

NT'06. June 19 2006, Nagano, Japan.

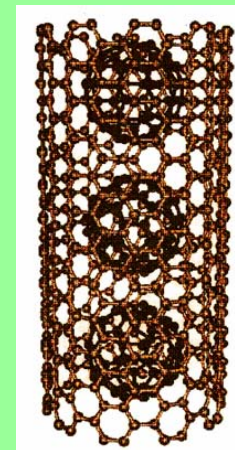
# Nanotube Peapods: A New Class of Carbon Nanotube Hybrids

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## Outline

1. Synthesis of Nano-Peapods
2. Carbon Nanotubes Encapsulating Fullerenes “Nano-Peapods”;
3. Peapods Encaging Linear Polyynes Molecules: Interstellar Molecules





# 善光寺

## Zenkoji Temple

It is said that Zenkoji temple was built in 642, which was the year of Emperor Kogyoku ascended. However, **it was first burnt down in 1179 and it subsequently caught fire on ten separate occasions.** The present main hall was set to rebuild in 1703 and completed in 1707.

**In a Japanese adage:**

**“If you miss to pay a visit to Zenkoji temple, it’s not worth coming to Nagano city.”**

**Superb Saving !** But we are still in a very difficult situation.....



**Japan vs. Croatia (0 : 0) in Nuremberg, Germany**

# Collaborators

## Synchrotron X-Ray

Prof. M. Sakata (Nagoya)

Dr. E. Nishibori (Nagoya)

Dr. M. Takata (Riken)

## HRTEM/EELS

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Dr. K. Suenaga (AIST)

Dr. S. Bandow (Meijo U)

Dr. K. Hirahara (Nagoya U)

## FET Measurements

Prof. T. Mizutani (Nagoya U)

Dr. Y. Ohono (Nagoya U)

## STM Experiments

Prof. Y. Kuk (SNU)

Dr. Jhin Hwan Lee (SNU)

## Peopod Syntheses & Characterization

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Dr. R. Kitaura (Nagoya U)

Dr. T. Tomiyama (Nagoya U)

Dr. G. Ning (Nagoya U)

Dr. R. Palanisami (Nagoya U)

Dr. T. Shimada (Nagoya, Stanford U)

Y. Ito (Nagoya U)

H. Okimoto (Nagoya U)

N. Kishi (Nagoya U)

D. Nishide (Nagoya U)

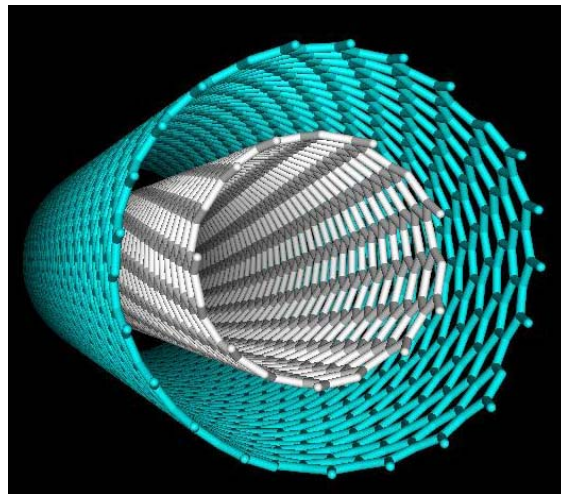
H. Yoshida (Nagoya U)

N. Fukui (Nagoya U)

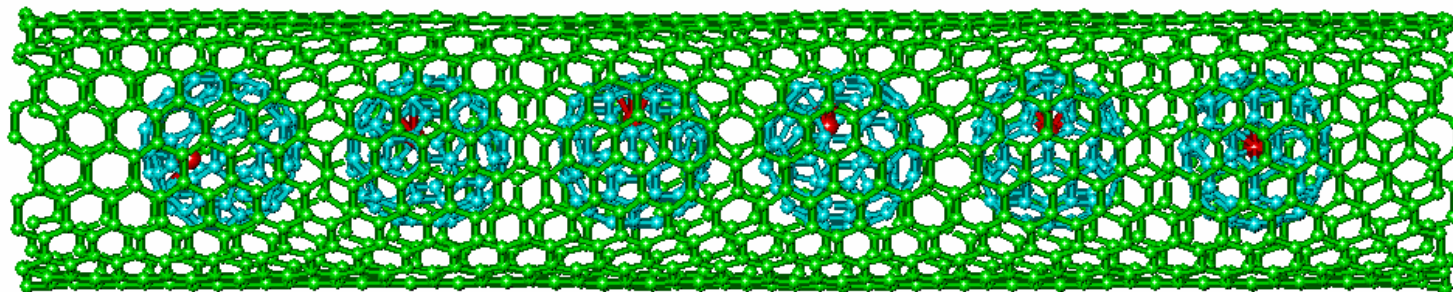
S. Kuwahara (Nagoya U)

K. Kobayashi (Nagoya U)

# Carbon Nanotubes of Our Interests

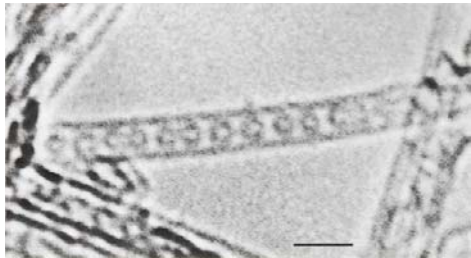


Double-Wall Carbon Nanotubes  
( DWNT )

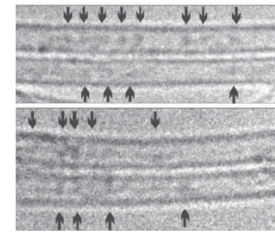


Peapod ( ピーポット )

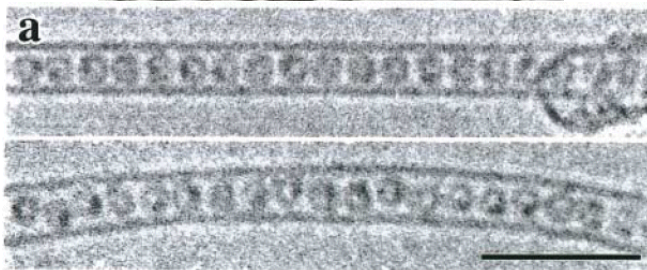
# Encapsulation into Nanotubes



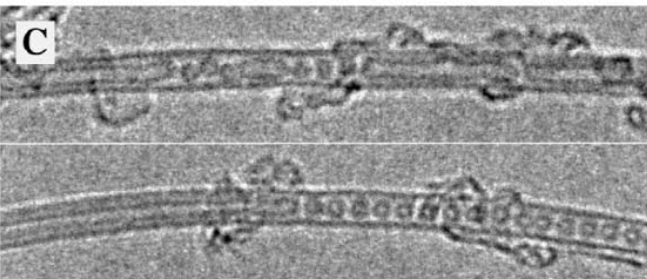
Smith (1998)



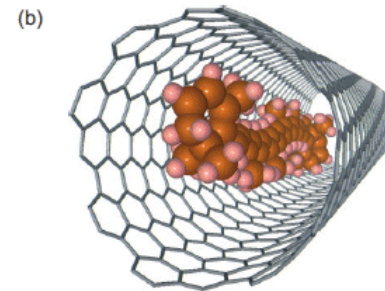
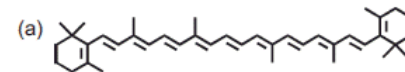
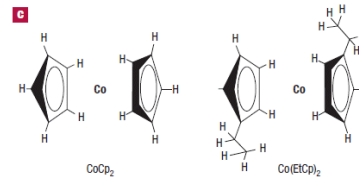
Li (2005)



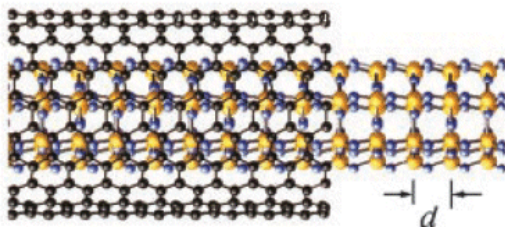
Hirahara (2000)



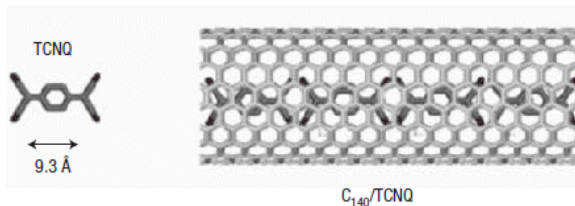
Bandow (2001)



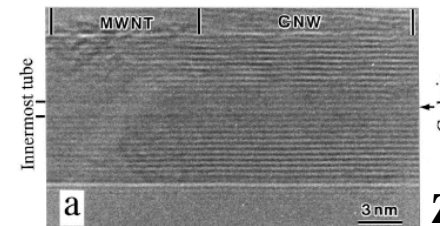
Yanagi (2006)



Maniwa (2002)

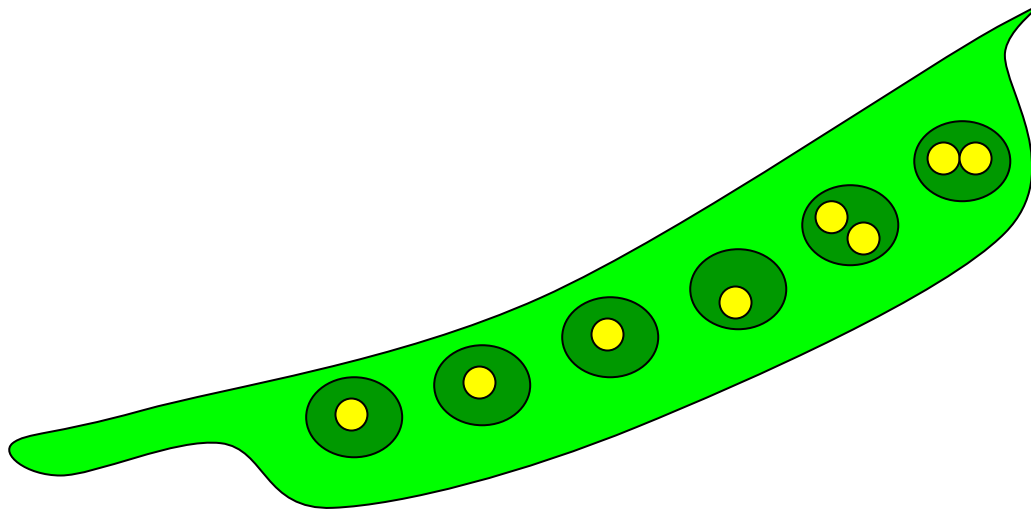


Takenobu (2003)



Zhao (2003)

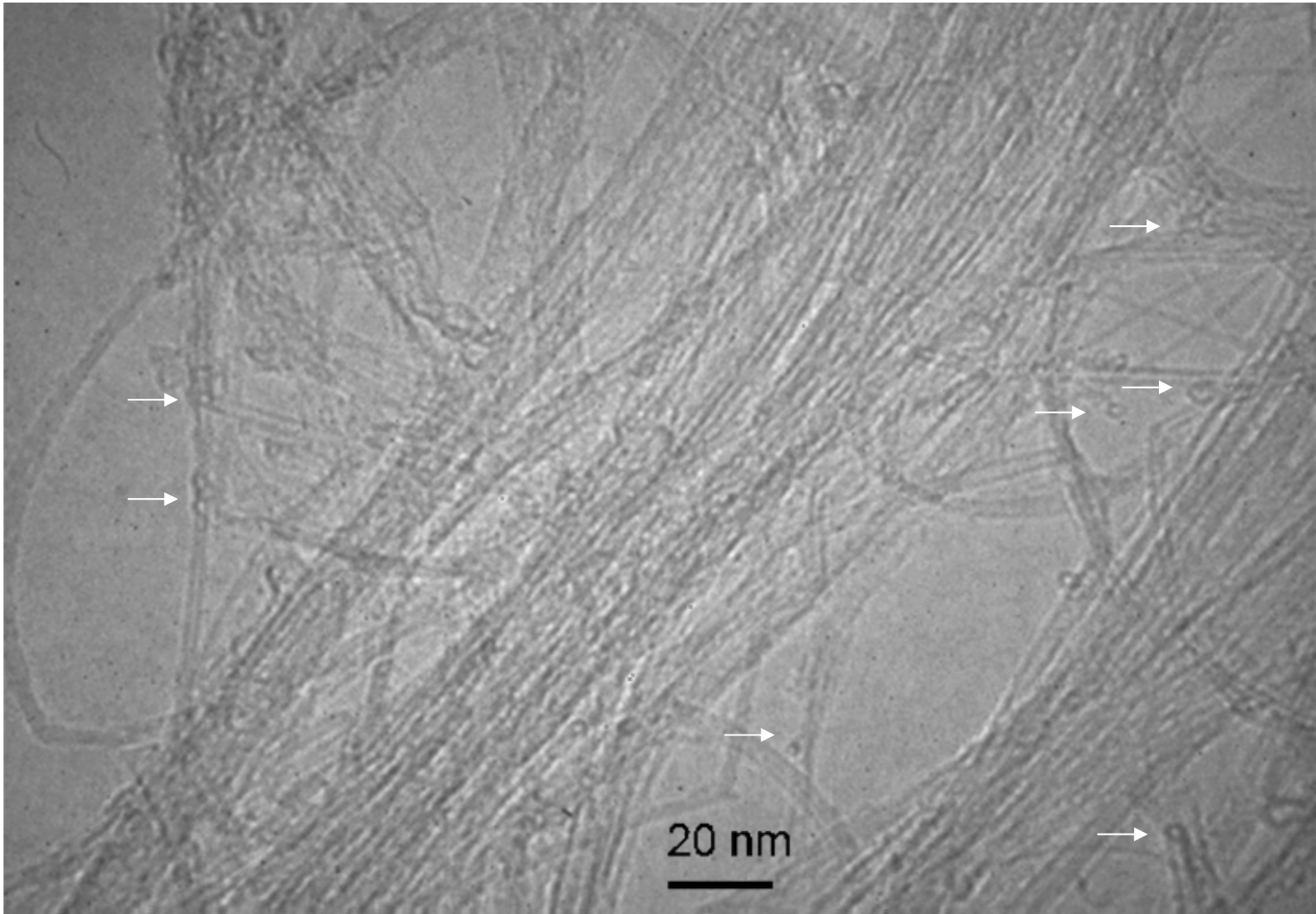
# “Peapod” Structure



さやえんどう



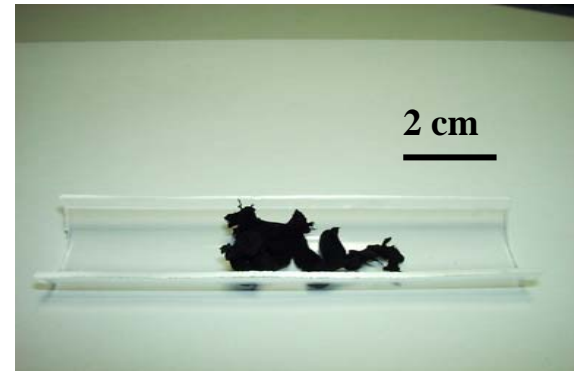
# Open-Ended Carbon Nanotubes



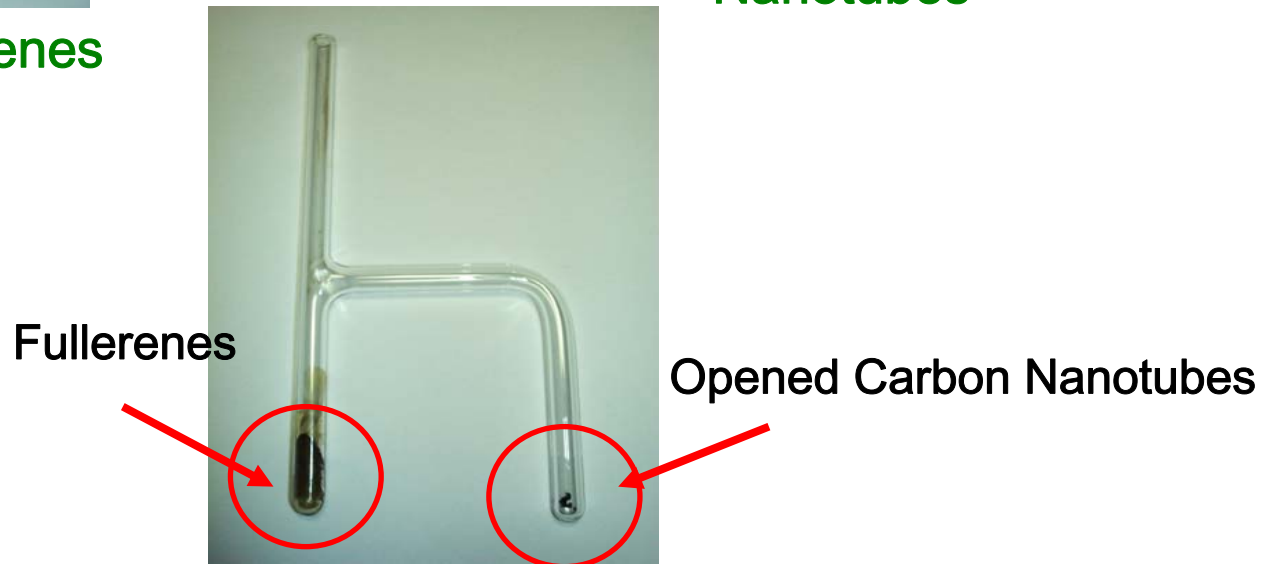
# Gas-Phase Synthesis of Peapods via Low Technology



Purified Fullerenes



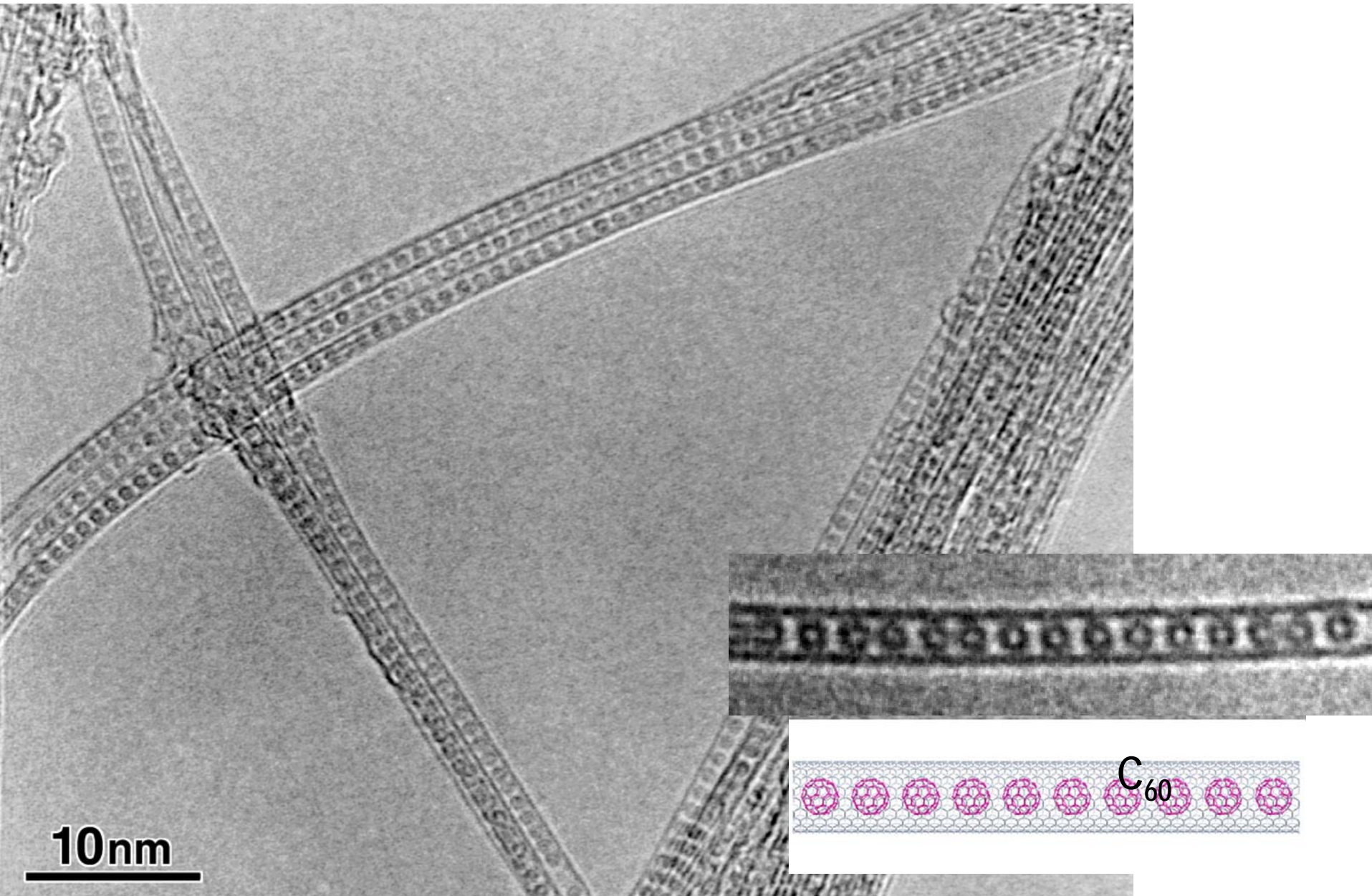
High-Purity Carbon  
Nanotubes

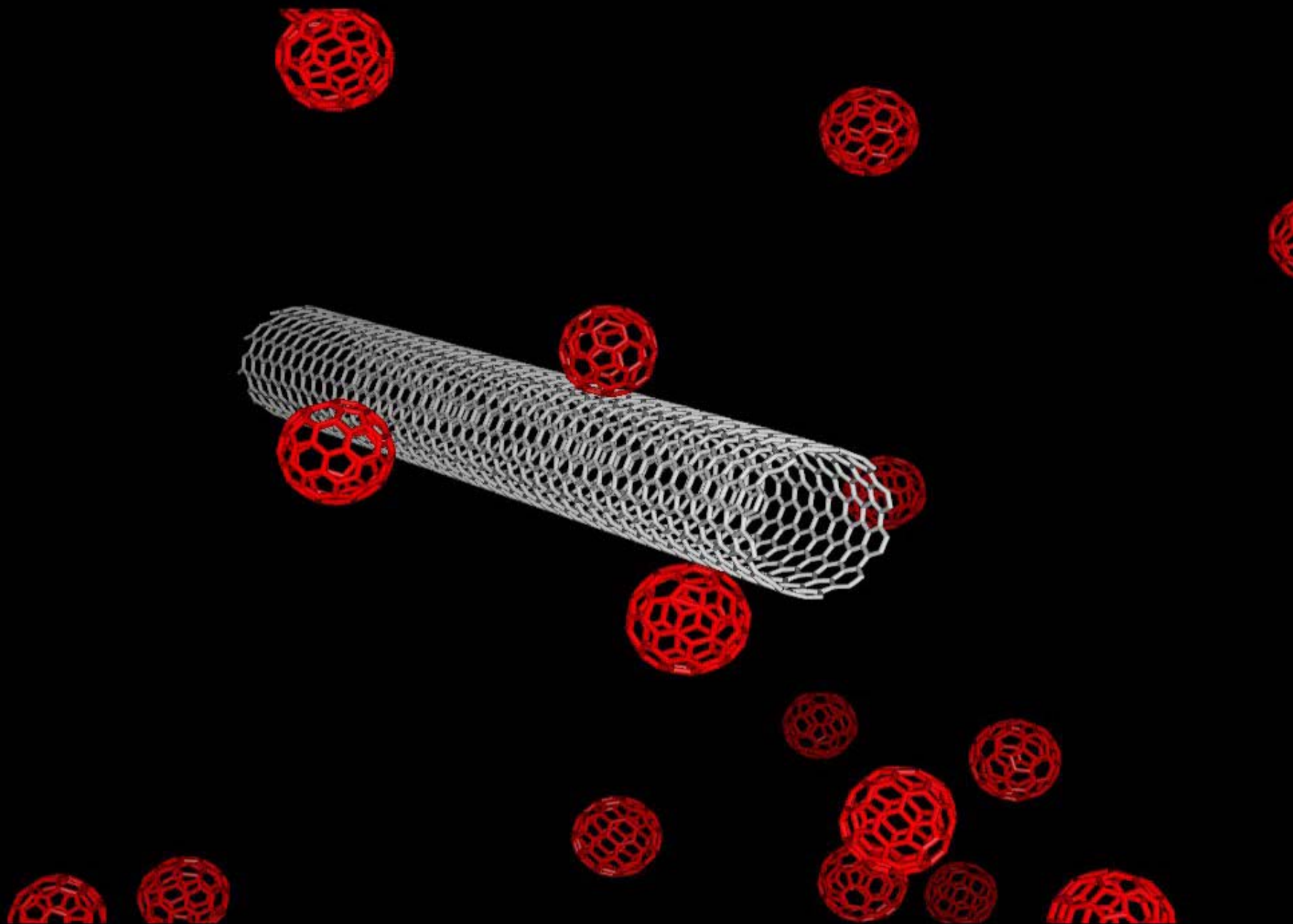


Fullerenes

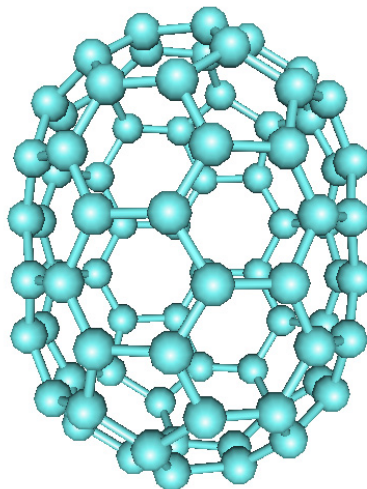
Opened Carbon Nanotubes

# C<sub>60</sub> molecules inside SWNTs

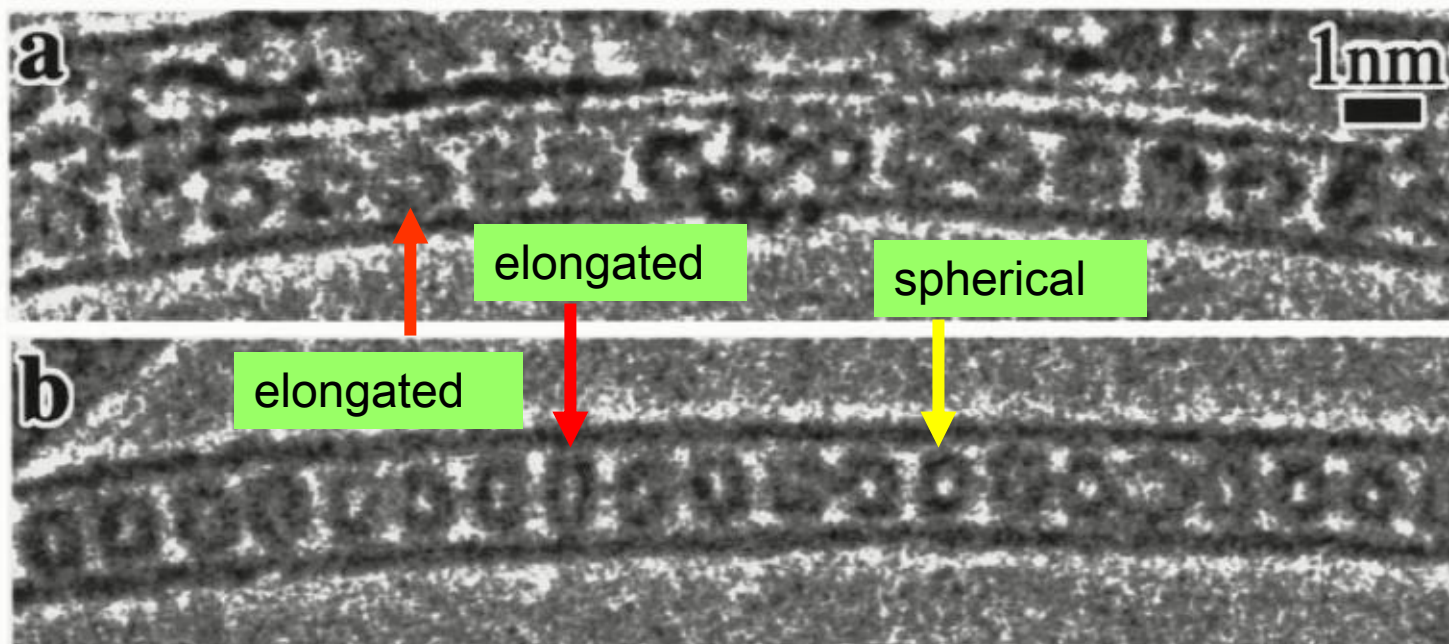




**C<sub>80</sub> (*D*<sub>5d</sub>)**



C-R.Wang et al.  
*Chem. Commun.*  
(2000).



**Syntheses of**

**C<sub>60</sub>@DWNT,**

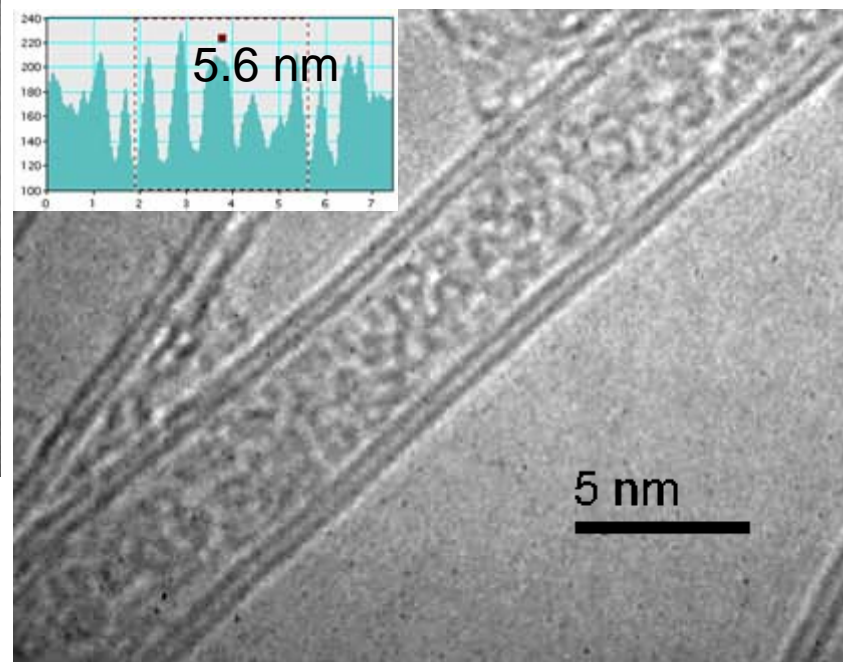
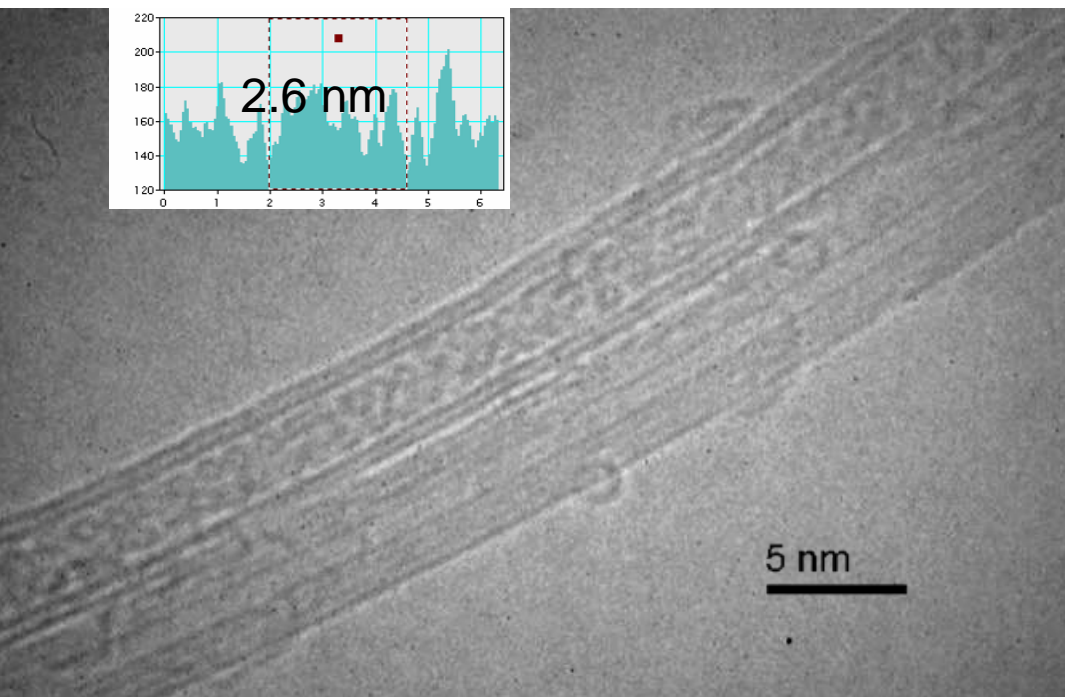
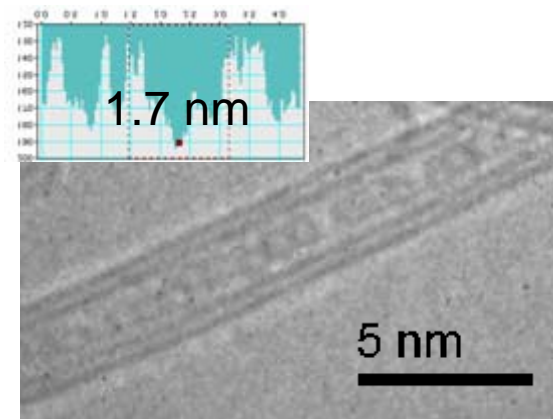
**C<sub>60</sub>@TWNT and**

**C<sub>60</sub>@MWNT**

# Peapods' Preparations

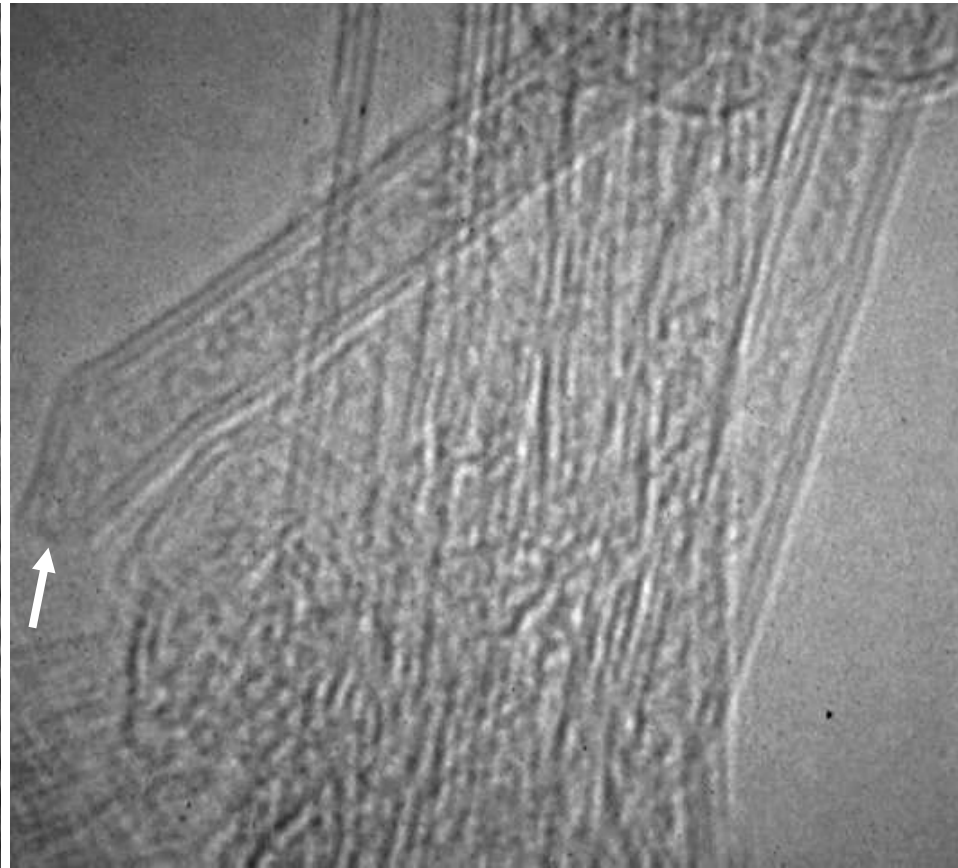
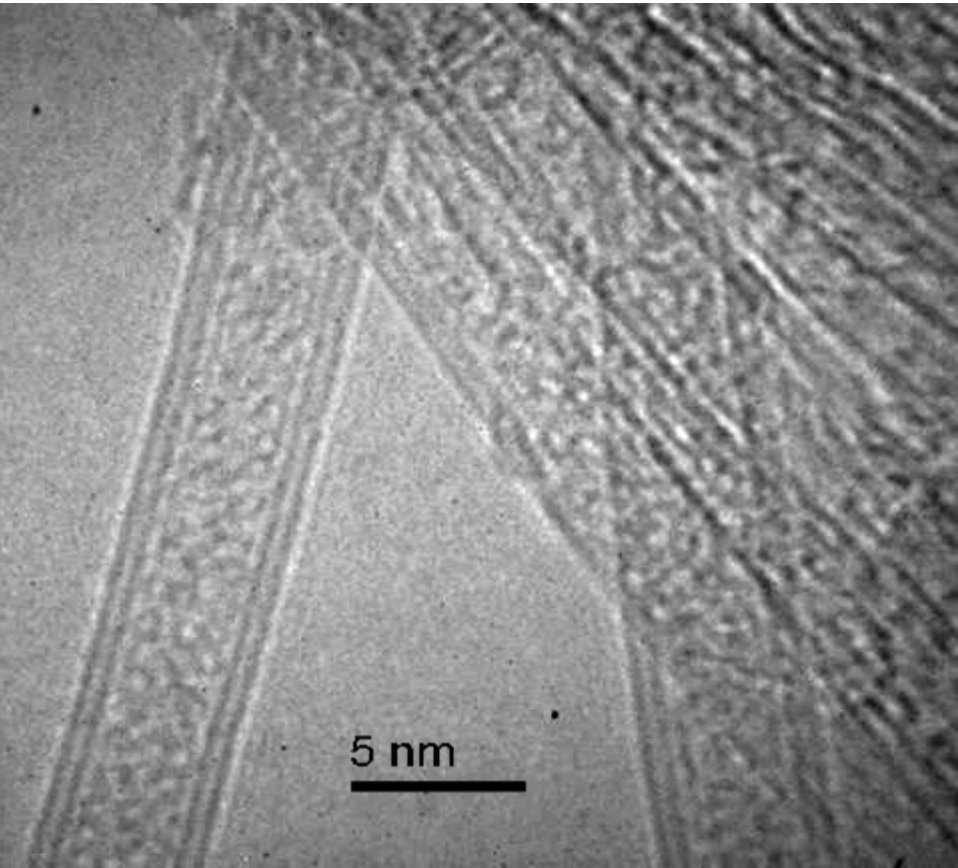
- **Growth, purification and opening of DWNTs**
  - **Growth of DWNTs**  
**Fe/MgO catalysts, CH<sub>4</sub> cracking at 900 °C for 10 min.**
  - **Open DWNTs by 450 °C heating in open air for 1 h.**
- **Synthesis of nano-peapods**
  - **DWNTs with excessive C<sub>60</sub> were sealed in a glass ampule under  $5 \times 10^{-5}$  Torr and heated at 500 °C for 2 days.**

# TEM images of $C_{60}@DWNTs$

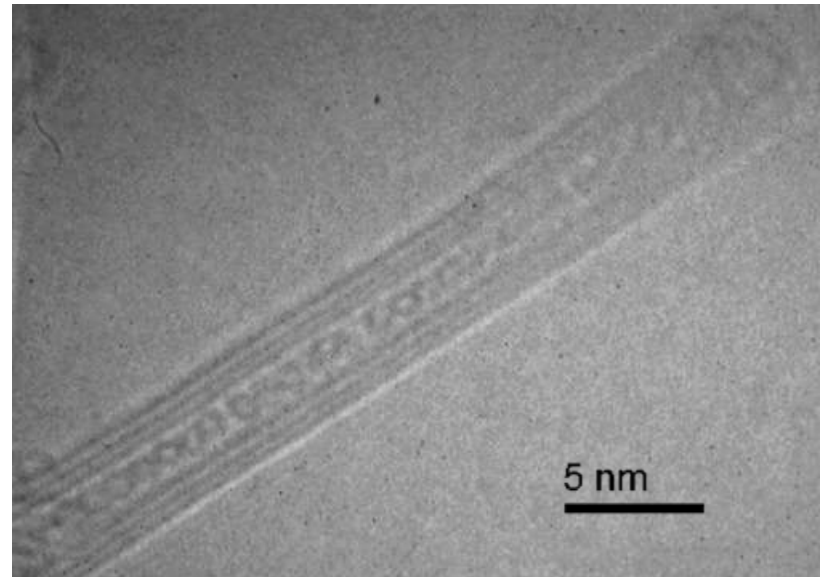
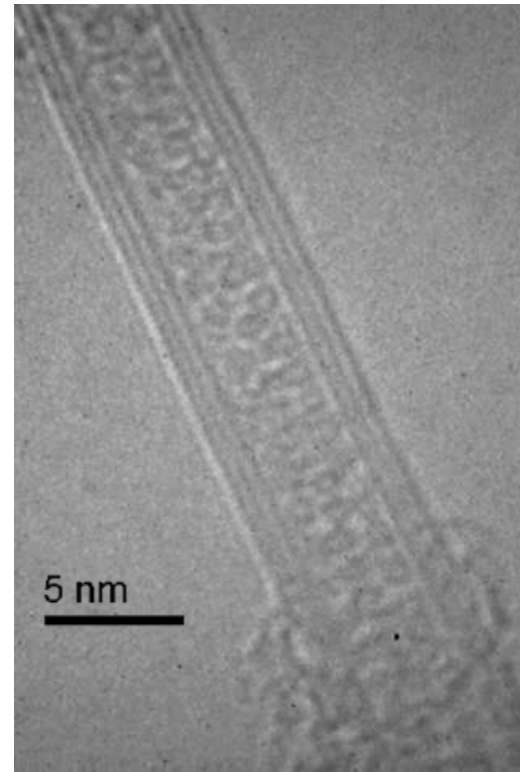
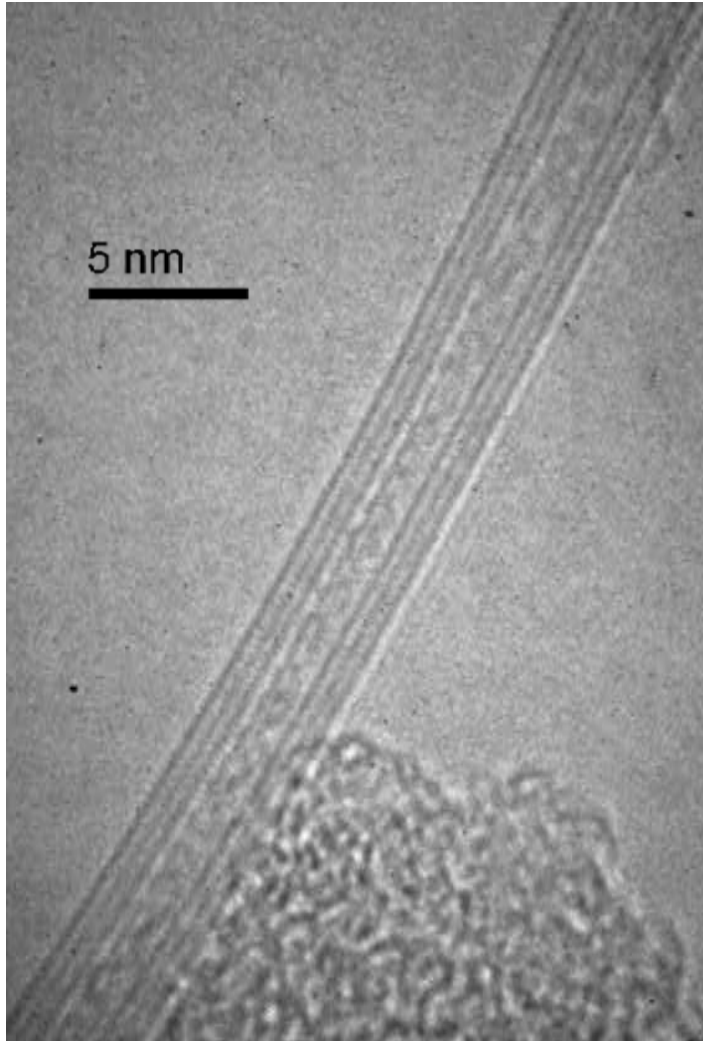




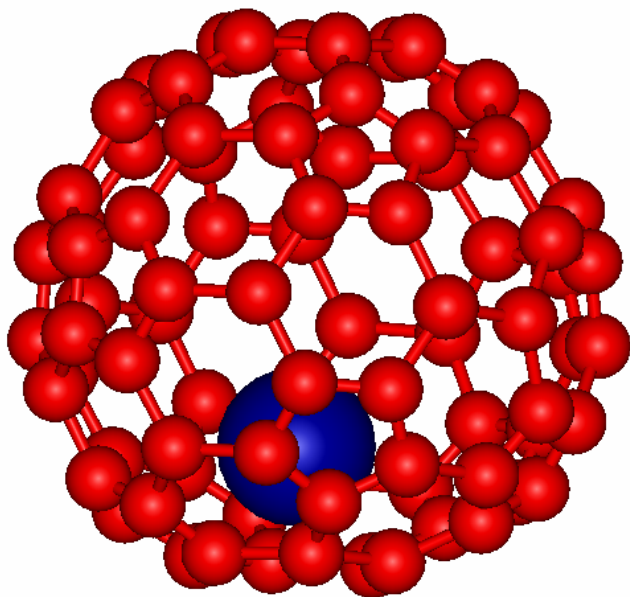
# High-Yield Synthesis of C<sub>60</sub>@DWNT



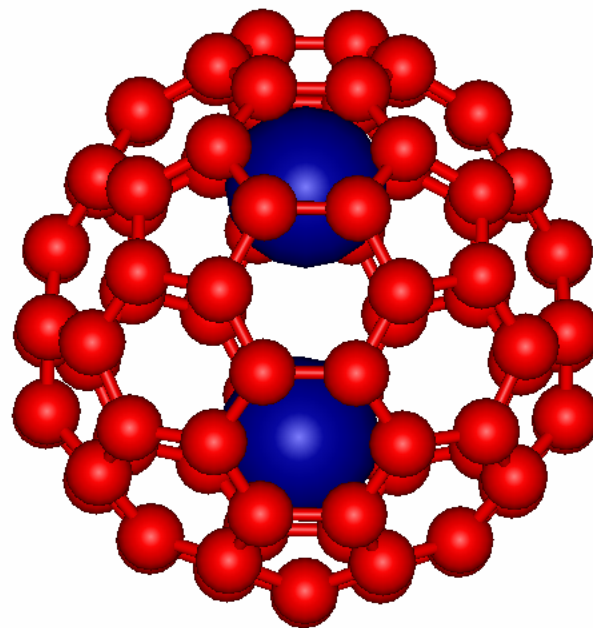
# C<sub>60</sub>@TWNT



# Endohedral Metallofullerenes

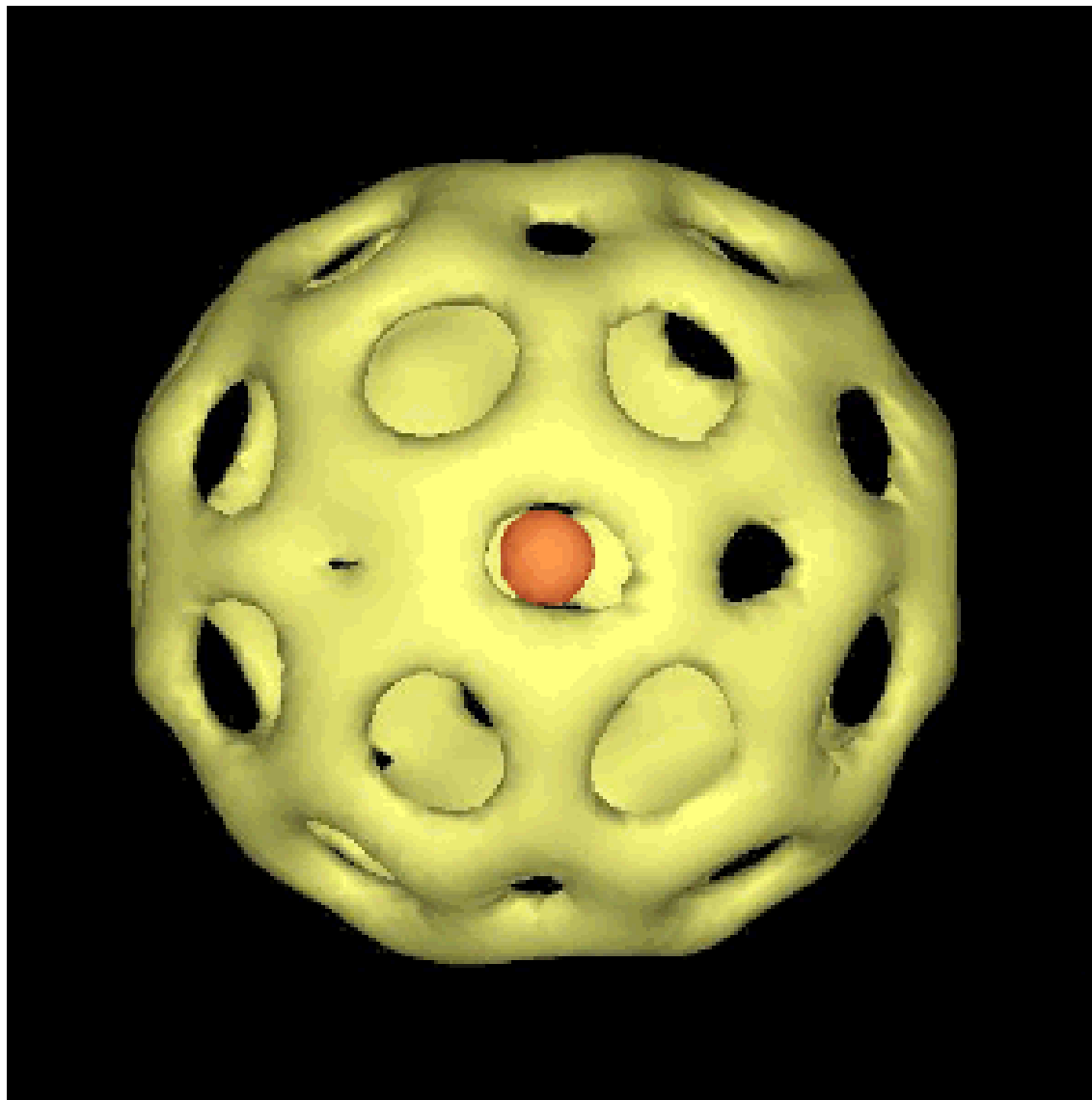


$\text{La@C}_{82}$   
 $\text{Gd@C}_{82}$



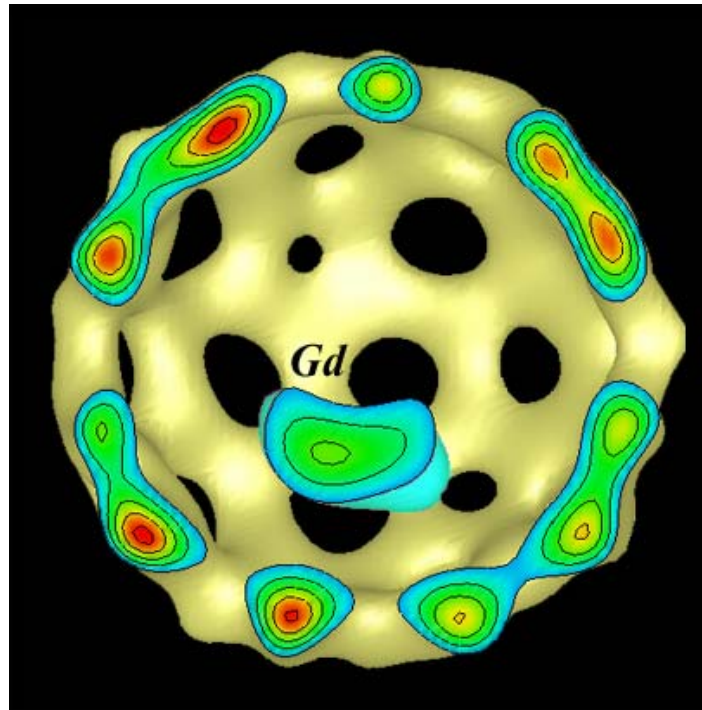
$\text{Gd}_2\text{@C}_{92}$

# Electron Charge Density of $Y@C_{82}$



M. Takata et al.  
*Nature* (1995)

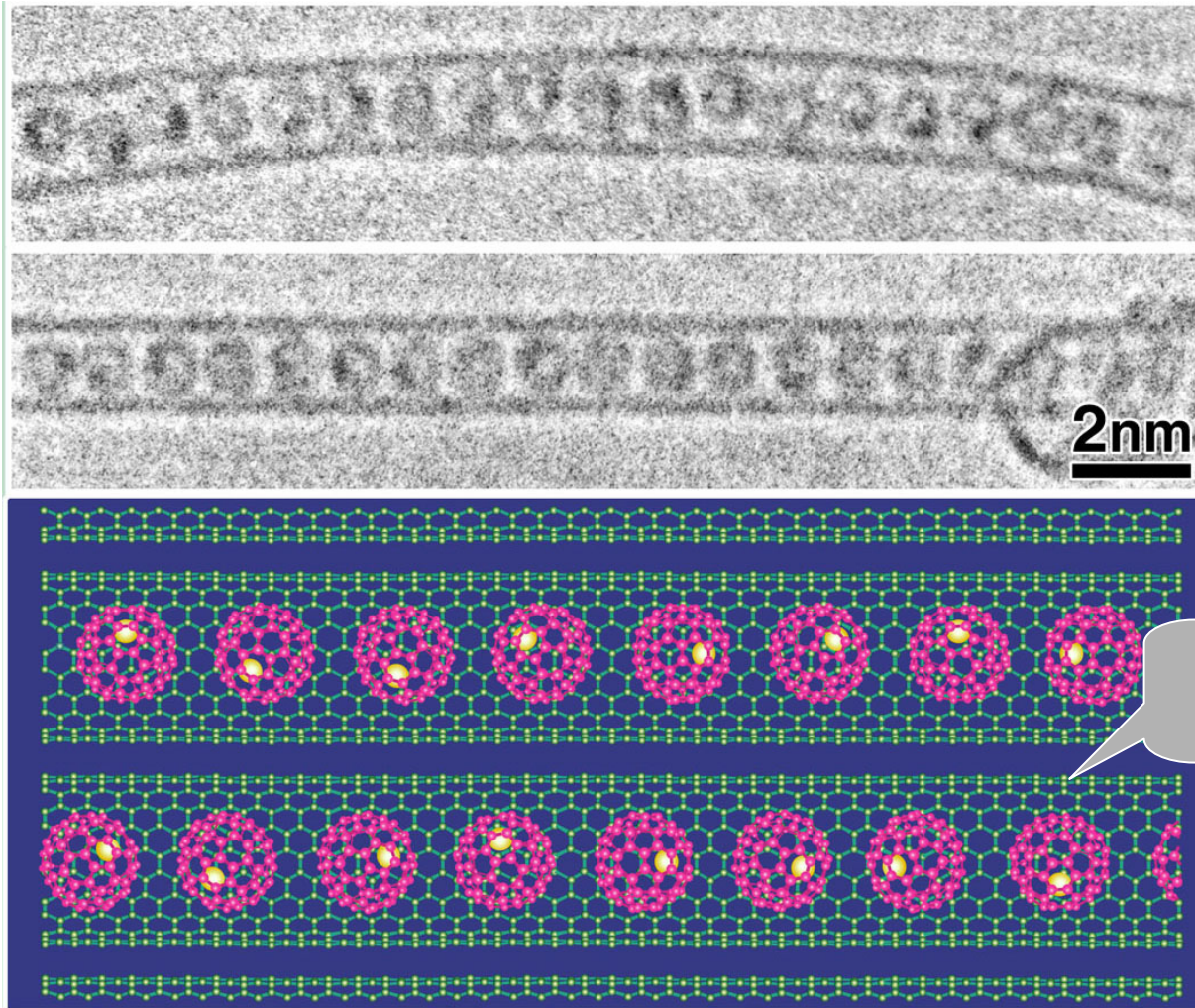
# The MEM Charge Densities of $Gd@C_{82}$



1.40 e/Å<sup>3</sup> equi-contour surface

E.Nishibori et al.  
*Phys.Rev.B* (2004)

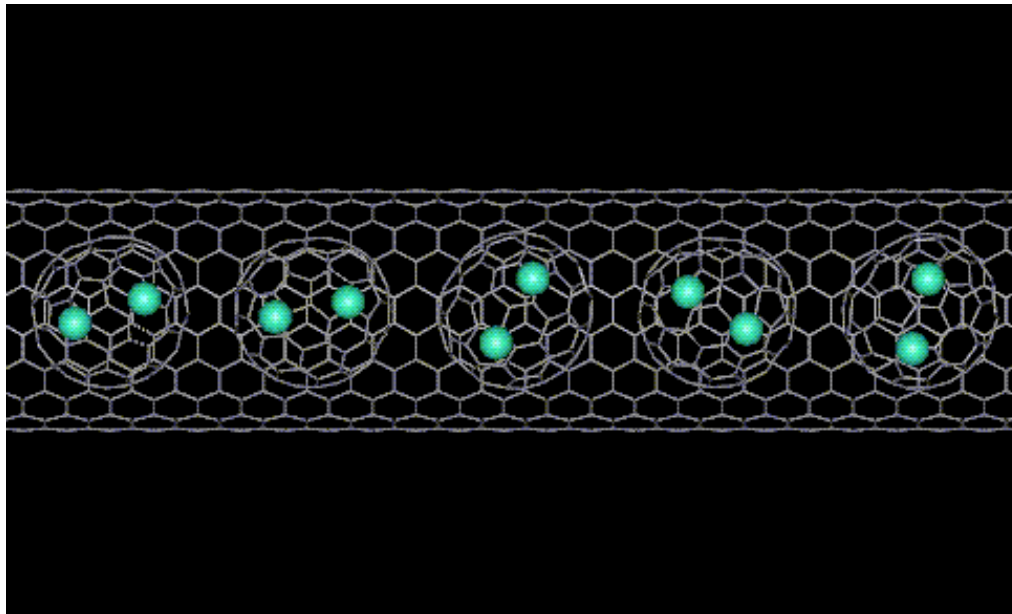
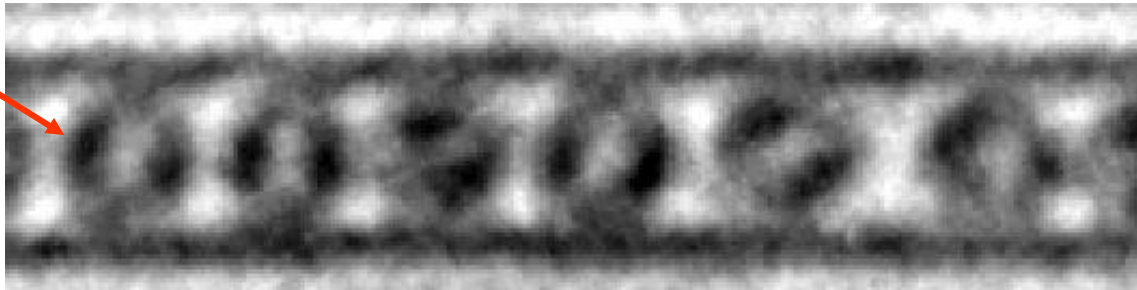
# Gd@C<sub>82</sub> peapods



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

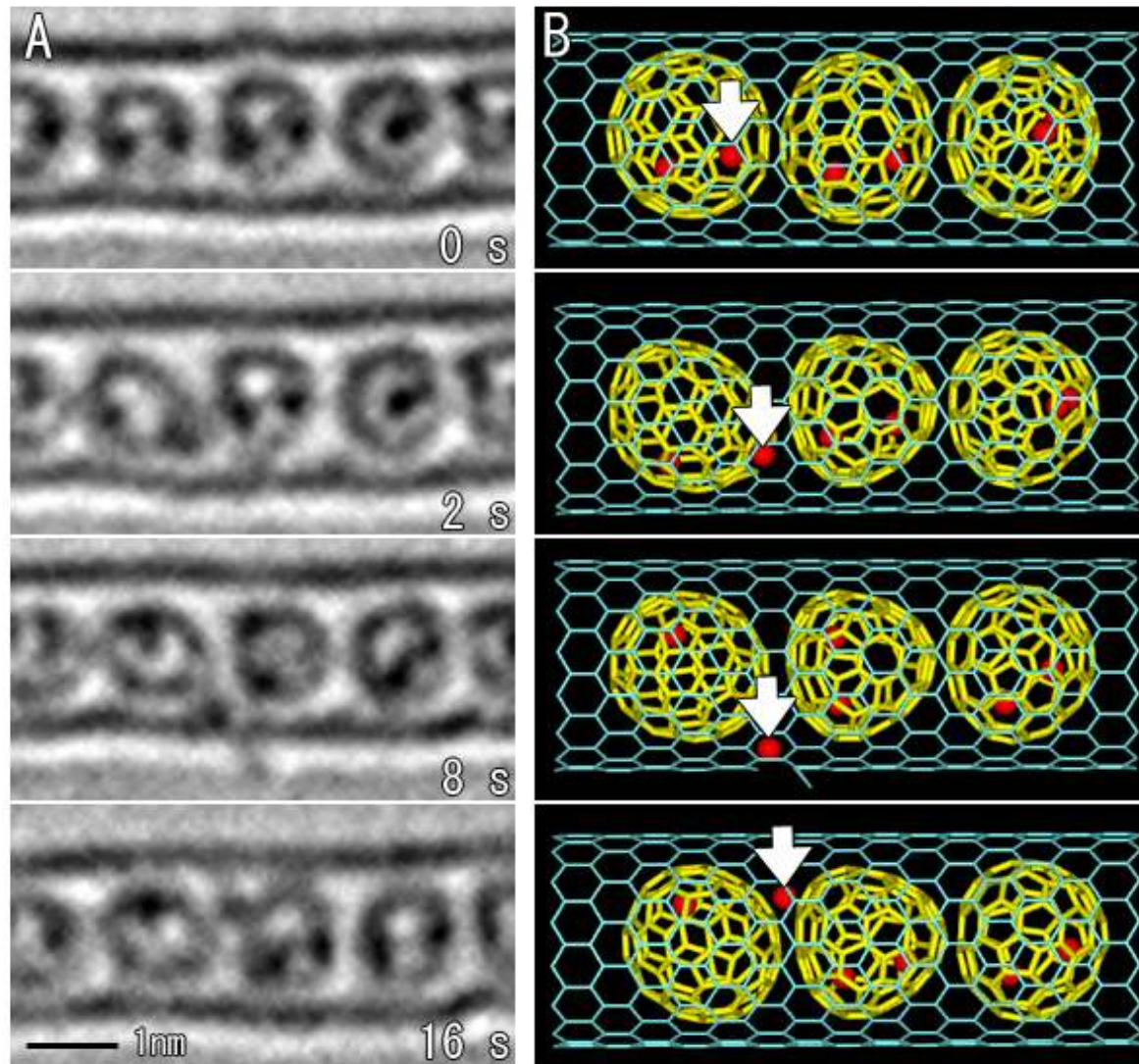
# HRTEM Image of $[(\text{Gd}_2)@C_{92}]@SWNT$ Peapod

Gd atom



K.Suenaga et al.  
*Nano Lett.* (2003).

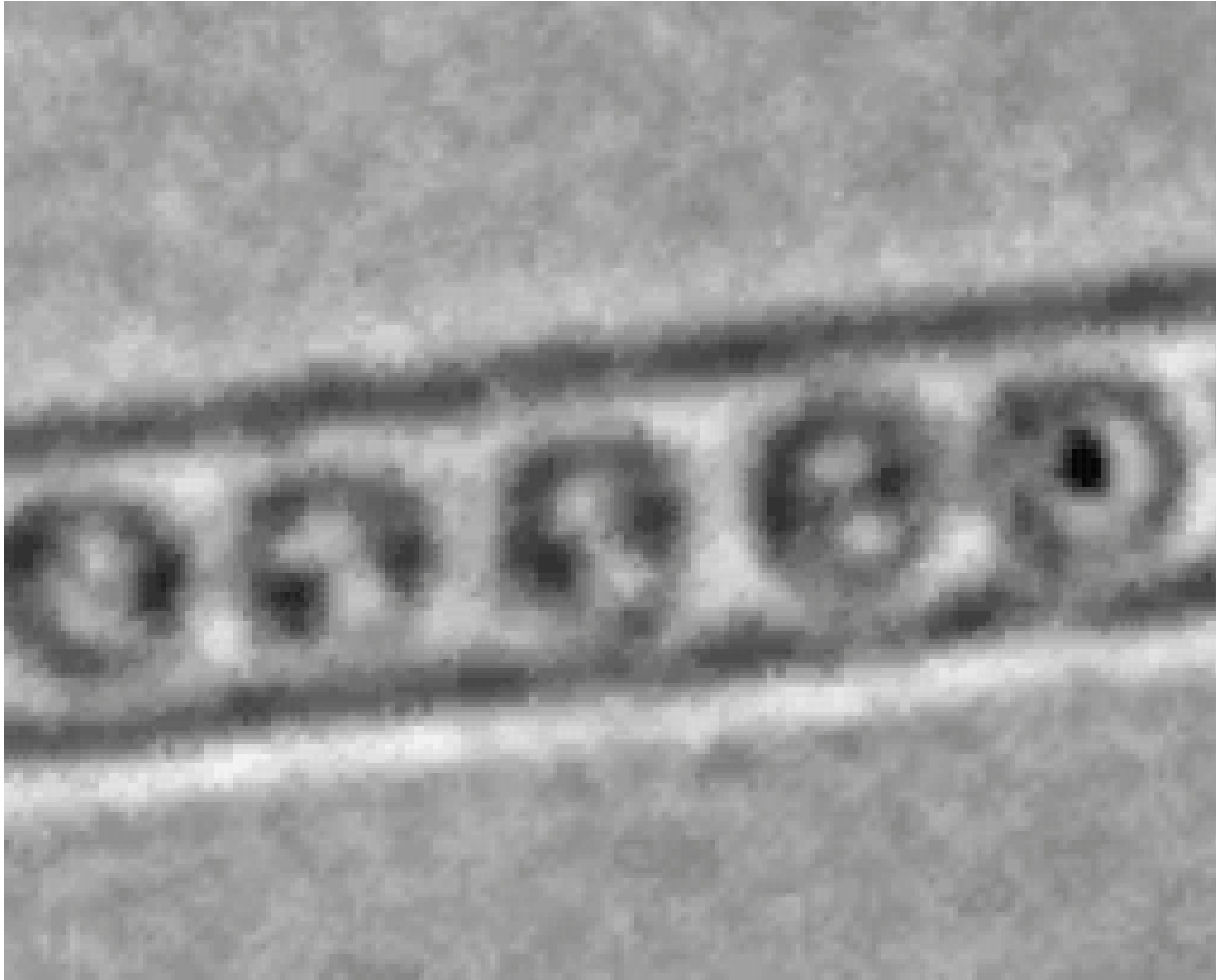
# Escaping of Tb atom from A C<sub>92</sub> Fullerene Cage



K.Suenaga et al. *Nano Letters* (2005).

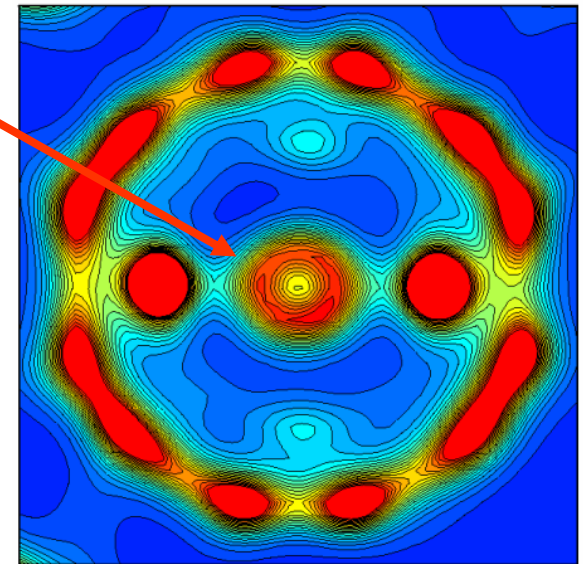
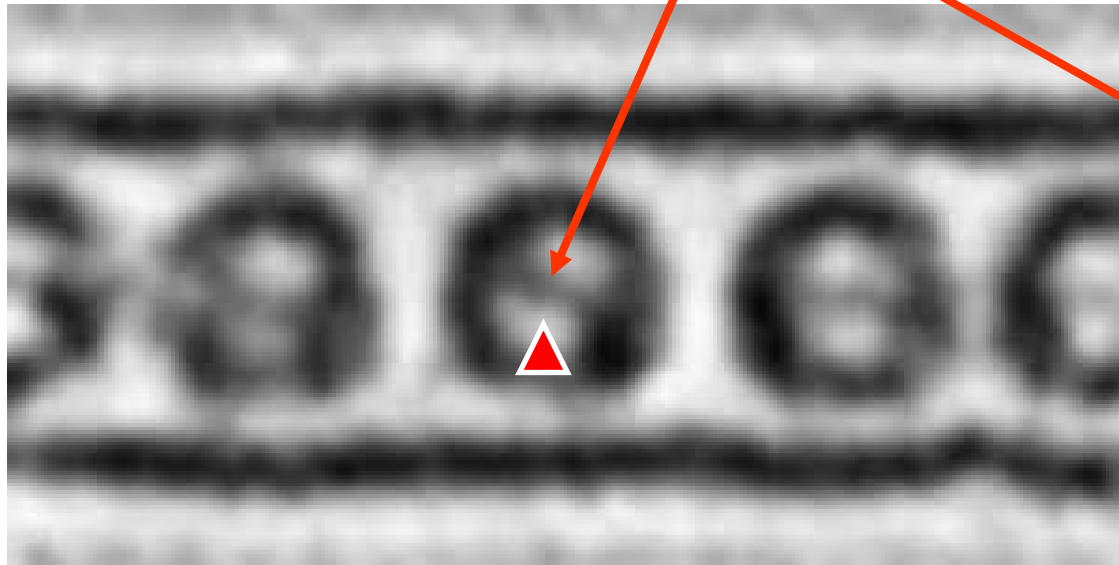


# Escaping of Tb atom from A C<sub>92</sub> Fullerene Cage

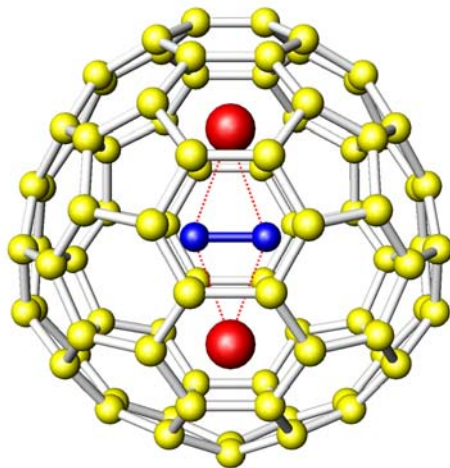


K.Suenaga et al. *Nano Letters* (2005).

# Ti<sub>2</sub>C<sub>2</sub>@C<sub>78</sub> Peapod

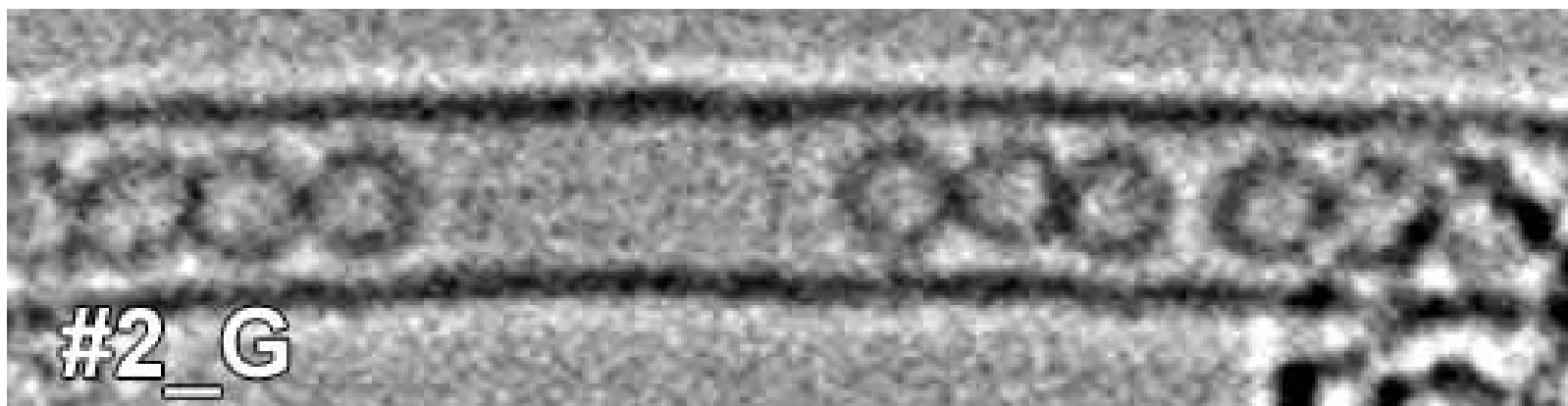
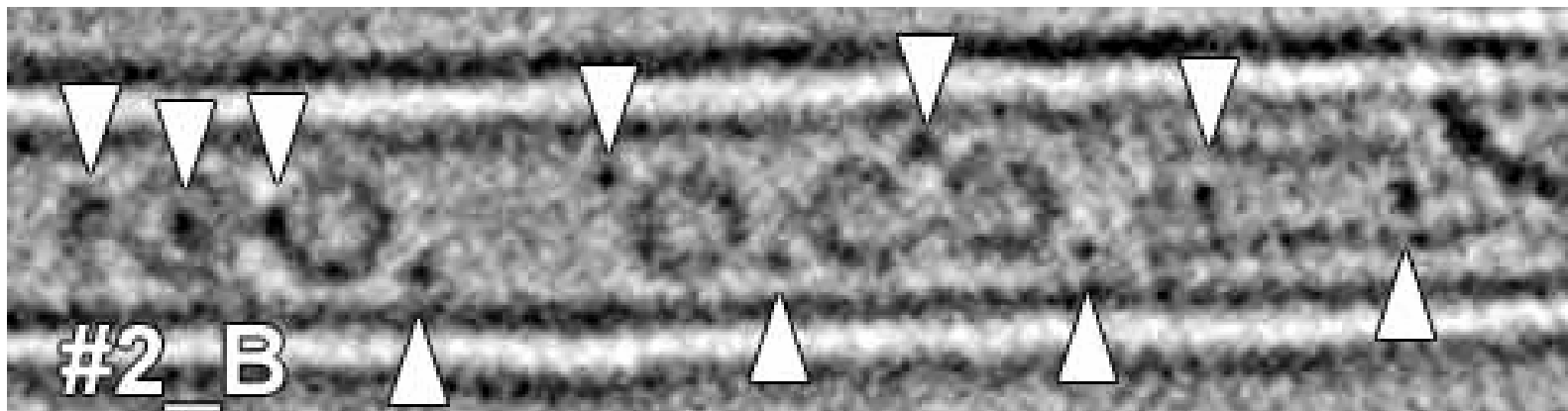


Range 0.0 - 2.0 [e/Å<sup>3</sup>]  
Step 0.1 [e/Å<sup>3</sup>]  
1 Å

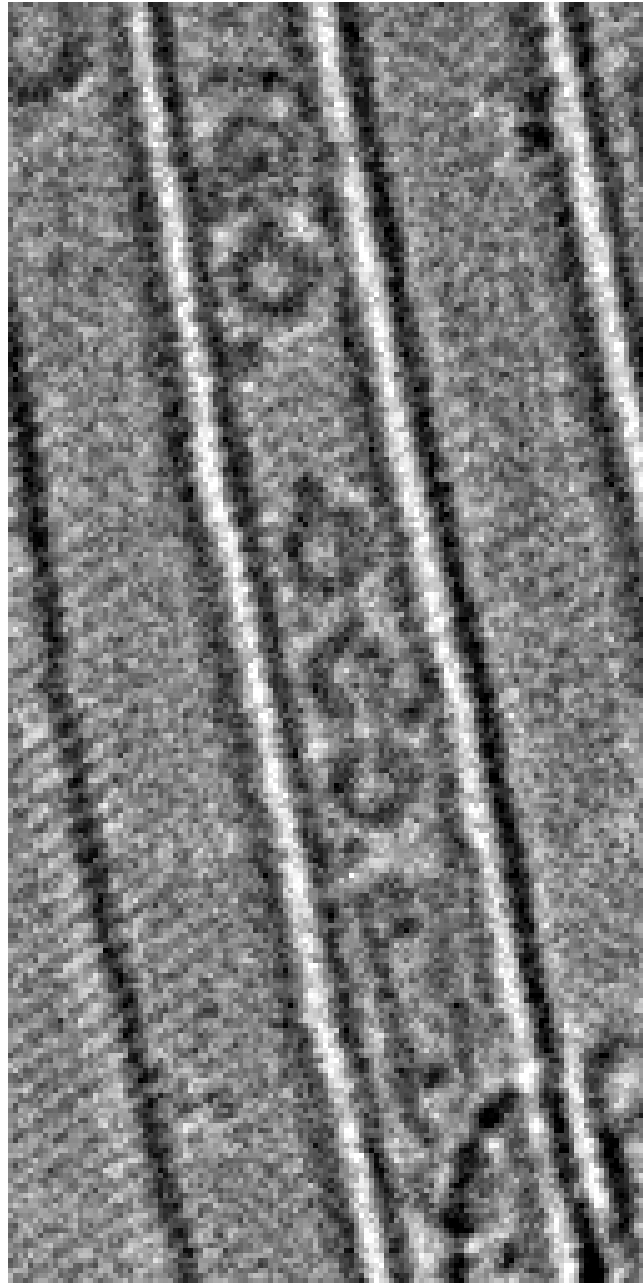


Sato et al. *Phys.Rev.B* in press

# The 1st Exohedral Metallofullerene Peapod: $(\text{Ce-C}_{60})_n@ \text{SWNT}$



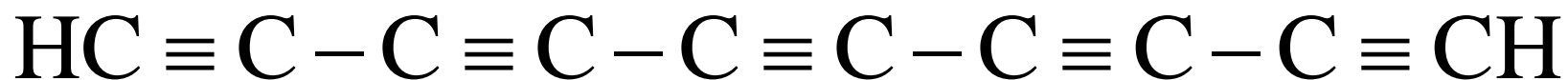
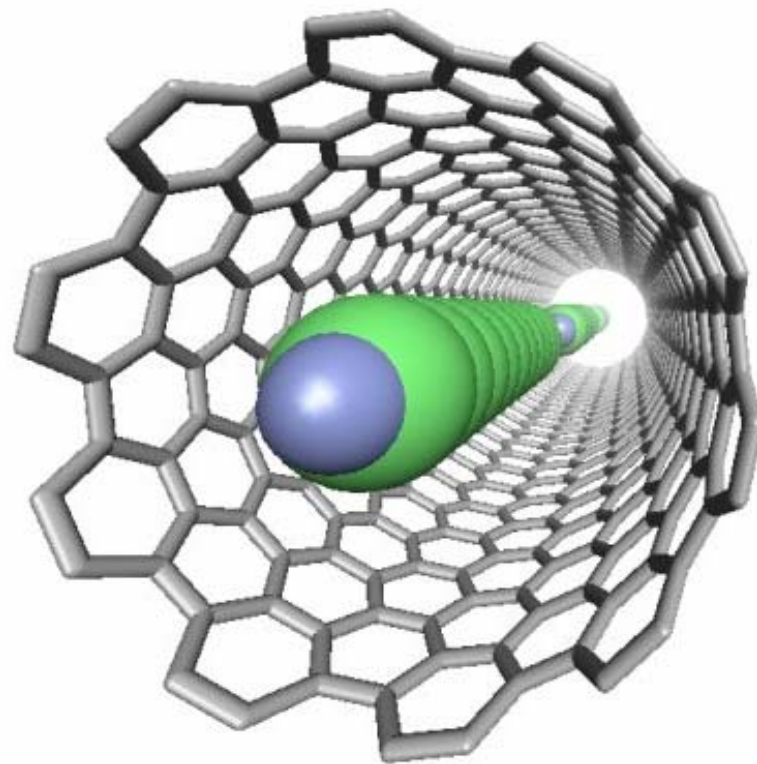
B.Sun et al. *J.Am.Chem.Soc.* (2005)



# Interstellar Molecules

## in Carbon Nanotubes

Encapsulated

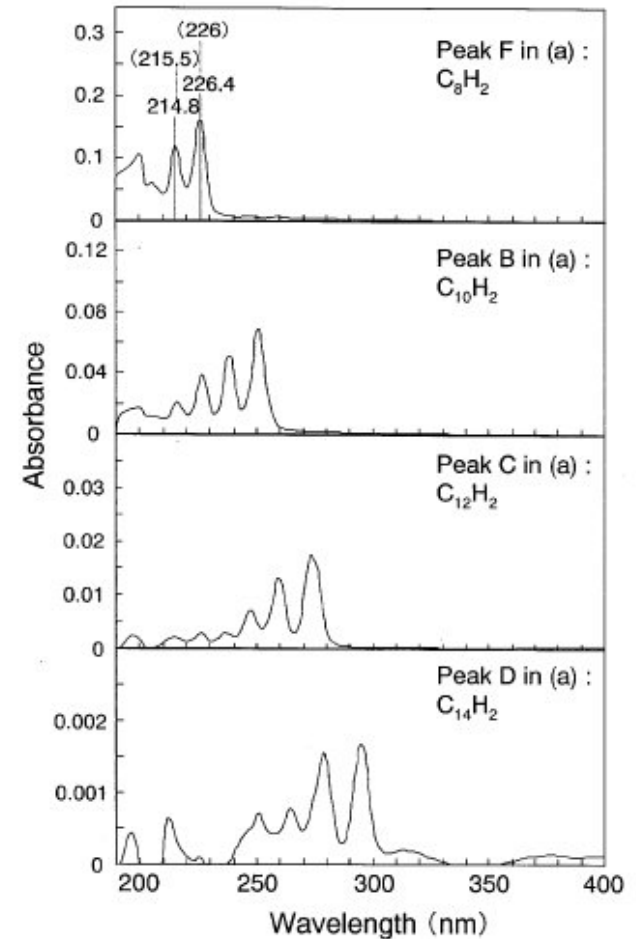
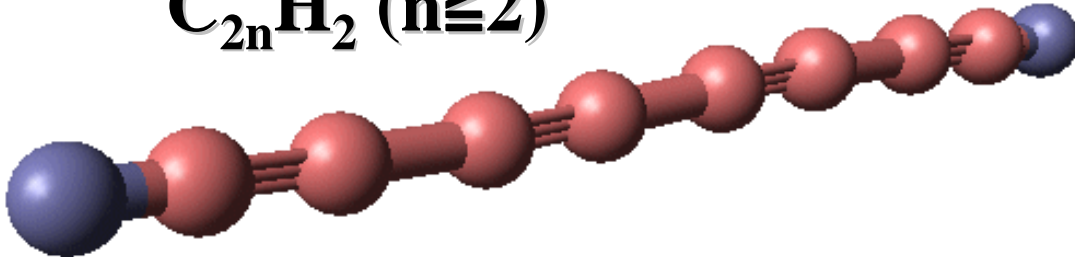


# Motivation

## Novel Nanotube-based Hybrid Materials

- Novel pi-conjugated system
- New Electronic Device
- Property in one-dimensional space

**"Linear-polyynes"**  
As target molecules



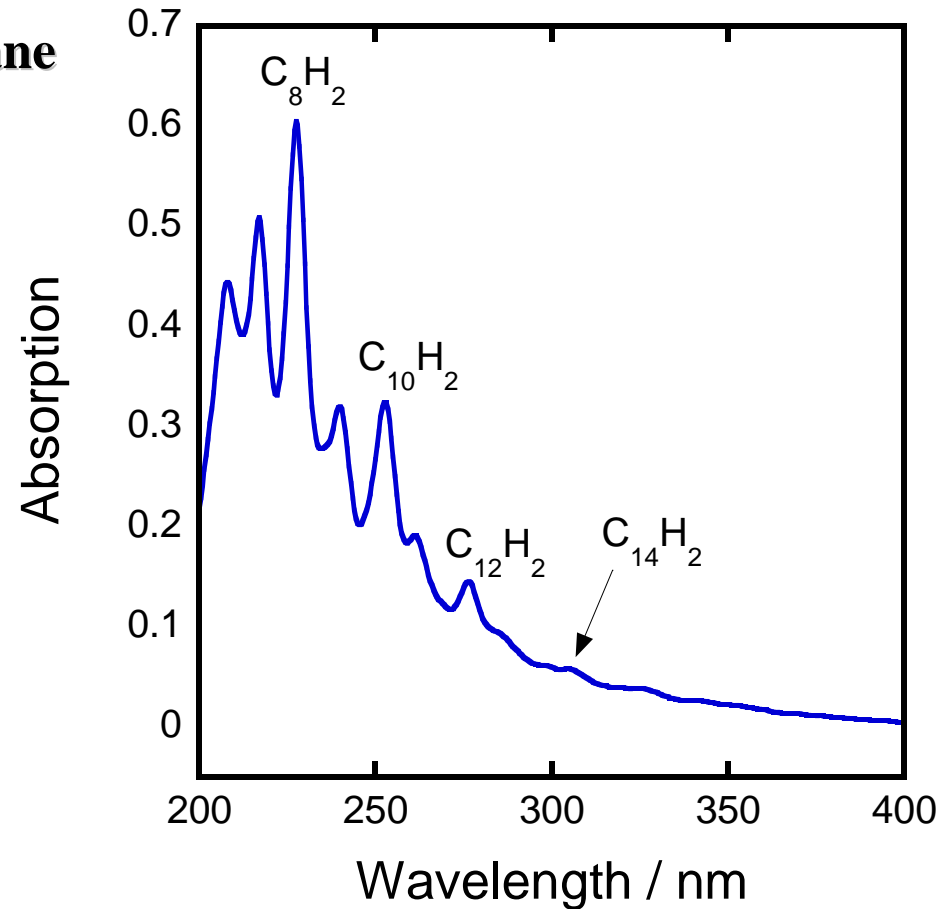
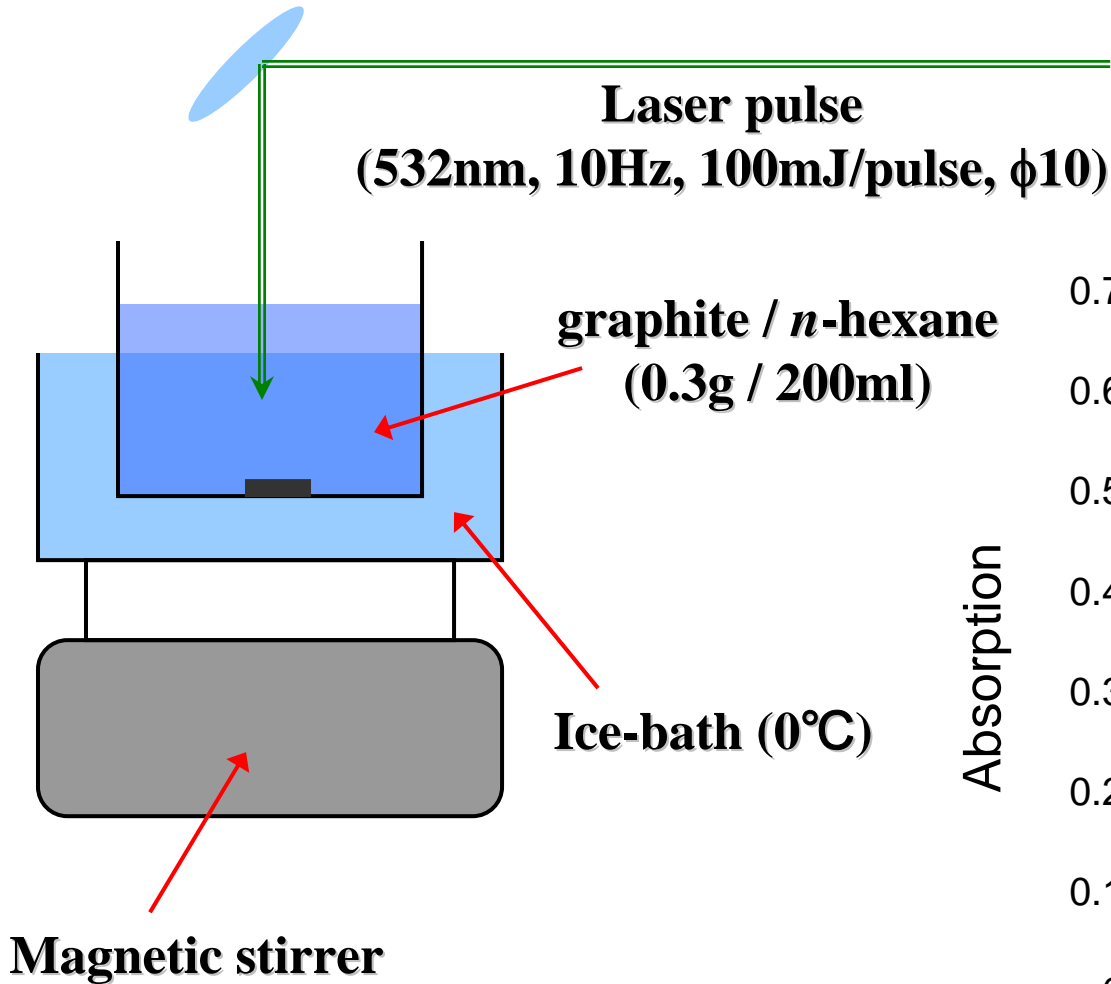
Tsuji *et al.*, CPL (2002)

# Interstellar Molecules Detected by Radio Telescopes ( as of September 2000 )

分子イオン	$\text{CO}^+$ , $\text{SO}^+$ , $\text{CH}^+$ , $\text{HCO}^+$ , $\text{HCS}^+$ , $\text{HOCO}^+$ , $\text{HOC}^+$ , $\text{HN}_2^+$ , $\text{HC}_3\text{NH}^+$ , $\text{H}_2\text{CN}^+$ , $\text{H}_3^+$ , $\text{H}_2\text{COH}^+$ , $\text{H}_3\text{O}^+$
無機化合物	$\text{H}_2$ , $\text{OH}$ , $\text{NO}$ , $\text{N}_2\text{O}$ , $\text{NH}$ , $\text{NH}_2$ , $\text{HNO}$ , $\text{NS}$ , $\text{SO}$ , $\text{SiO}$ , $\text{SiS}$ , $\text{SiN}$ , $\text{SiH}_4$ , $\text{HCl}$ , $\text{NaCl}$ , $\text{KCl}$ , $\text{AlF}$ , $\text{AlCl}$ , $\text{H}_2\text{O}$ , $\text{H}_2\text{S}$ , $\text{SO}_2$ , $\text{NH}_3$
アルコール、エーテル	$\text{CH}_3\text{OH}$ , $\text{C}_2\text{H}_5\text{OH}$ , $(\text{CH}_3)_2\text{O}$
アルデヒド、ケトン	$\text{H}_2\text{CO}$ , $\text{H}_2\text{CCO}$ , $\text{CH}_3\text{CHO}$ , $\text{HCCCHO}$ , $(\text{CH}_3)_2\text{CO}$ , $\text{HCO}$ 酸、
エステル	$\text{HCOOH}$ , $\text{CH}_3\text{OCHO}$ , $\text{CH}_3\text{COOH}$
アミン、イミン	$\text{NH}_2\text{CN}$ , $\text{NH}_2\text{CHO}$ , $\text{CH}_2\text{NH}$ , $\text{CH}_3\text{NH}_2$
シアン、イソシアン	$\text{CN}$ , $\text{HNC}$ , $\text{CH}_2\text{CN}$ , $\text{CH}_3\text{CN}$ , $\text{CH}_3\text{NC}$ , $\text{CH}_3\text{CH}_2\text{CN}$ , $\text{CH}_2\text{CHCN}$ , $\text{CH}_3\text{C}_3\text{N}$ , $\text{CH}_3\text{C}_5\text{N}$ , $\text{H}_2\text{CN}$ , $\text{HNCO}$ , $\text{MgNC}$ , $\text{MgCN}$ , $\text{NaCN}$
糖	$\text{CH}_2\text{OHCHO}$
含硫化合物	$\text{OCS}$ , $\text{HNCS}$ , $\text{H}_2\text{CS}$ , $\text{CH}_3\text{SH}$
含りん化合物	$\text{CP}$ , $\text{PN}$
環状化合物	$\text{C}_3\text{H}_2$ , $\text{C}_3\text{H}$ , $\text{SiC}_2$ , $\text{SiC}_3$ , $\text{C}_2\text{H}_4\text{O}$
直線炭素鎖化合物	$\text{HCN}$ , $\text{HC}_3\text{N}$ , $\text{HC}_5\text{N}$ , $\text{HC}_7\text{N}$ , $\text{HC}_9\text{N}$ , $\text{HC}_{11}\text{N}$ , $\text{CH}$ , $\text{C}_2\text{H}$ , $\text{C}_3\text{H}$ , $\text{C}_4\text{H}$ , $\text{C}_5\text{H}$ , $\text{C}_6\text{H}$ , $\text{C}_7\text{H}$ , $\text{C}_8\text{H}$ , $\text{C}_2$ , $\text{C}_3$ , $\text{C}_5$ , $\text{C}_2\text{H}_2$ , $\text{HCCN}$ , $\text{HNCCC}$ , $\text{HCCNC}$ , $\text{CO}$ , $\text{CCO}$ , $\text{C}_3\text{O}$ , $\text{C}_3\text{N}$ , $\text{C}_5\text{N}$ , $\text{CS}$ , $\text{CCS}$ , $\text{C}_3\text{S}$ , $\text{CSi}$ , $\text{C}_4\text{Si}$
その他の有機化合物	$\text{CH}_2$ , $\text{H}_2\text{C}_3$ , $\text{H}_2\text{C}_4$ , $\text{H}_2\text{C}_6$ , $\text{CH}_4$ , $\text{CH}_3\text{C}_2\text{H}$ , $\text{CH}_3\text{C}_4\text{H}$ , $\text{C}_2\text{H}_4$

115 Molecules and Ions

# Liquid Laser Ablation of Graphite



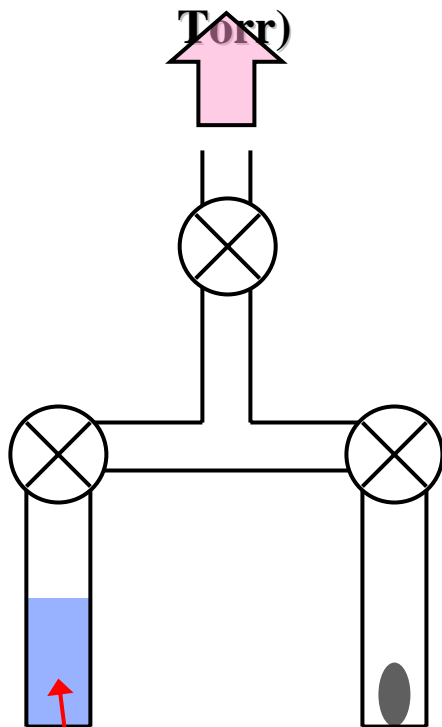


# Liquid Preparation of (C<sub>10</sub>H<sub>2</sub>)@SWNTs

①

R. P. ( $\sim 4 \cdot 10^{-3}$

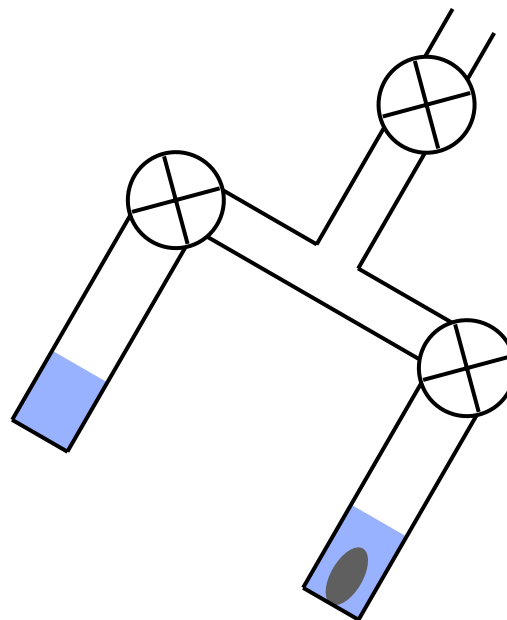
Torr)



Polyynes in *n*-hexane  
(Frozen)

Cap-Opened SWNT

②



Mixing & Standing  
(80°C, 2 Days, in  
Vacuum)

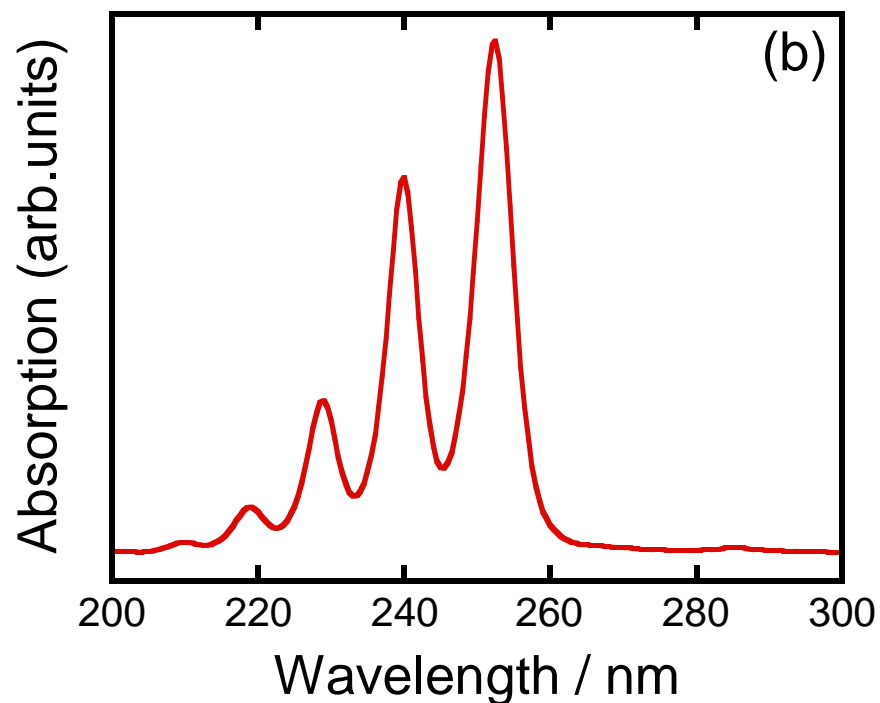
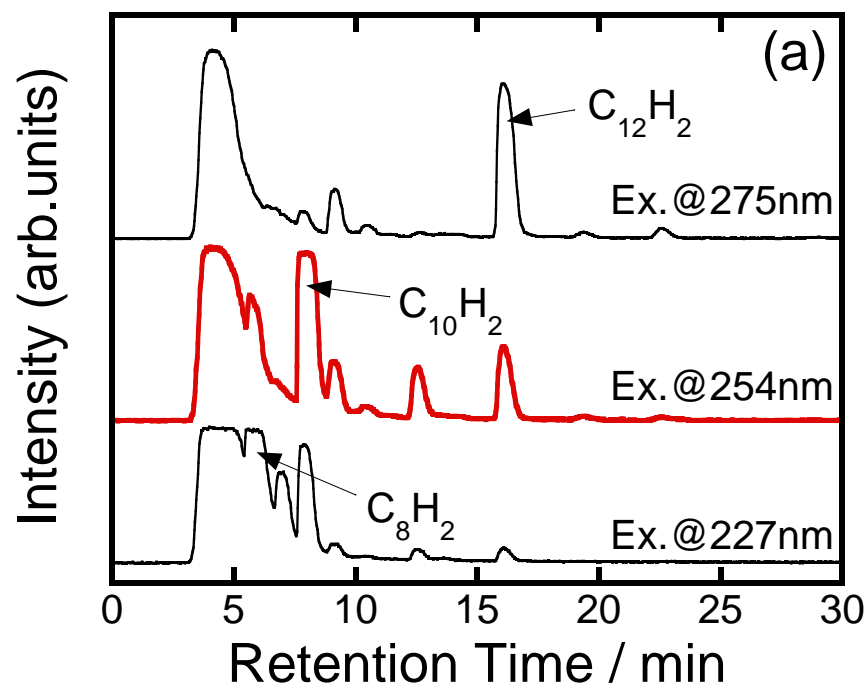


③

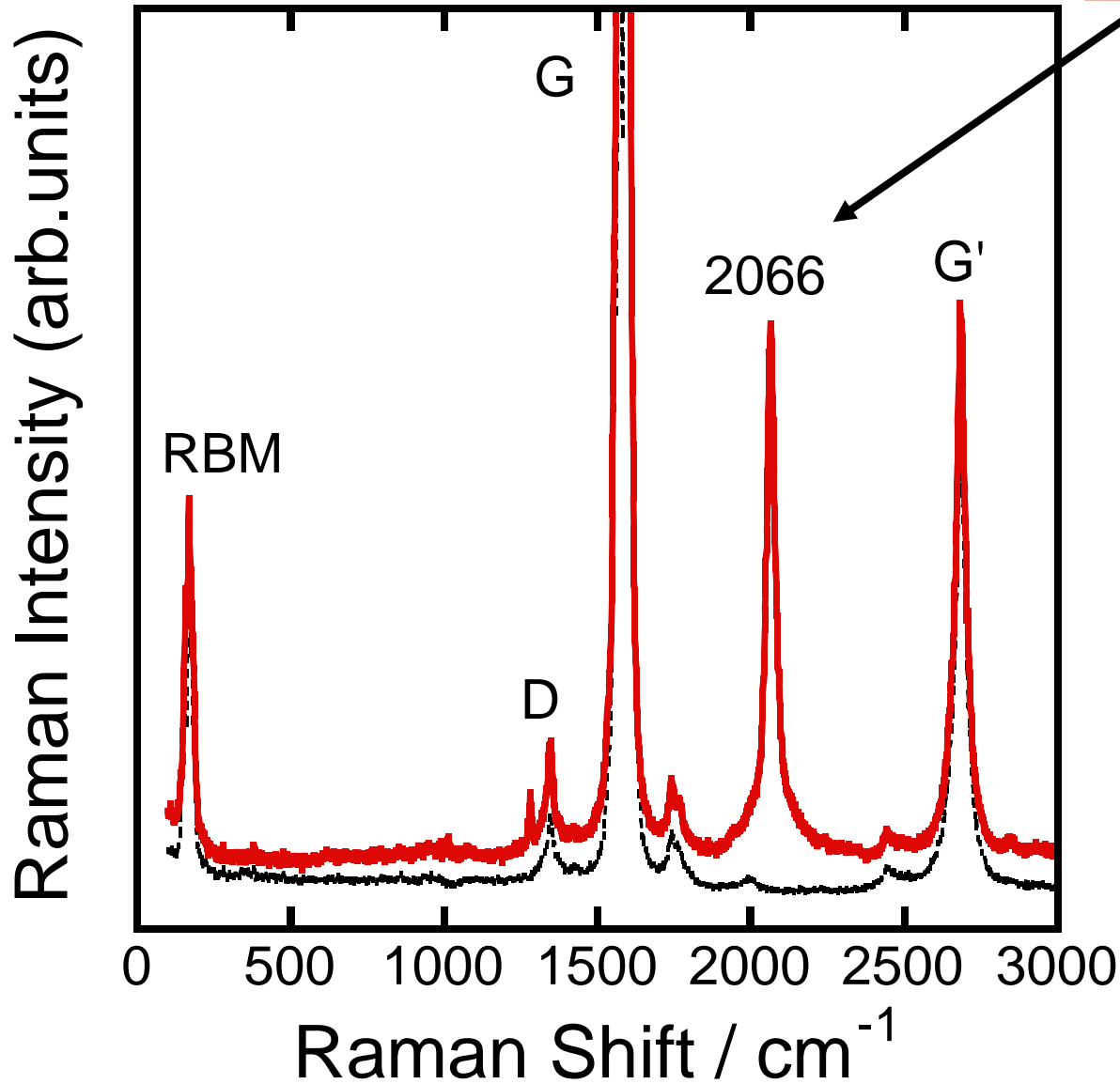


Drying under air atmosphere  
at 80 °C for overnight

# HPLC Separation & Isolation of Linear-Chain Polyene Molecules

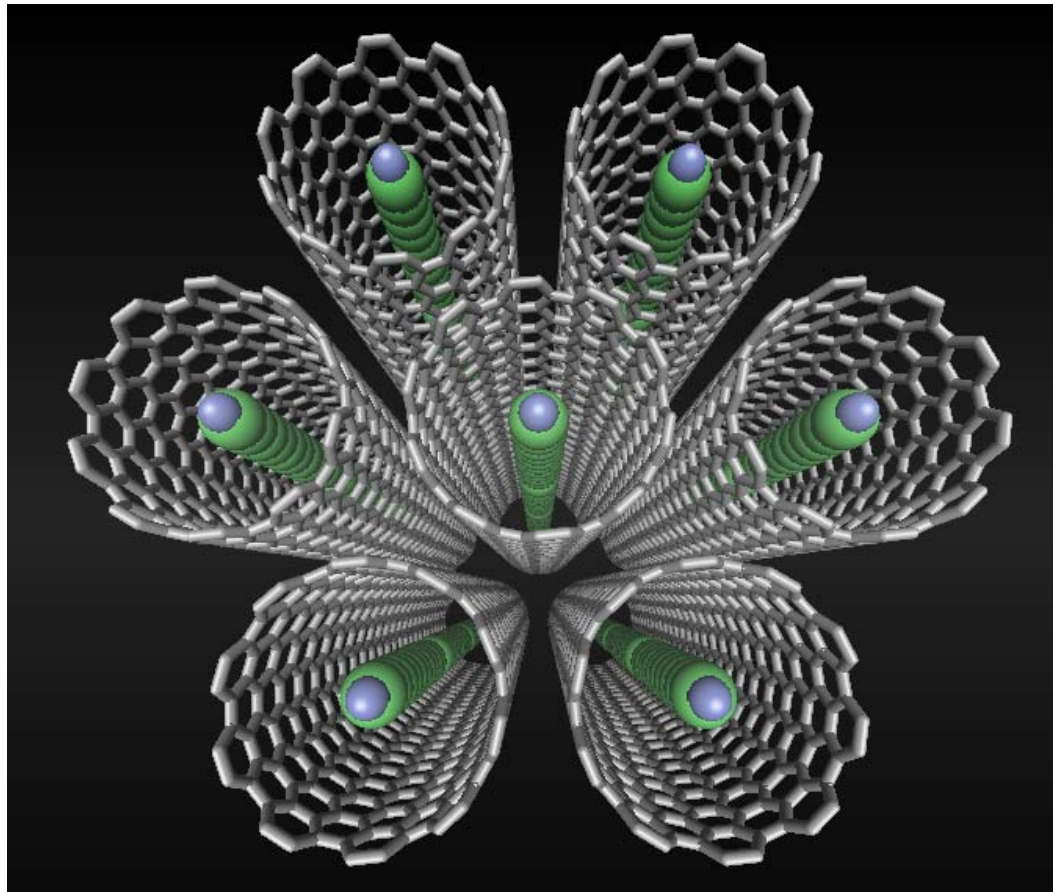


**C<sub>10</sub>H<sub>2</sub>@SWNT**



The first Raman detection of well-defined polyynes at room temperature !

**$C_{10}H_2$  molecules have been  
selectively encapsulated into SWNTs!!**



# Key Messages

1. High-yield synthesis of fullerenes/metallofullerenes **nano-peapods**.
2. Single-, Double- and Triple Nano-peapods provide **nano-templates** for TEM-imaging of fullerenes and molecules.
3. Even very unstable linear polyynes molecules can safely be encapsulated in SWNT.