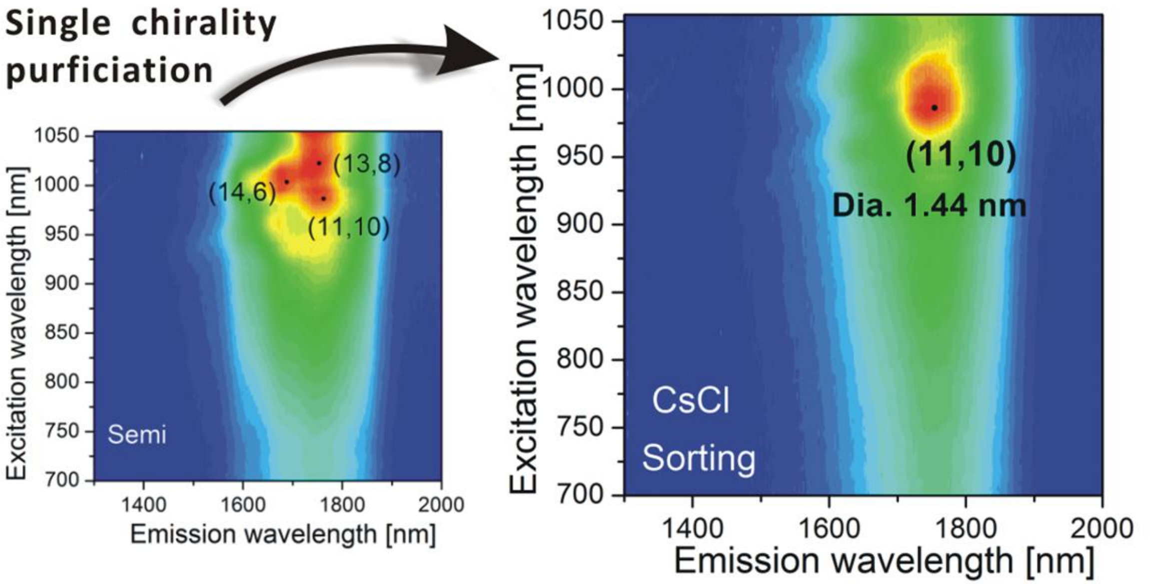
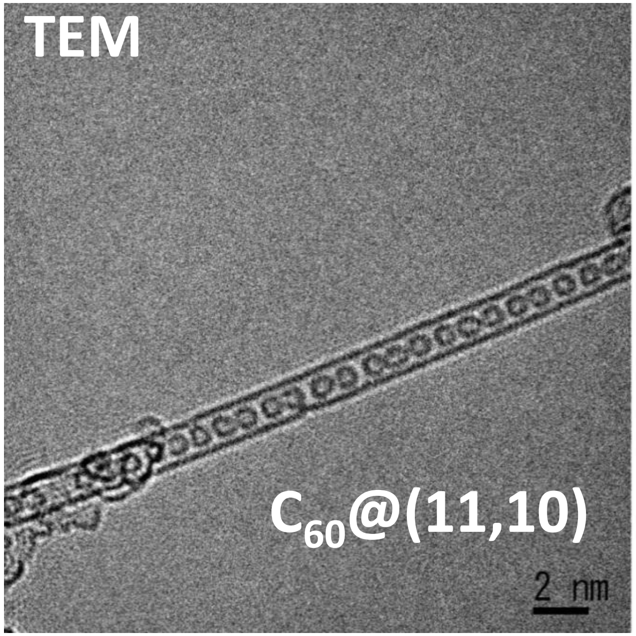
Single chiral extraction of single-wall carbon nanotubes for the encapsulation of organic molecules



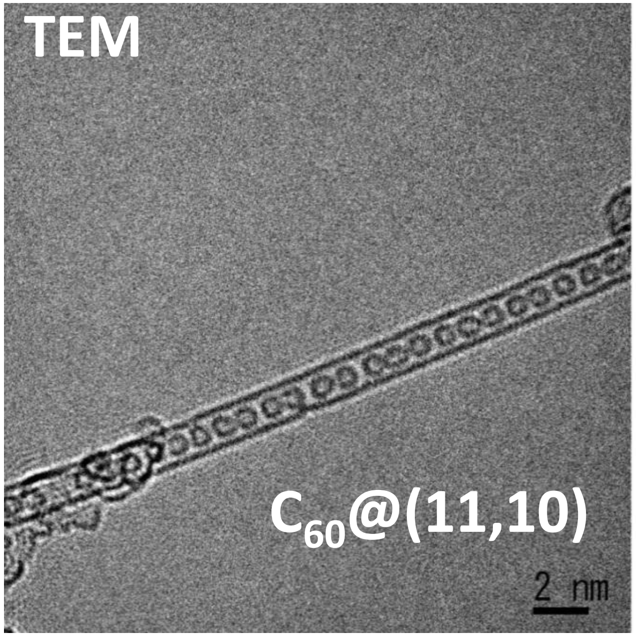


JACS 134, 9545 (2012)

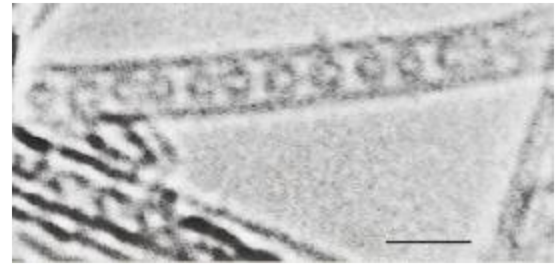
Kazuhiro Yanagi
Tokyo Metropolitan University

Contents

- Purpose of this study
- How to extract (11,10) SWCNTs
- How to produce C_{60}@(11,10) and their unique properties
- Summary

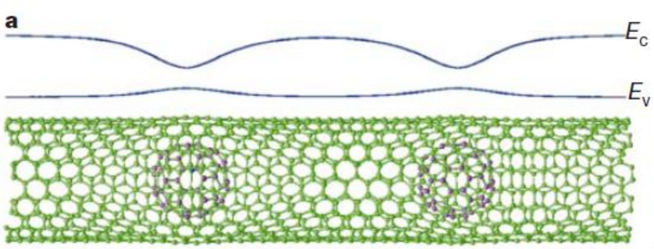


Research background



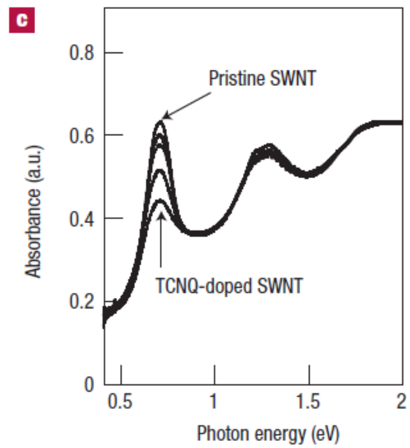
Smith et al., Nature 1998

- **Peapods**
  - **Control of physical properties of SWCNTs (doping etc)**
  - **Unique molecular reaction space**

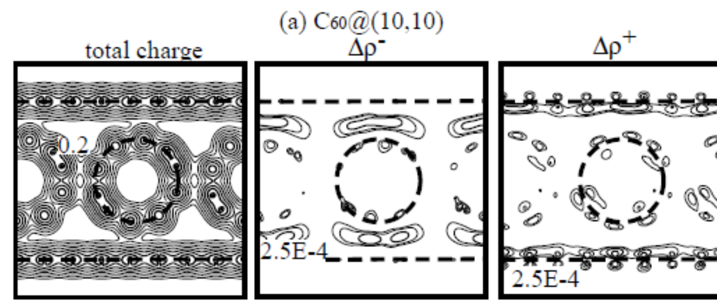


Lee et al., Nature 415, 1005 (2002)

Band-gap modulation

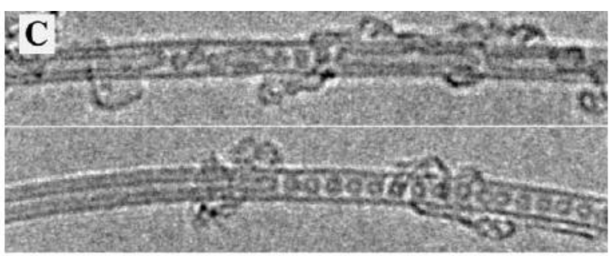


Takenobu, Nat. Mater. 2, 683 (2003)



Okada et al., PRL 86, 3835 (2001)

nearly free electron state



Double wall SWCNTs

Liu, Yanagi et al, Nature Nanotech. 2, 422 (2007)

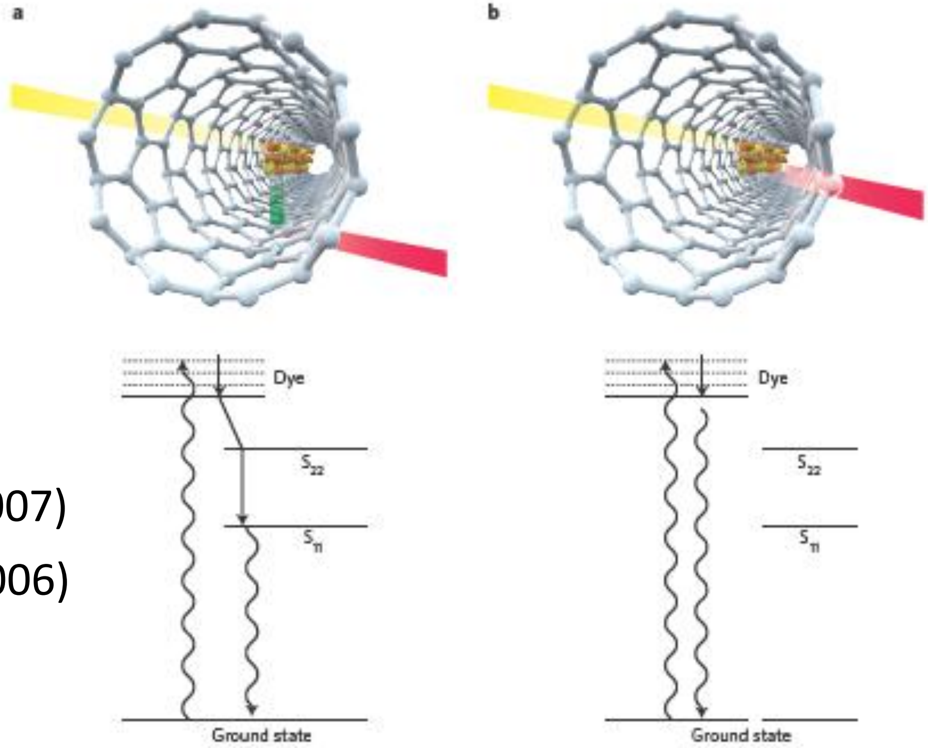
All the peapods are in a mixed chirality states of SWCNTs

Preparation of single-chirality state of peapods is important

Example:

JACS 129, 4992 (2007)

PRB 74, 155420 (2006)



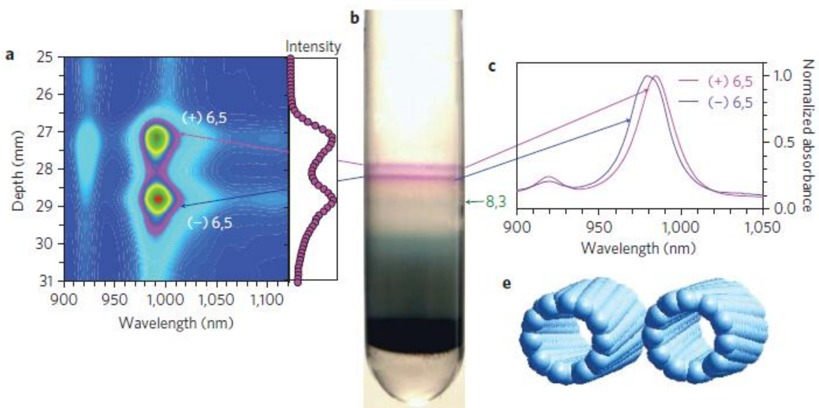
Okazaki et al., Angew. Chem. 50 4853 (2011)

Loi et al., Adv. Mater. 22 1635 (2010)

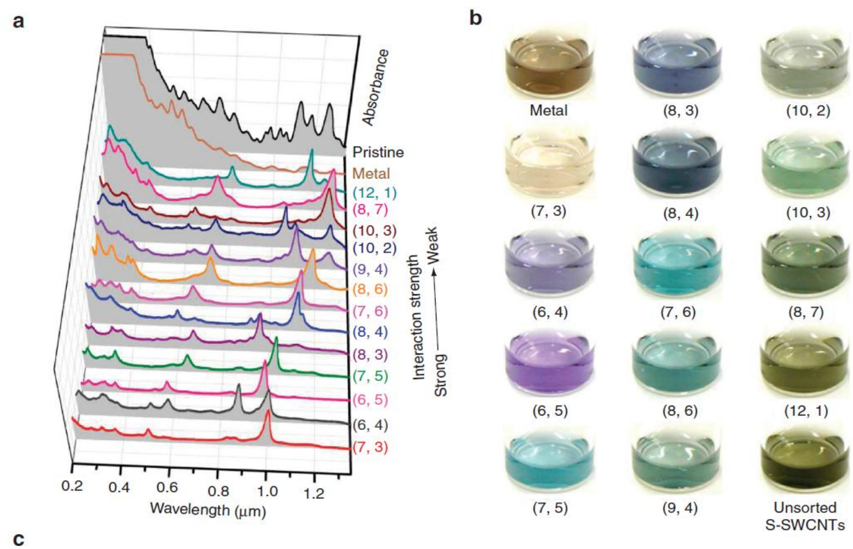
Two different excited-energy relaxation processes

Recent progress of purification techniques

SWCNTs with diameter less than 1.0 nm



Ghosh et al., Nat. Nanotechnology. 5, 443 (2010)

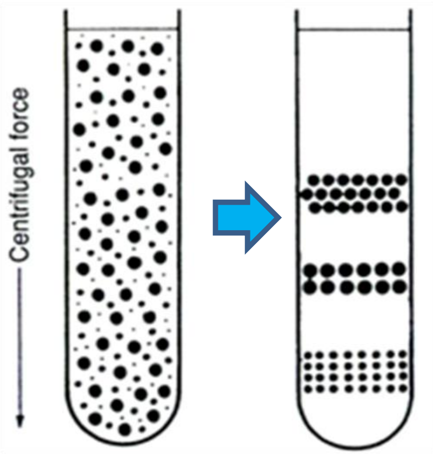


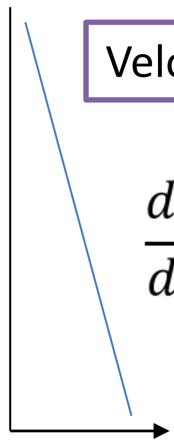
Liu et al., Nat. Comm. DOI:10.1038/ncomms1313 (2011)

Purpose of this study

—Preparation of single-chiral state of SWCNTs with diameter around 1.4 nm, which is large enough for molecular encapsulation

Our approach: Difference of densities of SWCNTs





Velocity of particle

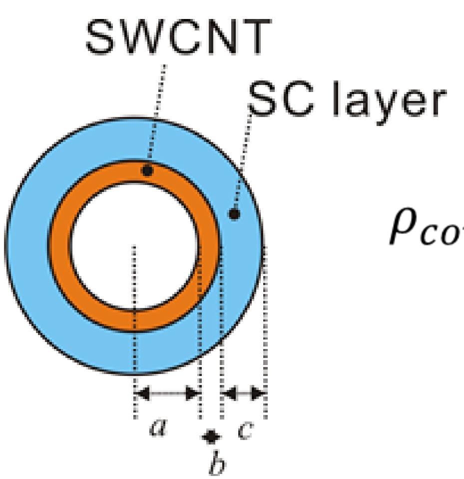
$$\frac{dr}{dt} = \frac{r_p^2\,(\rho_p - \rho_m)\,\omega^2 r}{K_\eta}$$

r_p = radius of the particle

ρ_p : density of the particle

ρ_m : density of the medium

K_η : Constant related to viscosity of the medium



Schematic model for the density of SWCNTs

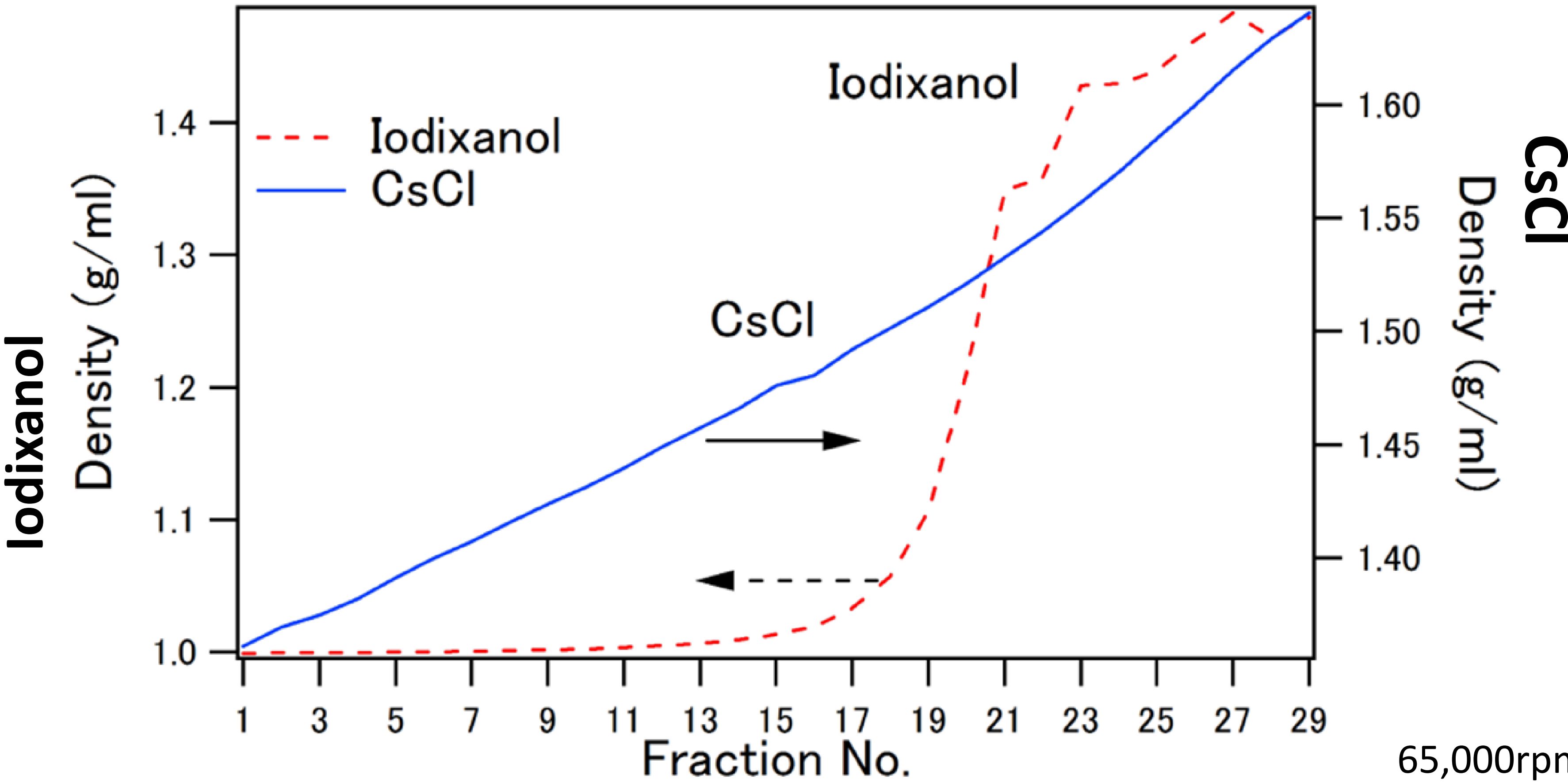
$$\rho_{complex} = \rho_{in}\left(\frac{a}{a+b+c}\right)^2 + \rho_c \frac{2ab + b^2}{(a+b+c)^2} + \rho_{sc} \frac{2c(a+b) + c^2}{(a+b+c)^2}$$

Difference of densities becomes small
as the diameters of SWCNTs become large

⇩

Improvement of sorting capability

Advantage of cesium chloride as gradient media



65,000rpm
9h

CsCl will improve the sorting capability!

Metal/Semi sorting → CsCl sorting "Diameter sorting"? → "Single chirality "?

CsCl sorting upon SWCNTs with diameters around 1.4 nm

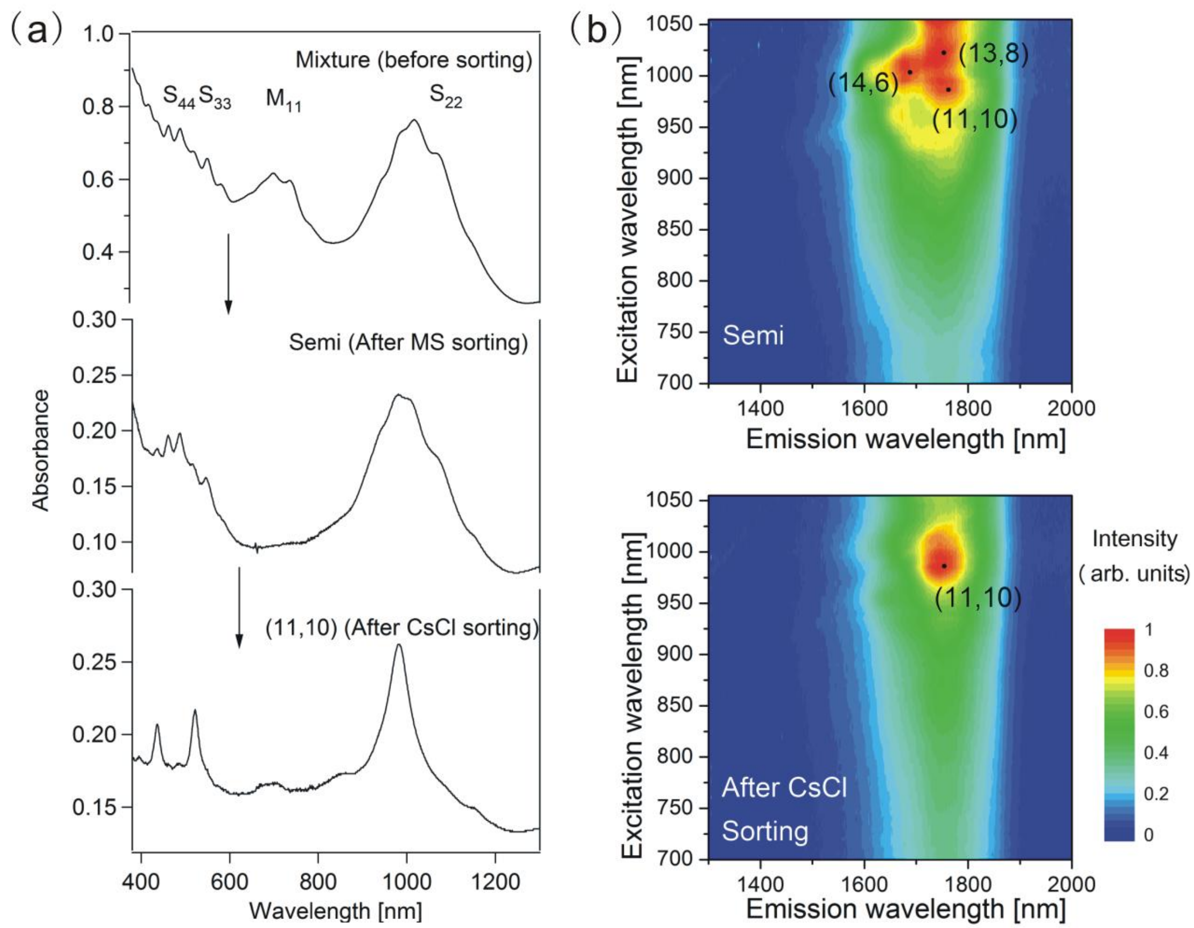
Pristine SWCNTs with diameter of 1.4 nm

MS sorting

Semiconducting SWCNTs

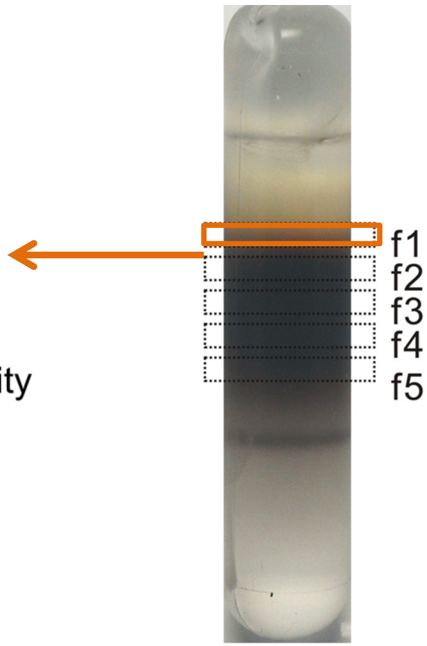
CsCl sorting

(11,10) SWCNTs



CsCl sorting upon SWCNTs with diamter of 1.4 nm

CsCl sorting

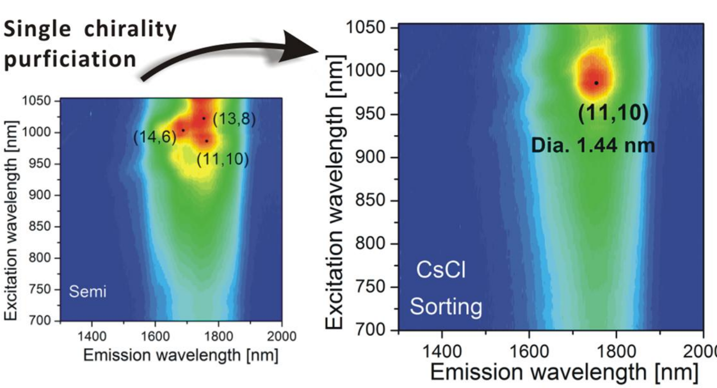


Diameter(nm) vs Chirality

1.41: (14,6)

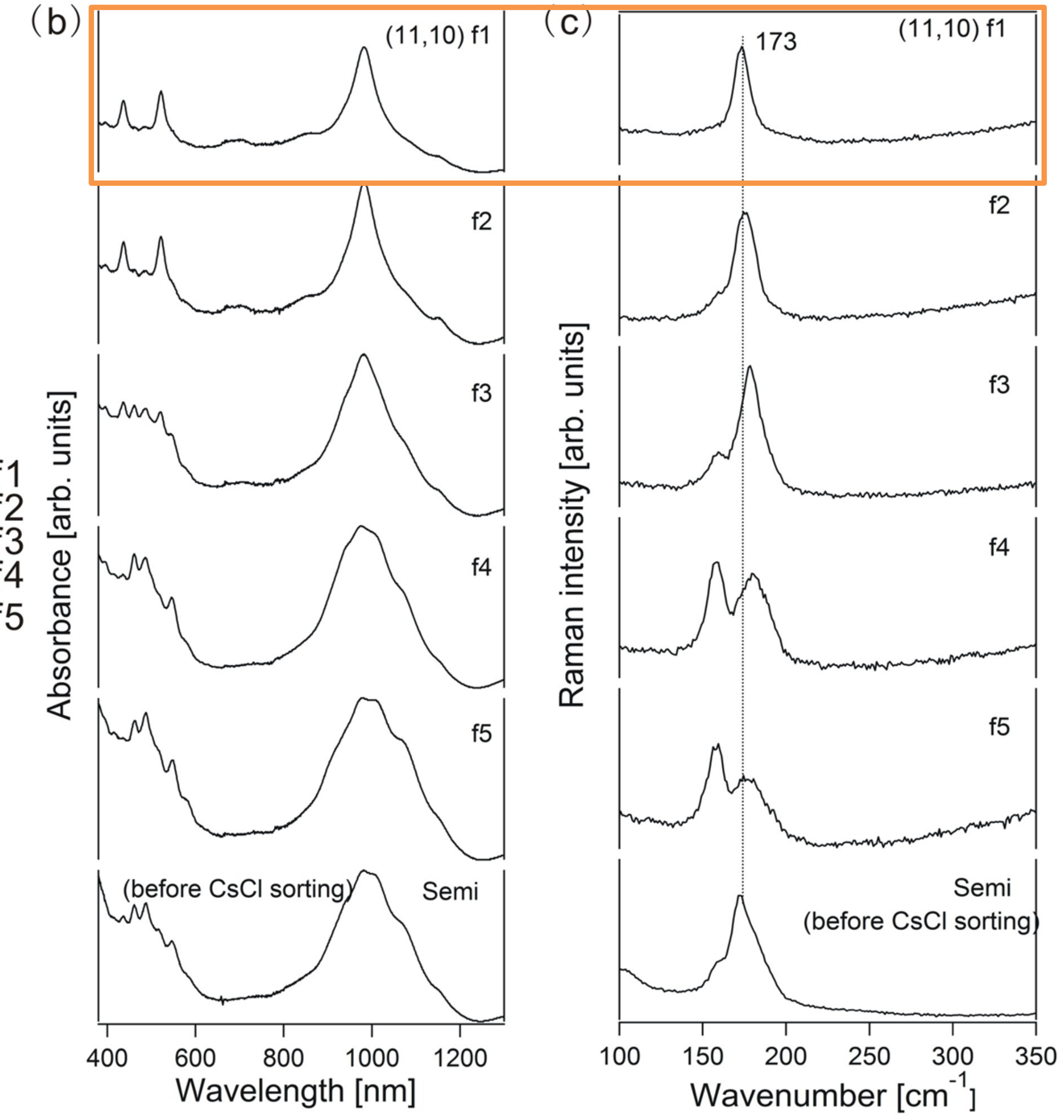
1.44: (11,10)

1.46: (13,8)



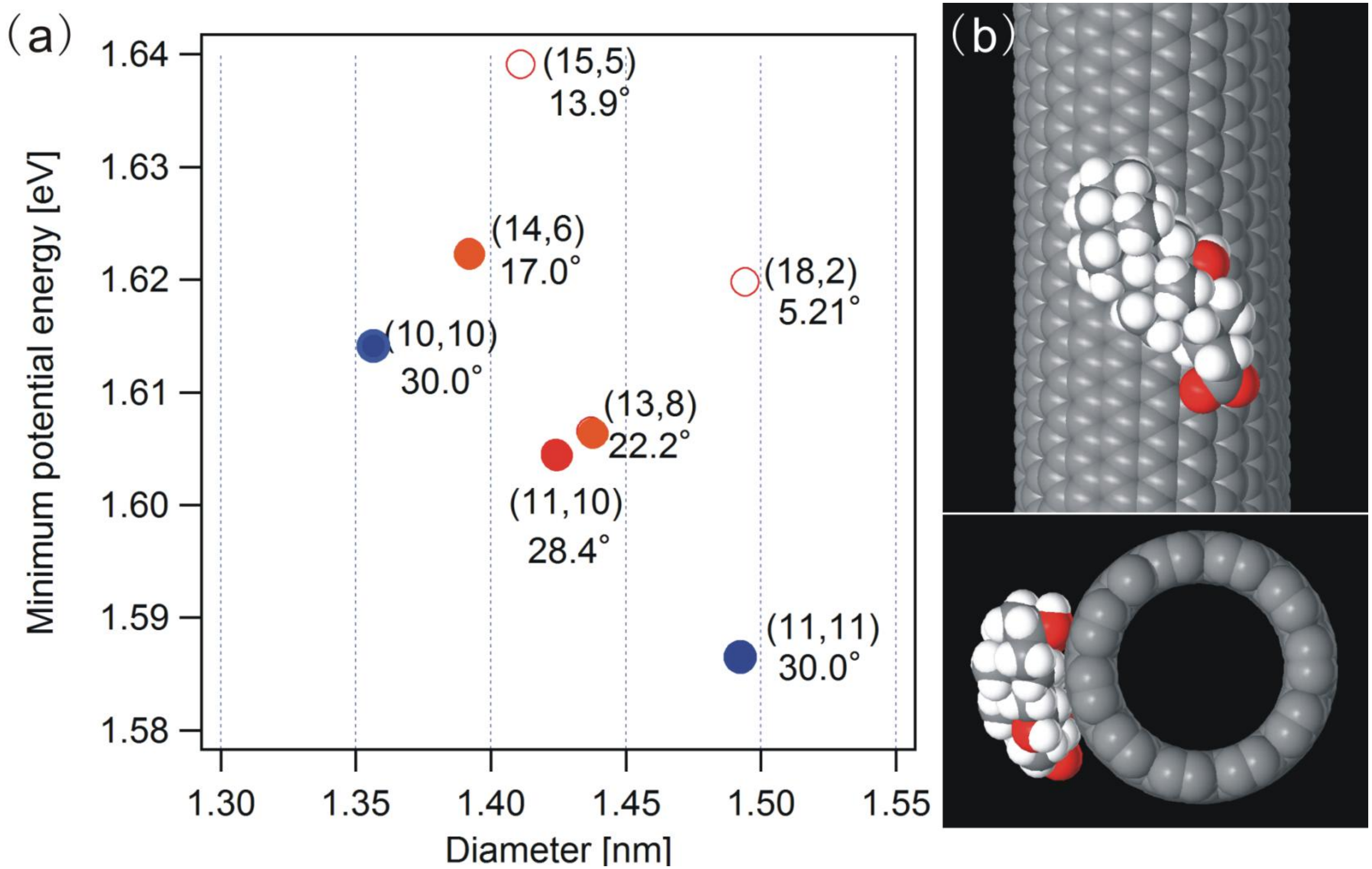
Optical absorption

Raman spectra（RBM）



Raman measurements: Excitation 514 nm

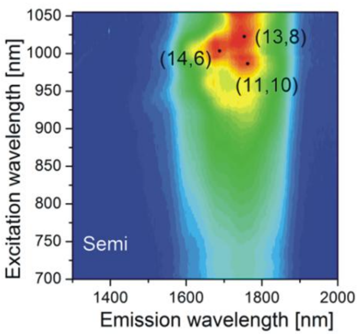
Sorting mechanism
~MD simulation to estimate potential energy for a surfactant to adsorb on SWCNTs~

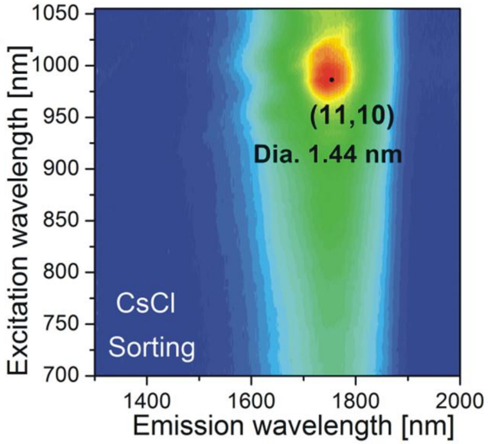


- Potential energy at (11,10) is lowest among other semiconducting chiralities
- Potential energy tends to be small as the chiral angle becomes large

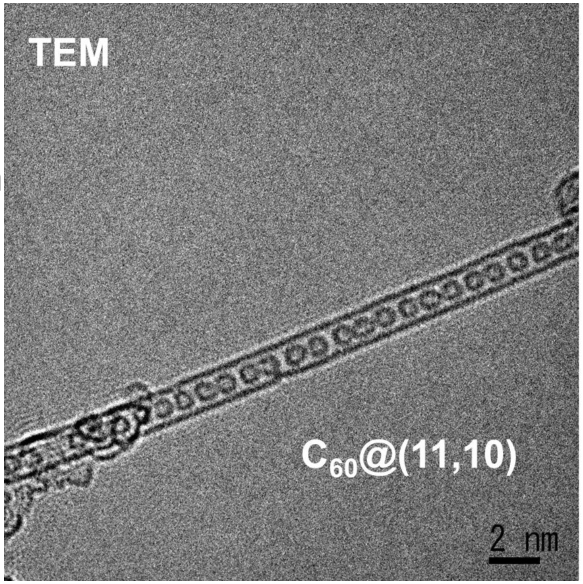
Encapsulation of C_{60} into (11,10) SWCNTs

Single chirality purfiication





C_{60}
encapsulation



How to encapsulate C60 inside (11,10) SWCNTs

Encapsulation of C_{60} into a thin film of (11,10) SWCNTs

Procedure

Formation of a thin film upon a glass substrate

Anneal at 500 ˚C

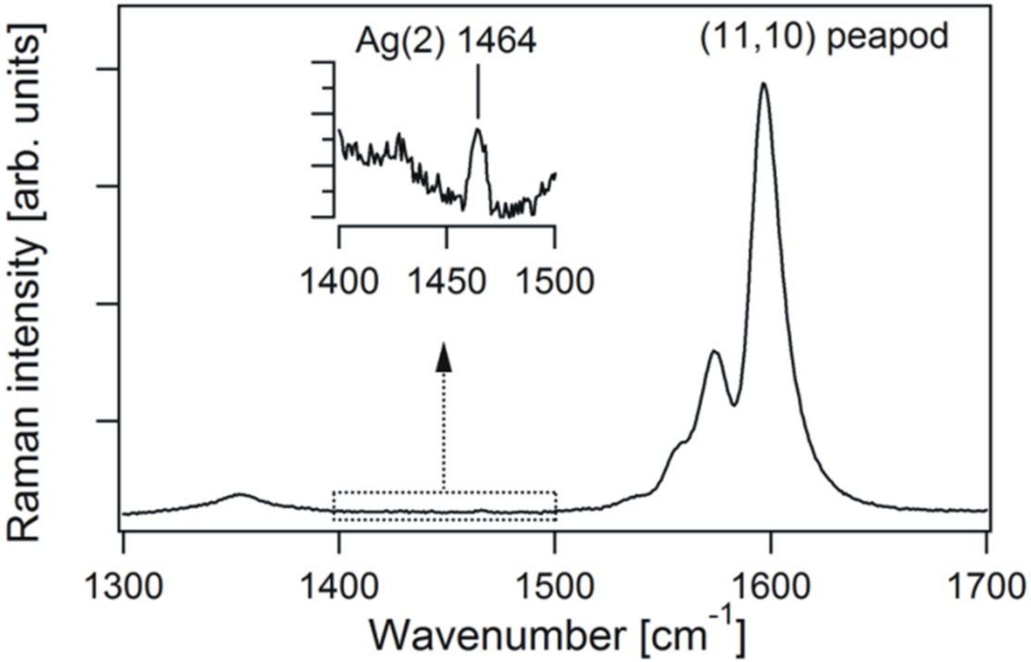
Sublimation at 600 ˚C for 24hrs

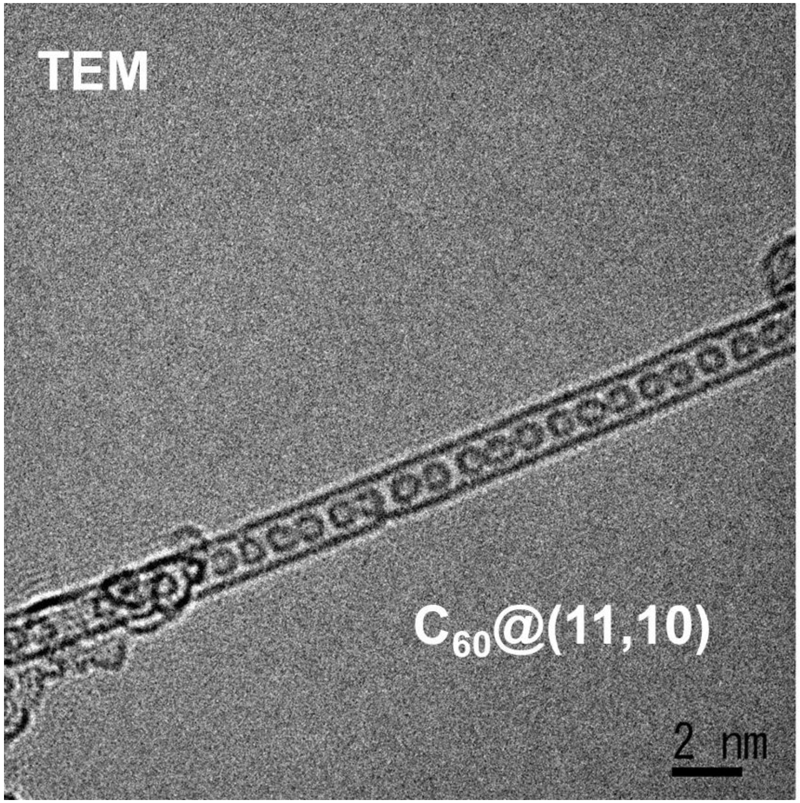
Wash with toluene and anneal in vacuum

(11,10) peapods

C_{60} encapsulated into (11,10)SWCNTs

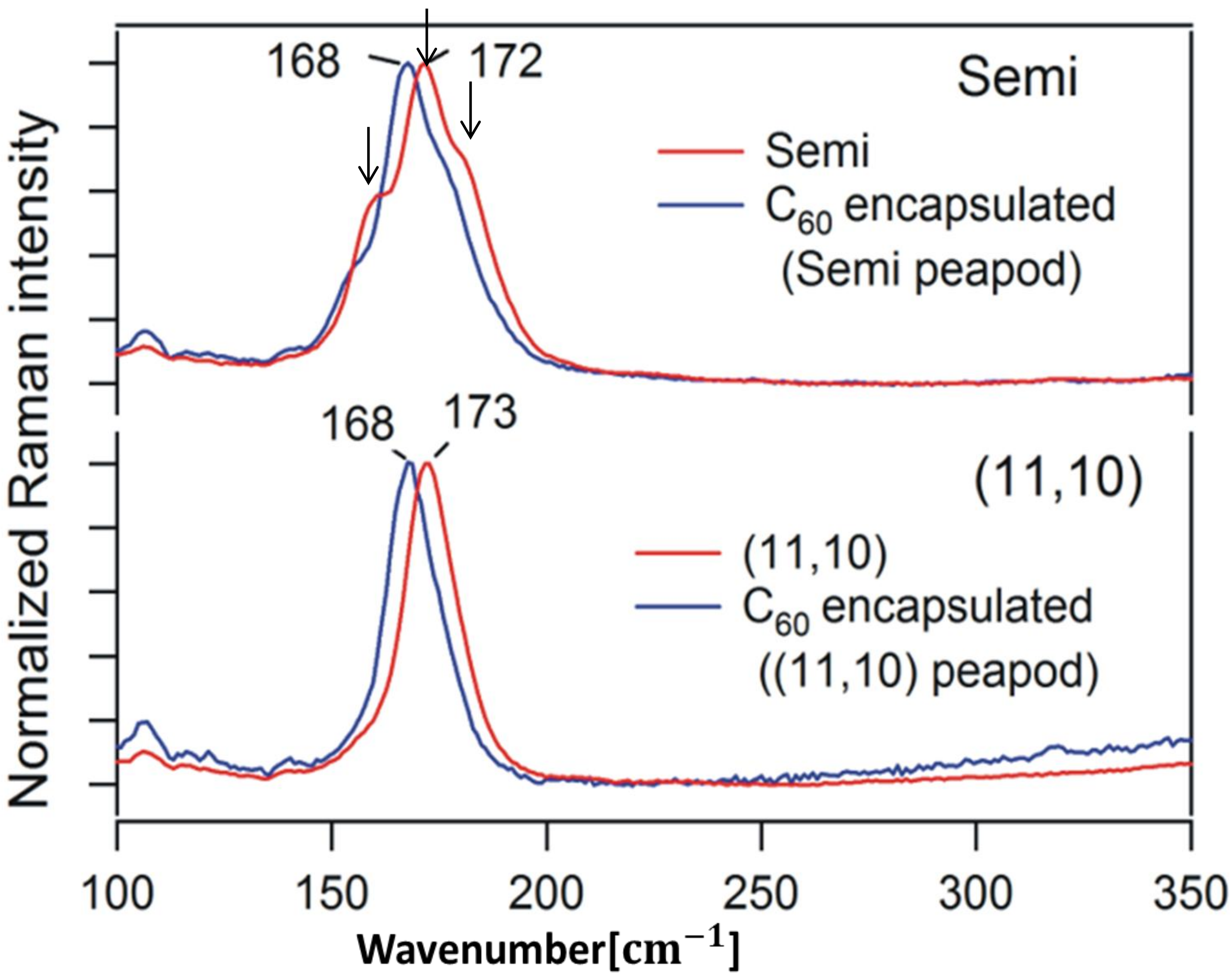
C_{60}:Ag(2) mode
(excitation wavelength of 488 nm)



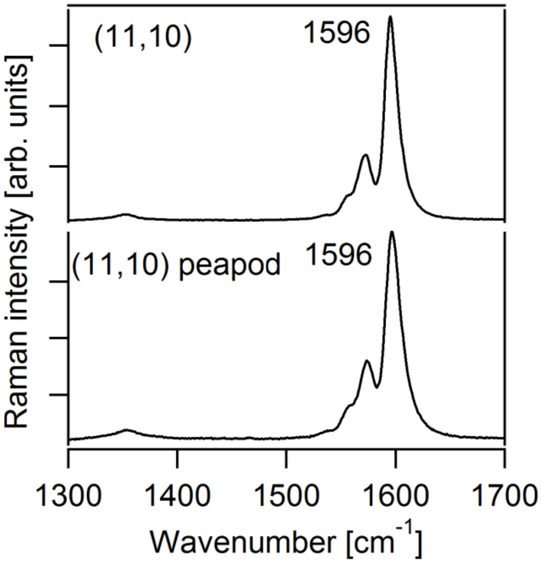


<u>Single-chirality peapod</u>

Shift of Radial breathing mode



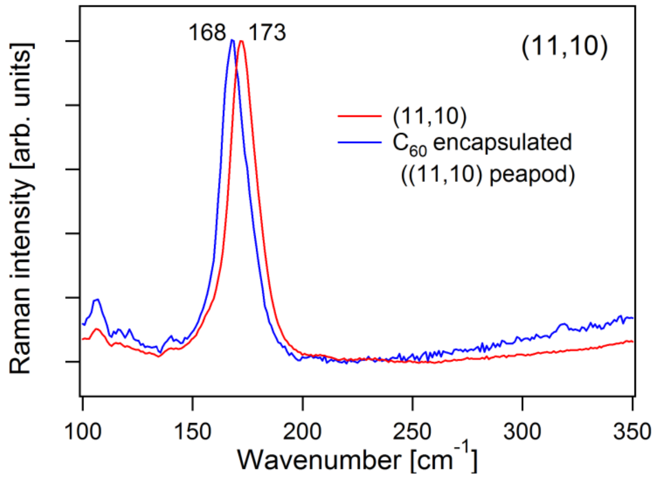
Raman measurements: Excitation 514 nm

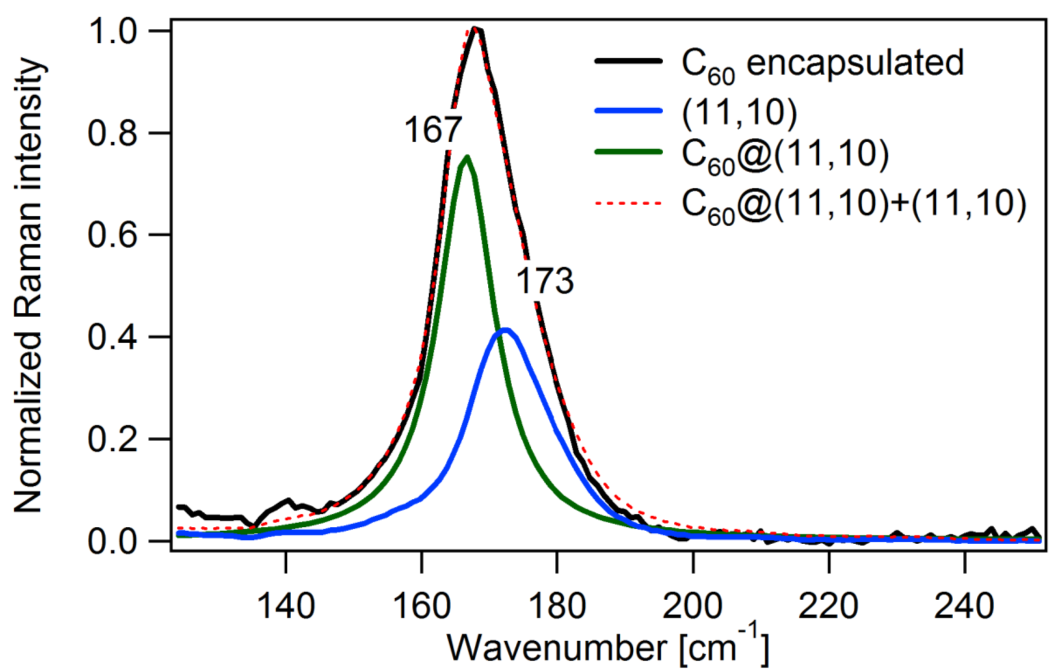


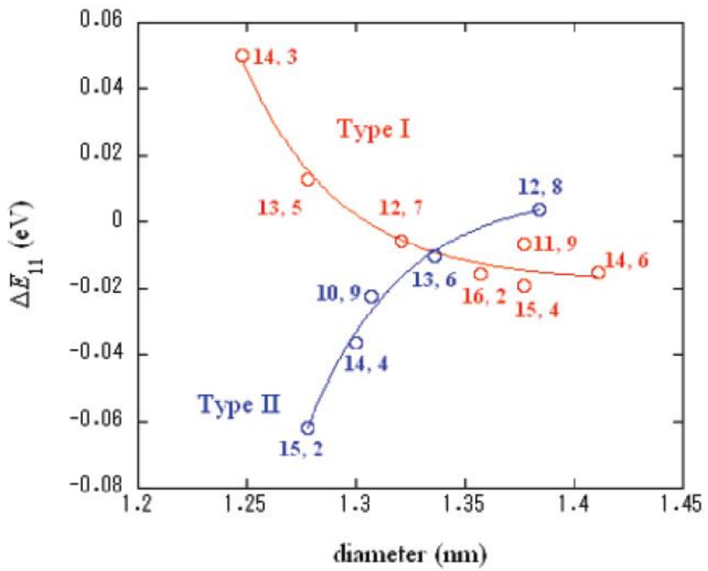
G-band

Clear softening of RBM by encapsulation

RBM of C_{60}@(11,10)





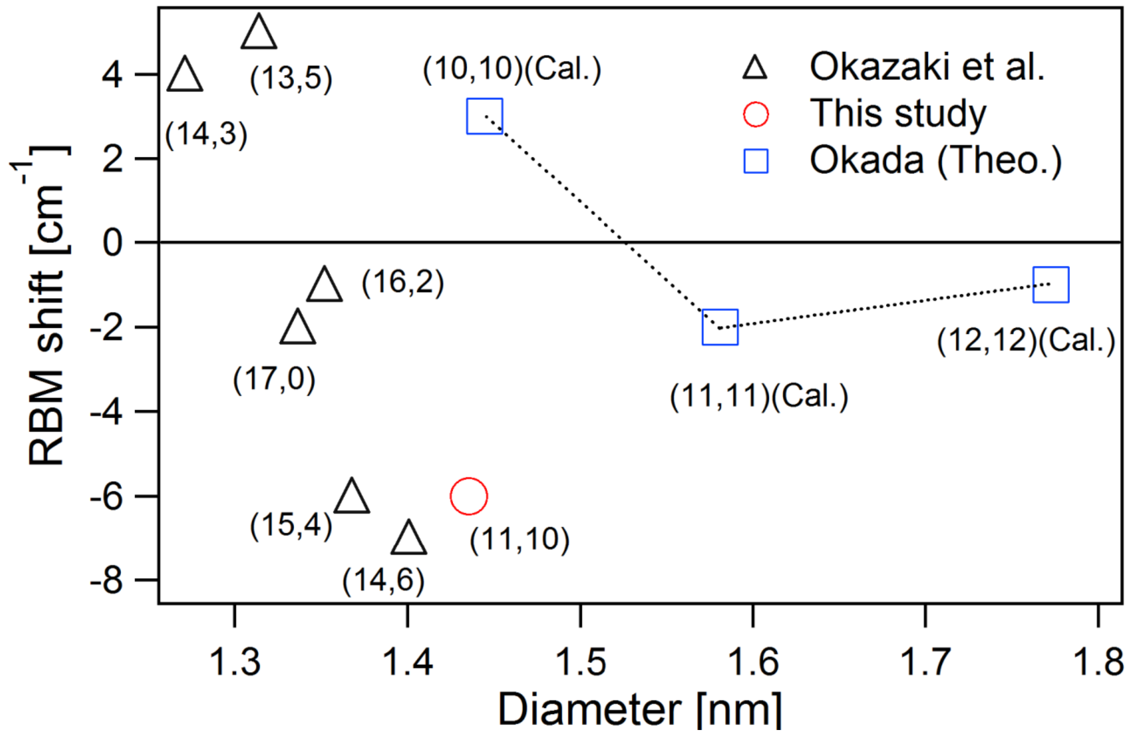


Okazaki et al., JACS 130, 4122 (2008)

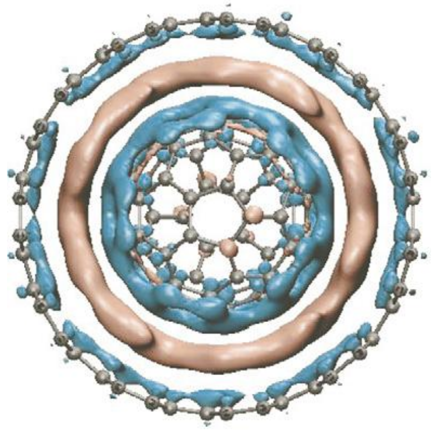
Shift of 6 cm^{-1}

Yield of 65%

Relationships between RBM shift and diameters

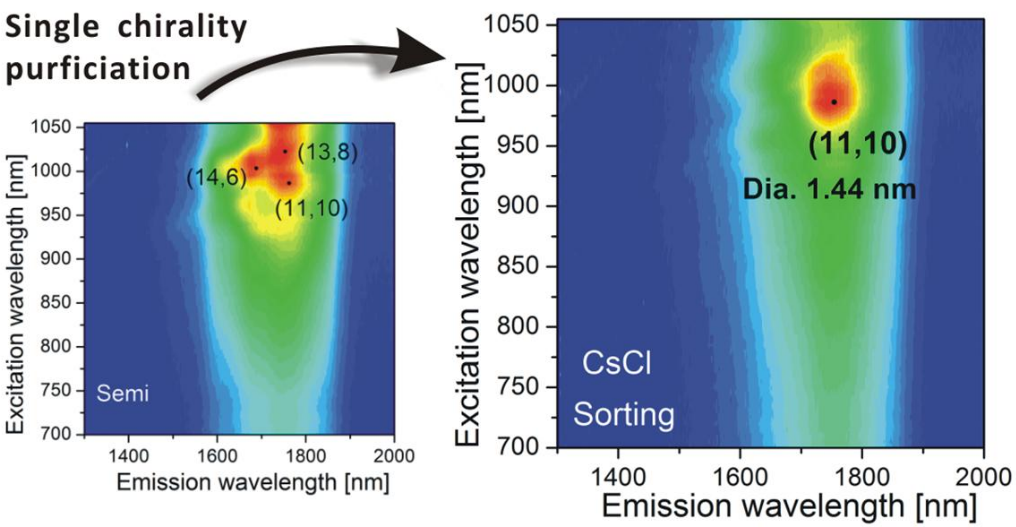


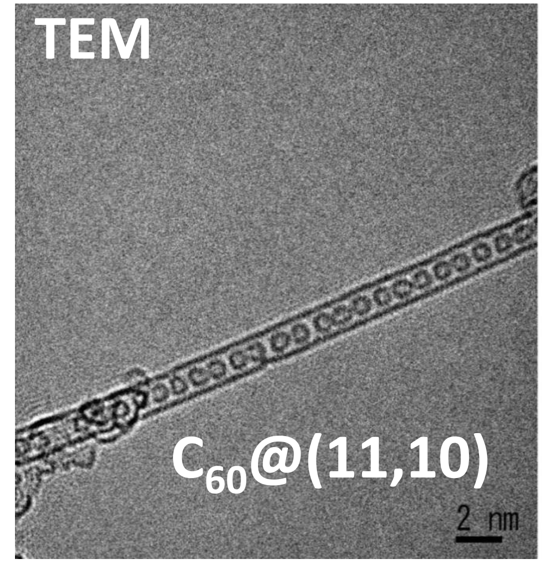
RBM shift:
Positive: Steric hindrance
Negative: hybridization of
Nearly free electron state



Okazaki et al. PRL 103, 027403 (2010)
Okada, CPL 438, 59 (2007)

Summary





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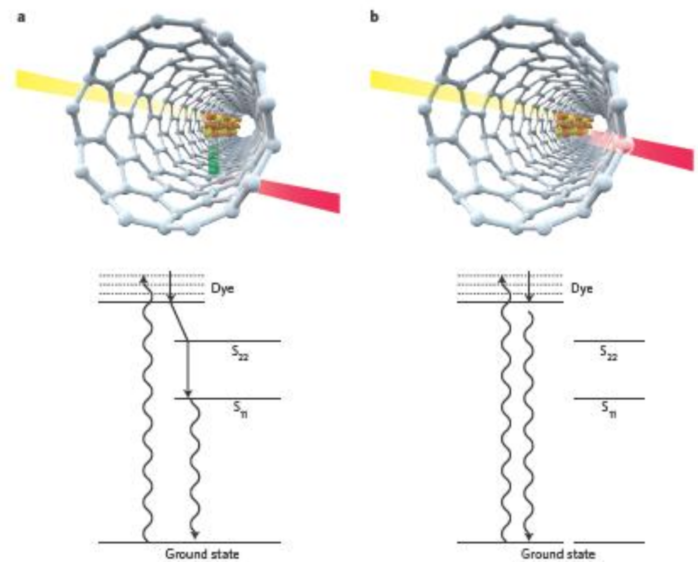

Single-chirality peapods:
Key to clarify unsolved-phenomena observed in peapods