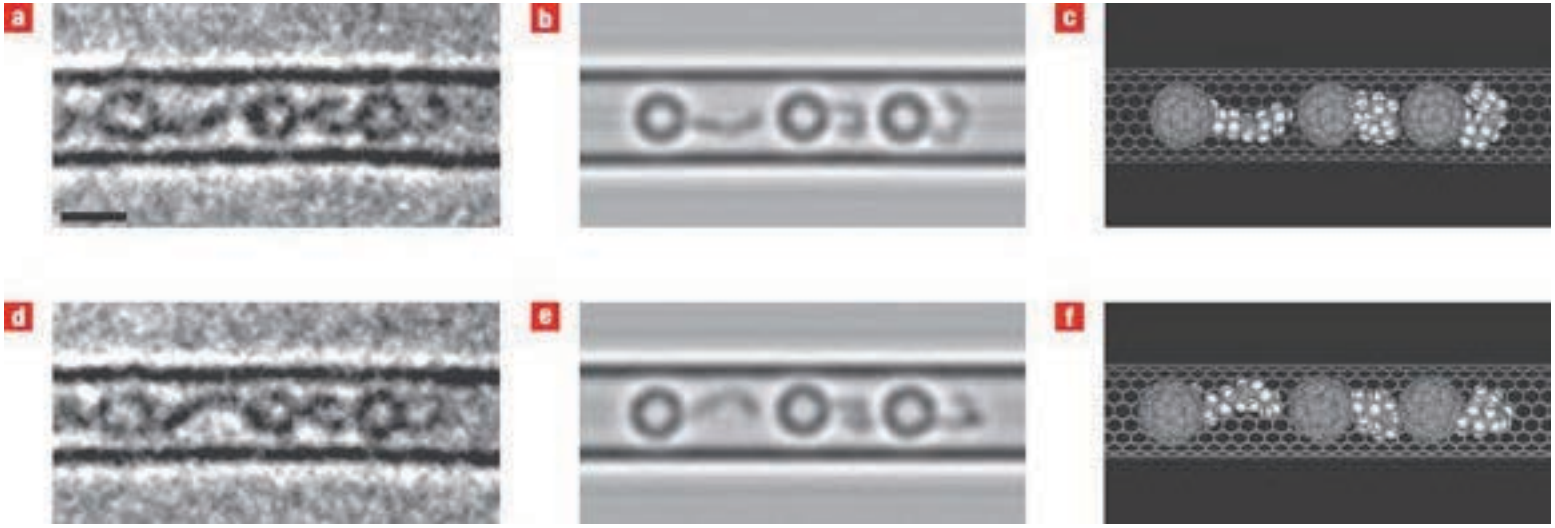

10nm
C_{60}

$Gd@C_{82}$ peapods

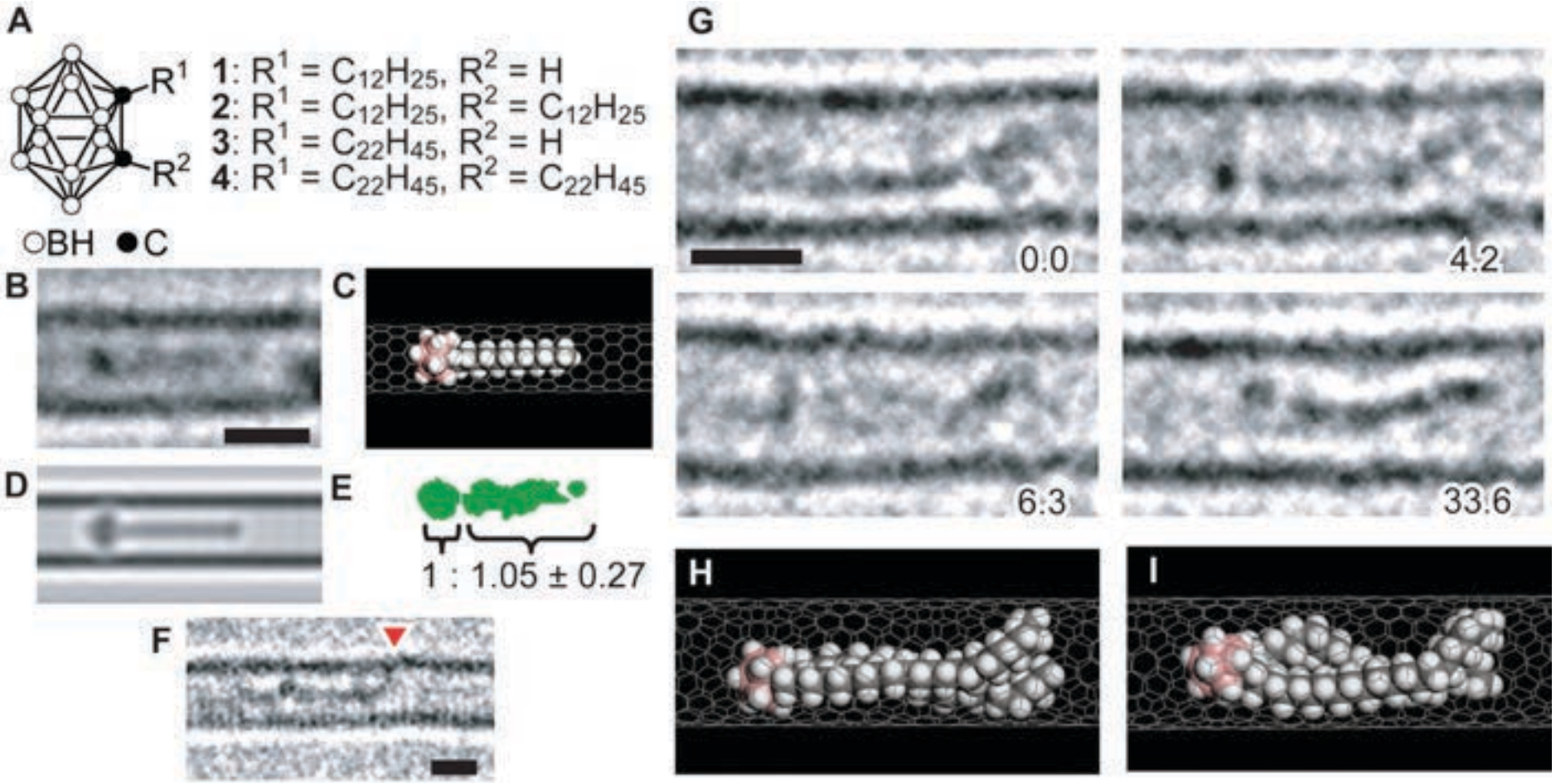


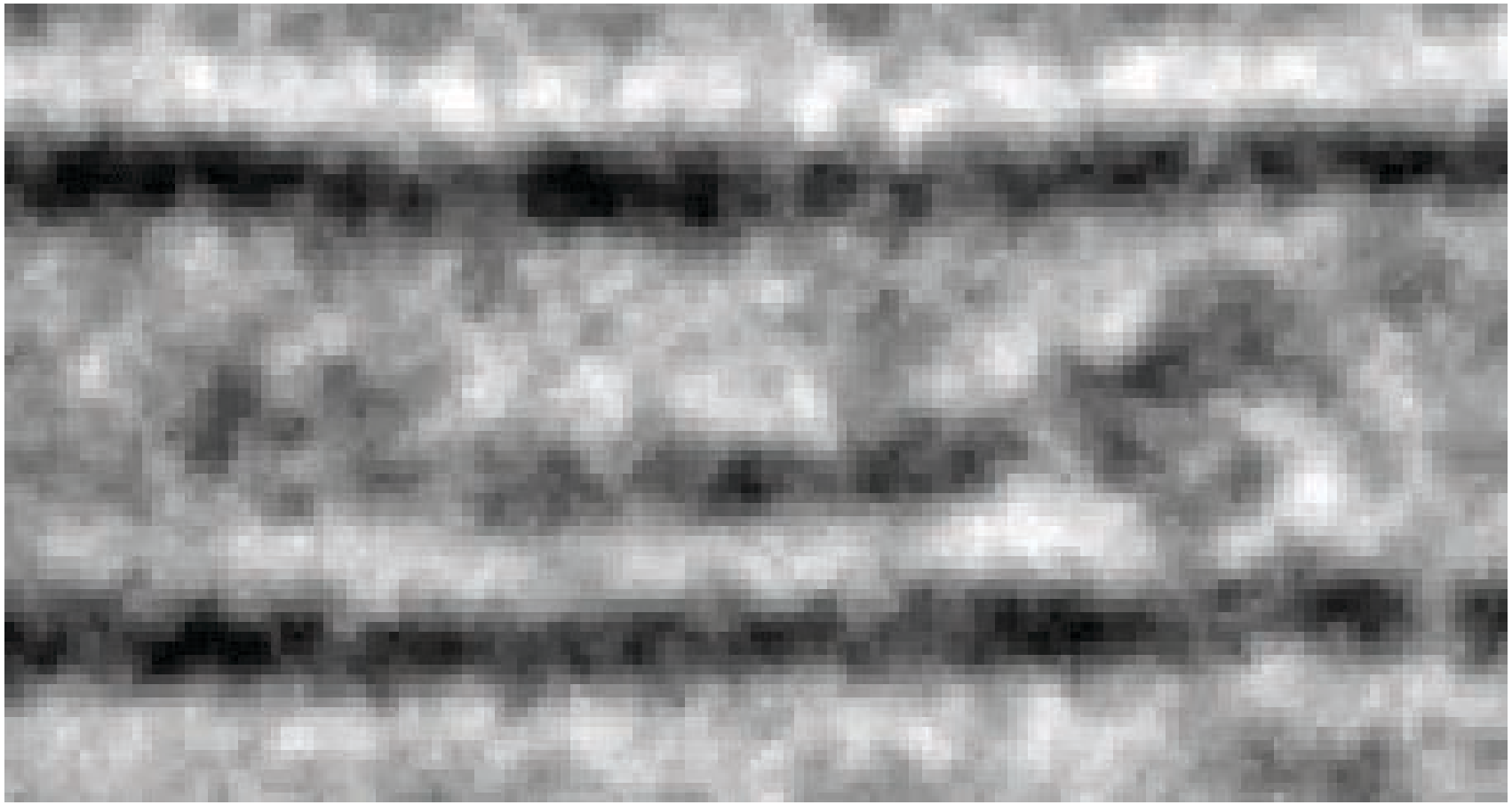
Suenaga et al. *Phys. Rev. Lett.*, (2000)
Hirahara et al. *Science*, (2000)





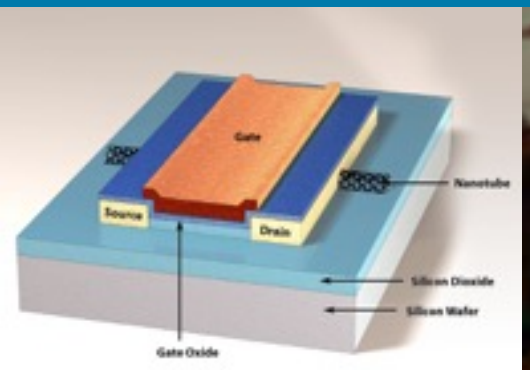
Nature Nanotechnology ***3****, 595–597 (2008)*

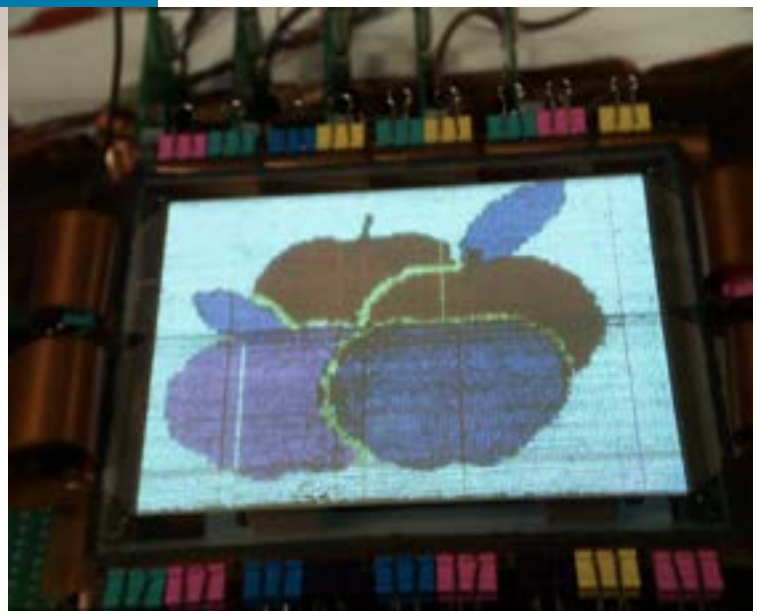

A
R1
R2
1: R1 = C12H25, R2 = H
2: R1 = C12H25, R2 = C12H25
3: R1 = C22H45, R2 = H
4: R1 = C22H45, R2 = C22H45
BH
C
B
C
D
E
1 : 1.05 ± 0.27
F
G
0.0
4.2
6.3
33.6
H
I

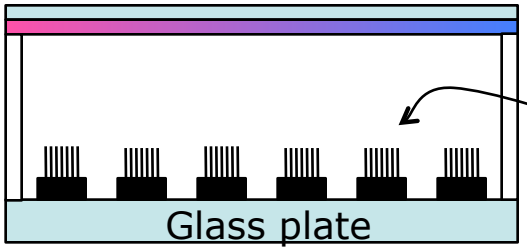


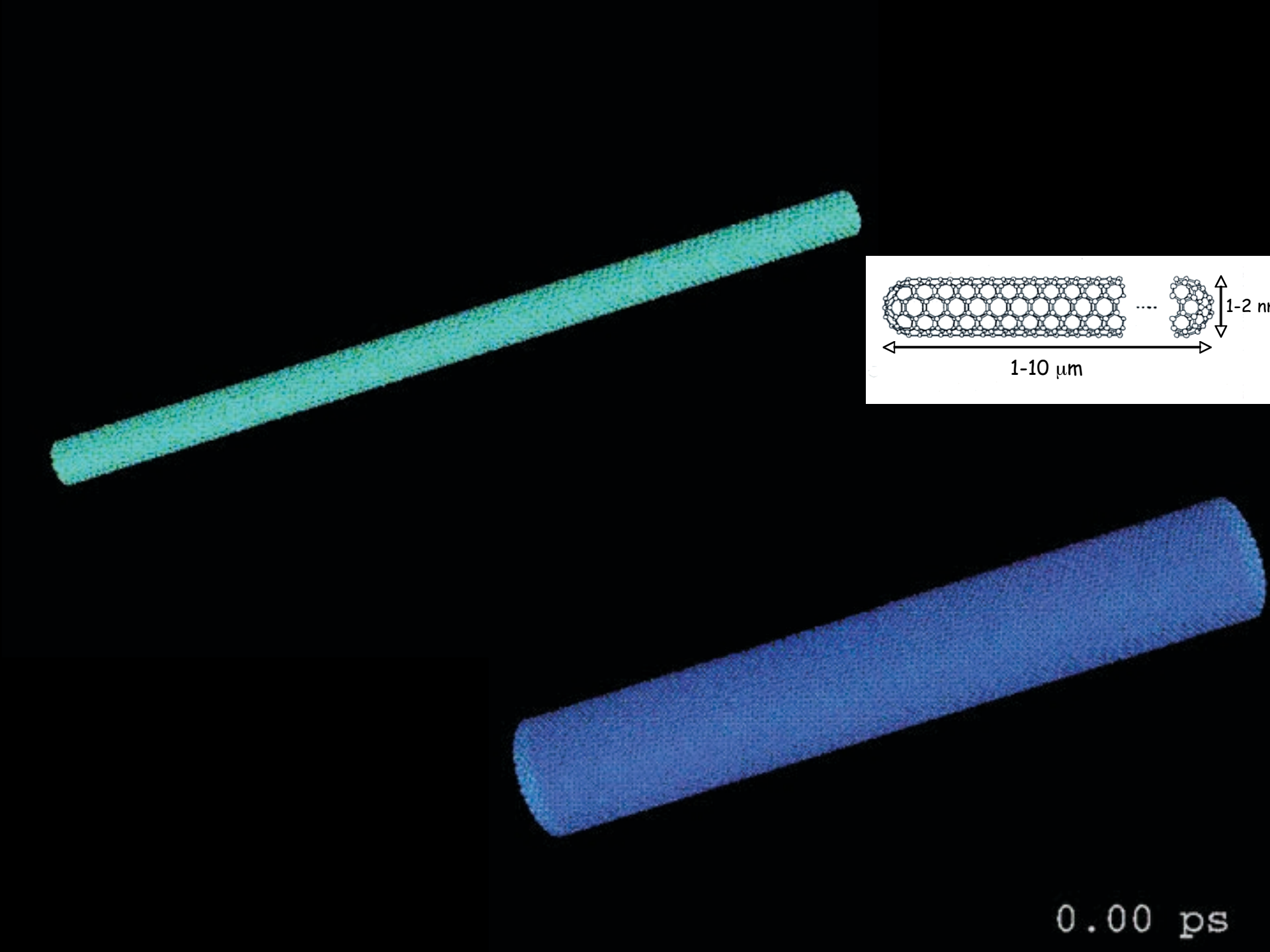
Nanotube Applications

IBM Creates World's Highest Performing Nanotube Transistors



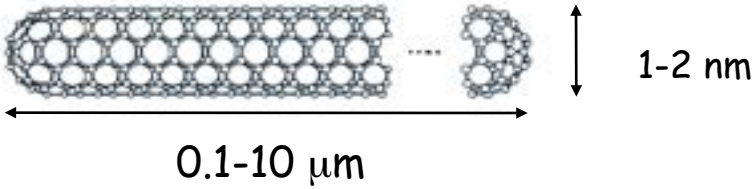





1-2 nm
1-10 μm
0.00 ps

Physico-Chemical Properties of Carbon Nanotubes

SWNT possess an ordered structure



Diameter 1 – 2 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

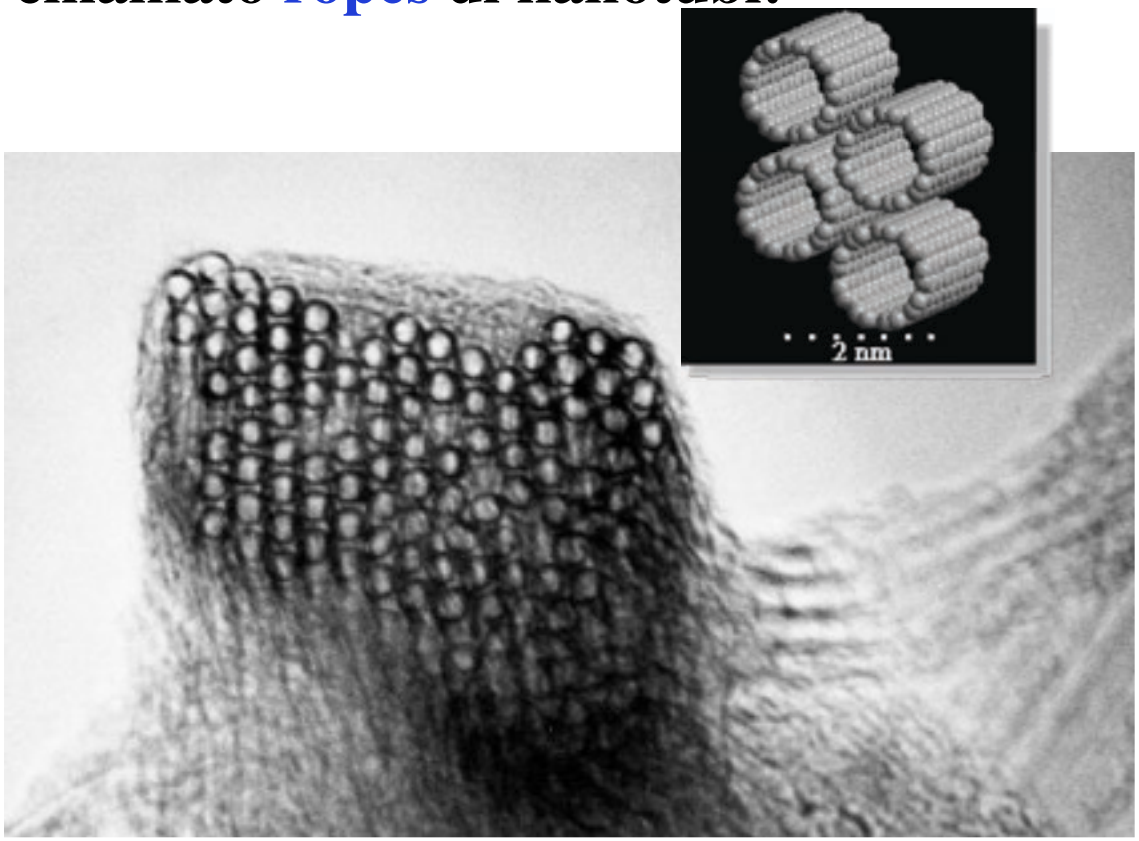
- Metallic
- Semiconducting-Insulating

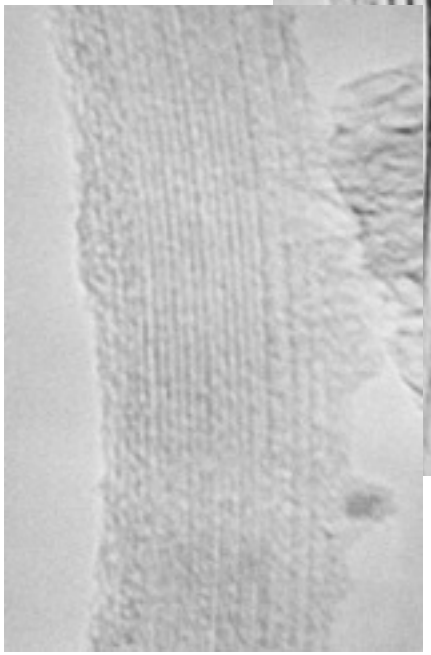
CNT are insoluble in any organic solvent or aqueous solution

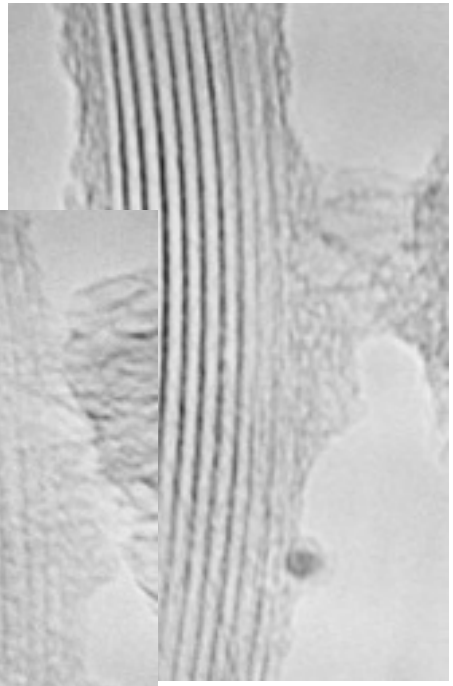
Carbon Nanotubes (CNTs)

I SWCNT sono in genere impaccati in strutture triangolari che prendono il nome di bundles (costante reticolare ≈ 1.7nm; distanza di separazione inter-tubo ≈ 0.32nm).

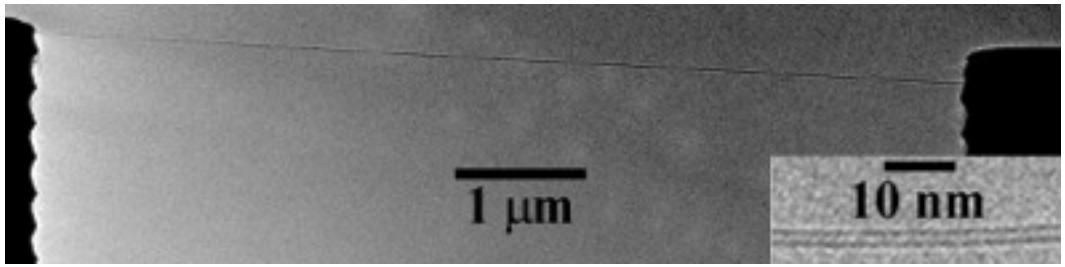
L'insieme di bundles costituisce ciò che comunemente viene chiamato ropes di nanotubi.

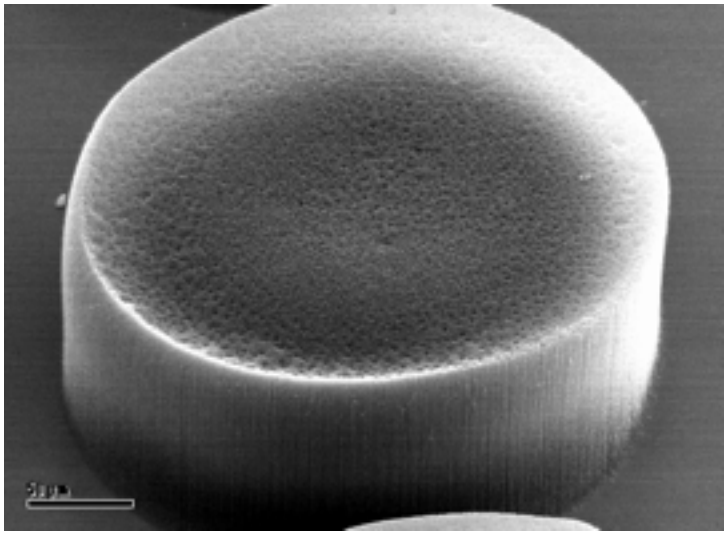


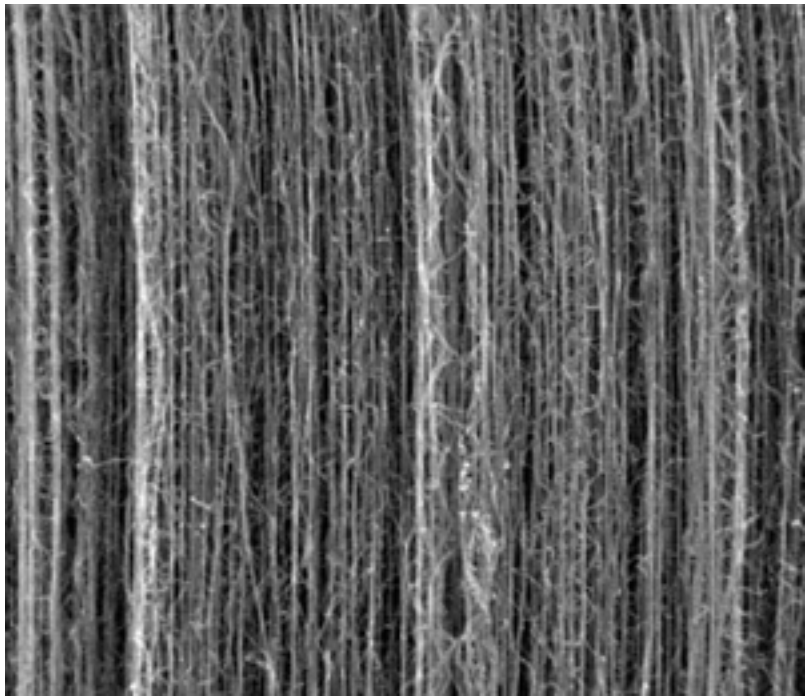


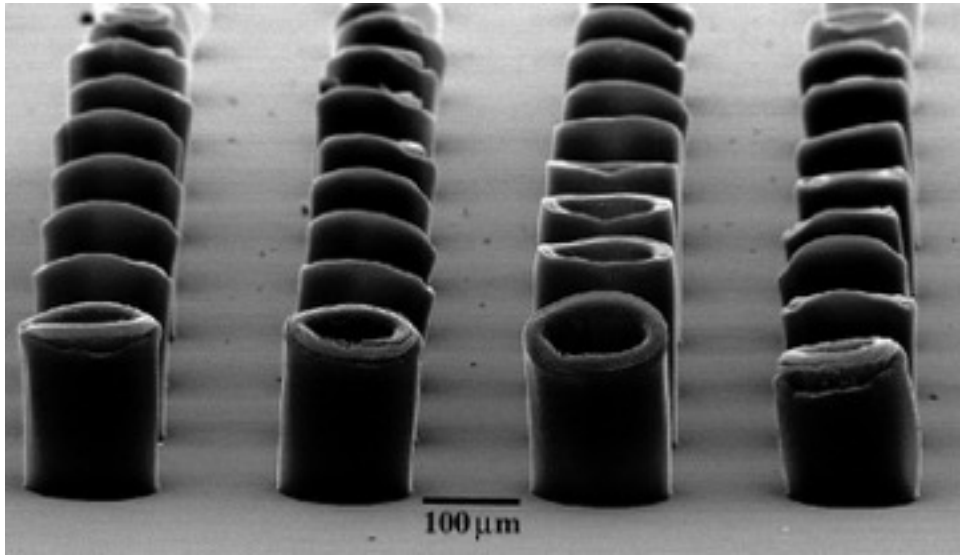


Crescita controllata di CNT su strutture

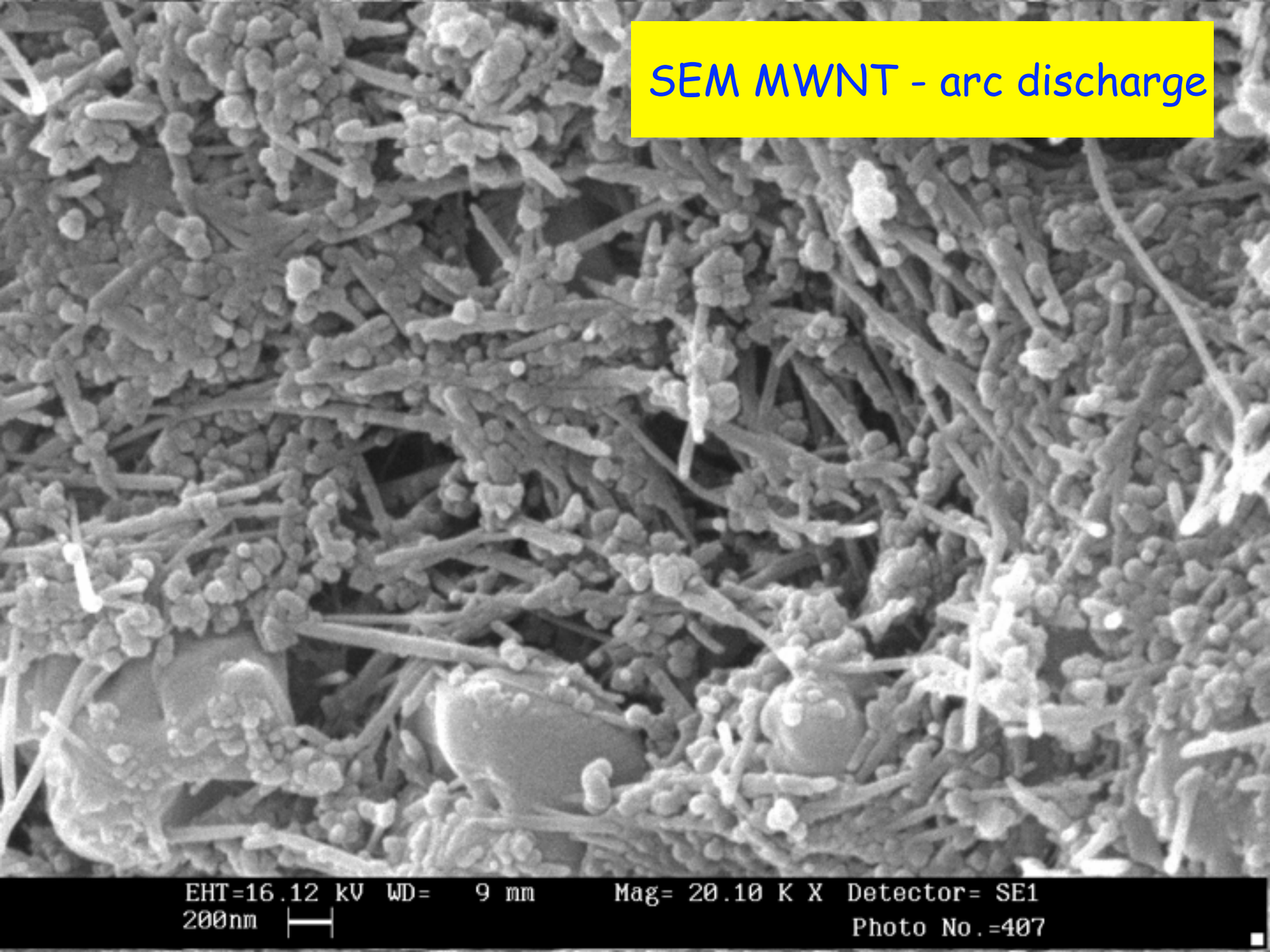




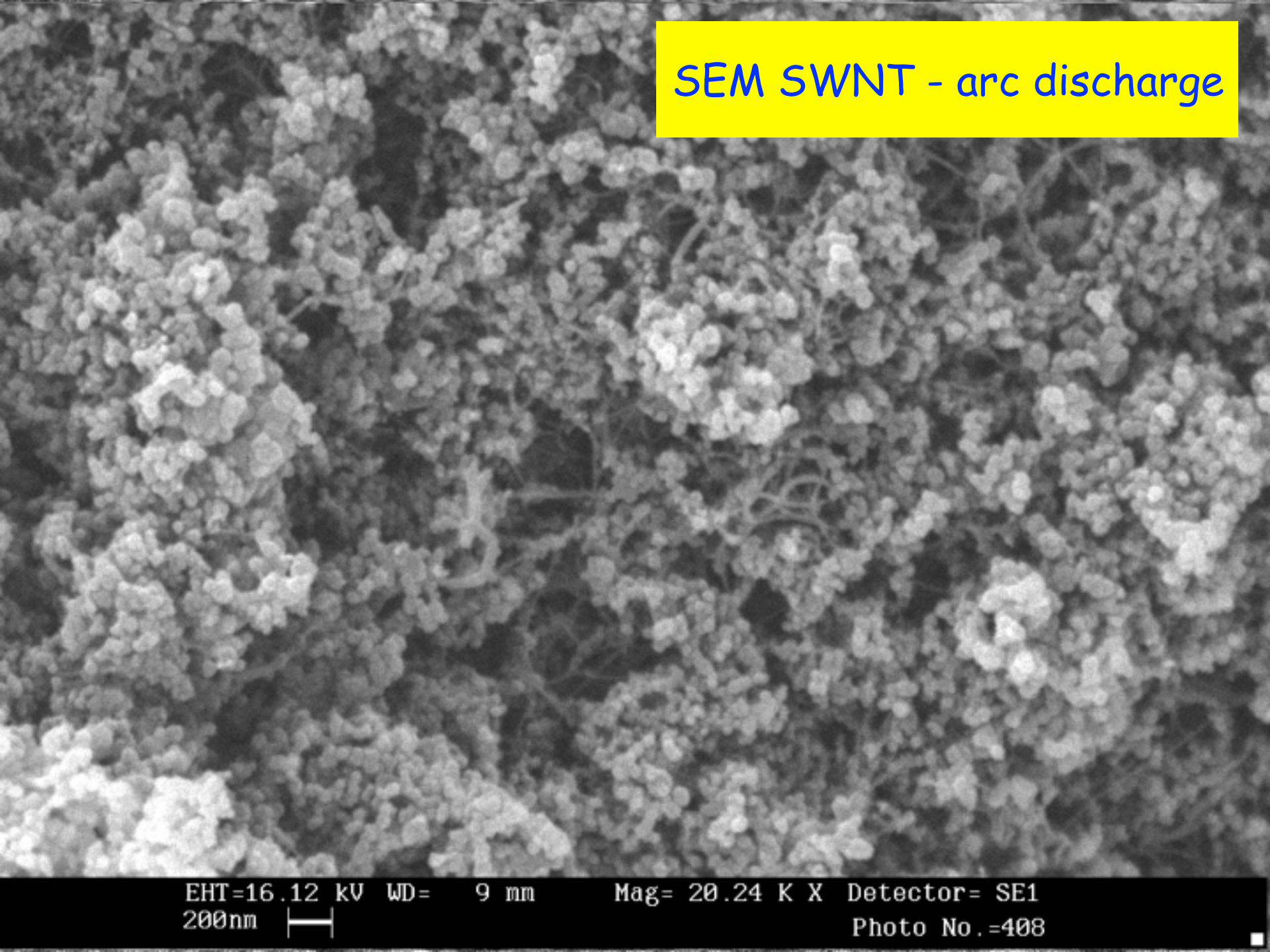


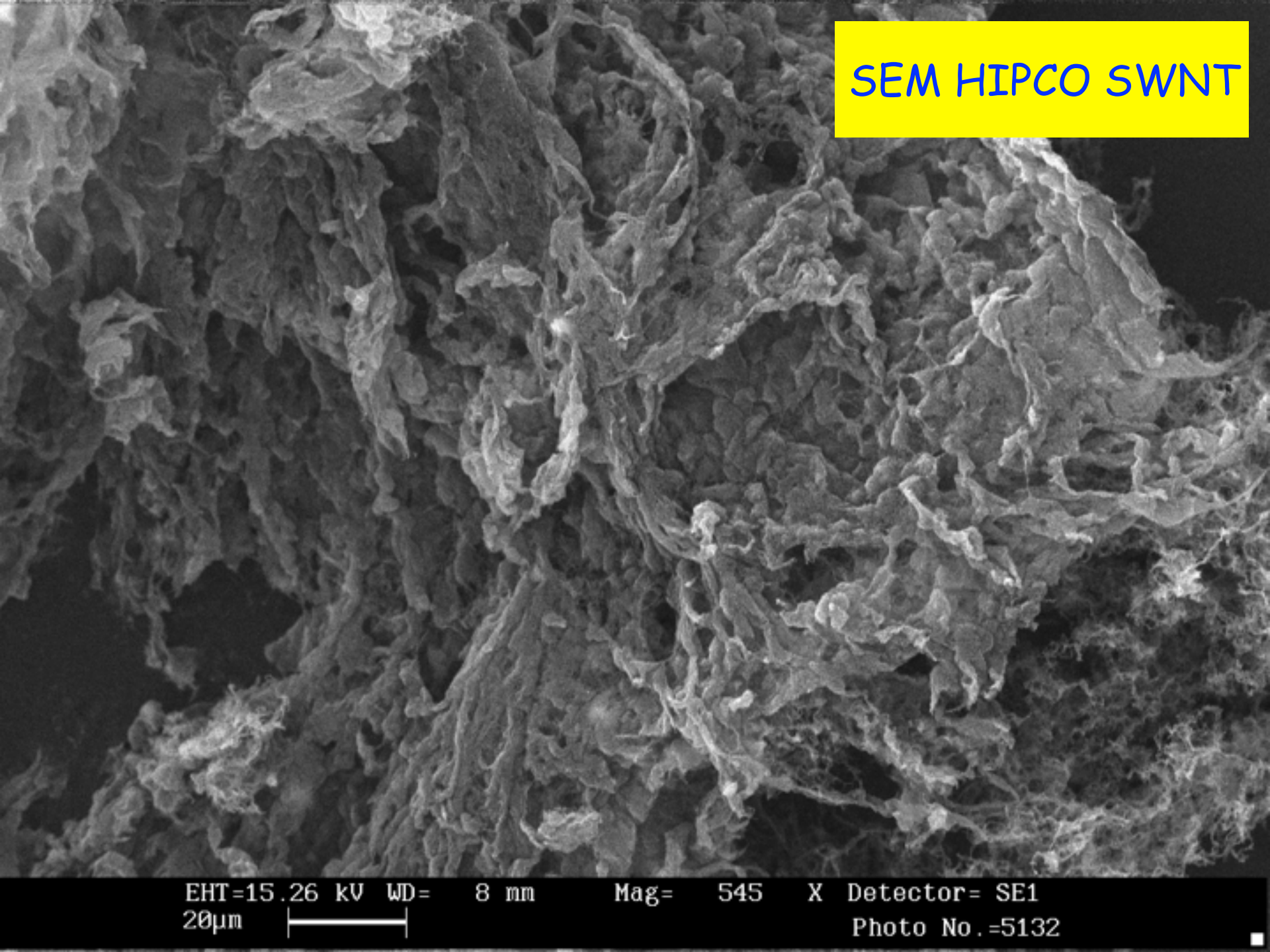


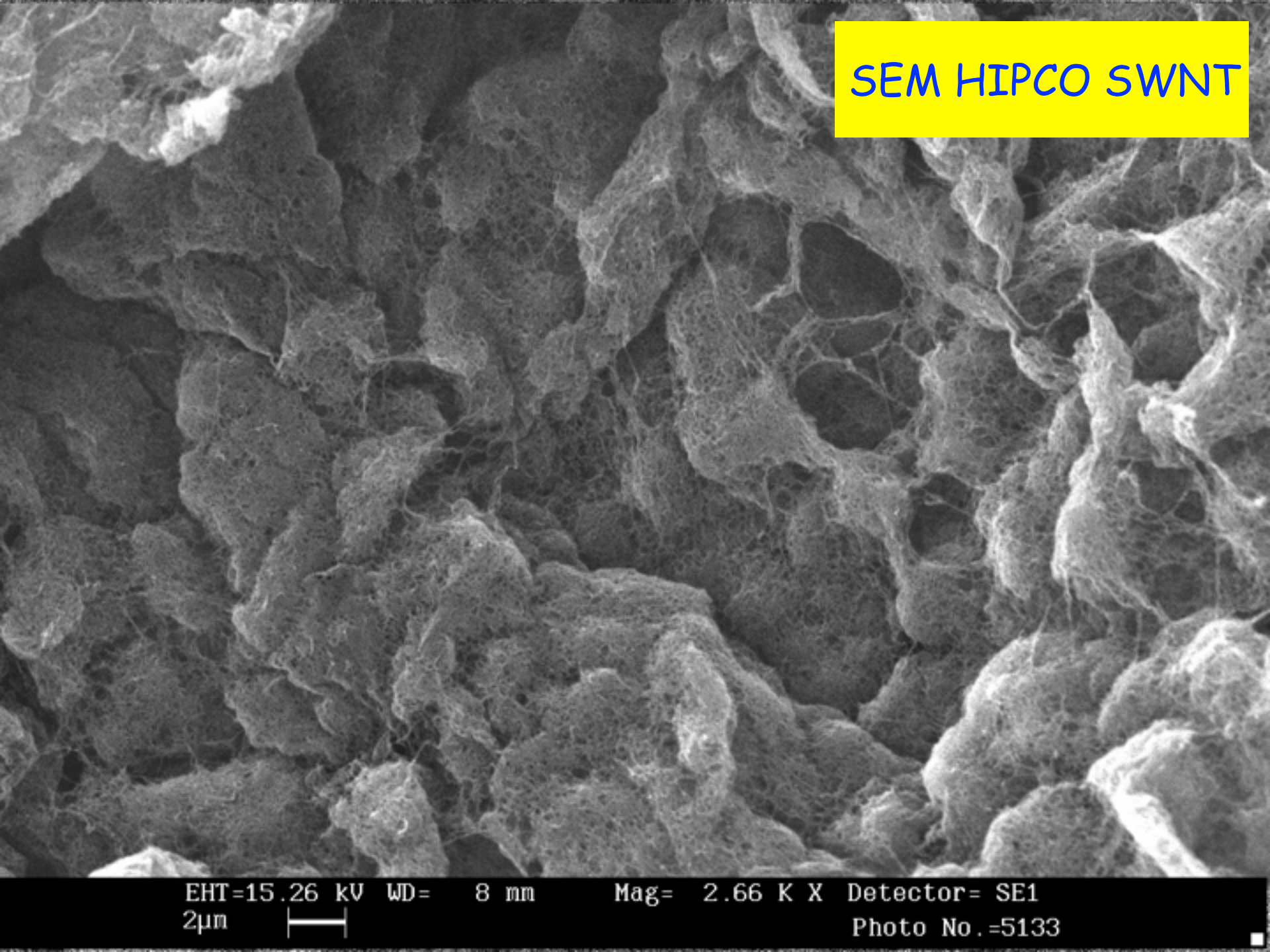
SEM MWNT - arc discharge



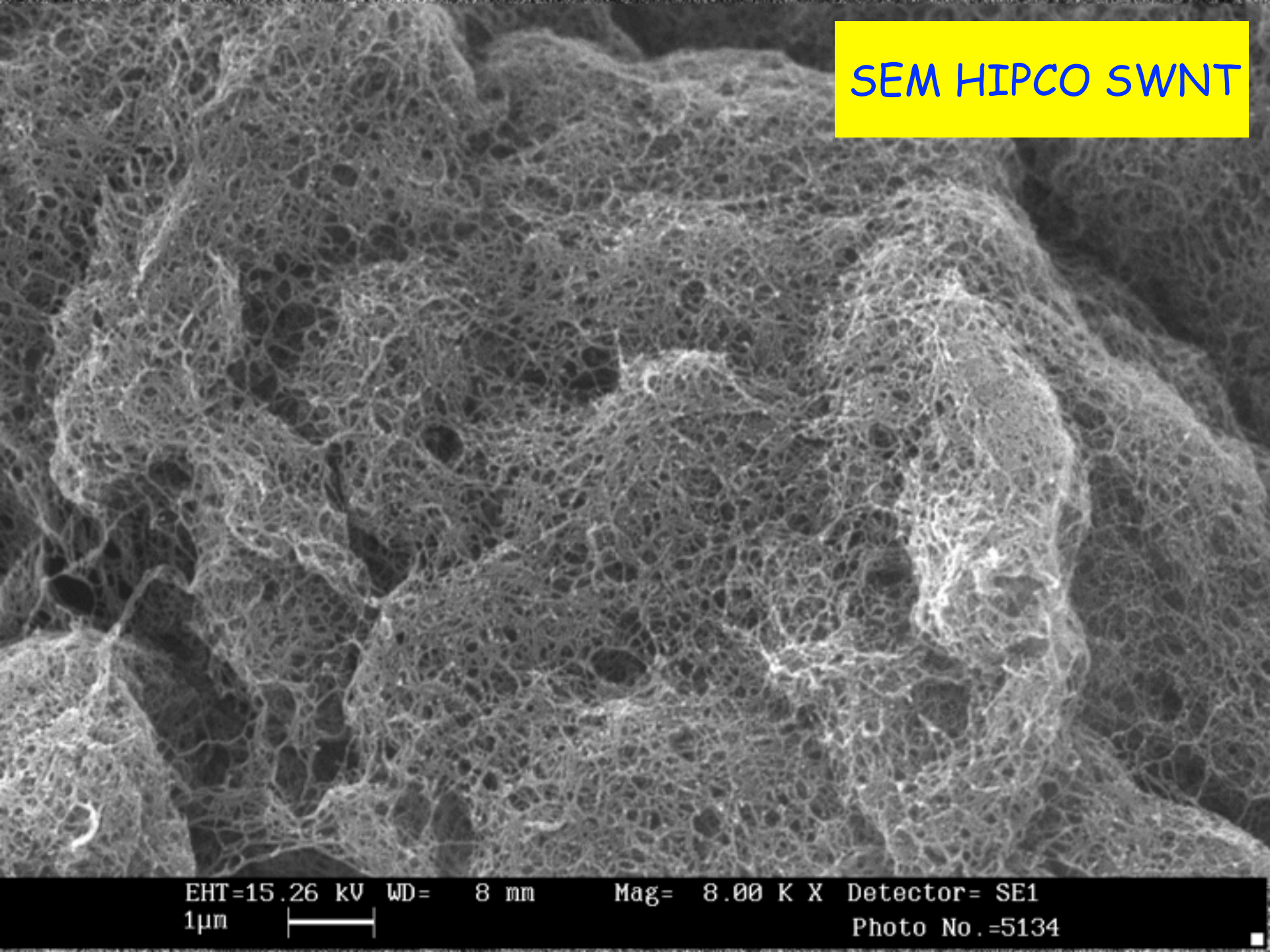
SEM SWNT - arc discharge

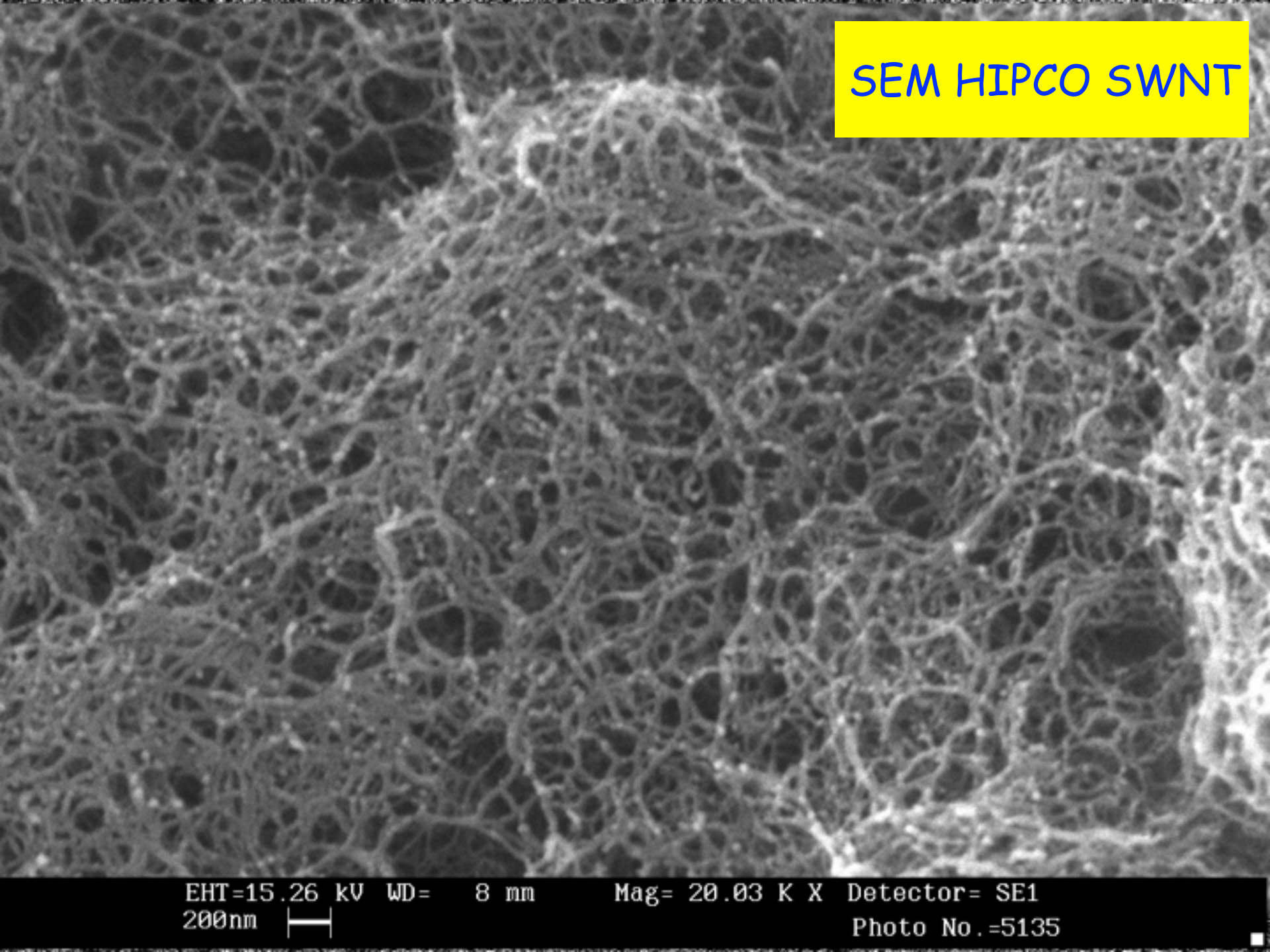



SEM HIPCO SWNT
EHT=15.26 kV WD= 8 mm Mag= 545 X Detector= SE1
20µm
Photo No.=5132


SEM HIPCO SWNT
EHT=15.26 kV WD= 8 mm Mag= 2.66 K X Detector= SE1
2µm
Photo No.=5133

SEM HIPCO SWNT

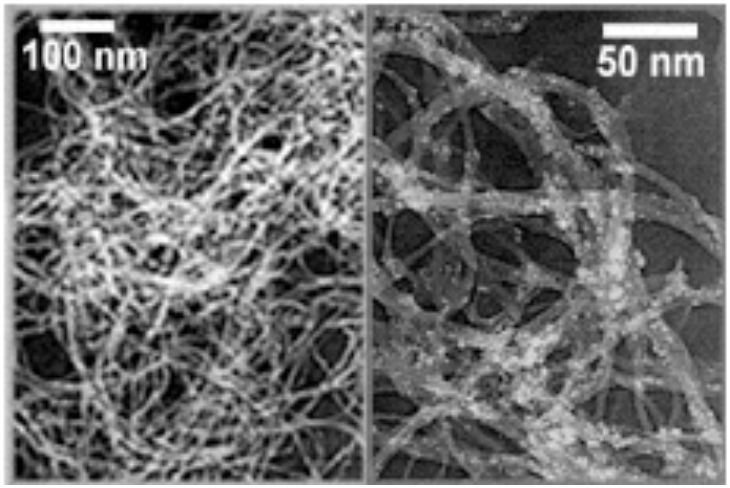



SEM HIPCO SWNT
EHT=15.26 kV WD= 8 mm
Mag= 20.03 K X
Detector= SE1
200nm
Photo No.=5135

Purification

- *Dominant impurities in SWNTs*

  - Metal catalyst
  - Amorphous carbon

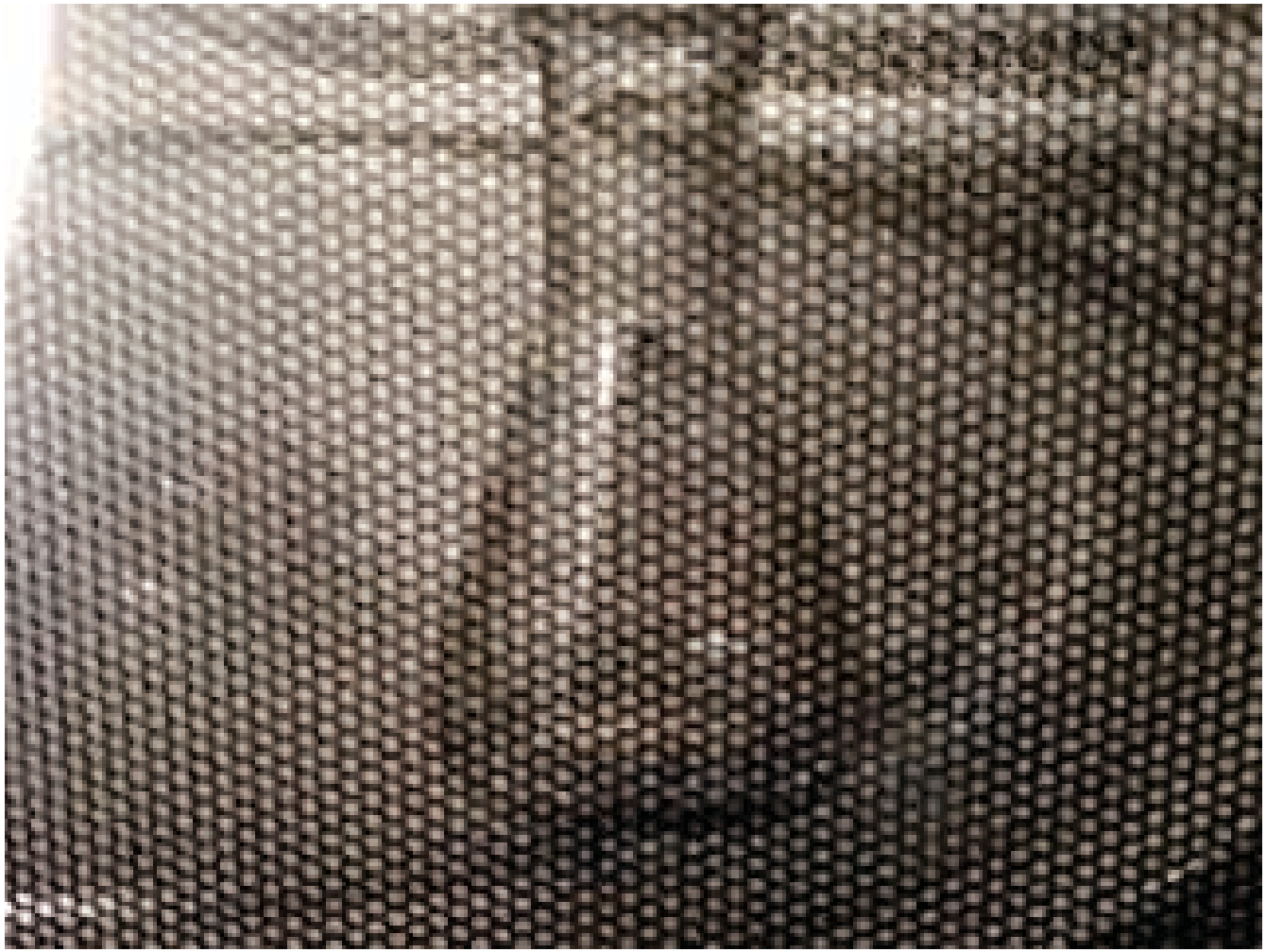


- *Principal purification process:*

  ✓ Treatment with strong oxidizing acids

  ✓ Air oxidation at high temperatures

Problem: purify without damaging the tubes

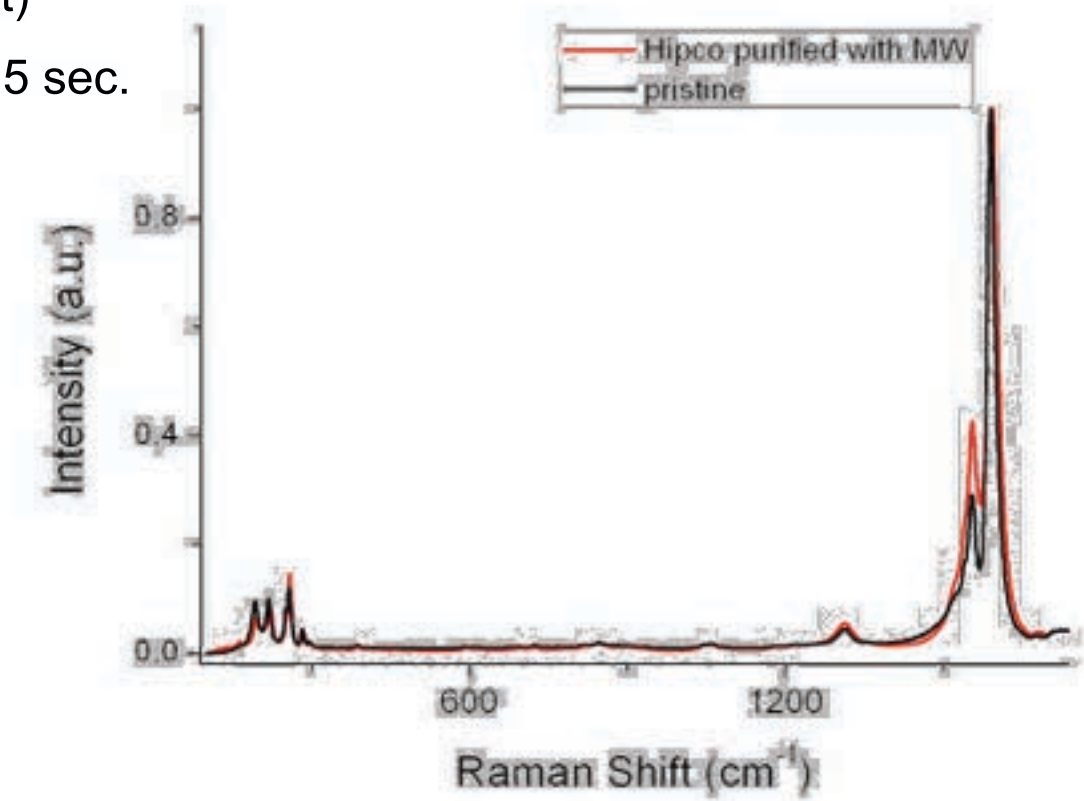


Purification

- ✓ Packed HIPCO SWNTs

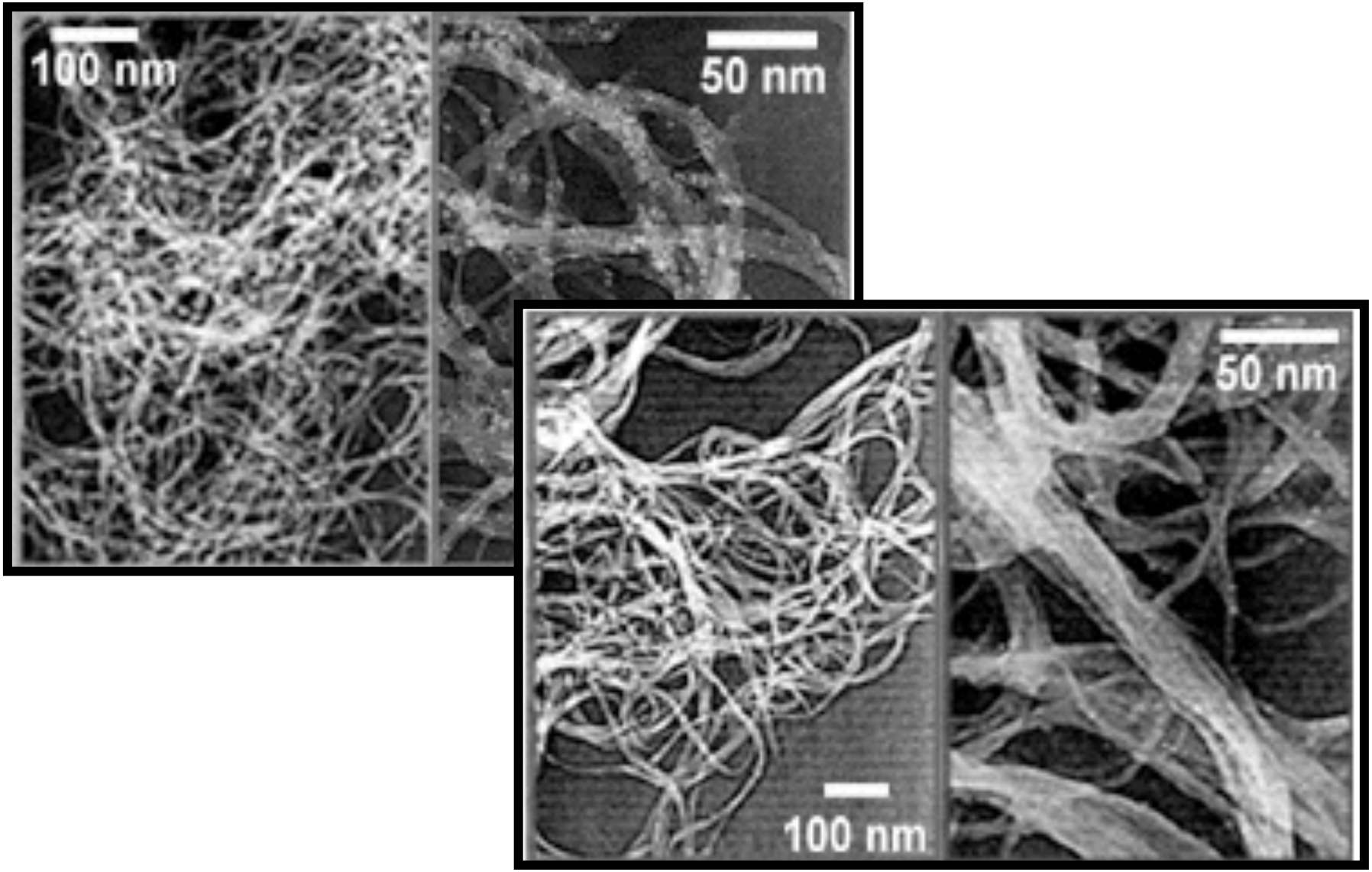
  (26%(w/w) iron content)
- ✓ Domestic microwave / 80 W / 5 sec.
- ✓ Red “material”!!! (Fe_2O_3)
- ✓ Washed with HCl cc. ---

  yellow solution (Fe^{3+})
- ✓ 7% (w/w) iron content



Chem. Commun. 2002, 2308-2309

before purification



after purification

naturenews

Published online 20 May 2008 | Nature | doi:10.1038/news.2008.845

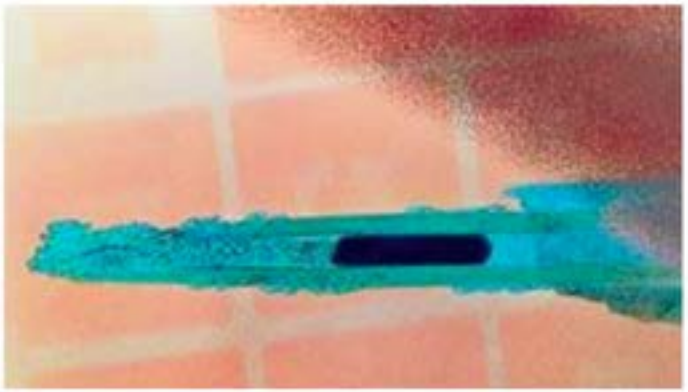
News

Carbon nanotubes: the new asbestos?

Calls for caution as nanotubes cause precancerous growths in mice.

Katharine Sanderson (/news/author/Katharine+Sanderson/index.html)

Nanotechnology experts are calling for prompt government action to ensure that carbon nanotubes are properly regulated, after researchers discovered that some carbon nanotubes can cause precancerous growths in the same way that asbestos does.



Straight carbon nanotubes may have the potential to damage lung tissue.

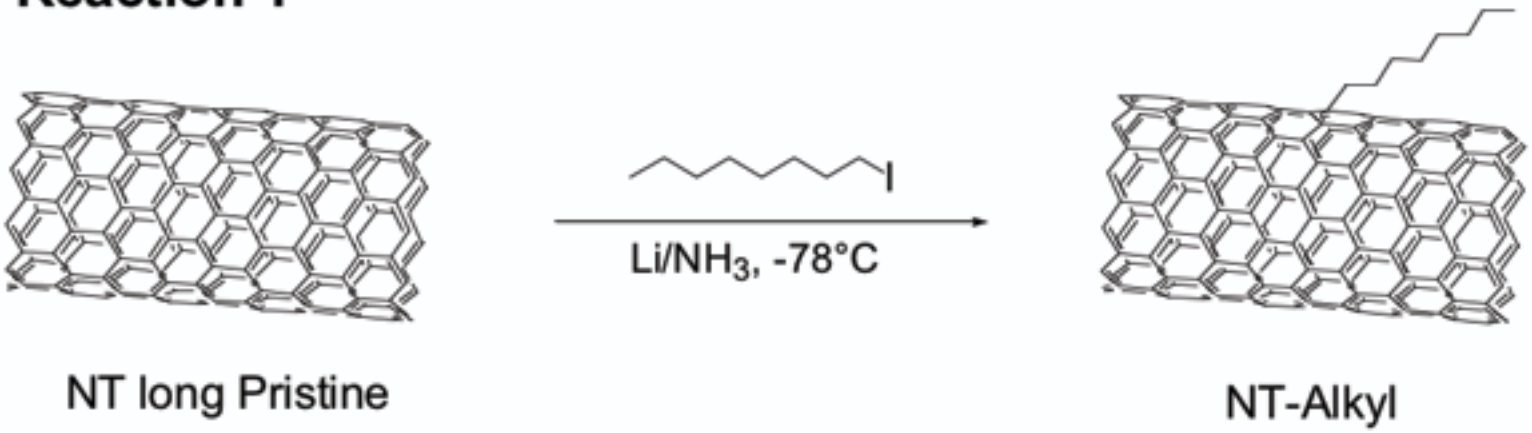
PETER HARRIS / SPL

Researchers led by Ken Donaldson of the University of Edinburgh's Centre for Inflammation Research, UK, found that in mice, long, straight, multi-walled carbon nanotubes can cause the same kind of damage as that inflicted by asbestos fibres when they are injected into the lung's outer lining, called the mesothelium.

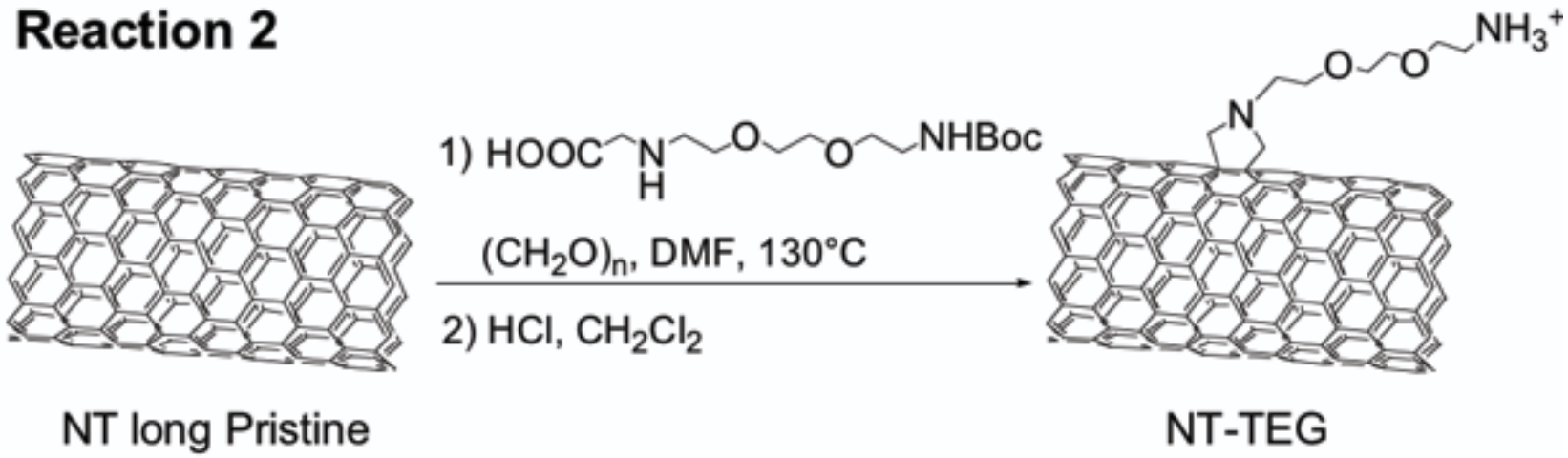
We investigated whether chemical functionalization of long, reactogenic MWNTs could diminish or completely abolish the inflammatory response and granuloma formation

Same long MWNTs used in: C. A. Poland, R. Duffin, I. Kinloch, A. Maynard, W. A. H. Wallace, A. Seaton, V. Stone, S. Brown, W. MacNee, K. Donaldson, *Nat. Nanotechnol*. **2008**, *3*, 423-428

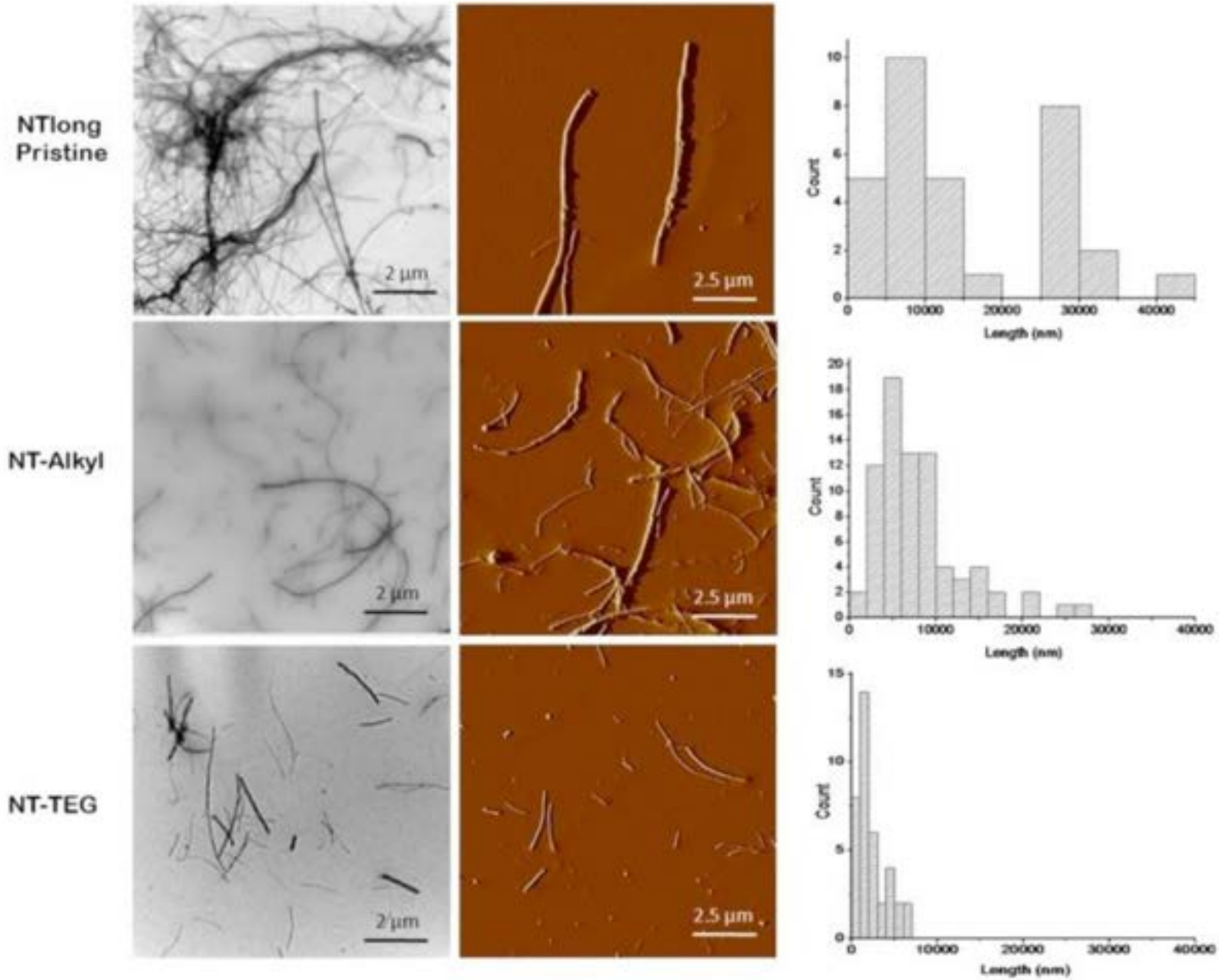
Reaction 1



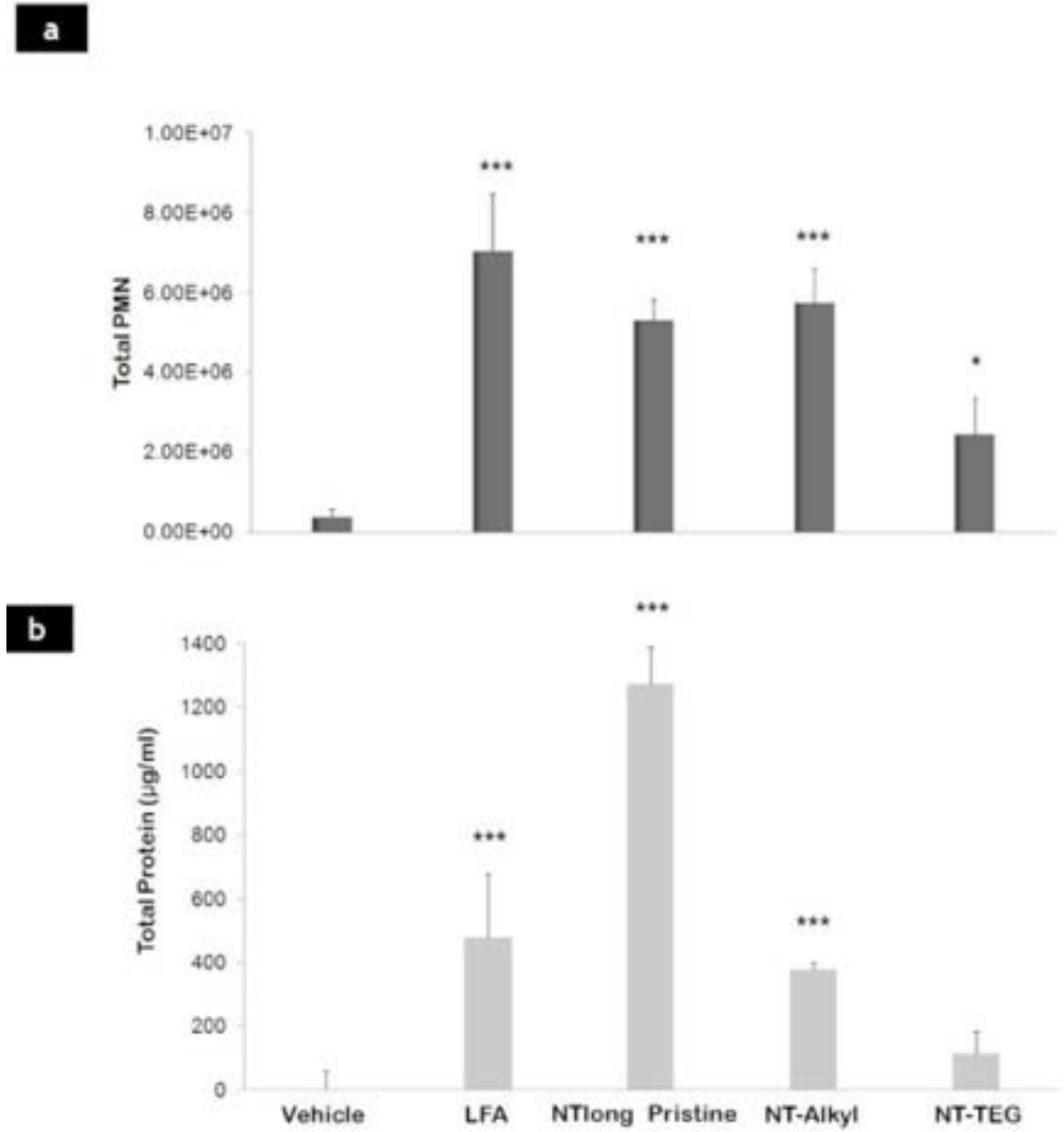
Reaction 2



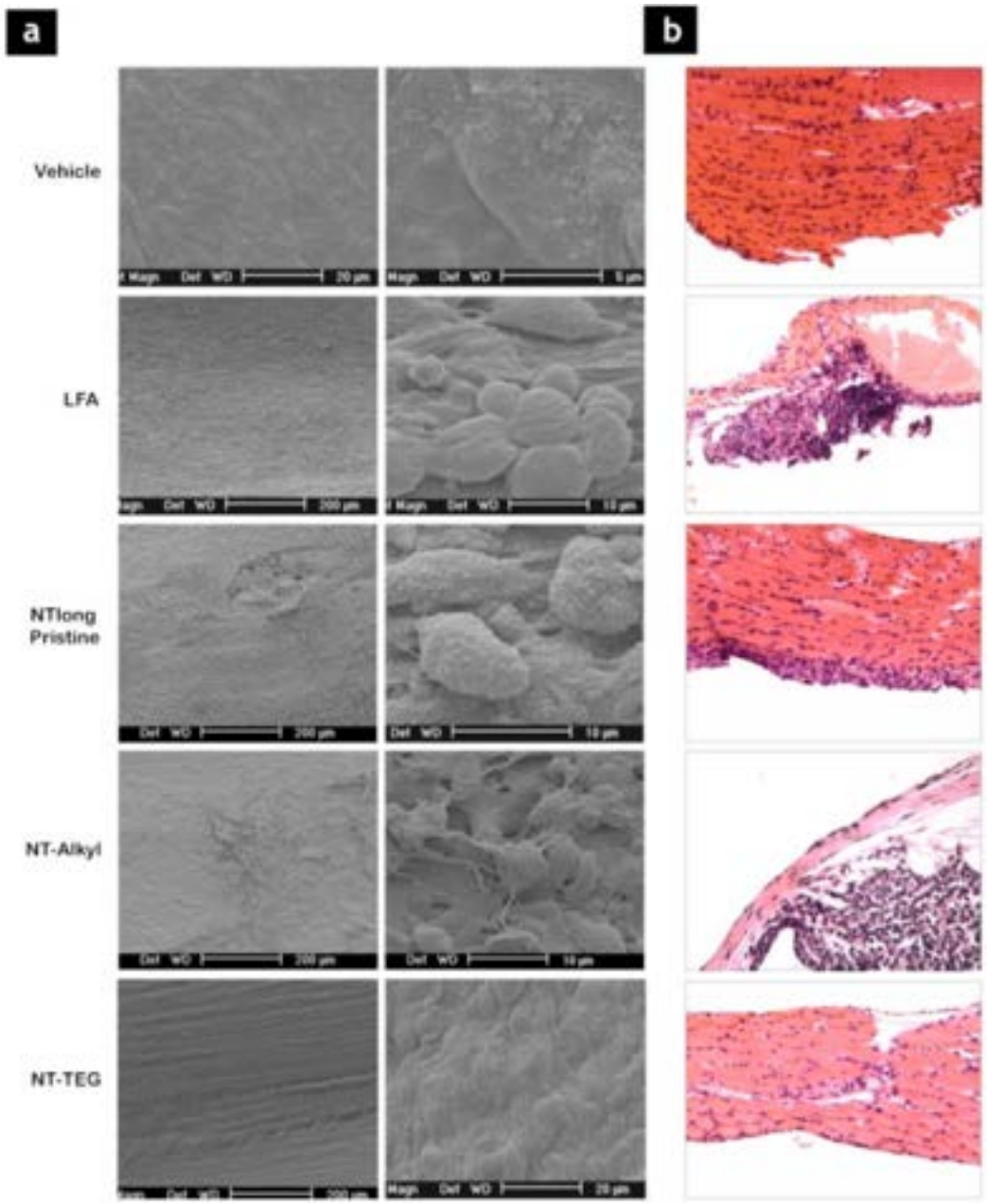
ANGEWANDTE CHEMIE-INTERNATIONAL EDITION Volume: **52** Issue: **8** Pages: **2274-2278**: **2013)**



ANGEWANDTE CHEMIE-INTERNATIONAL EDITION Volume: **52** Issue: **8** Pages: **2274-2278**: **2013)**



Inflammatory reaction in the peritoneal cavity 24 hours post injection with nanotubes. Female C57Bl/6 mice were intraperitoneally injected with 50 µg of vehicle control (0.5% BSA/saline), pristine MWNTs (NTlong Pristine) and the two chemically functionalized MWNTs (NT-Alkyl and NT-TEG) and long-fibre amosites (LFA) as positive control, the mice were killed and peritoneal cavity lavaged with saline. Inflammatory response was evaluated by (a) the total polymorphonuclear leukocytes (PMN) and (b) total protein (protein exudation) after 24 hours



The effect of fibres on the diaphragms after 7 days. Female C57Bl/6 mice were intraperitoneally injected with 50 µg of vehicle control (0.5% BSA/saline), pristine MWNTs (NTlong Pristine) and the two chemically functionalized MWNTs (NT-Alkyl and NT-TEG) and long-fibre amosites (LFA) as positive control, the mice were killed after 7 days and the diaphragms excized, fixed and prepared for visualization. SEM images of the diaphragm surface (a) and the histology using H&E staining (b) highlights the presence of granulomatous inflammation with NTlong Pristine, LFA and NT-Alkyl but not with NT-TEG.

ANGEWANDTE CHEMIE-INTERNATIONAL EDITION Volume: **52** Issue: **8** Pages: **2274-2278**: **2013)**

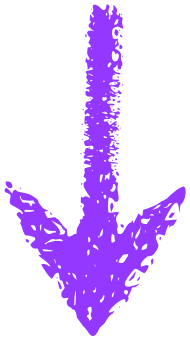
We confirm the inflammatory responses obtained from exposure of the peritoneum to long NT and LFA fibers with subsequent granuloma formation after 7 days.

Nanotubes treated with 1,3-dipolar cycloaddition reaction lead to reduction of the effective length, most likely due to efficient debundling and disaggregation of nanotube fibers, owing to the presence of the hydrophilic chains. No pathogenic responses were observed in this case.

Alkyl-functionalized MWNTs retain the toxicological profile of the pristine, long MWNTs, leading to inflamation.

ANGEWANDTE CHEMIE-INTERNATIONAL EDITION Volume: **52** Issue: **8** Pages: **2274-2278**: **2013)**

Conclusion: Only chemical functionalization reactions that lead to shortening or untangling of long MWNT bundles will be able to resolve the toxicological risks and concerns associated with long fiber exposure



Chemical functionalization of CNTs is an important step for applications in any field!

ANGEWANDTE CHEMIE-INTERNATIONAL EDITION Volume: **52** Issue: **8** Pages: **2274-2278**: **2013)**

Reasons for functionalization

1) To allow an easier manipulation

2) To help purification: in principle, this should be easier if CNT were soluble

3) Potential toxicity issues can be avoided if CNT are functionalized

4) Preparation of composites (e.g. with plastics) should give more homogeneous materials

5) Combination of their properties with those of other interesting classes of materials (photoactive or electroactive moieties, etc.)

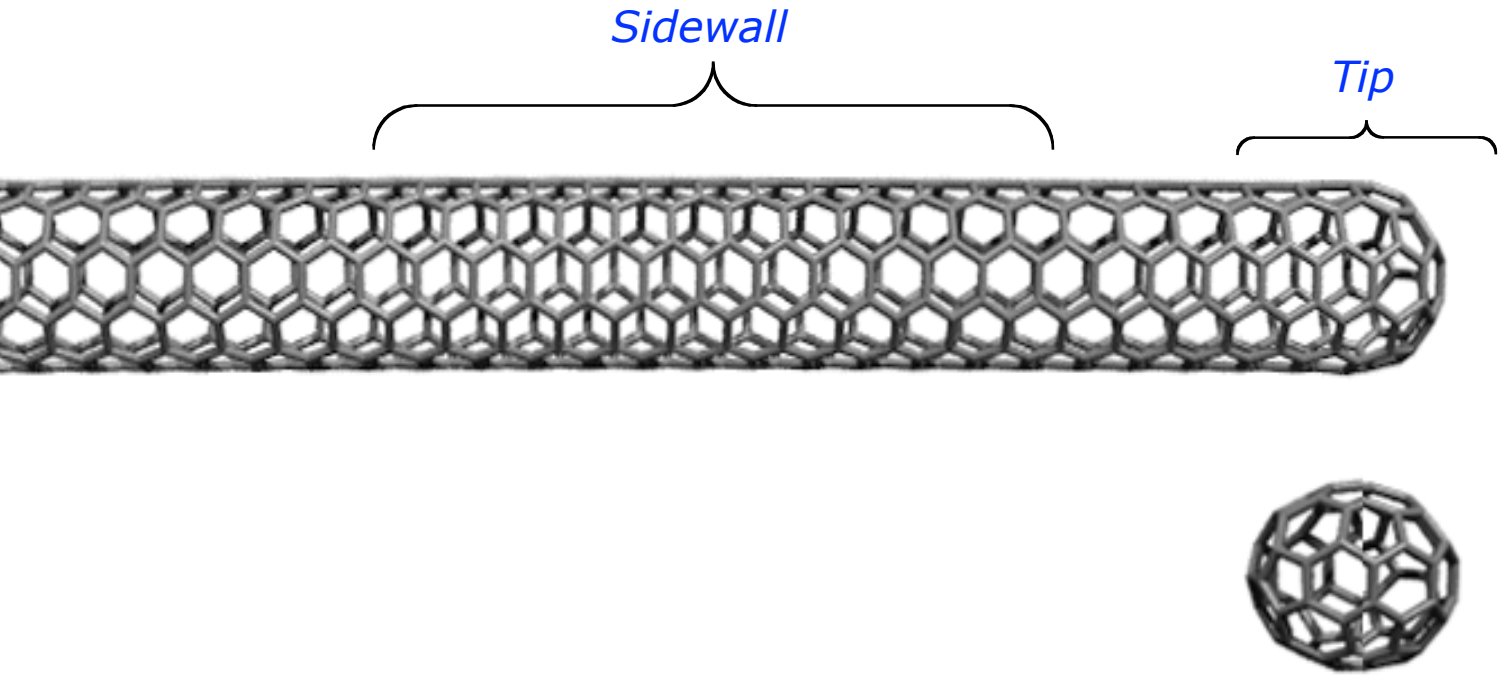
6) The solution properties of these species could be investigated

Scope of the work

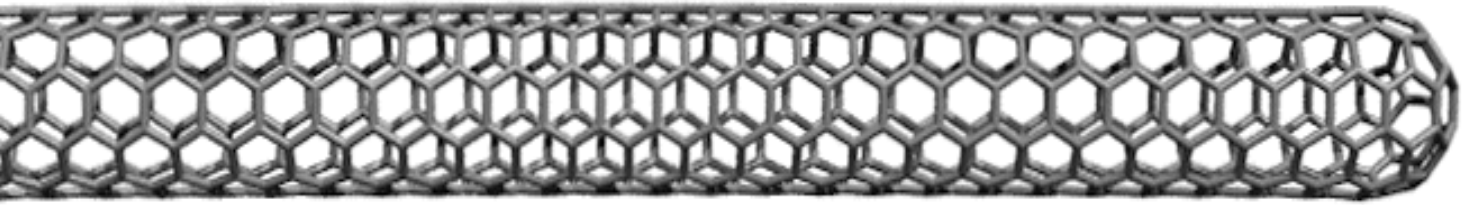
Applications in Materials Science (e.g, photovoltaics, composites)

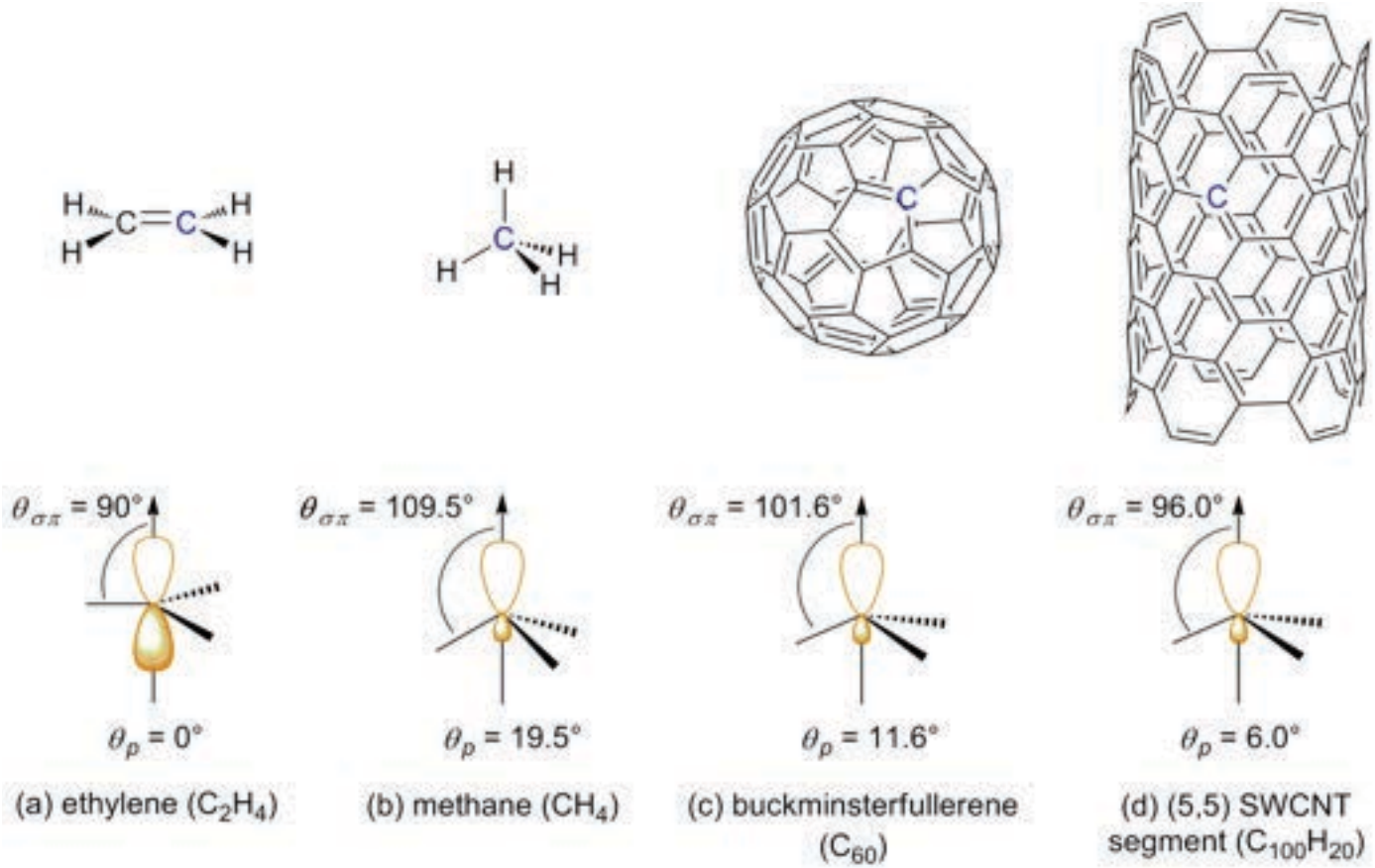
Applications in Biomedicine (e.g, drug delivery, neuron substrates)

CNTs have 2 topologically different zones

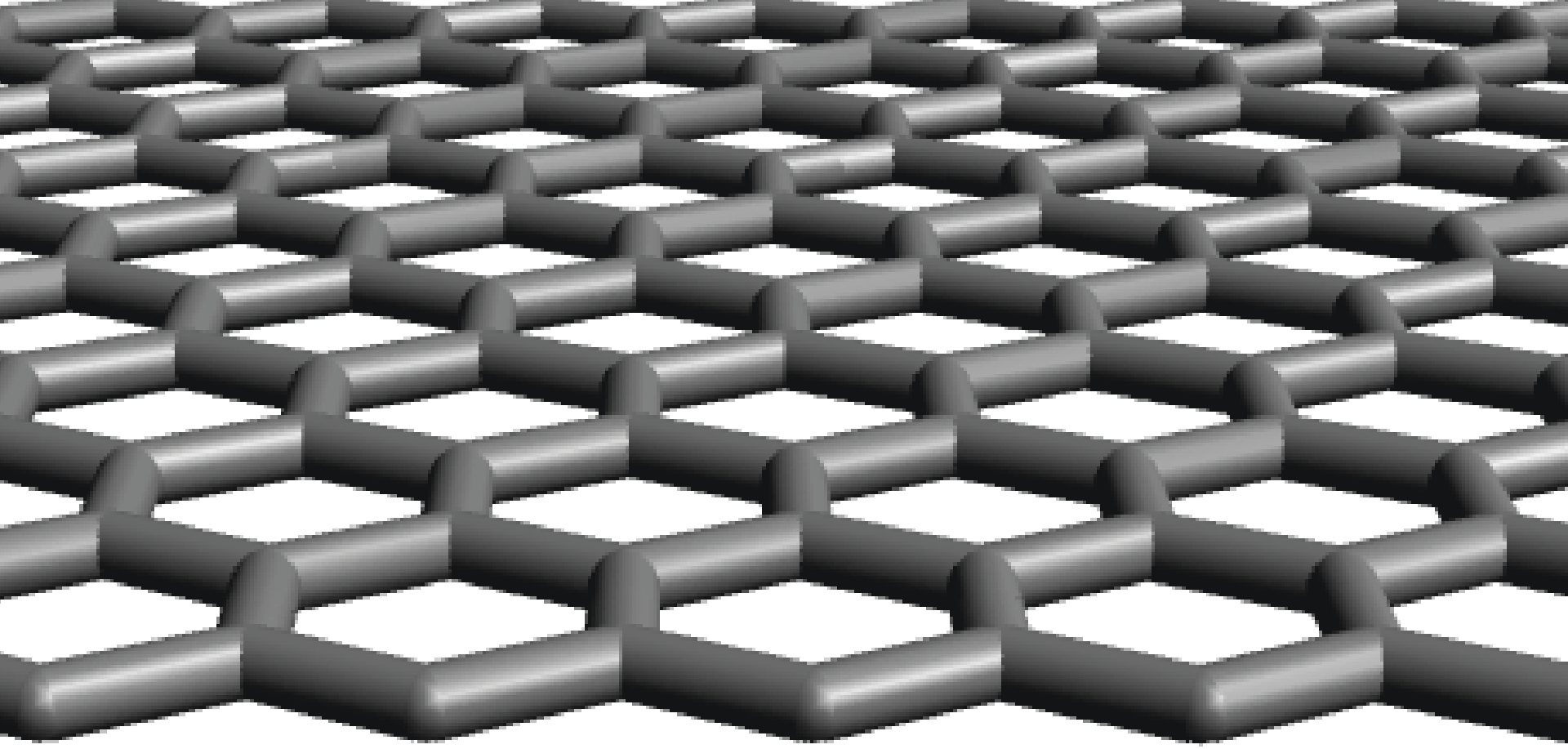


CNTs have 2 topologically different zones

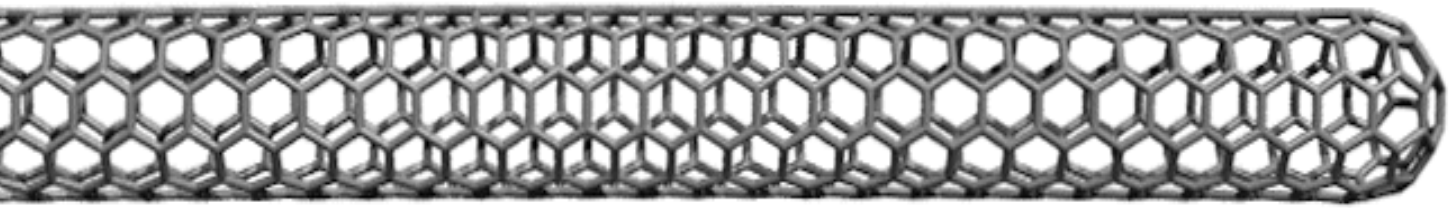


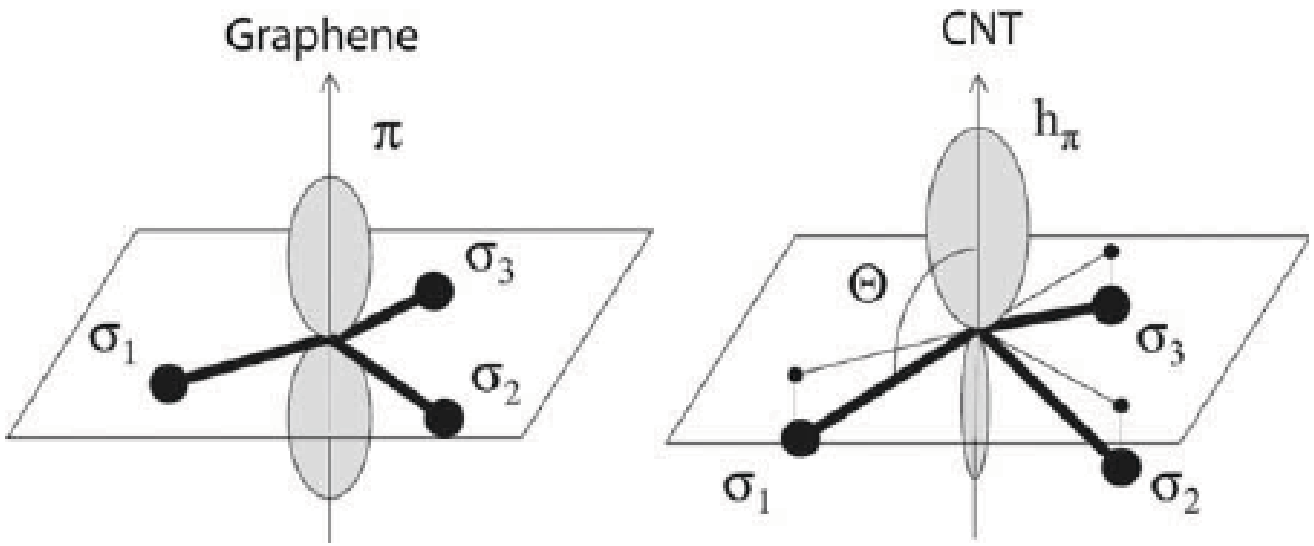


Charles See Yeung, Ya Kun Chen and Yan Alexander Wang

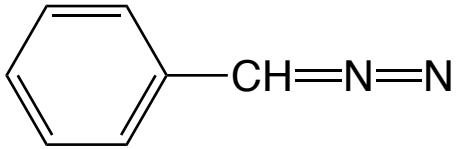


The order of reactivity is:
fullerenes > CNT > graphene

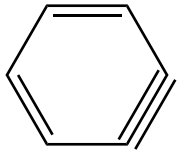




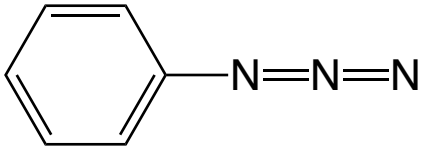
More reactive



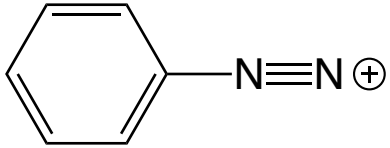
diazo compounds



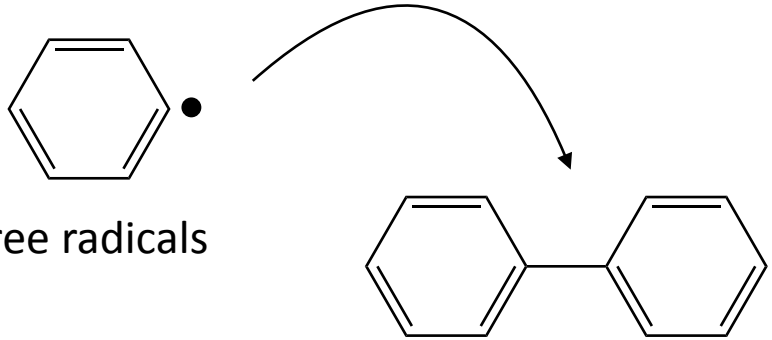
benzyne



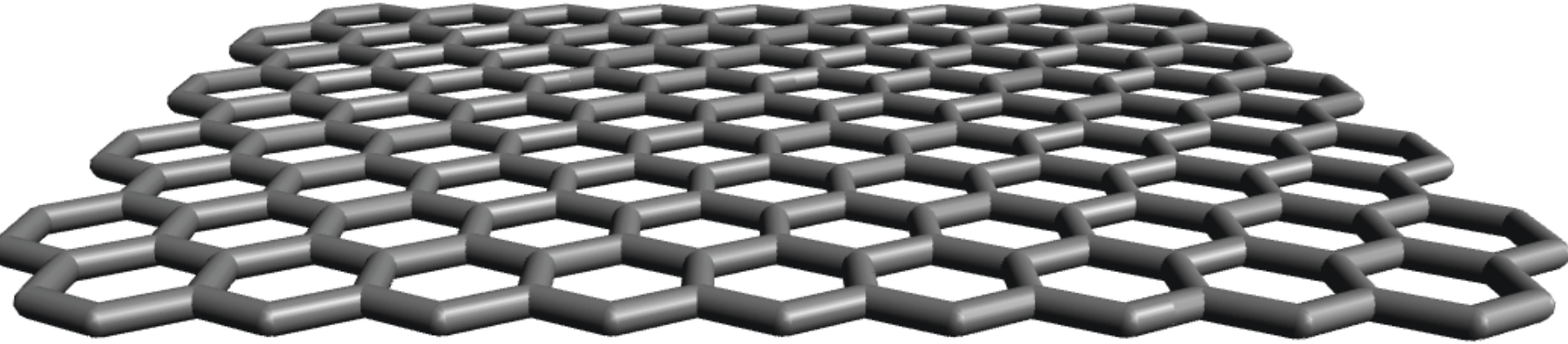
azides



diazonium salts



free radicals

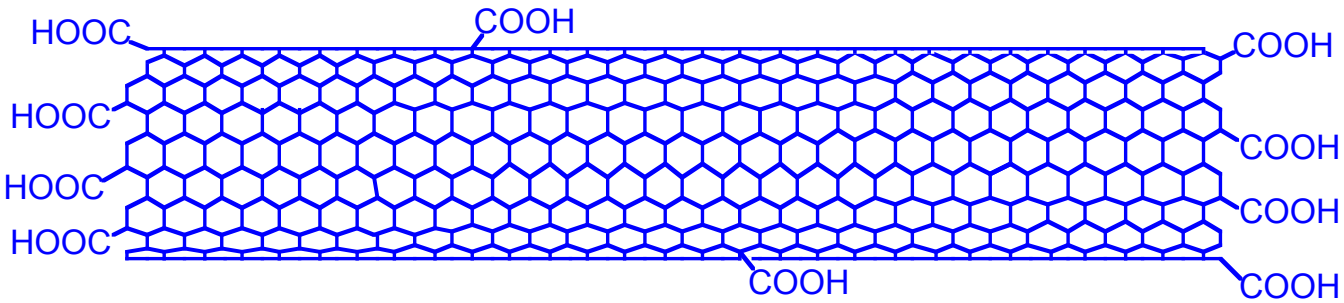


graphene

Most common way to purify SWNT

HNO_3

)))



Disadvantages:

partial loss of structure

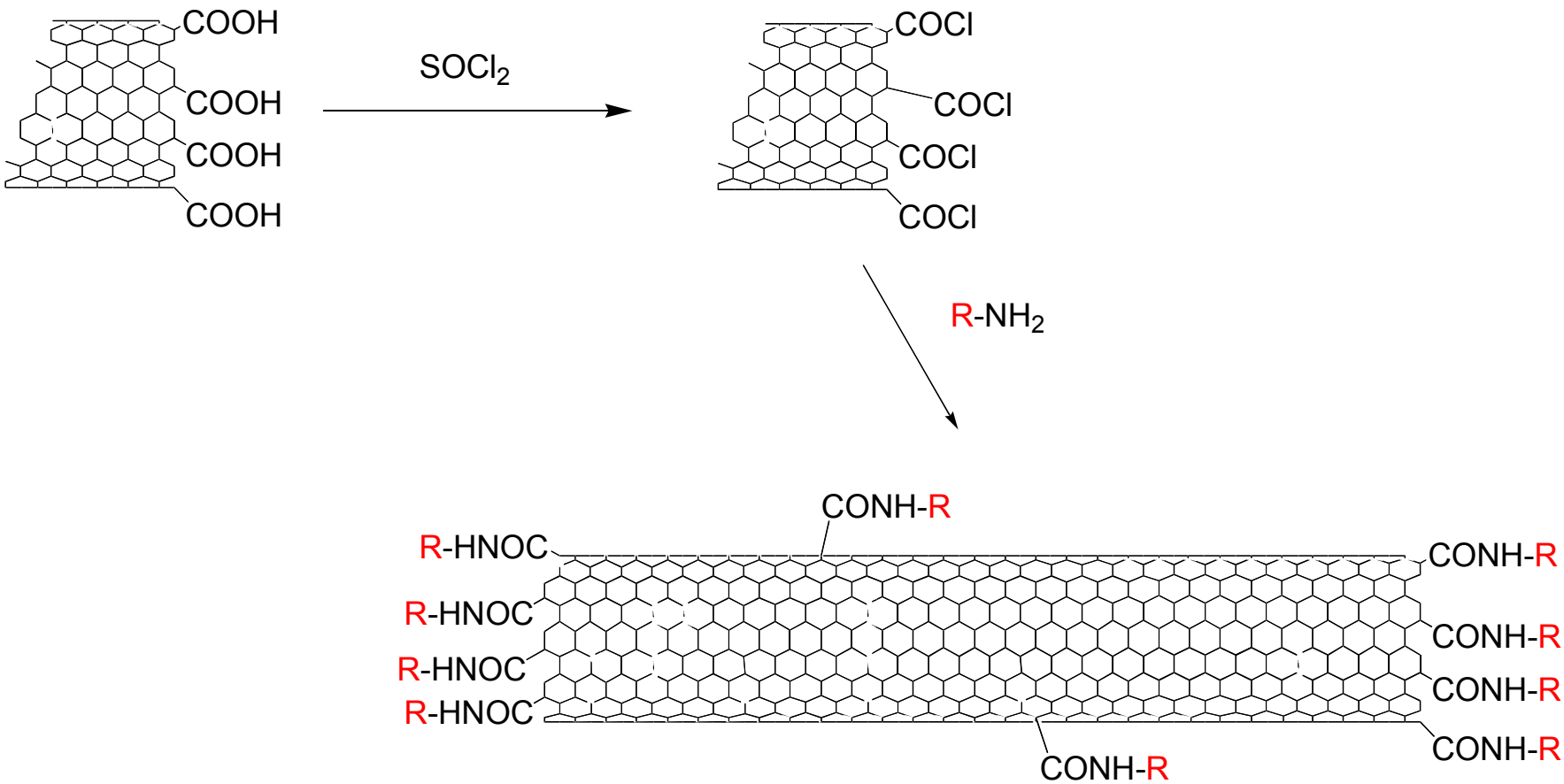
loss of material

increased number of defects

Advantages:

cleaner materials

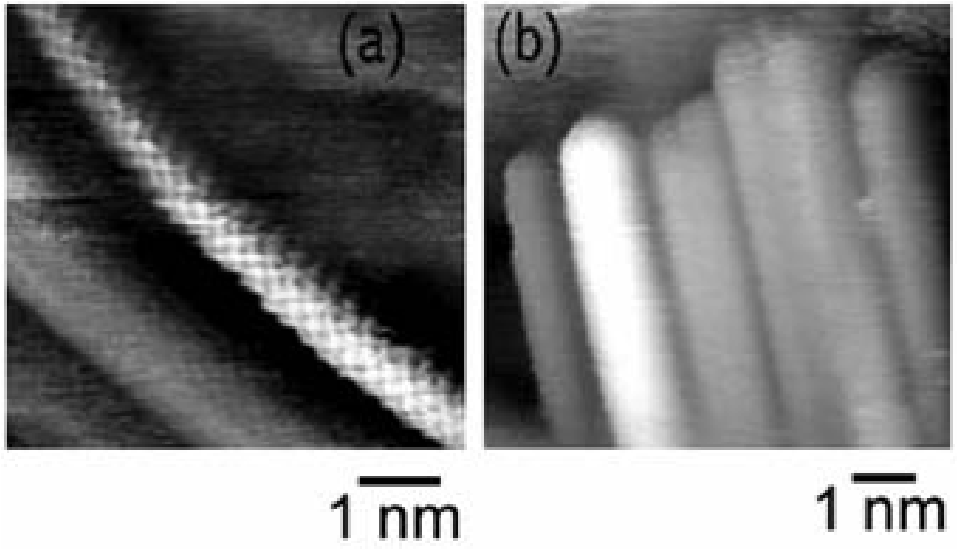
carboxylic groups allow for further functionalization



R = $CH_3(CH_2)_{16}CH_2$-

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

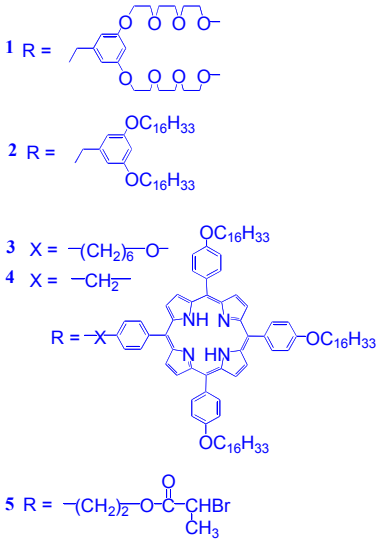
STM (coll. with Prof. S. Modesti, Trieste)

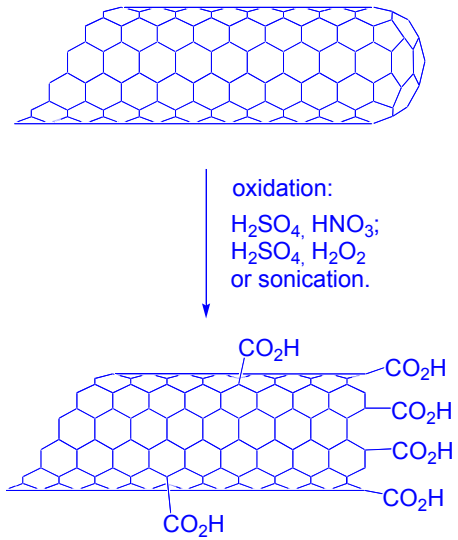


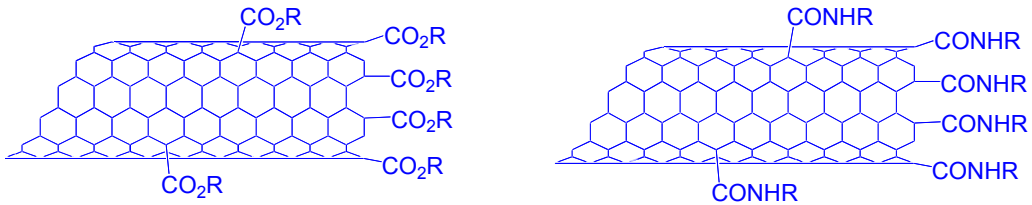
Pristine HiPCO

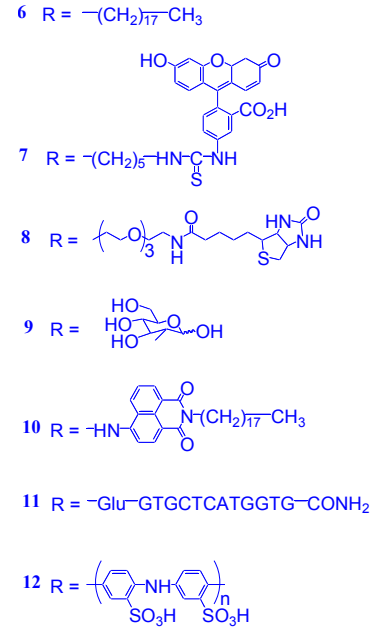
D. Bonifazi et al. Nano Letters, 2006

Oxidation followed by condensation with solubilizing groups (Haddon's approach)





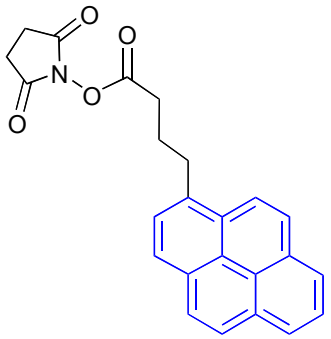


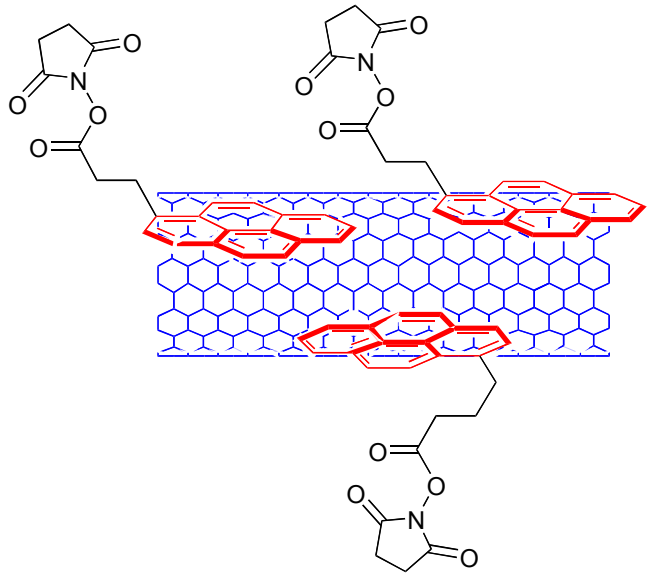


Chem.Phys.Lett. 2004 p342, JACS 2004 p170, AC 2004 p896, CM 2001 p2864,

JACS 2003 p14893, AFM 2004 p71, JACS 2004 p6850, JMC 2003 p2196, JMC 2004 p 1924, NL 2002 p369, Nature 2002 p761

Two general ways





b

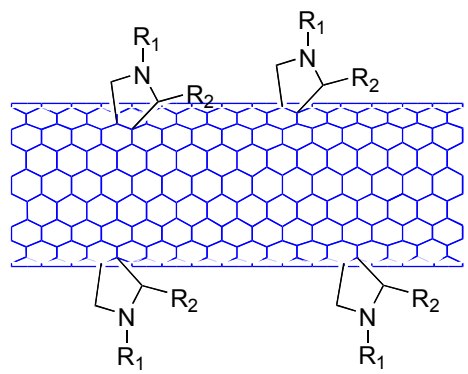
SWNT

leaves CNT electronic properties unaffected

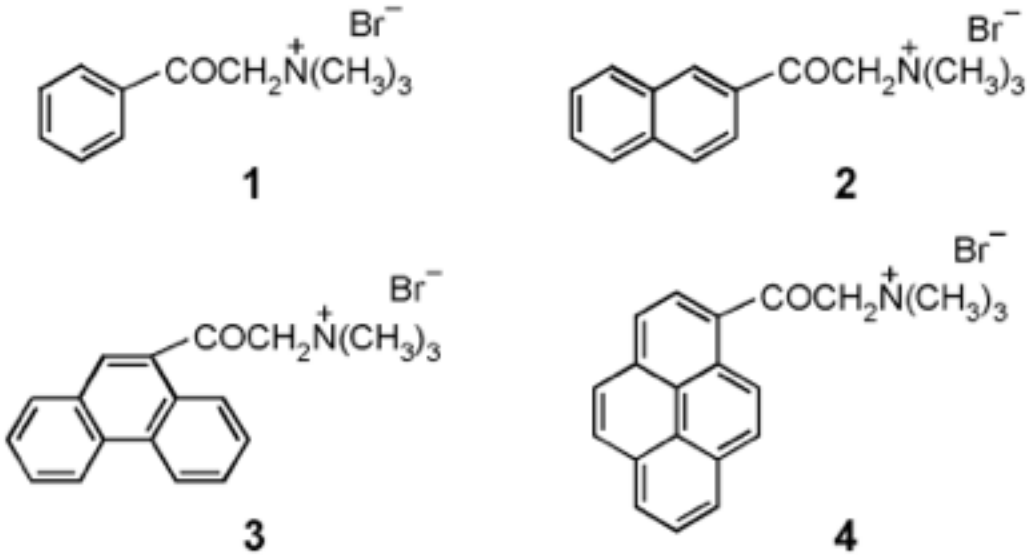
a

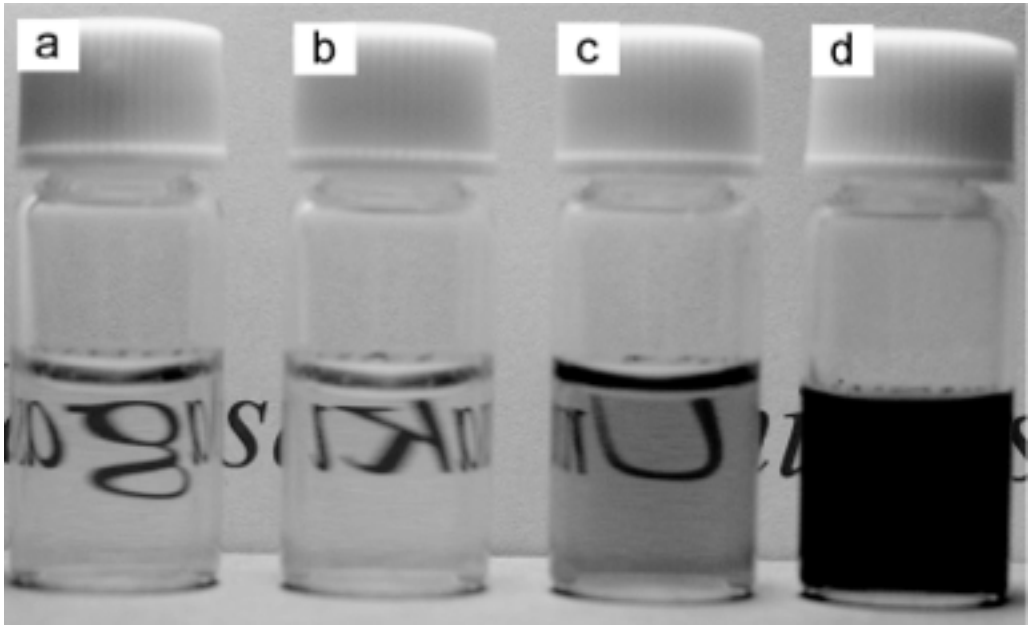
R_1-NH_2CH_2COOH

R_2CHO, DMF, 130° C



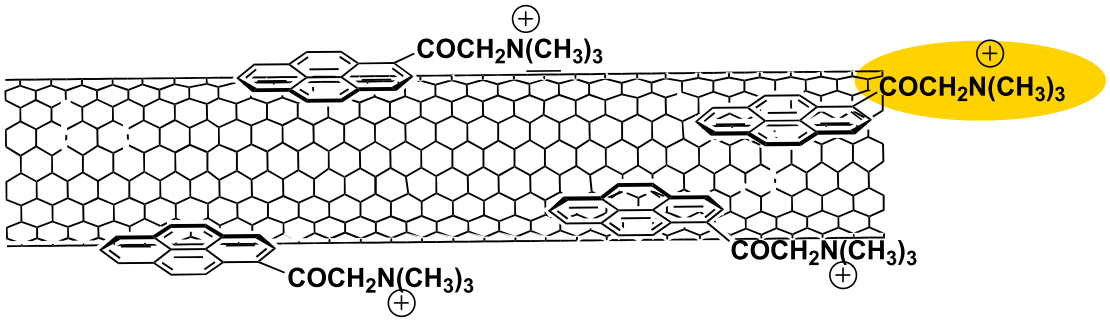
can affect CNT electronic properties

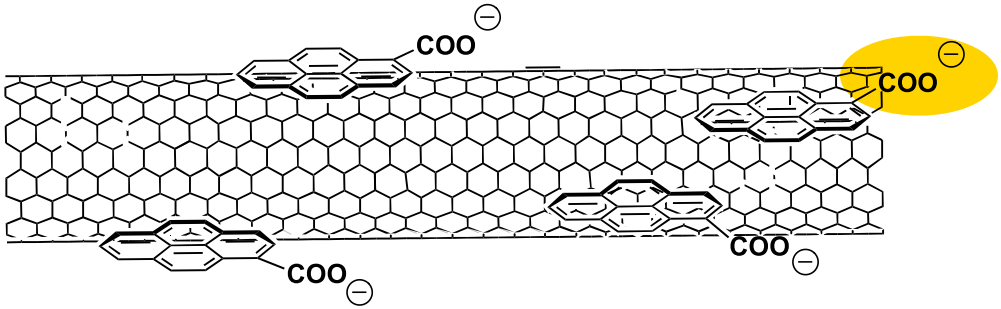




Nakashima et al. Chem Eur J. **12**, 4027 (2006)

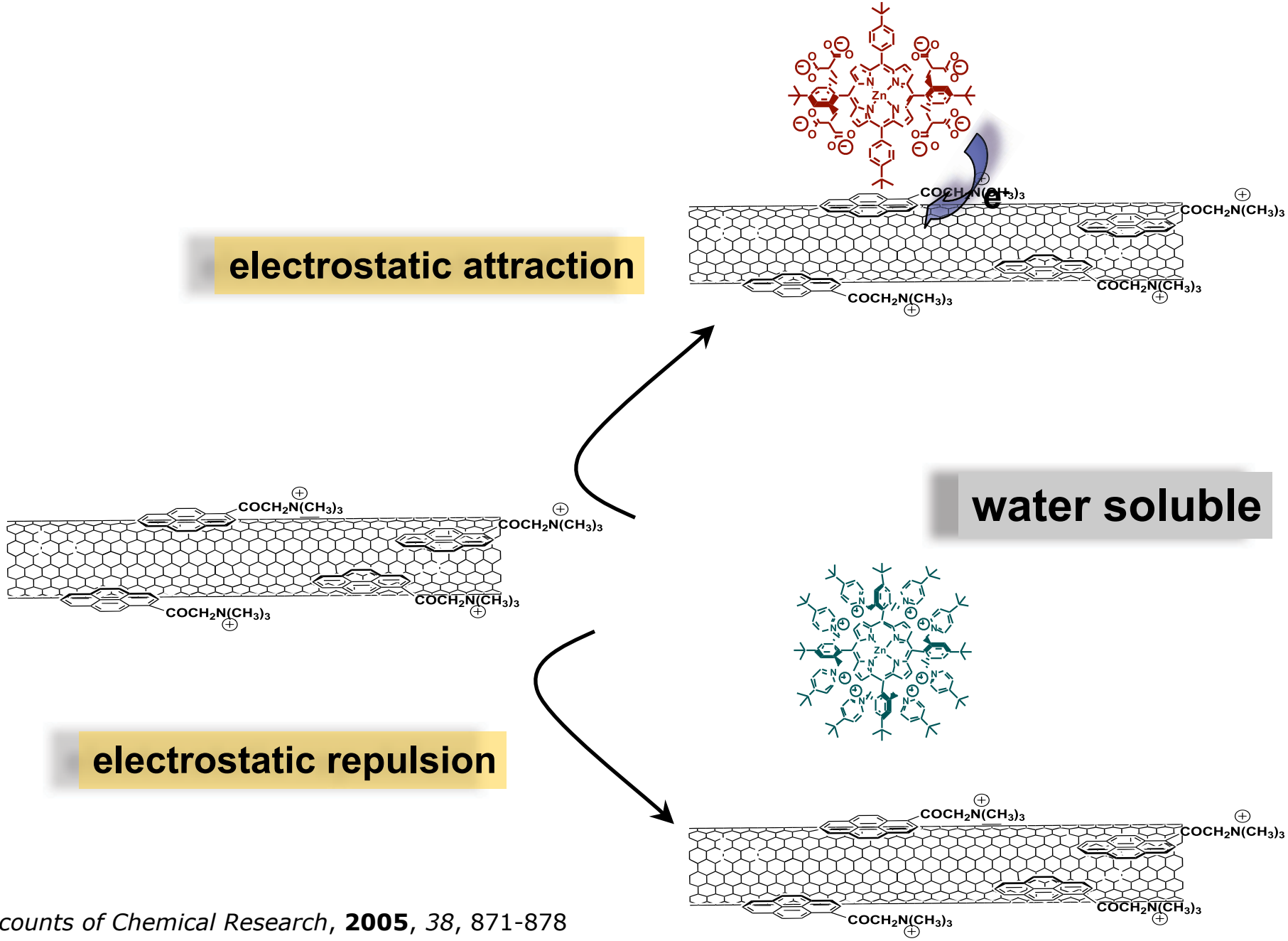
approaches to preserve the electronic structure of SWNT





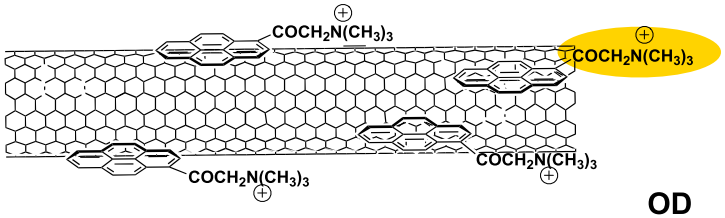
SWNT•pyrene$^{+/-}$ nanohybrids

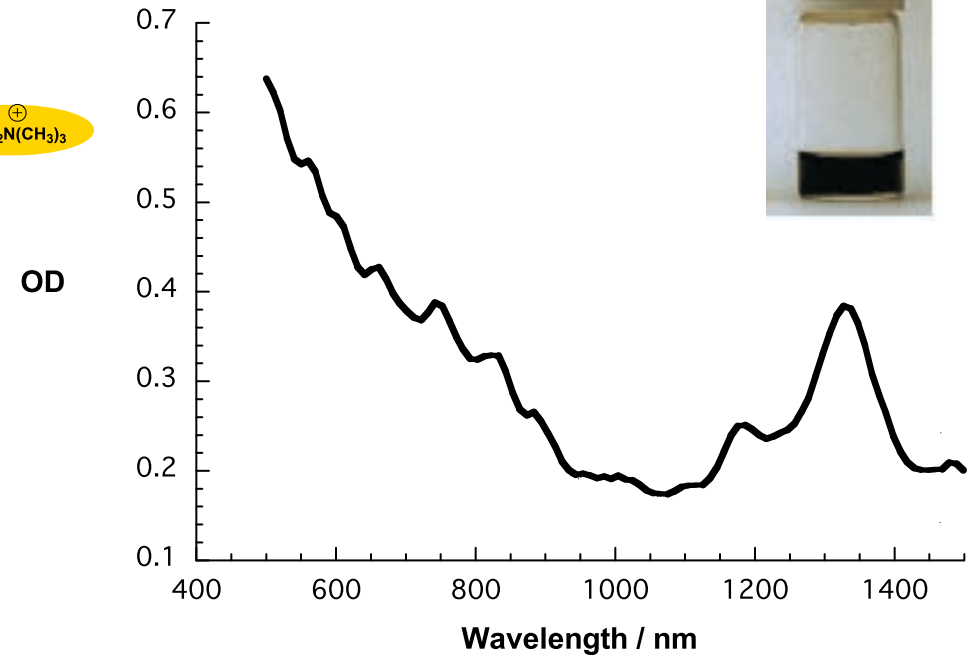
SWNT•pyrene^{+}•ZnP^{8-} donor-acceptor nanohybrids

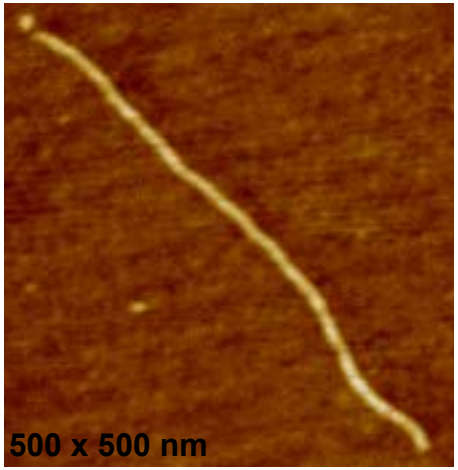


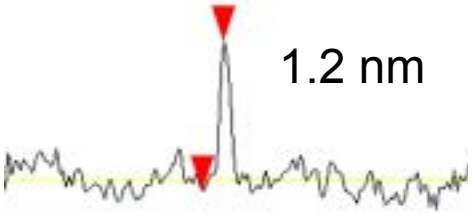
Accounts of Chemical Research, **2005**, *38*, 871-878

SWNT•pyrene$^+$ nanohybrids

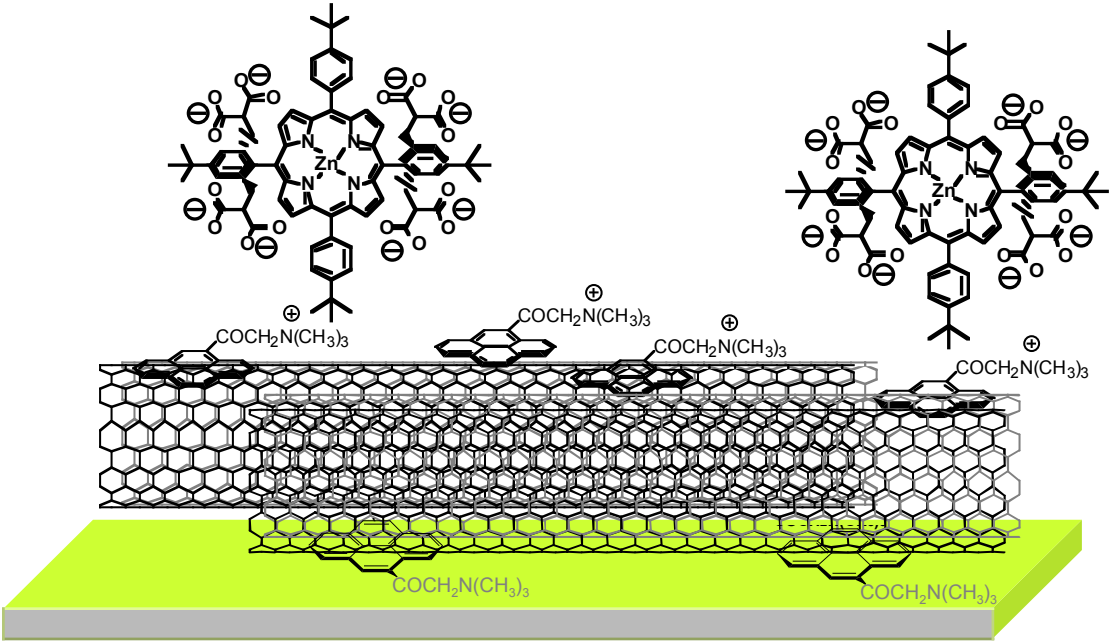






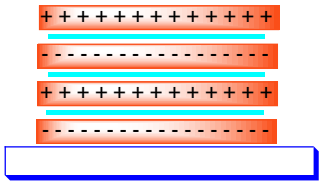


LBL deposition on ITO of photoactive components SWNT•pyrene^{+} nanohybrids

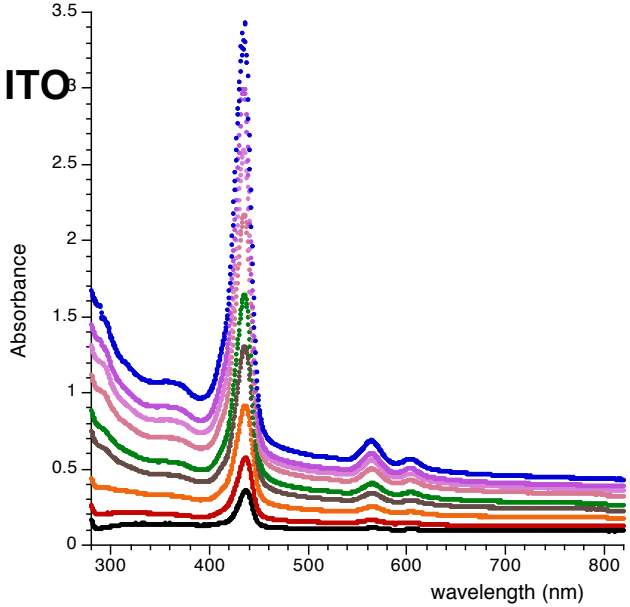


ZnP^{8-}

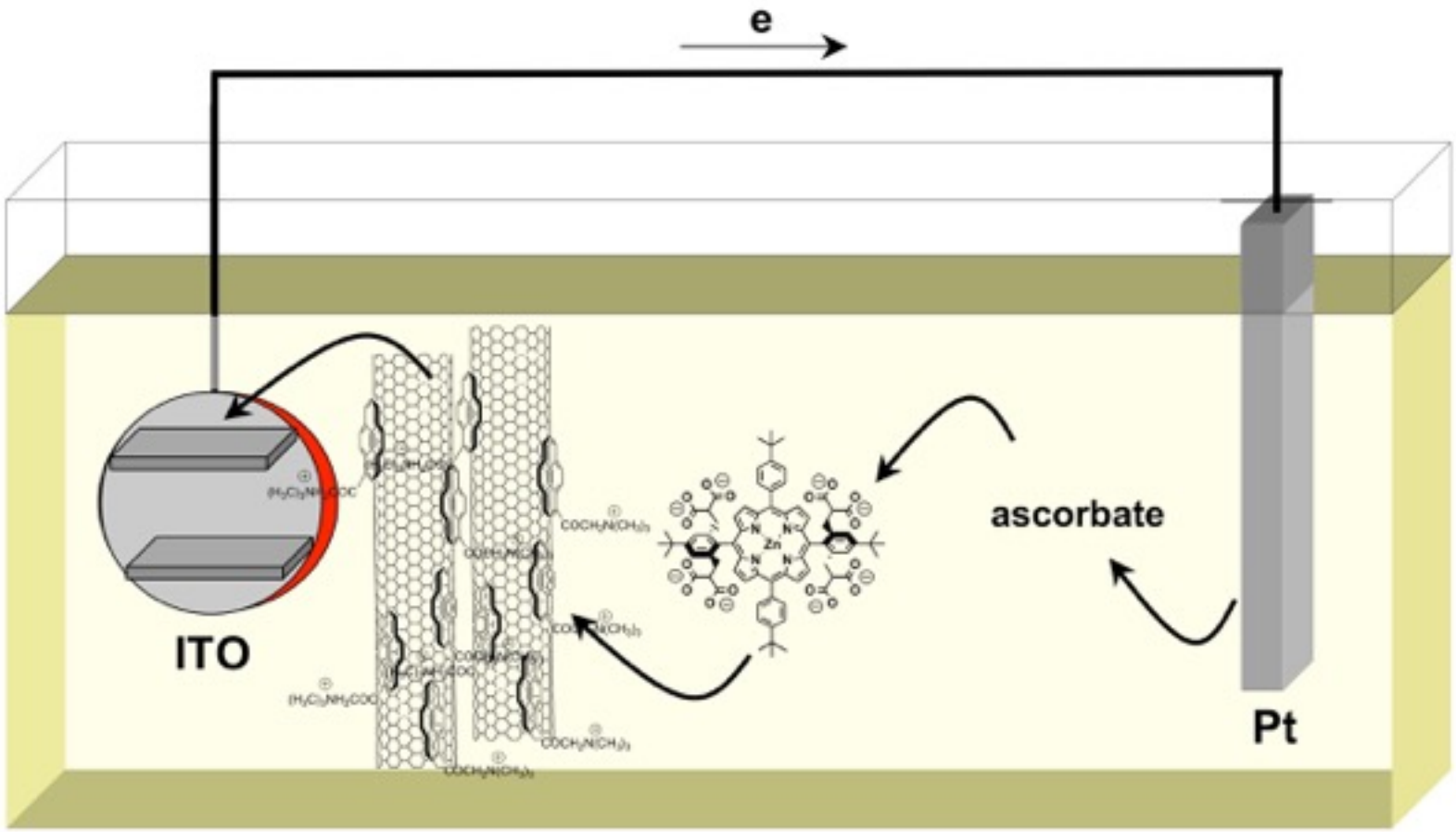
SWNT•pyrene^{+}



ITO



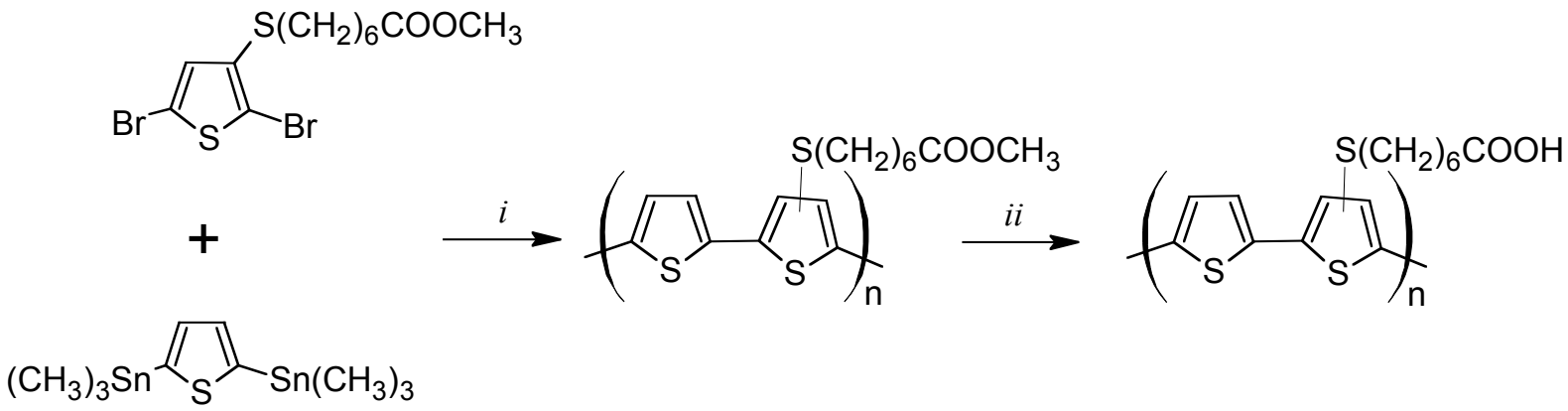
nanostructured ITO•SWNT•pyrene^{+}•ZnP^{8-} cells



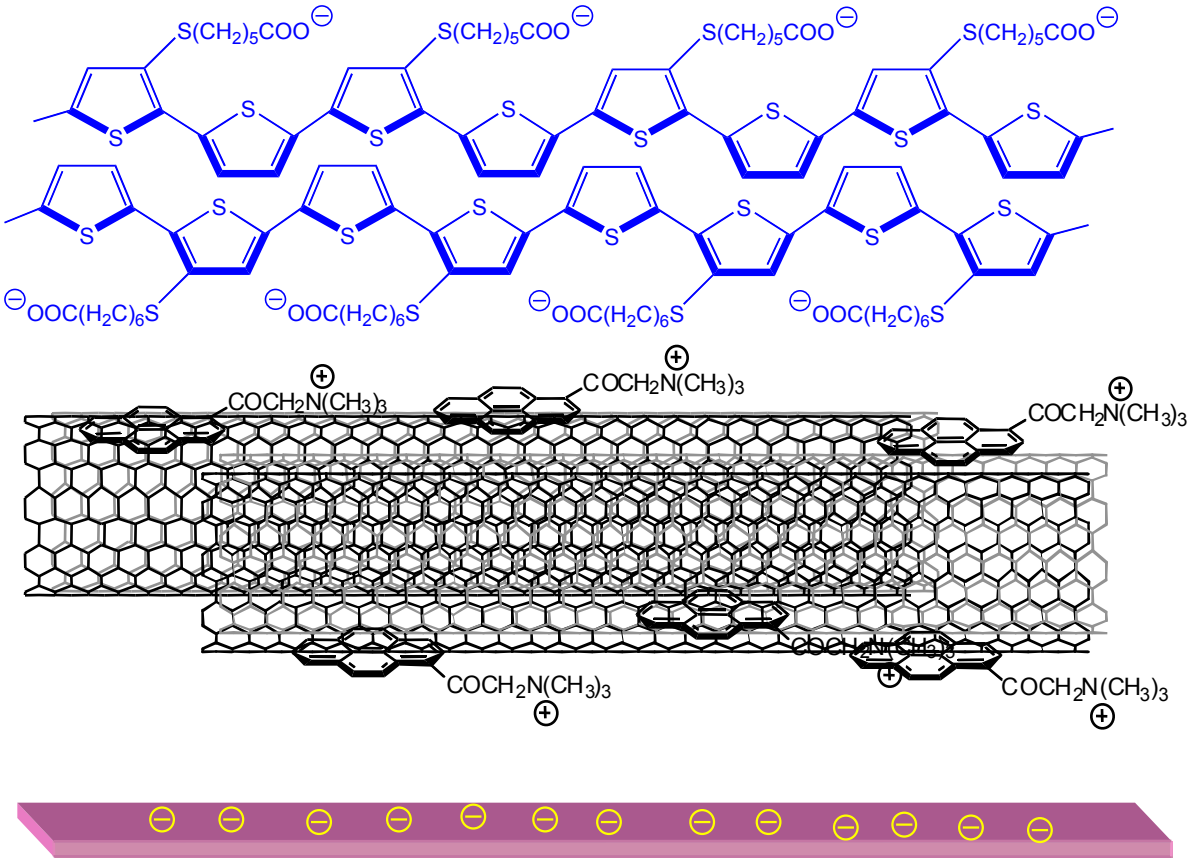
Monochromatic efficiency 8.5%

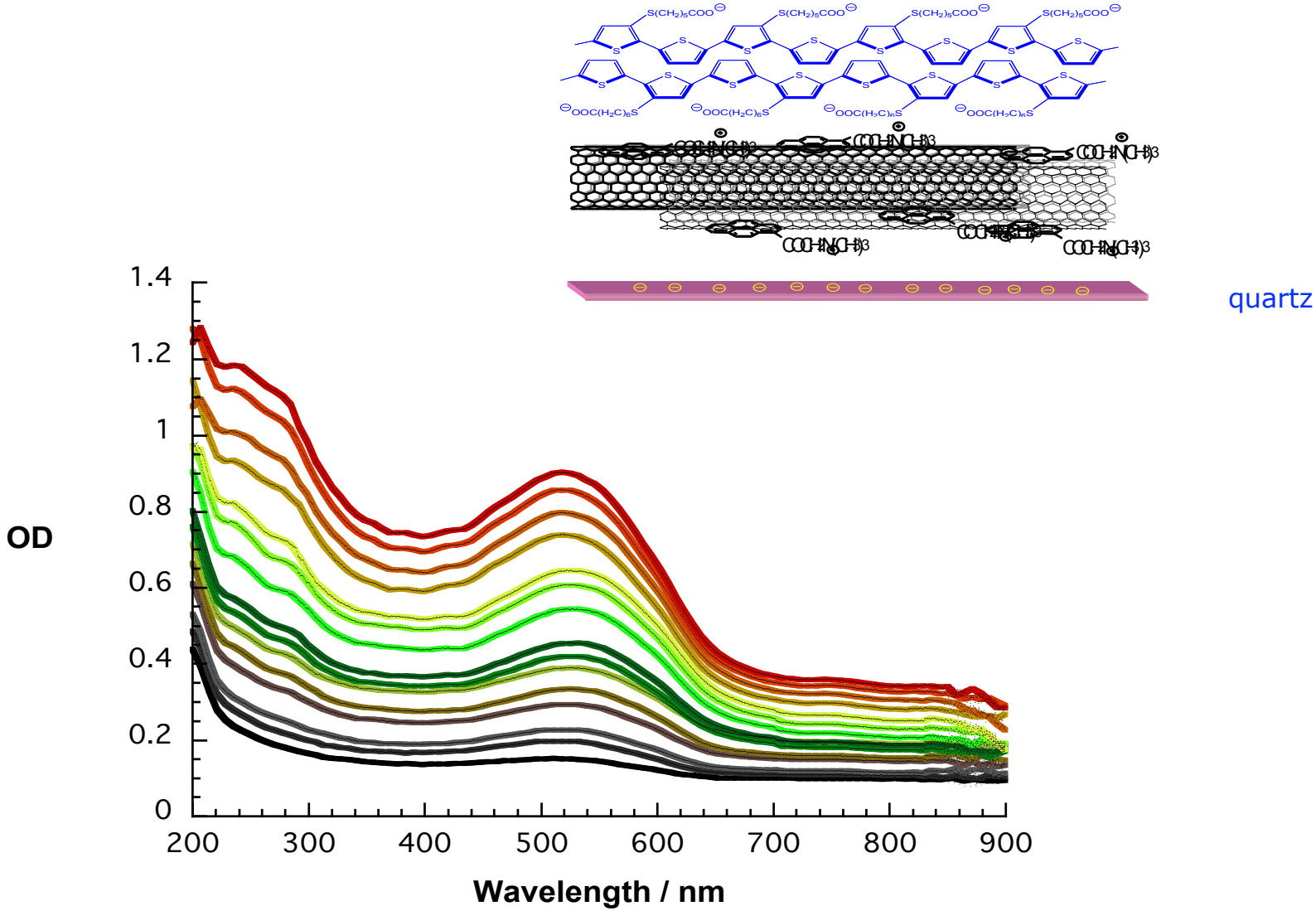
D. M. Guldi et al. *Angew. Chem. Int. Ed.* **2005**, *44*, 2015

Synthesis of a photo- and electroactive polymer

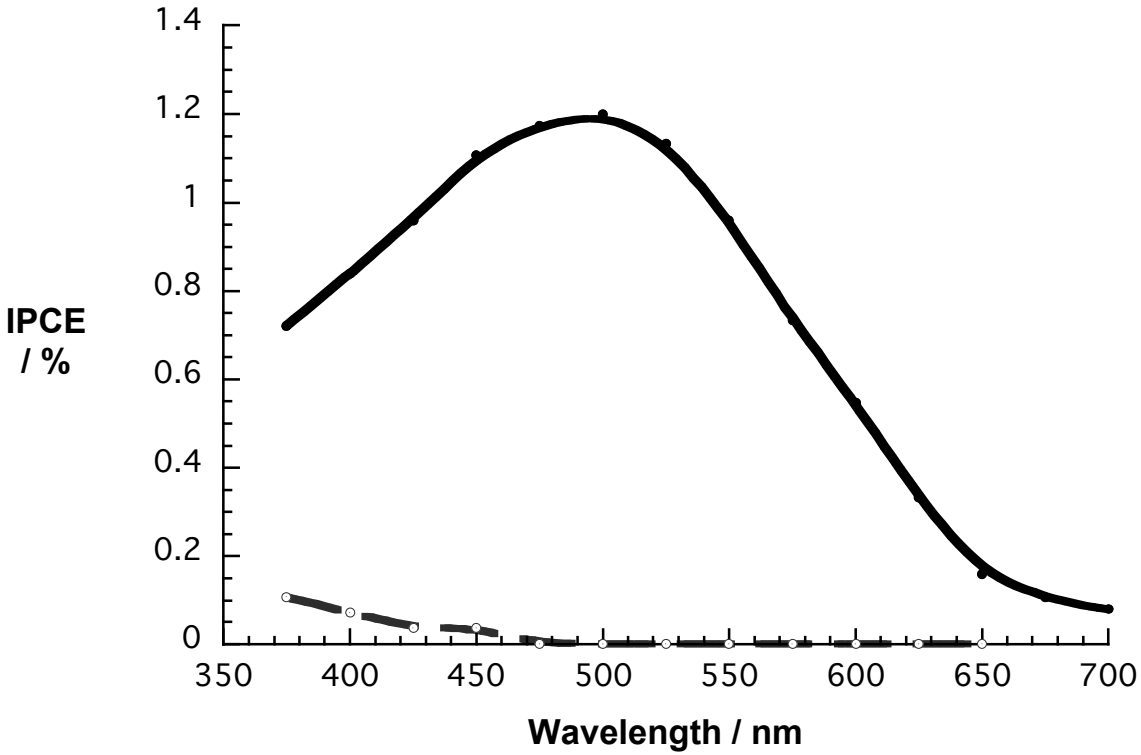


i) $Pd(PPh_3)_4$, THF/DMF 1:1, 90 °C, 60 h; *ii*) NaOH, CH_3OH/THF, 70 °C, 3 h


S(CH2)5COO⊖
S
⊖OOC(H2C)6S
COCH2N(CH3)3
ITO



Absorption spectra of **SWNT pyrene⁺ / PSCOOH**)$_n$ sandwich layers on quartz (up to 15)

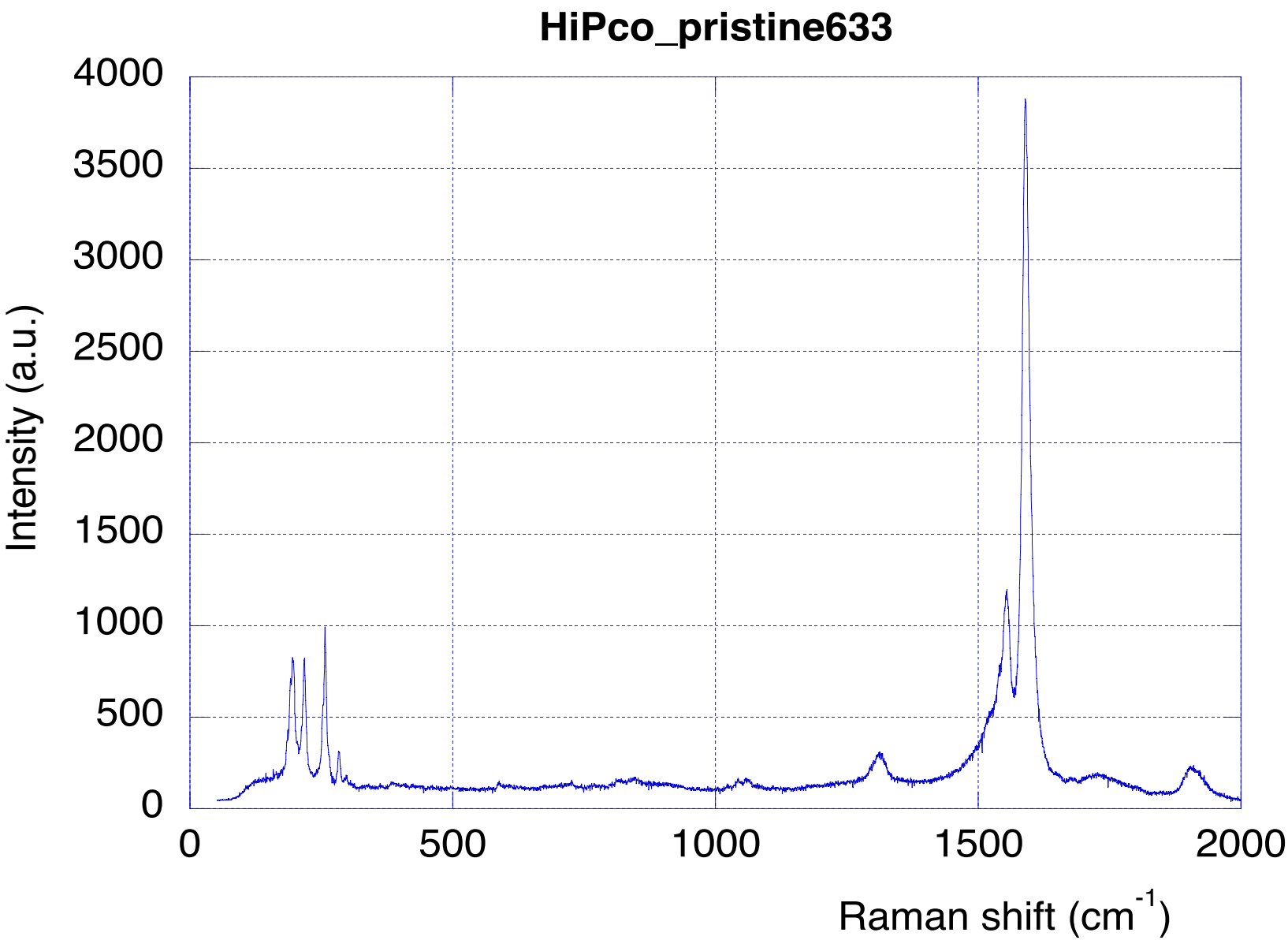


Photoaction spectrum of **SWNT pyrene$^+$** (dashed line) and a single **SWNT pyrene$^+$ / PSCOOH** (solid line) sandwich layer – 0.1 M Na_3PO_4, 1 mM sodium ascorbate, no electrochemical bias. monochromatic incident photoconversion efficiencies (IPCE) in the range of 1.2 % and 9.3 % for a single and eight sandwich layers, respectively

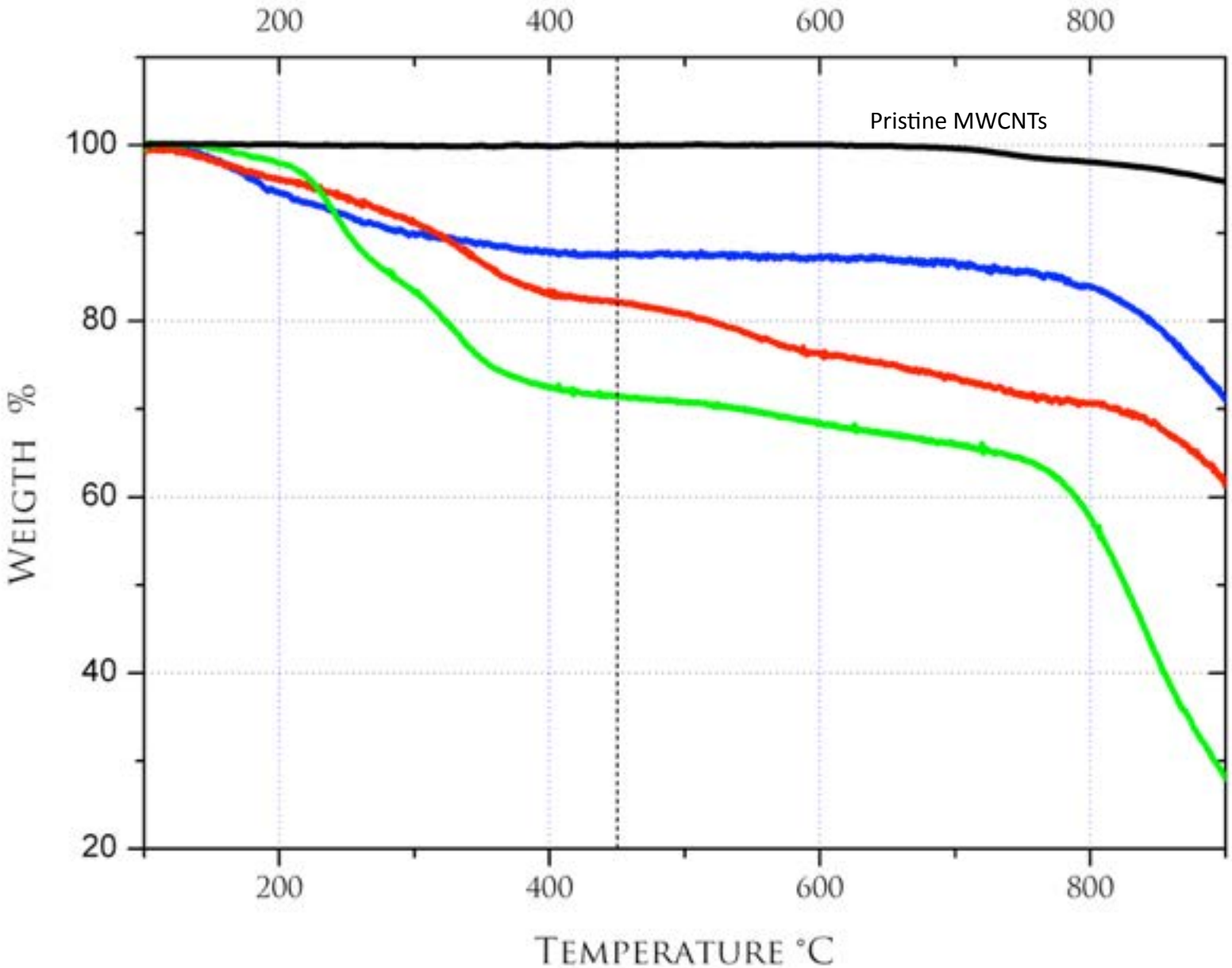
J. Amer. Chem. Soc., **2005**, *127*, 10051

Covalent Chemistry

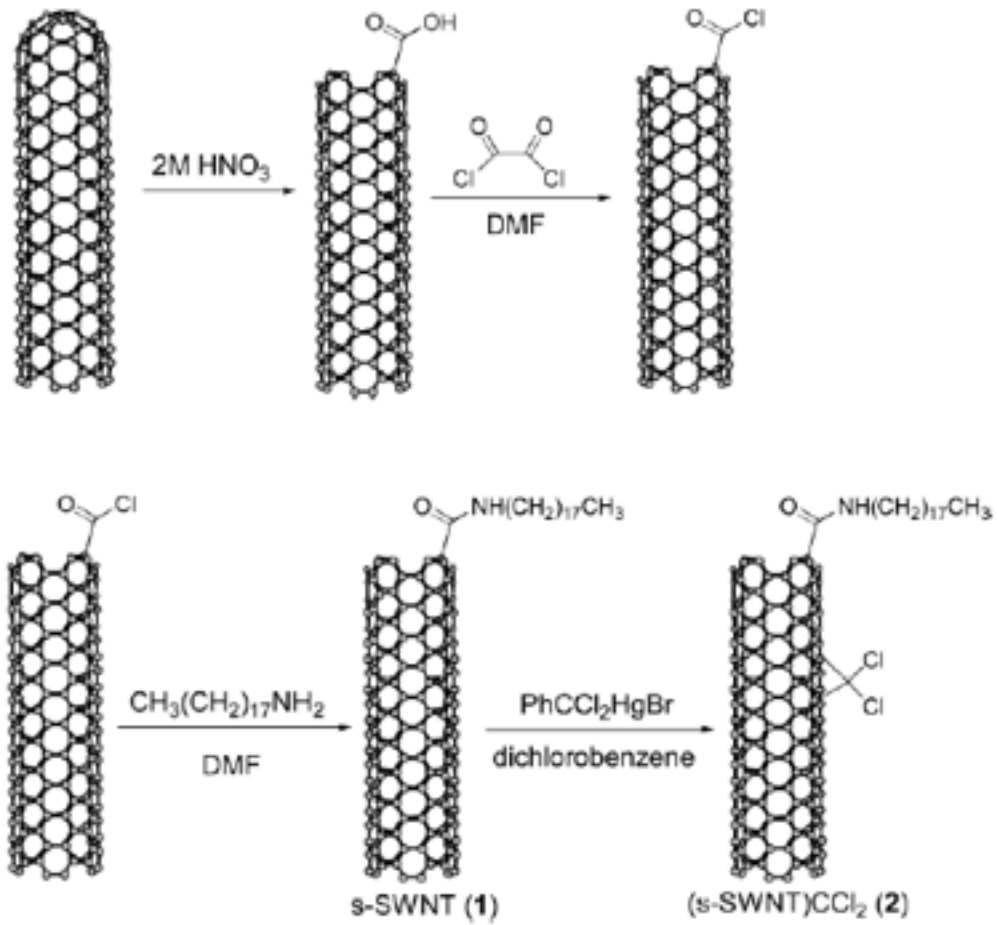
Raman Spectroscopy



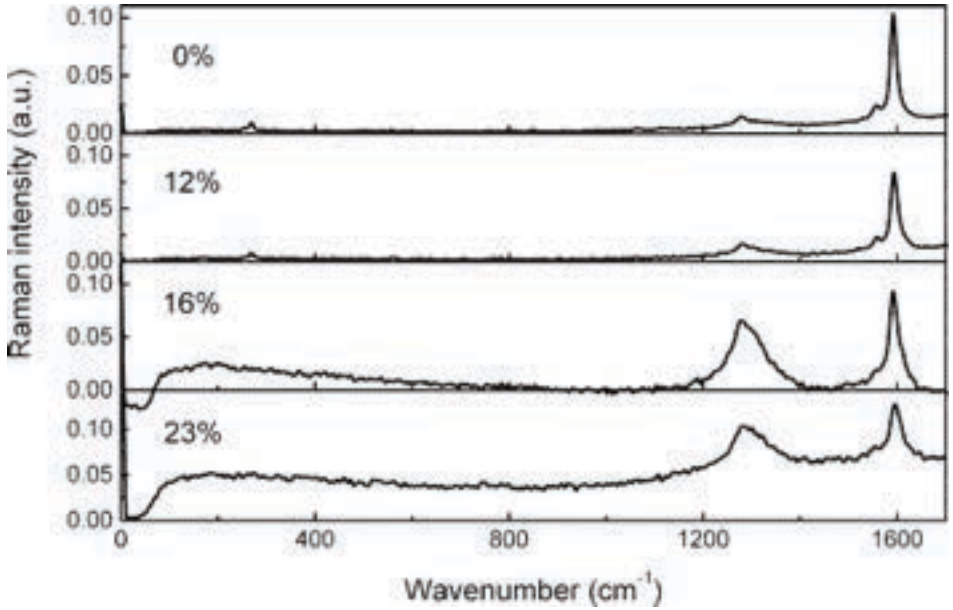
Thermogravimetric Analysis



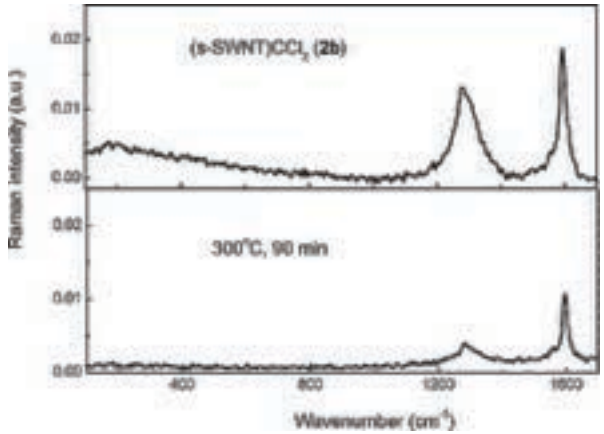
Addition of dichlorocarbene



JACS 2003, 125, 14893

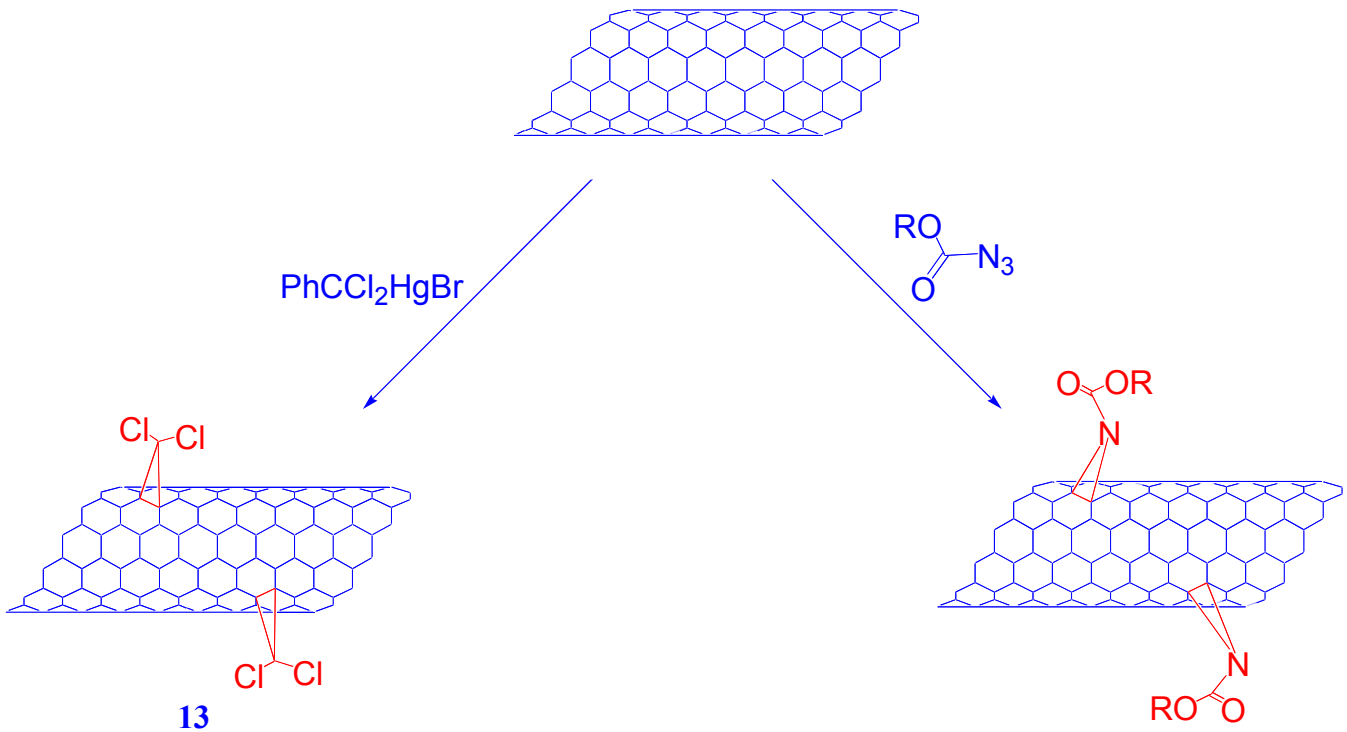


Raman spectra (film on Zn-Se substrate) of s-SWNT (1) (0%); (s-SWNT)CCl2 (2a) (12%); (s-SWNT)CCl2 (2b) (16%); (s-SWNT)CCl2 (2c) (23%). The spectra are labeled with the degree of functionality (Cl/Cwall)%.



Raman spectra (film on Zn-Se substrate) of (s-SWNT) CCl2 (2b) and (s-SWNT)CCl2 (2b) heated at 300 C for 90 min.

Addition of carbenes and nitrenes



13

Science 2003 p1501, JACS 2003 p14893

14 R = Ethyl

15 R = *tert*-Butyl

16 R =

17 R =

18 R =

19 R =

20 R =

21 R =

22 R =

23 R =

24 R =

25 R =

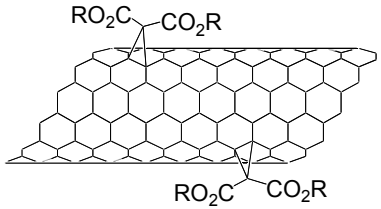
26 R =

27 R =

28 R =

AC 2001 p4002, JACS 2003 p8566

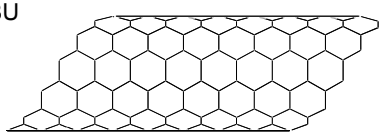
Cycloadditions

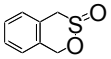


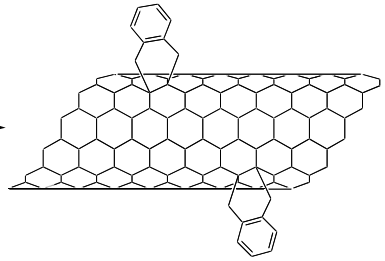
1) EtO_2C–CH(Br)–CO_2Et DBU

2) HO–CH_2CH_2–SCH_3 or MO–CH_2CH_2–C_8F_{17}

M = Na, Li







29 R = $-(CH_2)_2-SCH_3$

30 R = $-(CH_2)_2-(CF_2)_7-CF_3$

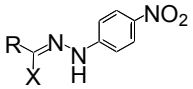
JACS 2003 p8722

39

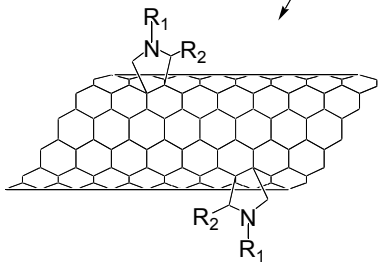
CC 2004 p3714

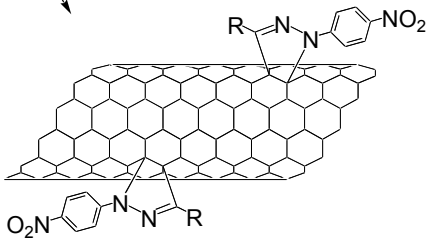
R_1HN–CH_2CO_2H

R_2CHO



X (Br, Cl)

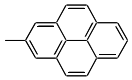




31 R_1 = –O–CH_2CH_2–O–CH_2CH_2–O– R_2 = H

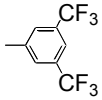
32 R_1 = $-(CH_2)_7-CH_3$ R_2 = H

33 R_1 = –O–CH_2CH_2–O–CH_2CH_2–O– R_2 = –C6H4–OCH_3

34 R_1 = –O–CH_2CH_2–O–CH_2CH_2–O– R_2 = 

35 R_1 = –O–CH_2CH_2–O–CH_2CH_2–NHBoc R_2 = H

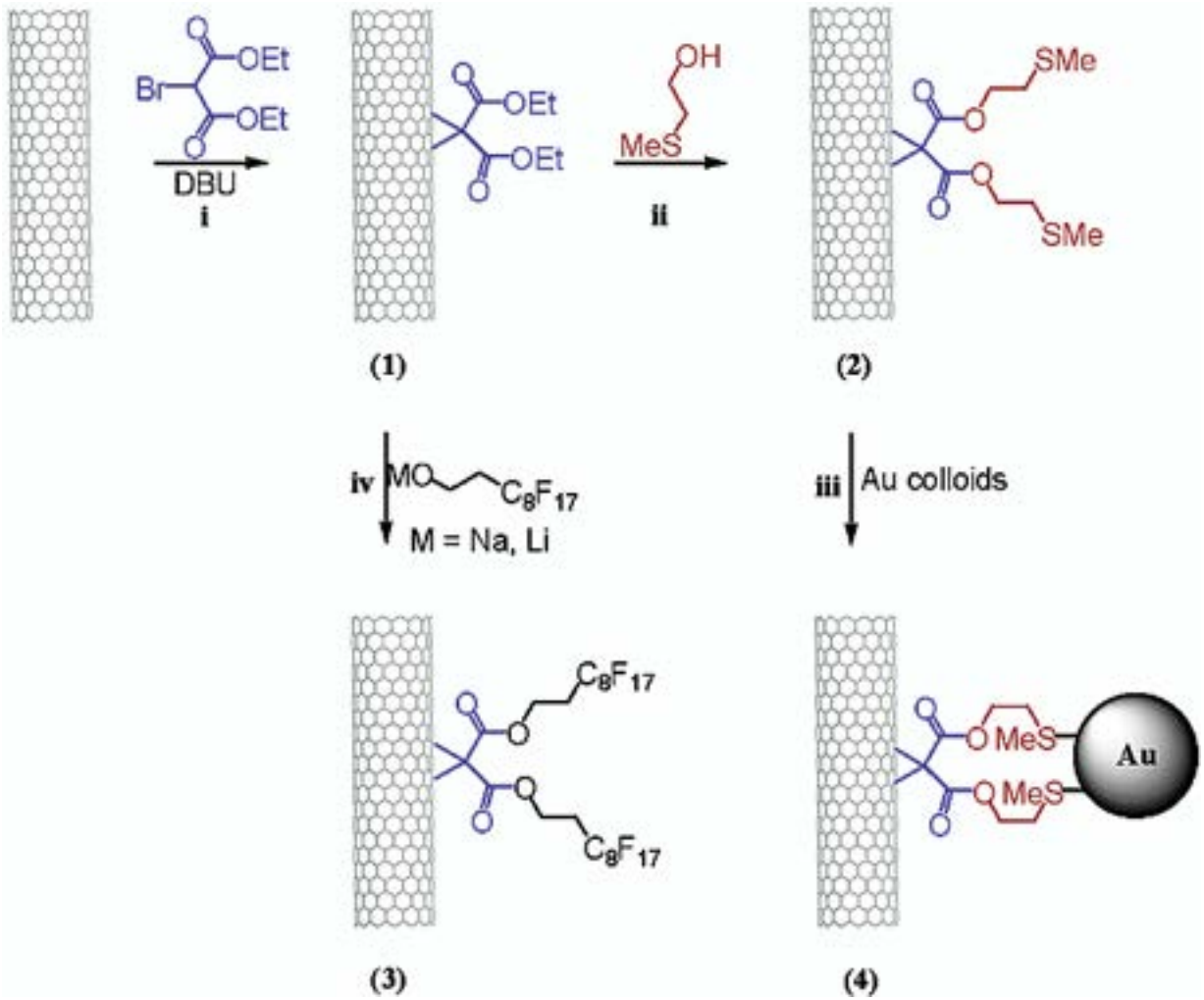
36 R_1 = –C6H4–OH R_2 = $-C_8H_{17}$

37 R_1 = 

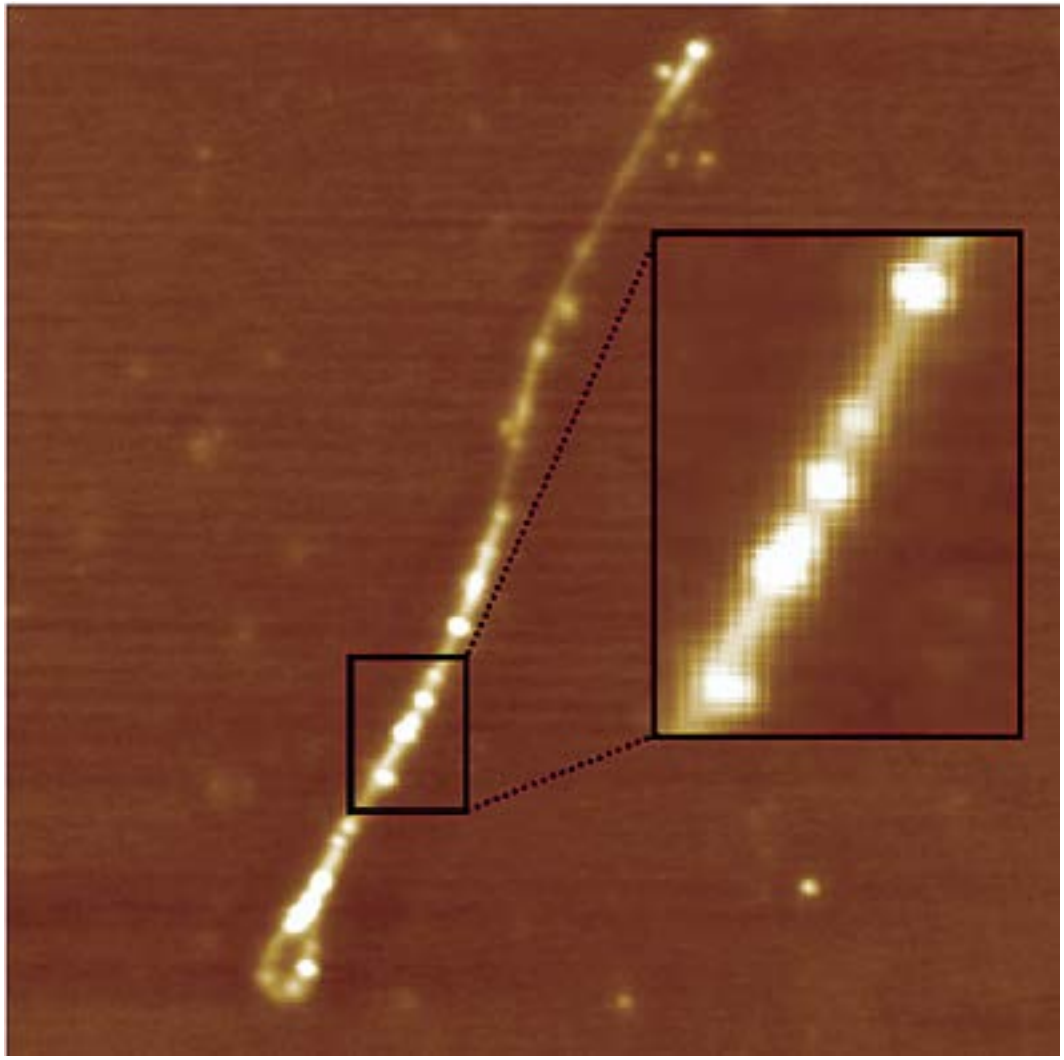
38 R_1 = –C6H4–NMe_2

JPCB 2004 p12691

JACS 2002 p760, CC 2002 p3050, JACS 2003 p16015



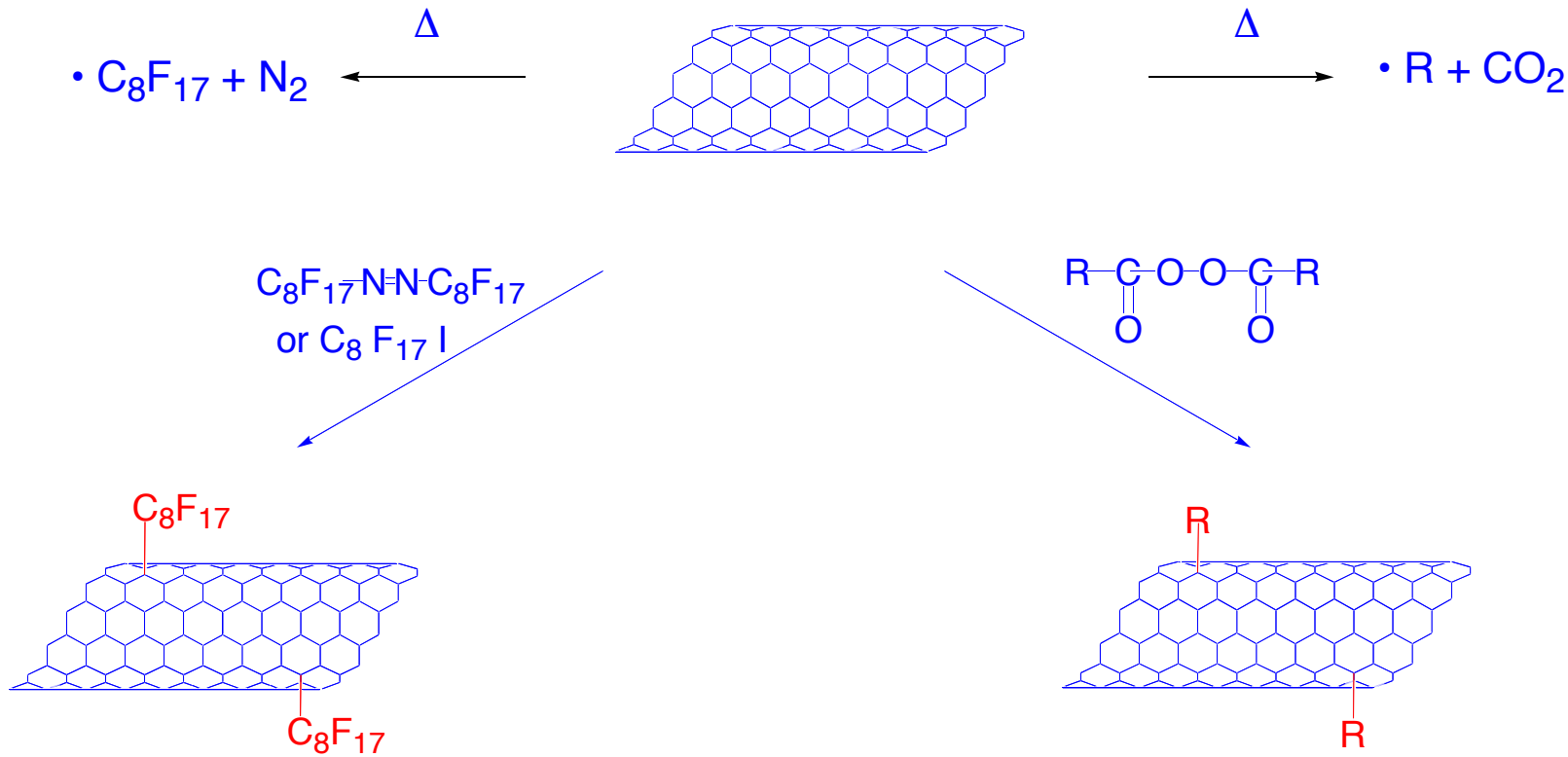
J. Am. Chem. Soc., 125 (29), 8722 -8723, 2003



A typical tapping mode AFM (height) image of a SWNT functionalized by the Bingel reaction, [(COOCH2CH2SMe)2C<SWNT], and after exposure to ~5 nm Au colloids (4). The image shown is 900 nm × 900 nm, z scale 0–5 nm. The Au colloids can be seen (light colored features) decorating the complete length of the nanotube.

J. Am. Chem. Soc., 125 (29), 8722 –8723, 2003

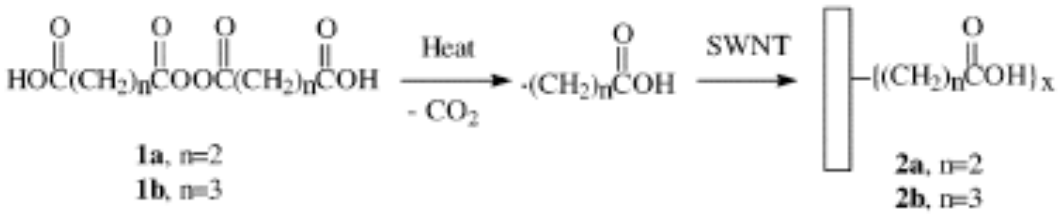
Radical additions



AC 2001 p4002, CC 2004 p1336

45 R = $-(CH_2)_{17}-CH_3$
46 R = $-(CH_2)_3-CH_3$
47 R = $-CH(CH_3)-CH_2-CH_3$
48 R = $-CH_2-CONH_2$
49 R = $-(CH_2)_3-Cl$
50 R = $-CH_2CN$
51 R = $-(CH_2)_3-OTHP$

CC 2003 p362, JACS 2003 p15174, OL 2003 p1471



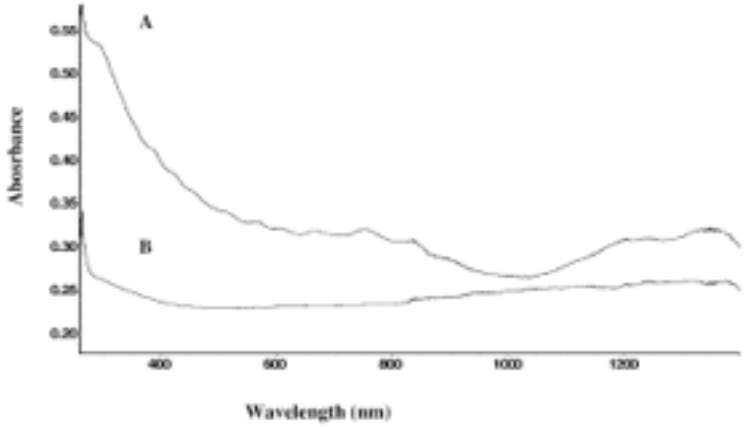


Figure 2. UV–vis–NIR spectra of (A) pristine SWNTs and (B) SWNT derivative 2a.

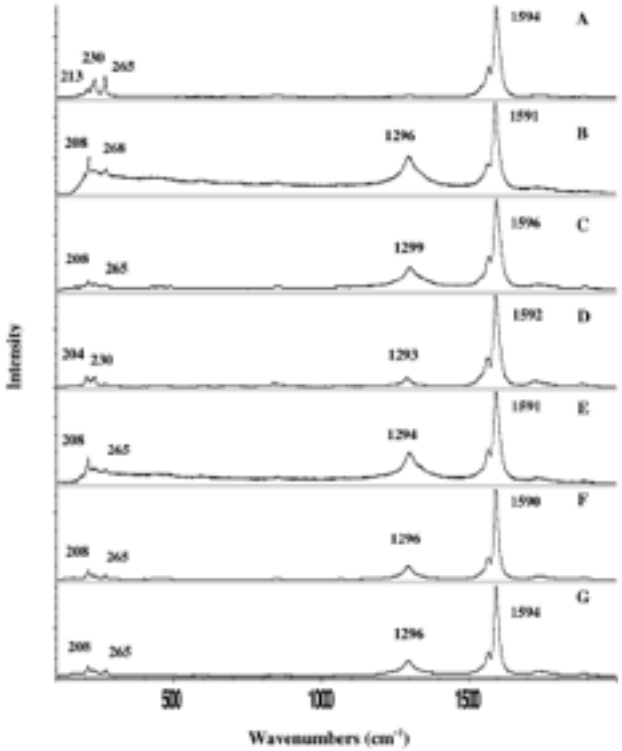
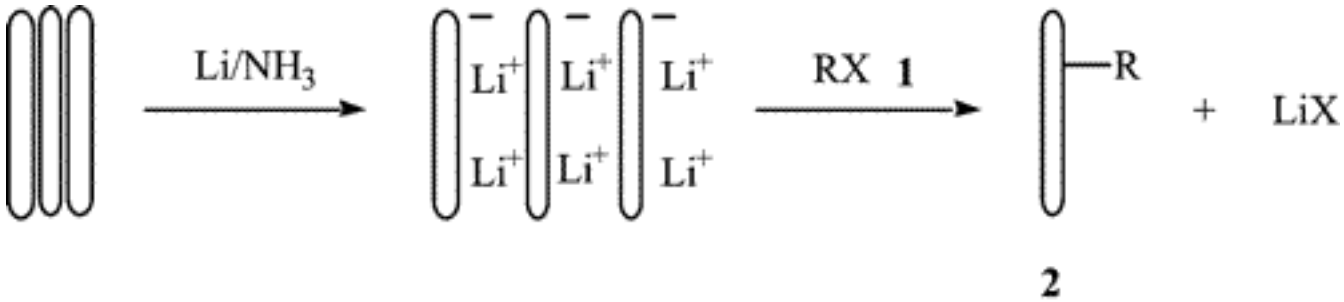
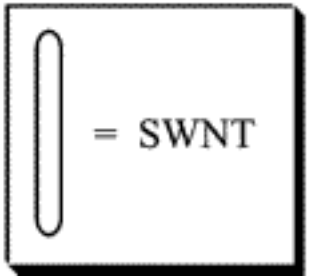


Figure 1. Raman spectra of SWNT materials: (A) pristine SWNTs, (B) 2a, (C) 2b, (D) SWNT residue after TGA of 2a, (E) 3, (F) 4, (G) 5.

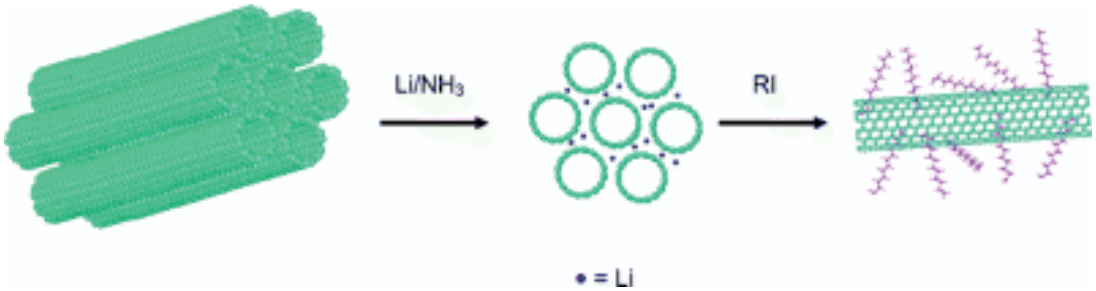
Margrave, JL, Khabashesku, VN J. AM. CHEM. SOC. 2003, *125*, 15174–15182

“Billups” Reaction





1a $CH_3(CH_2)_{11}I$
1b $CH_3(CH_2)_3I$
1c $CH_3(CH_2)_3Br$
1d $CH_3CH_2CHICH_3$
1e THP-O-$(CH_2)_3I$
1f H_2NCOCH_2I



NL 2004 p1257

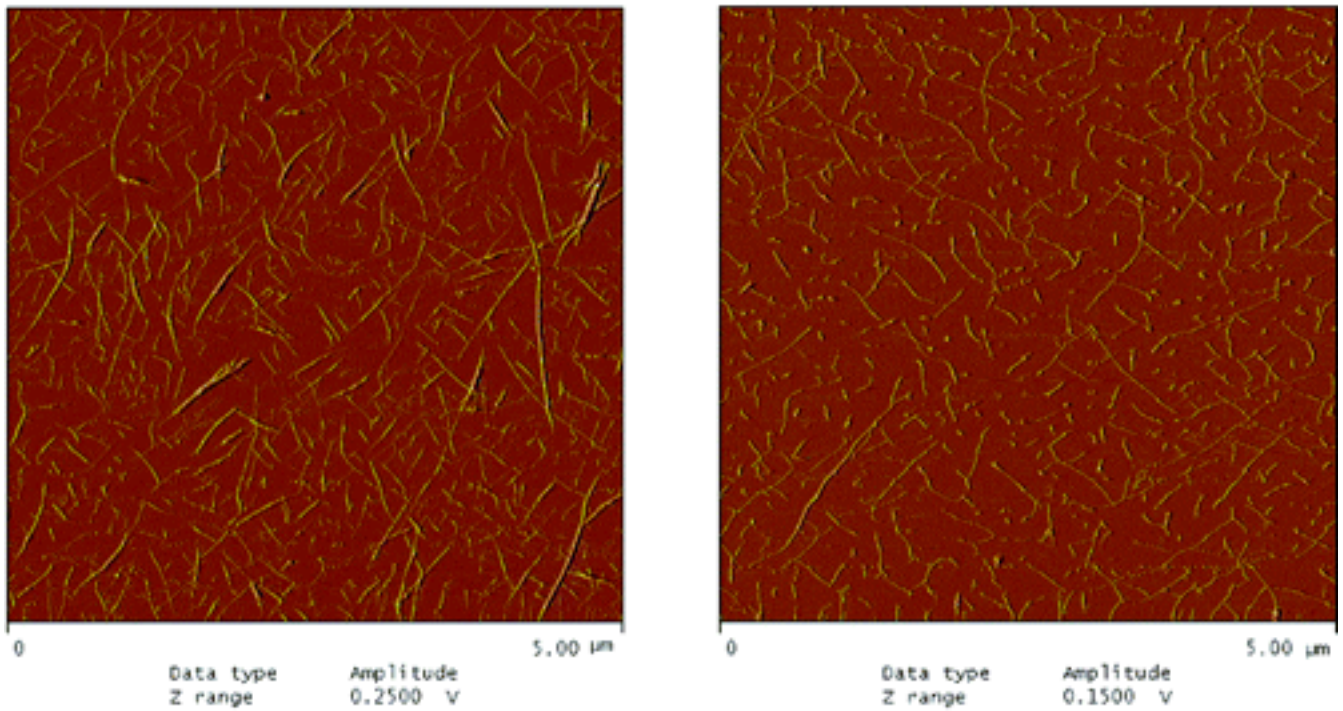


Figure 1 Tapping mode AFM images of dodecylated purified SWNTs (left) and raw SWNTs (right) spin-coated onto mica from chloroform.

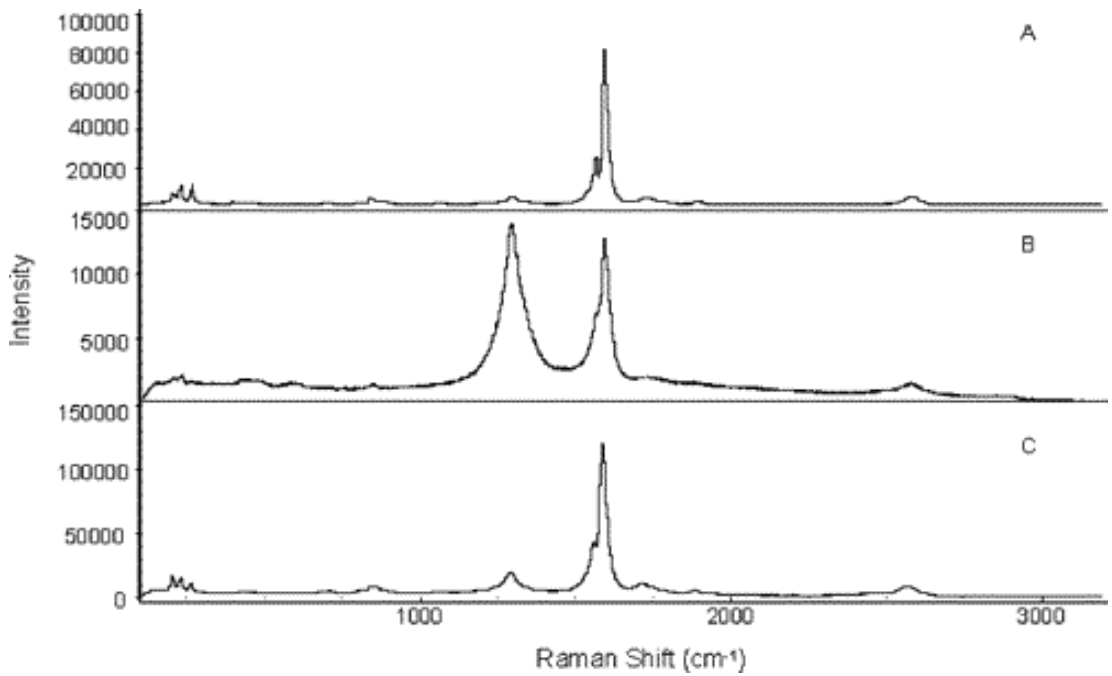
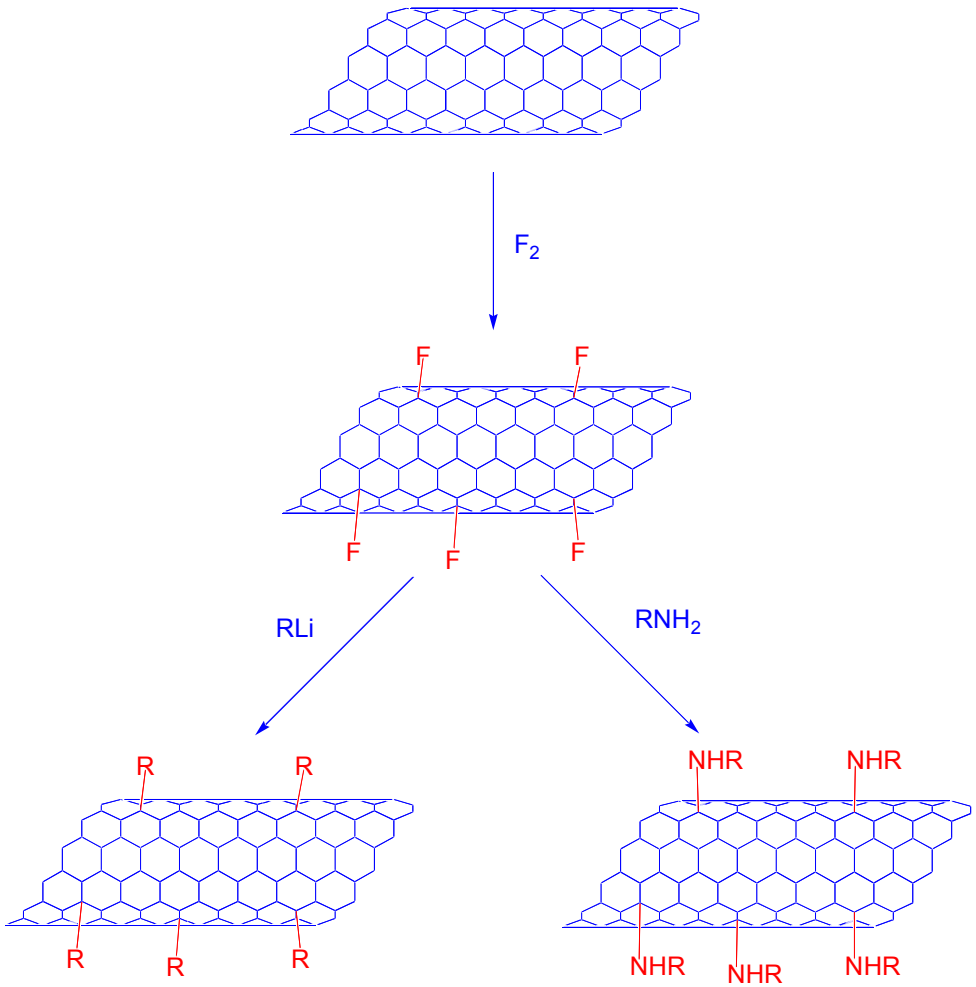


Figure 3 Raman spectra (780 nm excitation) of (A) purified SWNTs, (B) dodecylated product 2a, and (C) product 2a after TGA analysis (30 min hold at 80 C, ramp 10 C min−1 to 800 C, 20 min hold at 800 C) in argon showing the recovery of the pristine SWNTs.

Fluorination followed by displacement

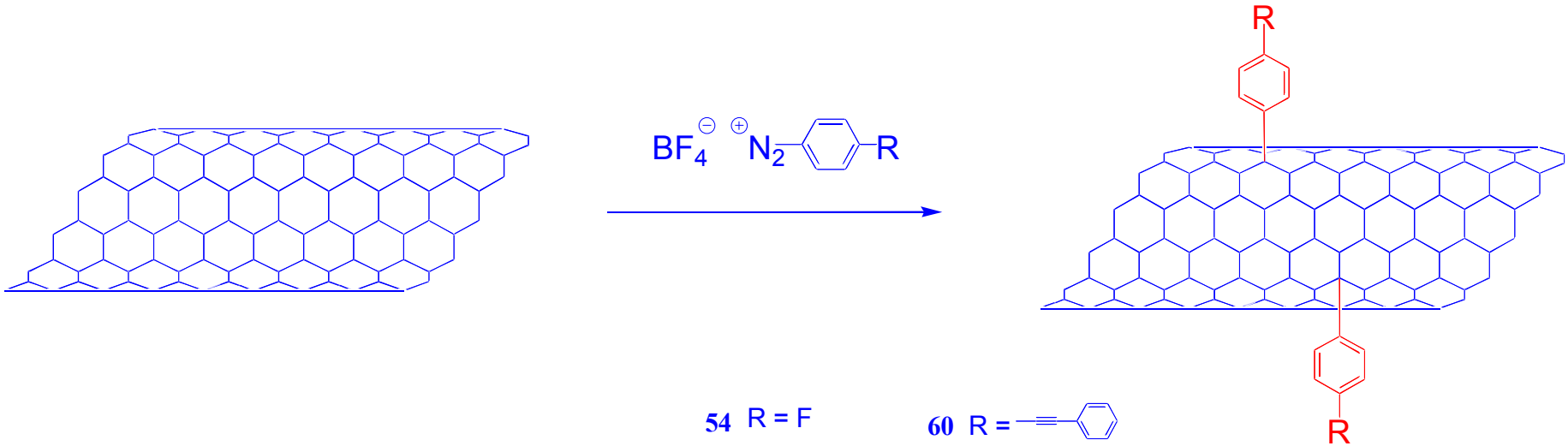


65 R = $-CH_3$
66 R = $-(CH_2)_3-CH_3$
67 R = $-(CH_2)_5-CH_3$

68 R = $-(CH_2)_2-NH_2$
69 R = $-(CH_2)_3-NH_2$
70 R = $-(CH_2)_4-NH_2$
71 R = $-(CH_2)_6-NH_2$

NL 2003 p 331, JACS 2003 p3617, CPL 1999 p367

Diazonium salts (Tour's approach)

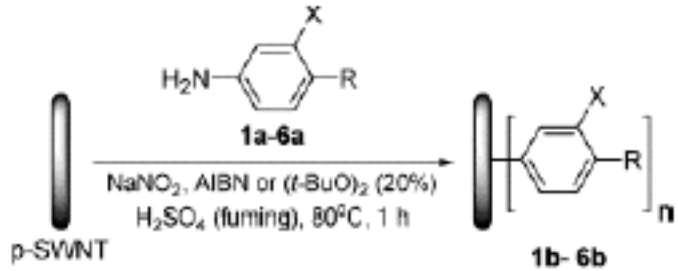


54 R = F
55 R = Cl
56 R = Br
57 R = *t*-Butyl
58 R = CO_2CH_3
59 R = NO_2

60 R =
61 R = $-C_{14}H_{29}$
62 R =
63 R =

JACS 2001 p6536, Science 2003 p1519, NL 2003 p1215

Scheme 1. Functionalization of SWNTs Dispersed in Oleum[a]



1a, R = H, X = H to 1b, R = SO_3H, X = H
2a, R = NO_2, X = H to 2b, R = NO_2, X = SO_3H
3a, R = Cl, X = H to 3b, R = Cl, X = SO_3H
4a, R = *t*-butyl, X = H to 4b, R = *t*-butyl, X = H and SO_3H (~1:1)[b]
5a, R = CH_2CH_2OH, X = H to 5b, R = CH_2CH_2OH, X = SO_3H[c]

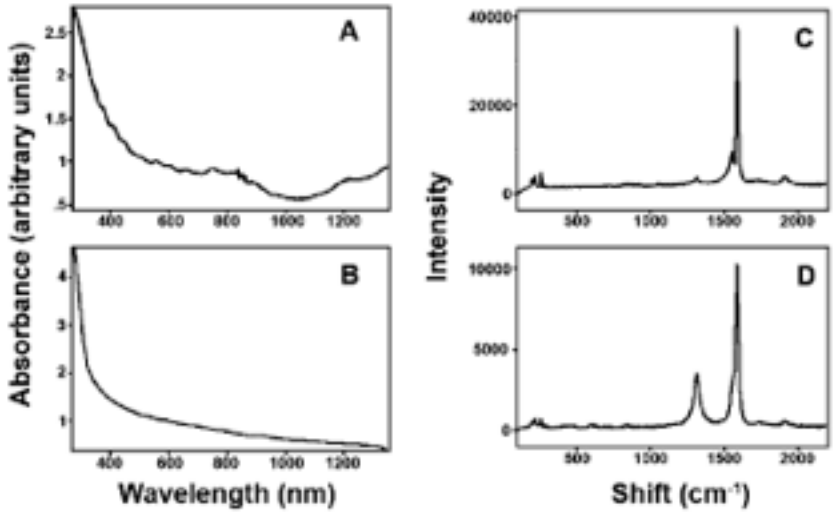
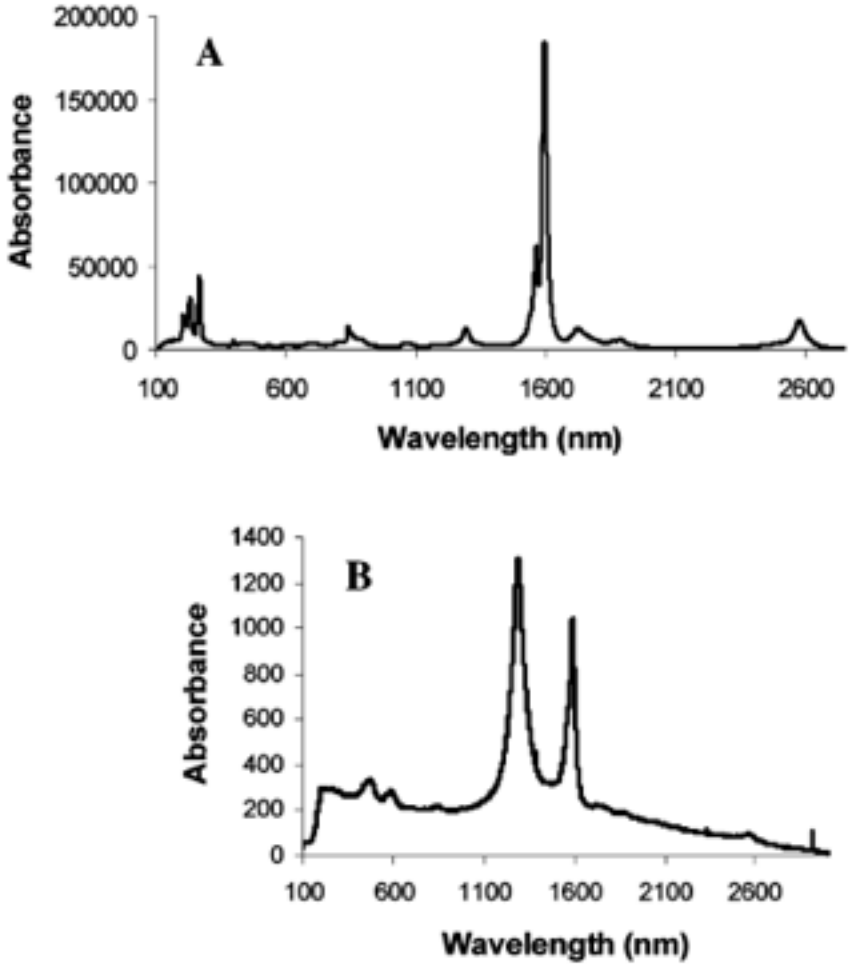


Figure 1. Absorption spectra of (a) p-SWNT in DMF. (b) 3b in DMF. Raman spectra (solid, median scan of five different areas per sample, 633 nm) of (c) p-SWNT and (d) 3b.

Tour, JM

J. AM. CHEM. SOC. 2004, *126*, 11158–11159



Raman (780-nm excitation) of (A) pristine SWNTs and (B) heavily functionalized individual carbon nanotubes.

Dyke and Tour *J. Phys. Chem. A, Vol. 108, No. 51, 2004*

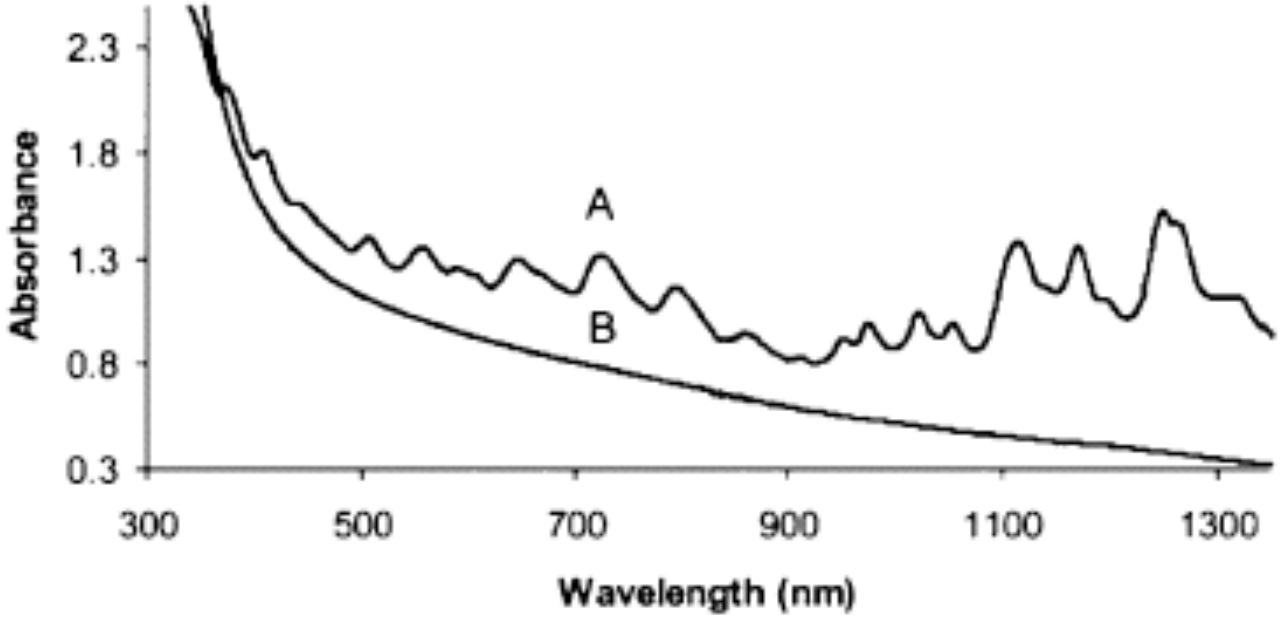


Figure 2. Absorption spectroscopy of A) SDS-coated SWNTs and B) functionalized SWNTs that are SDS-free.

Tour, JM

Chem. Eur. J. **2004**, *10*, 812–817

Metallic NT reacts better!

11156 *J. Phys. Chem. A, Vol. 108, No. 51, 2004* Dyke and Tour

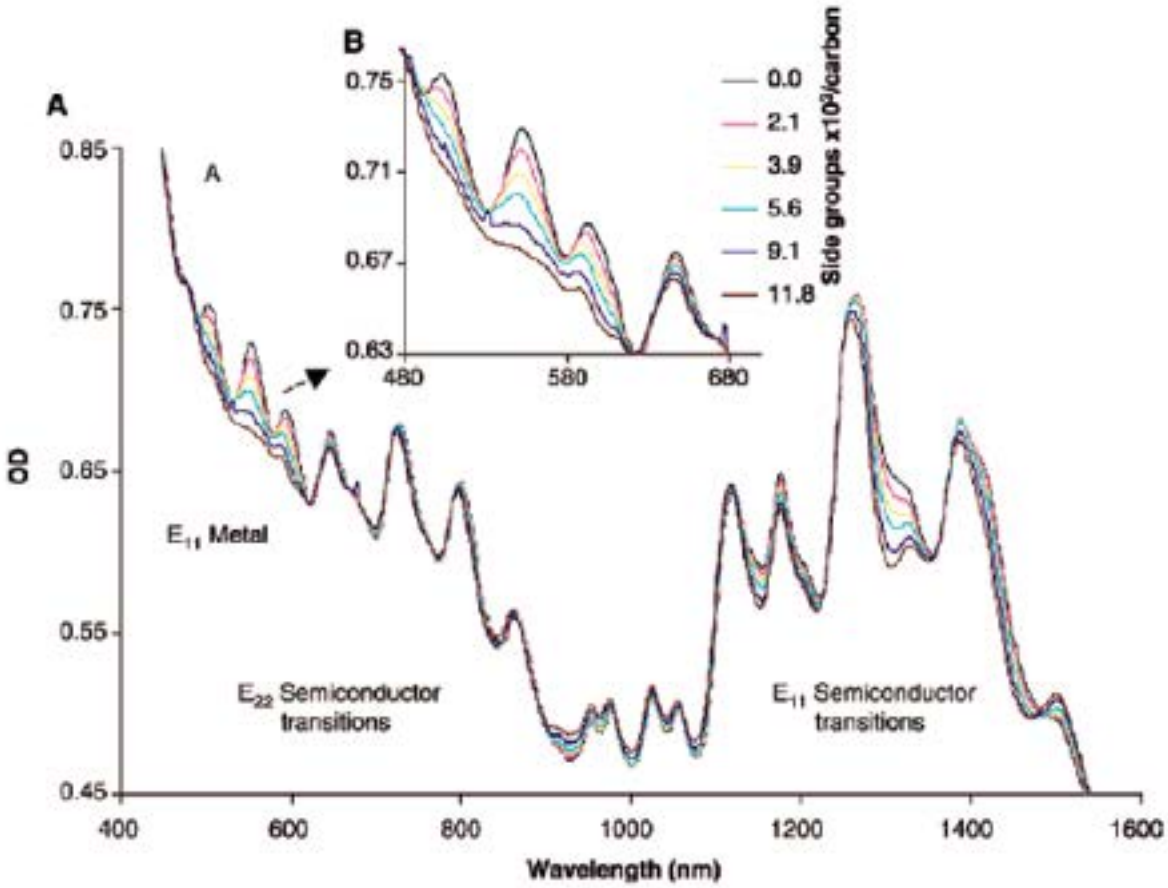
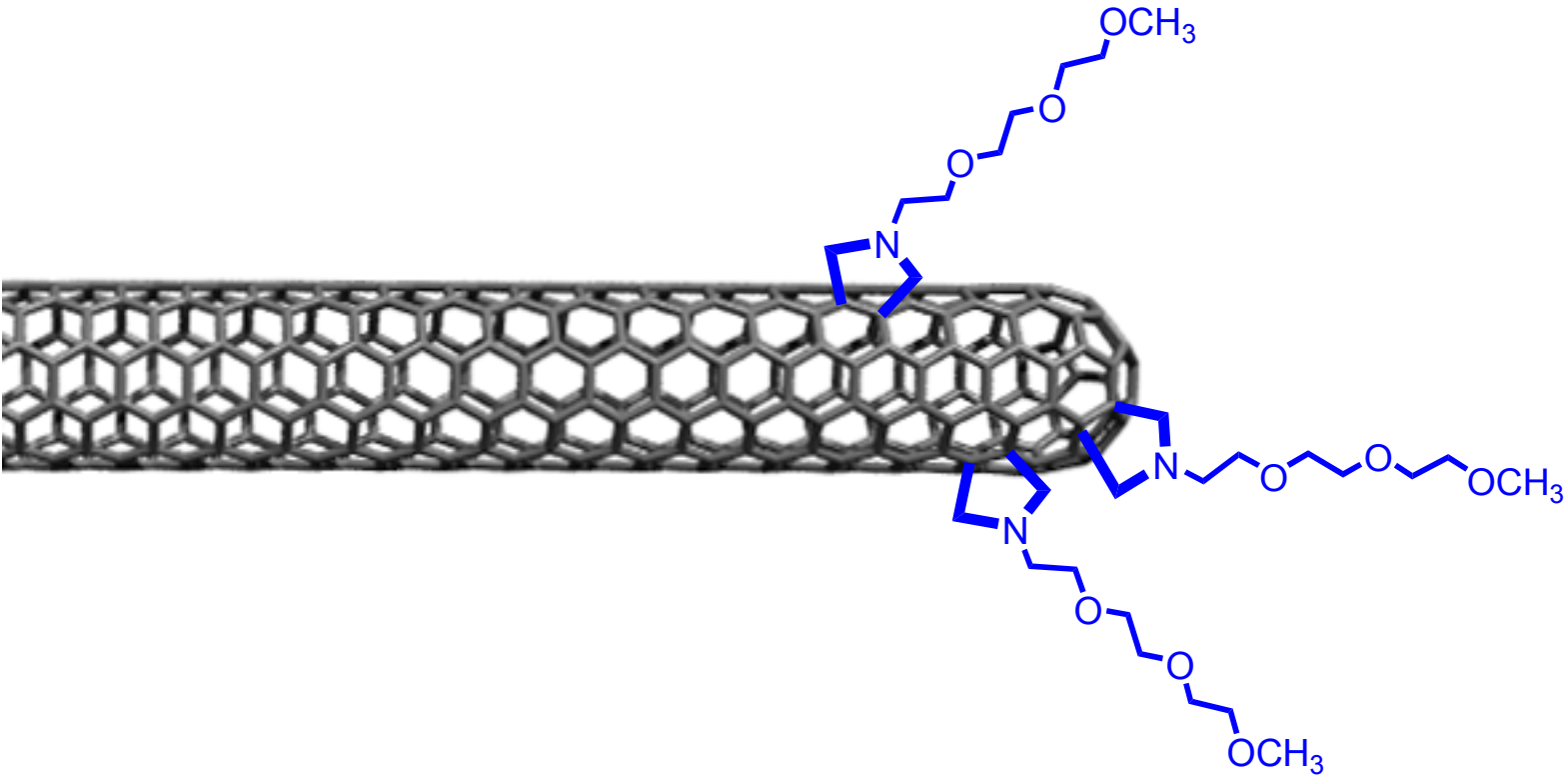


Figure 6. Progressive loss of the van Hove absorption bands of the three metallic/semimetallic peaks in the region from 480 to 600 cm^{-1} during the slow addition of an arene diazonium salt. The semiconducting SWNTs' bands remain largely unaffected.

$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2NHCH_2COOH$ + HCHO

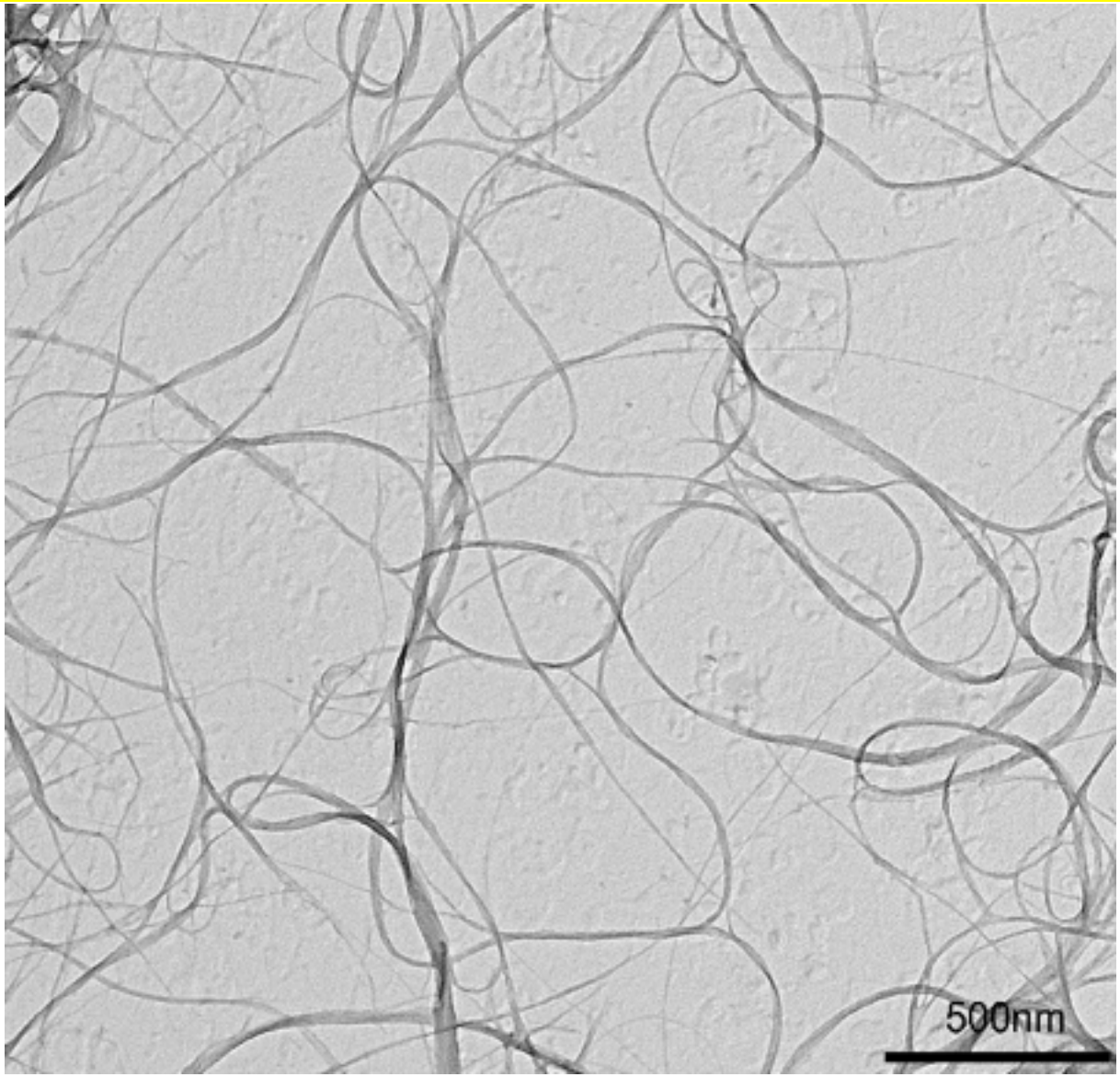
$\xrightarrow[\text{DMF, 10-70\%}]{\text{SWNT}}$

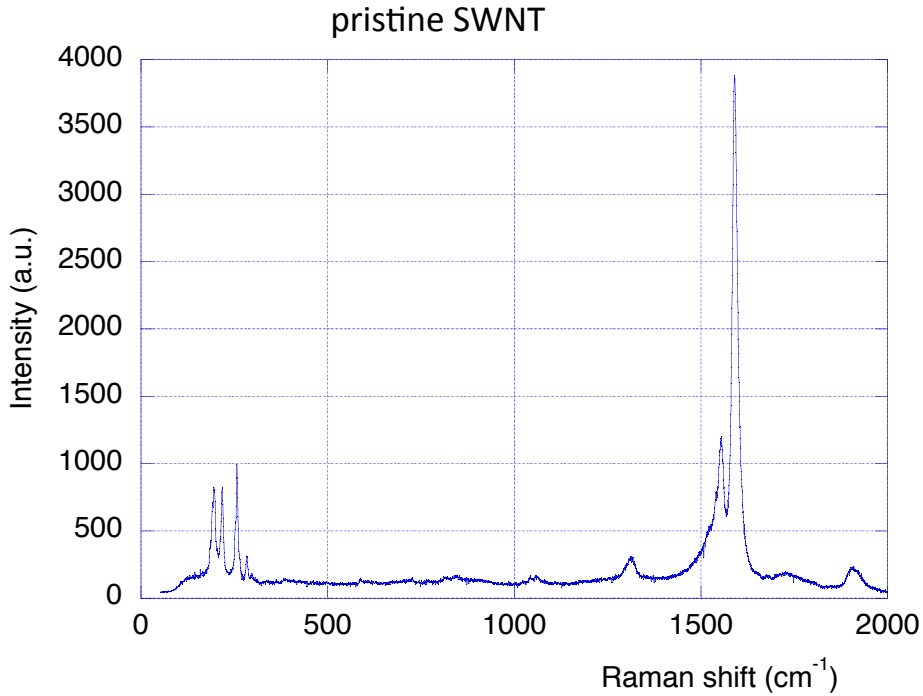


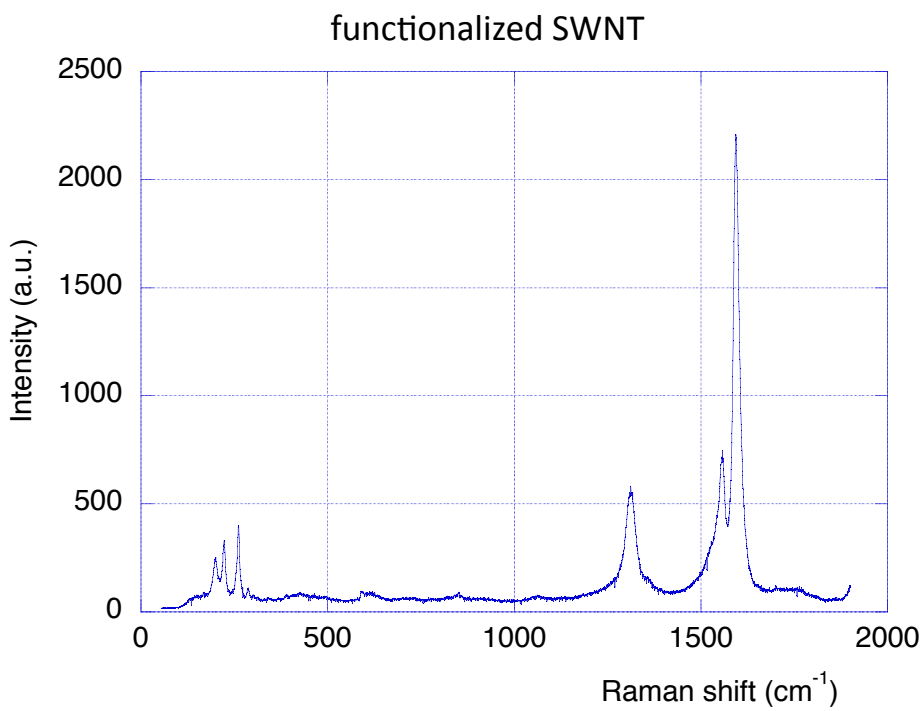
Degree of functionalization: 1 pyrrolidine group every 100 carbon atoms

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

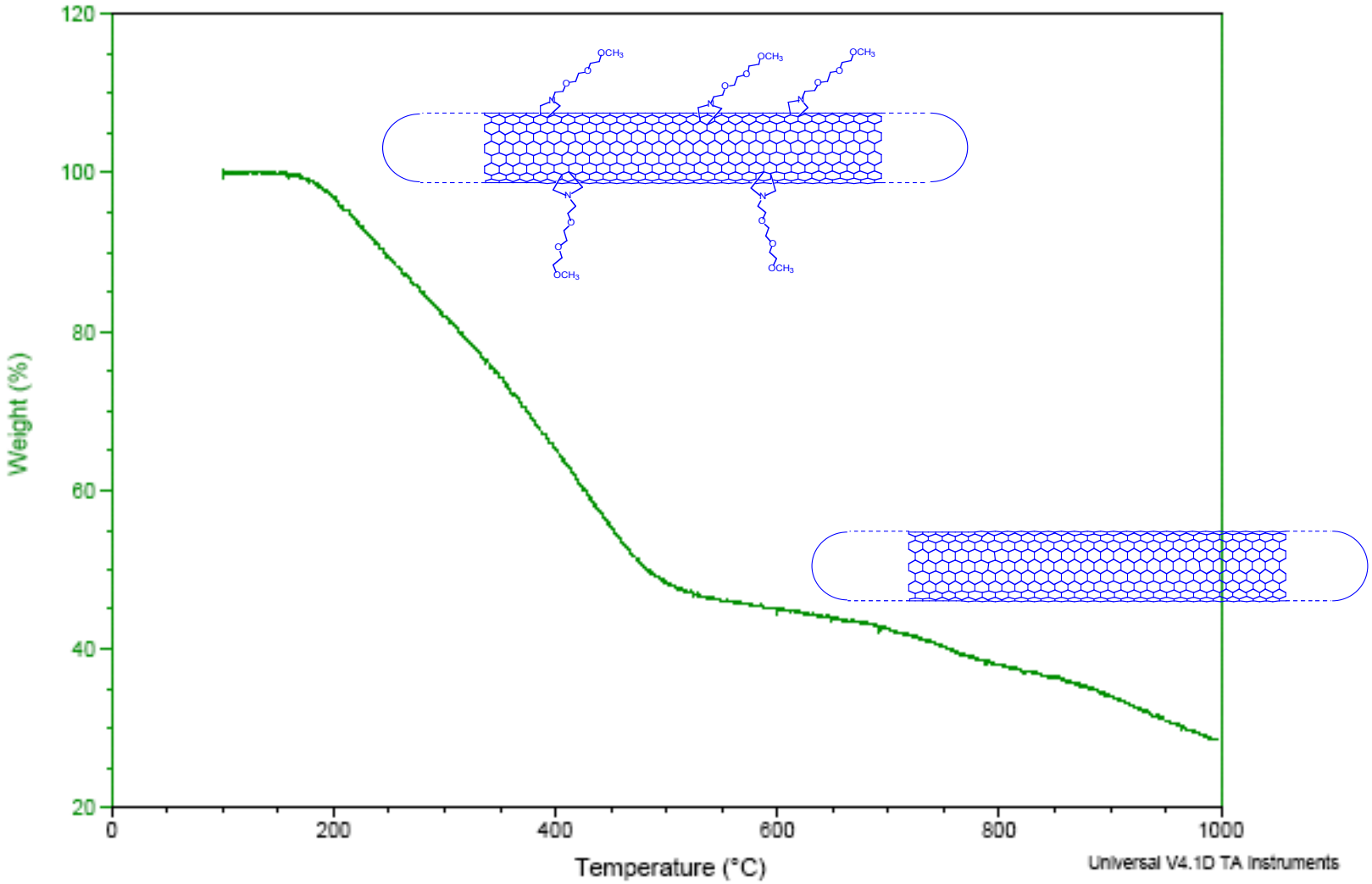
TEM HIPCO FUNCTIONALIZED SWNT



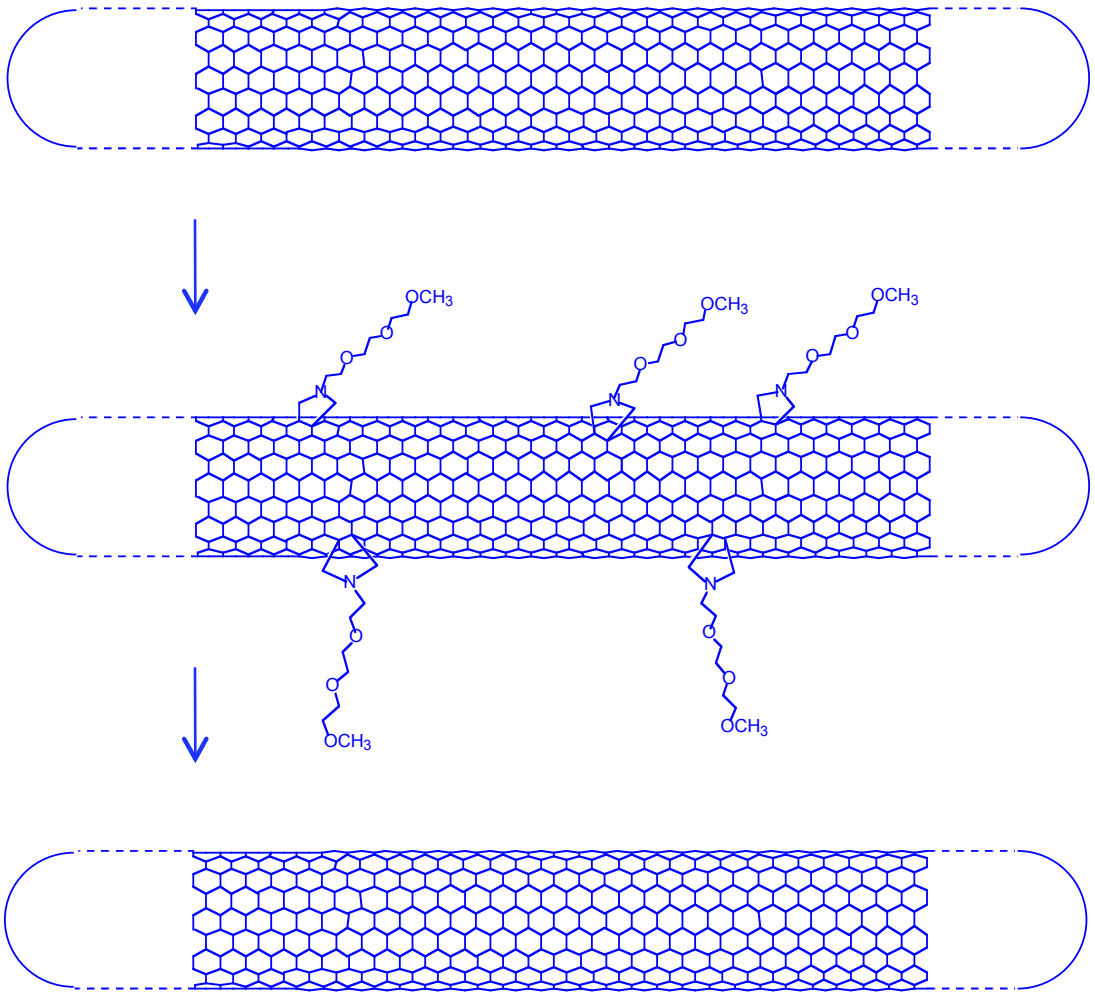

pristine SWNT
Intensity (a.u.)
4000
3500
3000
2500
2000
1500
1000
500
0
0
500
1000
1500
2000
Raman shift (cm-1)


functionalized SWNT
Intensity (a.u.)
2500
2000
1500
1000
500
0
0
500
1000
1500
2000
Raman shift (cm-1)

Thermogravimetric Analysis (TGA)



An Alternative Methodology for the Purification of SWNTs

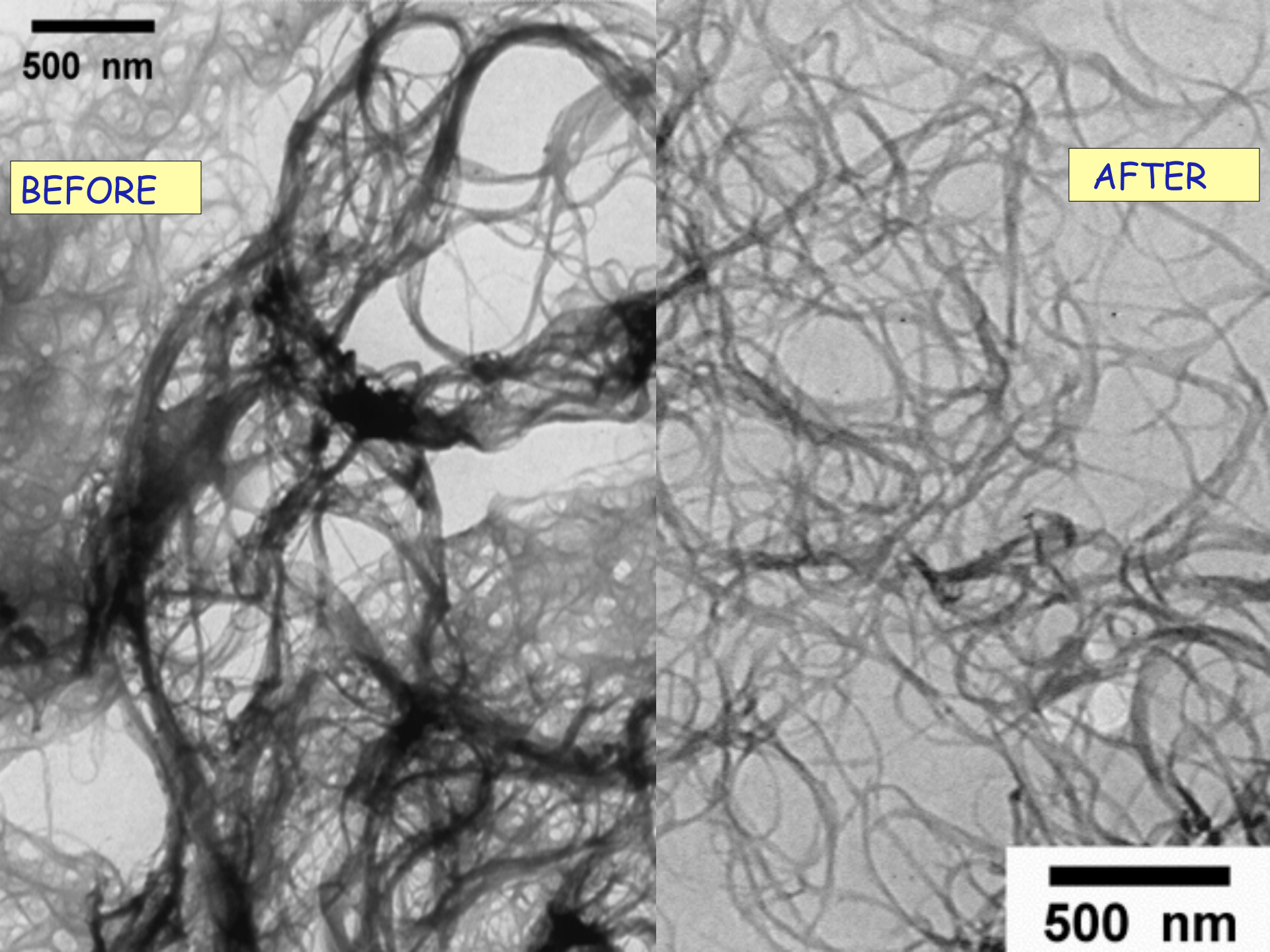


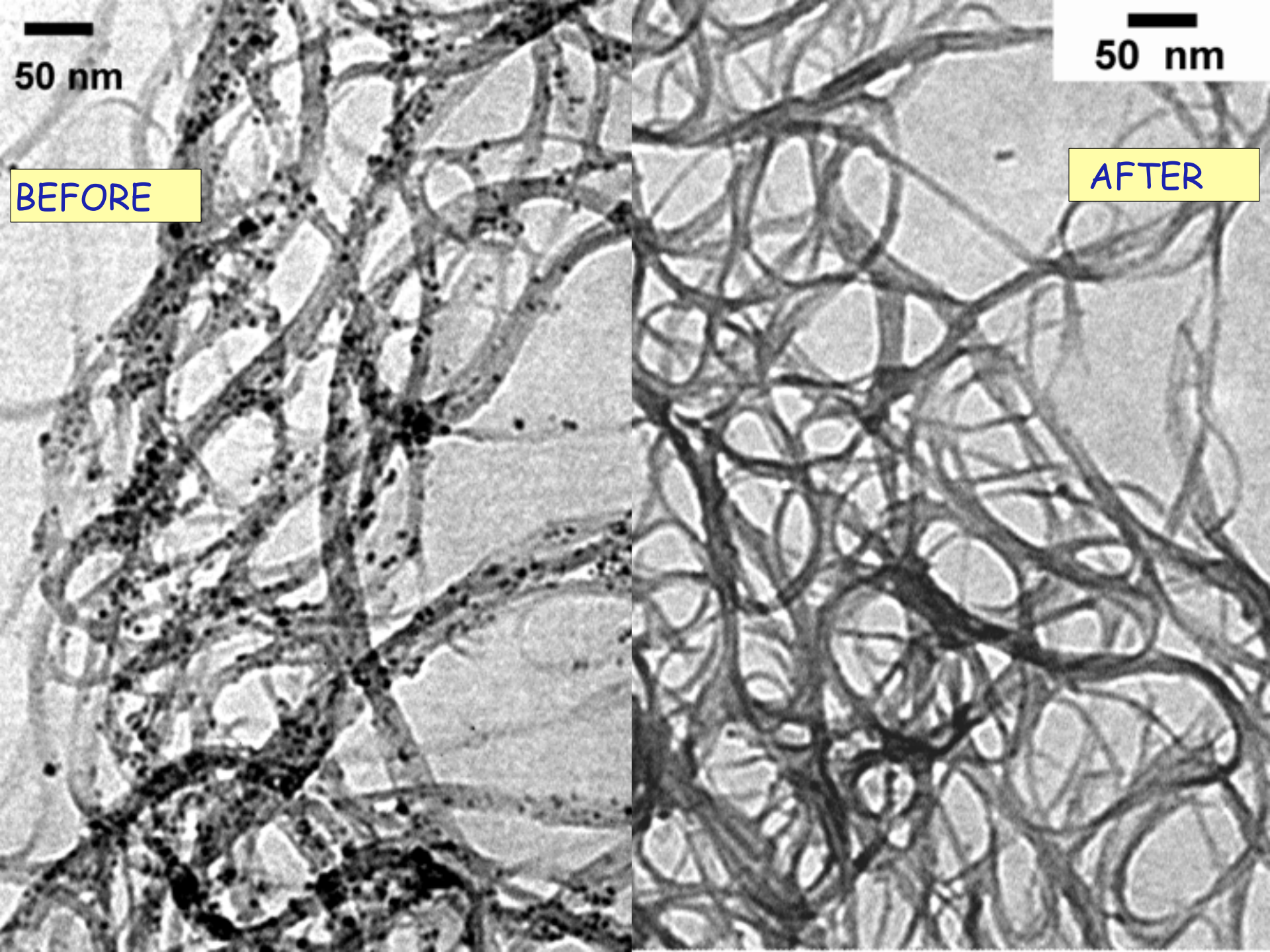
+ amorphous carbon
+ metallic nanoparticles

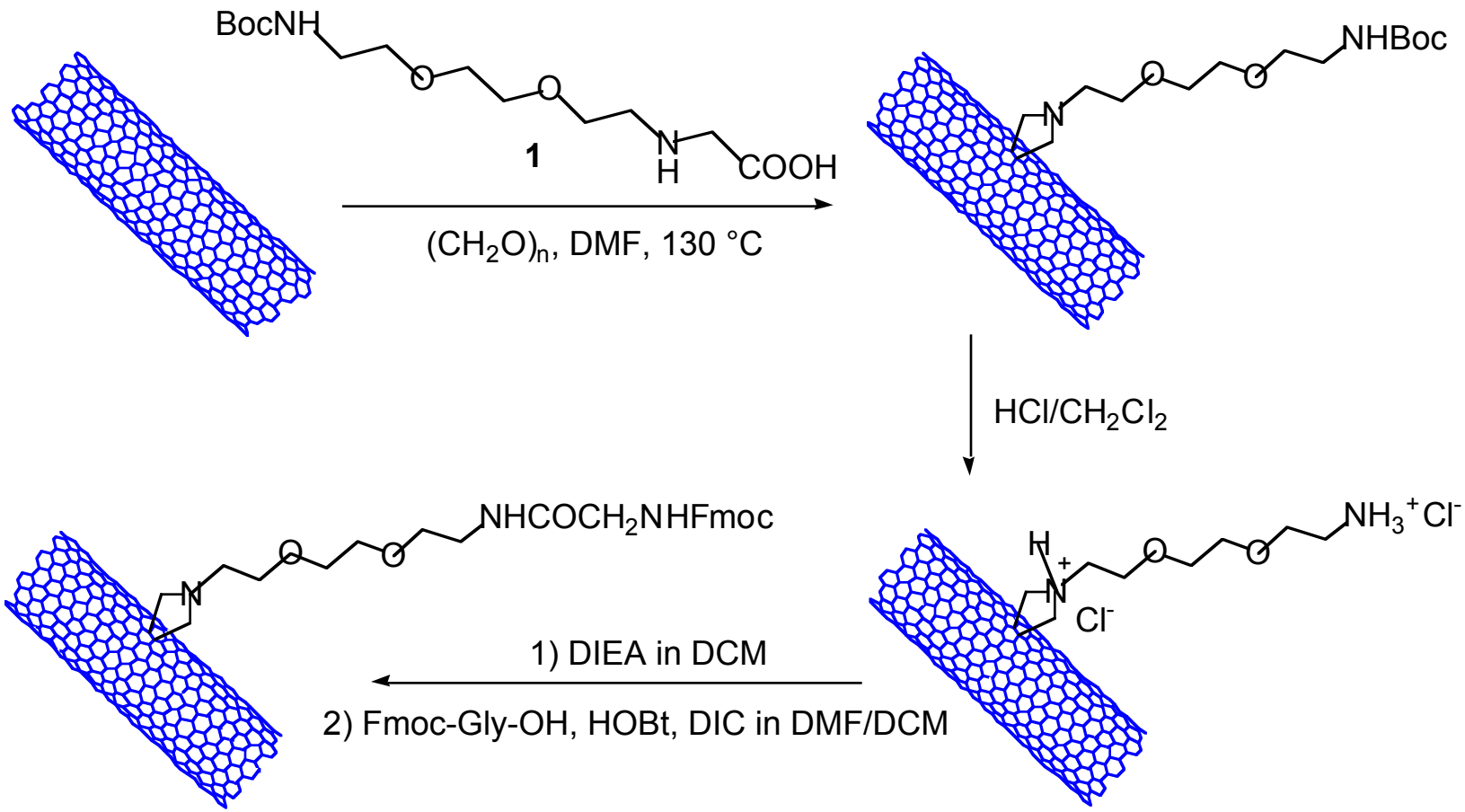
easy to handle, soluble
Can be purified!

PURE! No amorphous carbon, no metal

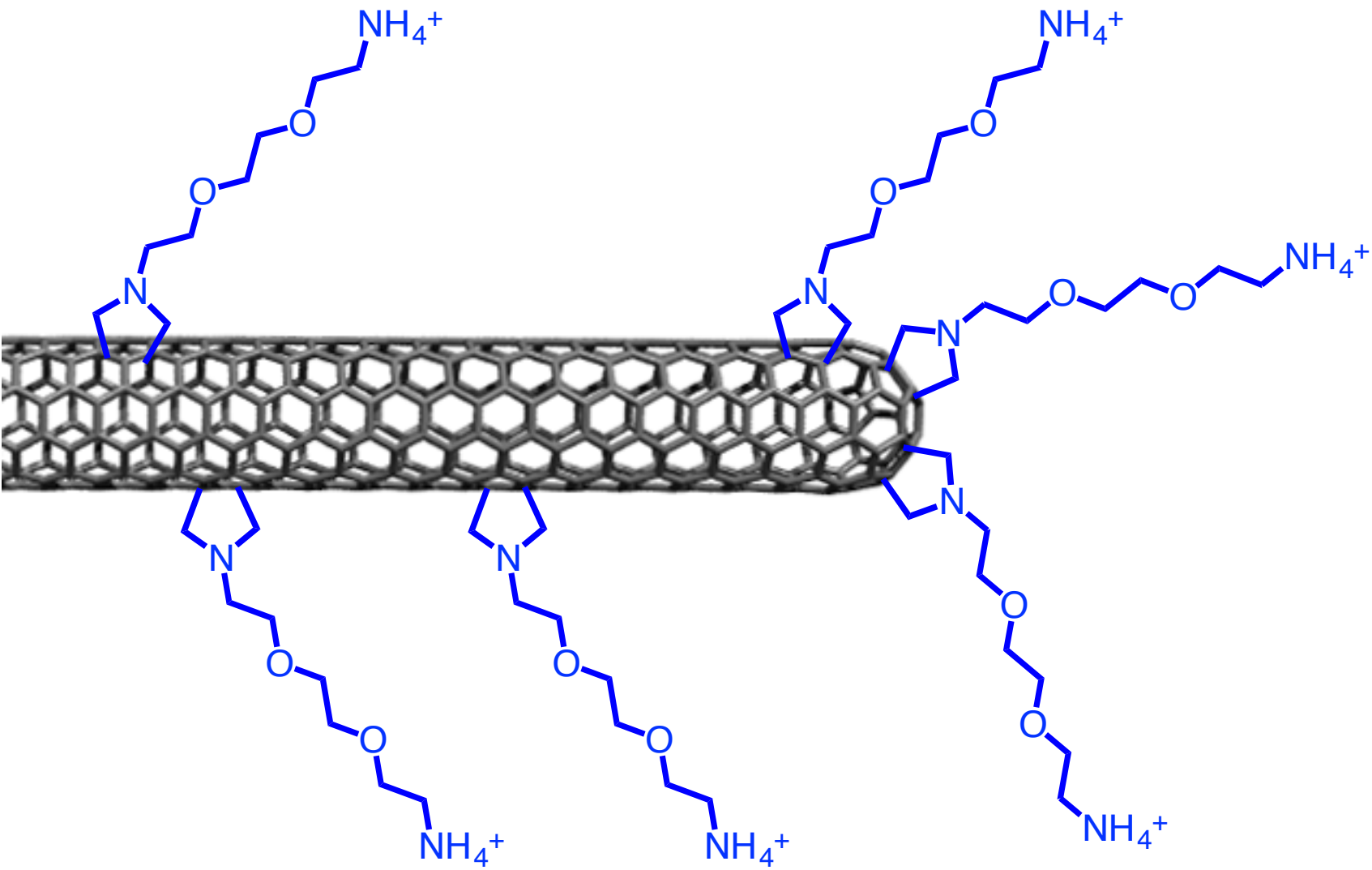
J. Am. Chem. Soc. **2002**, 124, 14318-14319


500 nm
BEFORE
AFTER
500 nm


50 nm
BEFORE
50 nm
AFTER

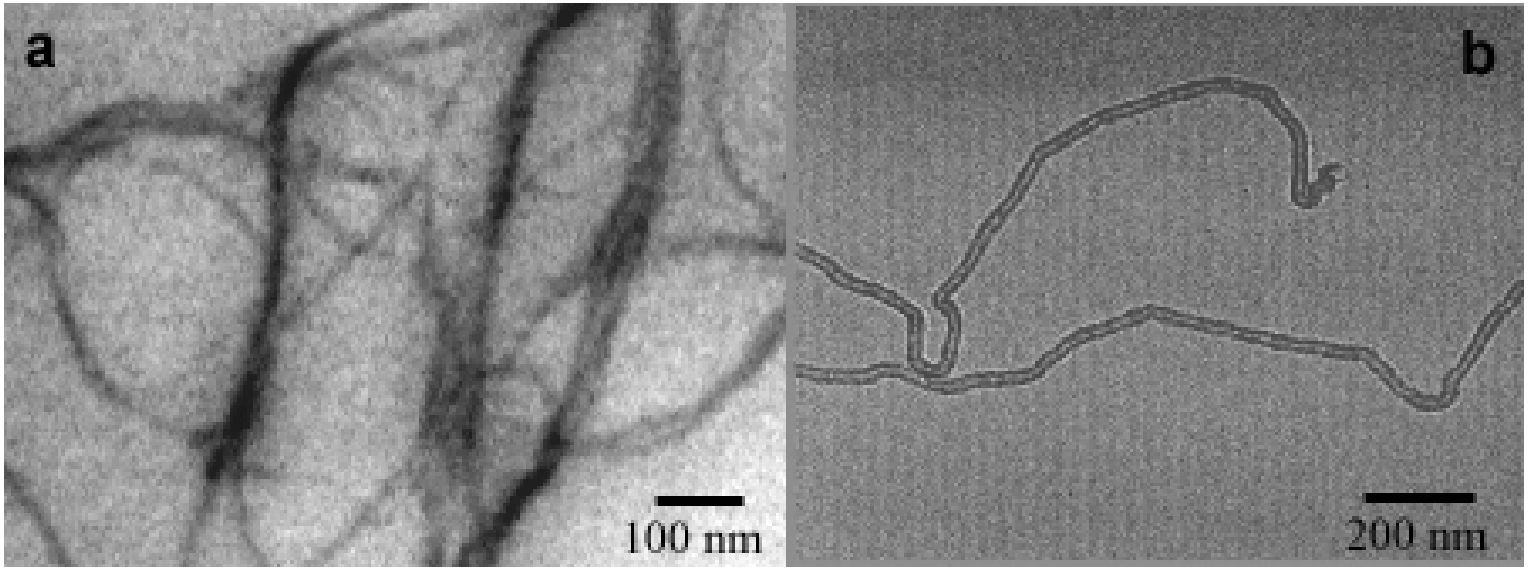


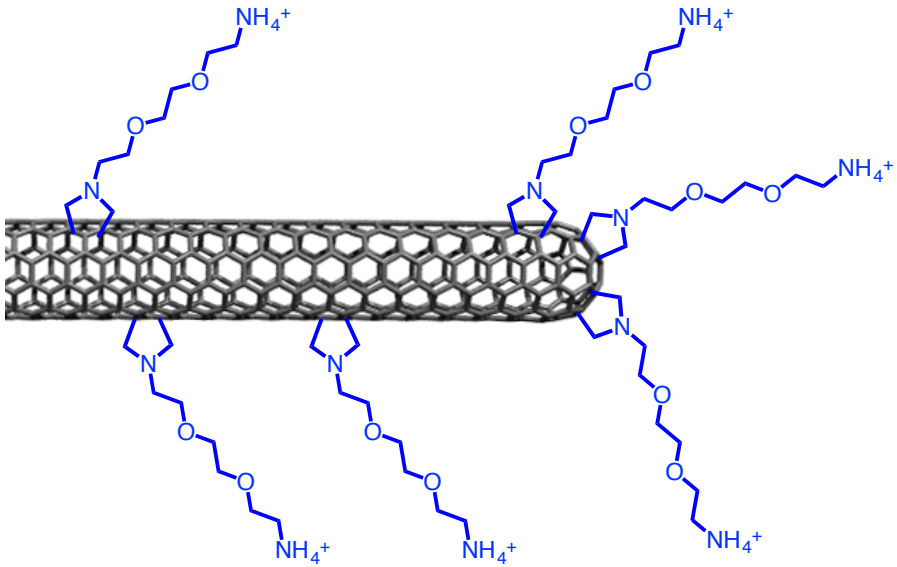
Chem. Commun. **2002**, 3050-3051



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

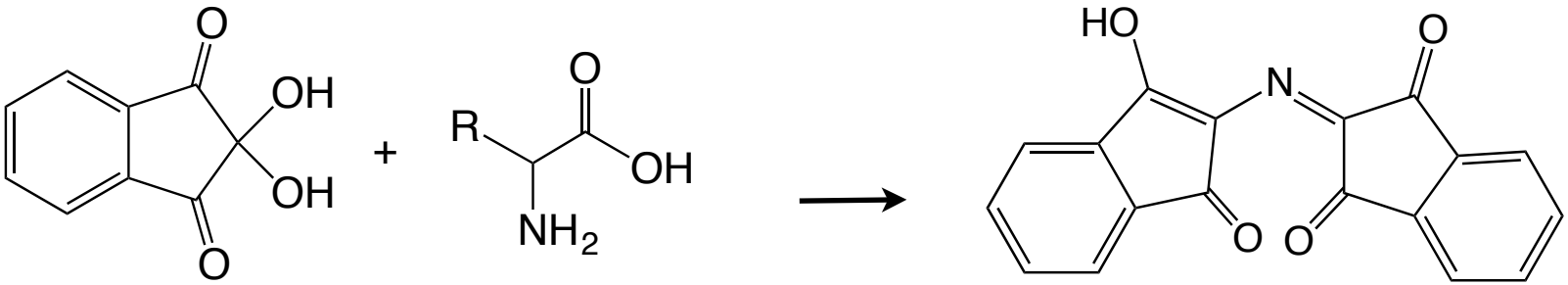
TEM OF WATER SOLUBLE SWNT AND MWNT



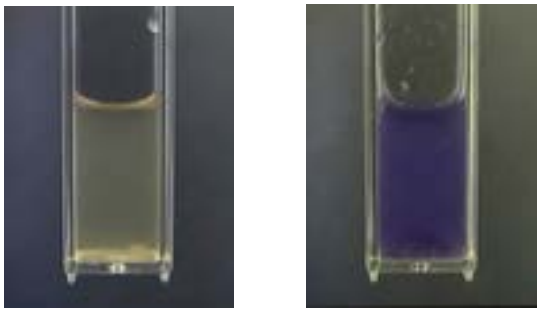


Chem. Commun. **2002**, 3050-3051

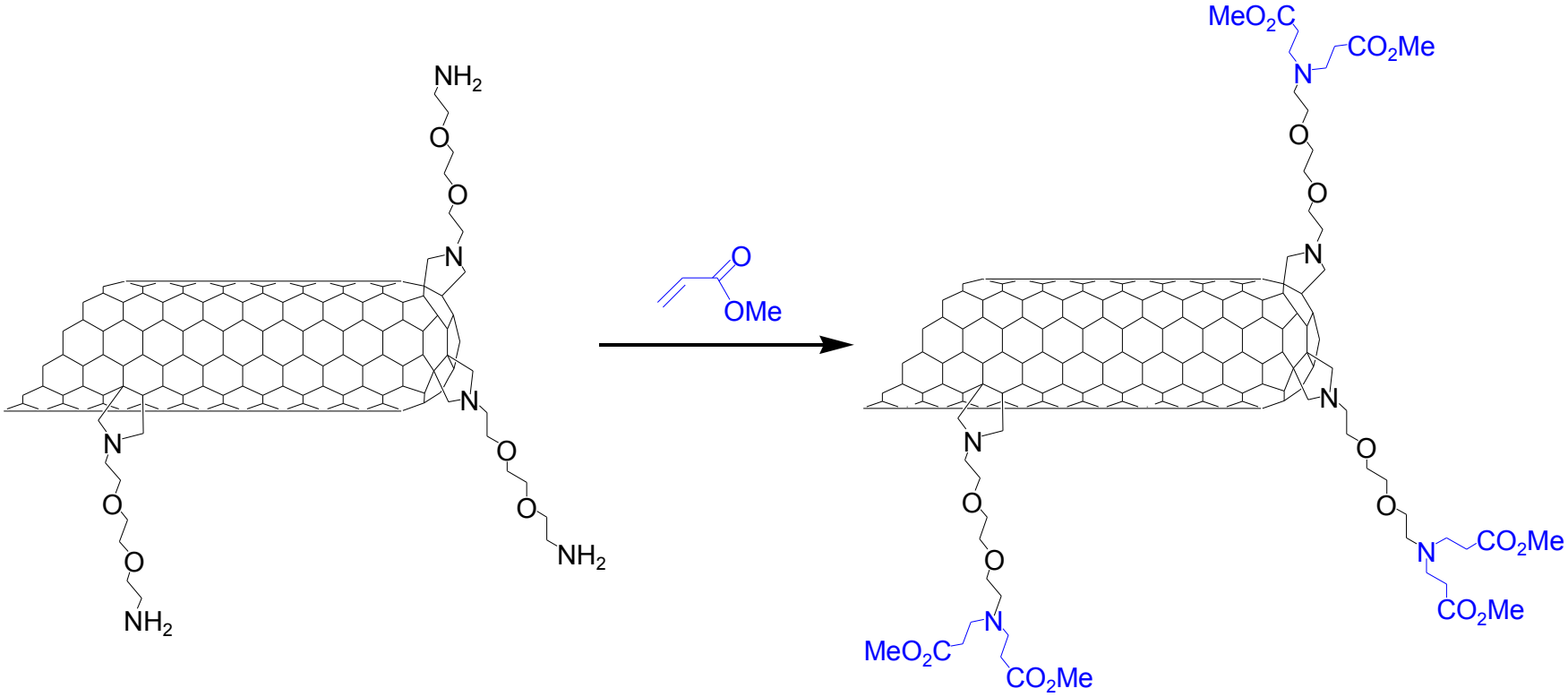
Kaiser test (Ninhydrin test)

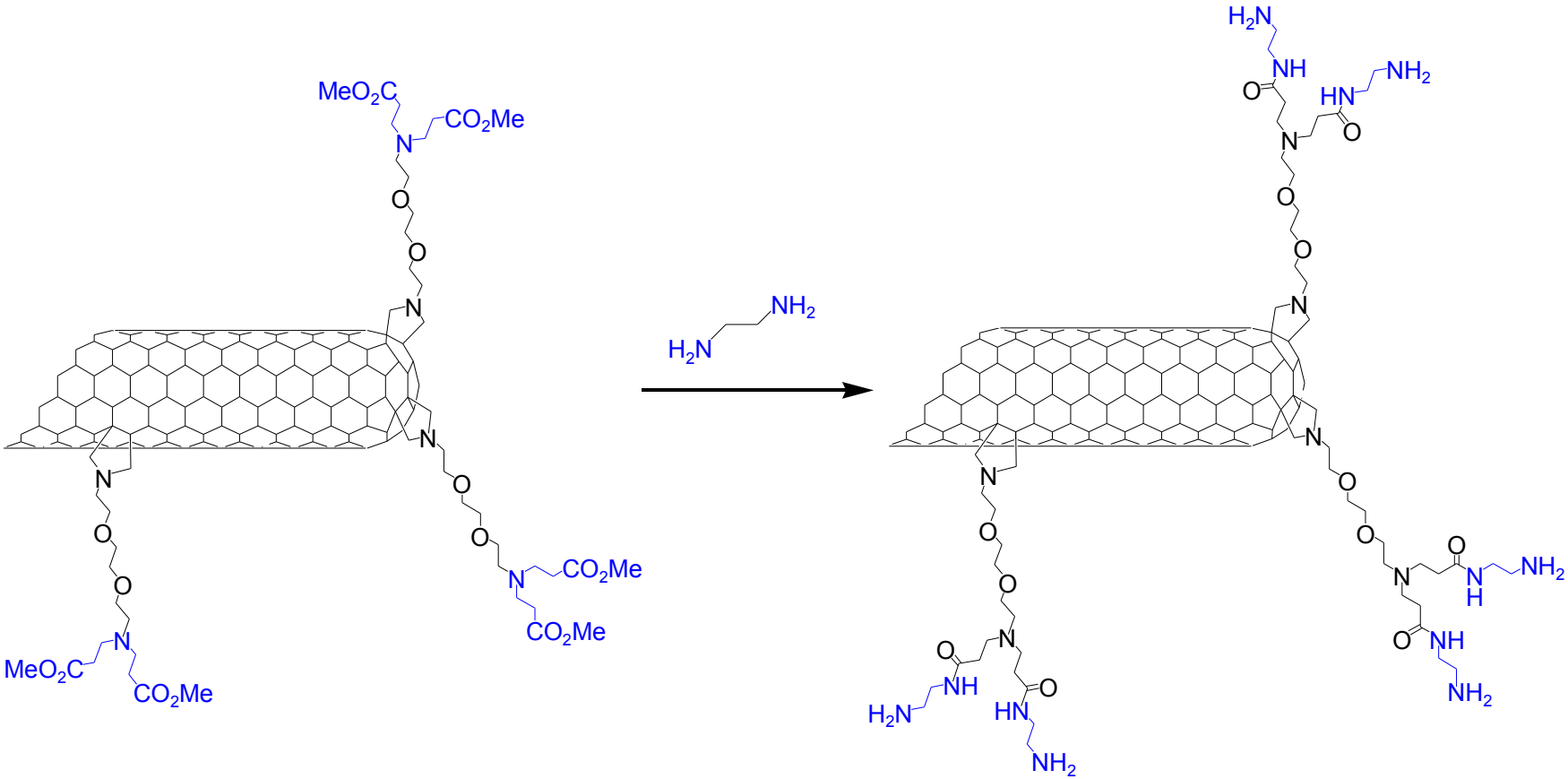


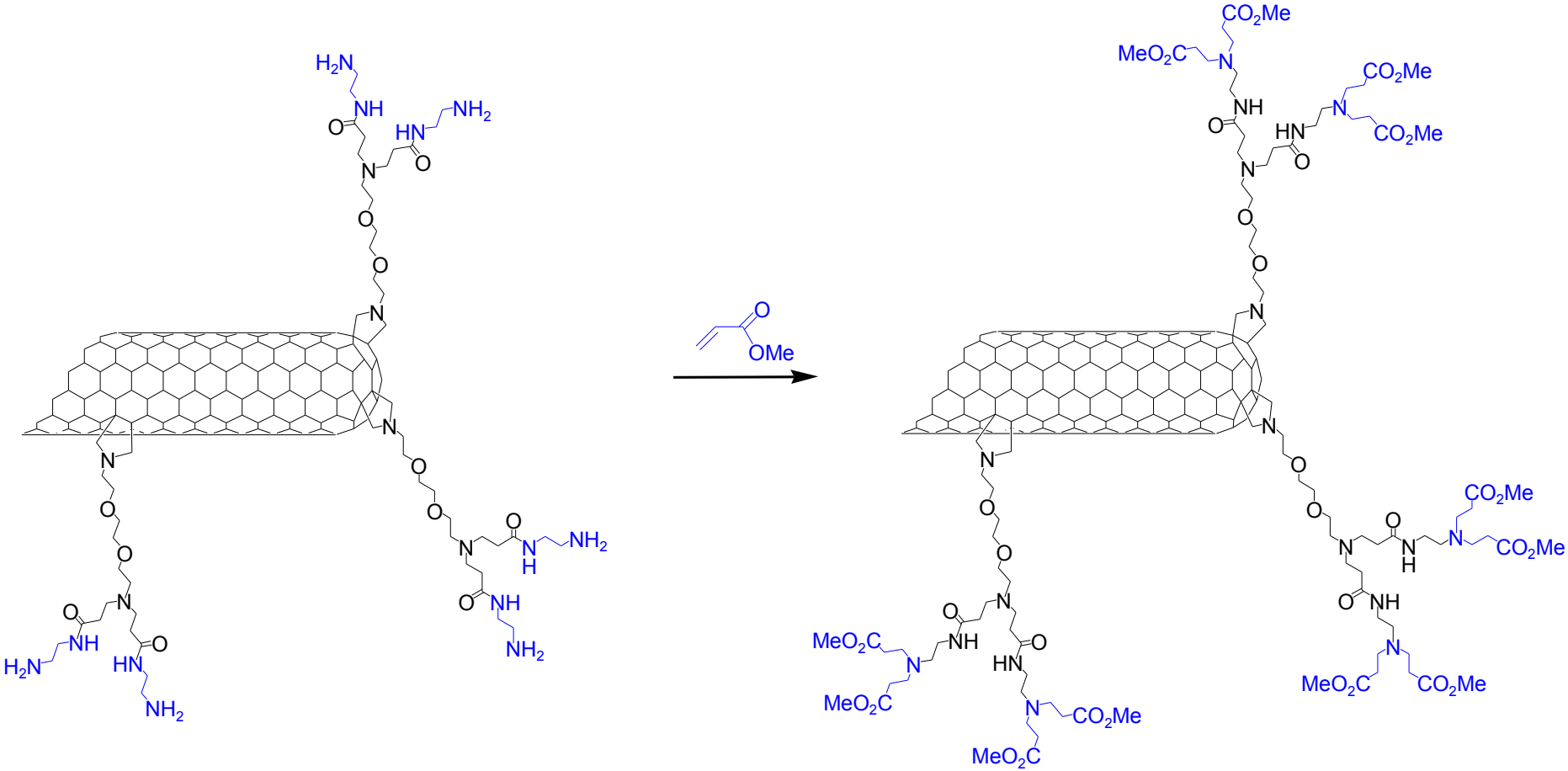
Amine detection and quantification using Kaiser test:
69 µmol/g

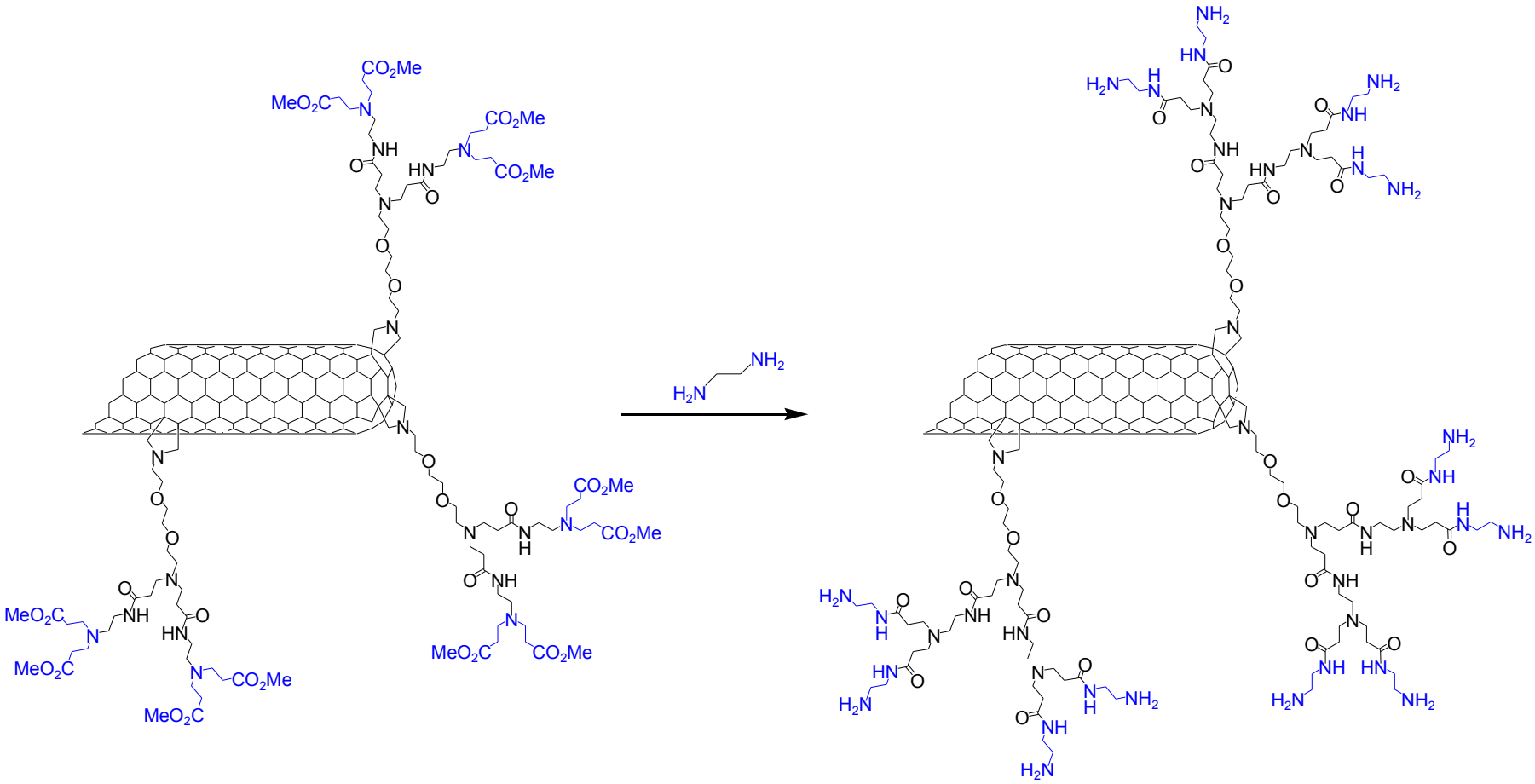


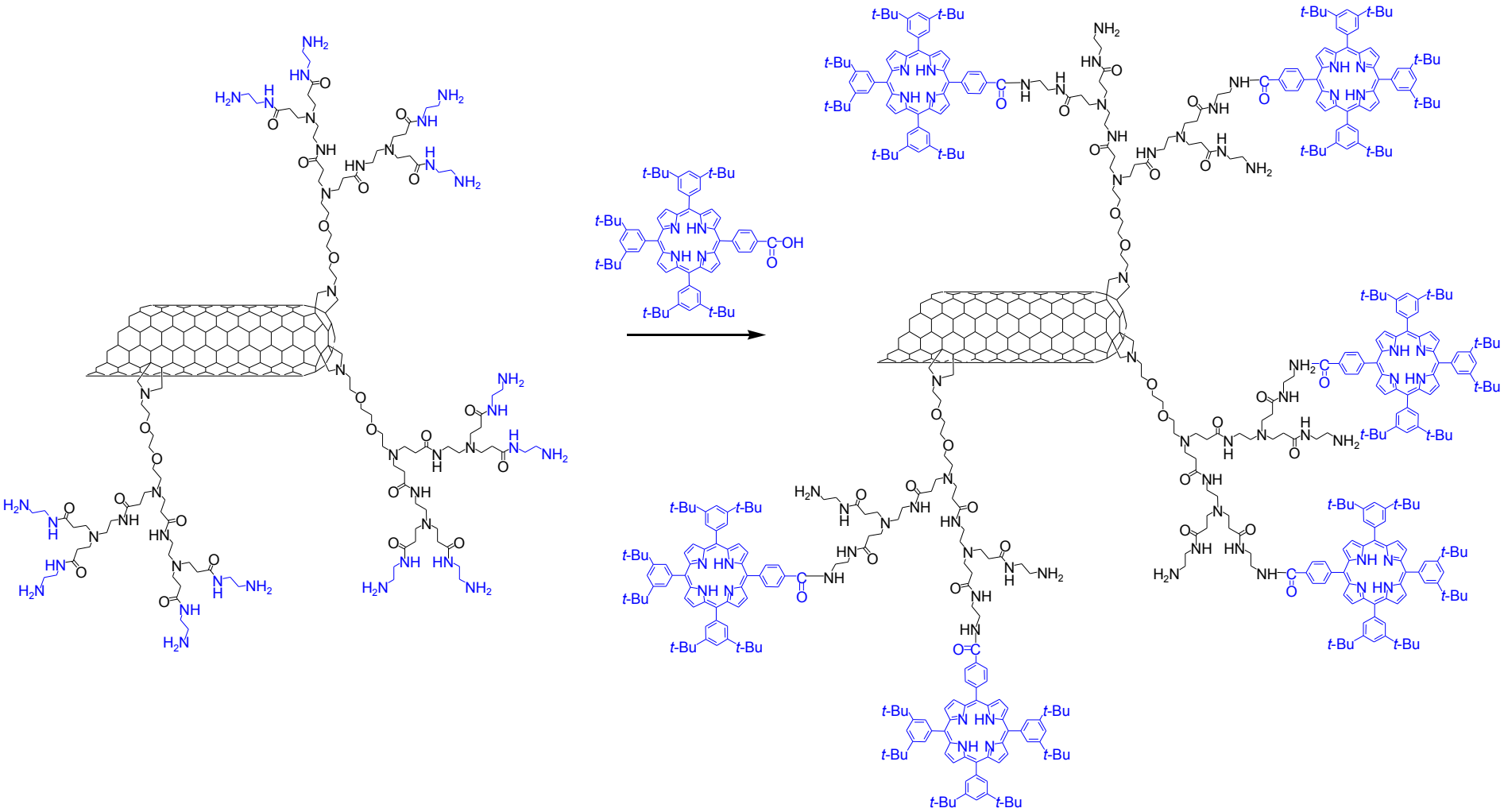
Synthesis of a polyfunctional dendrimer-CNT

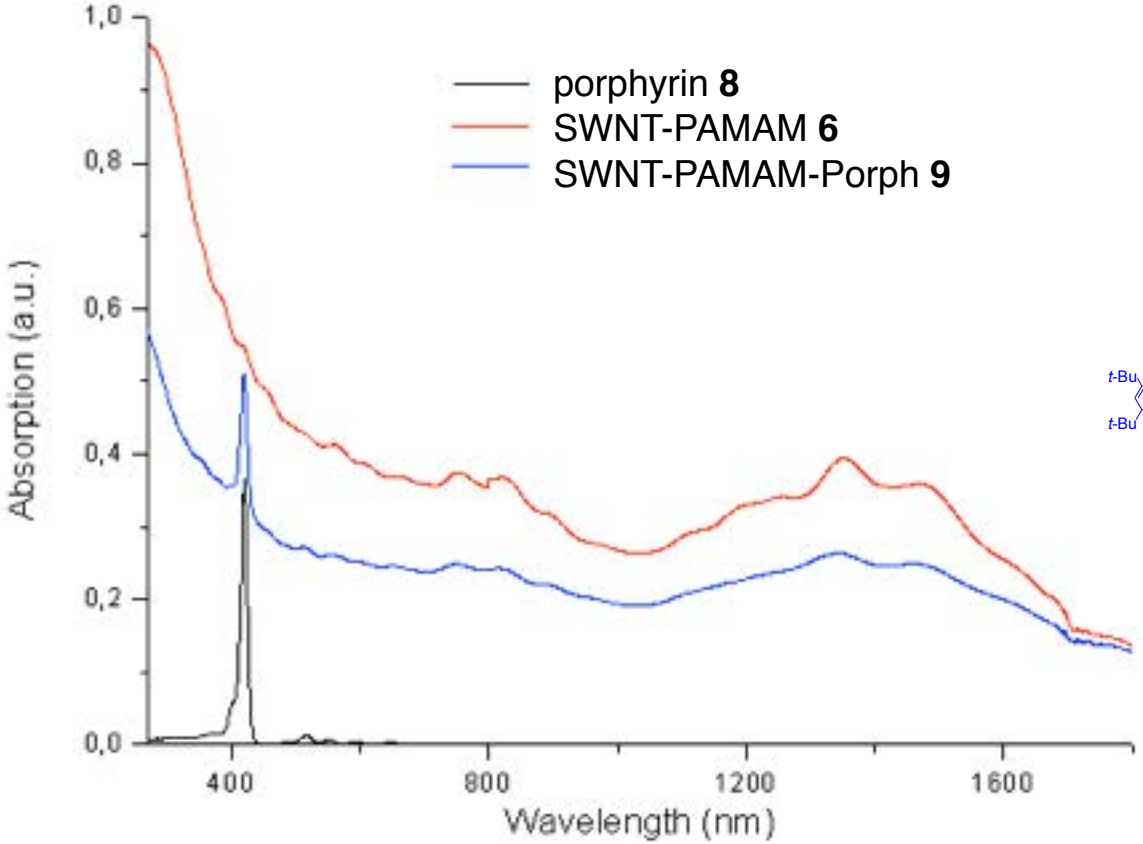


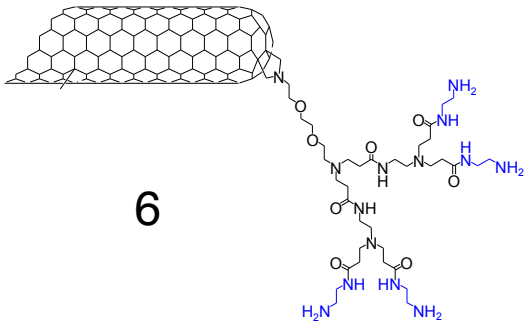

MeO2C
CO2Me
N
O
O
N
N
N
O
O
N
CO2Me
CO2Me
O
O
N
MeO2C
CO2Me
NH2
H2N
H2N
NH
NH2
O
HN
O
N
O
O
N
N
N
O
O
O
O
N
O
N
NH2
H
O
NH
NH2
O
N
O
NH
H2N
HN
O
NH2


H2N
NH
NH2
HN
O
N
O
OMe
CO2Me
MeO2C
H
MeO2C

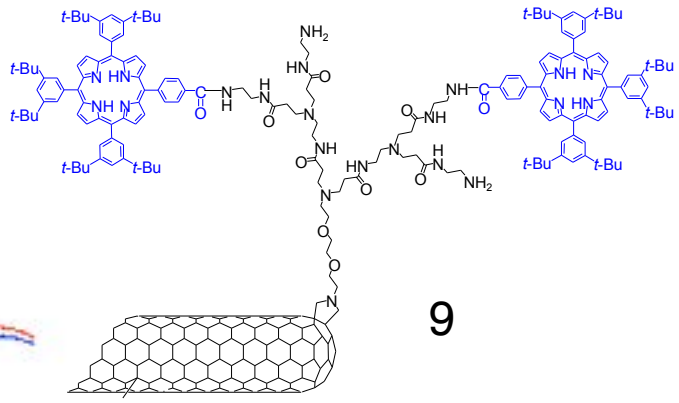

CO2Me
MeO2C
NH
HN
O
N
H2N
NH2



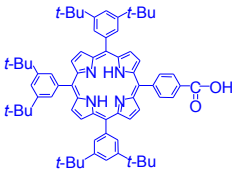

porphyrin **8**
SWNT-PAMAM **6**
SWNT-PAMAM-Porph **9**
Absorption (a.u.)
Wavelength (nm)
1,0
0,8
0,6
0,4
0,2
0,0
400
800
1200
1600



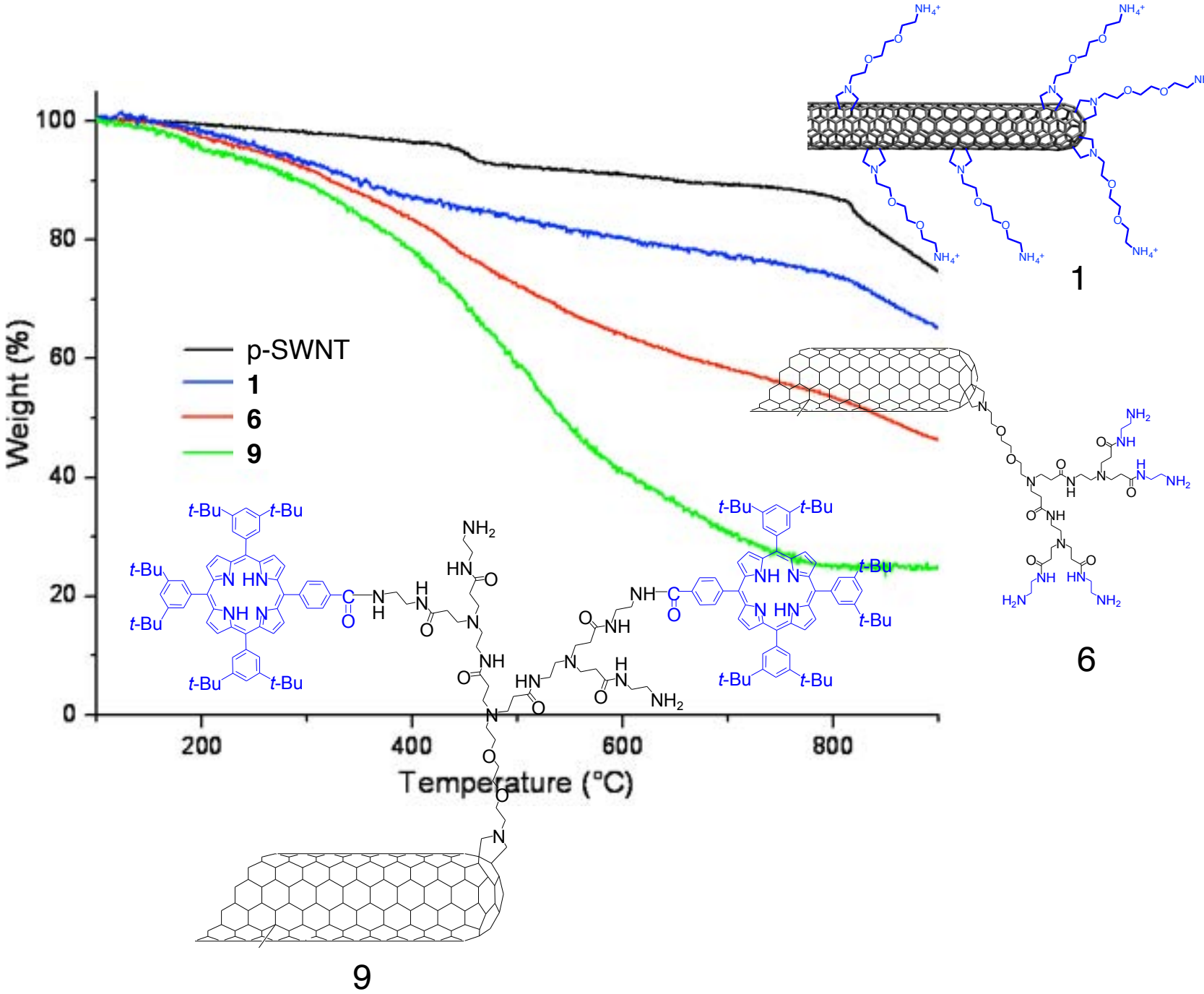
6

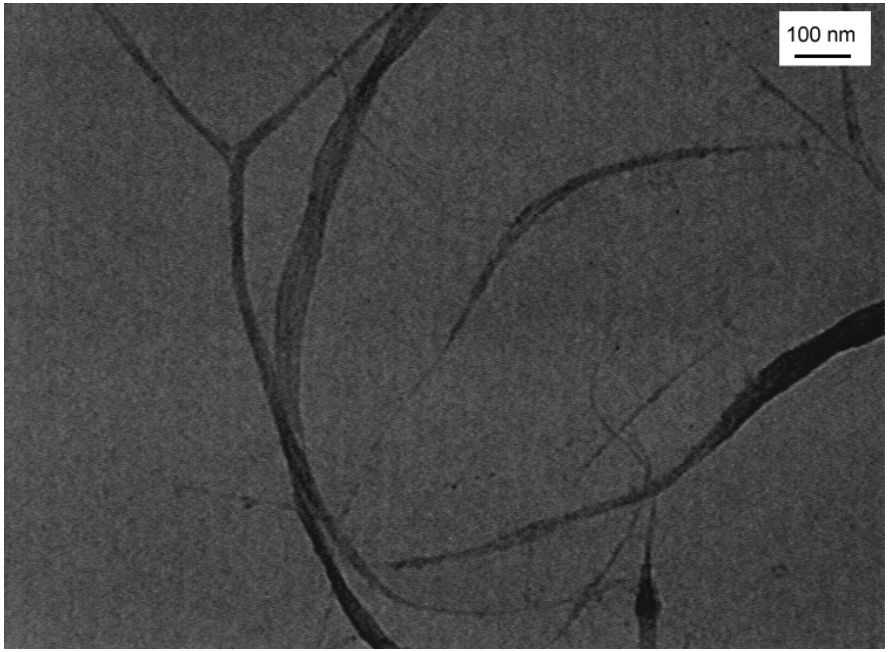


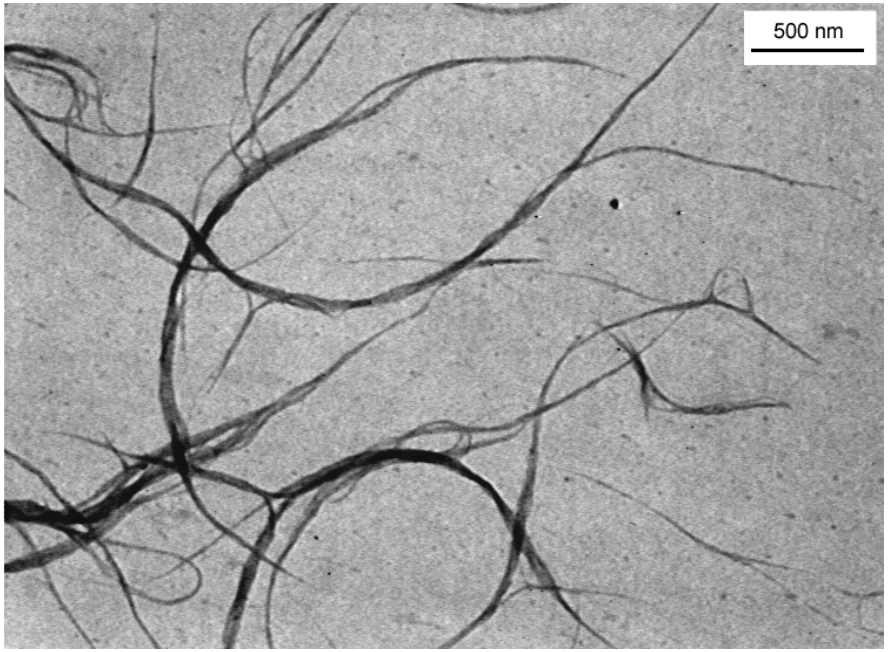
9

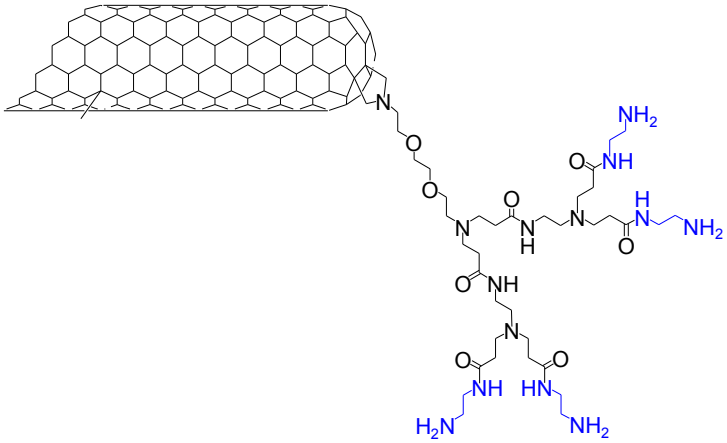


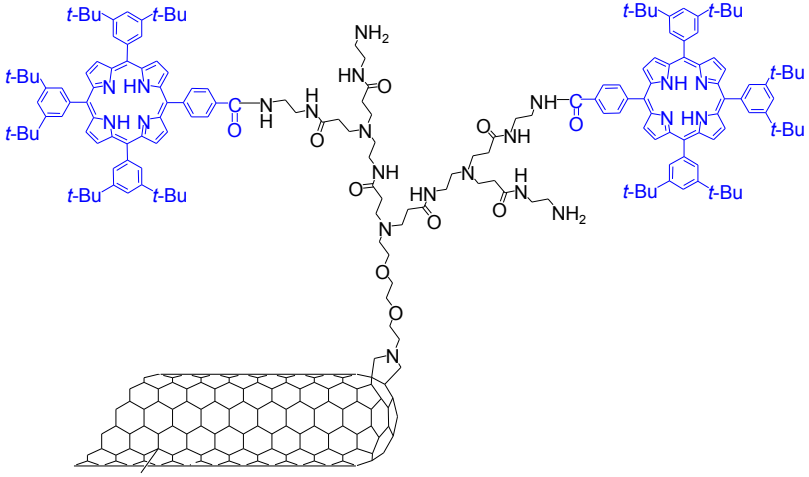
8

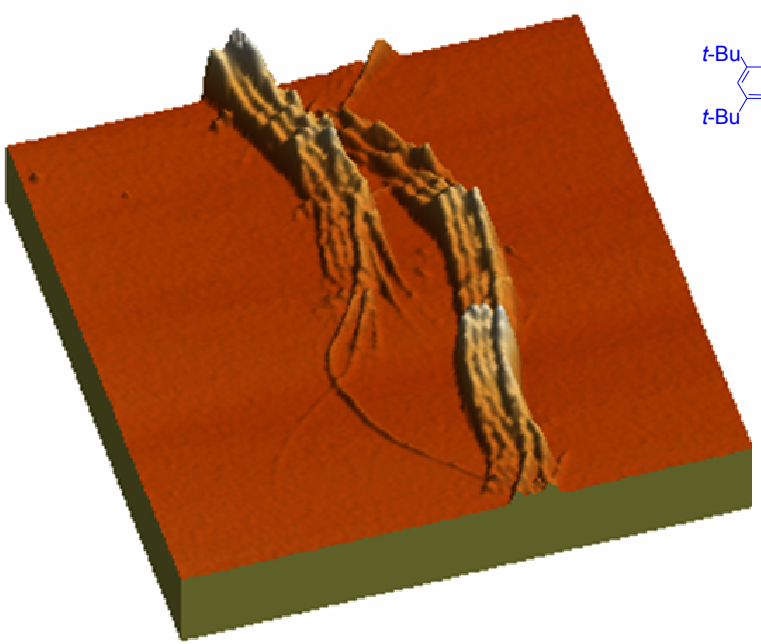

Weight (%)
Temperature (°C)
p-SWNT
1
6
9
100
80
60
40
20
0
200
400
600
800
t-Bu
NH4+
NH2
1
6
9

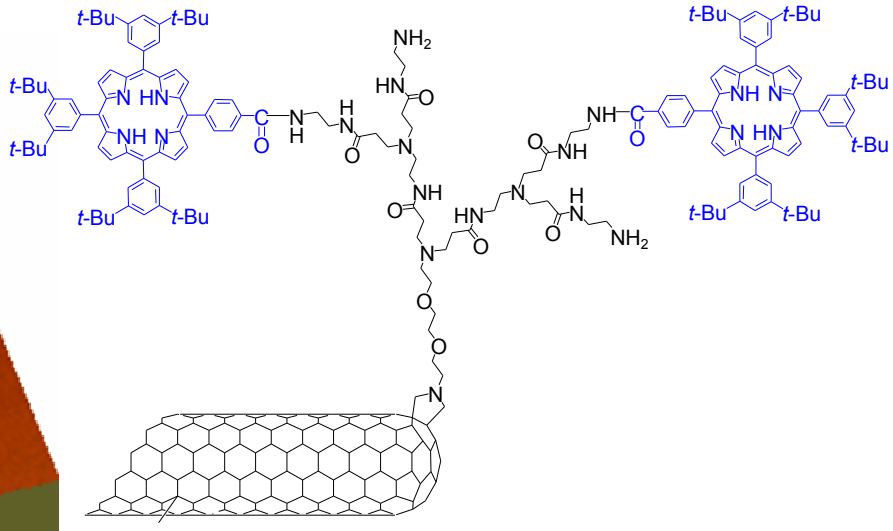

100 nm

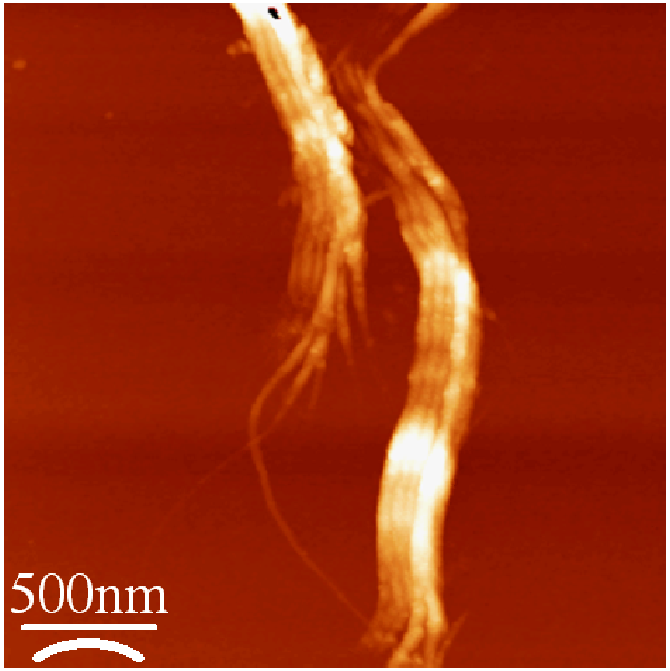

500 nm

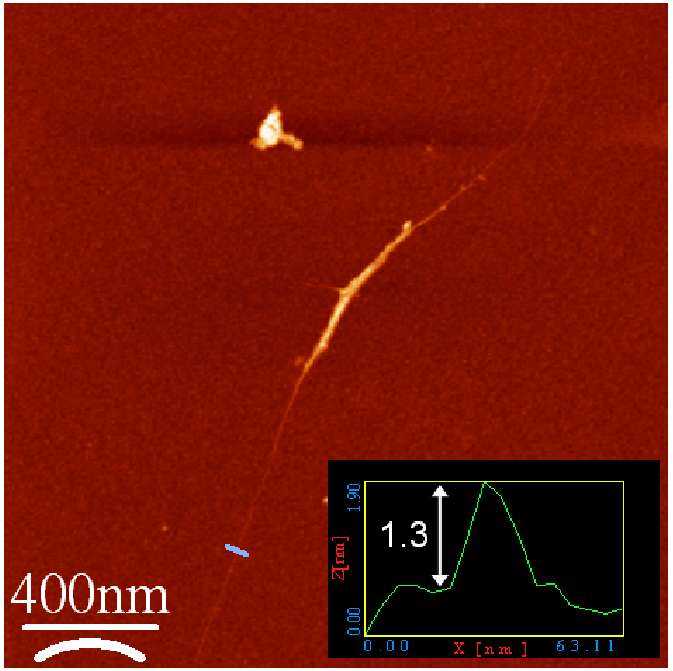




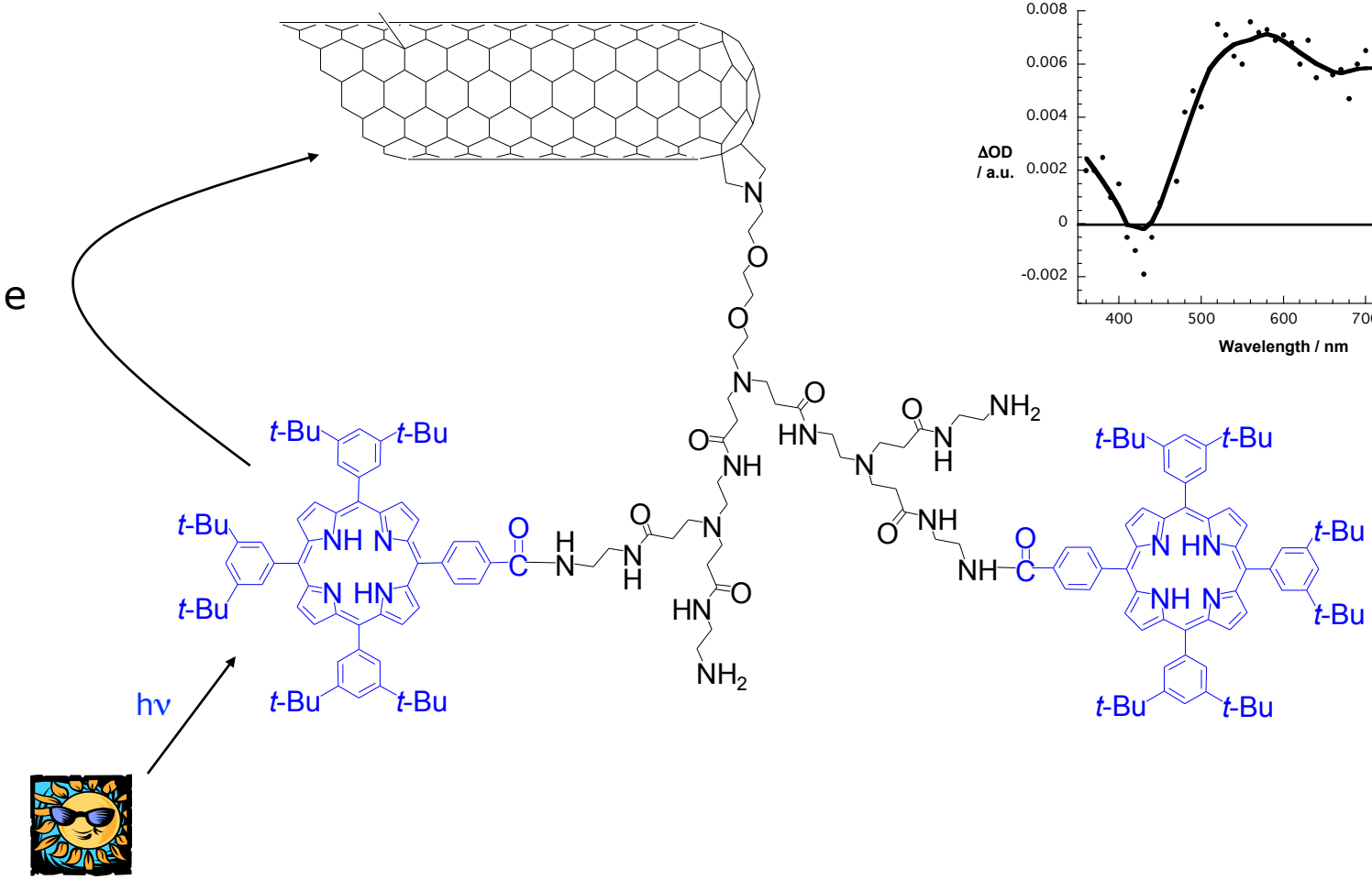


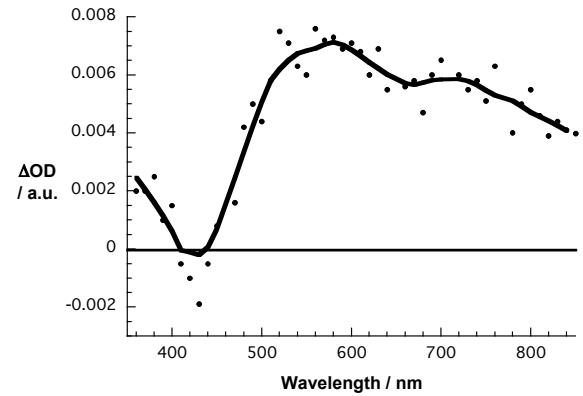

t-Bu
NH2
HN
O
N
H
NH
C
NH2


500nm

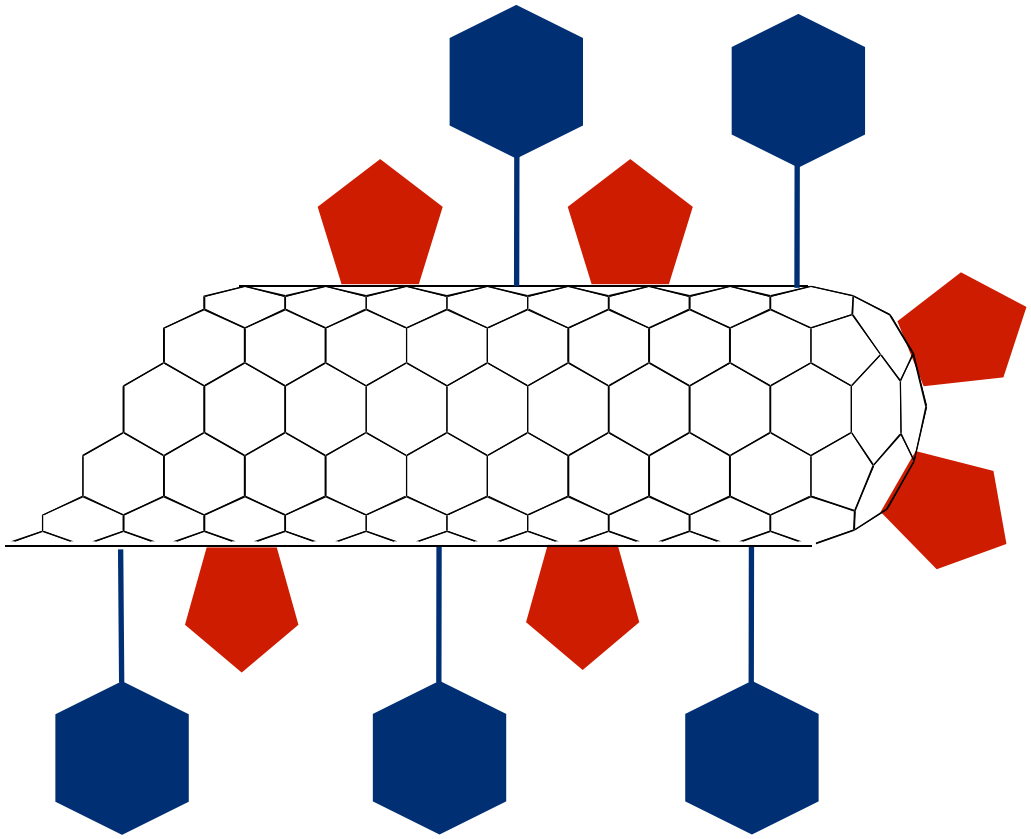

400nm
1.3
Z [nm]
1.90
0.00
0.00
X [nm]
63.11

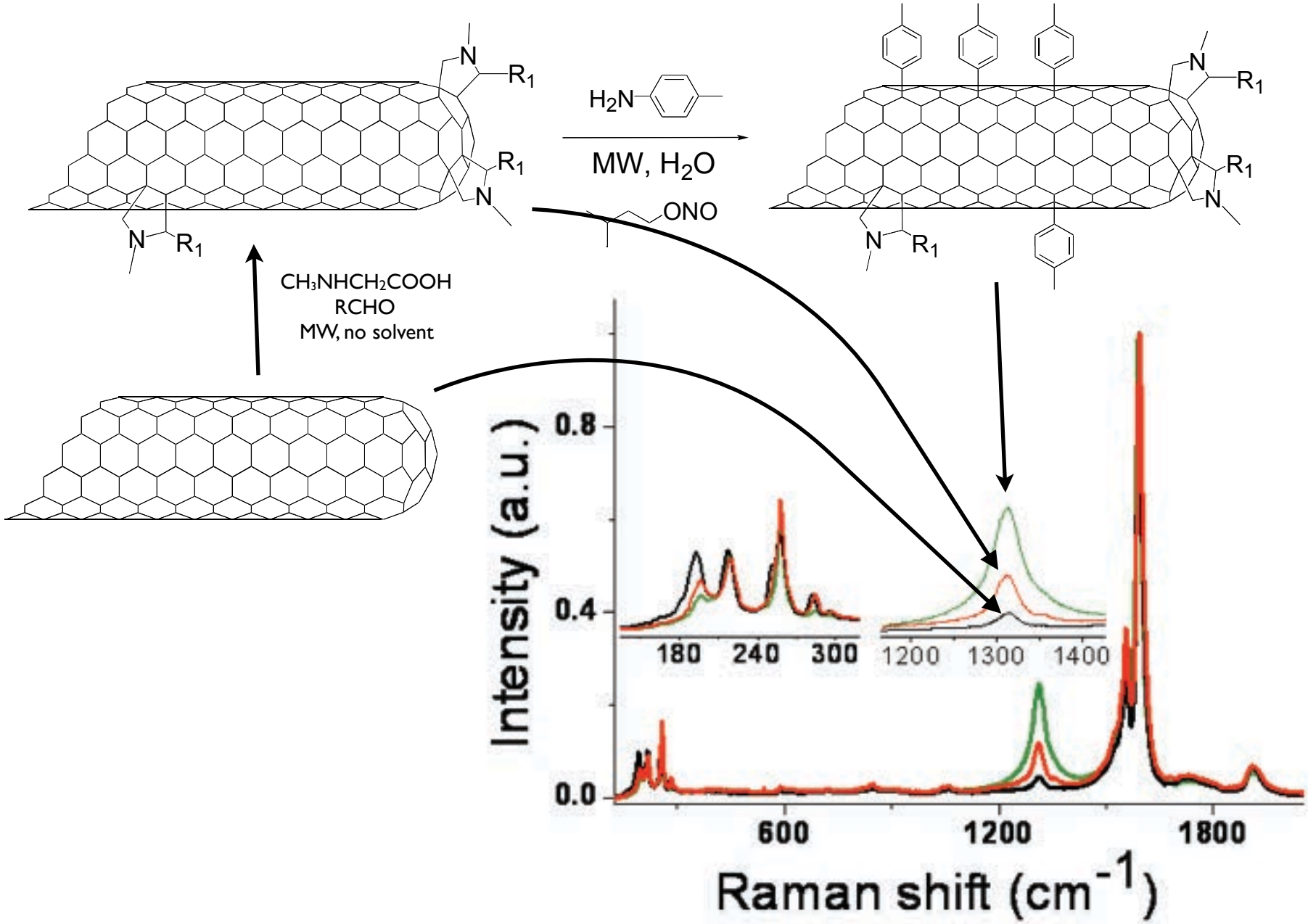
Photoinduced electron transfer from porphyrin to CNT





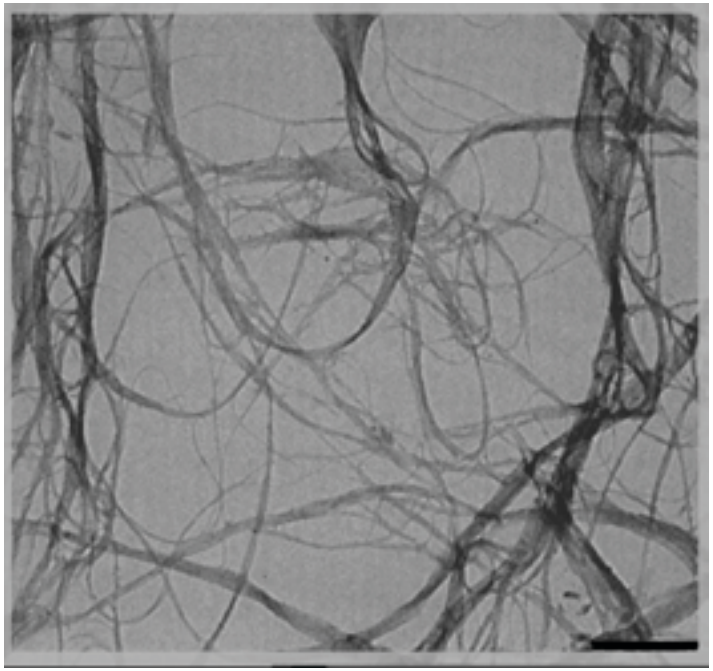
Time-resolved spectroscopy (D. Guldi, U Erlangen) gives lifetimes of charge-separated species of several microseconds

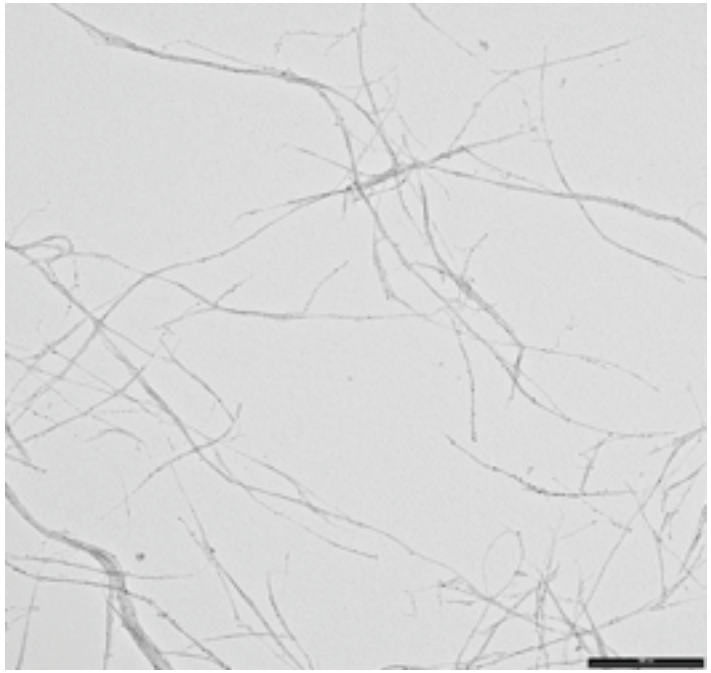


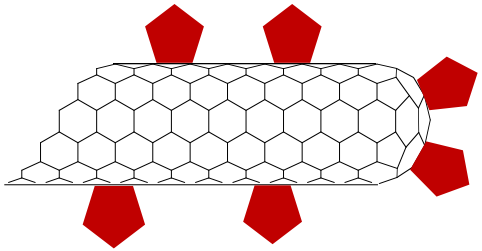


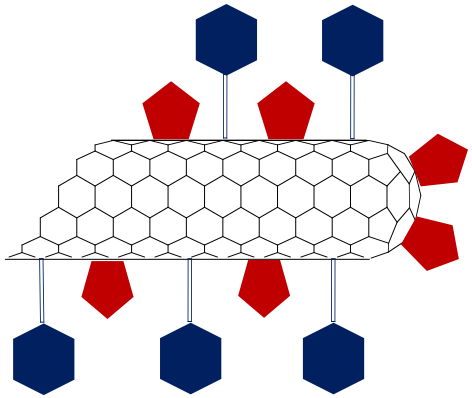
F. Brunetti, M. Herrero, J. Muñoz, M. Meneghetti, M. Prato, and E. Vázquez, J. Am. Chem. Soc., 2008, 130, 8094–8100

TEM Microscopy



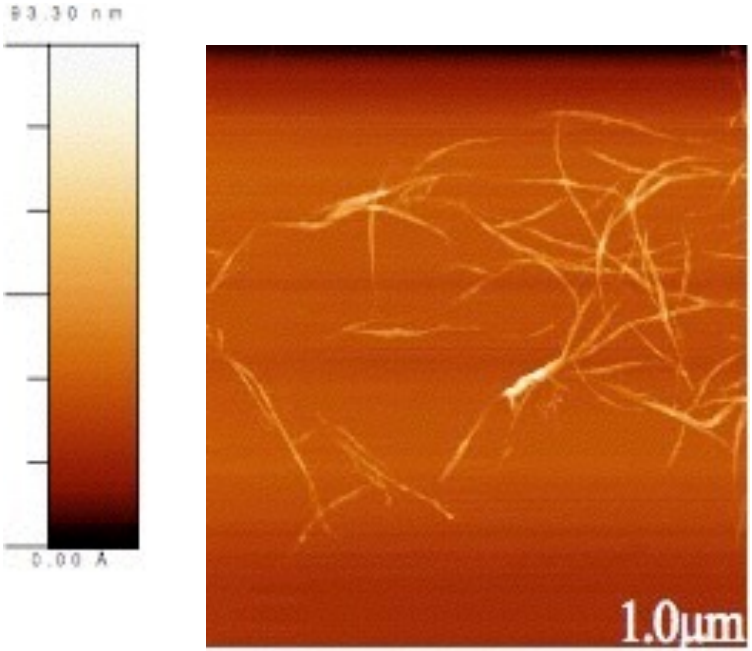


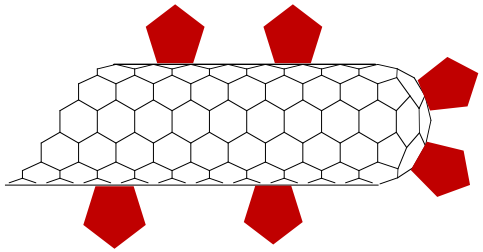


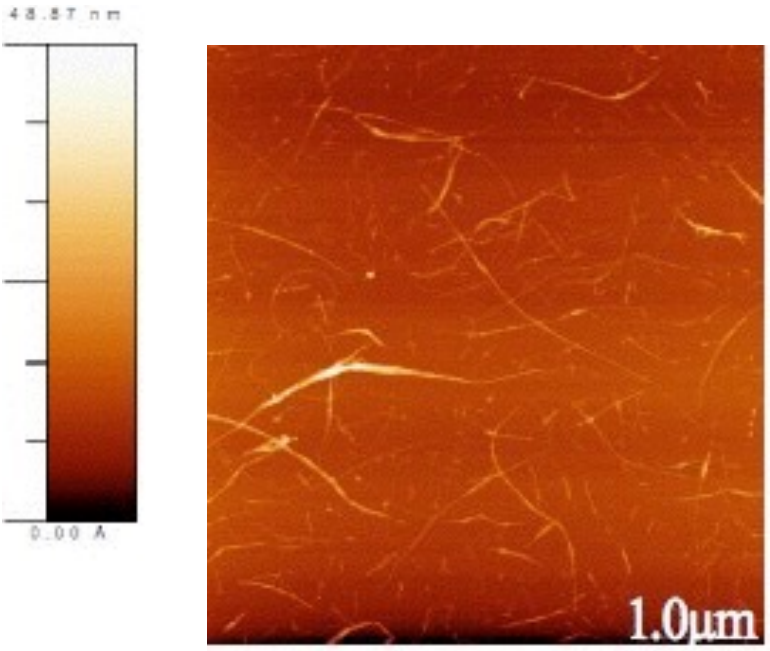


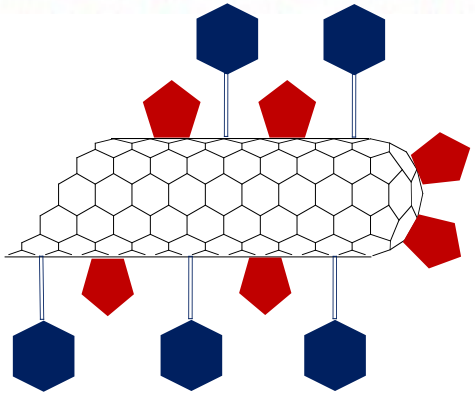
F. Brunetti, M. Herrero, J. Muñoz, M. Meneghetti, M. Prato, and E. Vázquez, J. Am. Chem. Soc., 2008, 130, 8094–8100

AFM Microscopy



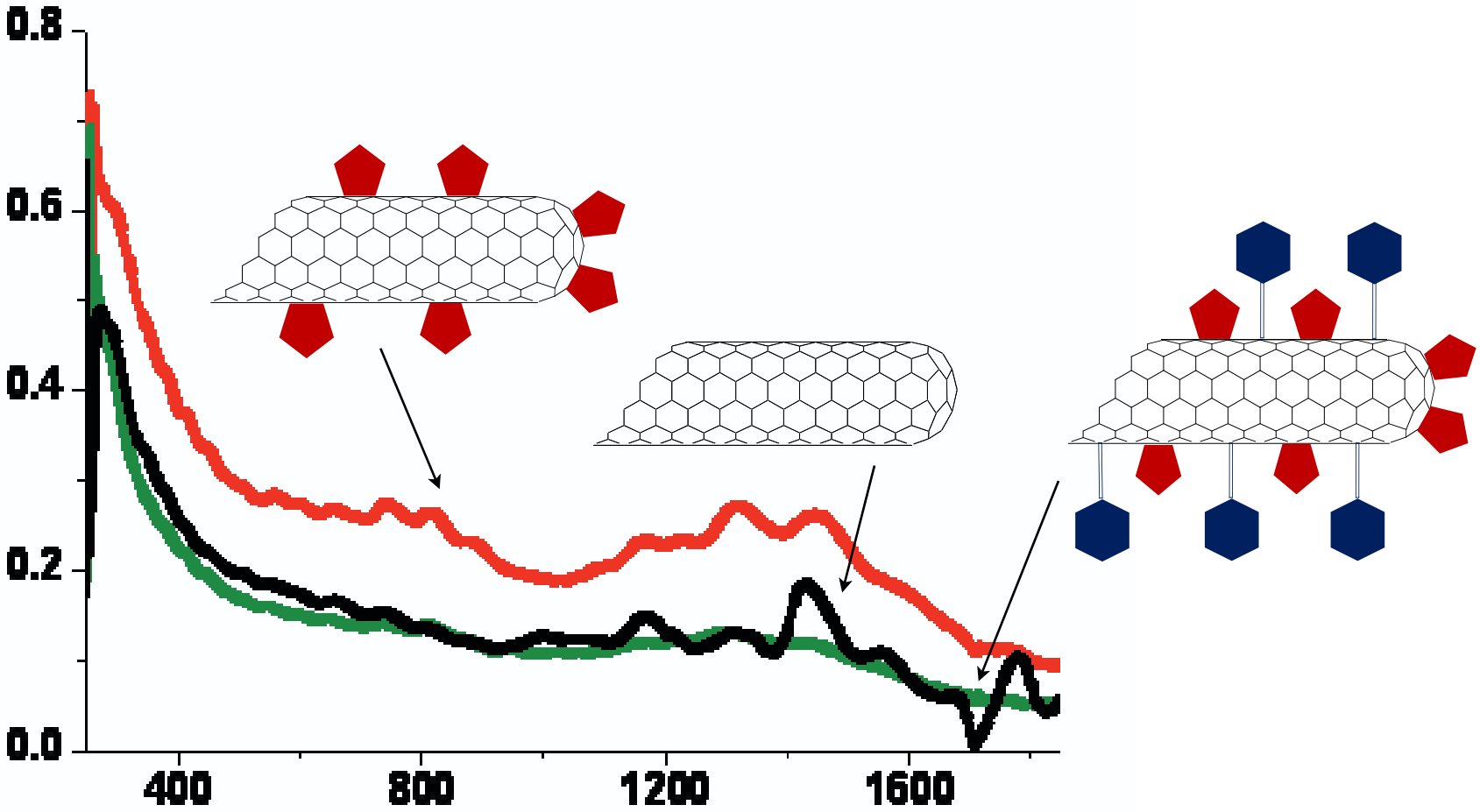






F. Brunetti, M. Herrero, J. Muñoz, M. Meneghetti, M. Prato, and E. Vázquez, J. Am. Chem. Soc., 2008, 130, 8094–8100

UV-Vis-NIR Spectra



F. Brunetti, M. Herrero, J. Muñoz, M. Meneghetti, M. Prato, and E. Vázquez, J. Am. Chem. Soc., 2008, 130, 8094–8100