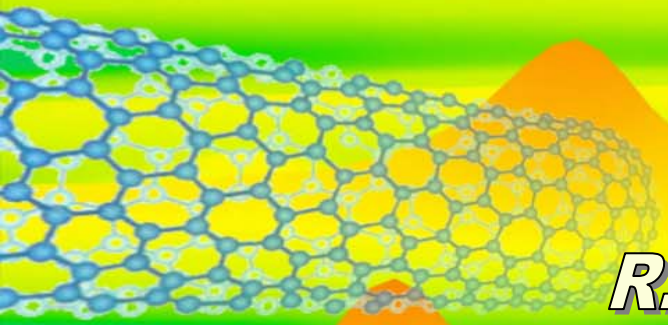
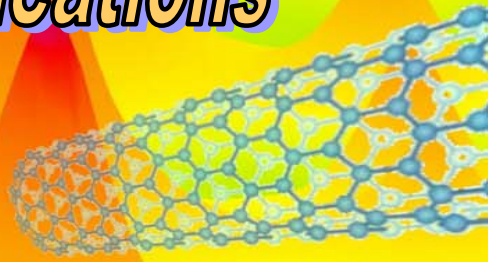
Fluorescence of Single-Walled Carbon Nanotubes: from Fundamental Studies to Applications

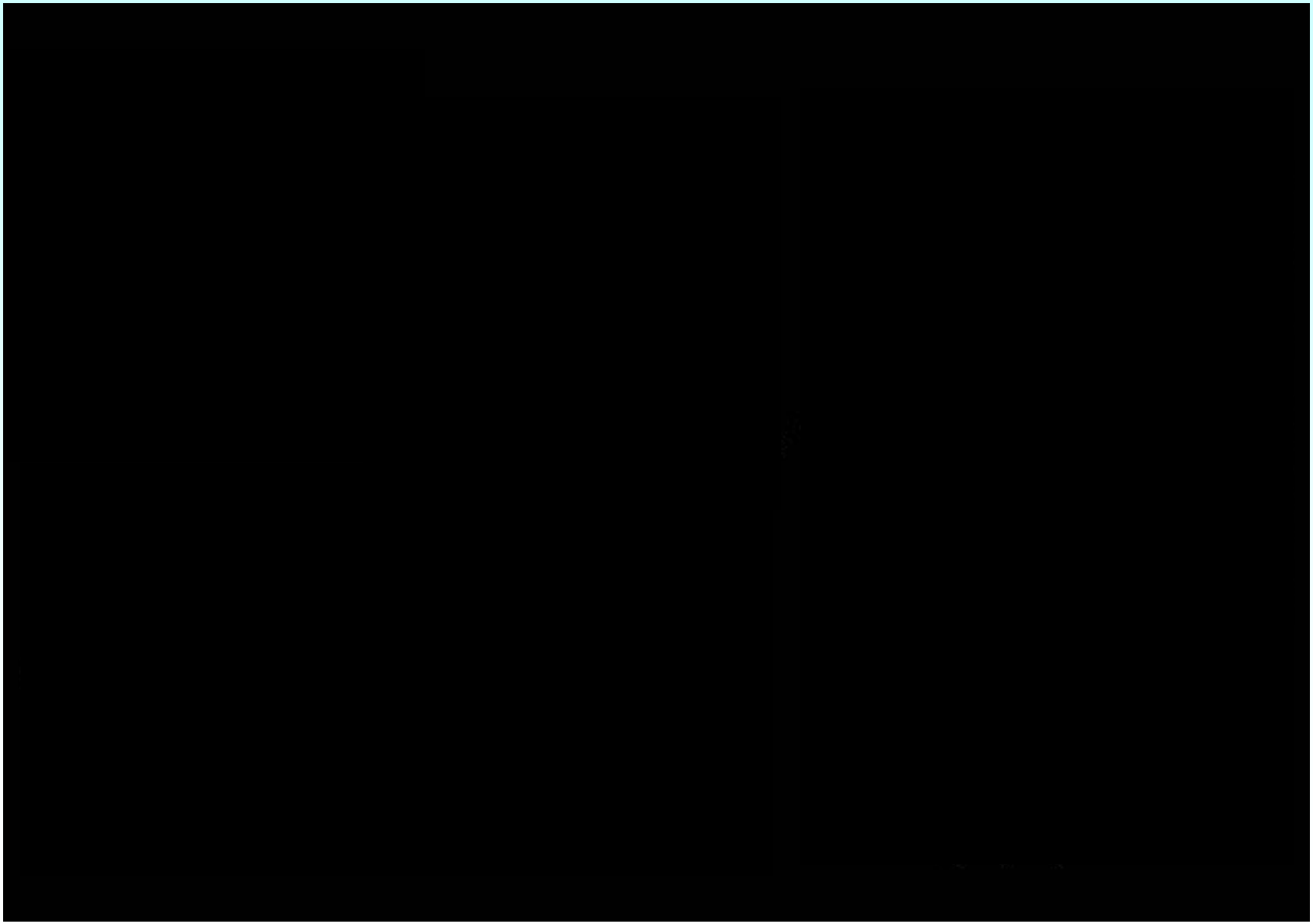




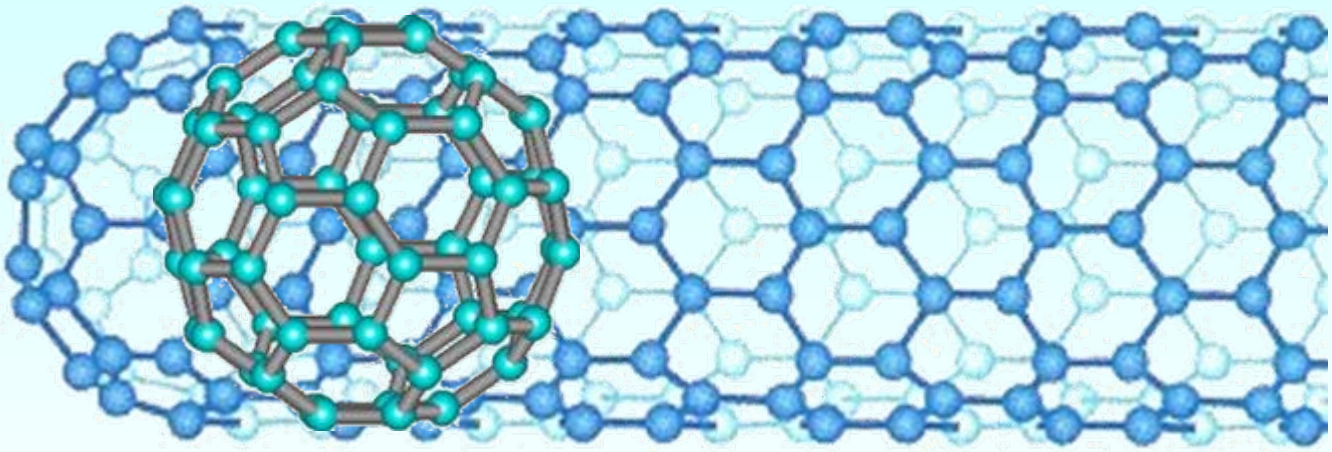
R. Bruce Weisman
Rice University
Houston, Texas

University of Houston Clear Lake March 28, 2013

Forms of Carbon



Carbon Nanostructures



Single-walled Carbon Nanotube (SWCNT)

C_{60} (Buckminsterfullerene)

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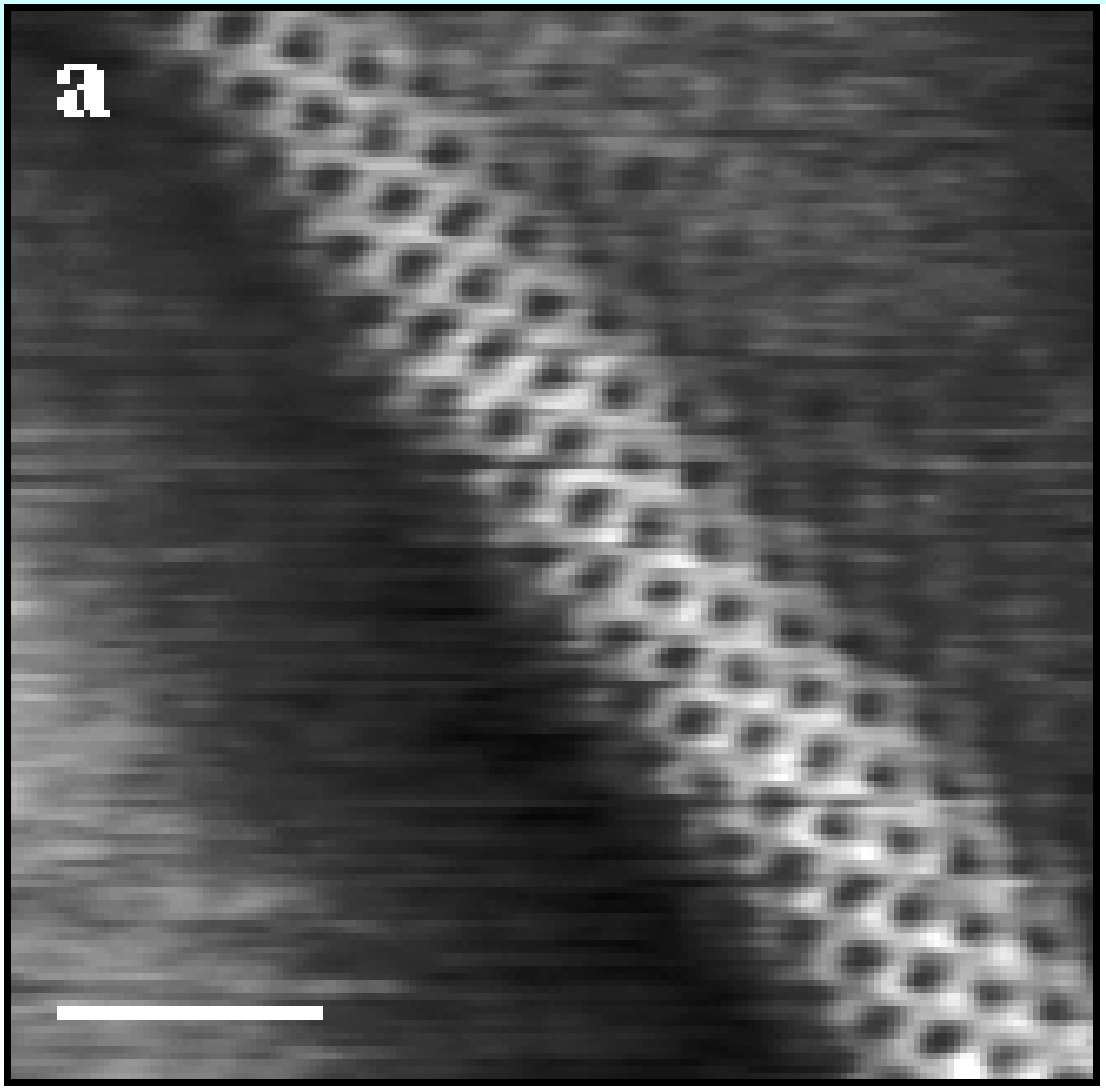
STM Image of a Single-Walled Carbon Nanotube



Prof. C. Lieber, Harvard Univ.

Relevant SWCNT Properties

Typical diameter: 0.6 – 3 nm

Typical lengths: 100 – 10,000 nm $\rightarrow$ large aspect ratios

Density: ~1.4 g / cm^3

Tensile strength: ~ 60 GPa $\rightarrow$ 50 x higher than steel

Persistence length: ~ 50 mm $\rightarrow$ very rigid

Surface area: > 1000 m^2 / g (every atom on surface)

Electrical transport: metallic or semiconducting

Optical spectra: intense π-π^* bands,
direct band-gap semiconductors

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Potential Uses of Carbon Nanotubes

Super-strong fibers

Lightweight electrical cable

High performance composite materials

Novel electronics (transistors, conductive films)

Physical / chemical / biochemical sensors

Medical diagnosis and therapy agents

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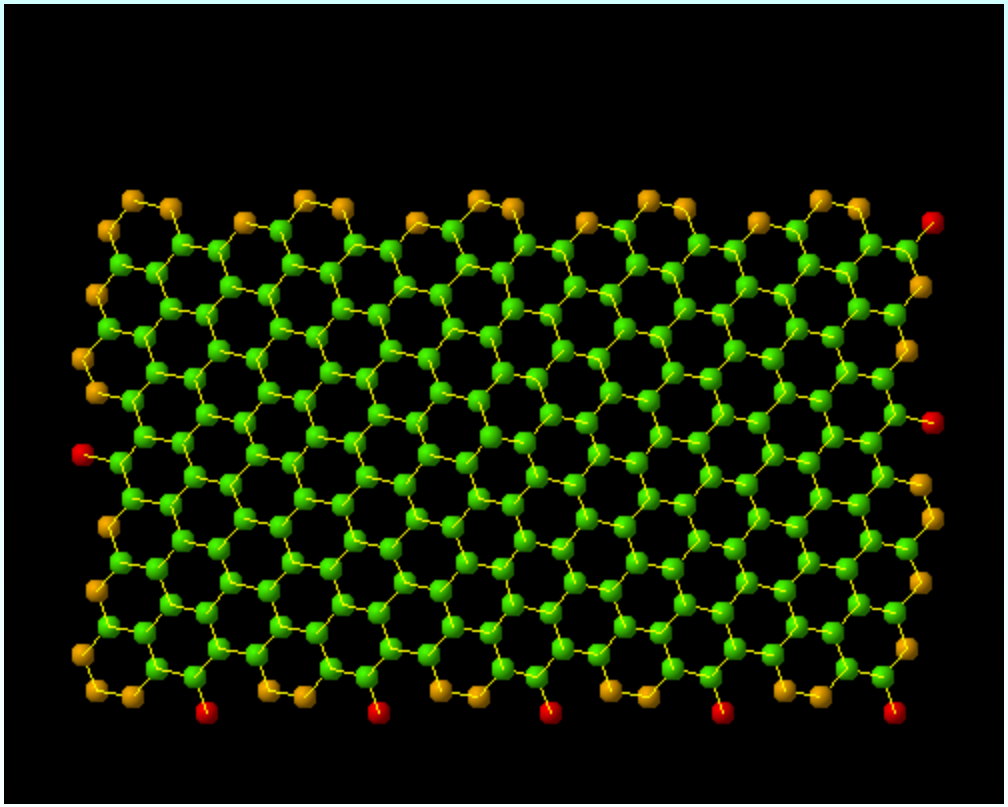
Rolling up graphene to make a SWCNT



from http://www.photon.t.u-tokyo.ac.jp/~maruyama/wrapping.files/frame.html

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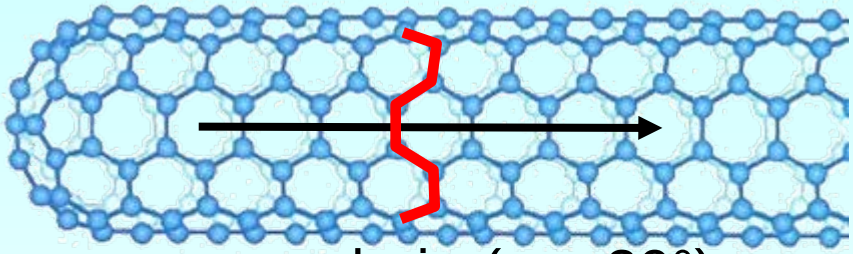
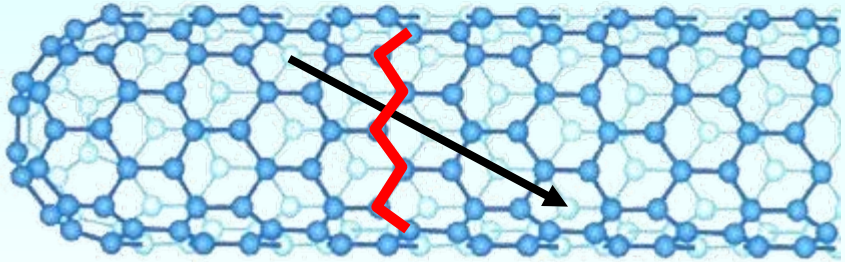
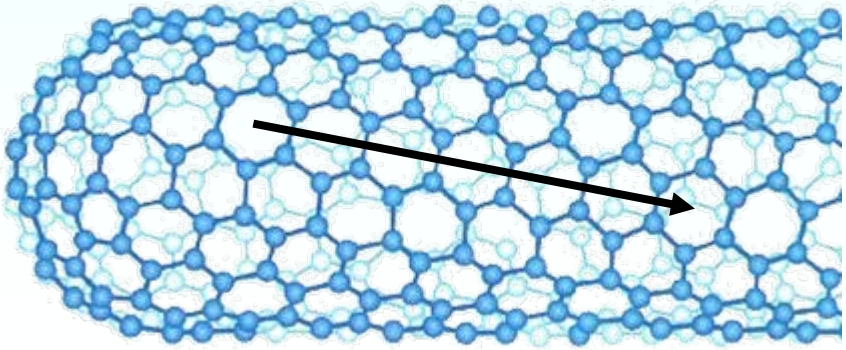
Many SWCNT structures exist (different diameters and angles)



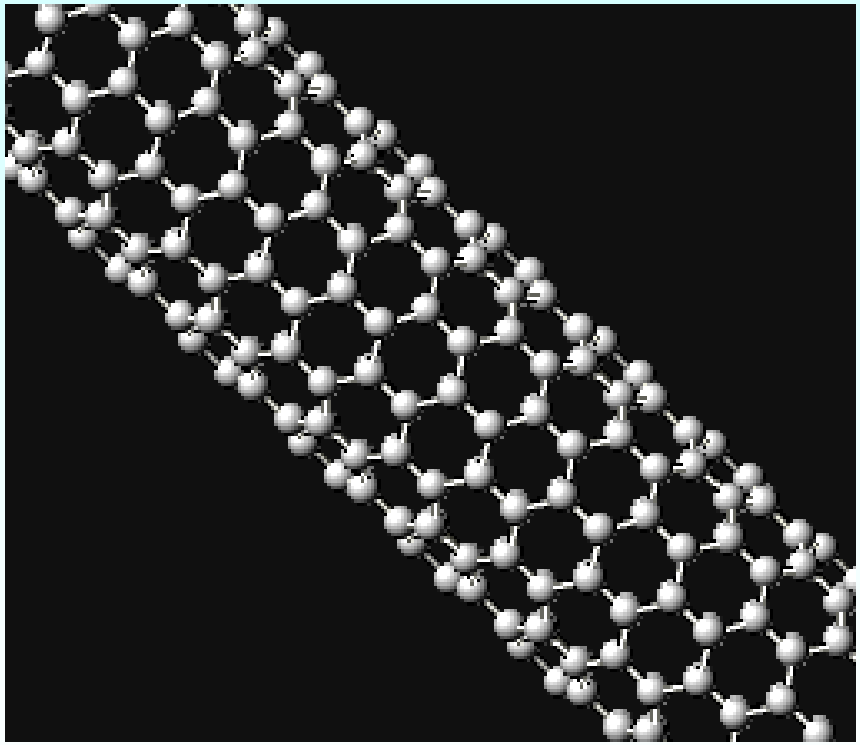
armchair ($\alpha = 30°$)



zigzag ($\alpha = 0°$)



intermediate ($0 < \alpha < 30°$)



zigzag

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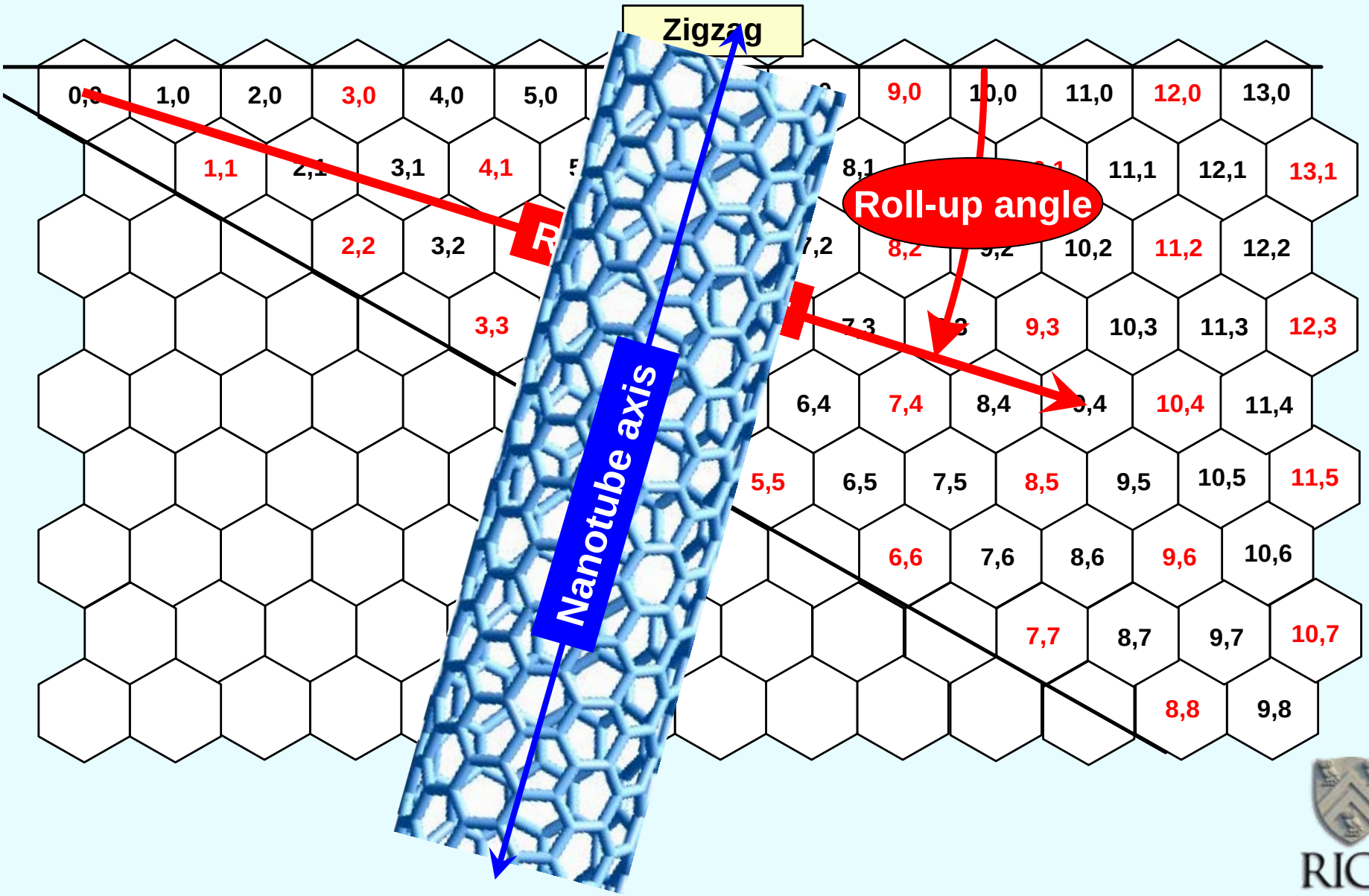
Constructing Nanotubes from a Graphene Sheet



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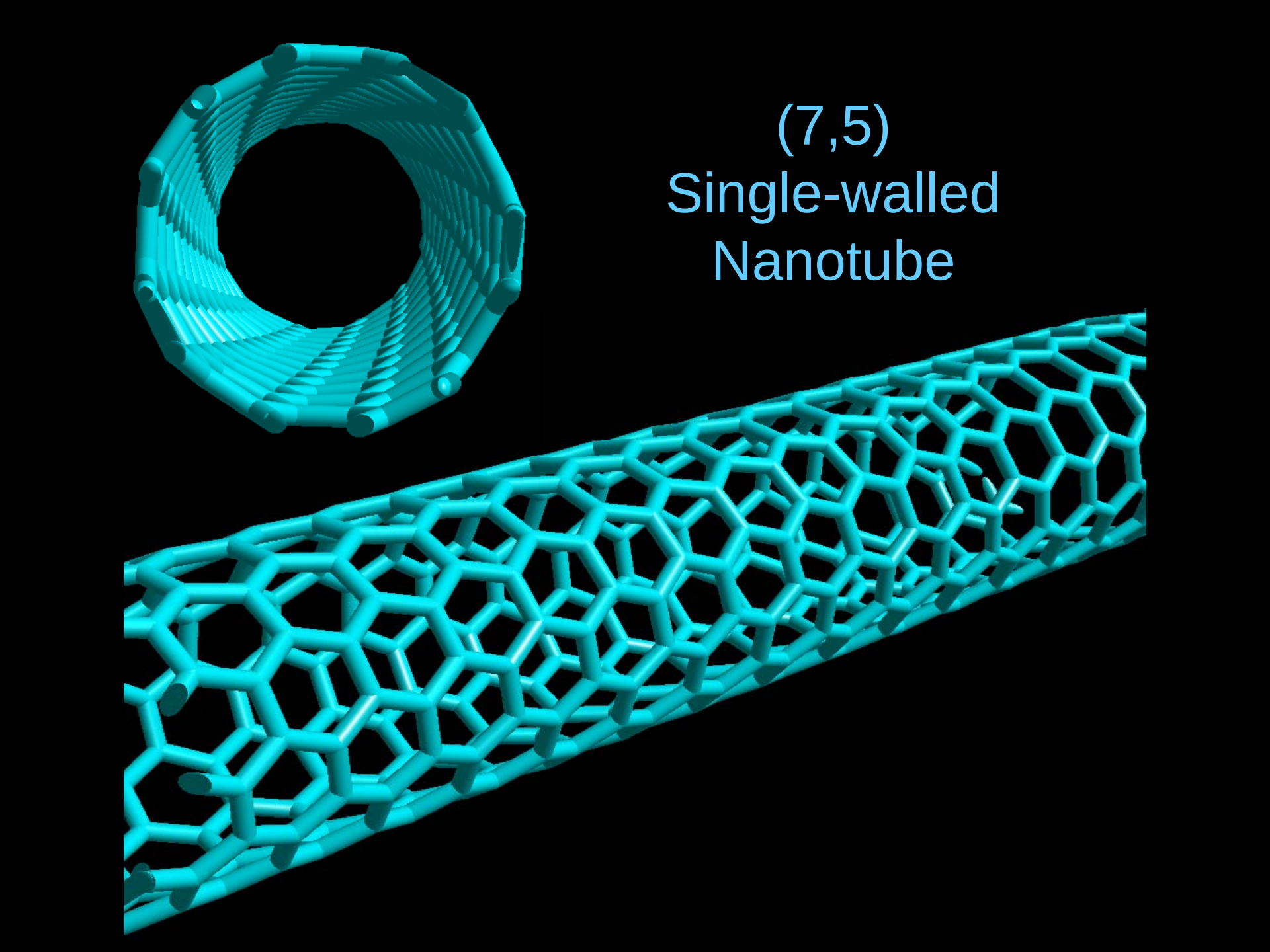
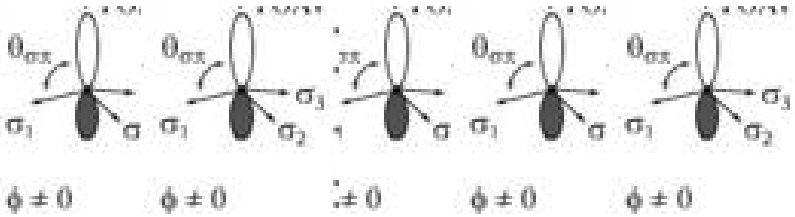

(7,5)
Single-walled
Nanotube

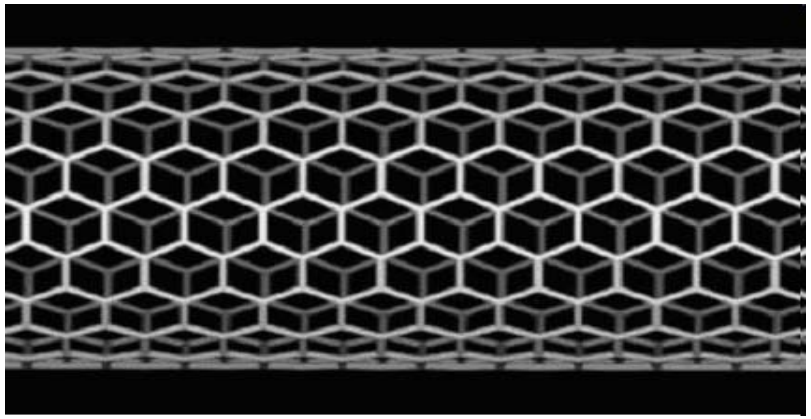
Forming bands from the p-orbitals

Carbon atom p-orbitals



vacant orbital (LUMO)

occupied orbital (HOMO)



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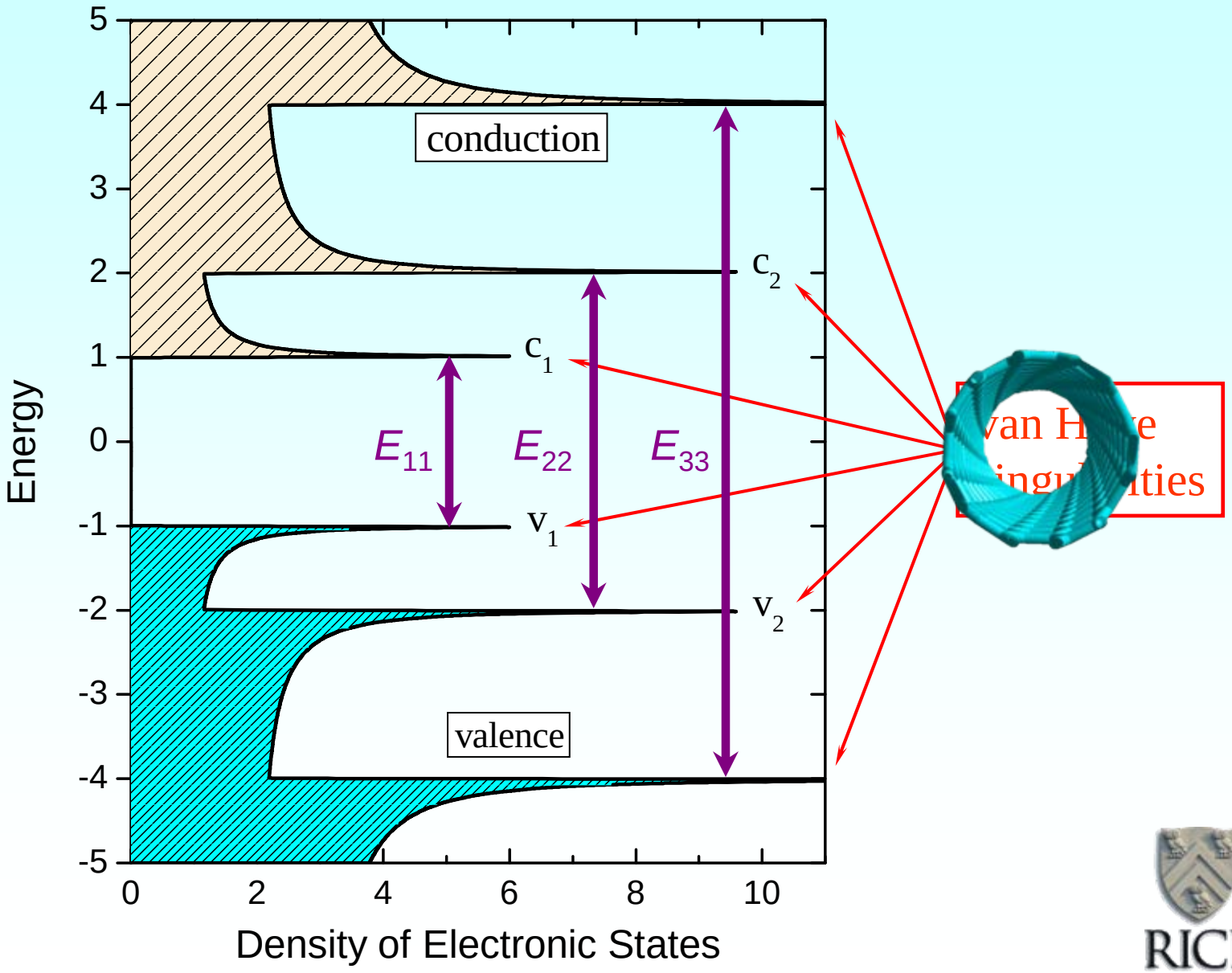
Electronic states of a semiconducting SWCNT



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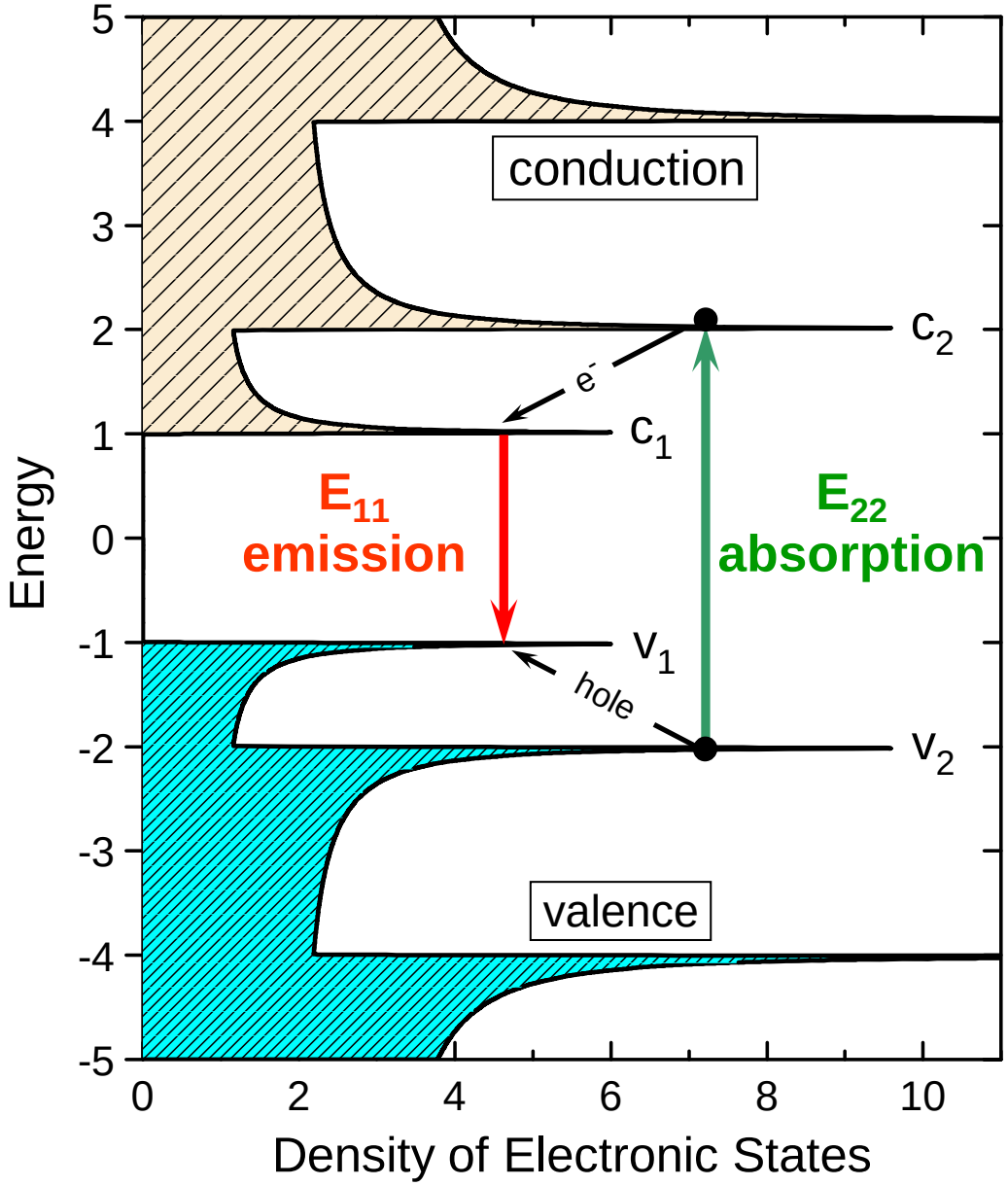
Nanotubes are produced as Complex Mixtures

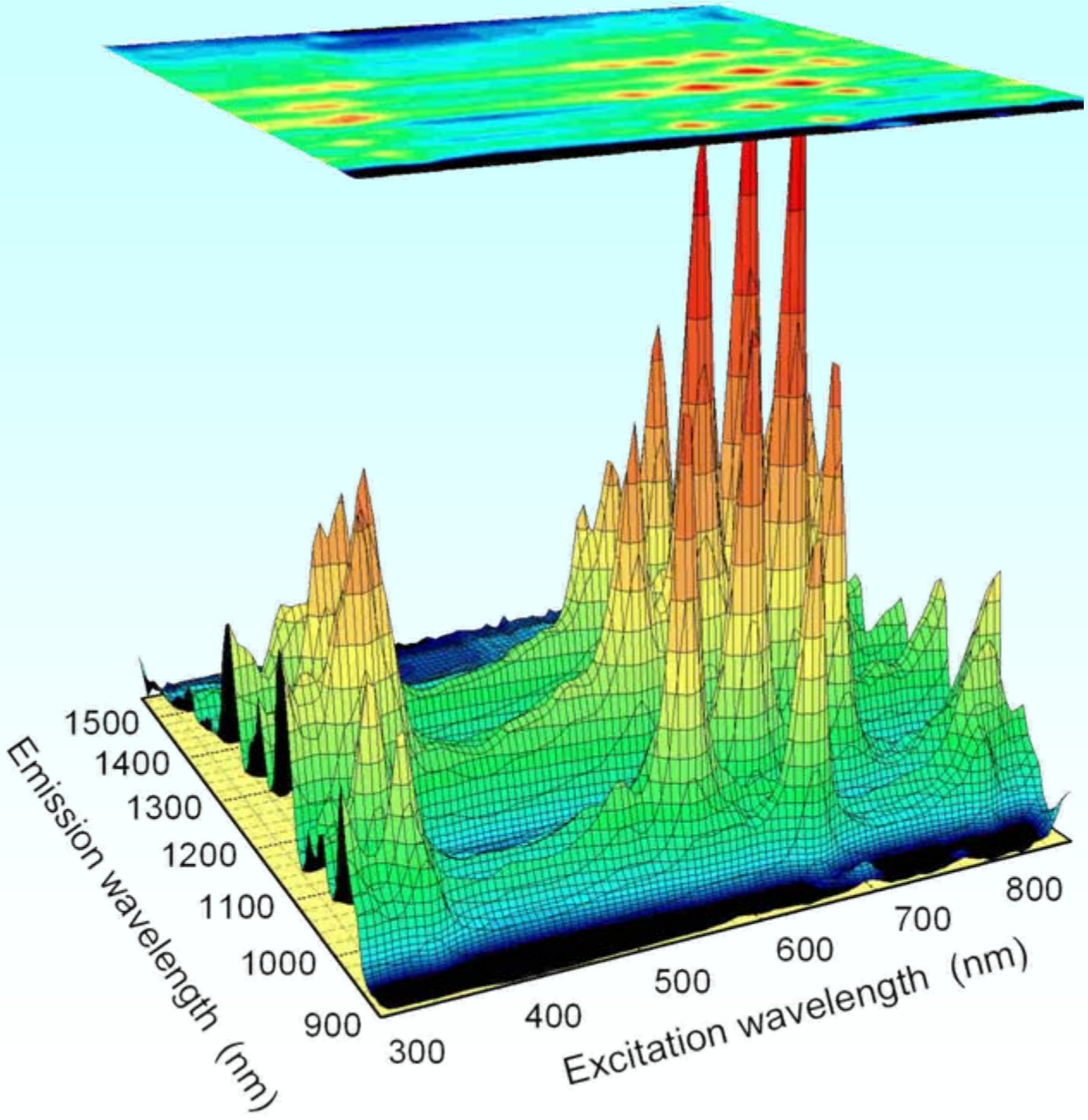
Even single-walled samples contain:

- many diameters
- many chiral angles
- many lengths (no effect on electronic structure)
- bundles of tubes bound by van der Waals forces
- impurities (residual catalyst, giant fullerenes,…)

Electronic states of a semiconducting SWCNT



RICE


1500
1400
1300
1200
1100
1000
900
Emission wavelength (nm)
300
400
500
600
700
800
Excitation wavelength (nm)

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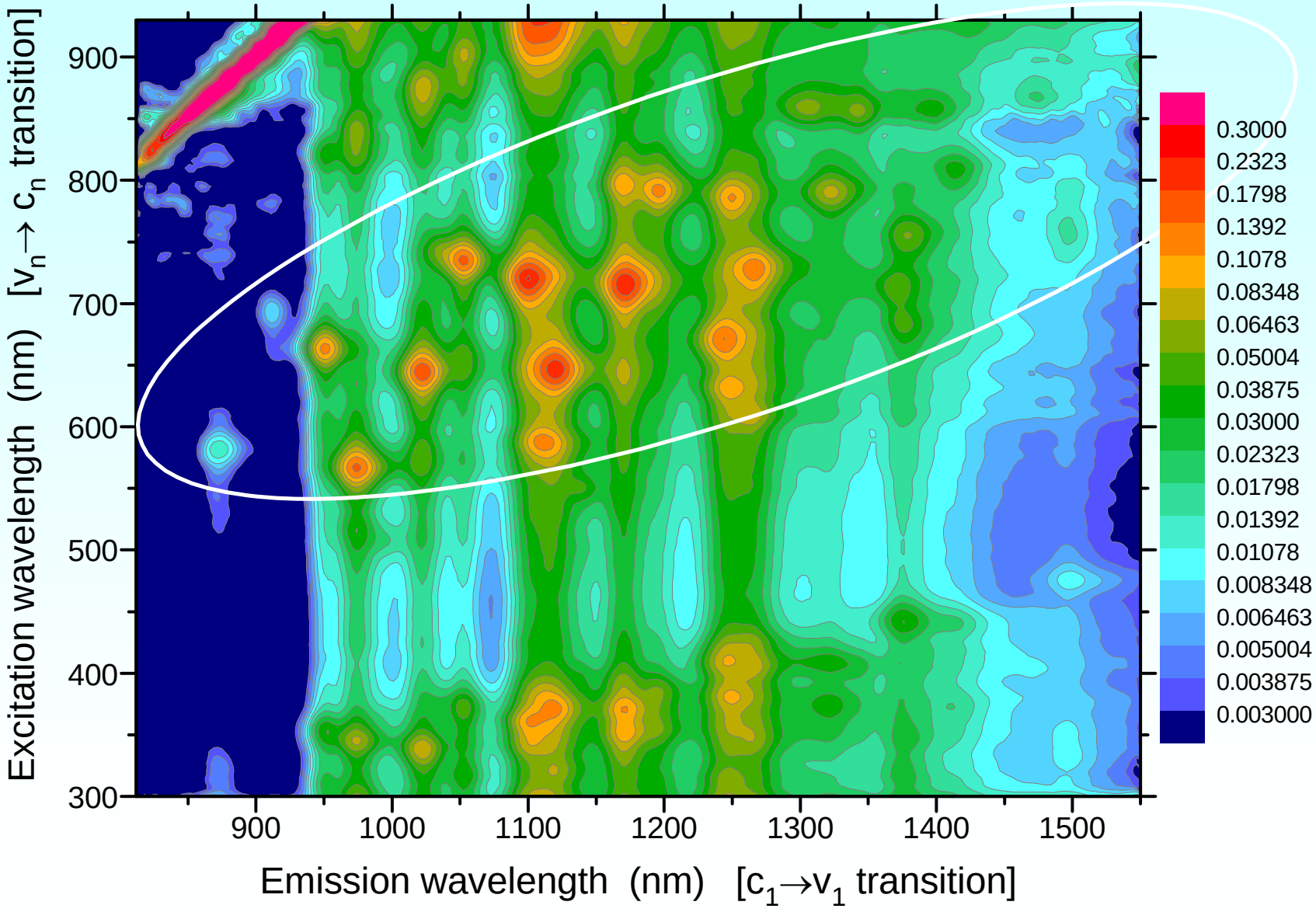
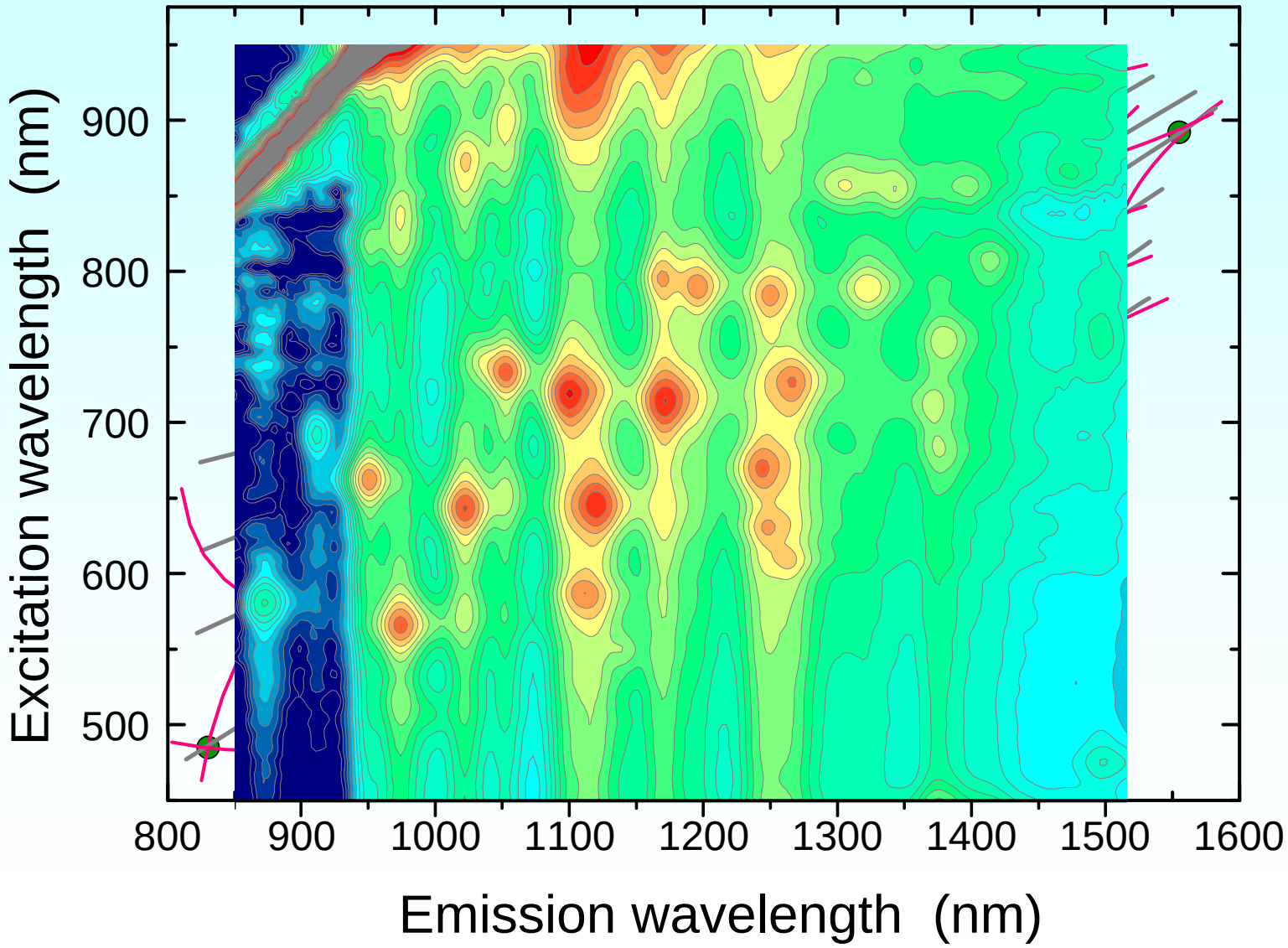
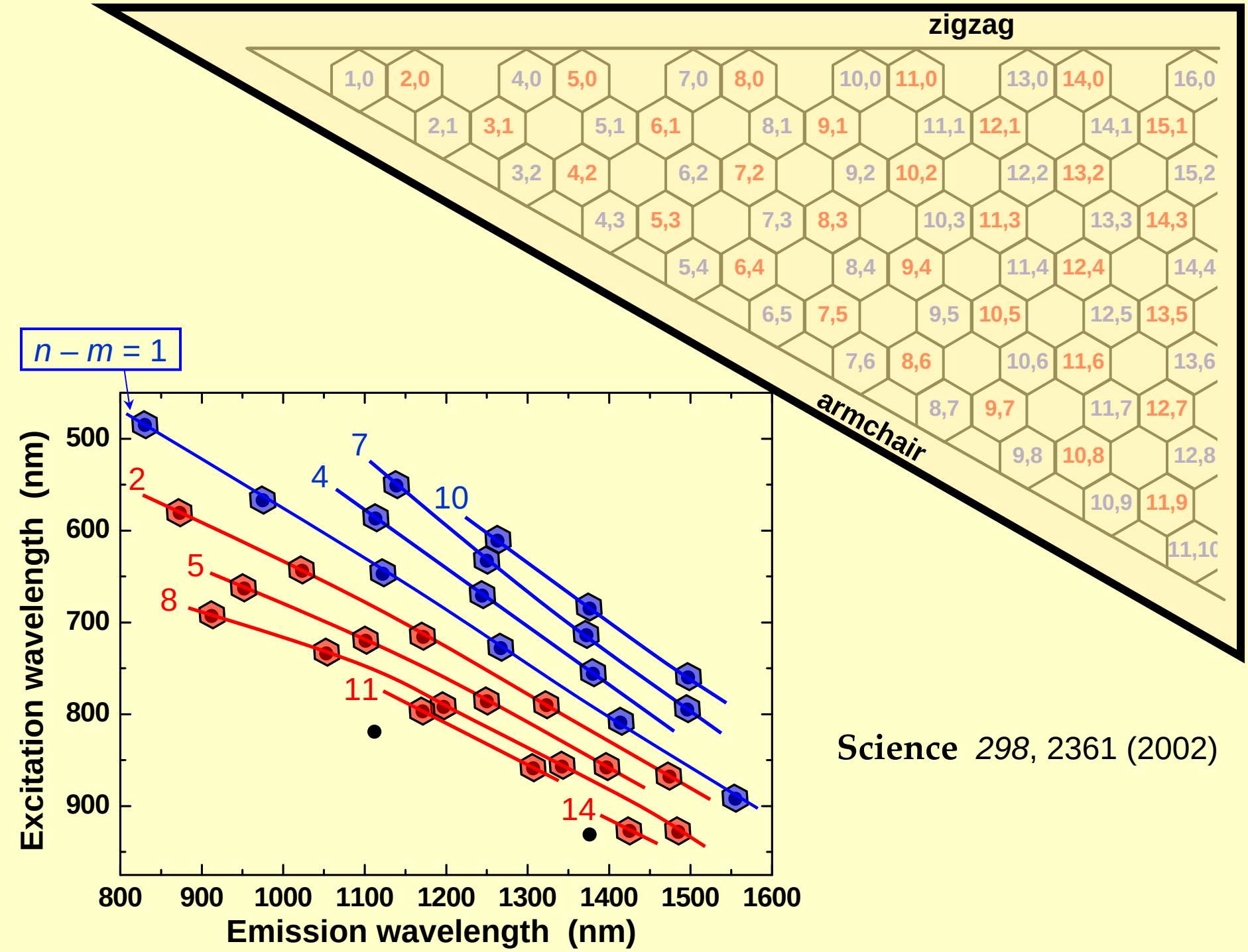
Contour plot of emission intensity



Patterns in the spectral data?

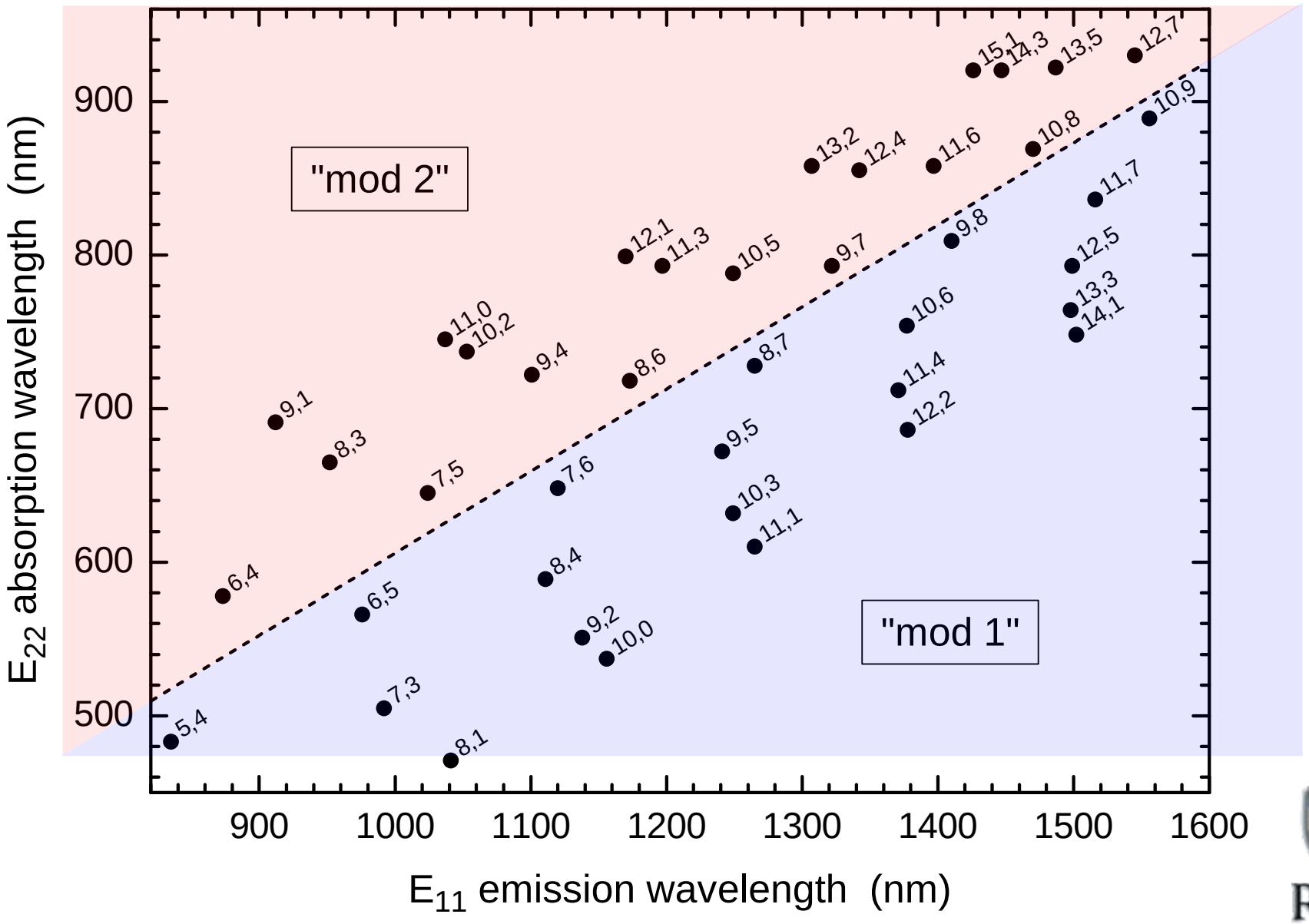
or just patterns in the noise?





Science *298*, 2361 (2002)

Structure-assigned spectral transitions



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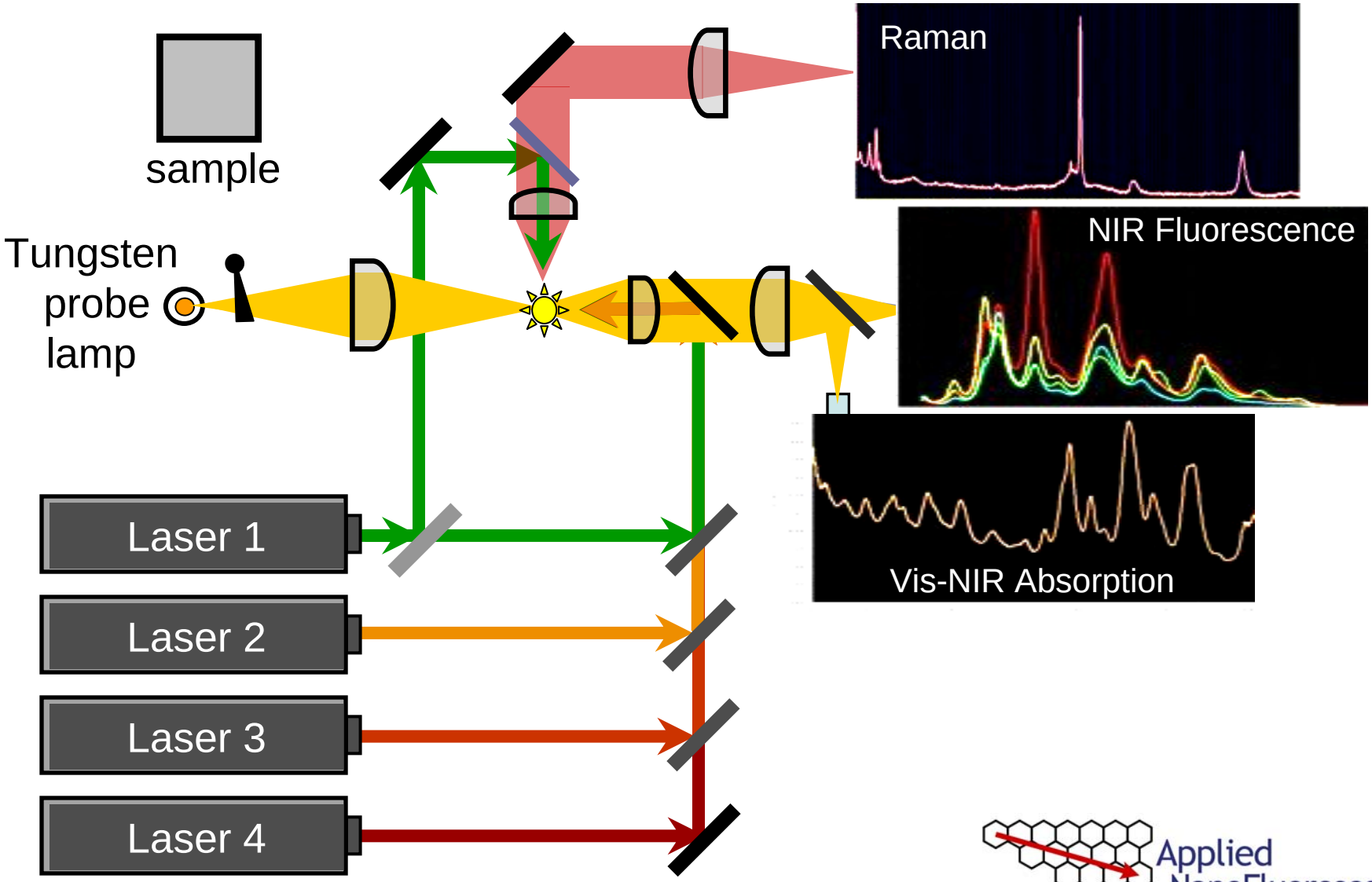
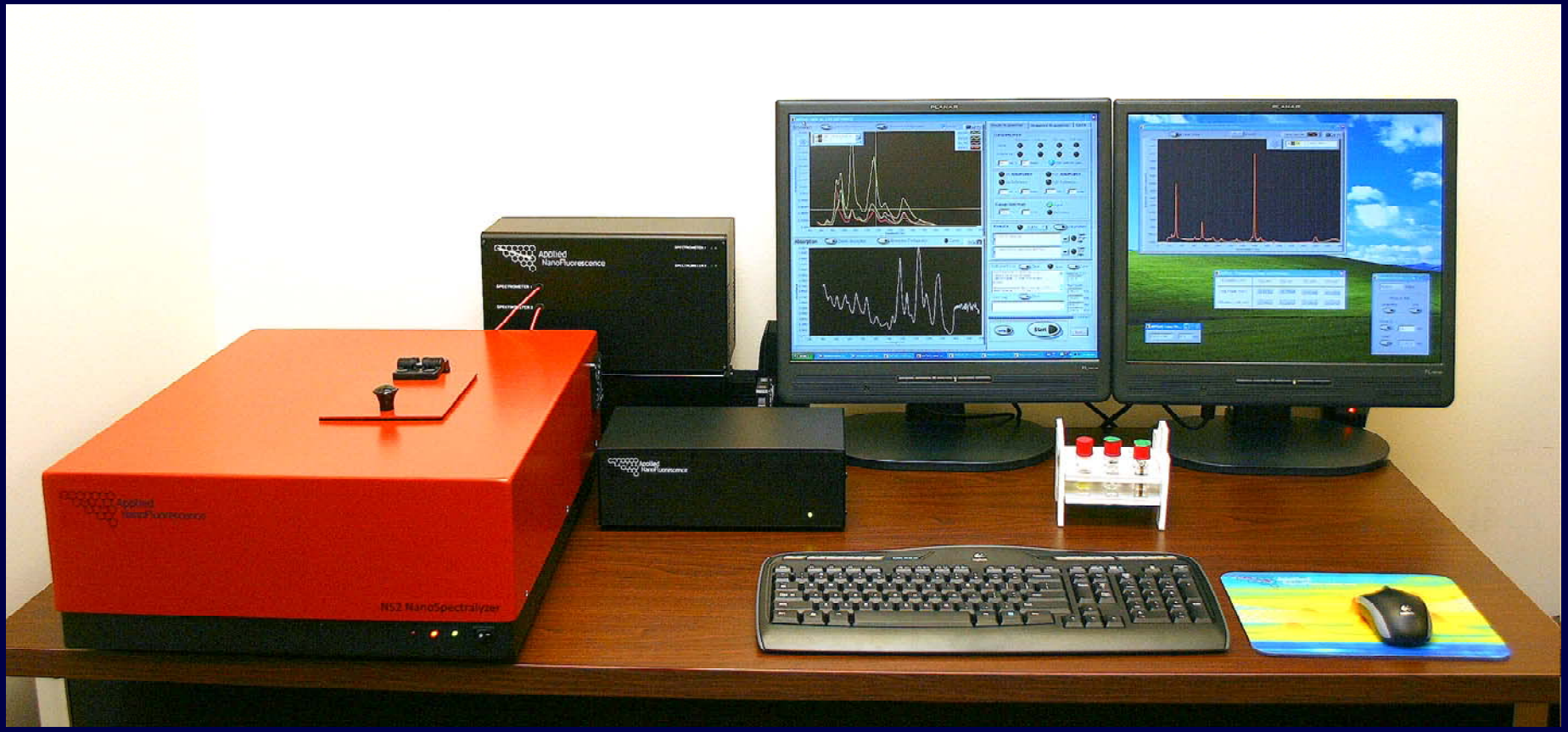
NS2 NanoSpectralyzer

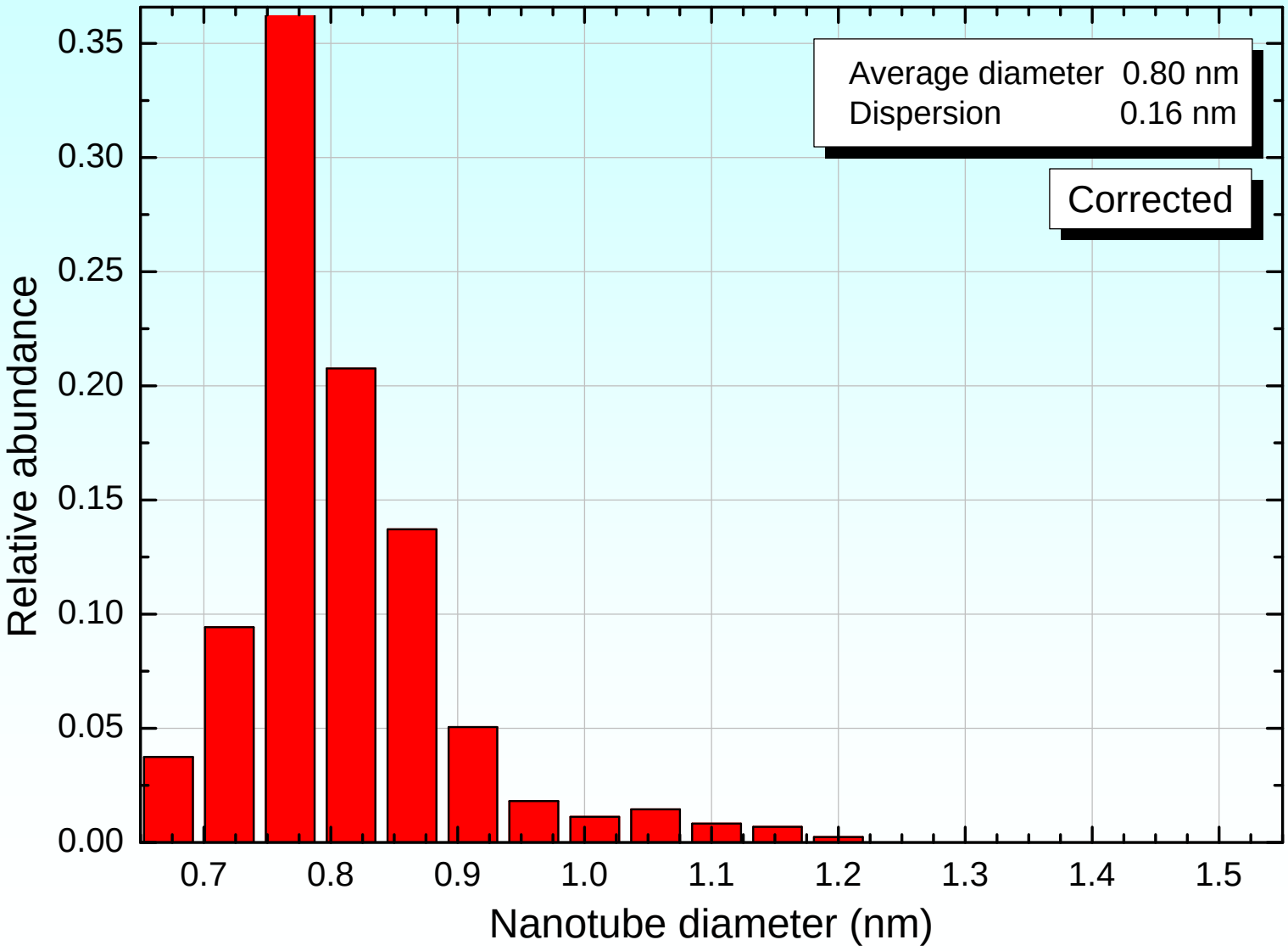


Applied NanoFluorescence

Model NS2 NanoSpectralyzer®



Diameter distribution of NIST-VAMAS sample
(from fluorimetric analysis, corrected)



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Chemical Application

Structural Sorting of SWCNTs

Ghosh, Bachilo, and Weisman, ***Nature Nanotechnology 5***, 443 (2010)

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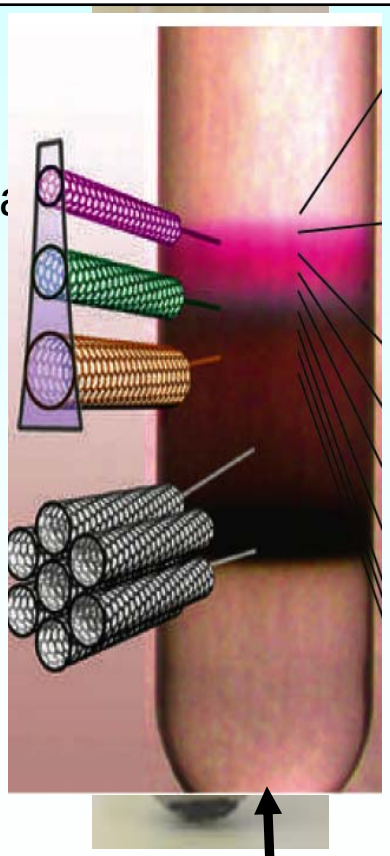
Ultracentrifugation processing of SWCNTs

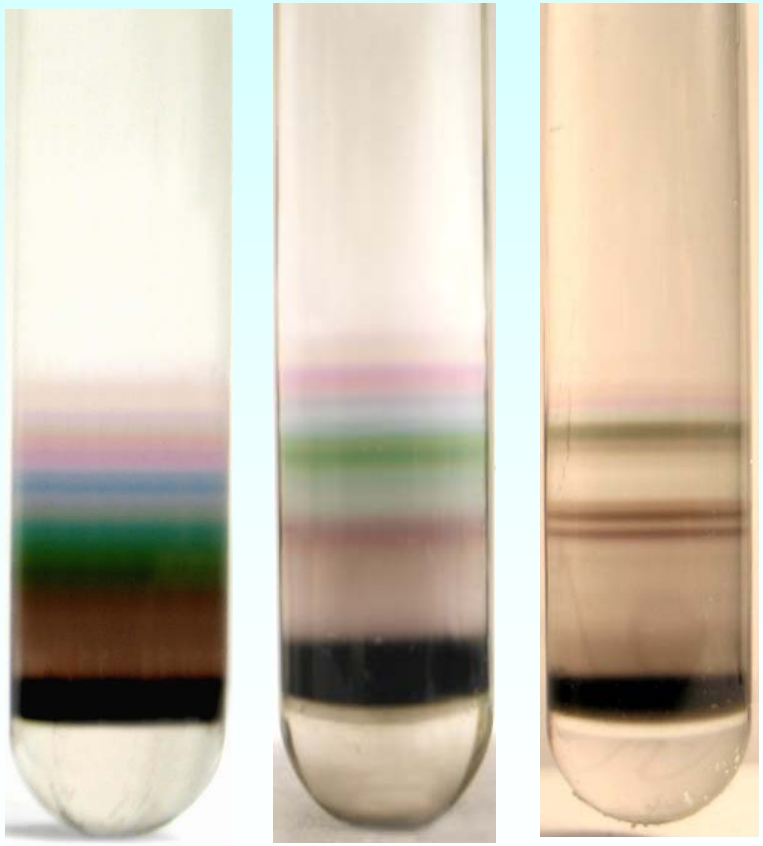
Density gradient (CoMoCAT)

SWCNT supernata



Arnold et al., *Nature Nanotech*. *1*, 60 (2006)

Refined DGU (HiPco)



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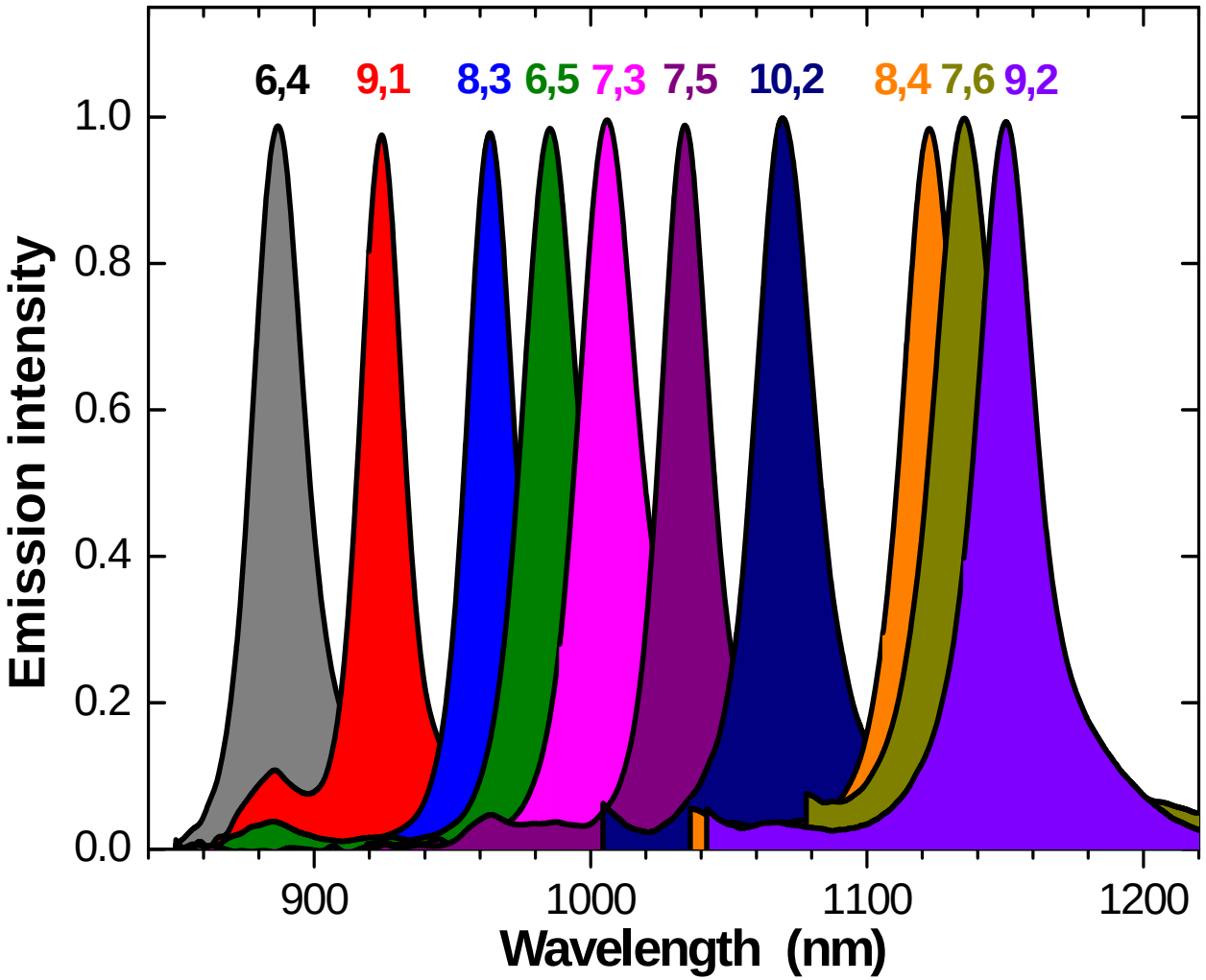
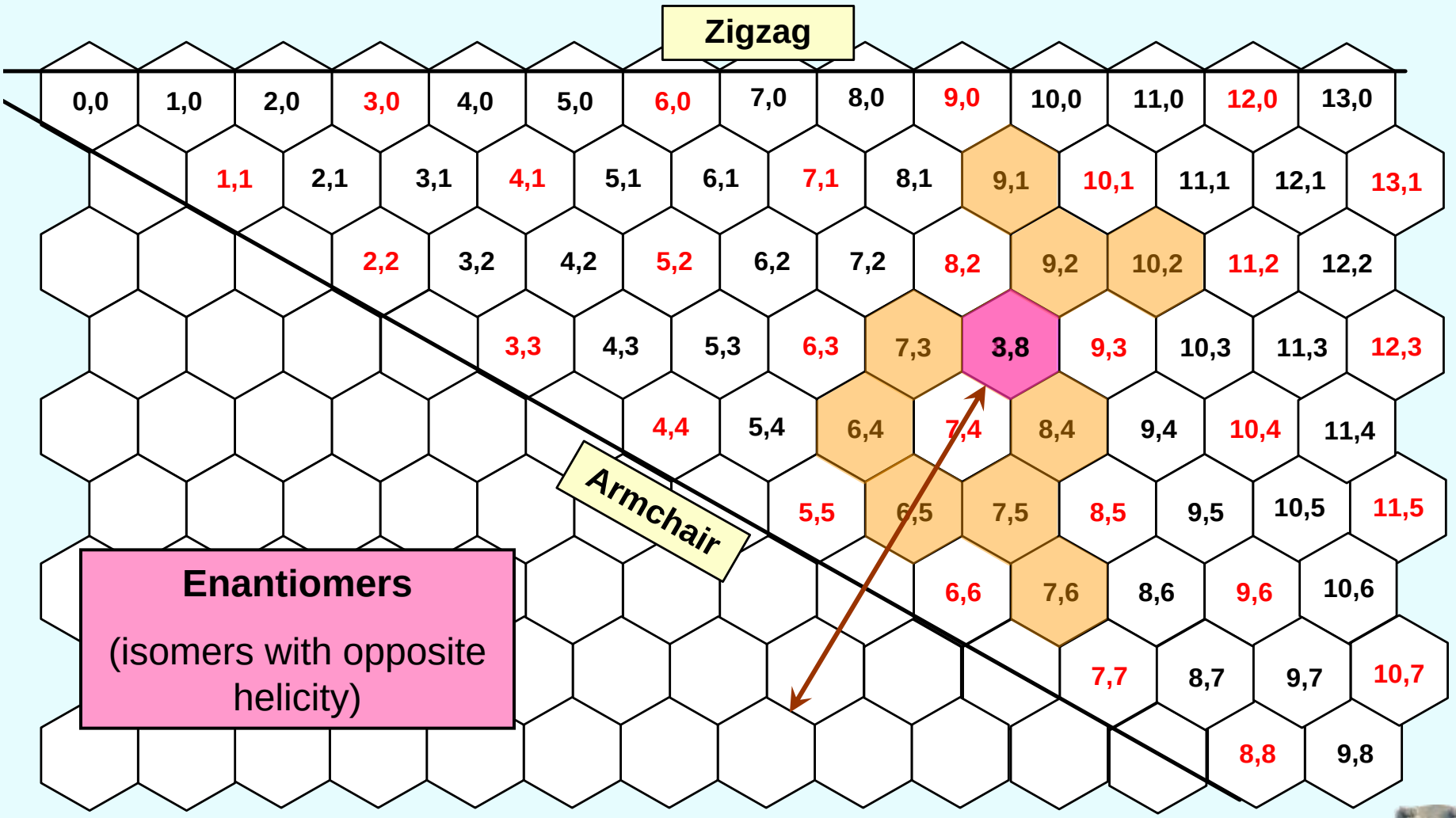
Separated fractions contain robust near-IR fluorophores with distinct emission peaks



Ghosh, Bachilo, and Weisman, ***Nature Nanotechnology 5***, 443 (2010)

Through the Looking Glass



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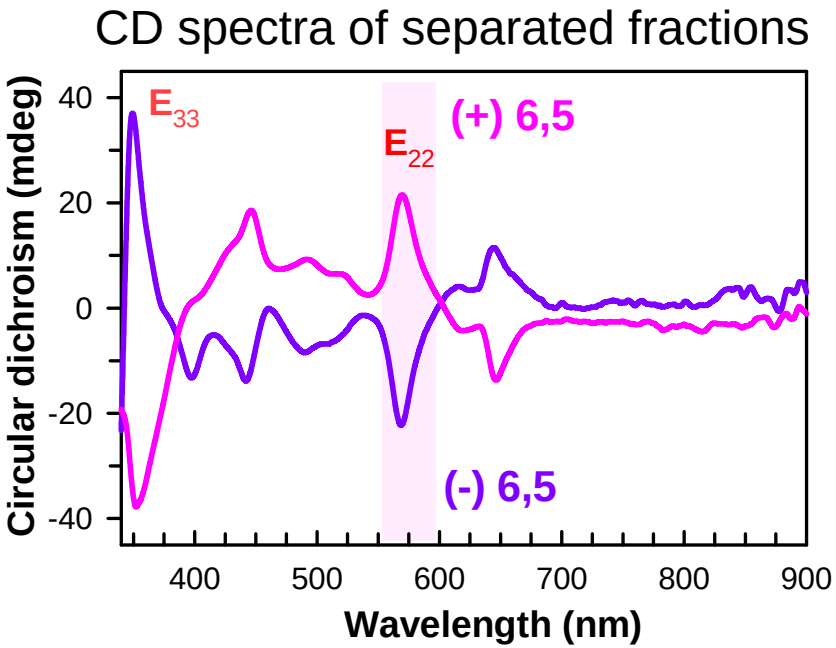
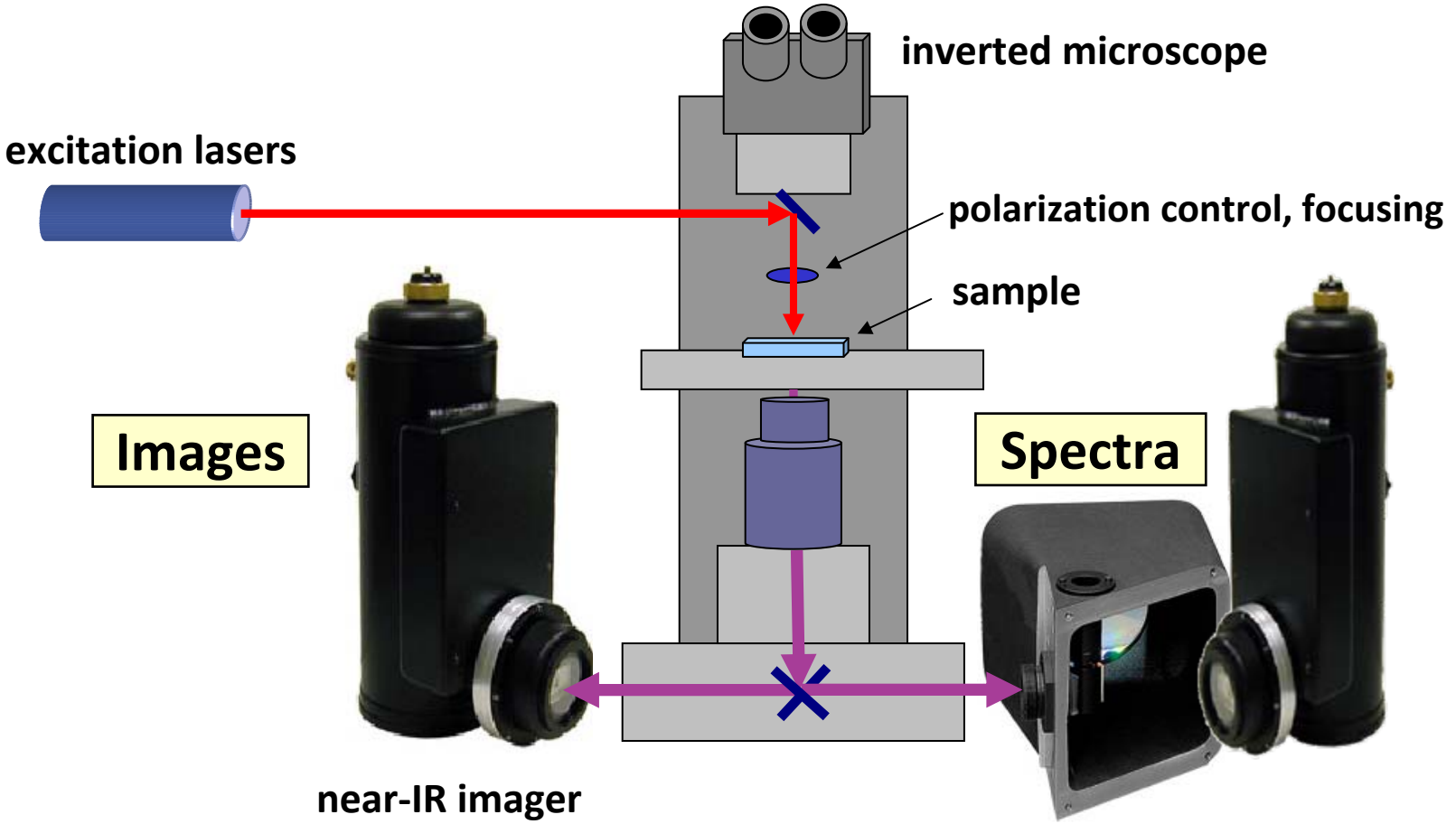
Separation of SWCNT enantiomers (left- and right-handed forms)



Apparatus for near-IR fluorescence microscopy

Tsyboulski, et al.
Nano Lett. 5, 975 (2005)



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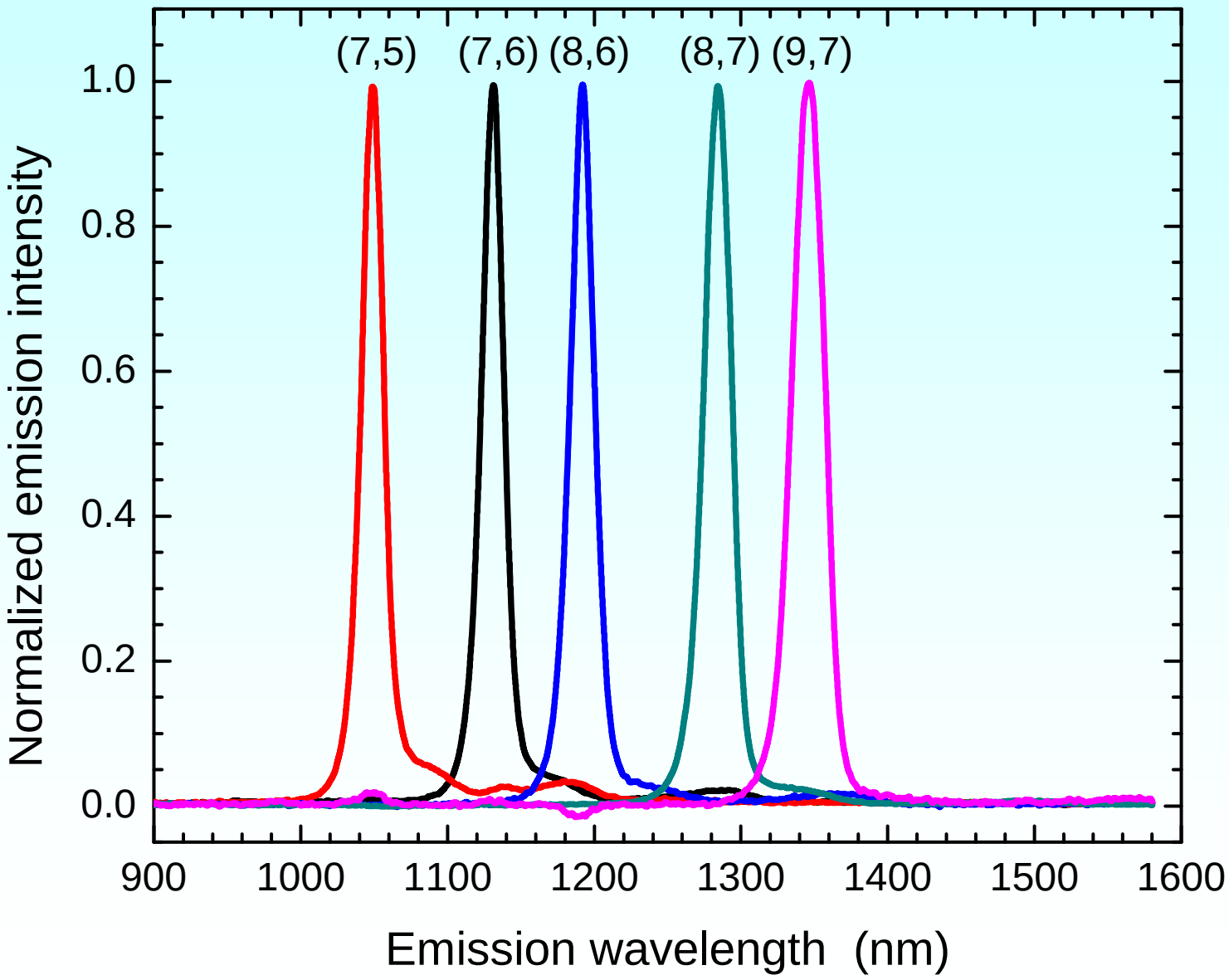
Emission spectra of individual SWCNTs



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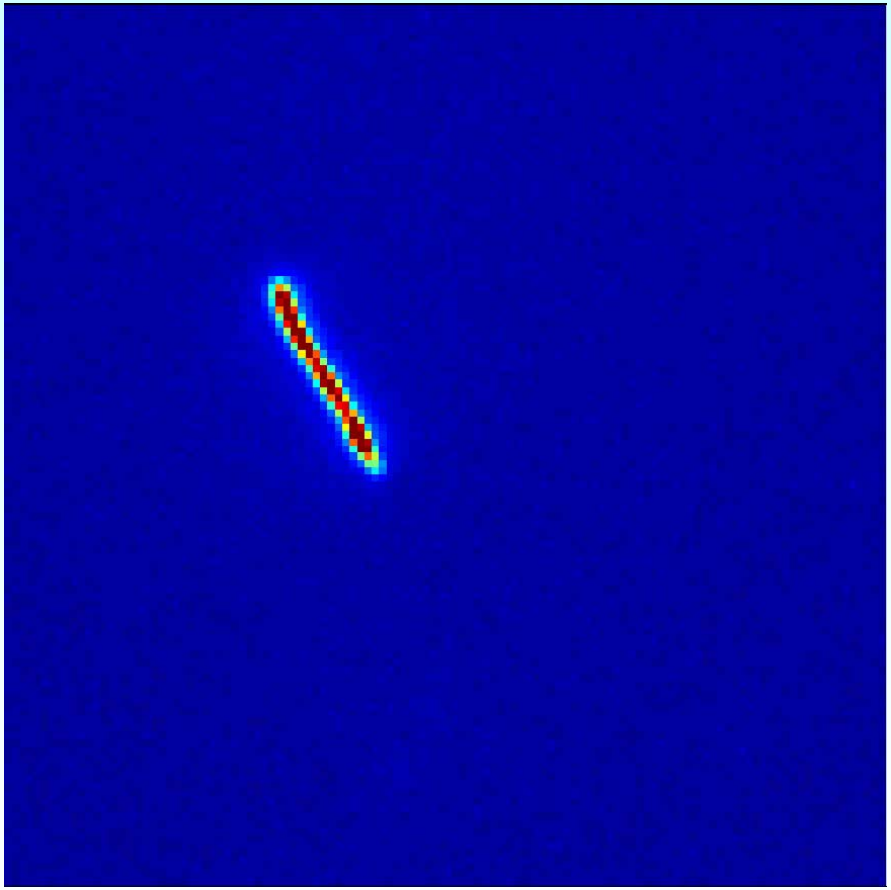
Fluorescence image of a free SWCNT in water suspension



Real time
Nanotube length = 10 μm

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Chemical Application

Observing Single-Molecule Chemical Reactions with Nanotubes

with L. Cognet, D. Tsyboulski, J.-D. Rocha, C. Doyle, J. Tour
Science 316, 1465 (2007)

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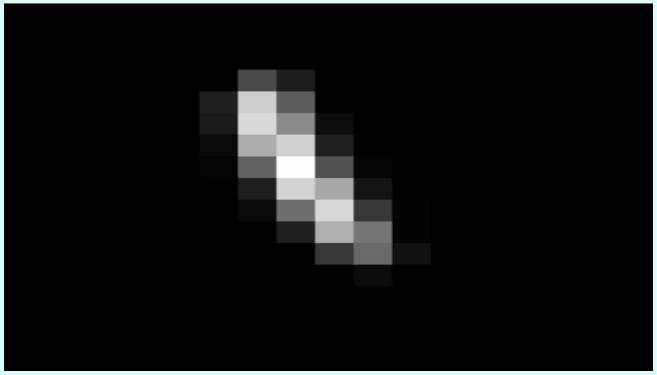
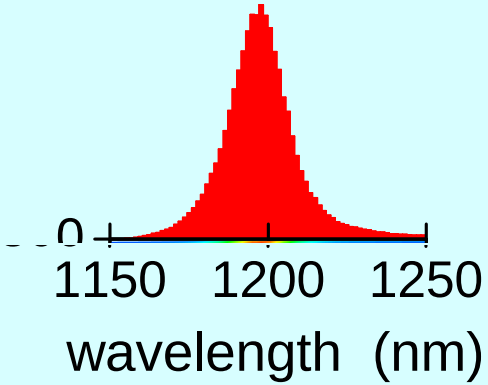
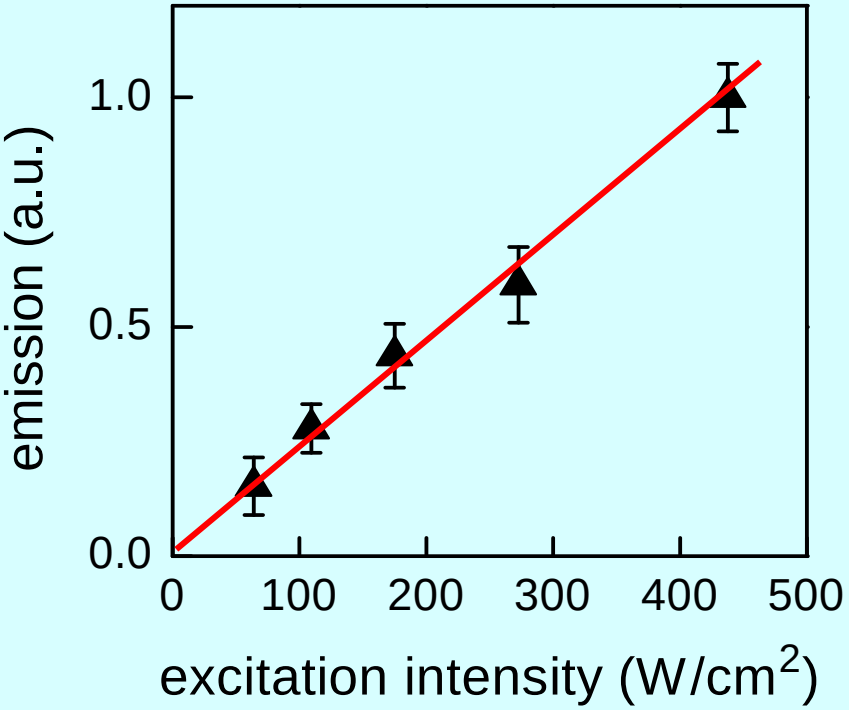
Stable fluorescence from single nanotubes







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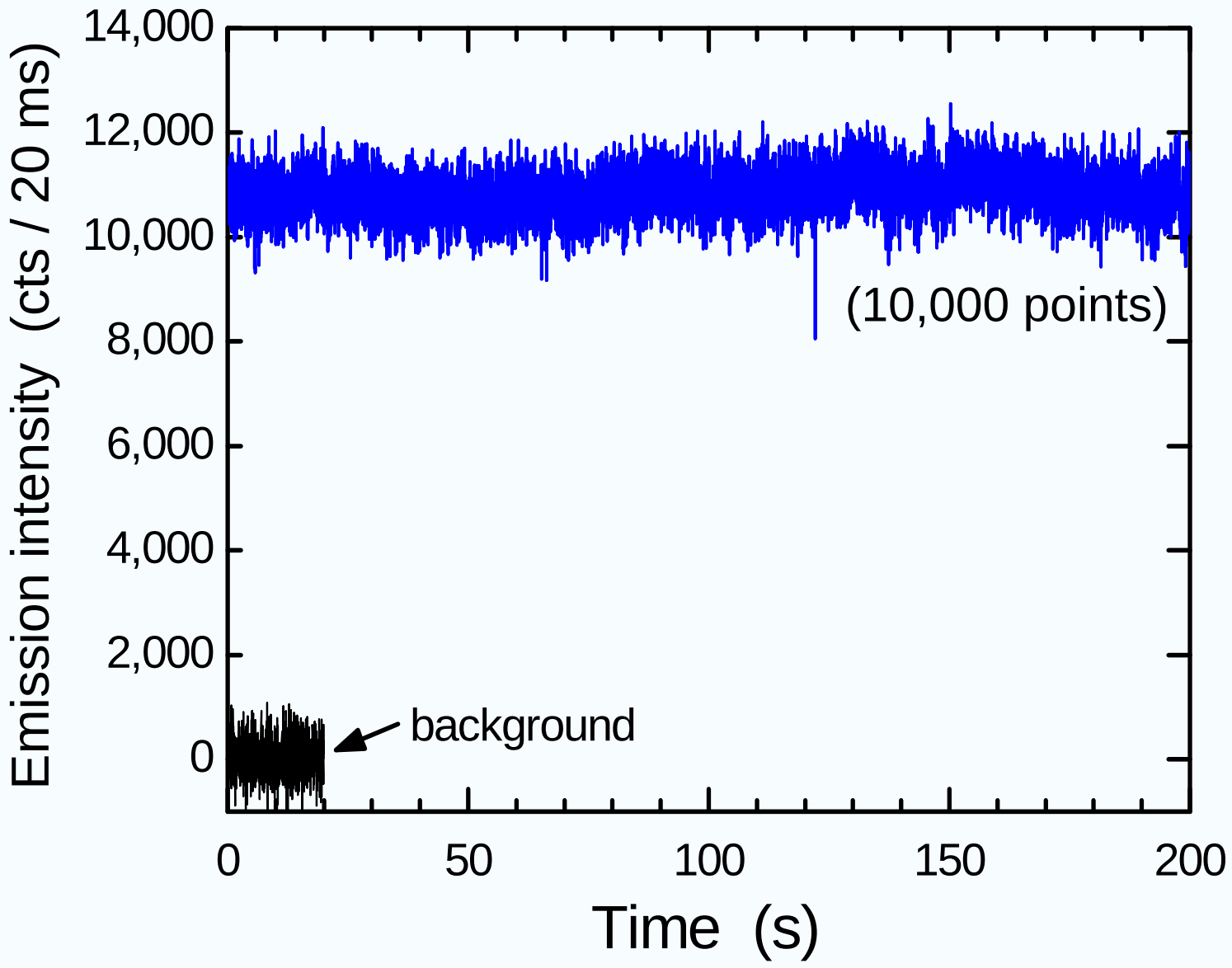
Single nanotube fluorescence at pH 7



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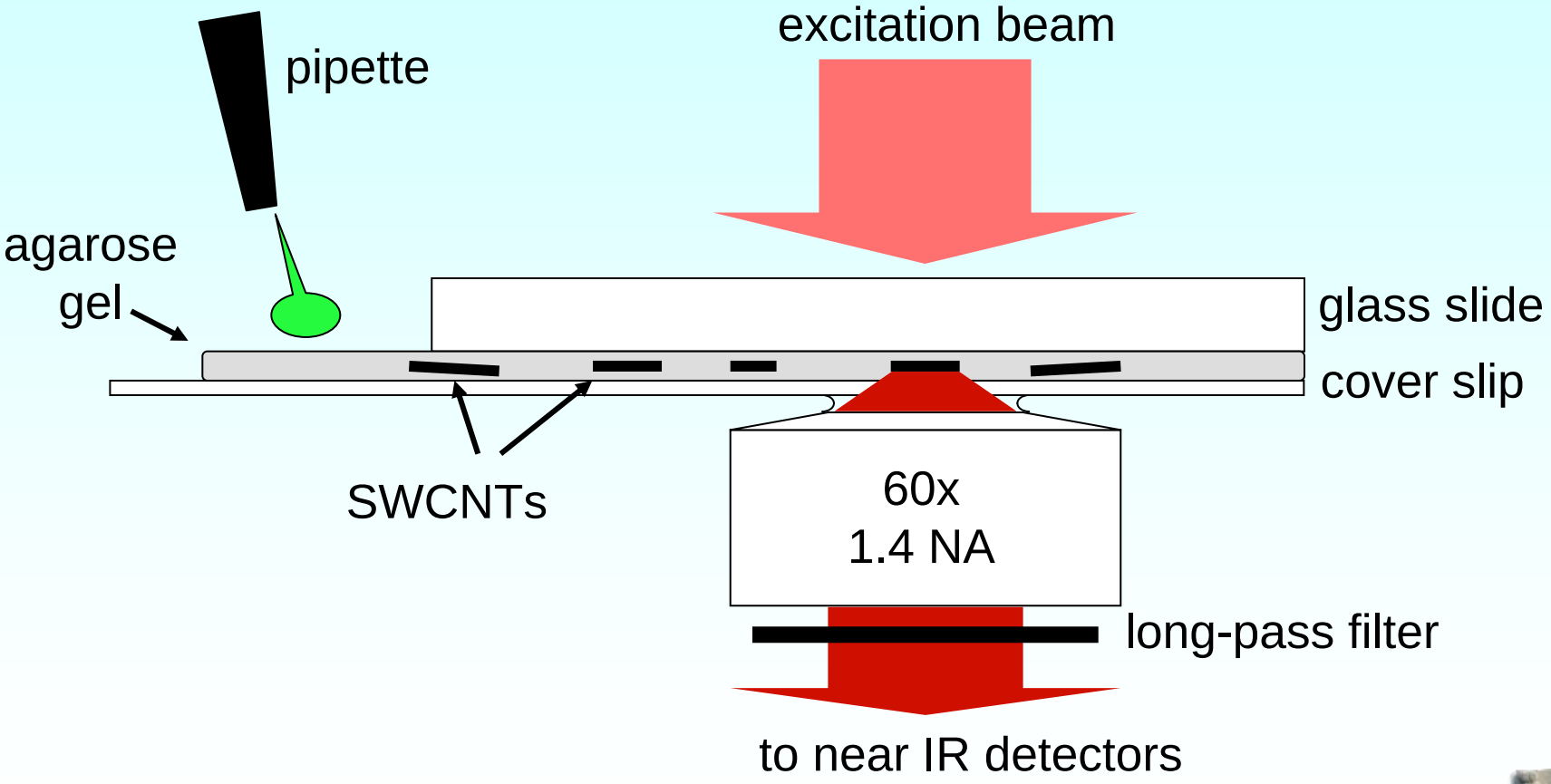
Quenching measurements on single nanotubes



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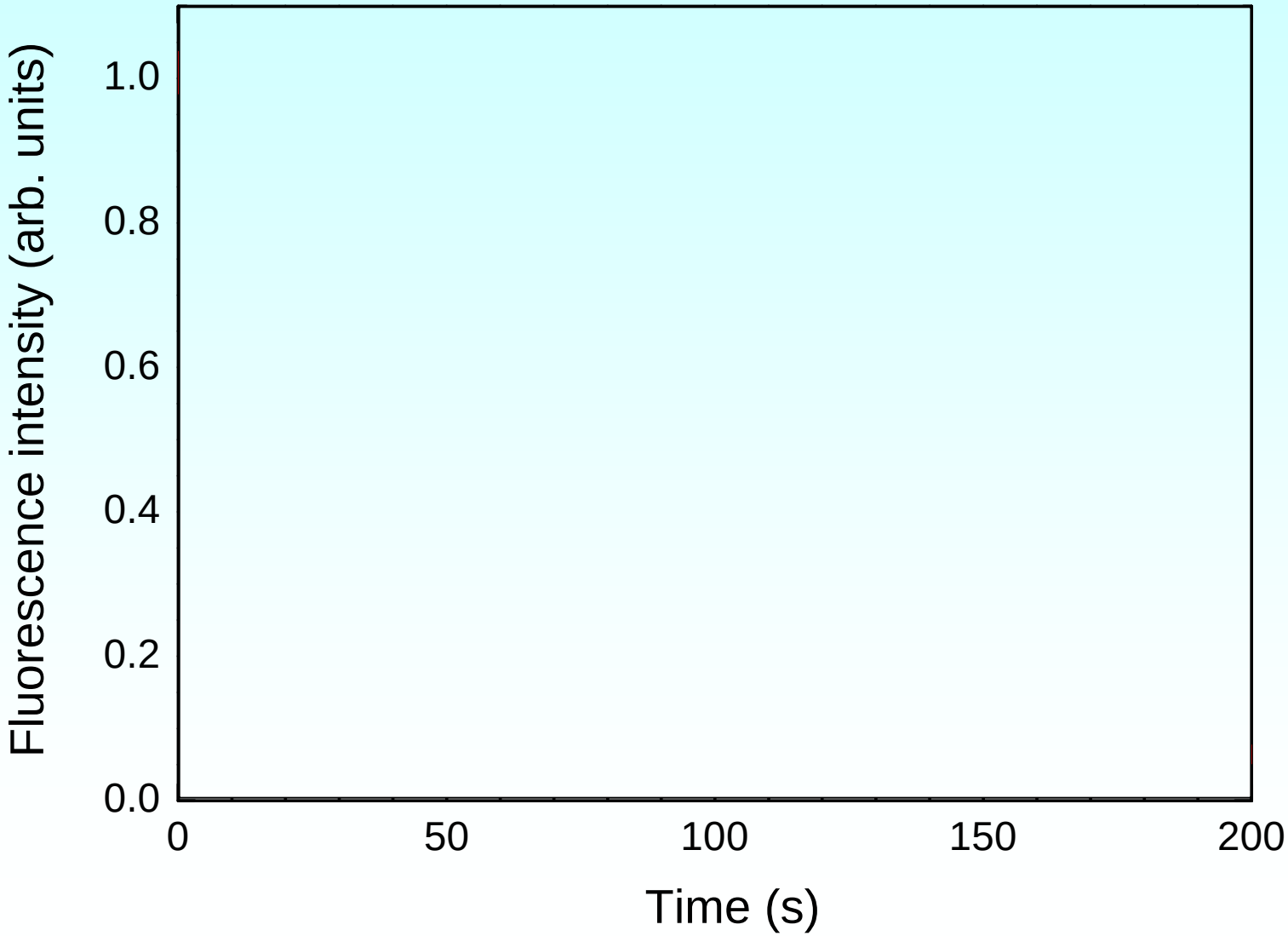
Stepwise fluorescence quenching by irreversible diazonium reaction



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Engineering Application

Using Nanotubes for Non-Contact Strain Measurement

P. Withey et al., *Nano Letters 12*, 3497 (2012).

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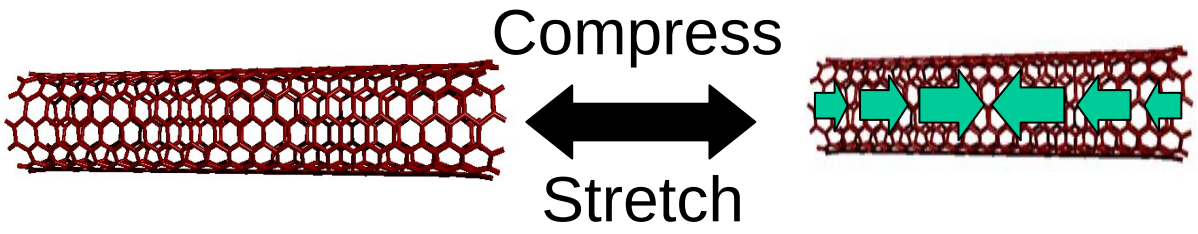
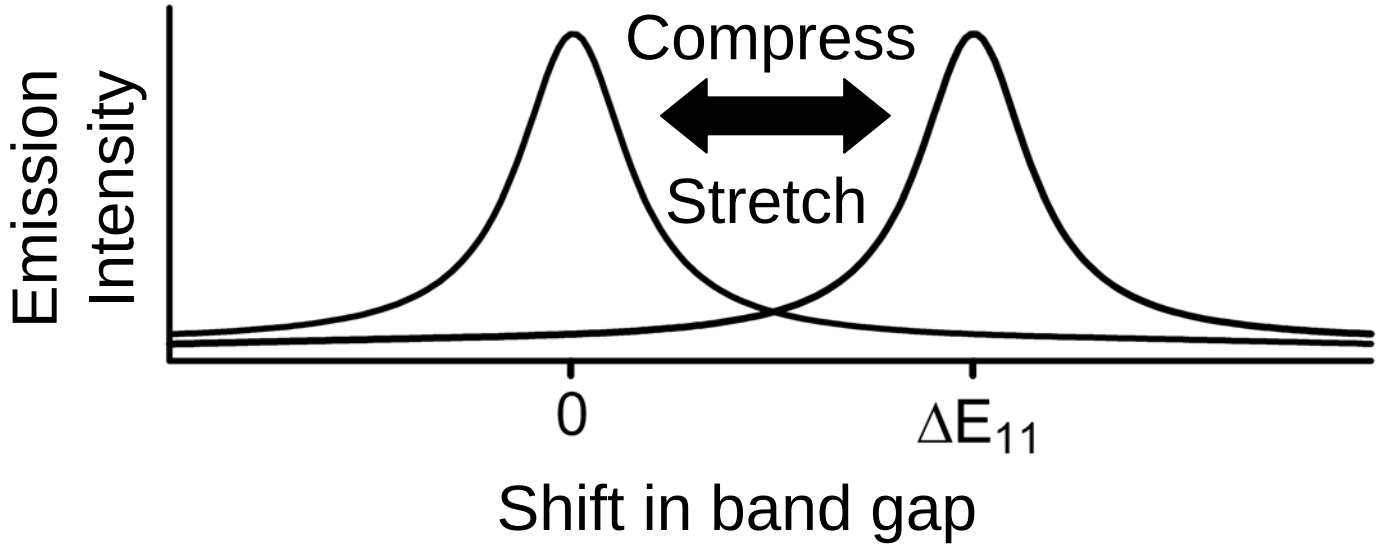
Axial strain alters the nanotube's band gap and causes spectral shifts





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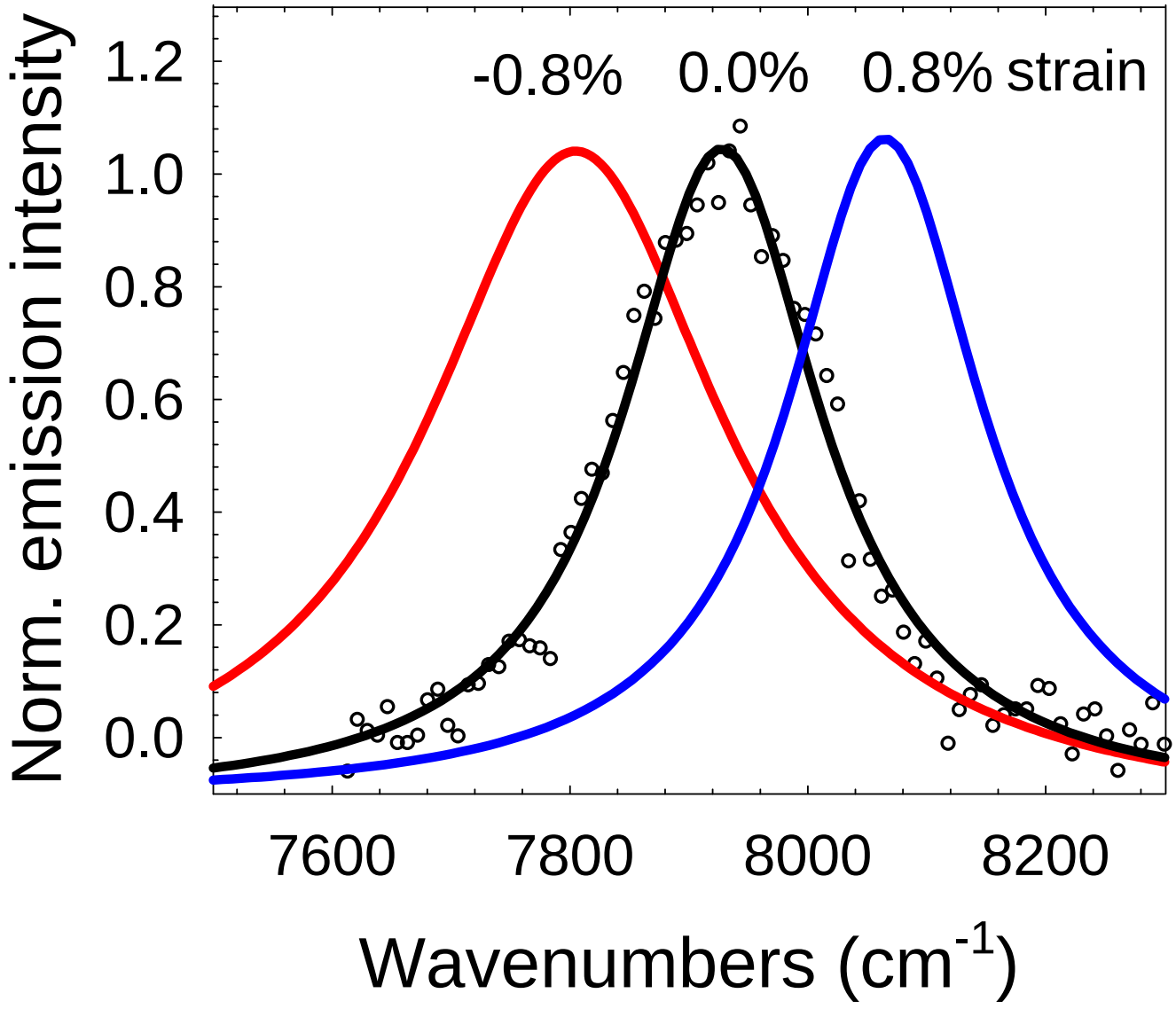
Fluorescence shifts in a single SWCNT



(8,7) nanotube

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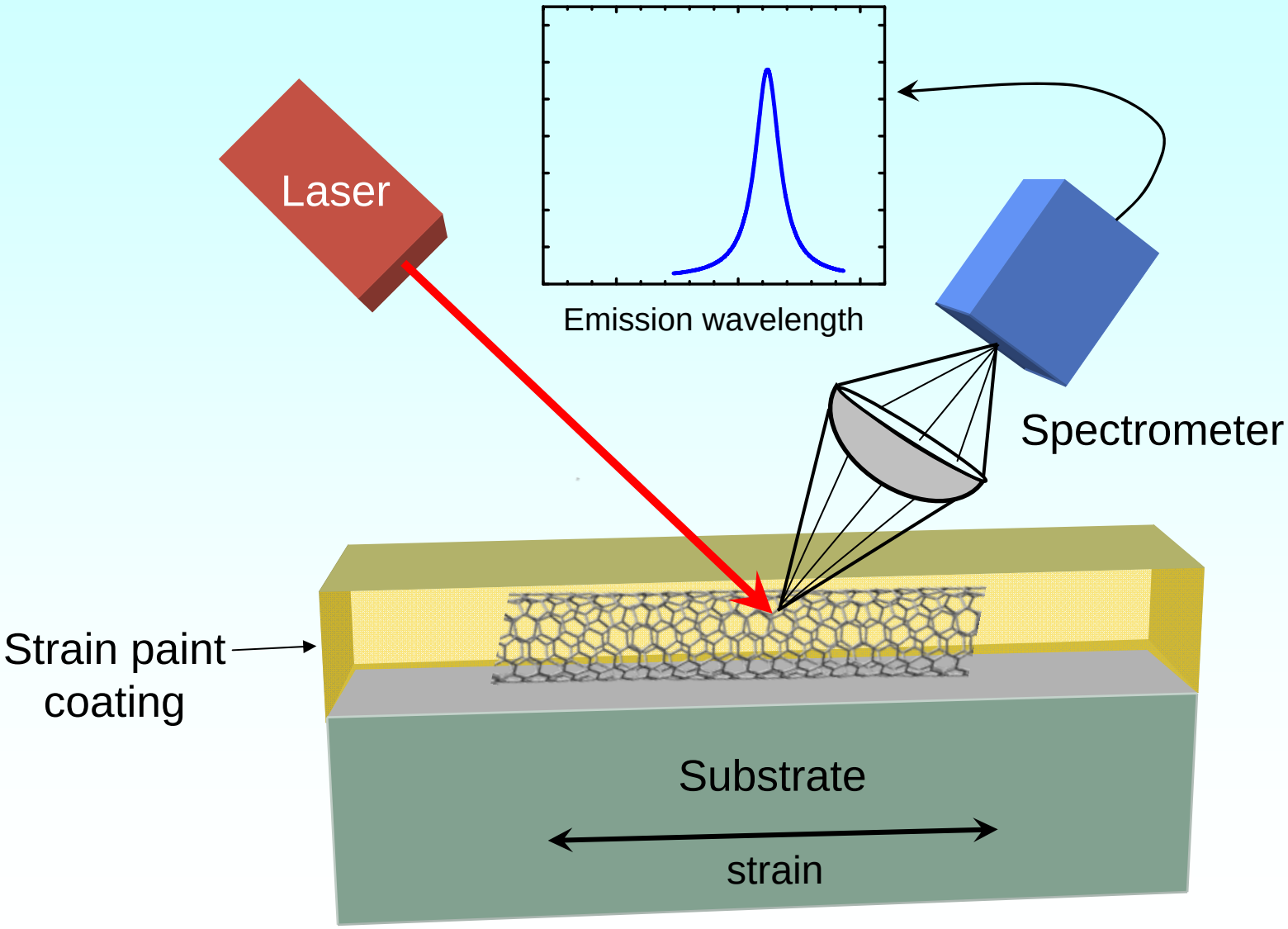
Basic scheme for non-contact optical strain measurement



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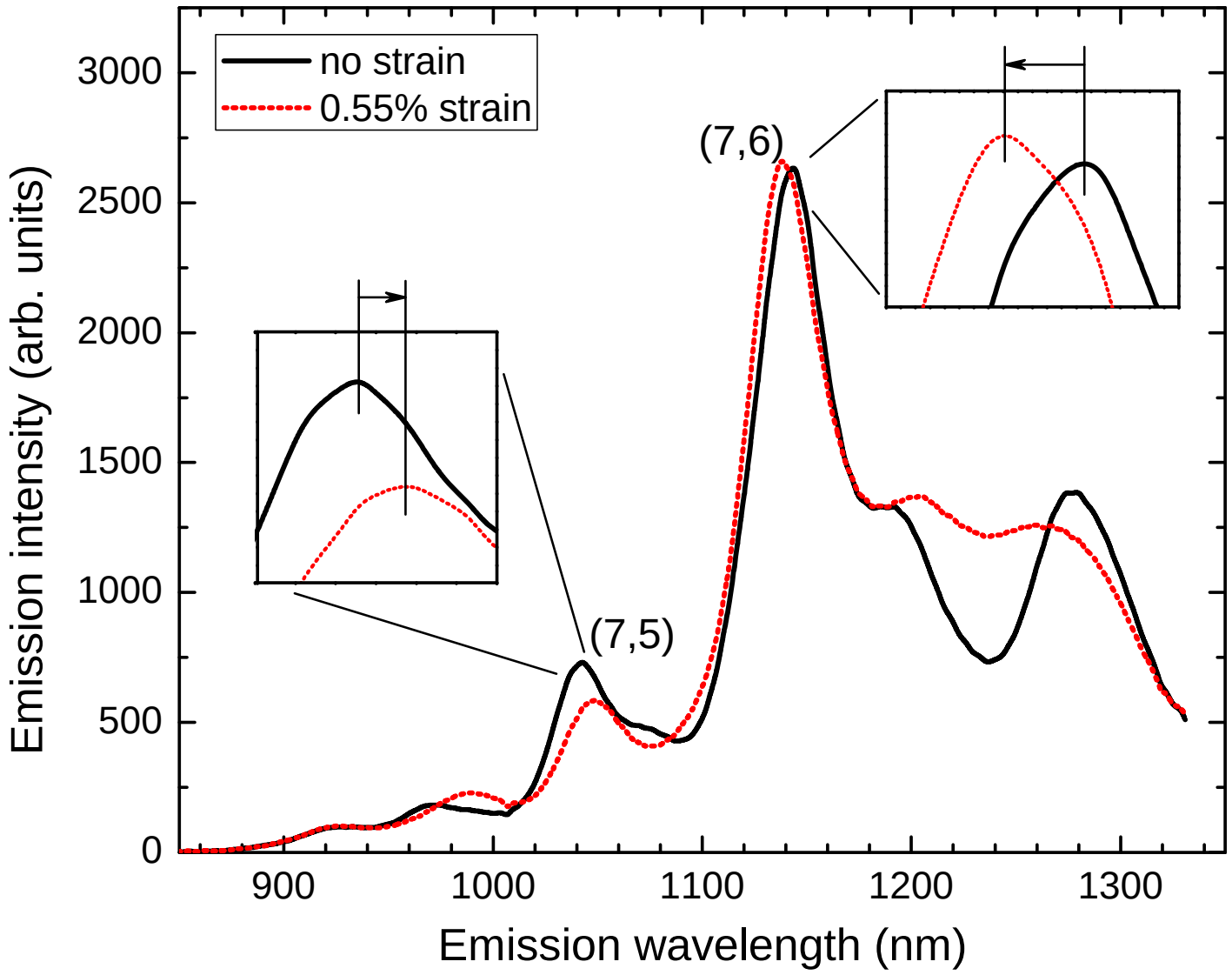
Strain-induced fluorescence shifts apparent from SWCNT/polyurethane coating (3-layer spin coat)



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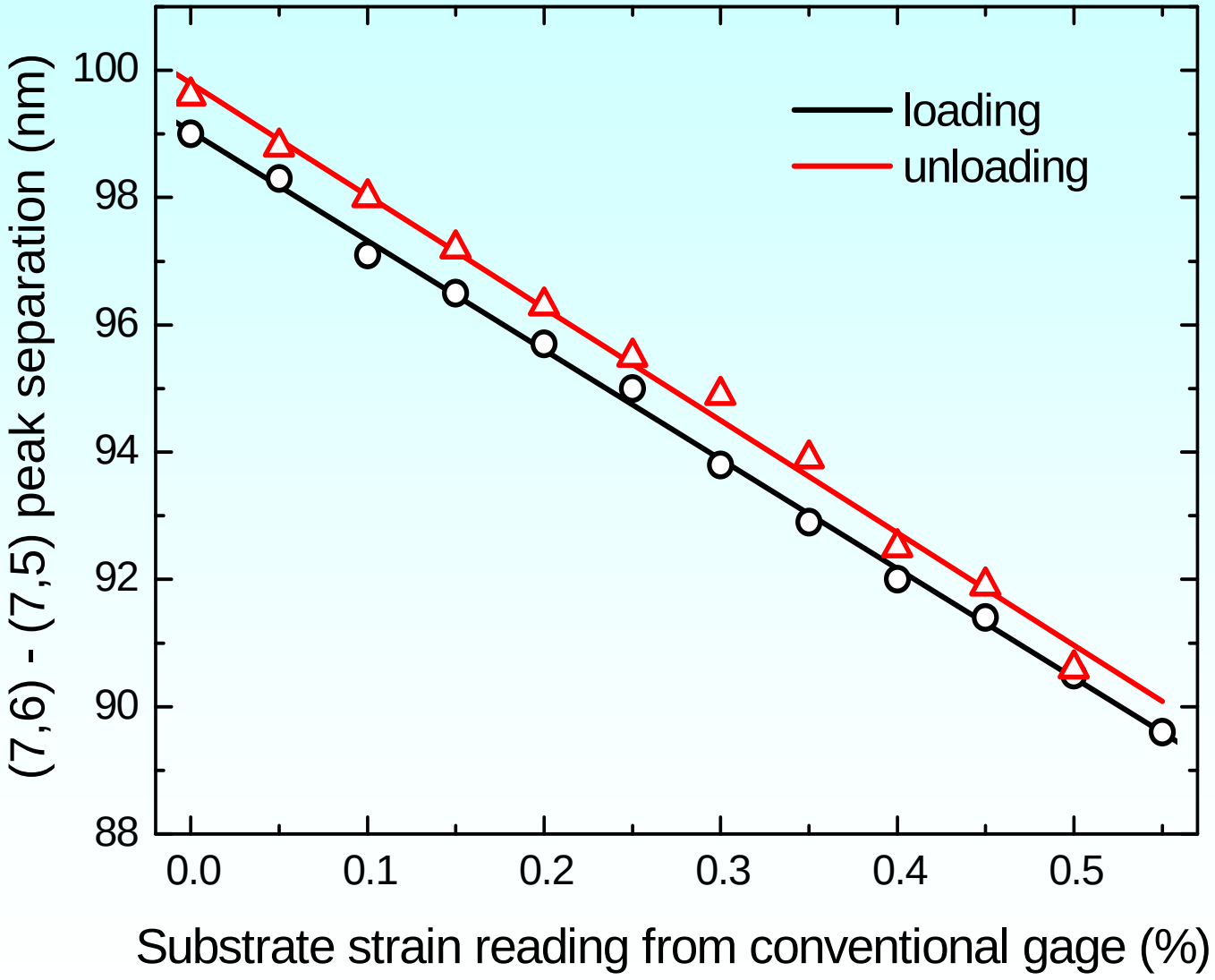
Spectral strain measurement using SWCNT / polyurethane coating



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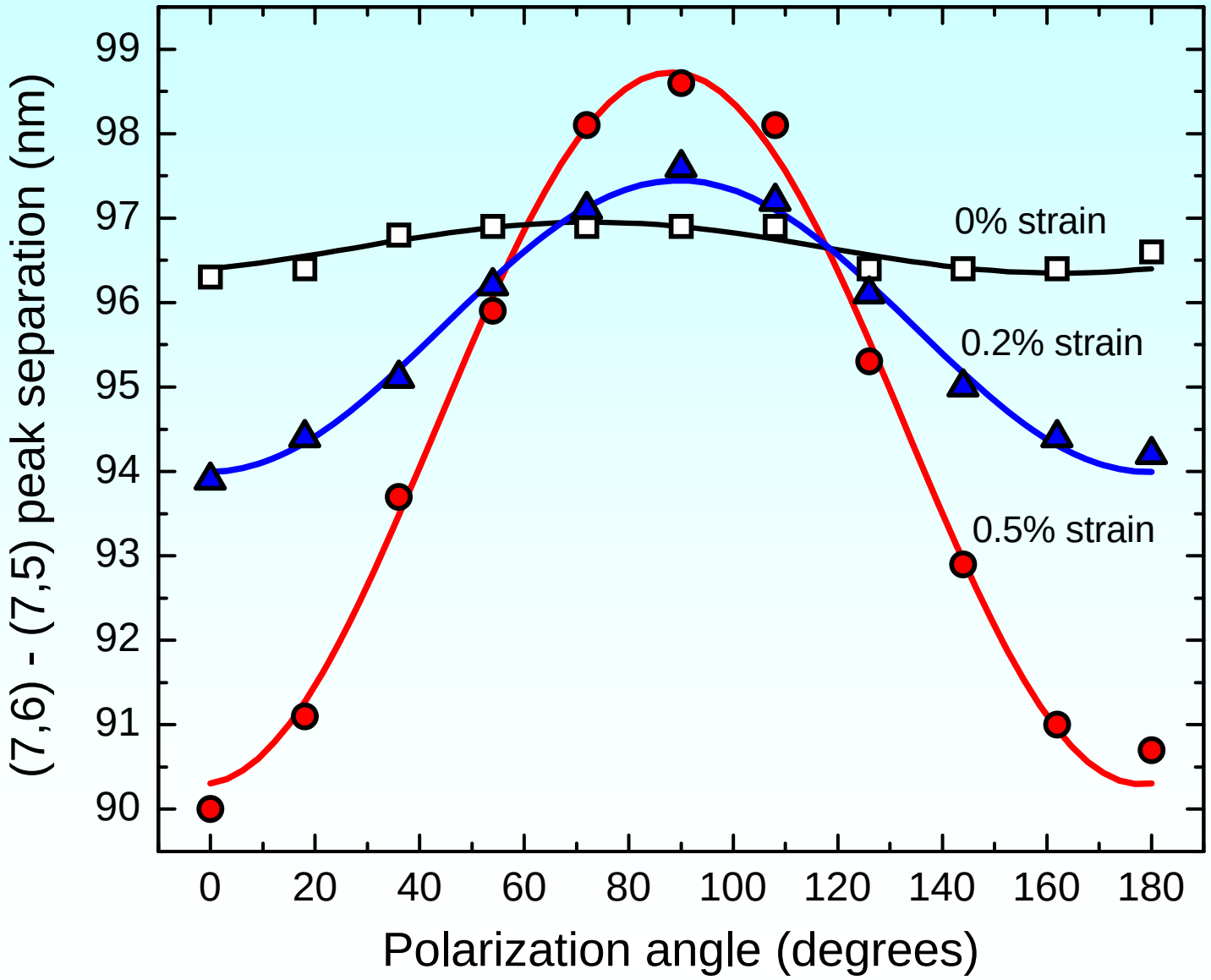
Rotate laser polarization to find the axis of strain



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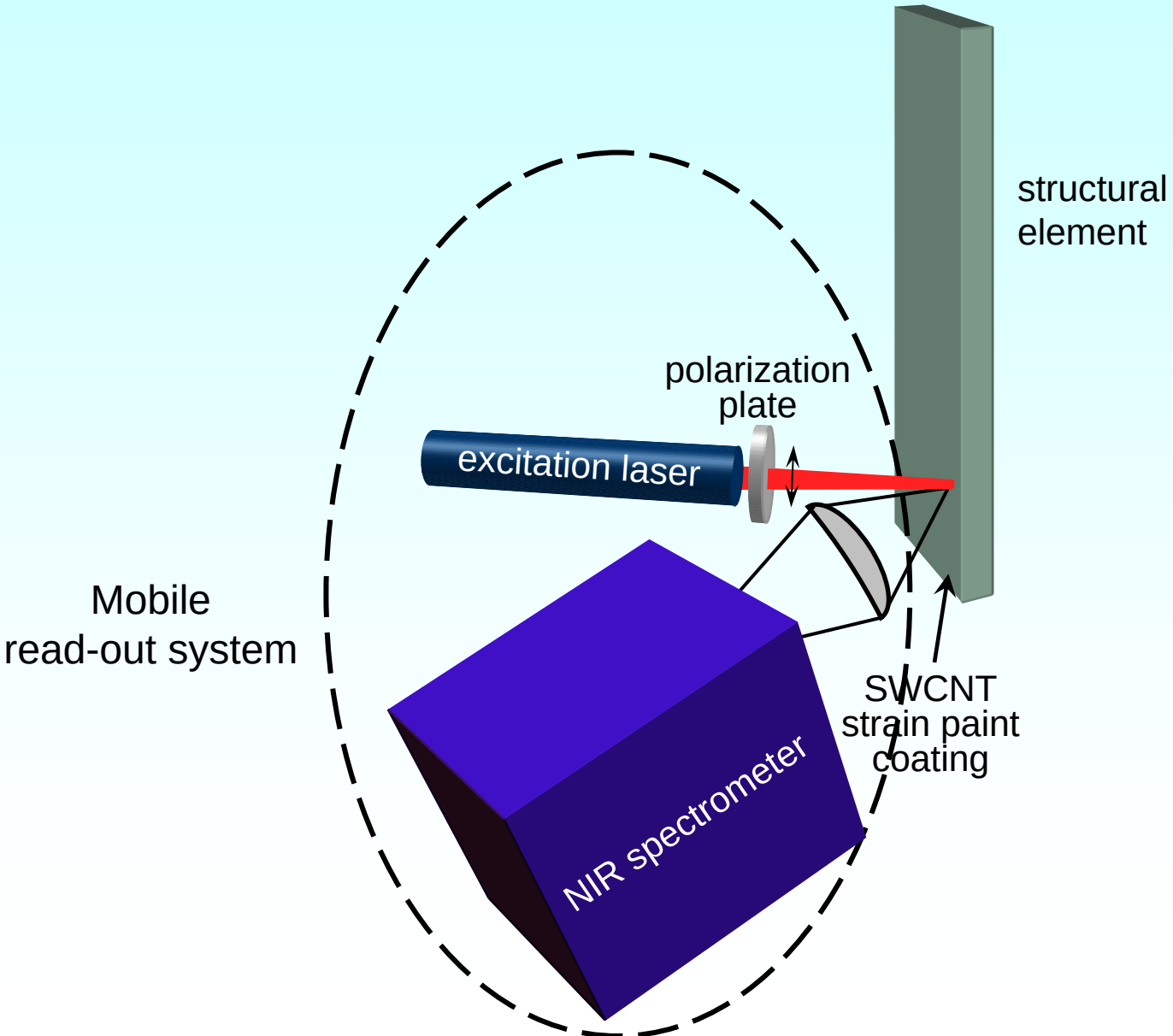
Field measurement scheme for non-contact strain measurements



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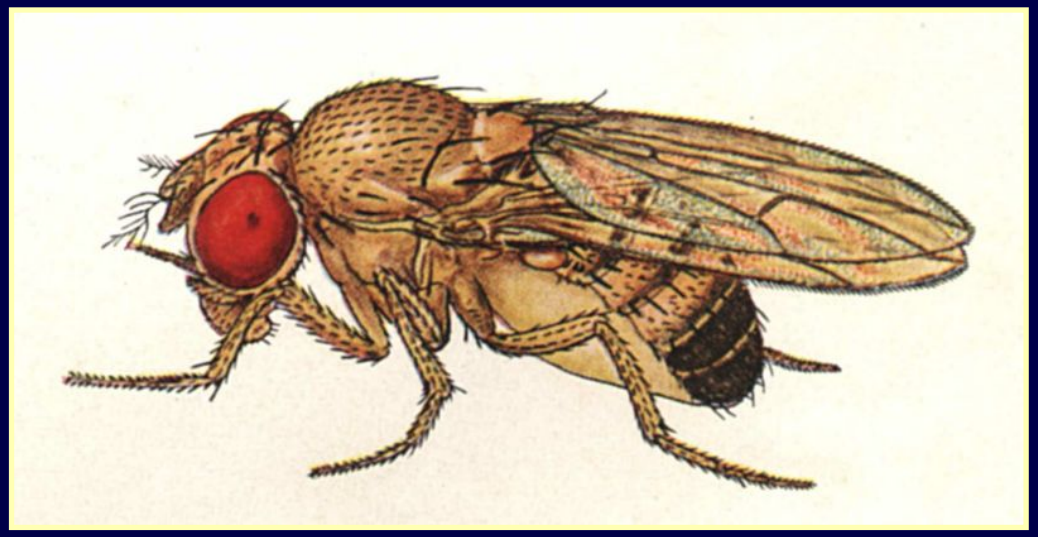
Fluorescence Studies of SWCNTs in Fruit Flies (Drosophila melanogaster)



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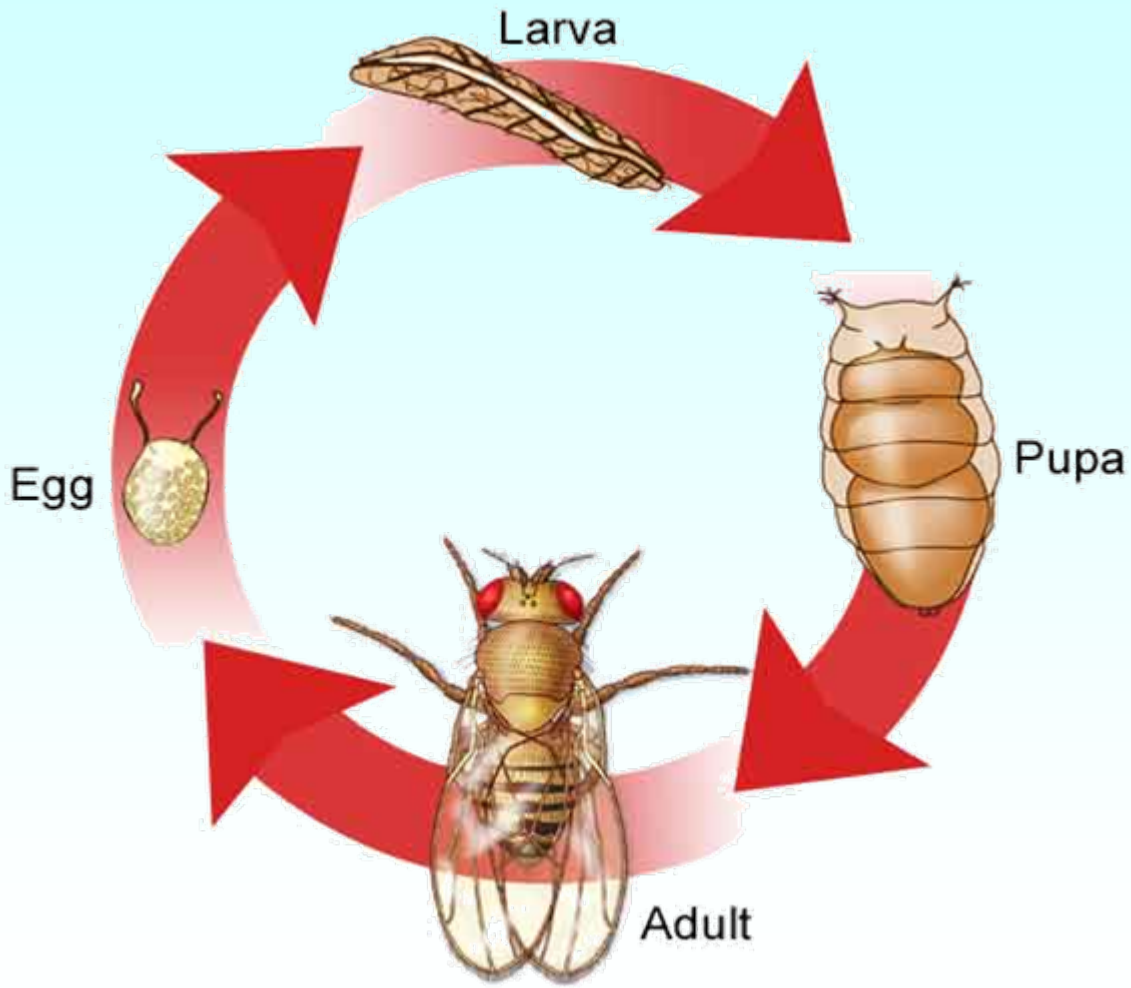
Drosophila life cycle



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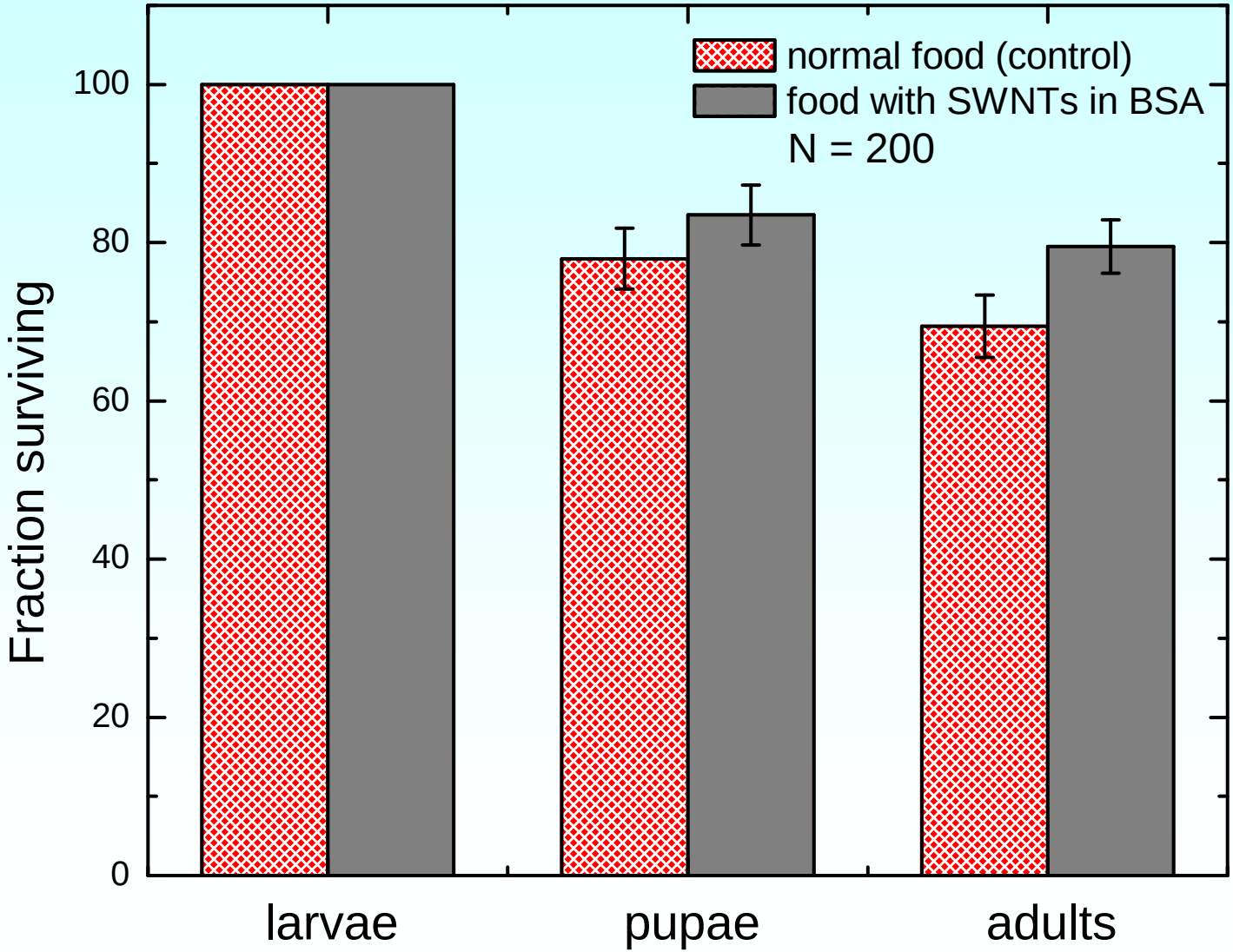
Drosophila viability not impaired by nanotubes in food



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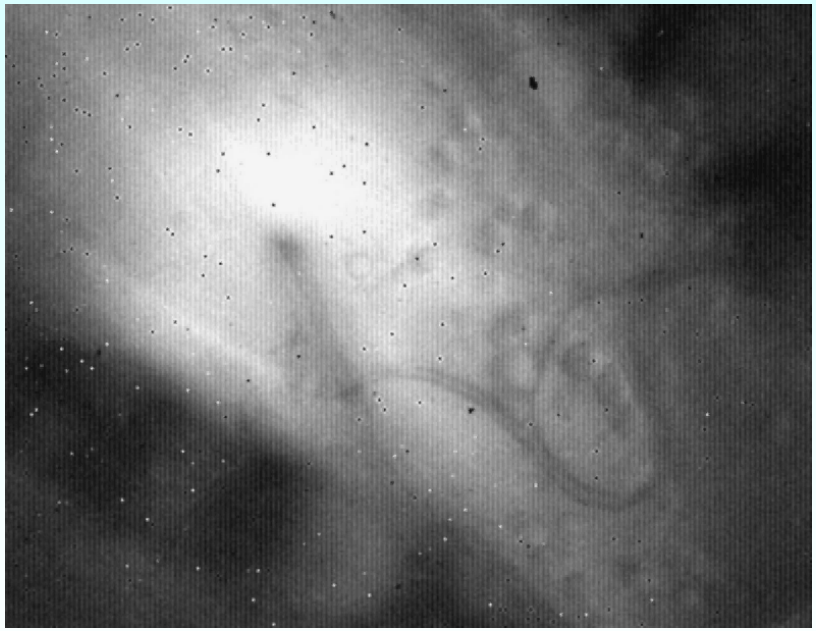
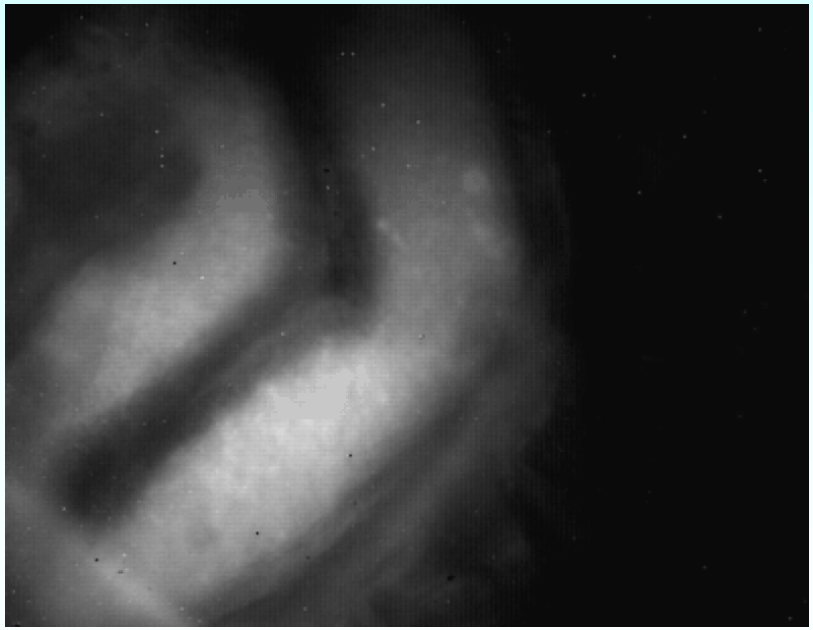
Fluorescence of SWCNTs inside gut of a living Drosophila larva





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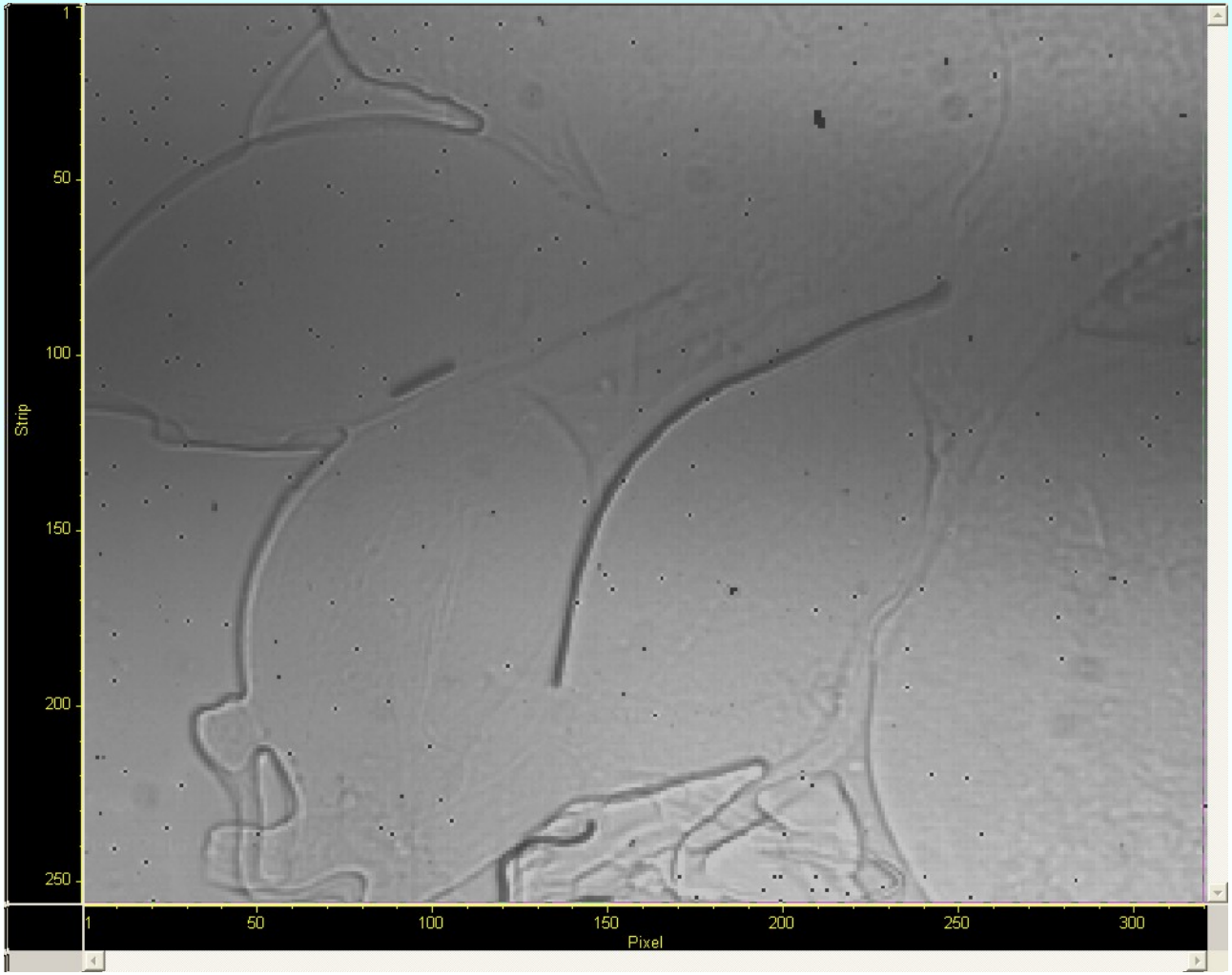
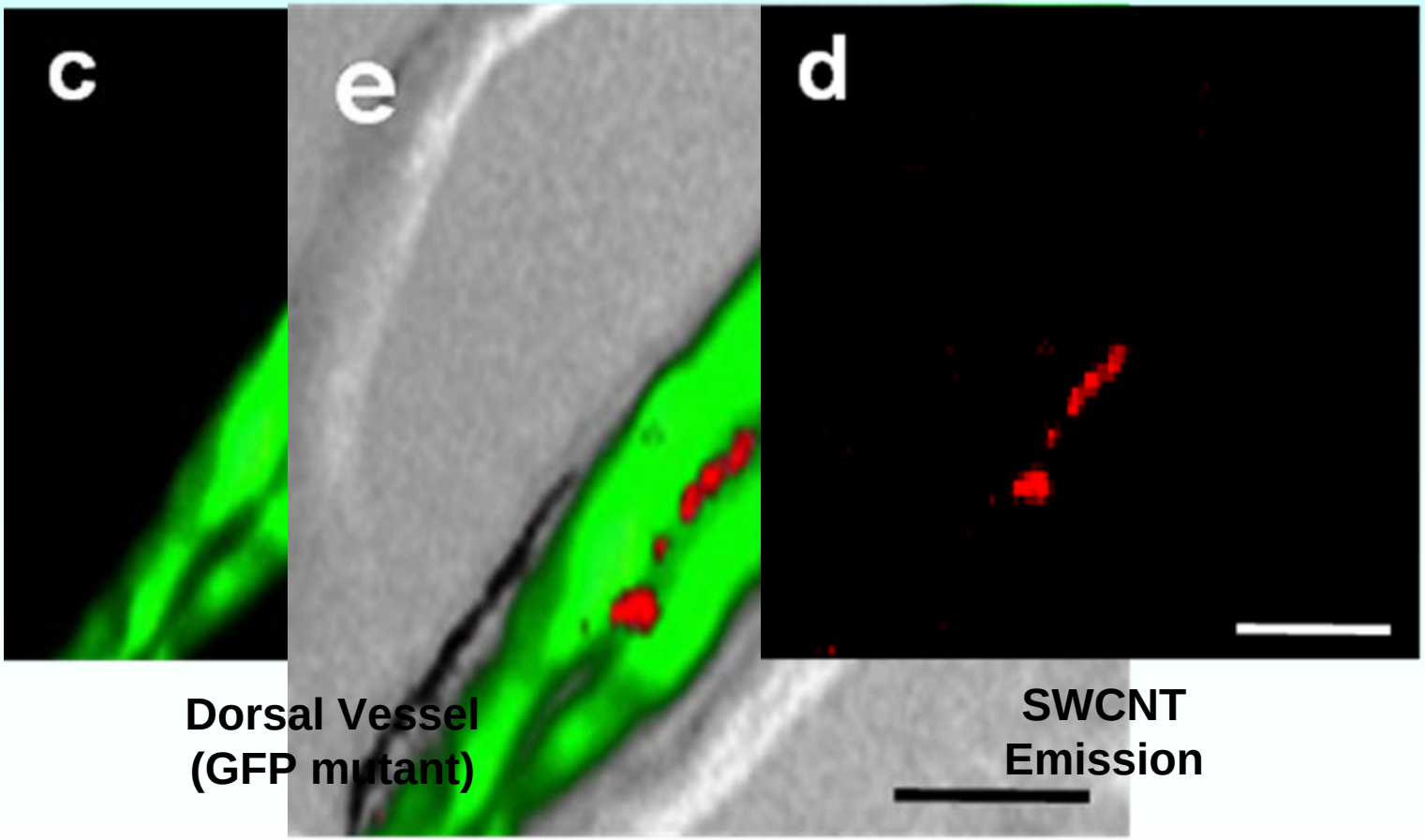
SWCNTs in the dorsal vessel of dissected Drosophila (fruit fly) larva after oral exposure



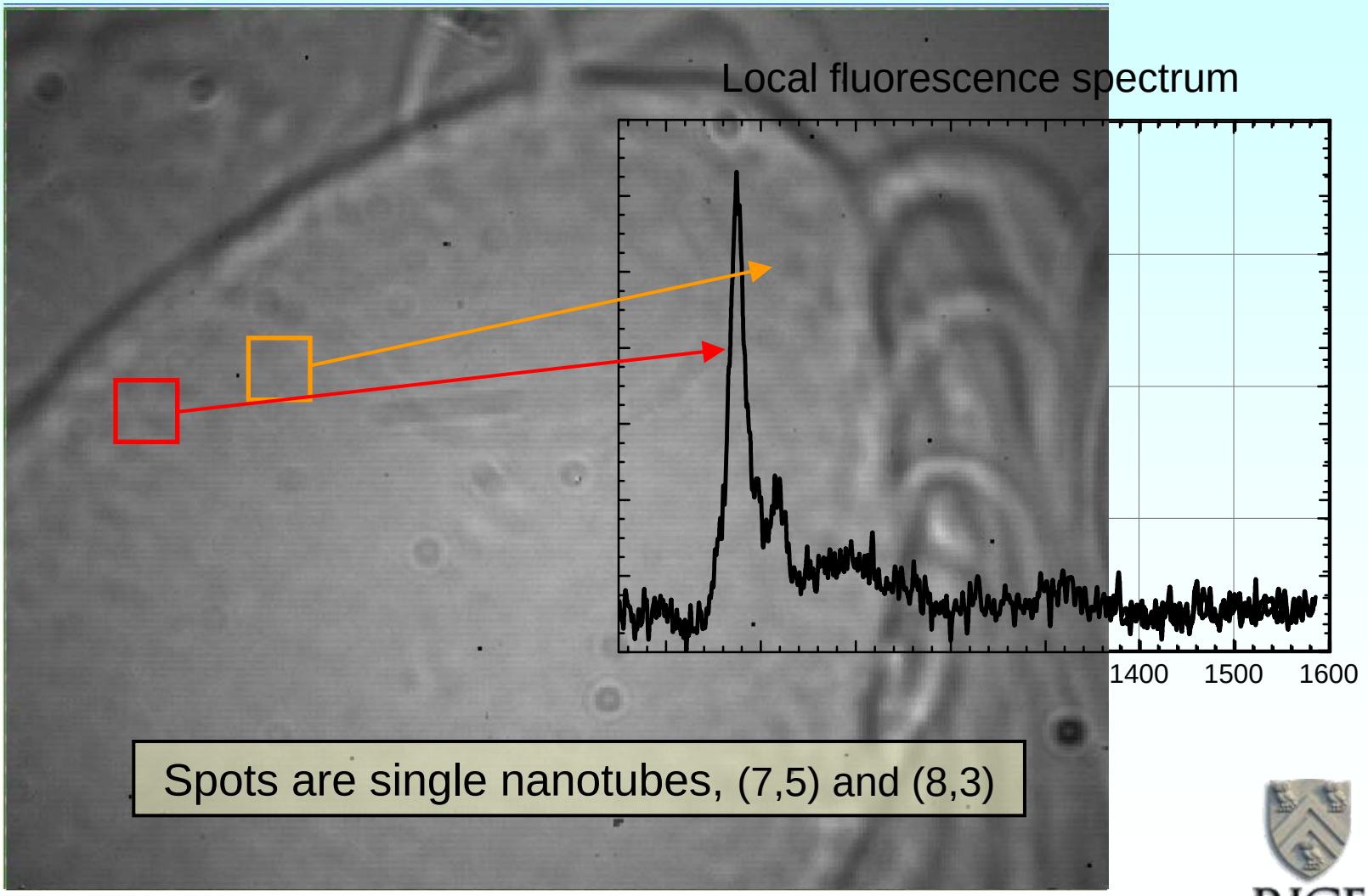
RICE

SWCNTs in the dorsal vessel



RICE

Dissected brain tissue of Drosophila larva fed with SWCNT-yeast paste



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Support

NSF Chemistry Division

Welch Foundation

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