The Chemistry of Single Walled Carbon Nanotubes

Applications to nanotube separation and biomolecule detection

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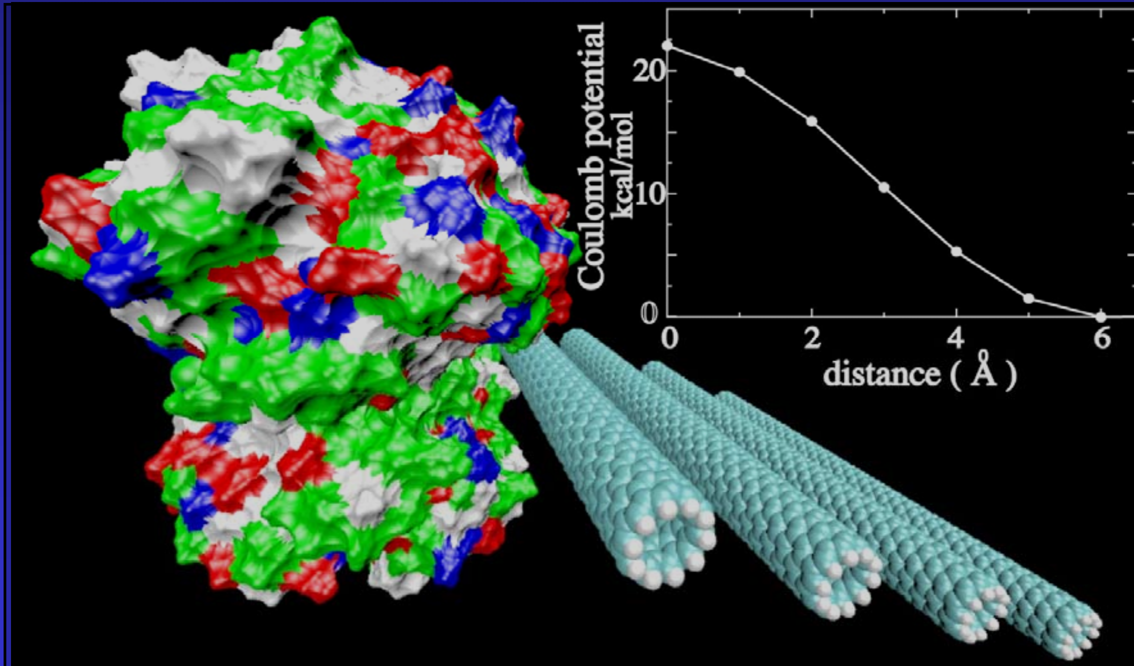

Department of Chemical & Biomolecular Engineering
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Outline

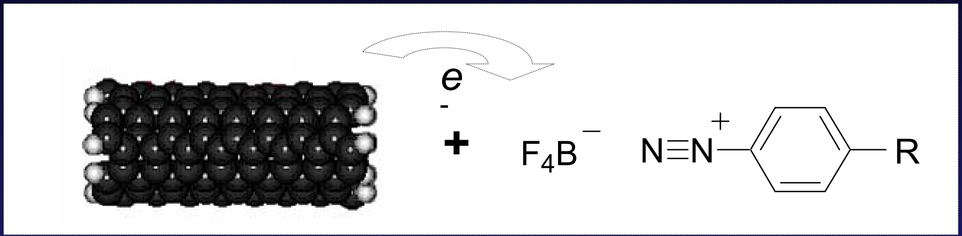
(n,m) selective, covalent chemistry of single walled carbon nanotubes

- Mechanism of electronic sensitive reactions
- Separation and sorting carbon nanotube by electronic type

Single walled carbon nanotubes as near infrared fluorescent biosensors

- Nanotube sub-cellular “molecular beacons”
- Tissue implantable biomedical devices

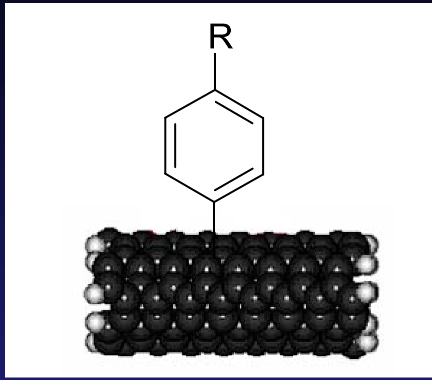
(n,m) Selective Chemistry on SWNT



M. S. Strano, C. Dyke, M. Usrey, el. al. Science 301 (2003) 1519-22

selective covalent reaction

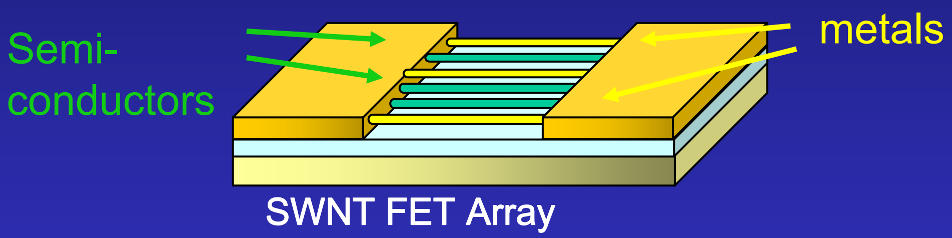
Rate = f(*n,m*)



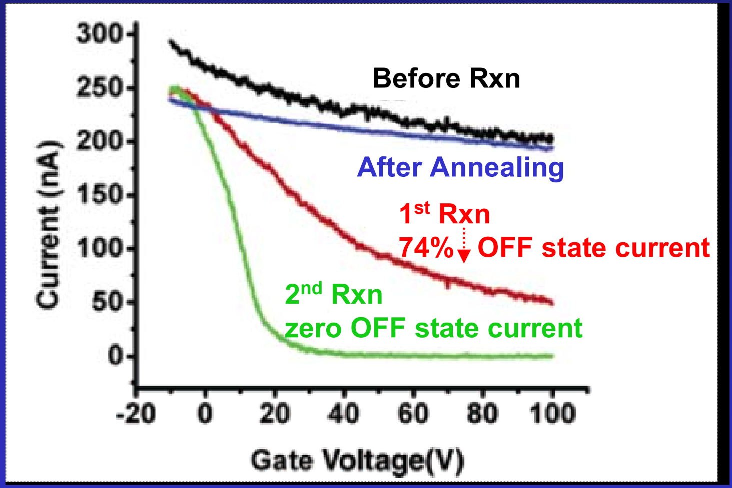
On-chip Modification of SWNT FETs

Functionalization carried out directly on SWNT array

- **ON / OFF current approaches 10^5**

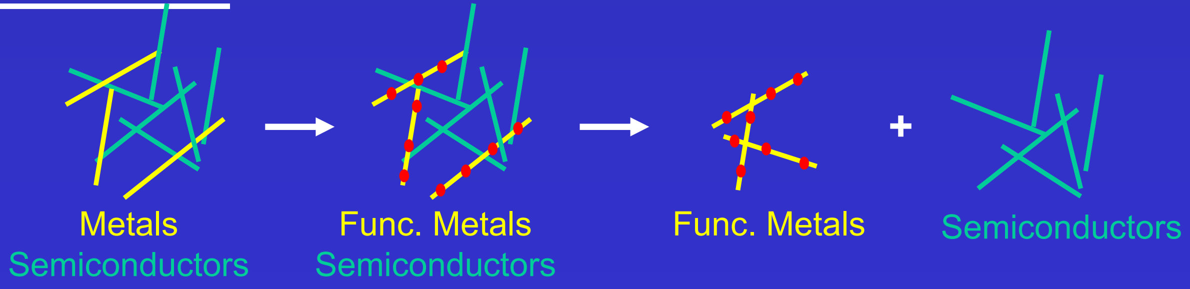


An, L., et. al. *J. Am. Chem. Soc.* **2004**, *126*, 10520.
Balasubramanian, K., et. al. *Nano Lett.*, **2004**, *4*, 827.
Wang, C., et. al. *J. Am. Chem. Soc.* **2005**. *127*, 11460.

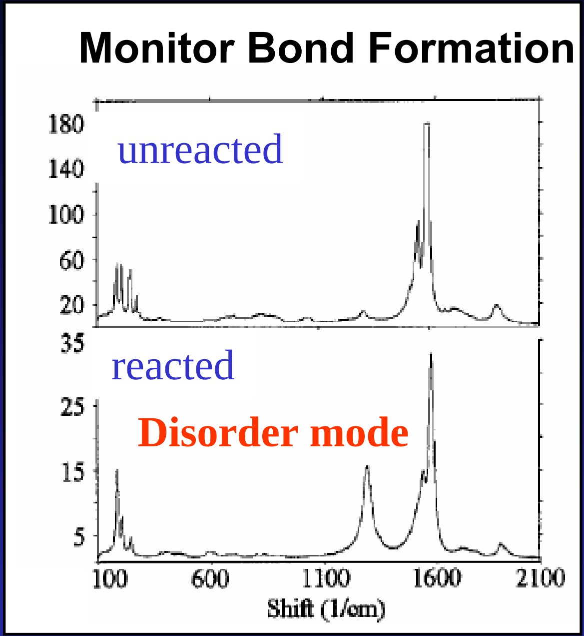


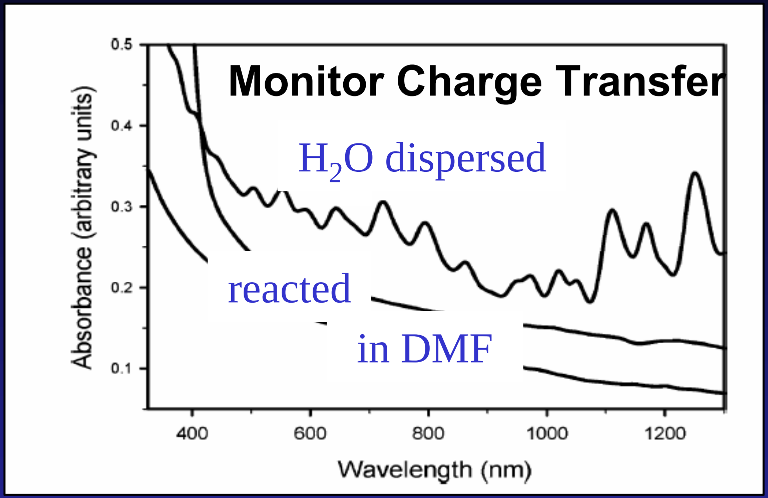
Scalable (n,m) Separation Method

Exploitation of functional group for preparative scale (n,m) separation

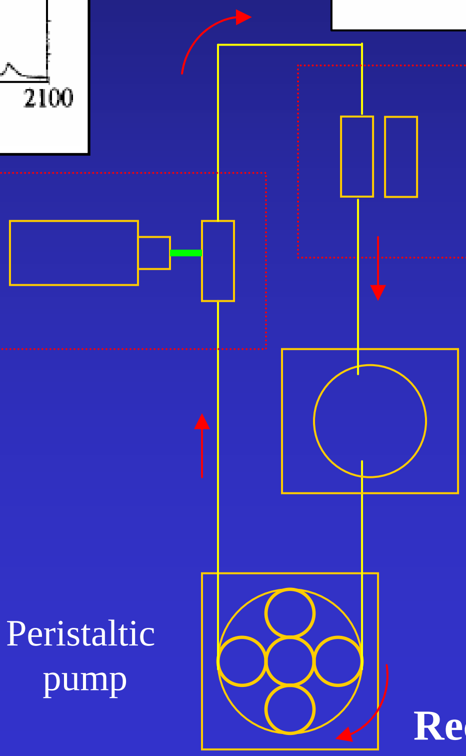


Apparatus for Studying SWNT Chemistry





Raman Spectrometer
532 nm excitation



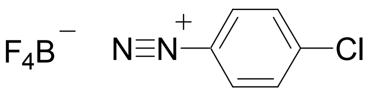
Spectrophotometer
UV-vis-nIR Absorbance
190 to 1800 nm

Reaction Vessel at 25 ºC
Stirred 3 neck flask
70 mL of aqueous dispersed SWNT
1% SDS/D_2O ~ 10 mg SWNT/L

Peristaltic pump

Sample Recirculation

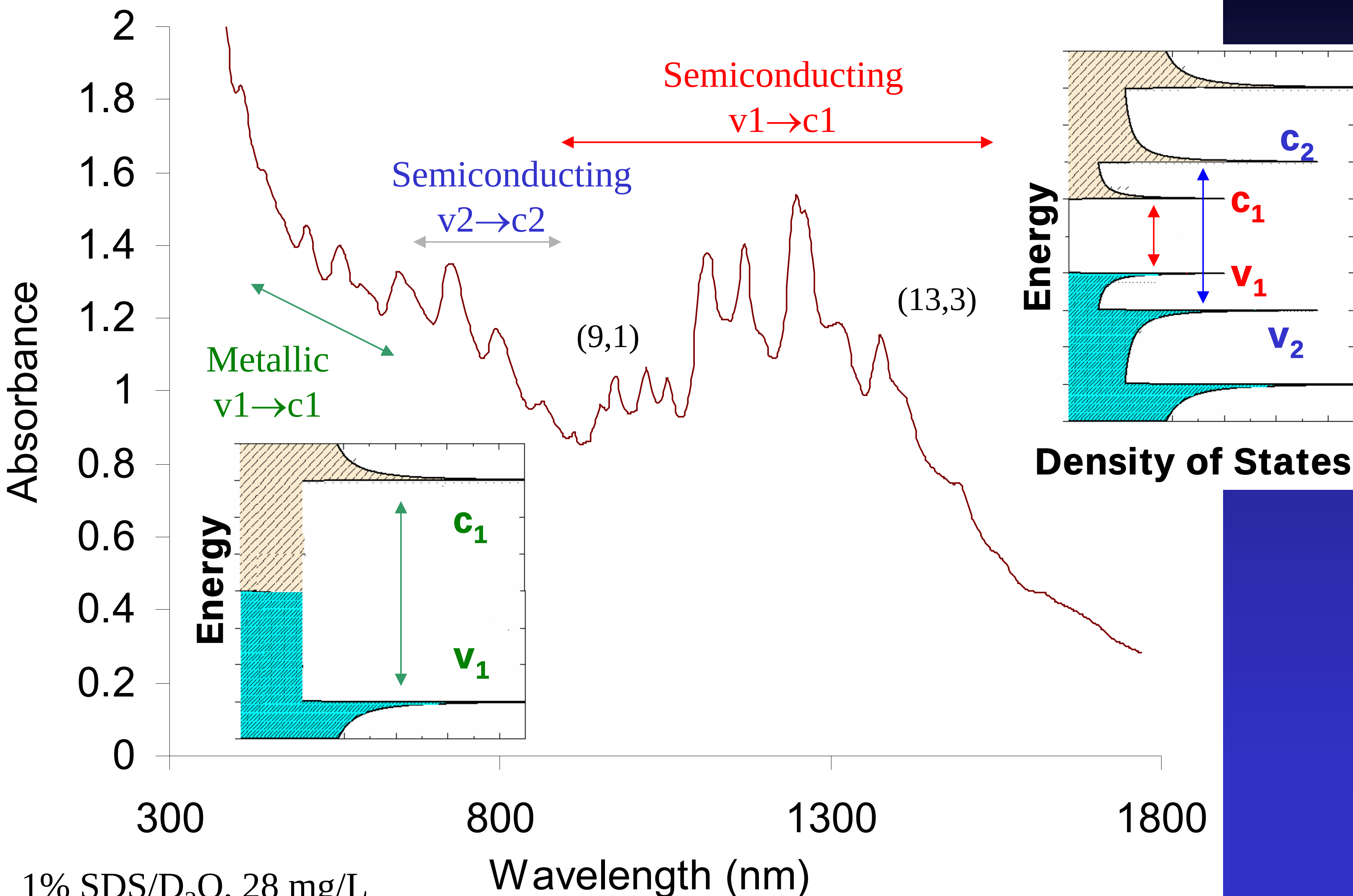
Reagent



0.25 mg/ml
Added in 100 μL aliquots

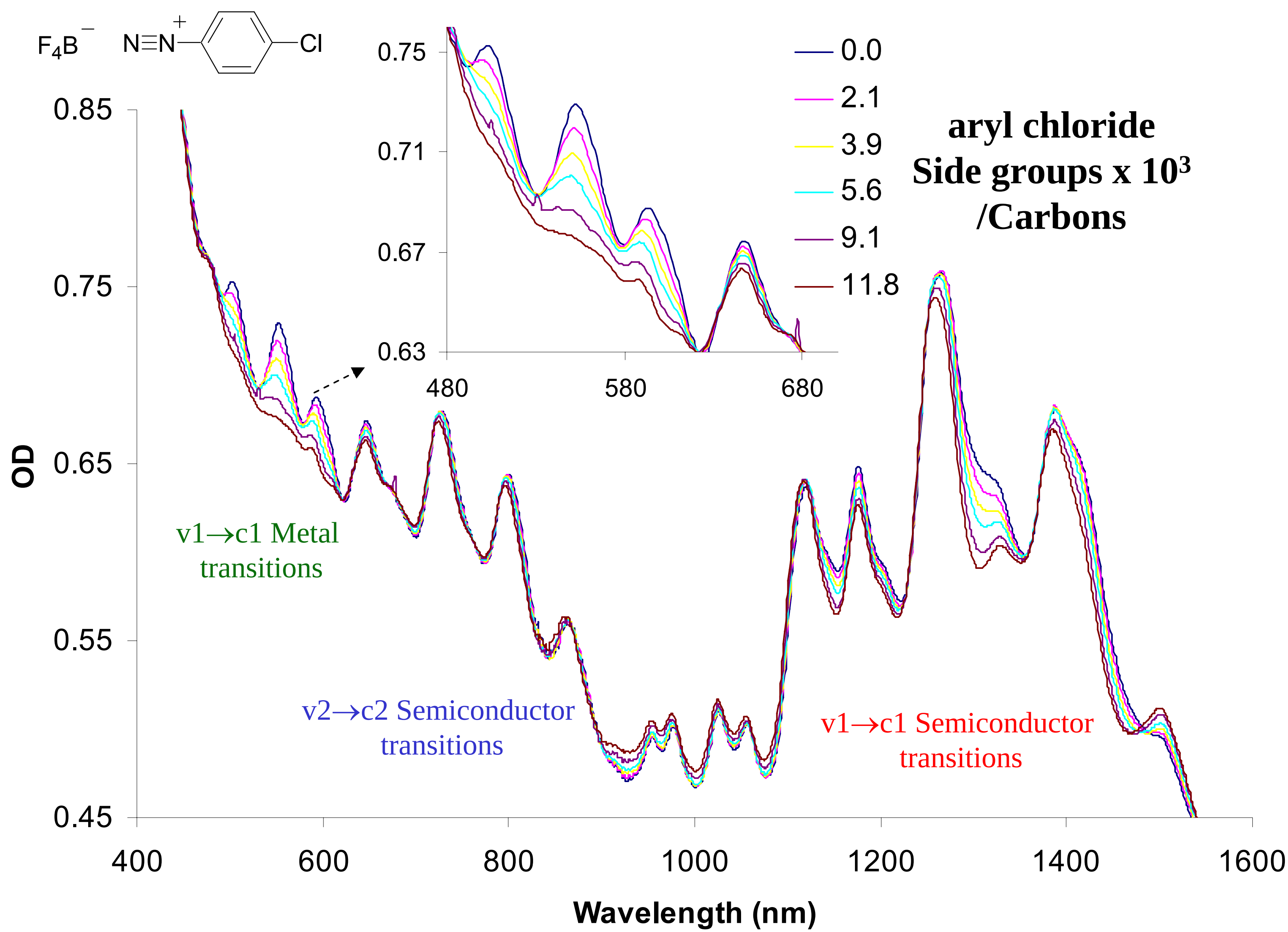
ML Usrey et al: JACS, 127 (2005) 16129-35.

Absorption Spectrum Allows Probing of Valence Electrons



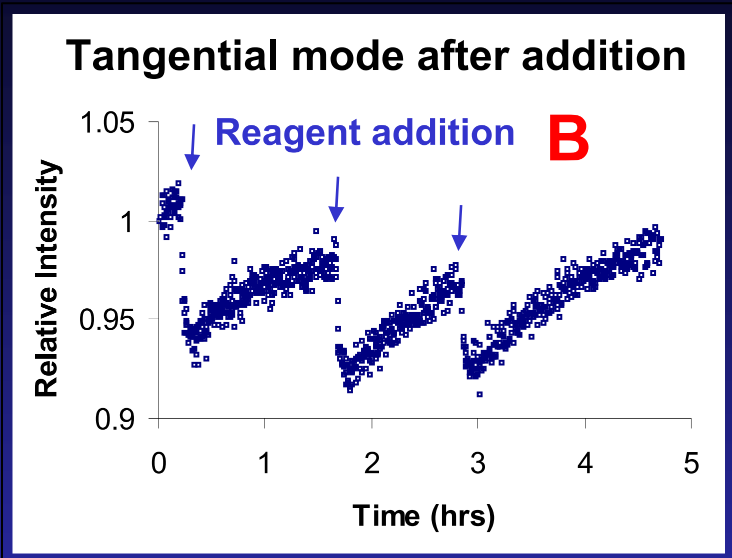
1% SDS/D_2O, 28 mg/L
exposed to air

Low Concentration: Selective Reaction of Metallic Nanotubes

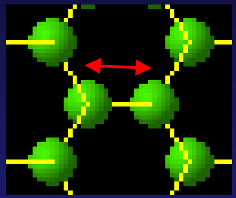


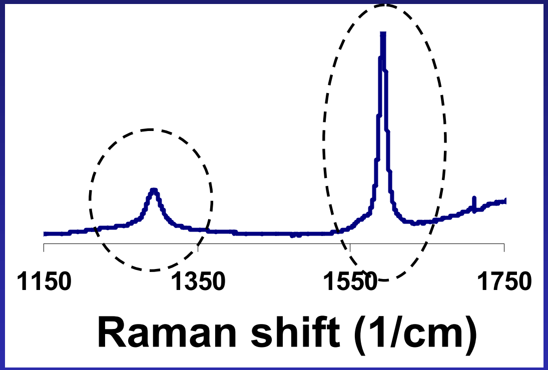
M. S. Strano, C. Dyke, M. Usrey, el. al. Science 301 (2003) 1519-22

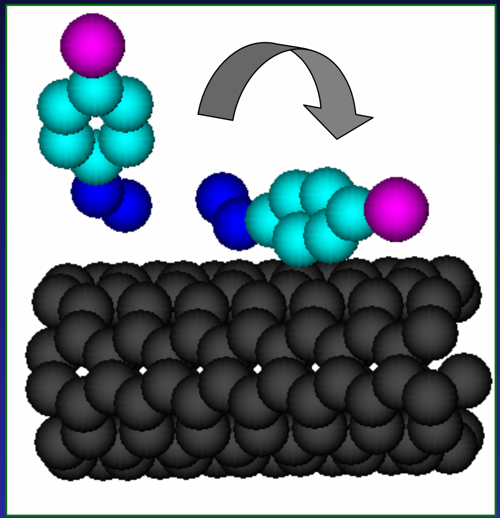
Two Step Mechanism from Raman Spectroscopy

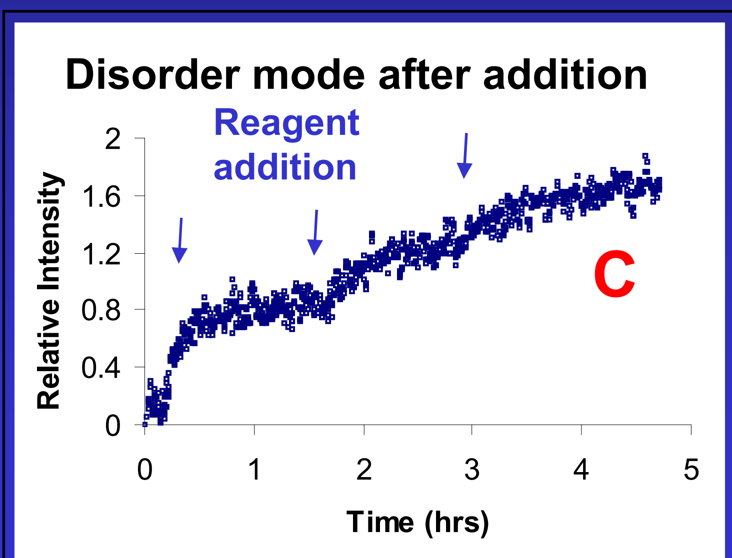


Measures electron withdraw

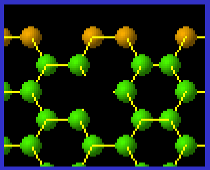


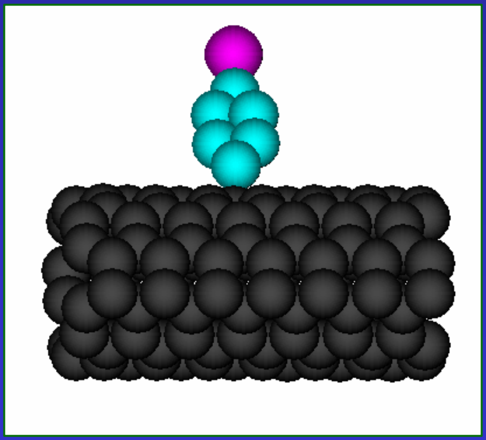






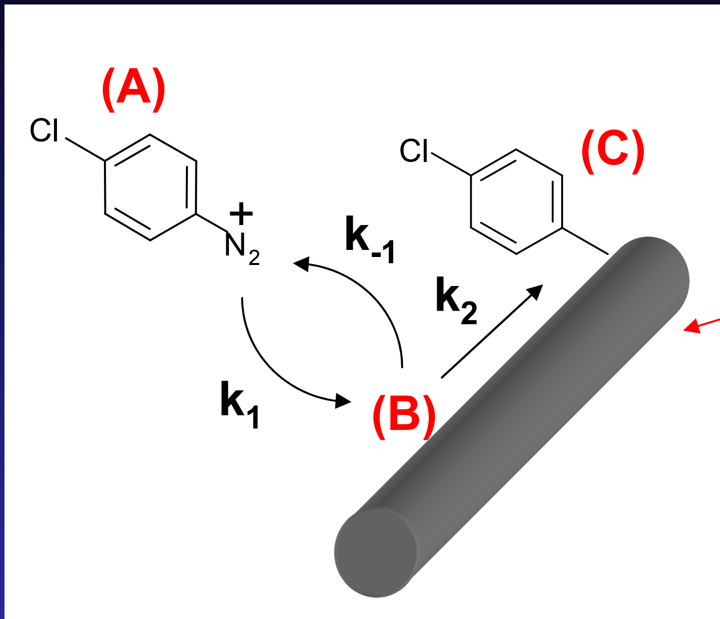
Measures sp3 "disorder" ∴ covalent bond formation





Looks like A → B → C

Understanding the Selective Mechanism

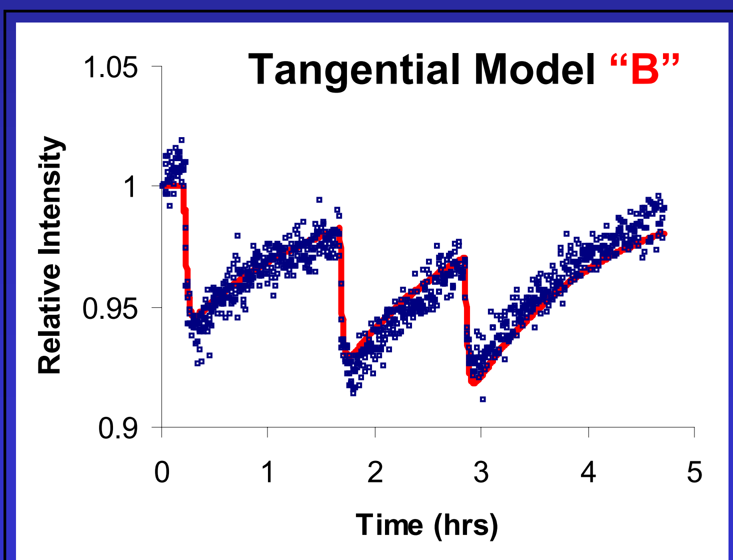


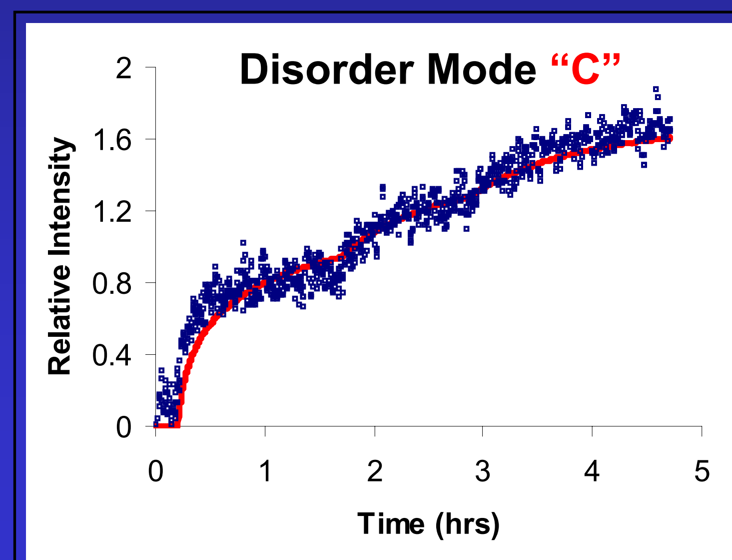
$$A + \theta \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B \xrightarrow{k_2} C$$

$$\theta = \theta_T - B[t] - C[t]$$

If coverage remains sparse,
$\theta[t] >> (B[t] + C[t],\quad k_{-1} \sim 0$

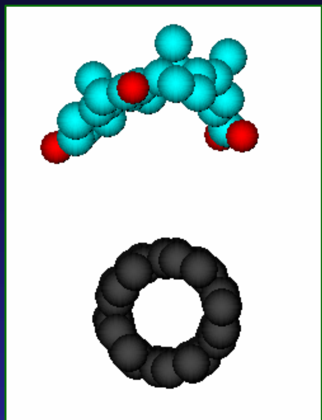
Resolves outstanding problems:
k_1 = selective and delocalized
k_2 = follows Pyramidalization





ML Usrey, ES Lippmann, MS Strano: JACS, 127 (2005) 16129-35.

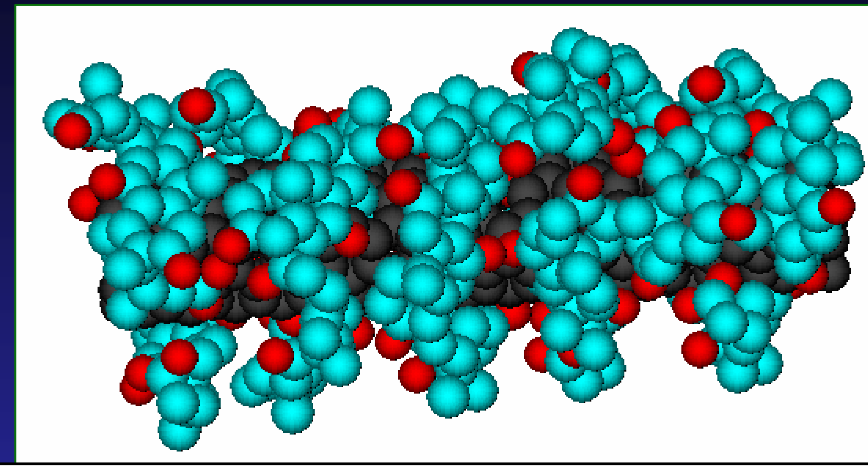
Further Evidence: Blocking the Second Step

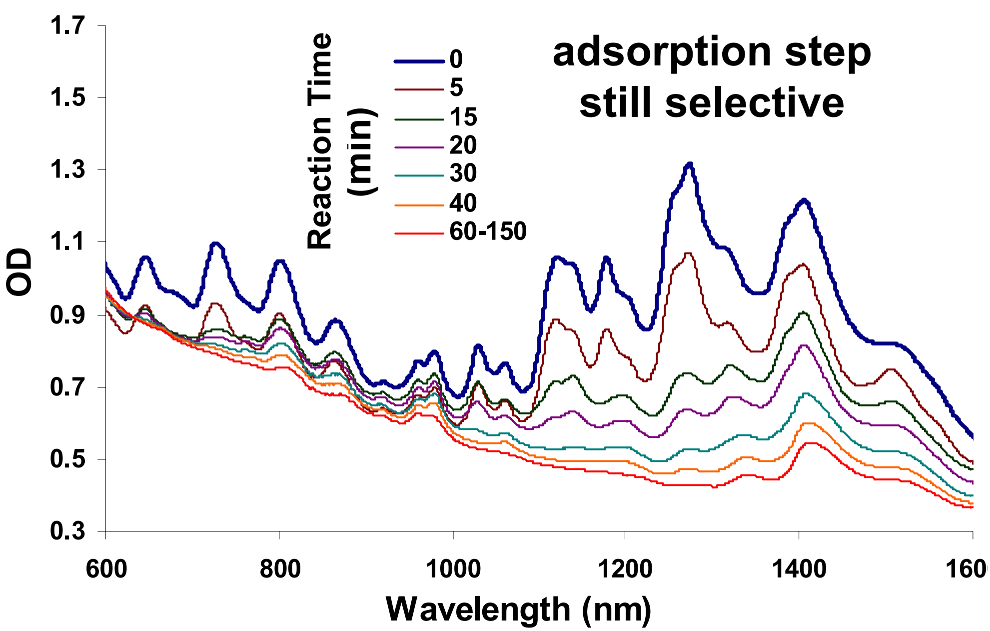


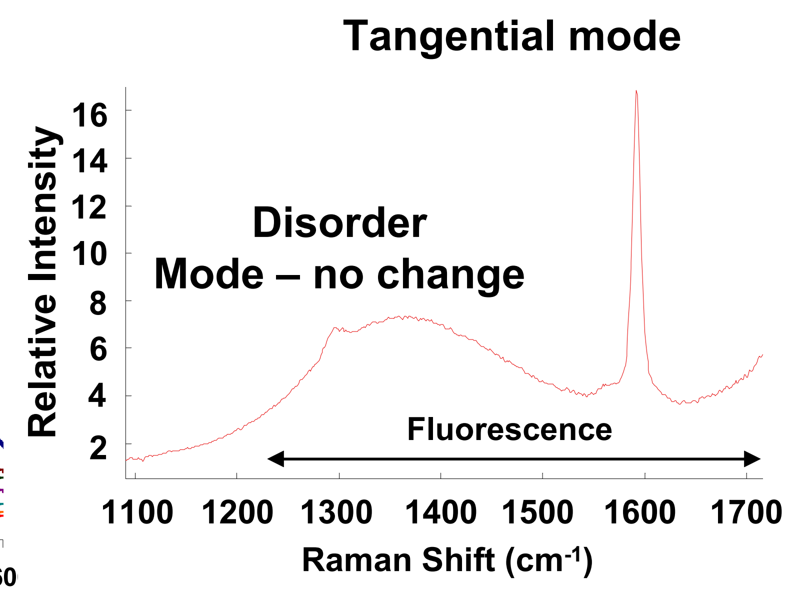
Sodium cholate:

closely packed adsorbed phase; steric hindrance

$A \rightarrow B \nrightarrow C$

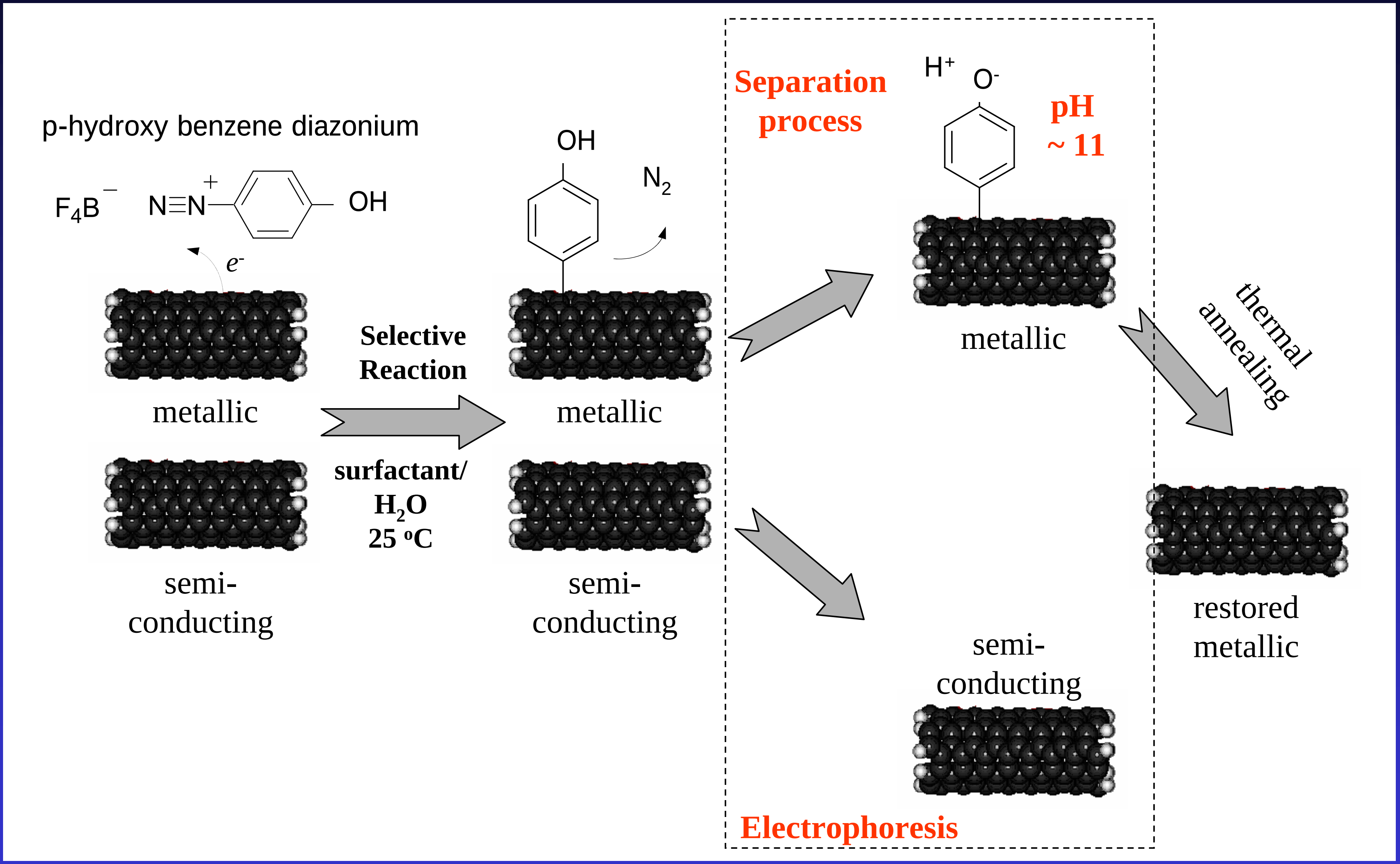






ML Usrey, ES Lippmann, MS Strano: JACS, 127 (2005) 16129-35.

Chemistry for Sorting Carbon Nanotubes

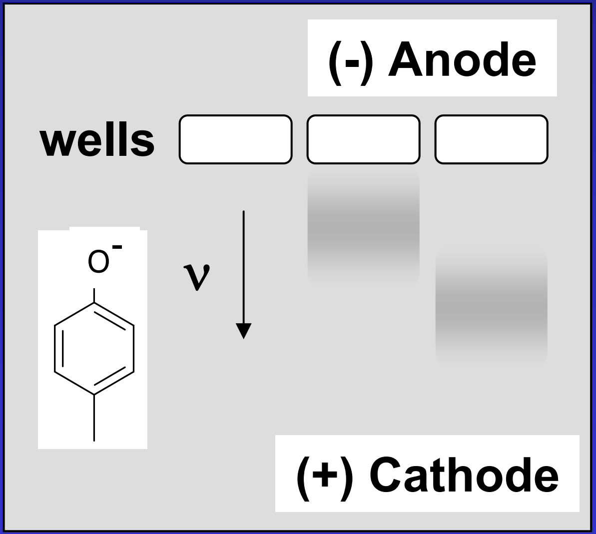


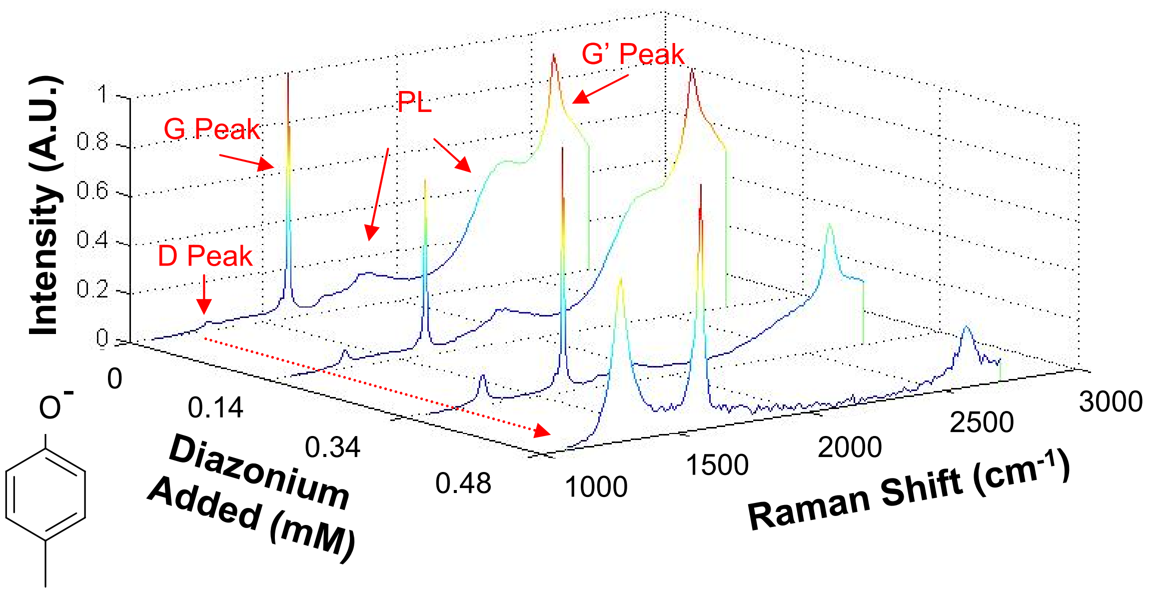
Usrey, M. A., Strano, M. S., in preparation (2006)

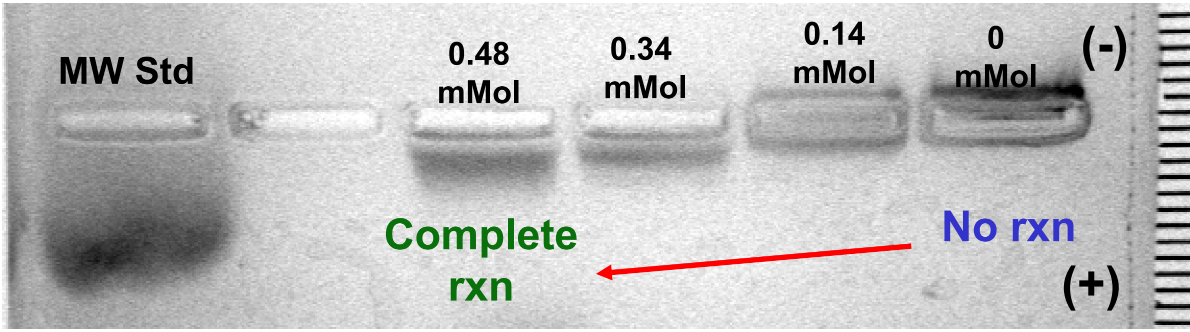
Chemistry Controls Electrophoretic Mobility

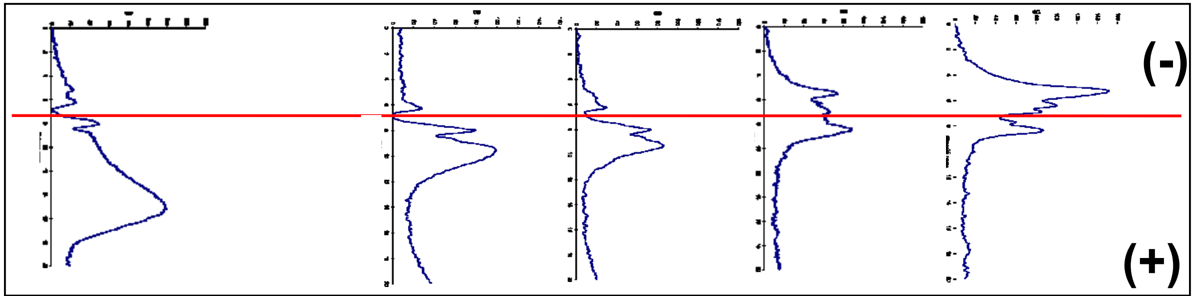
$\nu = (q/f)\,E$

ν = electrophoretic mobility
q = net charge
f = hydrodynamic factor
E = applied electric field









Outline

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Single walled carbon nanotubes as near infrared fluorescent biosensors

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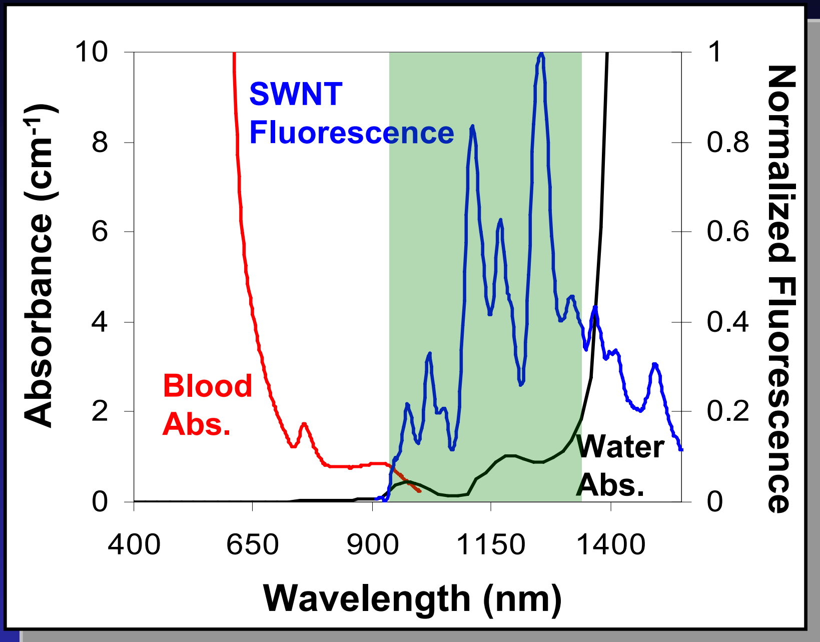
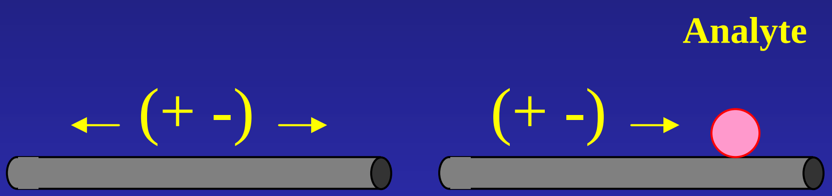
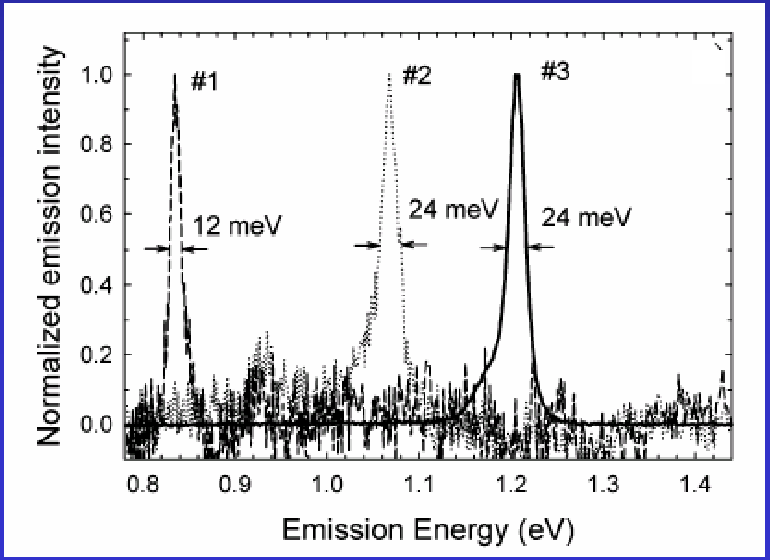
Advantages for Optical Sensing



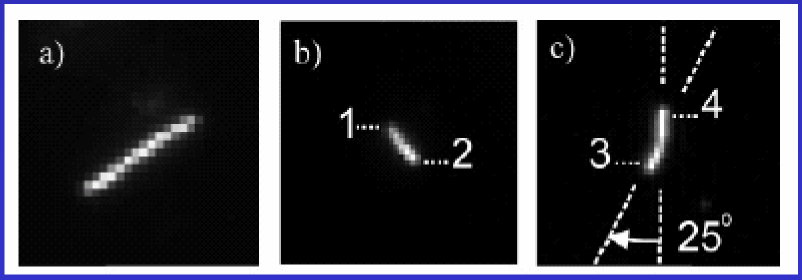
Semi-conducting single walled carbon nanotubes

- fluoresce in near infrared
- very photostable
- sensitive to environment





Single nano-particle spectroscopy = single molecule sensor

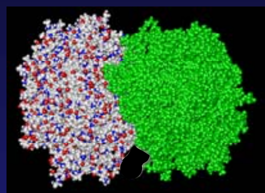


D. A. Tsyboulski, Nano Lett., Vol. 5, No. 5, 2005

Scheme for β-d-Glucose Sensor

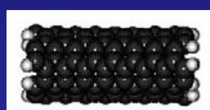
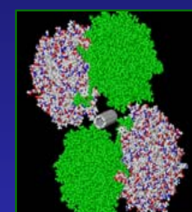
Two Step Synthesis

Glucose oxidase



Glucose + O_2 + H_2O $\xrightarrow{\text{(GOx)}}$ H_2O_2 + 1,5-gluconolactone

Step I: Immobilization of binding site (GOx) on SWNT

 + **(GOx)** $\xrightarrow{\text{Self assembly}}$ 

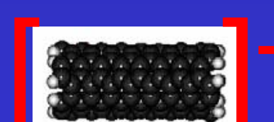
Colloidally stable
Nanotube-Glucose oxidase
complex

Step II: Coupling to electron transfer

$2[Fe(CN_6)]^{3-} + H_2O_2 \longrightarrow 2[Fe(CN_6)]^{4-} + 2(H^+) + 2e^- + O_2$

Ferricyanide — Ferrocyanide

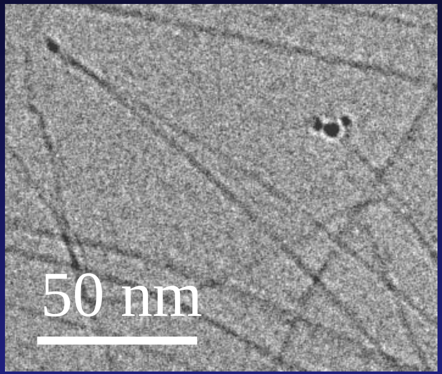
A nanotube redox couple:

 + e^- $\longrightarrow$  $\longrightarrow$ **Decrease in fluorescence intensity**

PW Barone, S Baik, DA Heller, MS Strano: Nature Materials 4 (2005) 86-92.

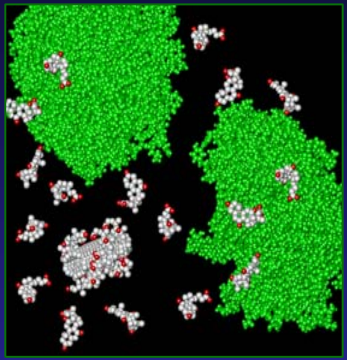
Step I: Immobilization of GOx Enzyme

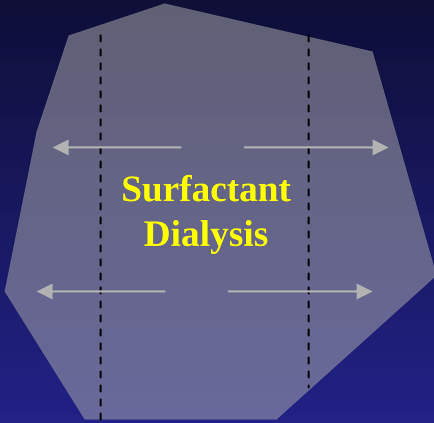
Band-gap fluorescence

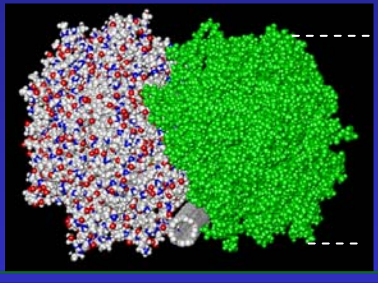


Cryo-TEM of individual nanotubes

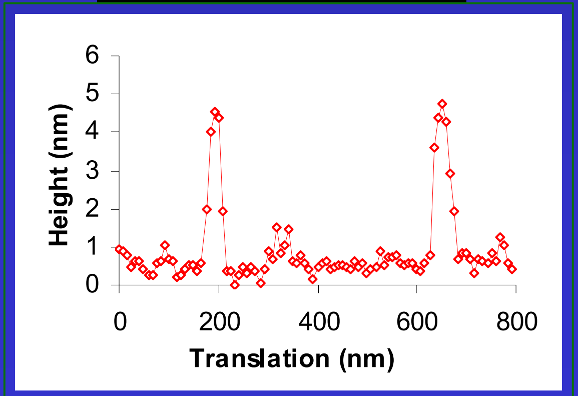
Add 1:200 Glucose Oxidase



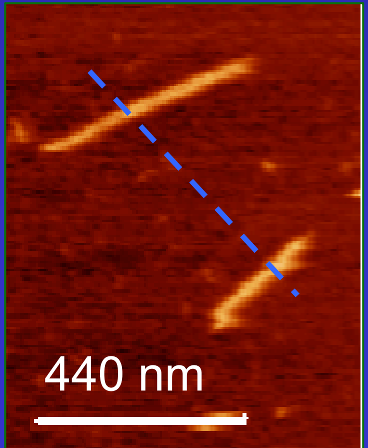


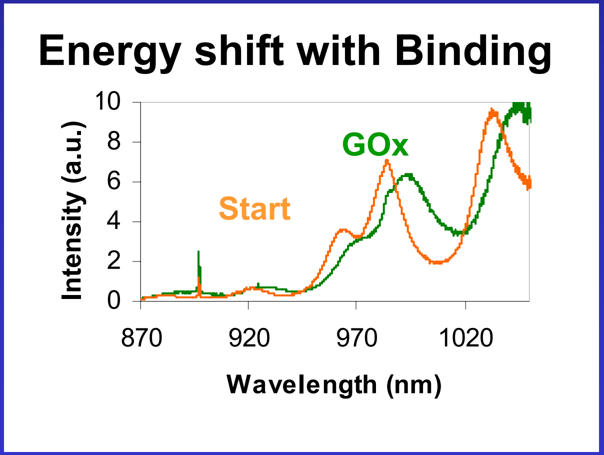


4.5 nm[1]



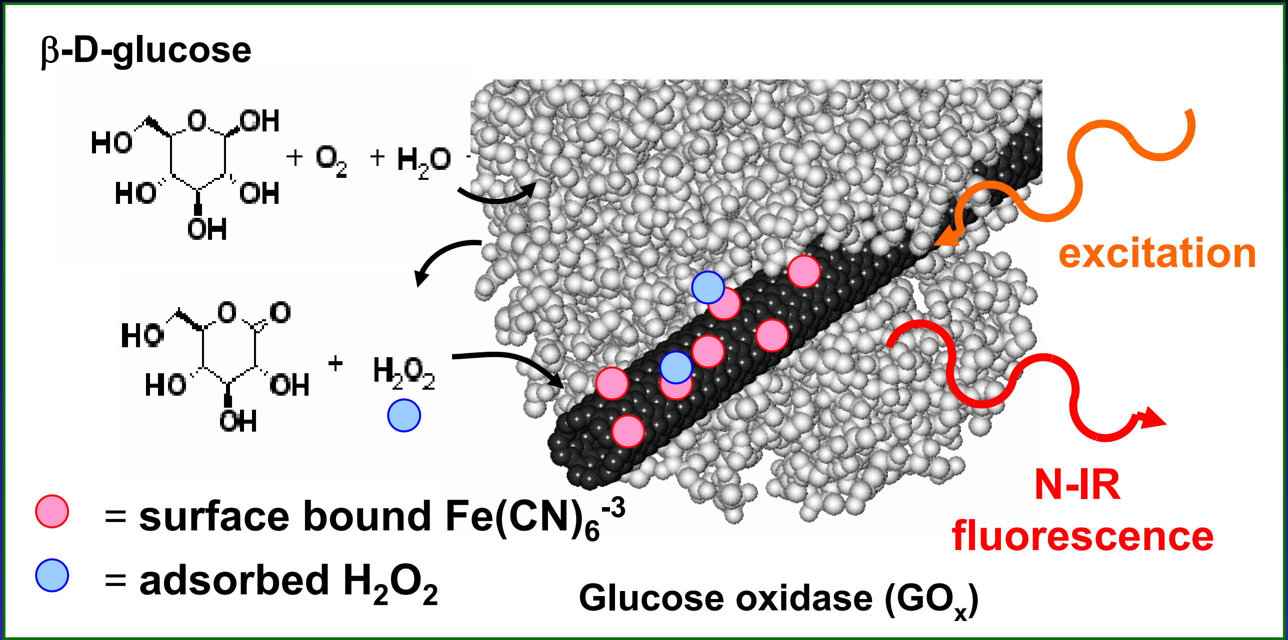
GO_x-SWNT

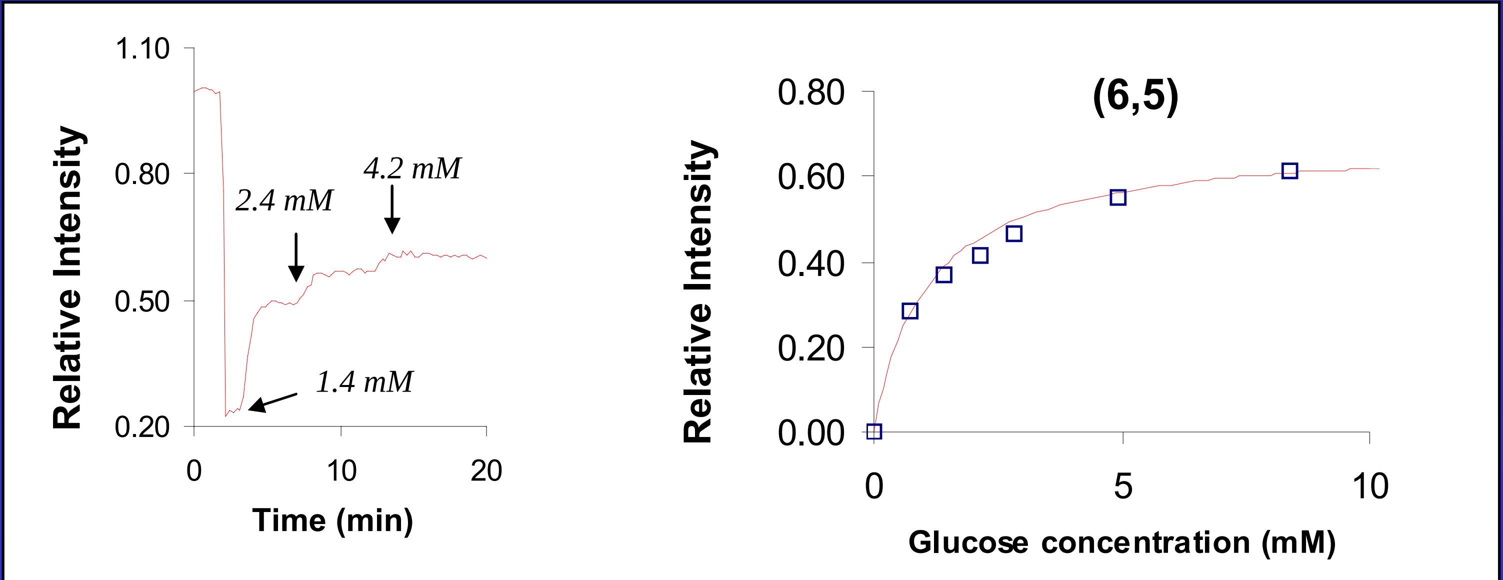




1. Saal, K. et al. *Bio. Eng.* **19**, 195-199 (2002).

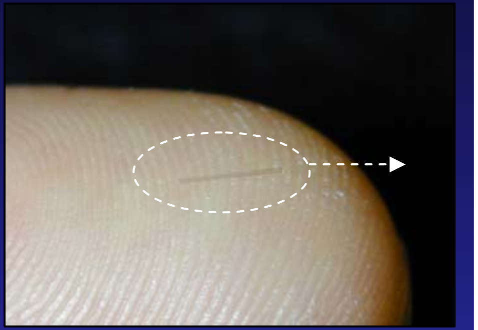
Step II: Functionalization with Ferricyanide

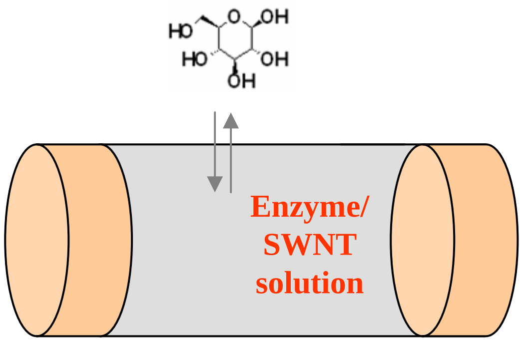




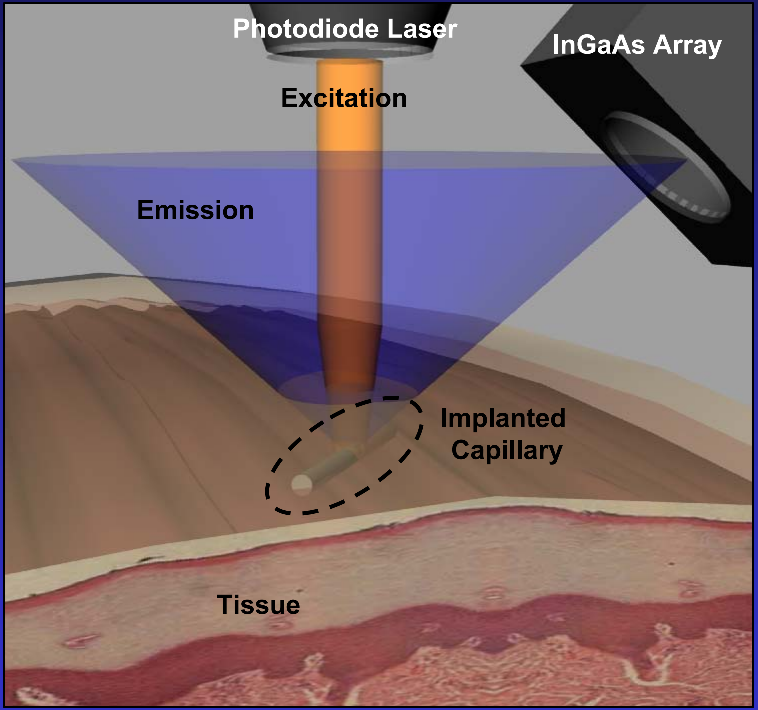
PW Barone, S Baik, DA Heller, MS Strano: Nature Materials 4 (2005) 86-92.

Tissue Implantable Biomedical Sensors

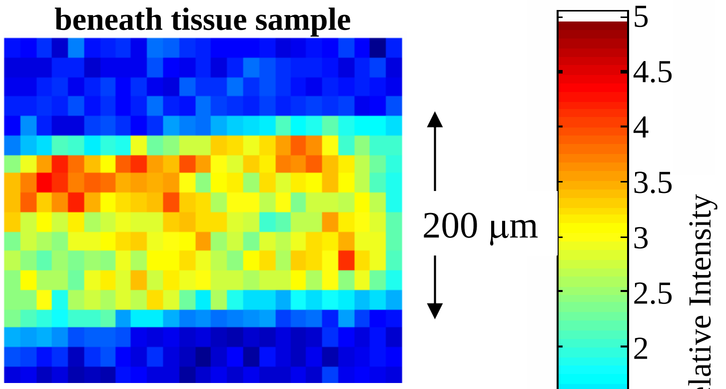




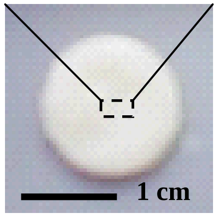
Porous dialysis capillary
13 kDa MW cutoff



nIR image of filled capillary
beneath tissue sample



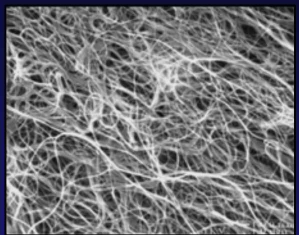
Epidermal
Tissue
Sample



PW Barone, RS Parker, MS Strano: Analytical Chemistry 77 (2005) 7556-62.

DNA Wrapped Carbon Nanotube Hybrids

Synthesis I: Sonication

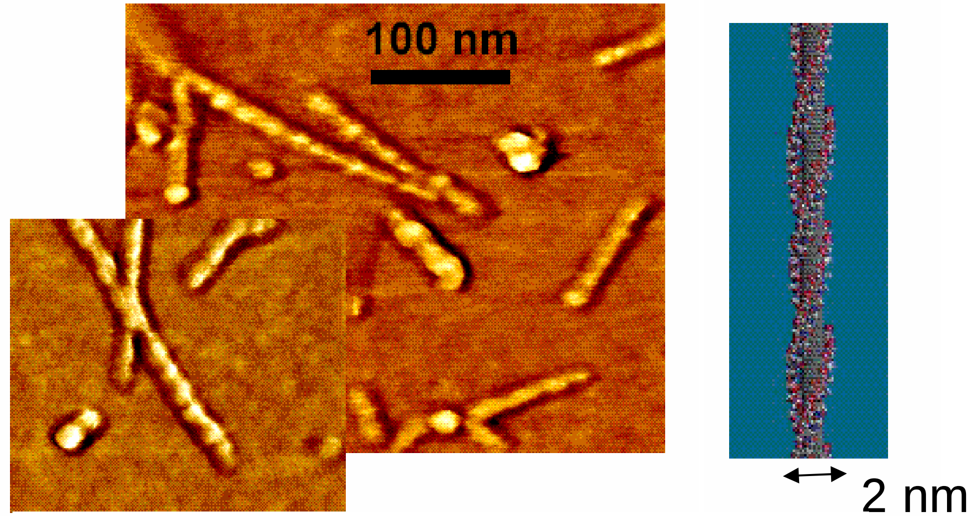


Raw material

ds(GT)$_{15}$ oligomers

Ultra -sonication
3 W, 4 °C

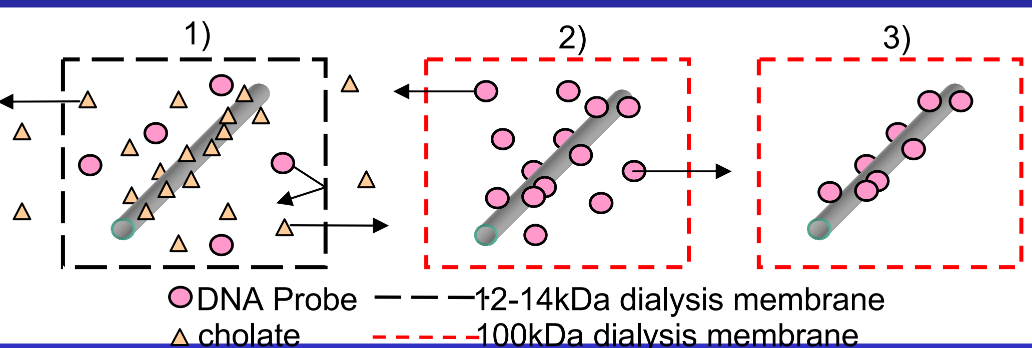
Centrifugation

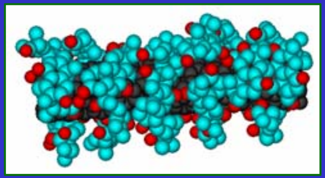


alternating guanine/thymine pairs – 20 mer

M Zheng, A Jagota, MS Strano, et al. Science 302 (2003) 1545-48.

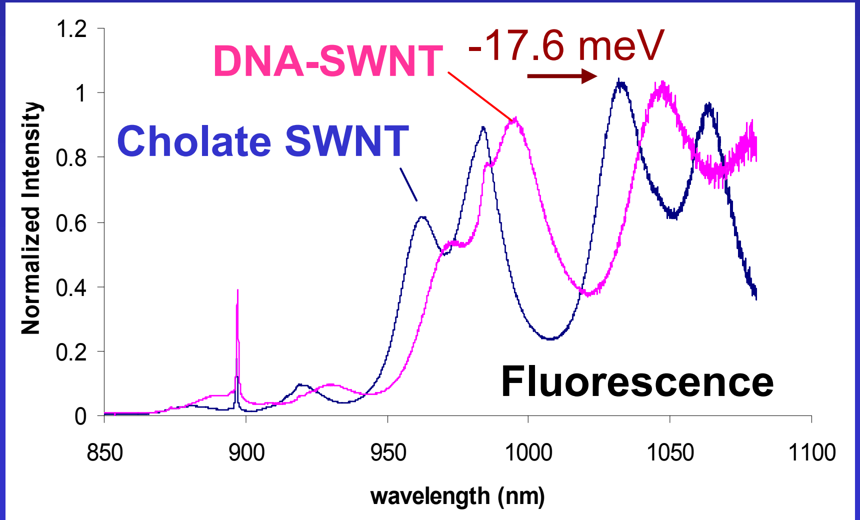
Synthesis II: Dialysis





Sodium cholate

ssDNA

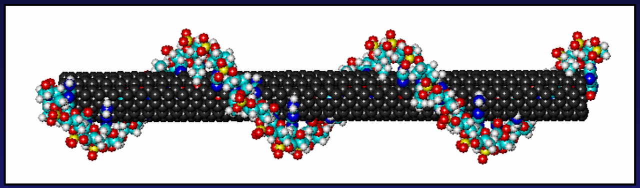


E. Jeng, M. Strano, Nano Letters, **ASAP** (2006)

Selective Detection of DNA Hybridization

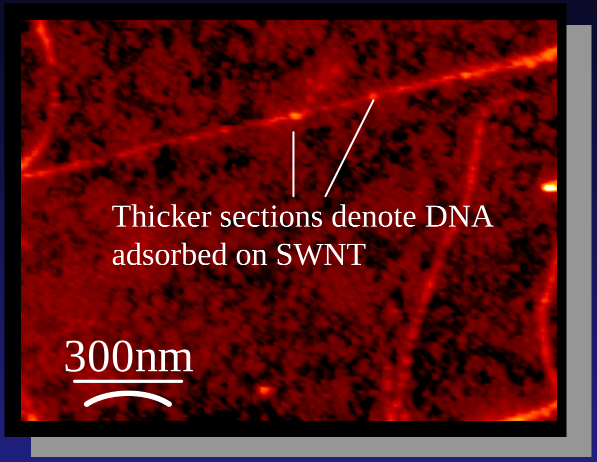
Sensor: SWNT decorated with ss-DNA

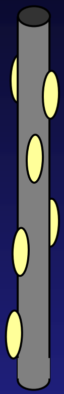
5' – TAG CTA TGG AAT TCC TCG TAG GCA – 3'

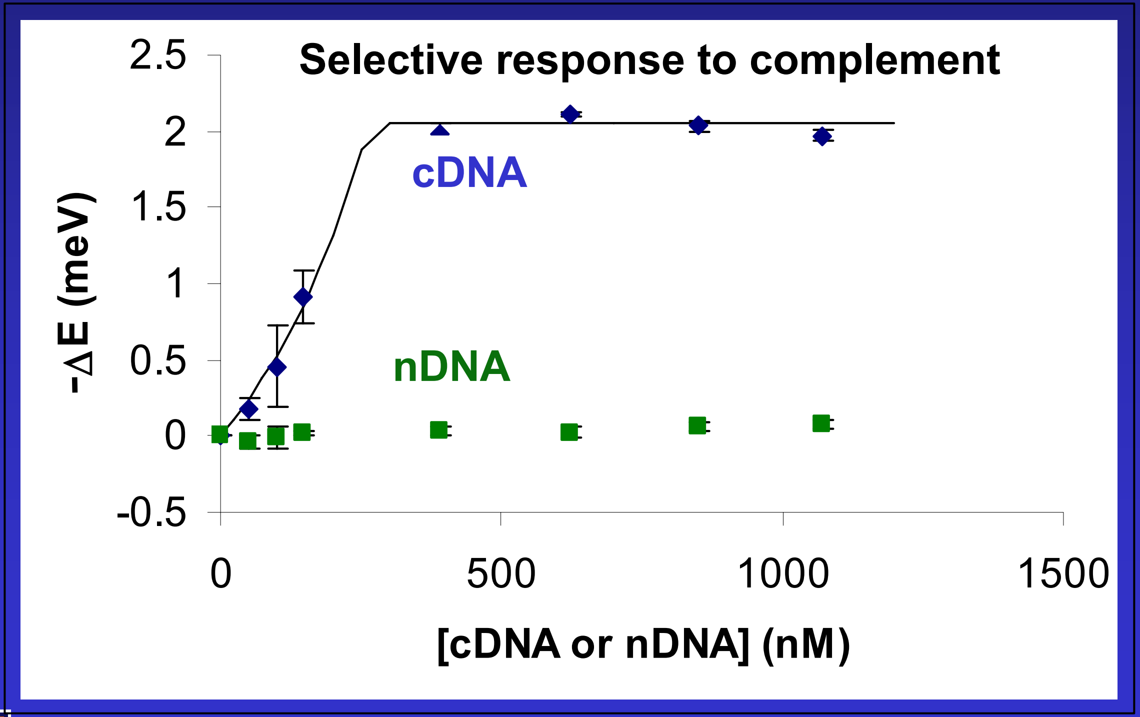


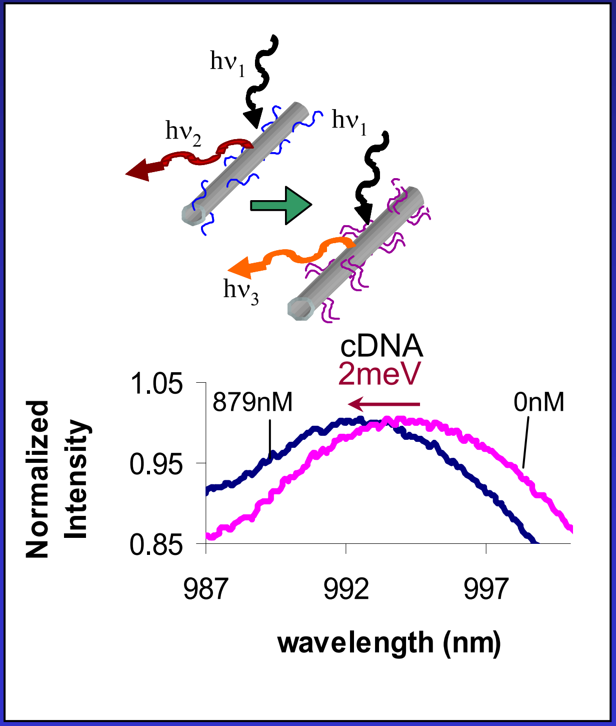
cDNA = 5'- GCC TAC GAG GAA TTC CAT AGC T – 3'

nDNA = 5'- TCG ATA CCT TAA GGA GCA TCC G -3'









Graduate Student Esther Jeng

Jeng, E.S., Strano, M.S. Nano Letters ASAP (2006)

Optical Transduction: Dielectric Modulation

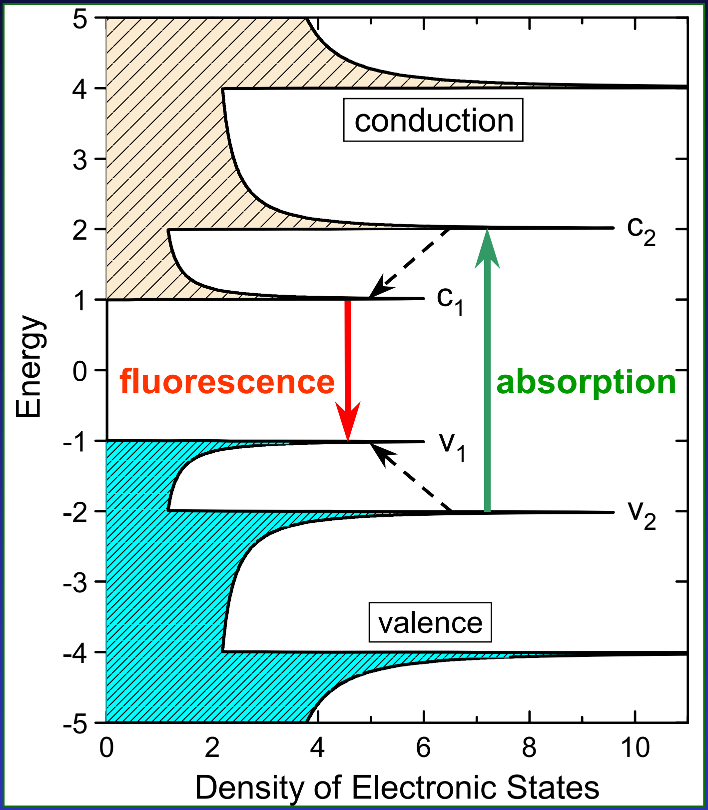
One dimensional structure confines exciton that forms on photo-absorption

Fluorescence energy : $E = E_{11} + E_b$

E_{11} = Energy of $V_1 - C_1$ transition

E_b = Exciton binding energy

E_b scales with effective environmental dielectric constant (ε)



Binding energy relation:

$$E_b \approx R^{n-2} m^{n-1} \varepsilon^{-n}$$

R = nanotube radius
m = nanotube effective mass
n = scaling value of 1.4

Nanotube fluorescence linked to analyte adsorption via surface area (α)

Effective medium approximation

$$\varepsilon = \alpha \varepsilon_{DNA} + (1-\alpha)\varepsilon_{water}$$

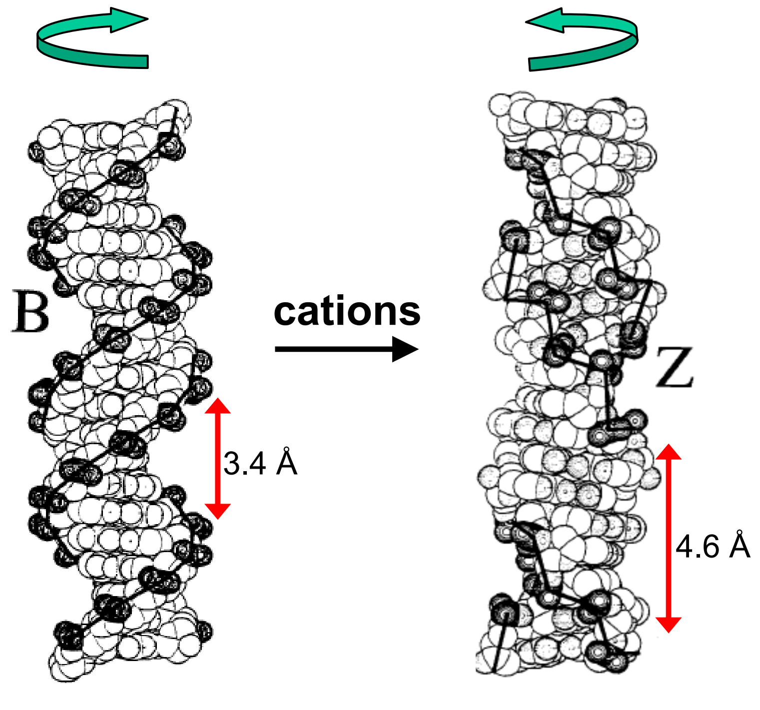
Perebeinos, et. al. PRL, **92** (2004)

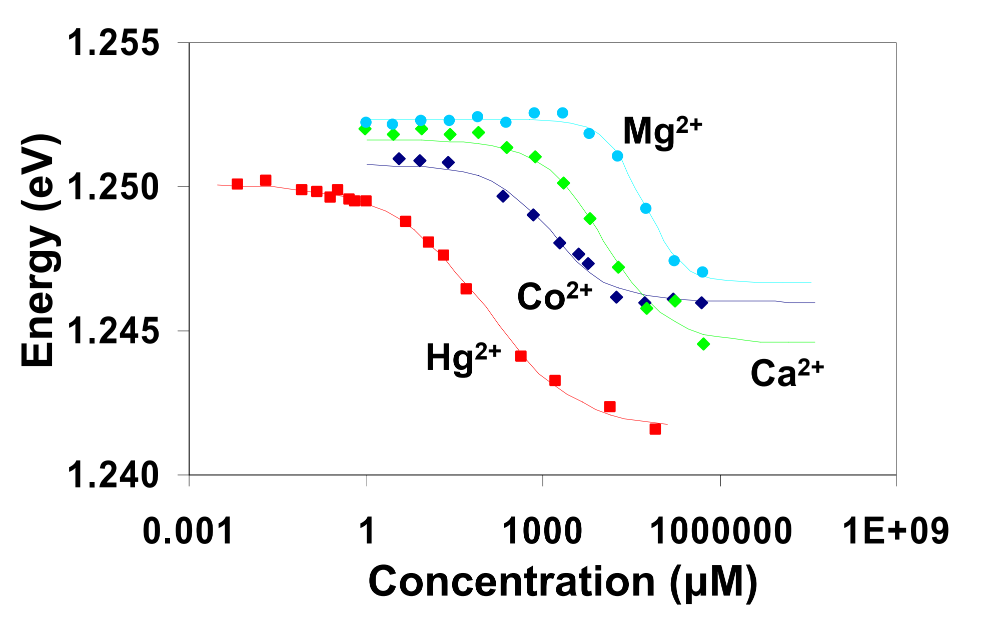
Detecting Changes in DNA Conformation

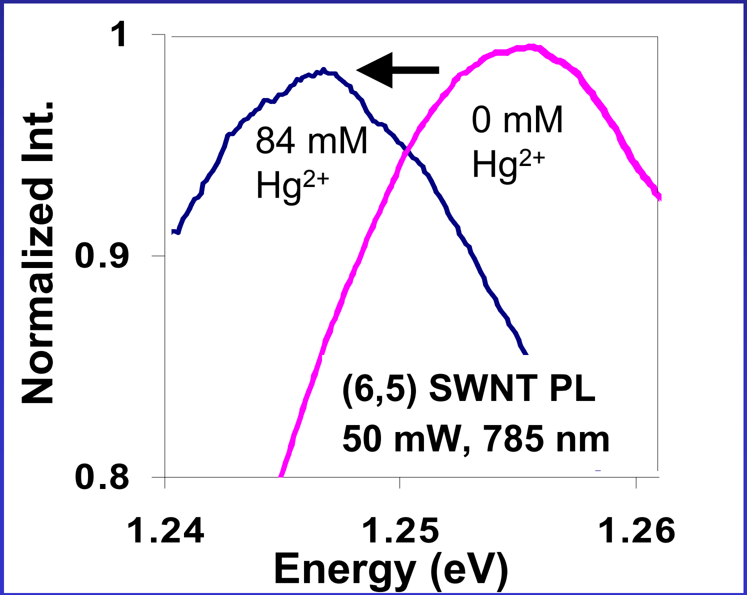
Divalent metal ions added to DNA-SWNT cause red shift in nanotube fluorescence

Conformational polymorphism of nanotube-bound DNA

Same relative sensitivity to divalent ions







Heller, D. A. et. al., *Science* **311** (2006)

Thermodynamic Comparison of DNA Transitions on and off SWNT

Compare CD and PL: common midpoints – Δ(ΔGibbs) ~ 0 thermodynamically similar transitions

Slopes at the inflections are different for SWNT-DNA and free DNA

$$K = \left(\frac{C}{C_o}\right)^{aN}\left(\frac{\beta_B}{\beta_Z}+\left(\frac{C}{C_o}\right)^{aN}\right)^{-1}$$

K = fraction of transition

C_0 = DNA length-independent conc.

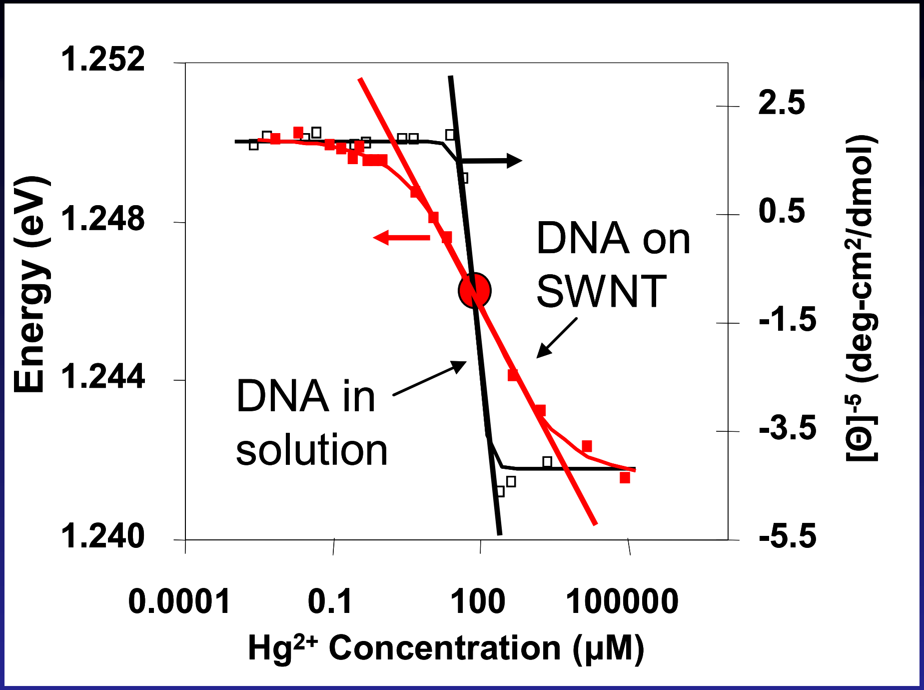
a = binding sites/DNA length

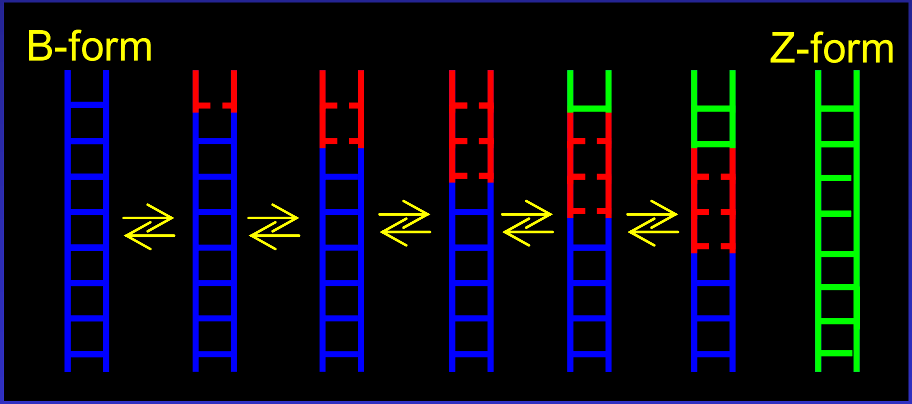
β_B/β_Z = ratio of nucleation rates

N = effective oligonucleotide length

Pohl F., Jovin, T, *J. Mol. Biol.* **67** (1972)

Pohl, F., *Cold Spring Harbor Quant. Biol.* **47** (1982)

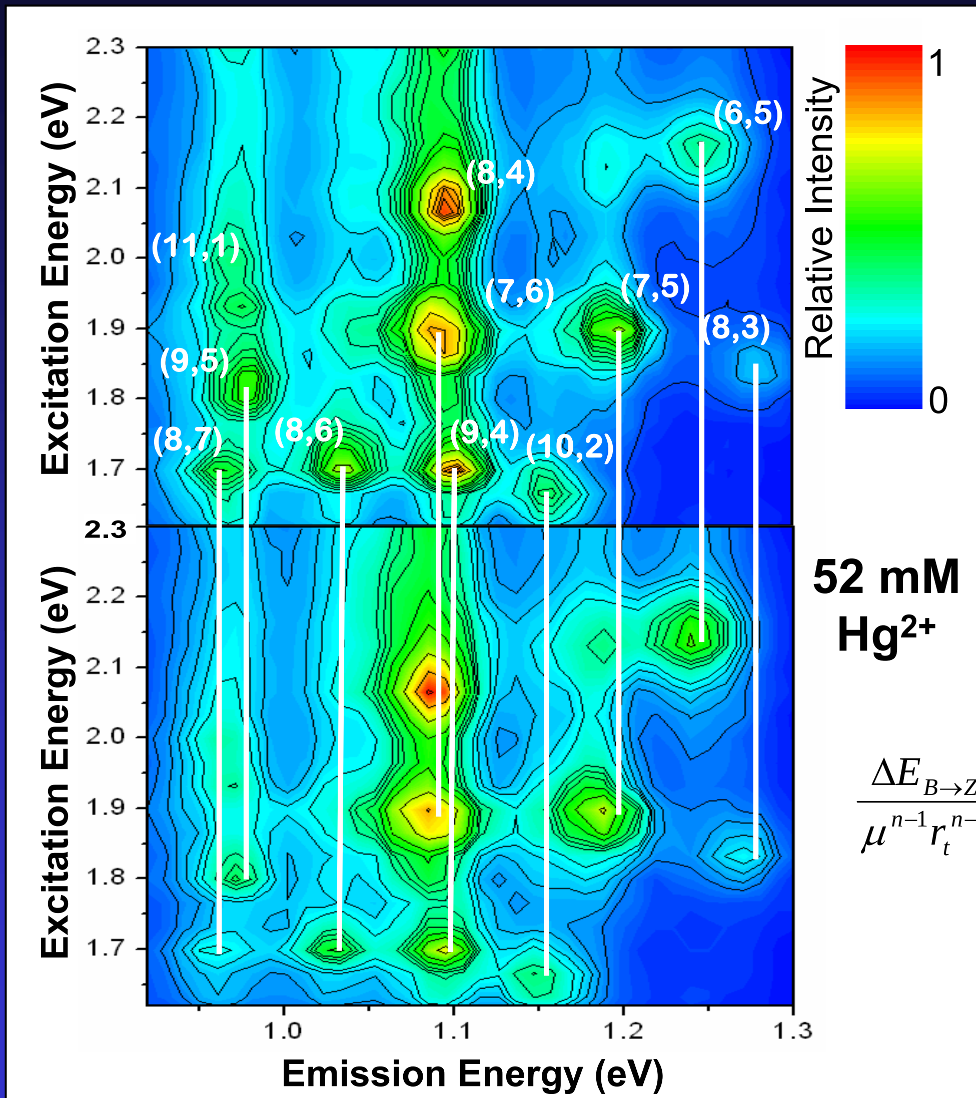




	C_0	a	β_B/β_Z	N
DNA	70.8 μM	0.118	1.04	30
DNA-SWNT	102 μM	0.118	1.21	5

Shorter effective length

Probing the Effects of Nanotube Diameter

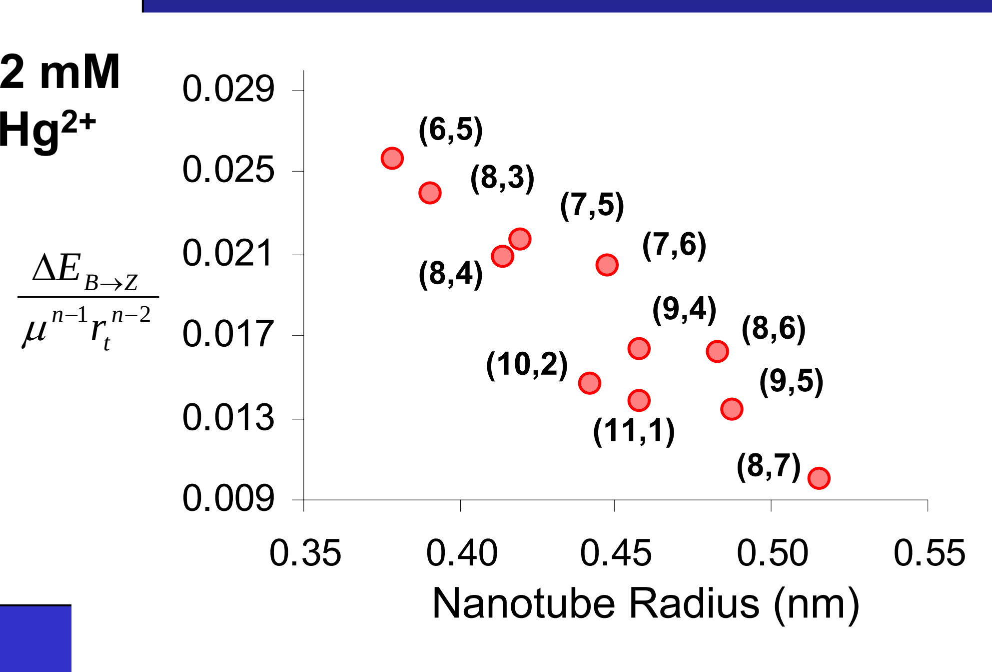


Scaling from 1-D Exciton Simulations[1]

$$\frac{\Delta E_{B \to Z}}{\mu^{n-1} r_t^{n-2}}$$

Effective mass

Nanotube radius



1. Perebeinos, et. al. PRL, **92** (2004)

Modeling Conformational Polymorphism on SWNT

Exciton binding energy difference of B and Z forms modeled on change in dielectric constant (ε)

$$\Delta E_{B\to Z} = A\mu^{n-1} r_t^{n-2}\left(\frac{1}{\varepsilon_Z^n} - \frac{1}{\varepsilon_B^n}\right)$$

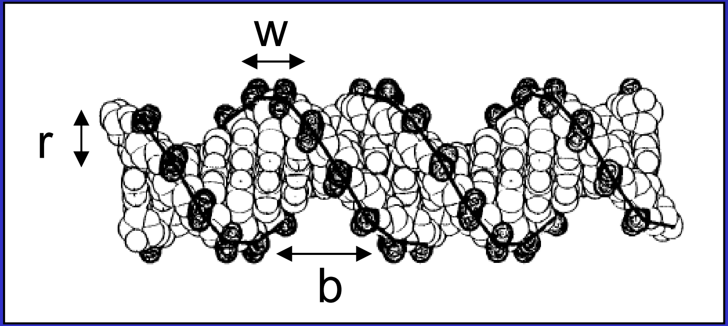
A, *n*, = empirical parameters
μ = SWNT reduced effective mass
r = SWNT diameter

Effective medium model accounts for changing ε using DNA surface area coverage on the nanotube

$$\varepsilon_i = (1-\alpha_i)\varepsilon_{H2O} + \alpha_i \varepsilon_{DNA}$$

ε_{DNA} = 4.0 and ε_{H2O} = 88.1
α = surface area

The surface area of the absorbed DNA helix is described by 3 parameters:



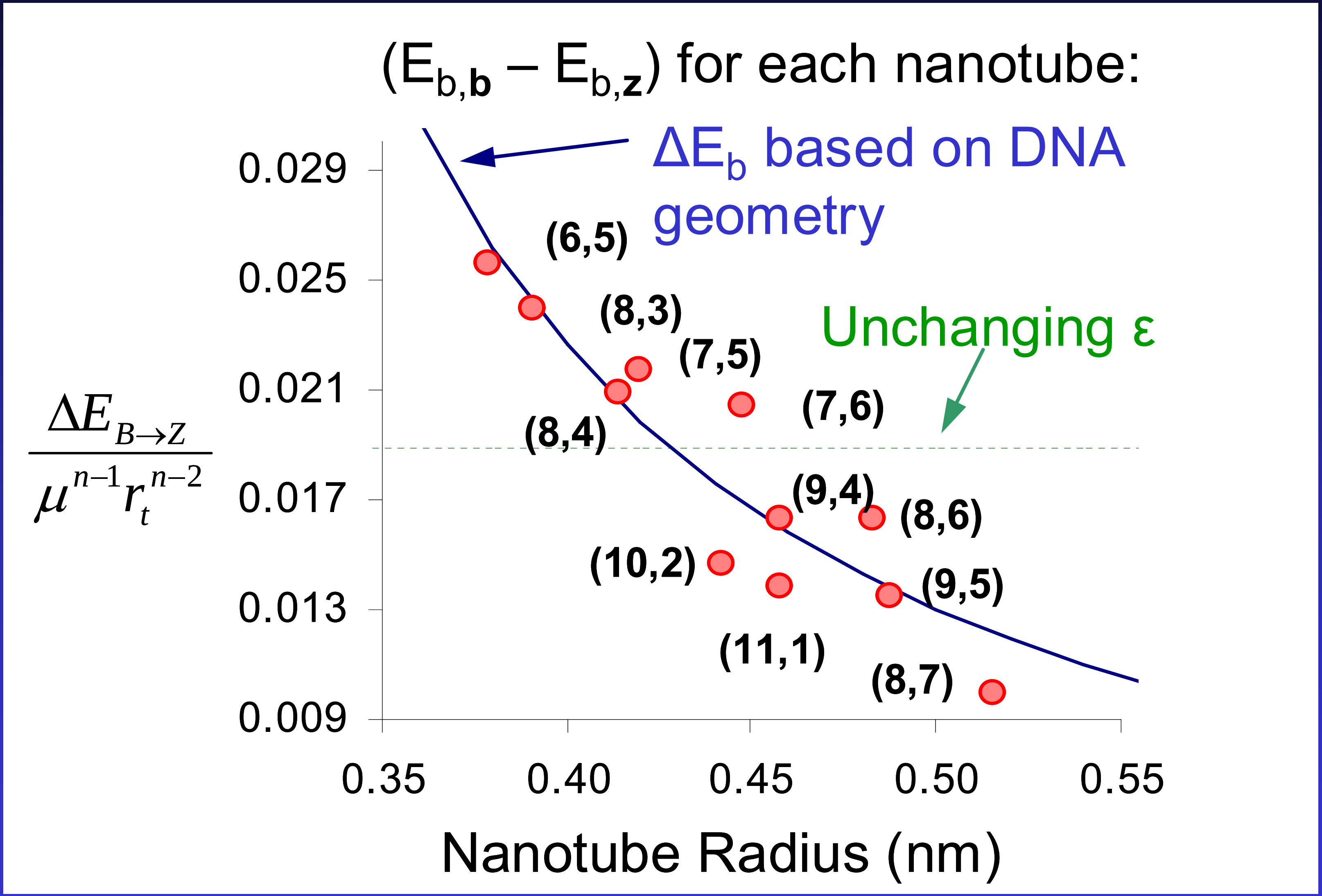
r = radius
w = strand width
b = pitch

Equilibrium values of radius and pitch in B and Z DNA:

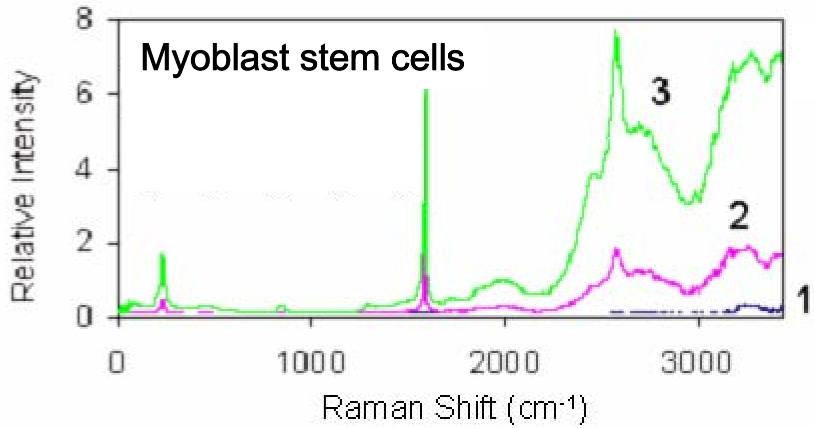
	r_0	b_0
B form	1 nm	3.32 nm
Z form	0.9 nm	4.56 nm

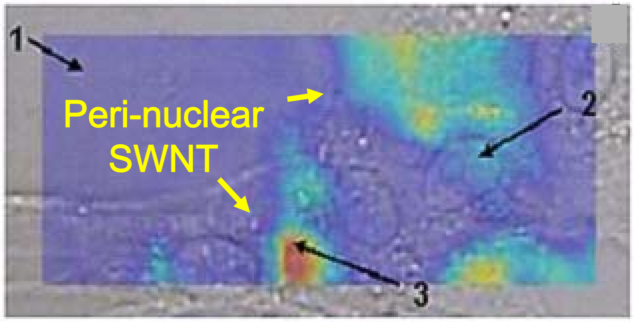
Heller, D. A. et. al., *Science* **311** (2006)

Transduction is Modeled using DNA Geometry

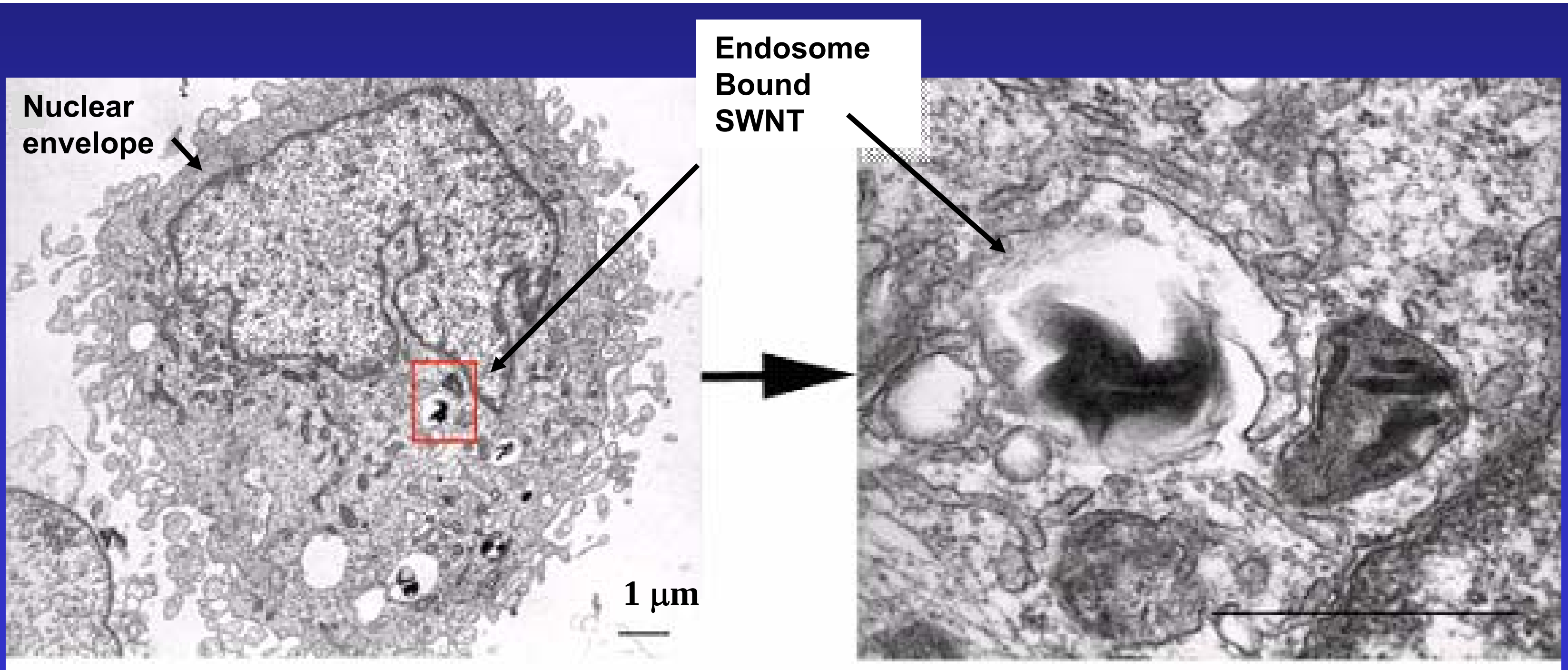


Endocytosis of DNA-SWNT "sensors" within live cells





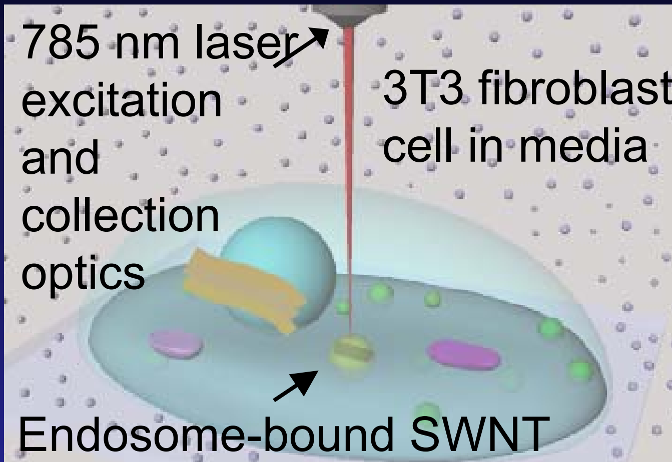
Fluorescence Mapping

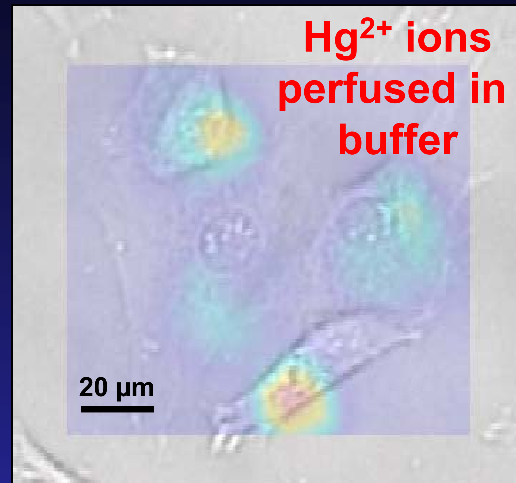


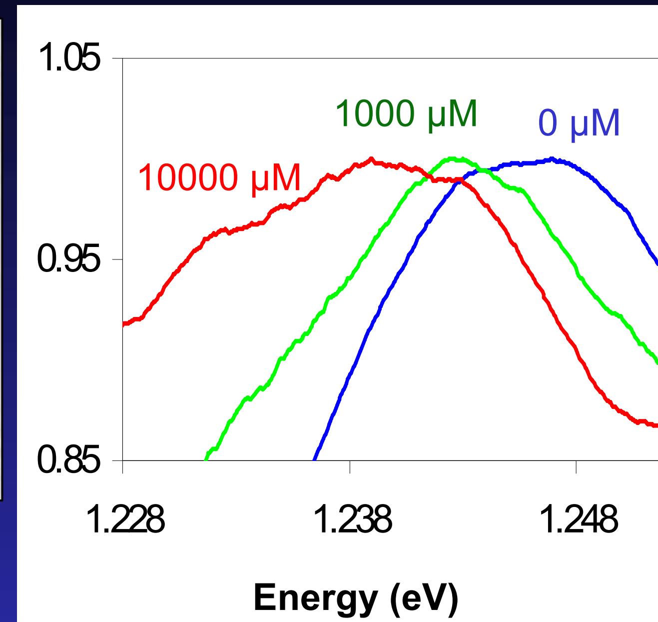
Transmission Electron Micrograph

DA Heller, MS Strano, Advanced Materials 17 (2005) 2793-99

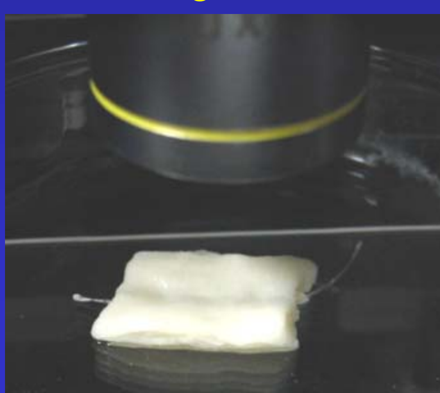
Applications for Metal Ion Detection



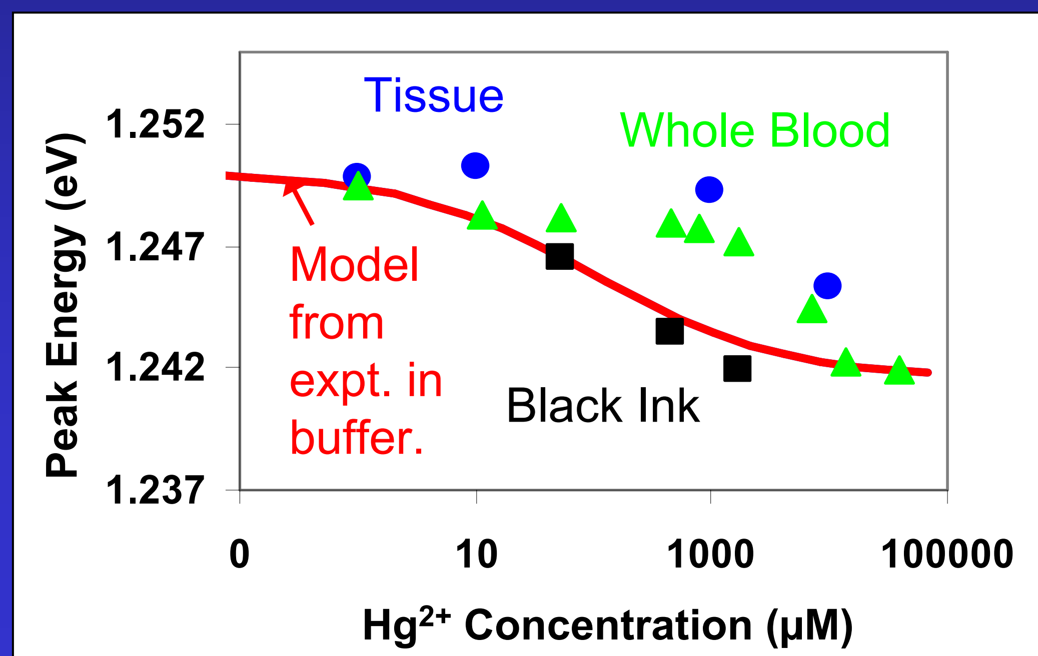




Near infrared fluorescence through tissue

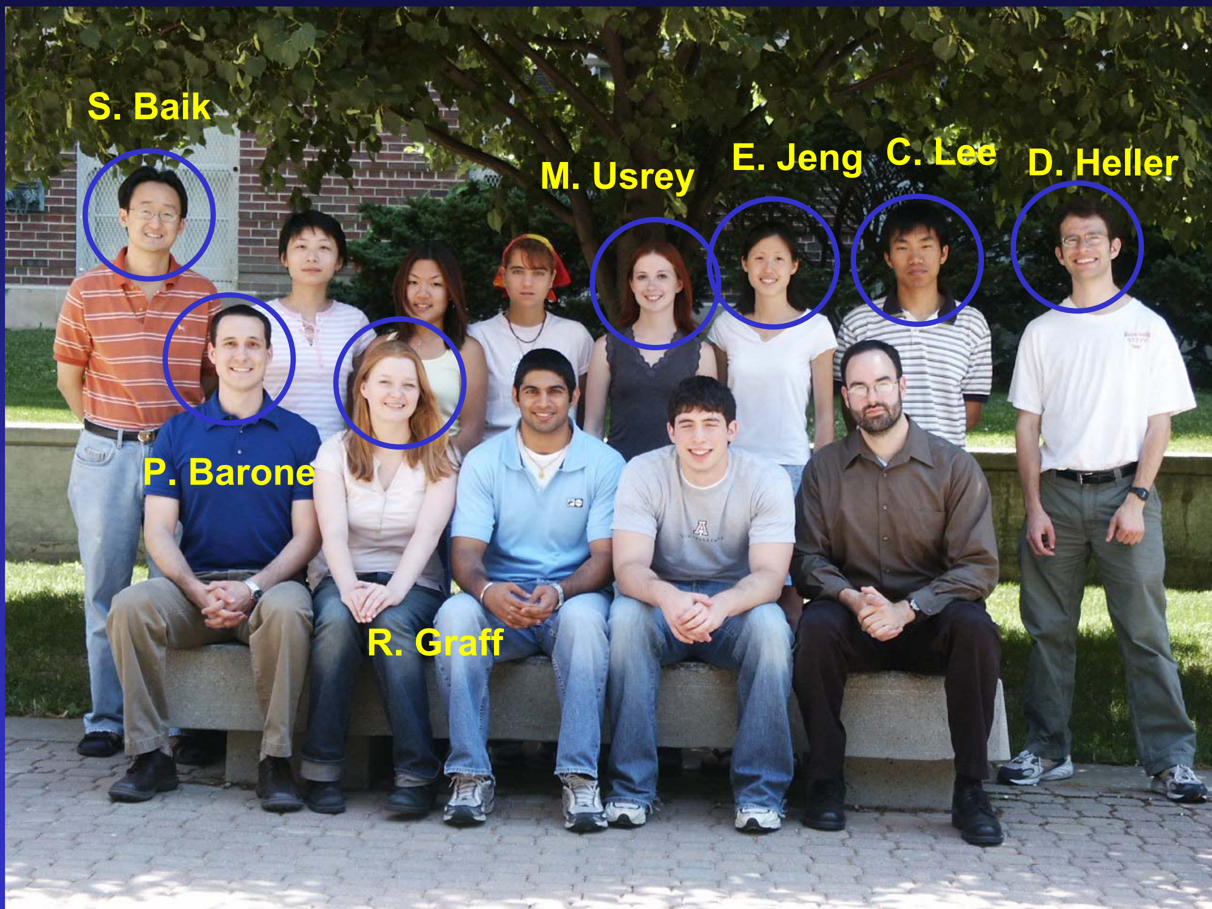


Whole blood



Heller, D. A. et. al., *Science* **311** (2006)

The Strano Group at University of Illinois



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Woo Jae Kim *(not shown)*

Jong Hyun Choi *(not shown)*

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M. Usrey

C. Lee

R. Graff

N. Nair (not shown)

H. Jin *(not shown)*

R. Sharma *(not shown)*)

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