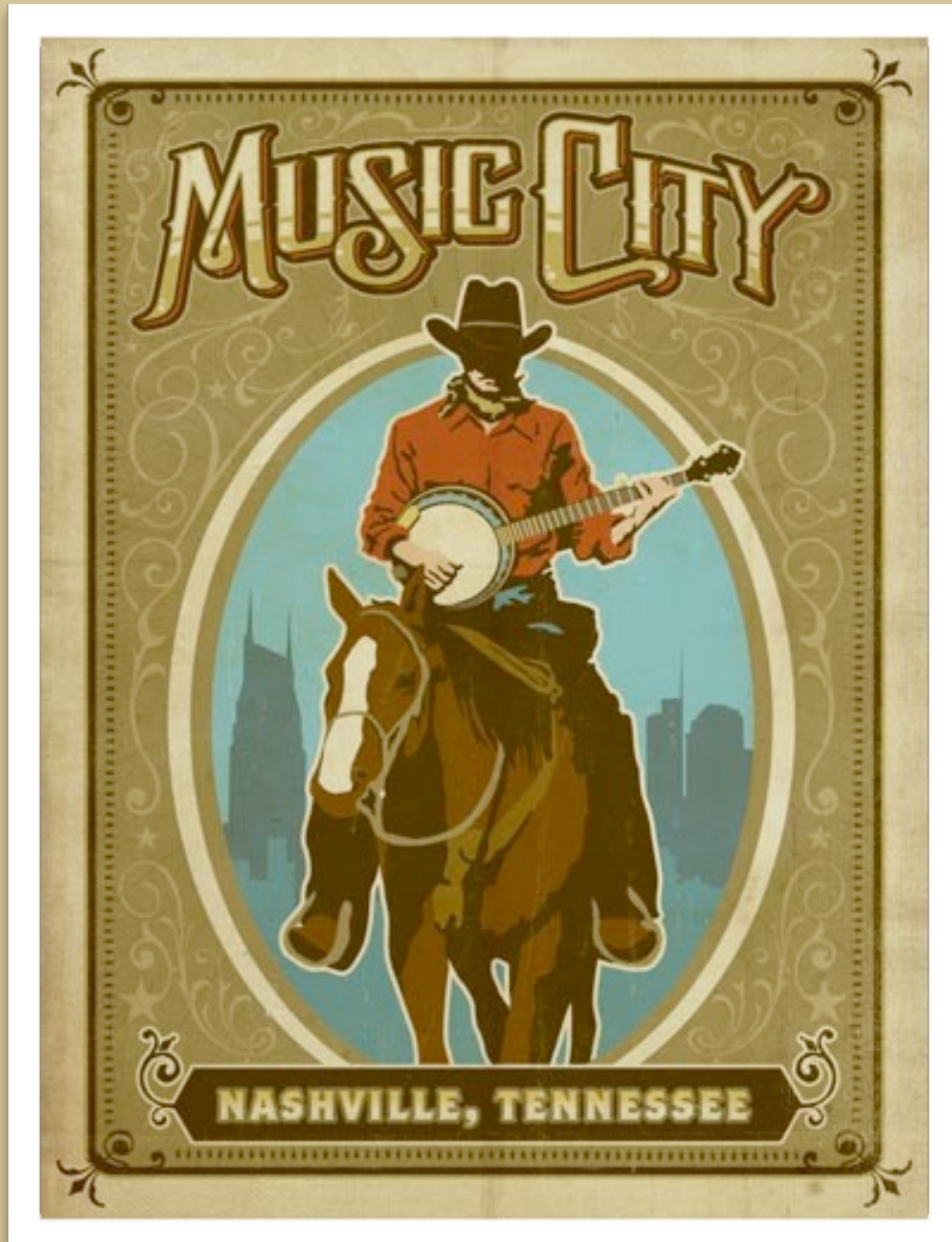
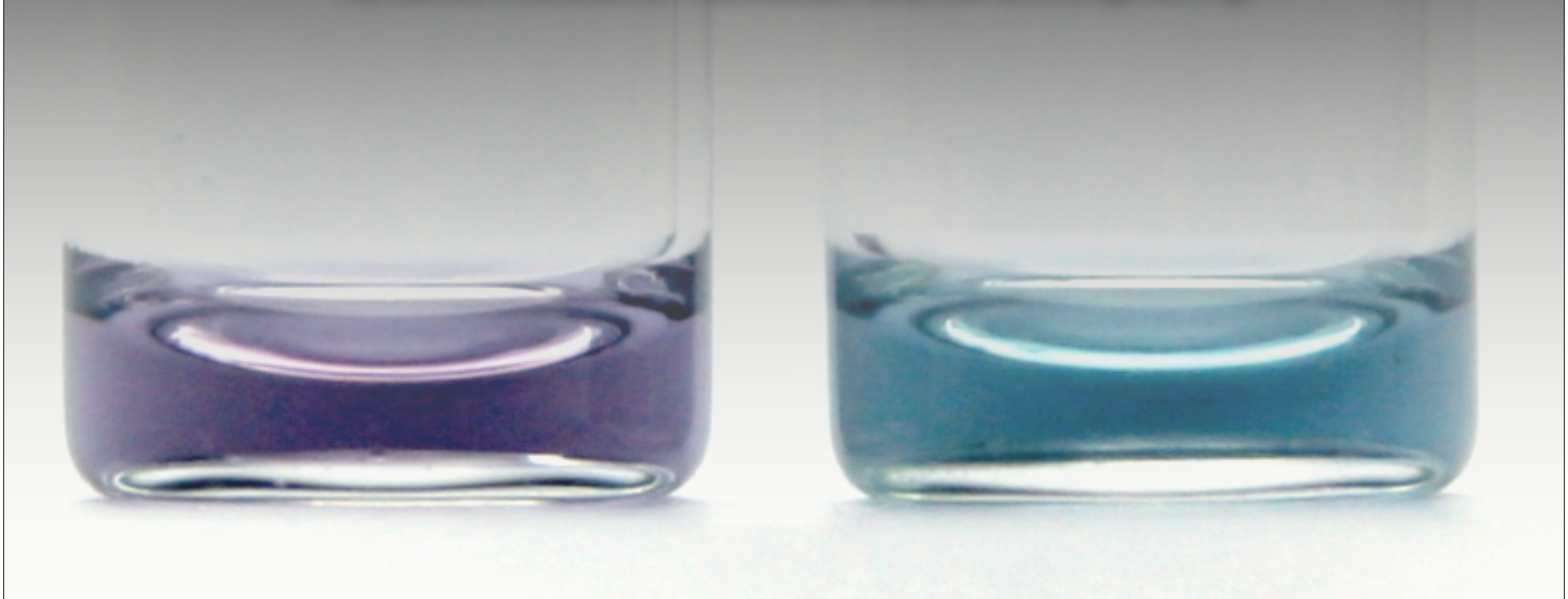

MUSIC CITY
NASHVILLE, TENNESSEE

Colorful Carbon:
Photophysics of Carbon Nanotubes

Tobias Hertel

Department of Physics and Astronomy &
Vanderbilt Institute for Nanoscale Science and Engineering



Small systems, big concerns

The Washington Post

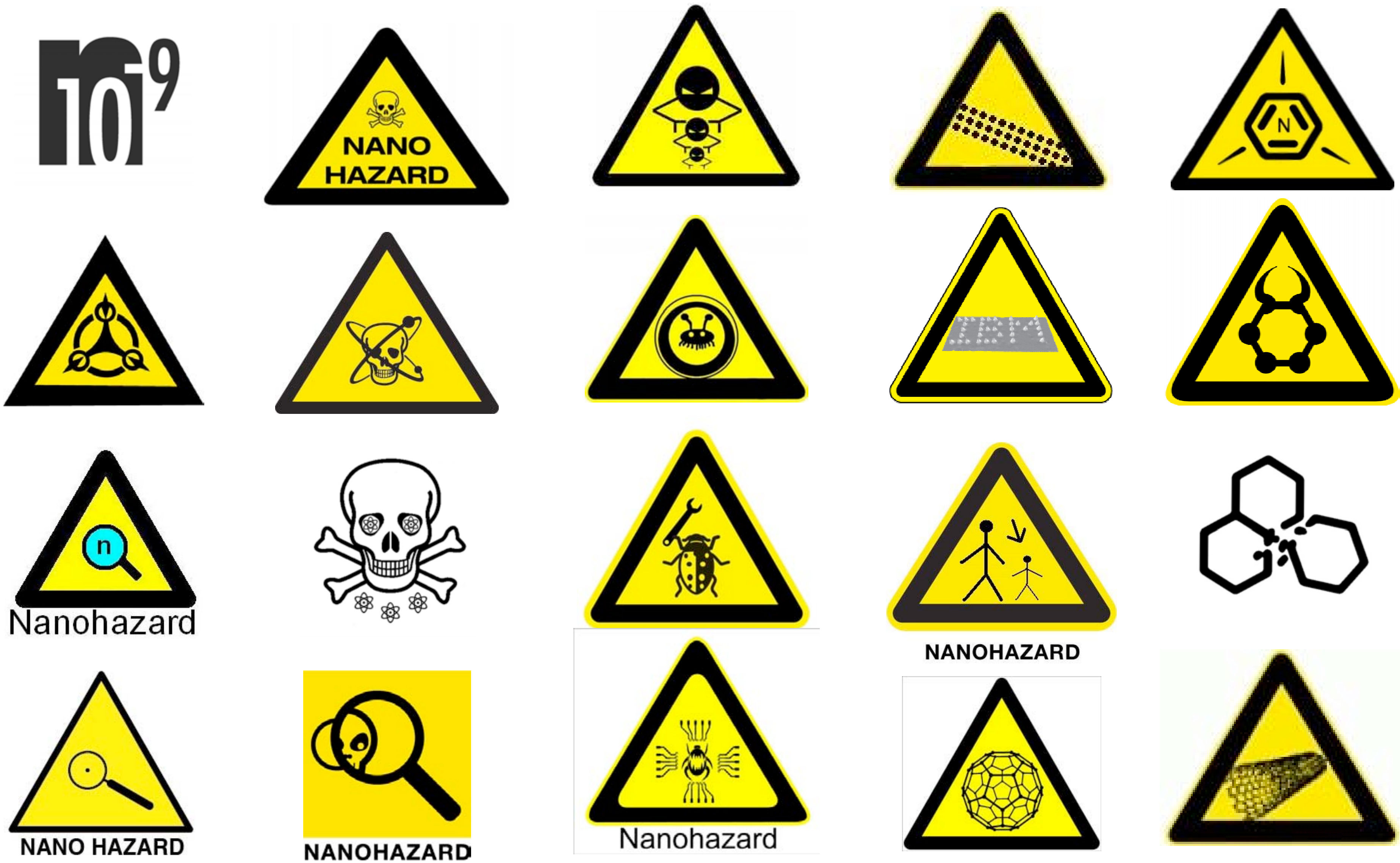
Sunday, 21. January 2007:

“Nanotechnology is the hot new science of the very small, in which researchers are engineering materials and devices as tiny as a billionth of a meter across. **At those scales, even mundane materials such as carbon perform extraordinary feats - conducting electricity, for example**, or triggering chemical reactions - that they'd never do in their chunkier forms.”

“Already, **hundreds of products** containing nanomaterial are on the market, including stain-resistant fabrics, high-tech tennis rackets, cosmetic creams and sunscreens, computer hard drives and **even a "Nanoceuticals Slim Shake,"** which claims to deliver nutrition directly into your cells in the form of "CocoaClusters" 100,000 times smaller than a grain of sand.”

Nanotechnology warning sign contest by the **Erosion, Technology and Concentration** (ETC) group.

A new nanotech warning sign



In the eye of the public ...

Economist.com

Thursday February 14th 2008

The risk in nanotechnology

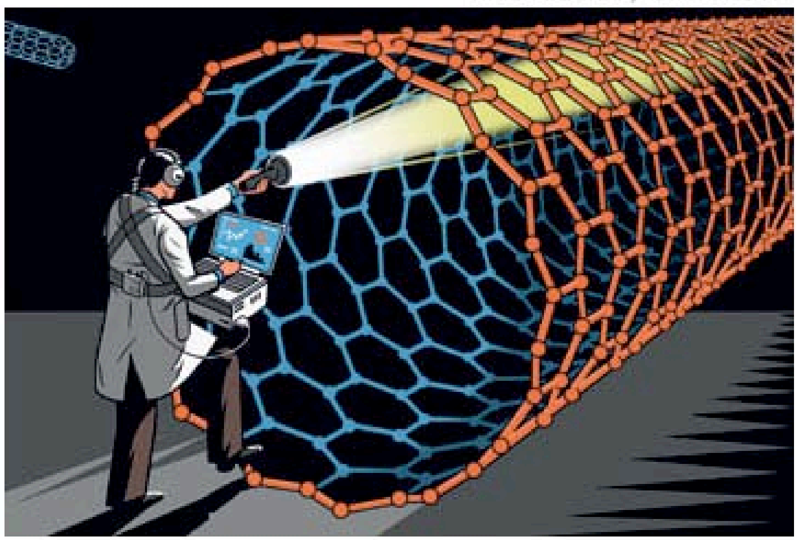
A little risky business

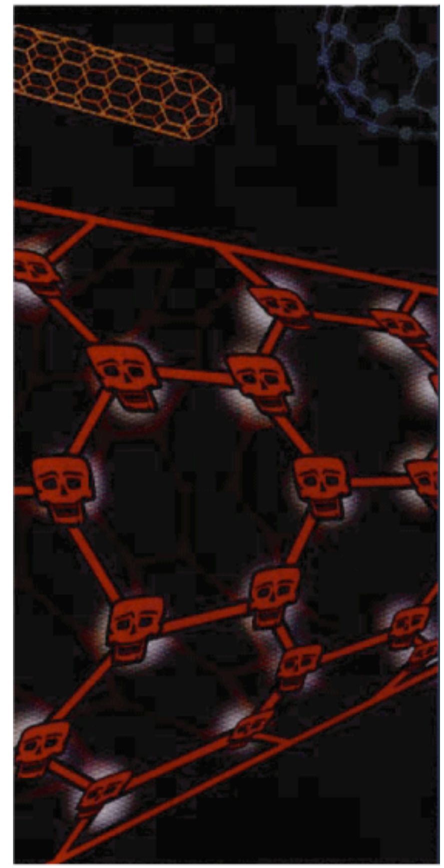
Nov 22nd 2007

From *The Economist* print edition

The unusual properties of tiny particles contain huge promise. But nobody knows how safe they are. And too few people are trying to find out

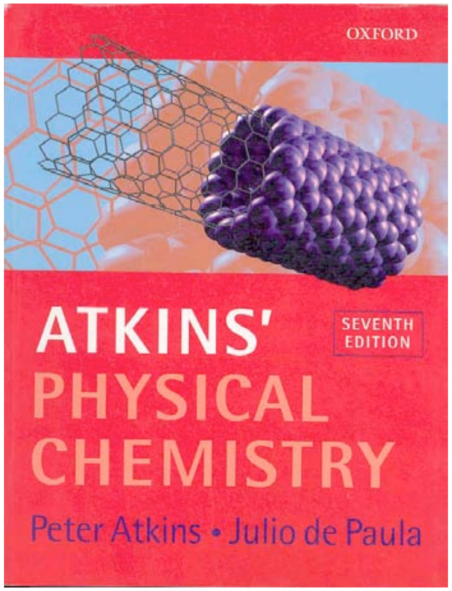
Illustration by Bill Butcher

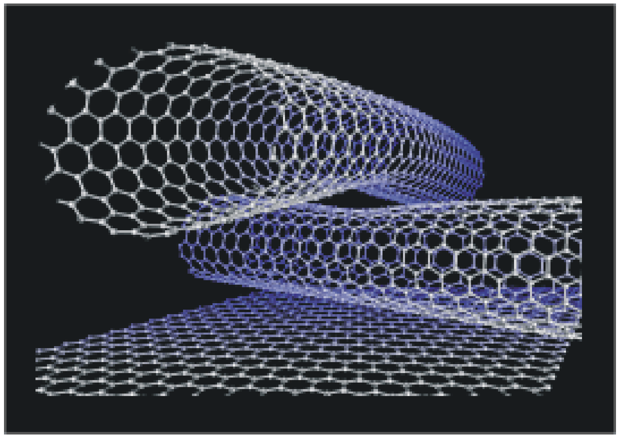




Today’s menu

- **Low-dimensional photophysics 101**
- **Optically excited states in CNTs**
- **Preparative developments**
- **Dynamics: introduction and some gory details**
- **Outlook**

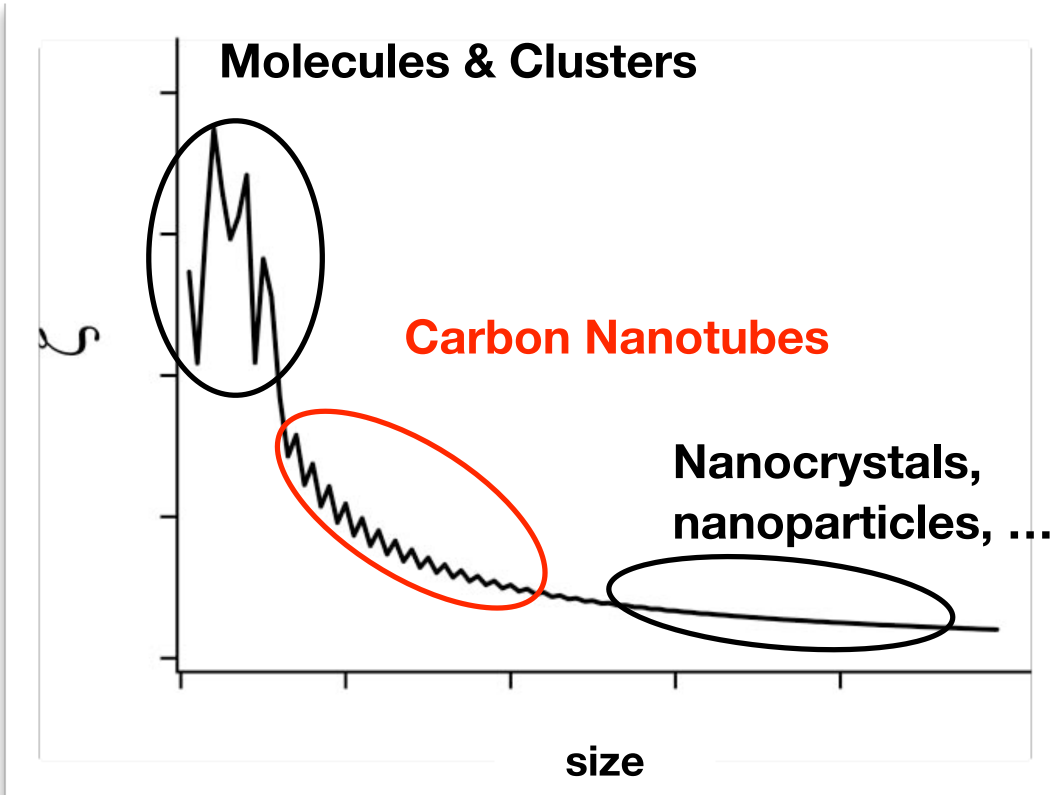




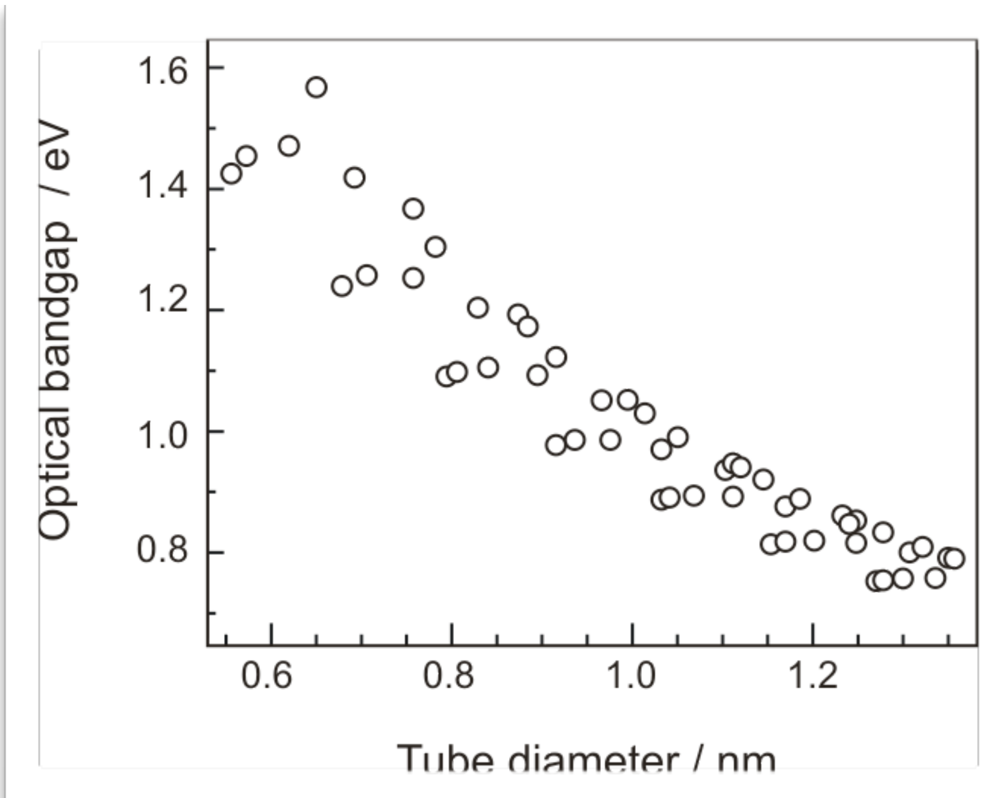
Hertel, Walkup, Avouris, Phys. Rev. B 58 (1998) 13870

Now also to be found in Germany’s high school standard for Chemistry "Elemente Chemie 1 – Unterrichts-Werk für die Sekundarstufe II“, Band 4179, page 175 B6, Klett Verlag.

Size matters

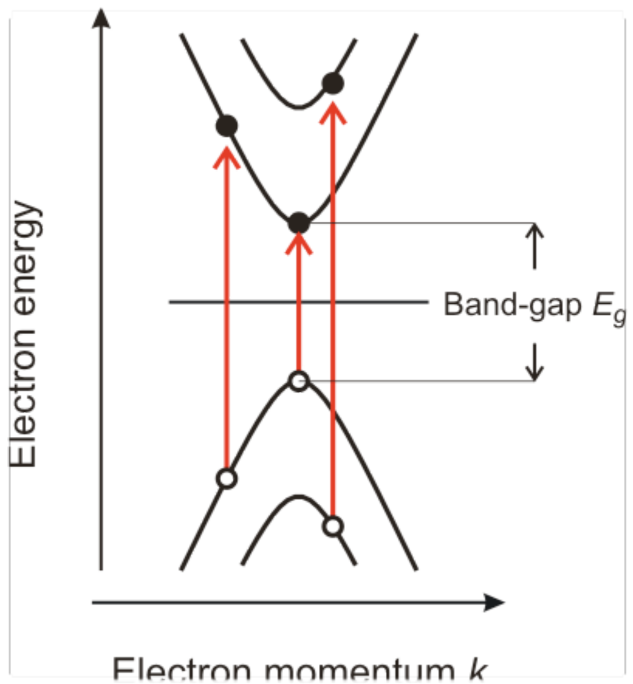


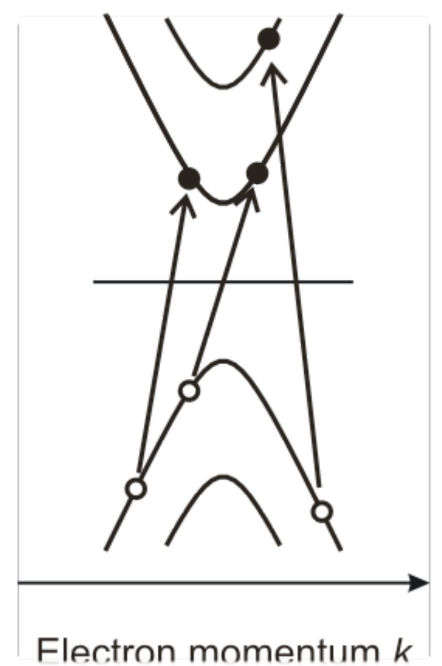
Optical band gap of carbon nanotubes

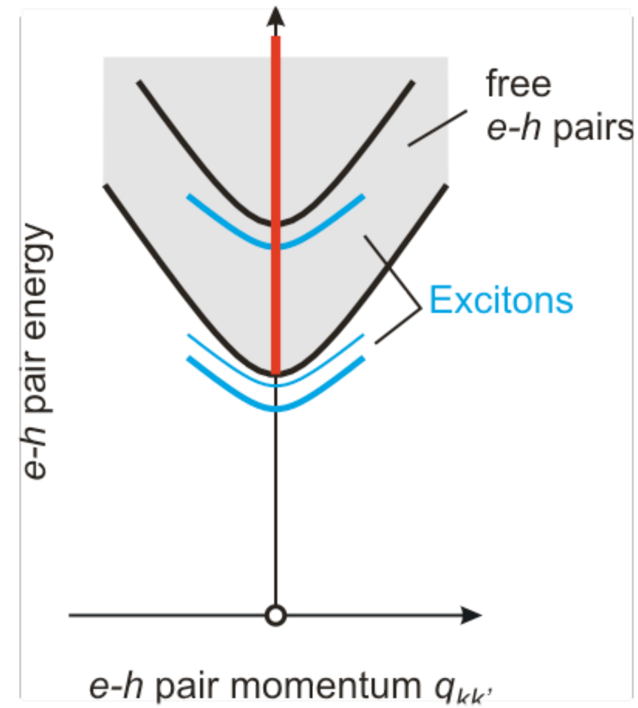


Low dimensional photophysics 101

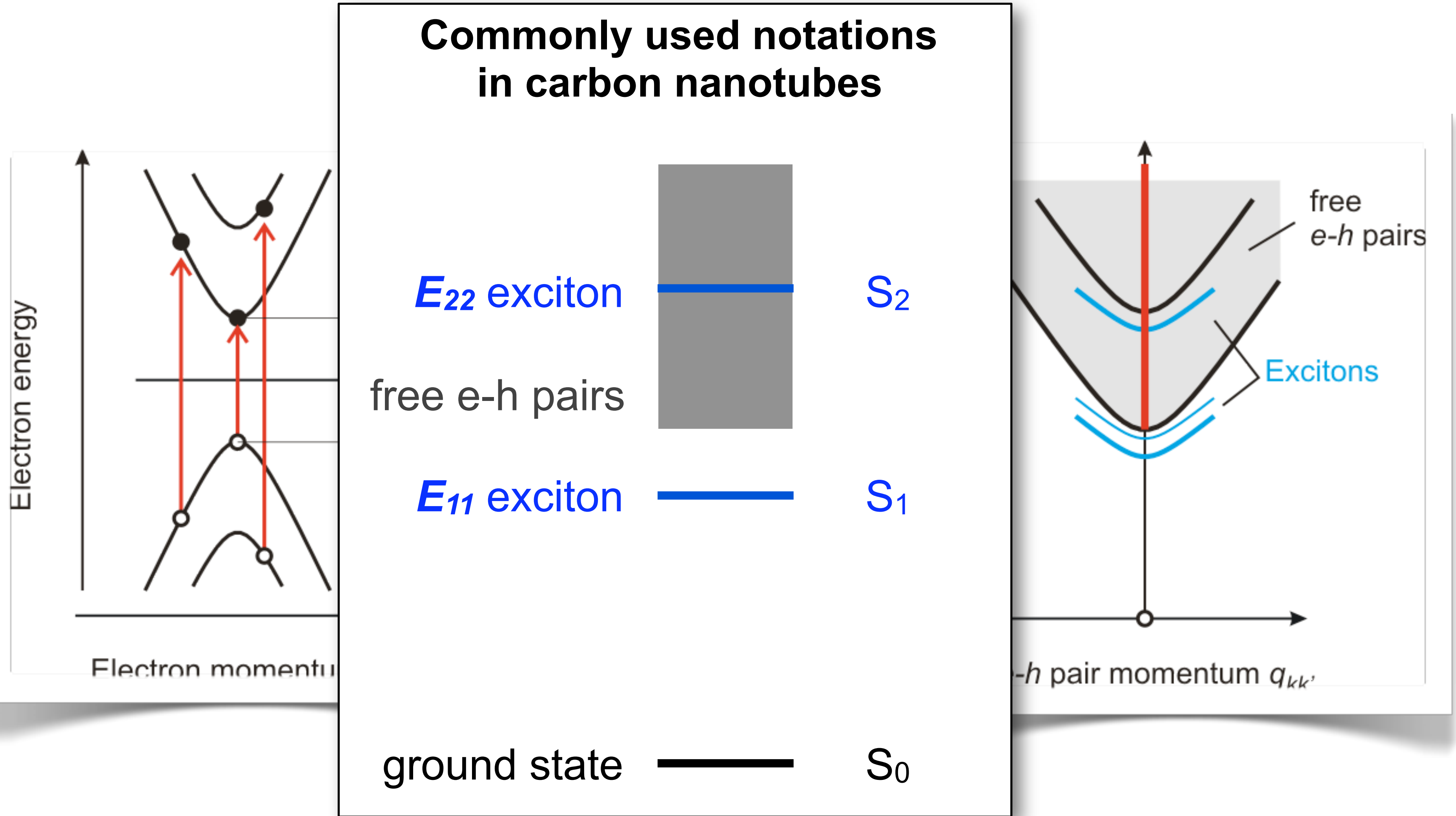
Excited states in semiconductors







Excited states in semiconductors

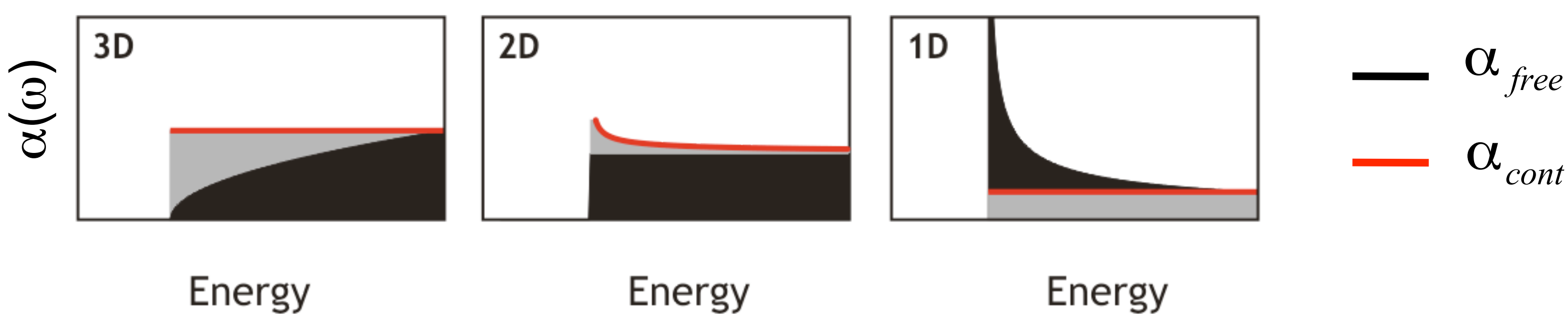


Free *e-h* pairs: 3D → 1D

Sommerfeld factors

(see for example Ogawa and Takagahara, PRB **43** (1991) 14325)

$$\alpha_{cont}(\omega) = \alpha_{free}(\omega)C(\omega)$$



Excitons: 3D → 1D

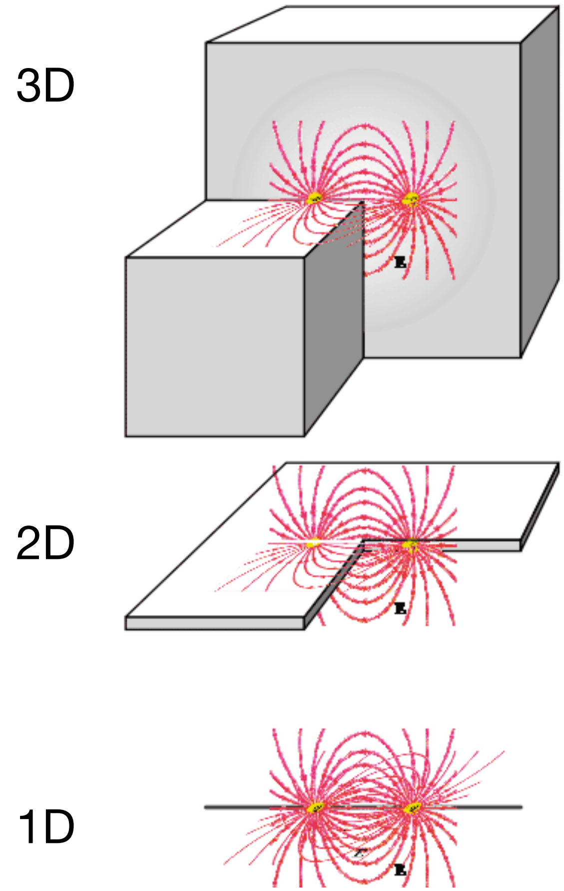
Effective medium Hamiltonian

$$H = \frac{p^2}{2\mu} - \frac{e^2}{(4\pi\epsilon_0)\epsilon r}$$

Binding energy of the 1s state:

$$E_b^{1s} = \left(\frac{\mu}{m_e\epsilon^2}\right)\left(\frac{2}{\alpha - 1}\right)^2 E_H$$

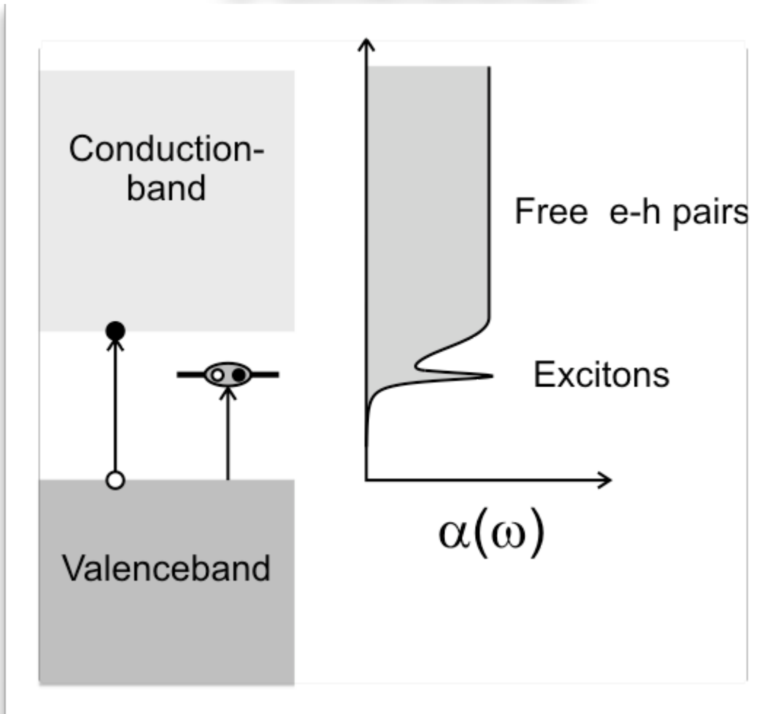
screening (ϵ^2) geometry ($\frac{2}{\alpha-1}$)



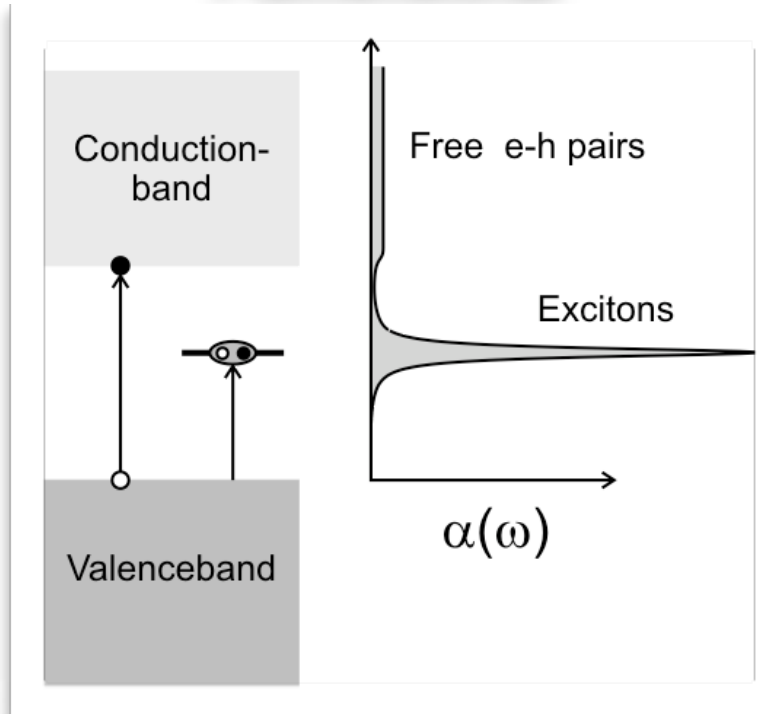
α - dimensionality (see He, PRB **43**, 2063 (1991))

1D systems are different

3-dimensional



1-dimensional



See for example:
Quantum theory of the optical and electronic properties of semiconductors
Haug and Koch, World Scientific (2004).

Carbon allotropes

The heritage

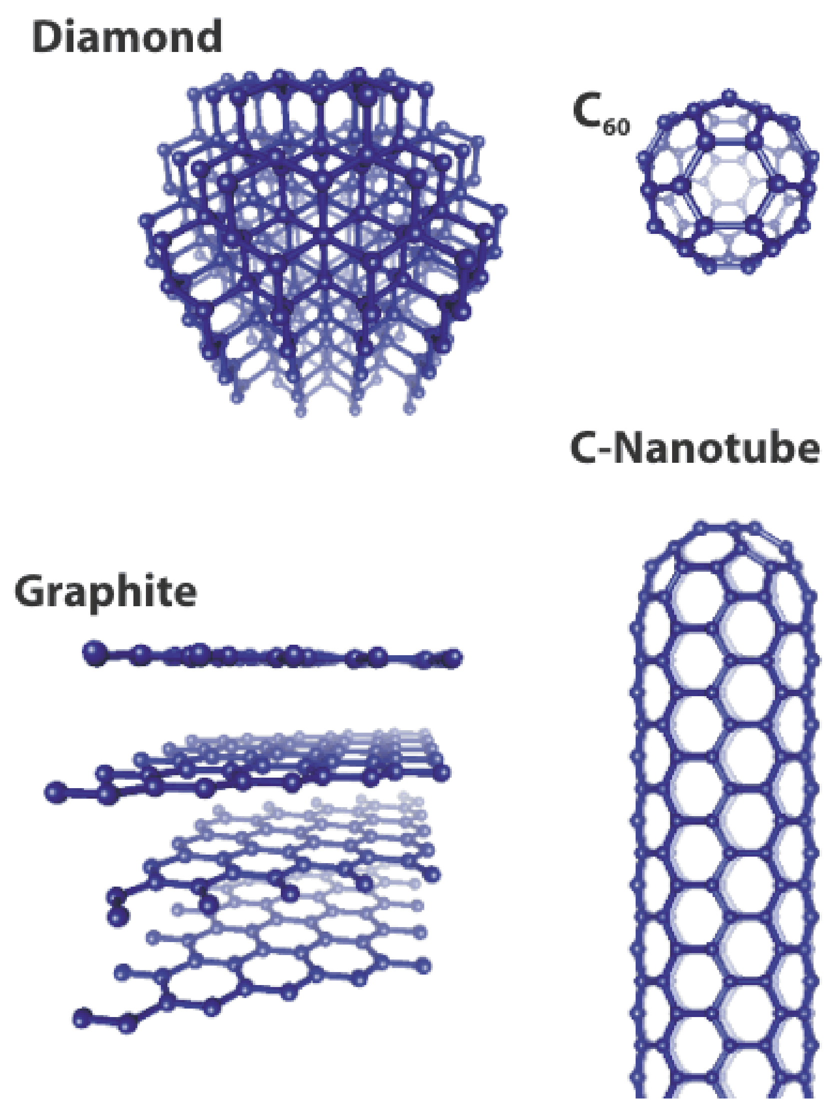
- Strong bonds, stiff orbitals
- Inert surfaces (sp^2)

Derived properties

- Mechanical, chemical, thermal, electrical and photostability

New qualities

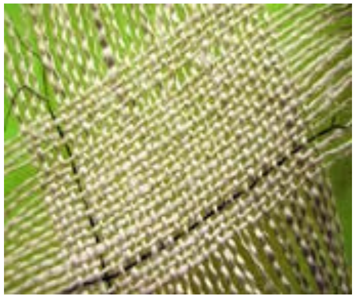
- Variable electronic character
- Variable band-gap
- Unsurpassed transport properties
- Sensitivity to environment

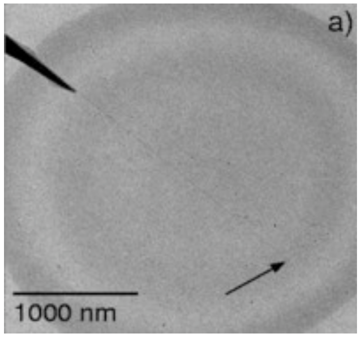


The promise

Most researched

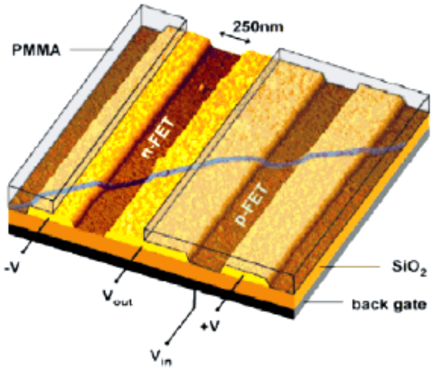
- Electronics
- Composites
- Field emission sources
- Membranes and host materials
- ...





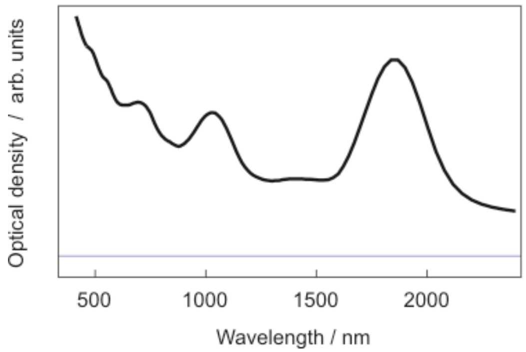
Our interests

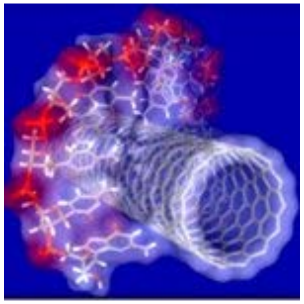
- **Photosensing**
  - specific surface area, chemical stability
- **Imaging & microscopy**
  - luminescence in the water window, chemical- and photostability
- **Agents and reporters in biological systems**
  - benign surface chemistry, low cytotoxicity



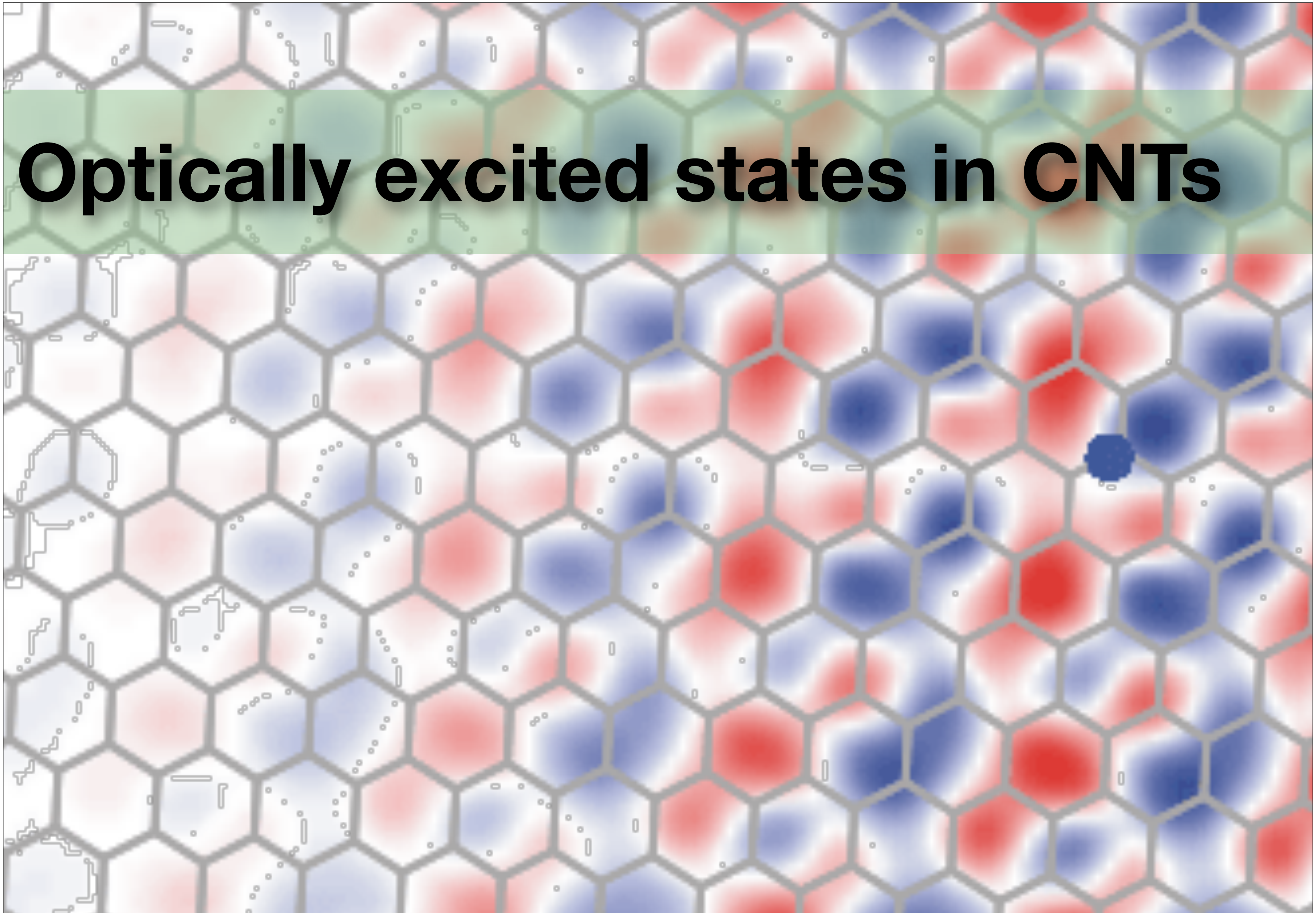
Practical challenges

- **Solubilization for use in various environments**
  - CNT soot is hydrophobic and insoluble in practically all organic solvents
- **Purification, structural sorting**
  - CVD synthesized material is polydisperse
  - Mixed metallic and semiconducting tubes
- **Soft functionalization**
  - graphitic surfaces not biocompatible
  - graphitic surfaces have no chemical specificity

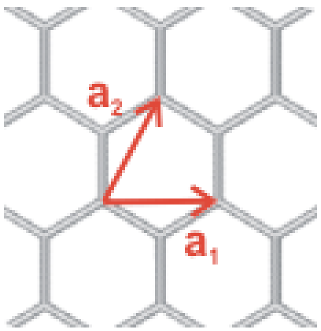




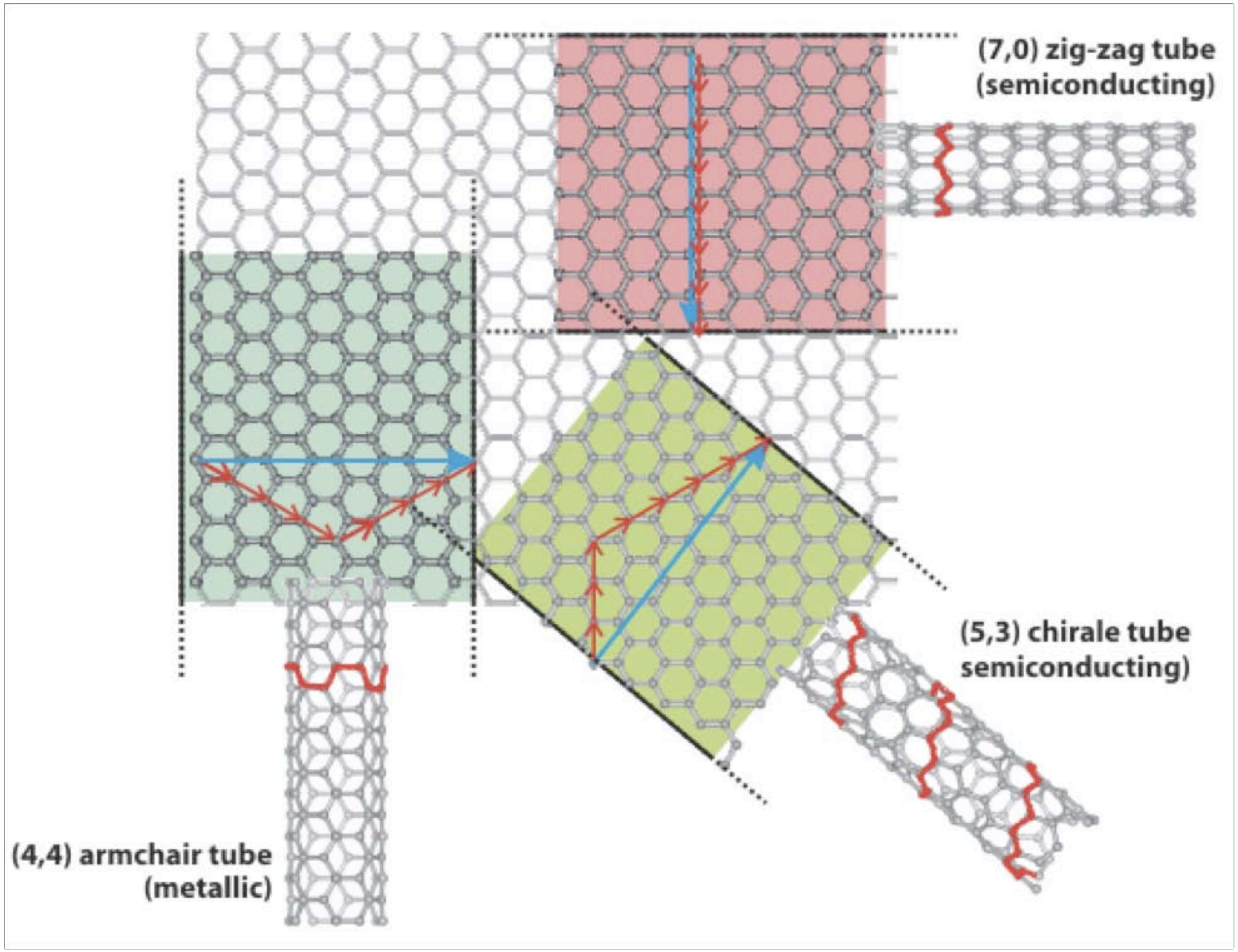
Optically excited states in CNTs



Wrapping graphene

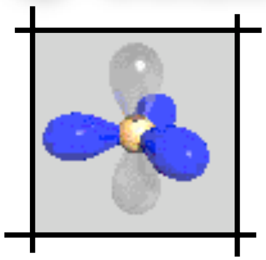


Chiral vector:
$\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$

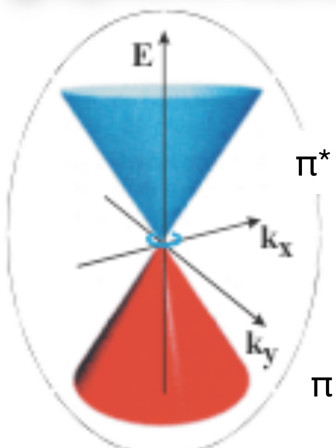


Chirality and diameter make a difference

*sp*² orbitals



p_z derived graphene bands



π* (LUMO)

π (HOMO)

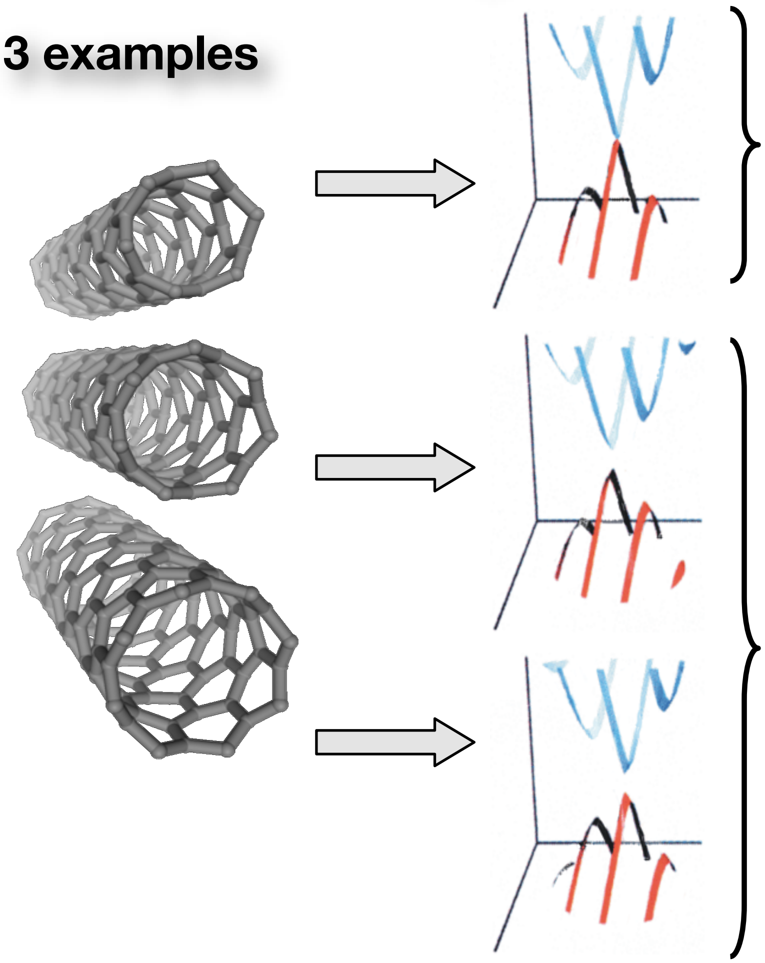
3 examples

(6,0)

(7,0)

(8,0)

quantization



character

metallic

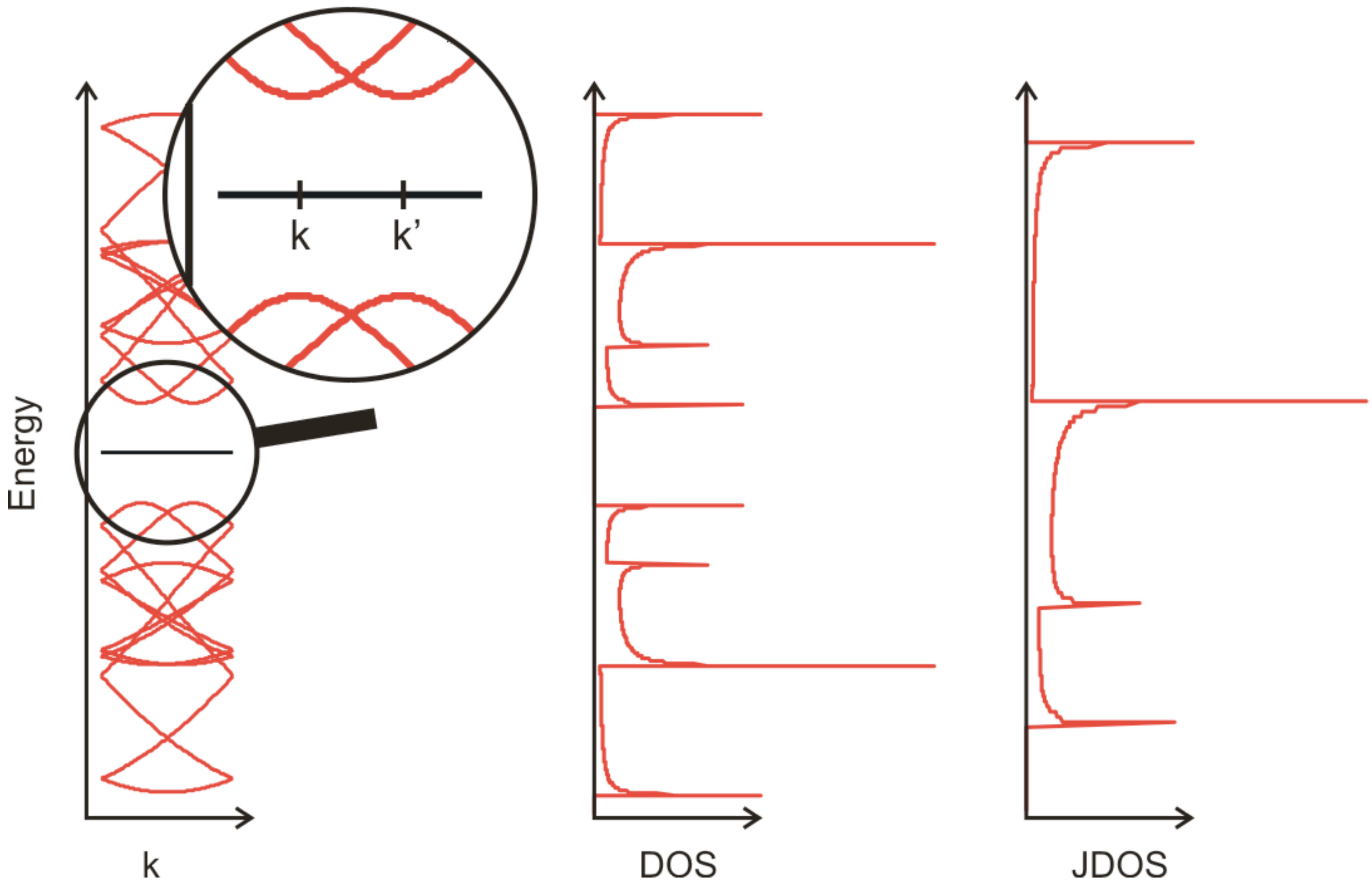
(n-m) *mod*(3) = 0

semiconducting

(n-m) *mod*(3) = ±1

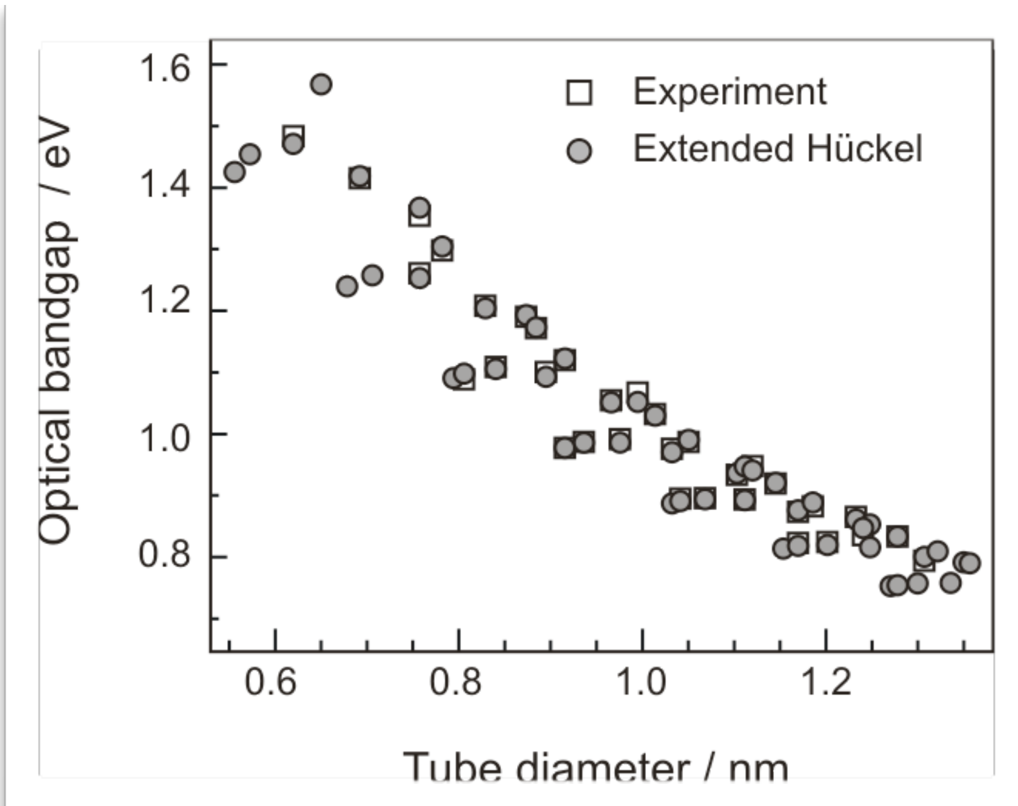
Tight binding example

(2,1) π-subbands



Diameter dependence of optical band gap

Band gap in semiconducting SWNTs



Free parameter: nearest neighbor hopping or transfer integral:

$$t = \langle p_a^A(r)|\mathbf{H}|p_z^B(r - r_{C-C})\rangle$$

Deviation from 1/d scaling because of curvature and chirality effects on π-π overlap.

Coulomb interactions give birth to excitons

Many particle problem with Coulomb interaction:
Solution of the Bethe-Salpeter equation

Perebeinos et al., PRL **92**, 257402 (2004).
Spataru et al., PRL **92**, 77402 (2004).

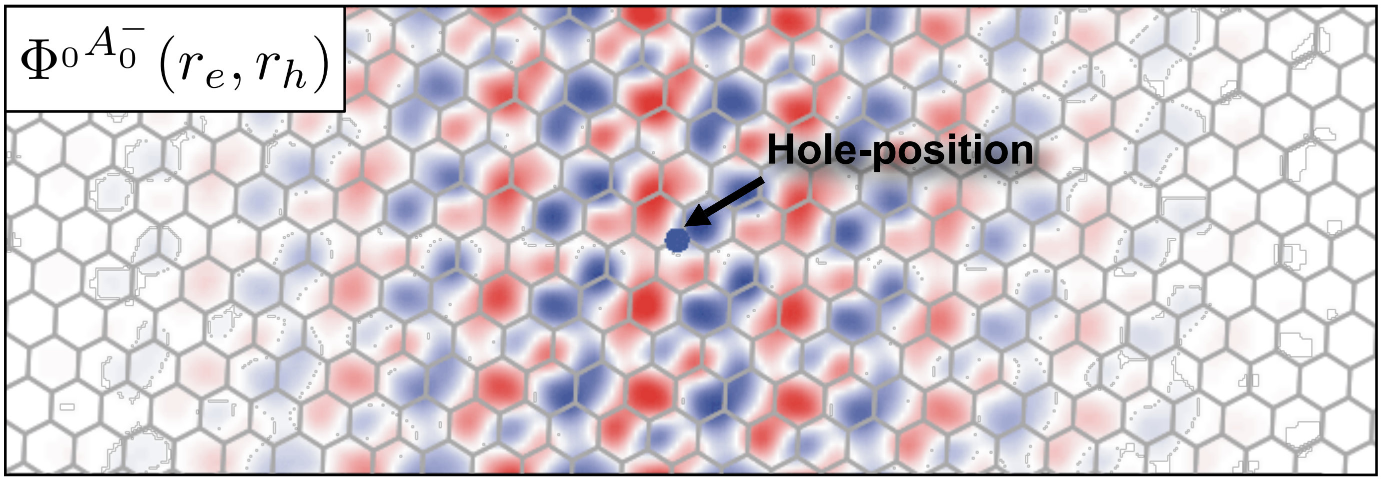
$$\Delta_k A_k^S \sum_{k'} K_{k,k'}^{eh} A_{k'}^S = \Omega_S A_{k'}^S$$

Δ_k - quasiparticle energie (not WW)

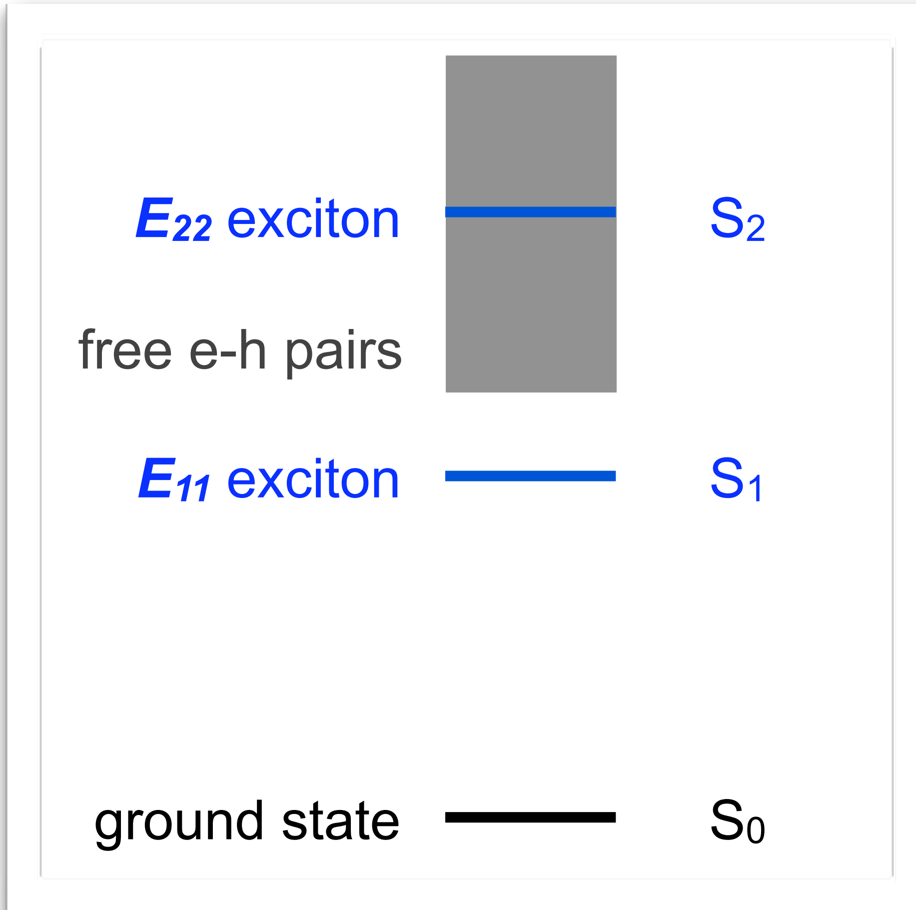
$K_{k,k'}^{eh} = K_{k,k'}^{d} + 2K_{k,k'}^{x}$ - direct and exchange terms

A_k^S - exciton amplitude

(6,5) tube

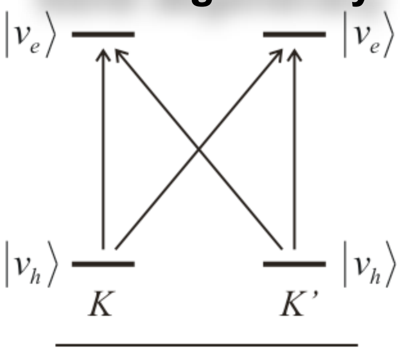


Simplified energy level scheme



Including spin and band degeneracy

band degeneracy



wavefunctions

$$|\nu_e \, \nu_h \, \sigma_e \, \sigma_h\rangle$$

$\lvert K'K'\rangle$	$\lvert\uparrow\uparrow\rangle$
$\lvert K\,K\rangle$	$\lvert\uparrow\downarrow\rangle$
$\lvert K\,K'\rangle$	$\lvert\downarrow\uparrow\rangle$
$\lvert K'K\rangle$	$\lvert\downarrow\downarrow\rangle$

spatial components

$$\tfrac{1}{\sqrt{2}}\left(|K\,K\rangle - |K'K'\rangle\right)$$

$$\tfrac{1}{\sqrt{2}}\left(|K\,K\rangle + |K'K'\rangle\right)$$

$$\tfrac{1}{\sqrt{2}}\left(|K\,K'\rangle + |K'K\rangle\right)$$

} Symmetr. WF.

$$\tfrac{1}{\sqrt{2}}\left(|K\,K'\rangle - |K'K\rangle\right)$$

} Antisymmetr. WF.

spin components

$$\chi^{1}_{0,0} = \tfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

} Antisymmetr. WF. (Singlet)

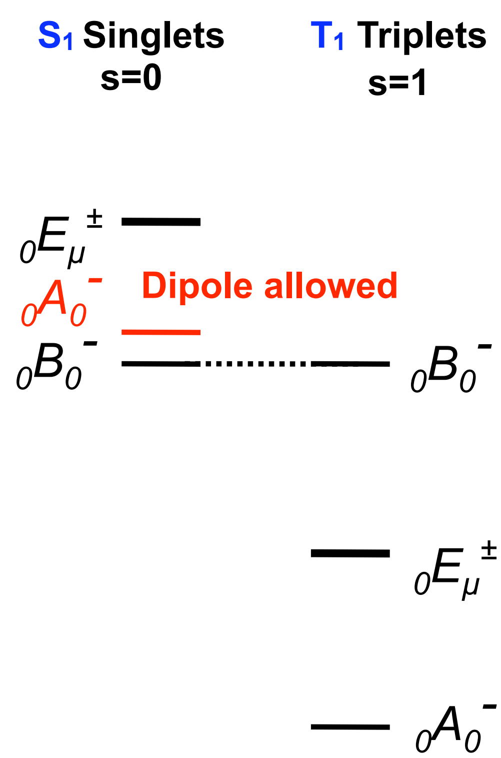
$$\chi^{3}_{1,+1} = |\uparrow\uparrow\rangle$$

$$\chi^{3}_{1,0} = \tfrac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right)$$

$$\chi^{3}_{1,-1} = |\downarrow\downarrow\rangle$$

} Symmetr. WF. (Triplet)

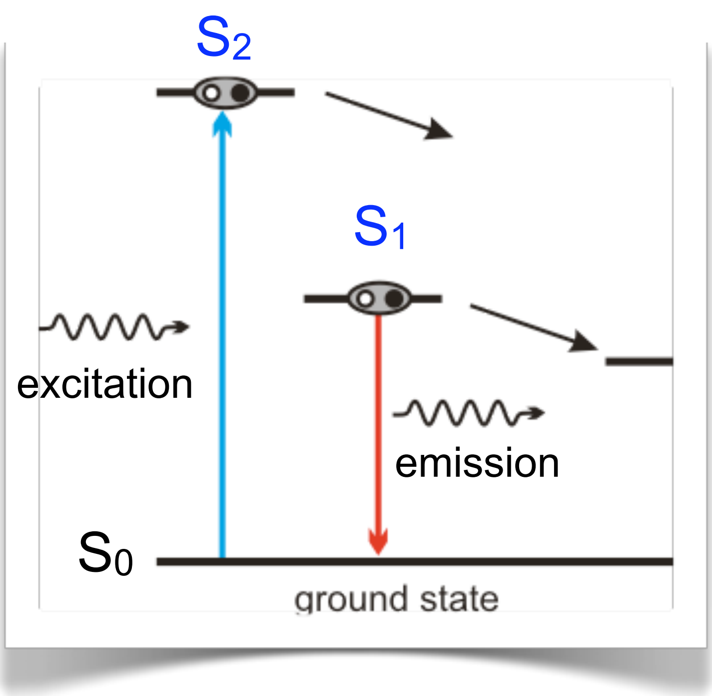
term scheme



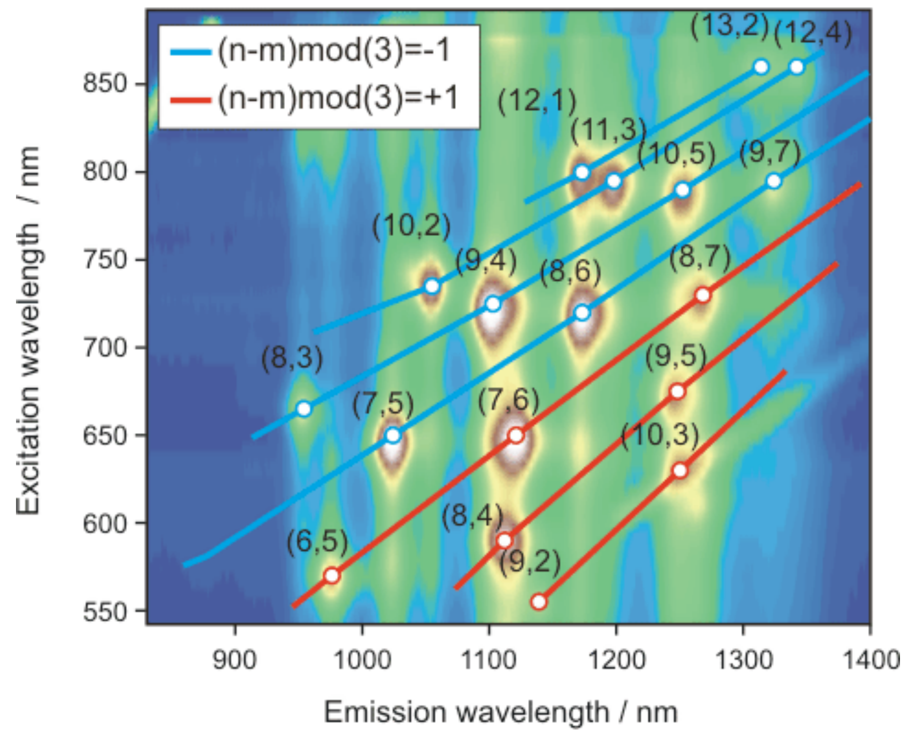
Ando, J. Phys. Soc. Jap. **75**, 24707 (2006).
Abe, Yu amd Su, PRB **45**, 8264 (1992).

Spectroscopic assessment

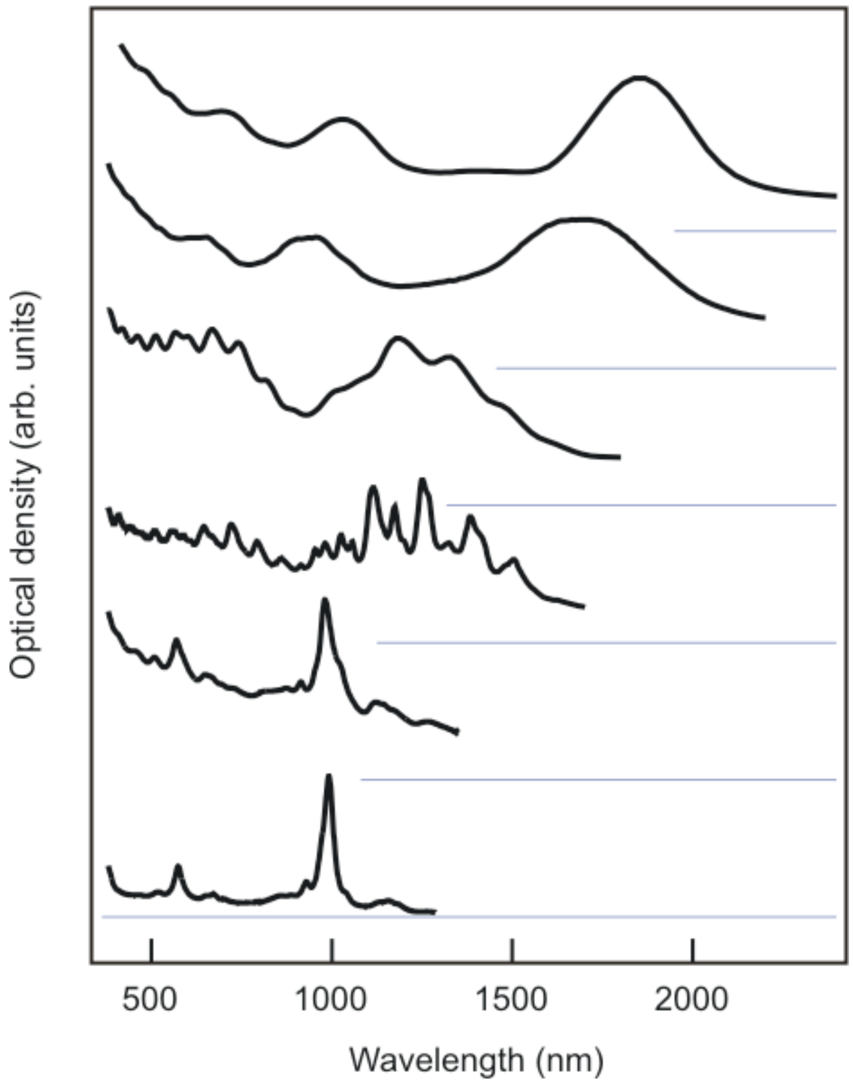
Absorption and photoluminescence



Photoluminescence excitation spectrum, poly-disperse CNT material



Absorption spectroscopy: samples 1999-2007



1999 Laseroven material: Ø ≈ 1.4 nm

1999 Laseroven material: Ø ≈ 1.2 nm

2000 CVD material (HIPCO): Ø ≈ 1.0 nm

2002 HIPCO colloidal

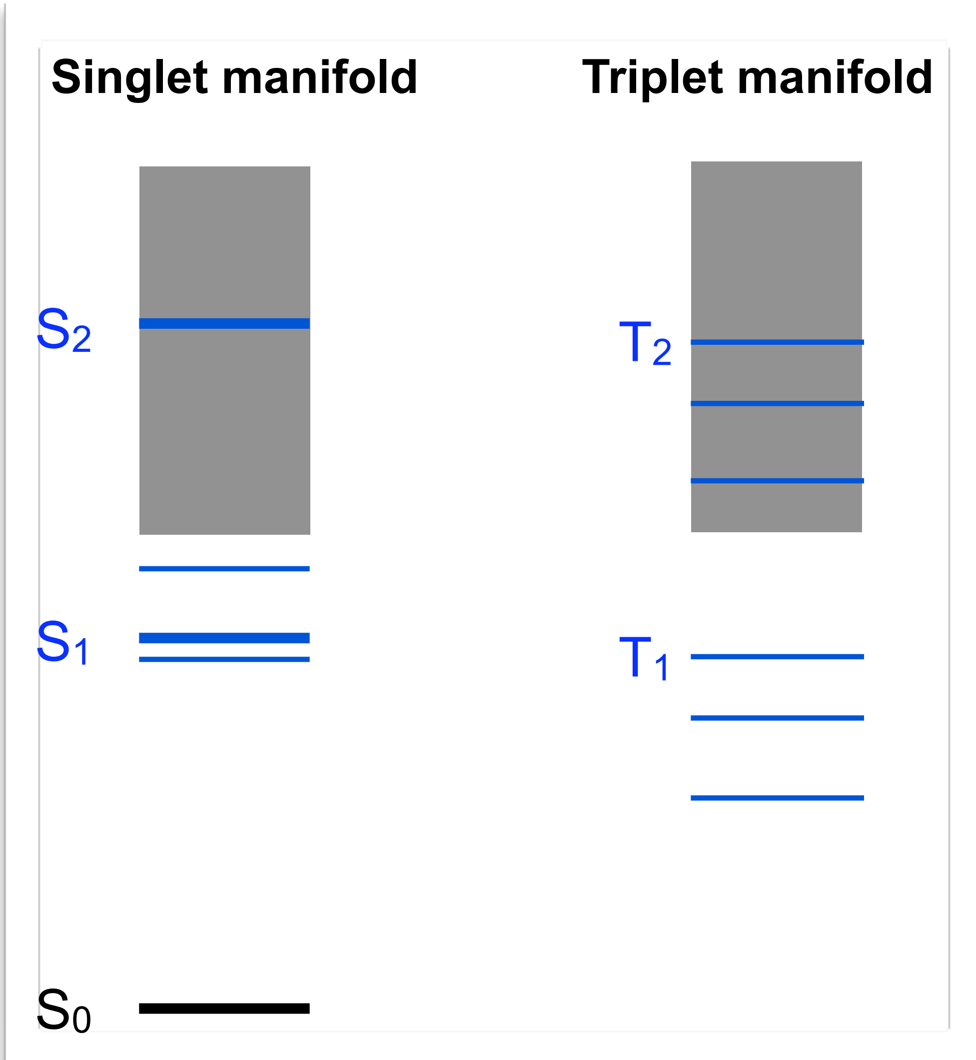
2003 CVD material (CoMoCAT) colloidal: Ø ≈ 0.8 nm

2005 CoMoCAT material: isopycnic fractionation .

2006 Fractionation of metallic tubes (isopycnic)

Kataura et al., Synth. Metals **103** (1999) 2555.
Hertel et al., Appl. Phys. A **75** (2002) 449.
O'Connel et al. , Science **297** (2002) 593.
Arnold et al., Nano Lett. 5 (2005) 713.
Arnold et al., Nature Nanotech. 1 (2006) 60.

Energetic landscape



Known to some degree

- Energetics of singlet manifold

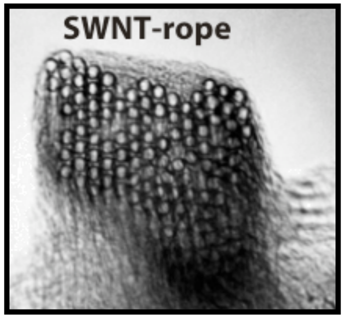
Unresolved

- Decay of excited states?
- Coupling to vibrations?
- Exciton size?
- Branching ratios?
- Energetics of triplet manifold?
- ...

Sample preparation

Colloidal Nanotube suspensions

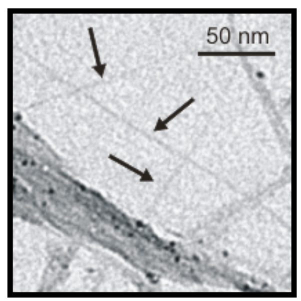
CNT soot



soap & water

energy (ultrasound)

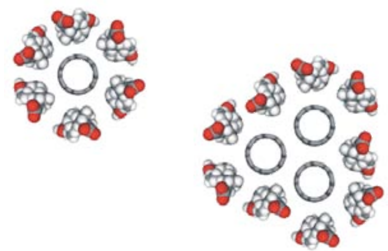
Mixture



sedimentation 100.000g, 4h

supernatant

SWNT micelles

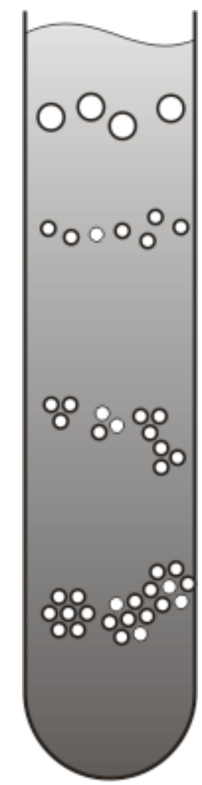


$\eta \approx \mathbf{10^{-4} - 10^{-3}}$

O'Connel et al. , Science **297** (2002) 593.

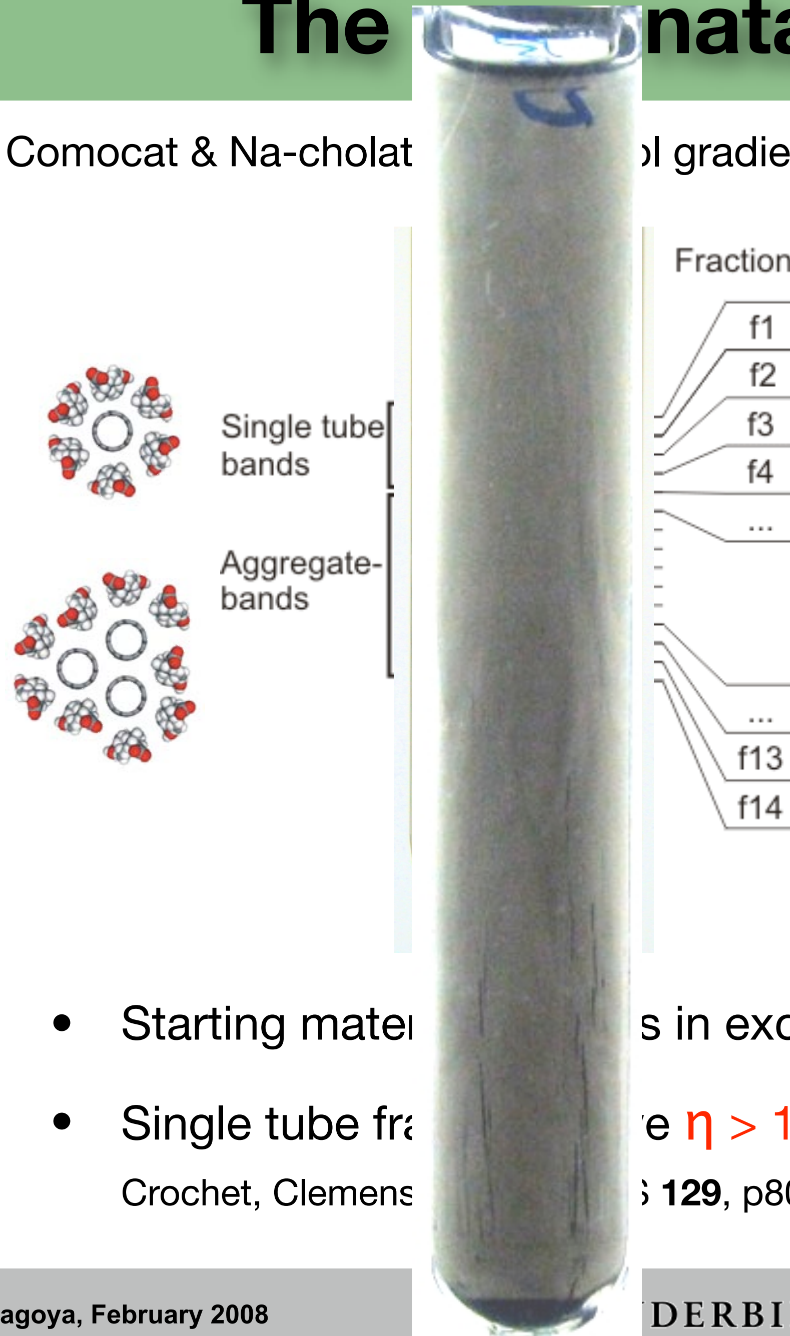
Density gradient ultracentrifugation (DGU)

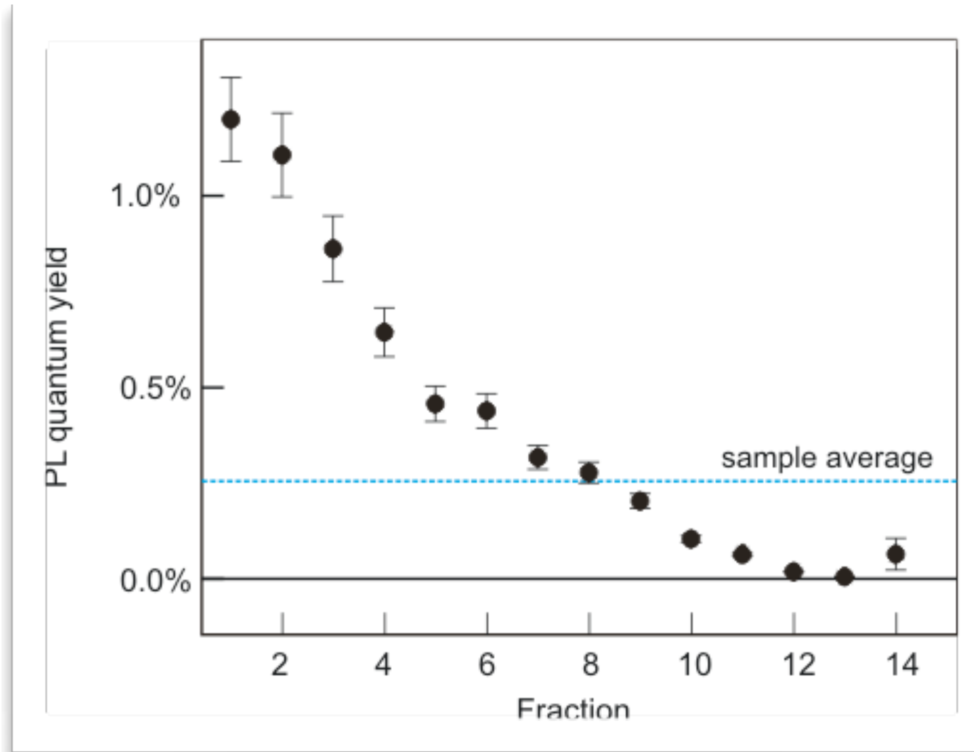
- Additives generating density gradients
  - CsCl: 1.0-1.9 g/cm^3
  - Sucrose: 1.0-1.35 g/cm^3
  - Iodixanol: 1.0-1.6 g/cm^3
  - …
- Ultracentrifugation at high accelerations
  - 100,000g -200,000g
- Fractionation by buoyancy (isopycnic fractionation)



The natant is polydisperse

Comocat & Na-cholat l gradient



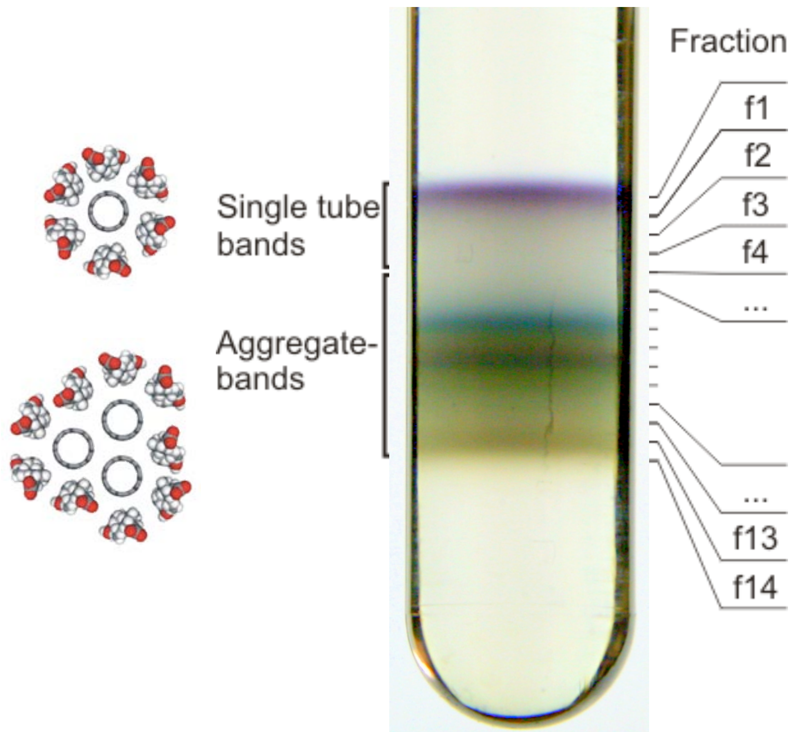


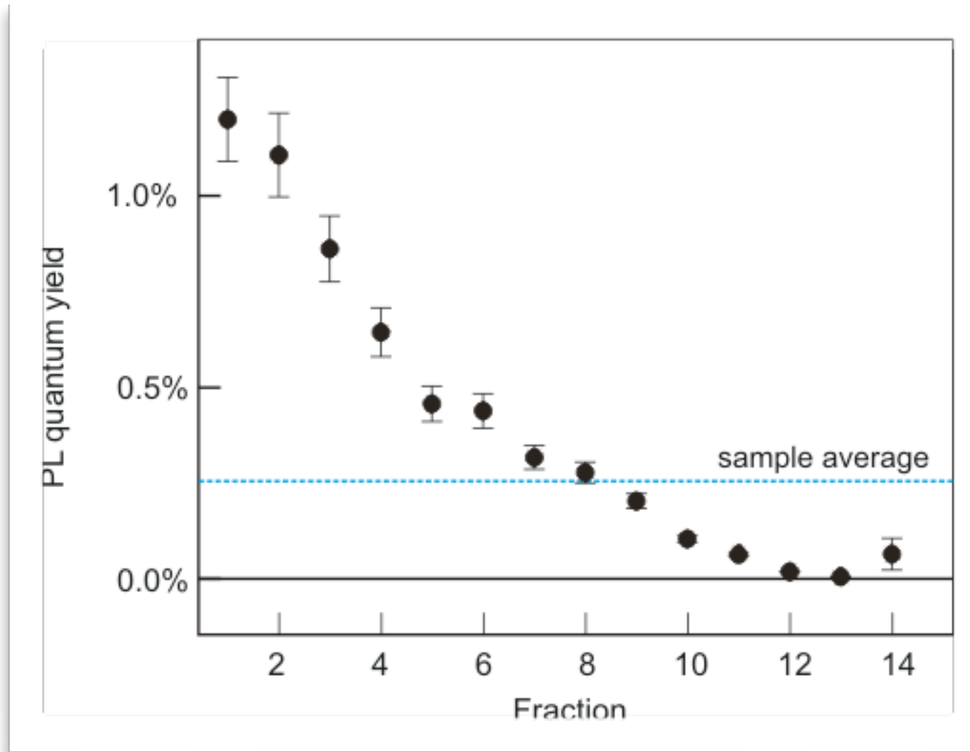
- Starting mate s in excess of 70 wt.% of small aggregates.
- Single tube fr e η > 1% .

Crochet, Clemens **129**, p8058 (2007)

The supernatant is polydisperse

Comocat & Na-cholate in iodixanol gradient





- Starting material contains in excess of 70 wt.% of small aggregates.
- Single tube fractions have η > 1% .

Crochet, Clemens, Hertel, JACS **129**, p8058 (2007)

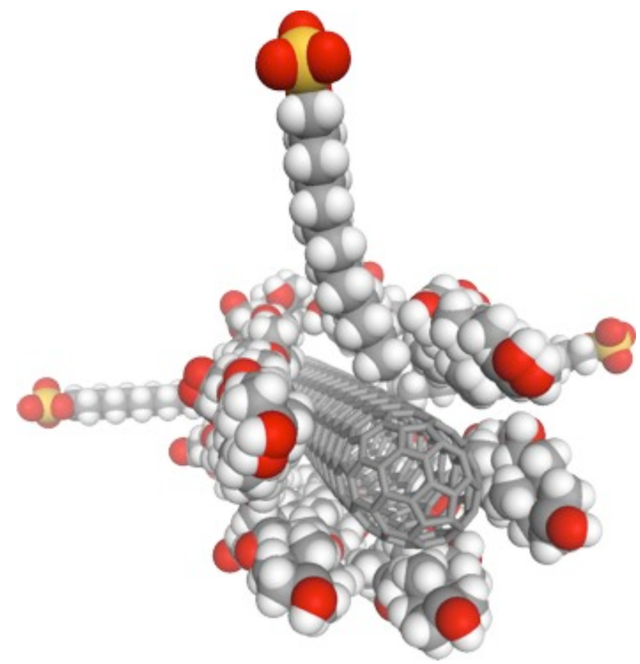
Cosurfactants introduce new flavor

- **Zero order energetics: amphiphilics in water with nanotube soot**
  - Minimization of hydrophobic interactions (CNT-H_2O)
  - Non-specific to tube metallicity or band-gap

- **Second order effects**
  - Optimization of van der Waals interactions
  - Hamaker constants can be shown to depend on polarizabilities (Lifshitz theory)

$$F(D) = -\frac{A(\epsilon_{\mathrm{CNT}}, \epsilon_{\mathrm{S}}, \epsilon_{\mathrm{water}})\, R}{12D^2}$$

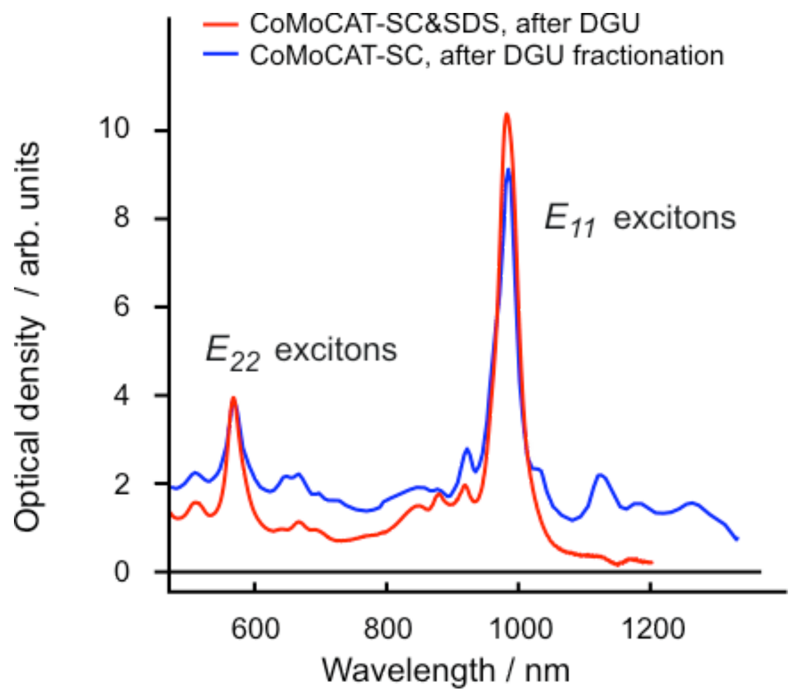
  - Selectivity towards band-gap and metallicity



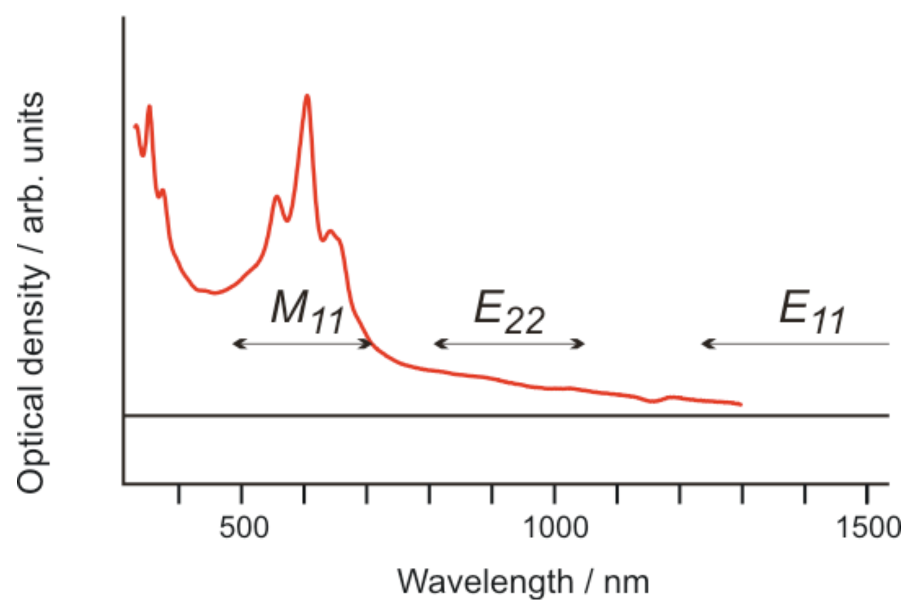
SC + SDS + SWNT

Better samples through cosurfactant DGU

Better diameter selectivity
(4:1 mixture of SC:SDS, 2 wt%)

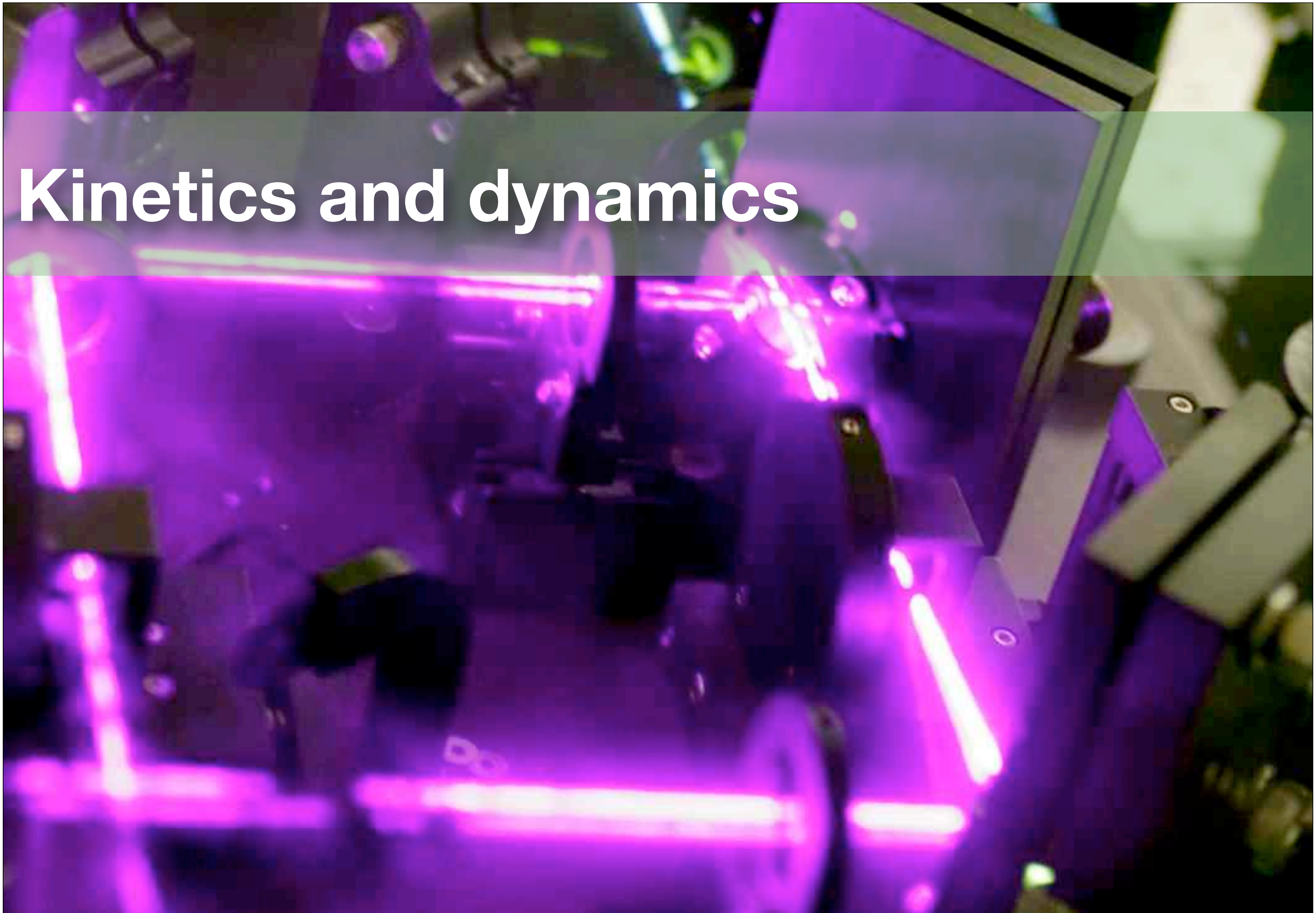


Separation of metallic and semiconducting SWTNs



sample by M. Arnold & M. Hersam

Kinetics and dynamics



Kinetics and dynamics: relevance

Selected applications

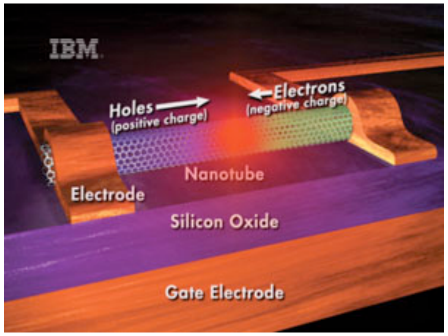
- Light emitting devices
- Fluorescent tags
- Saturable absorbers
- Photosensors

Role of excited state dynamics

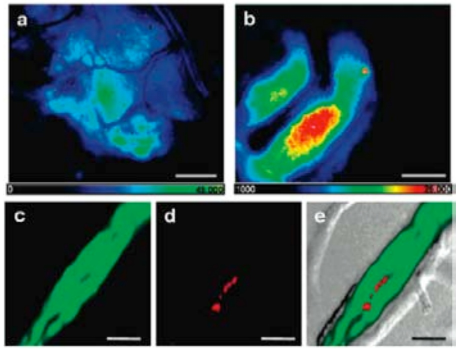
- determines efficiency (electroluminescence)
- determines quantum yields (photoluminescence)
- power, rep. rate, etc (modelocked ultrafast lasers)

Questions

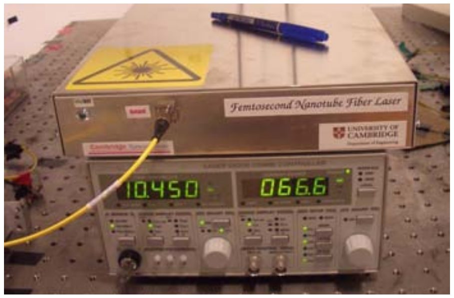
- rate constants for different relaxation channels
- branching ratios
- ...



IBM Group of Ph. Avouris

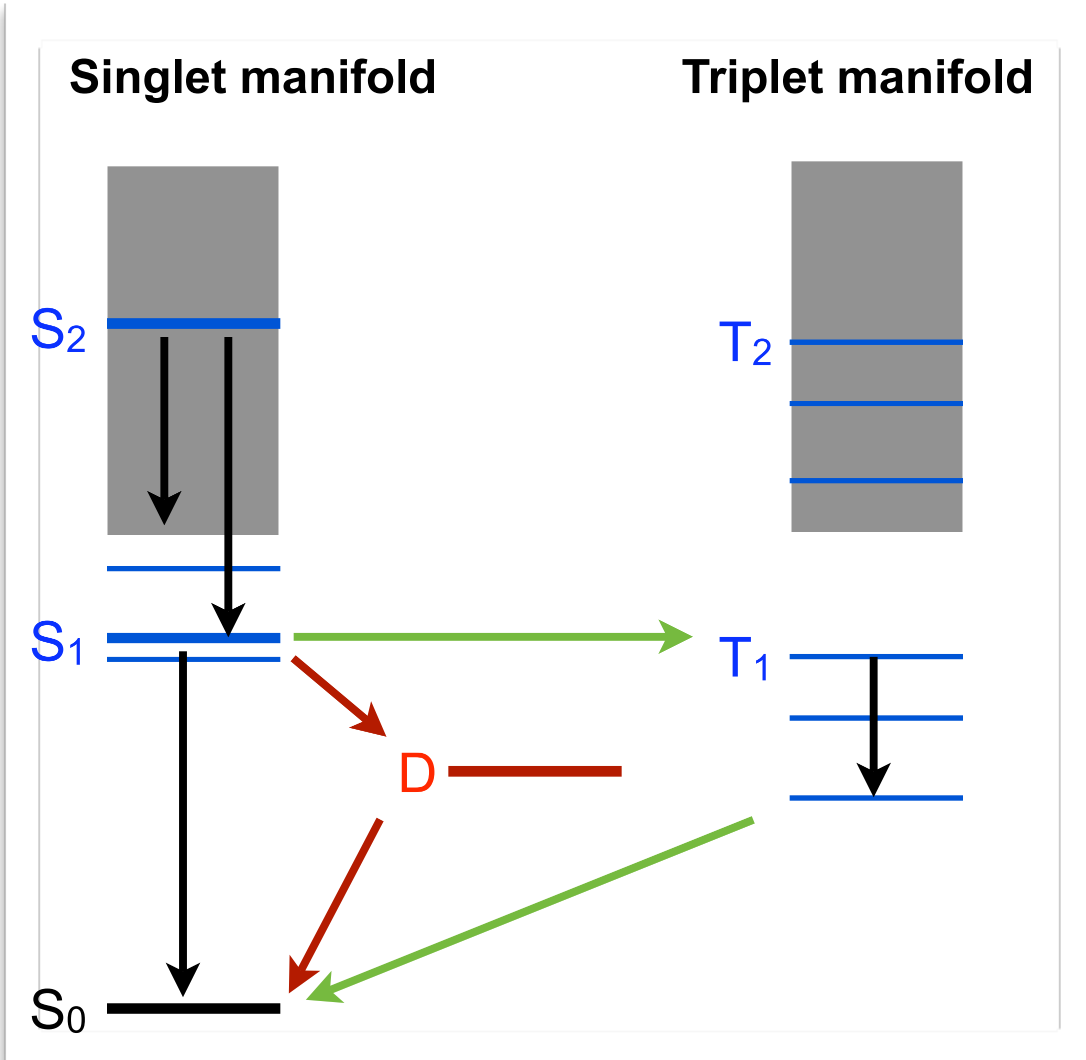


Leeuw et al., Nano Lett. 2007



Cambridge Group of A. Ferrari

Kinetics and dynamics: overview

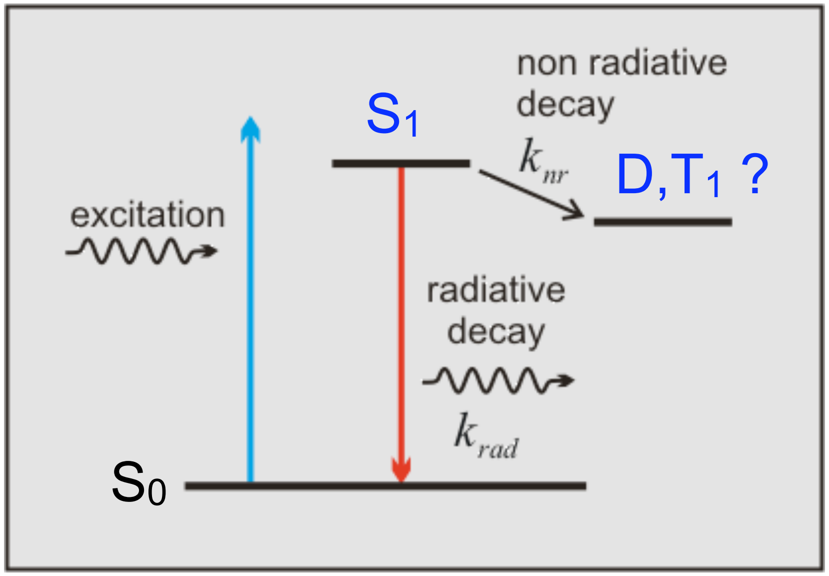


Processes of interest

- Internal conversion (IC)
- Intersystem crossing (ICS)
- Trapping

- Branching
- Radiative decay
- Non-radiative decay
- Ground state recovery
- ....

Radiative and non-radiative decay



PL quantum yields

Photon counting

$$\eta = \frac{N_{\mathrm{PL}}}{N_{\mathrm{abs}}}$$

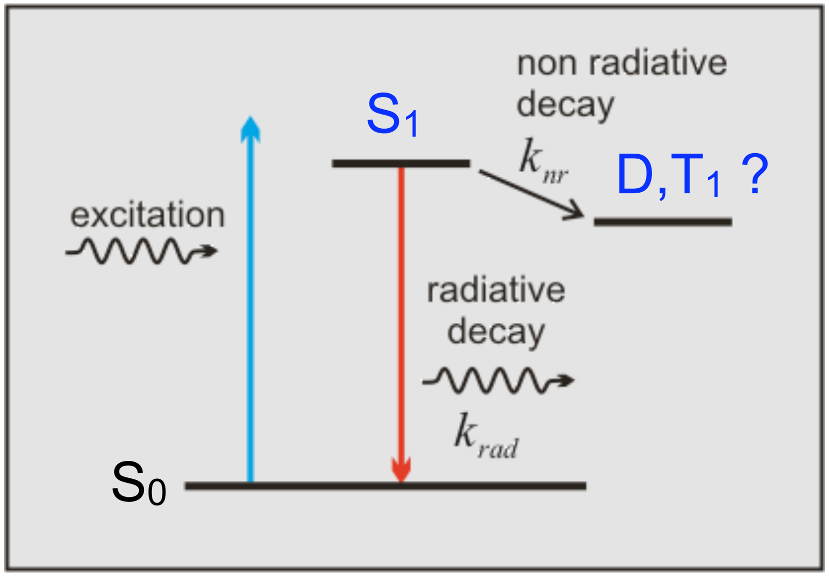
Kinetics

$$\eta = \frac{k_{\mathrm{rad}}}{k_{\mathrm{rad}} + k_{\mathrm{nr}}}$$

Lifetimes

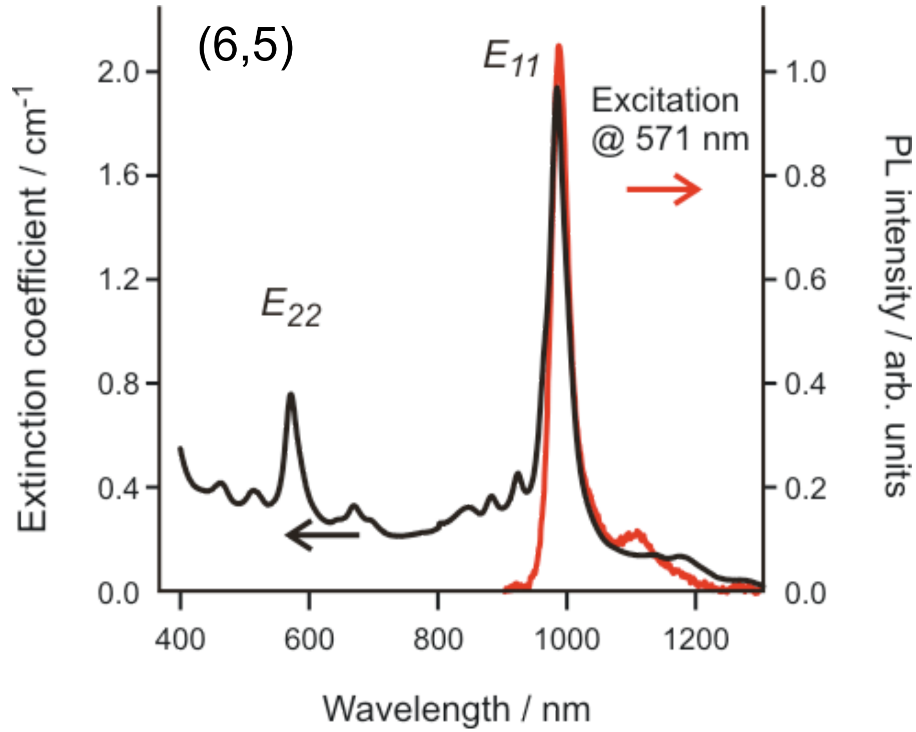
$$\eta = \frac{\tau_{\mathrm{PL}}}{\tau_{\mathrm{rad}}}$$

Non-radiative decay k_{nr} is efficient



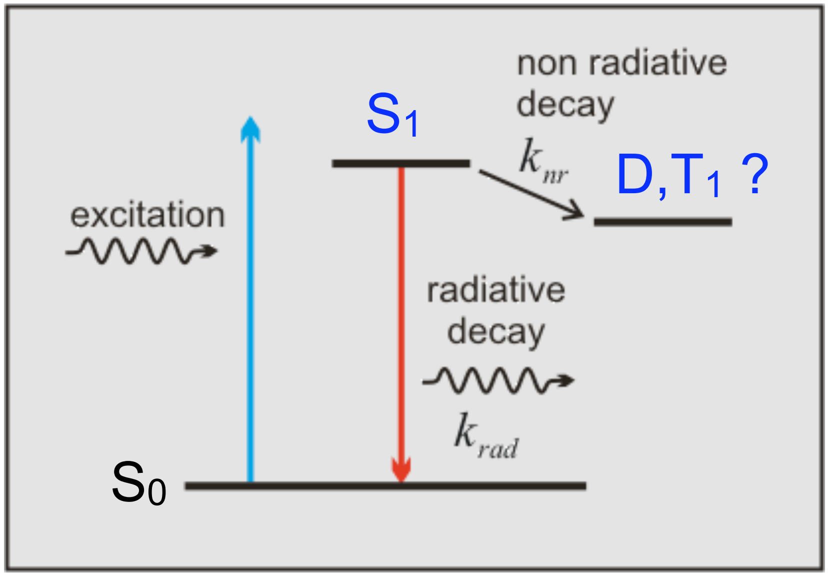
$$\eta = \frac{k_{\rm rad}}{k_{\rm rad}+k_{\rm nr}} \approx 3\%$$

$$\mathrm{k}_{\rm nr} \approx 30 \times k_{\rm rad}$$



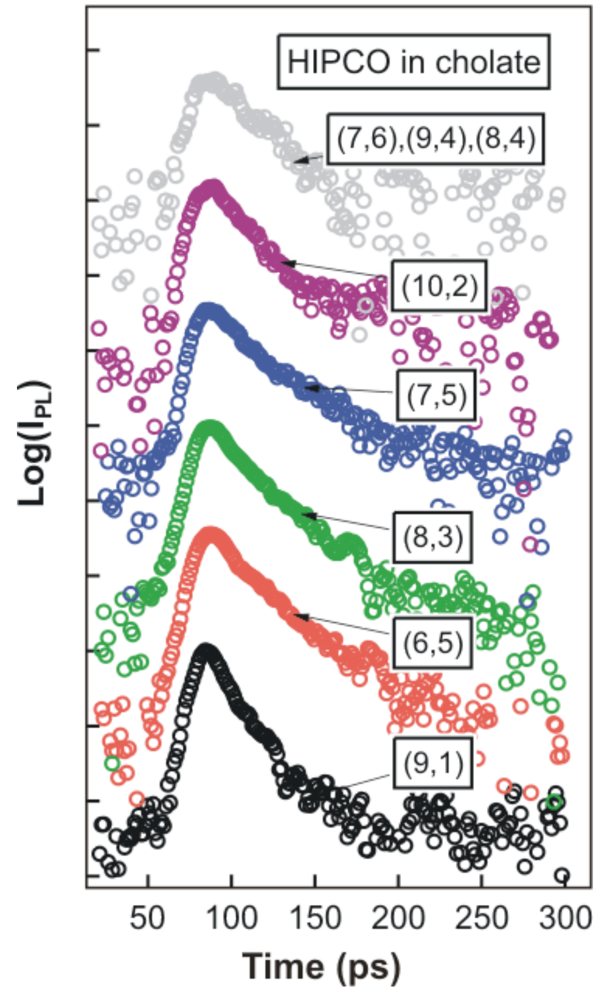
Crochet, Clemens, Hertel, JACS **129**, p8058 (2007)
Rajan, Strano, Heller, Hertel, Schulten, JPCB (in press)

Radiative decay τ_{PL} is on the order of ps



$$\eta = \frac{\tau_{\rm PL}}{\tau_{\rm rad}}$$

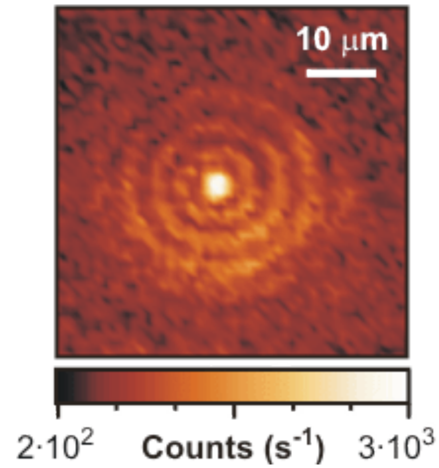
$$k_{\rm PL} \approx (30{\rm ps})^{-1}$$



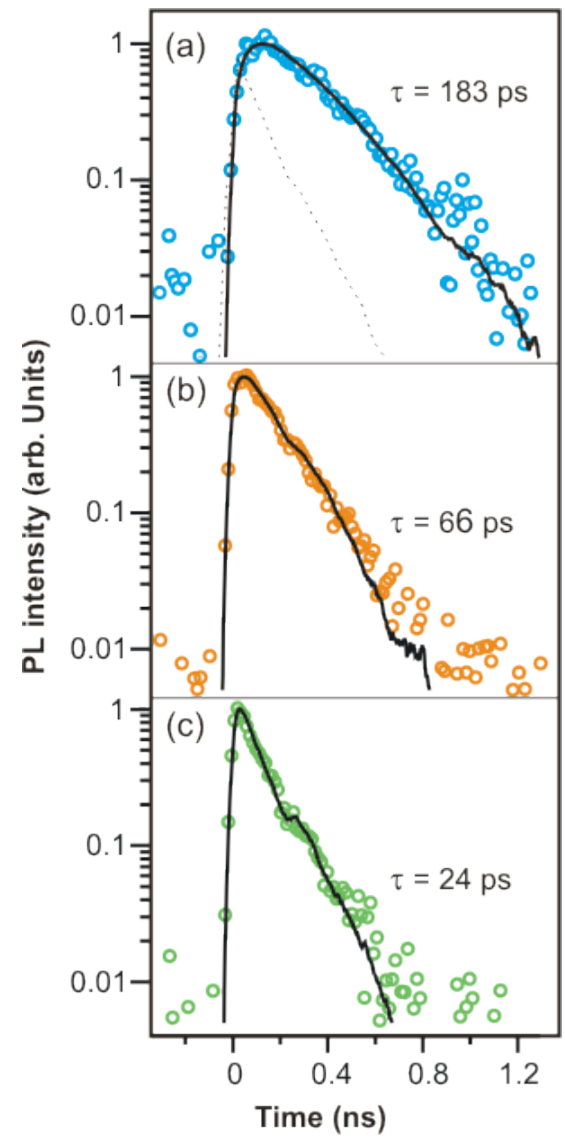
Hagen et al., Appl. Phys. A **78**, 1137 (2004)
Hertel, et al., Nano Letters (2005)

Inhomogeneities affect non-radiative decay

Time-correlated single photon counting of (6,4) tubes.



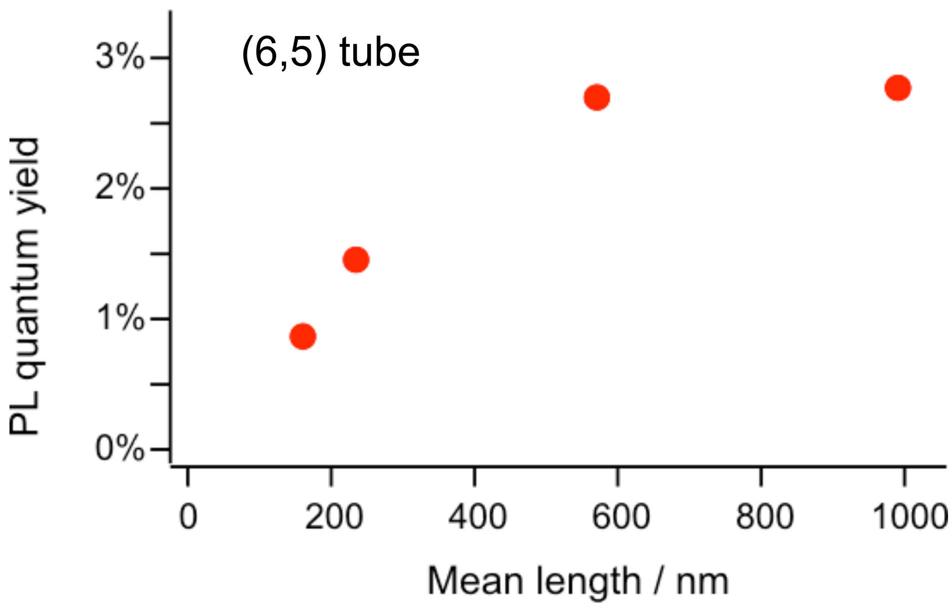
Hagen et al.,
PRL **95**, 197401 (2005)



$$k_{\mathrm{nr}}(\mathrm{tube1}) \neq k_{\mathrm{nr}}(\mathrm{tube2}) \neq k_{\mathrm{nr}}(\mathrm{tube3})\ldots$$

What kind of inhomogeneities? Defects, Bundles? ...

Long tubes shine brighter



Non-radiative decay at tube ends!

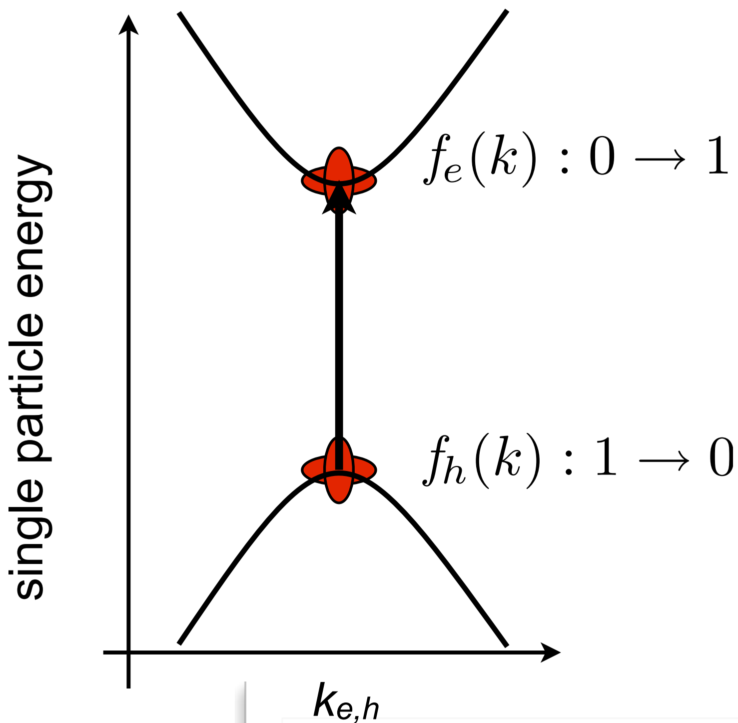
Diffusion is crucial!

Is diffusion one-dimensional?

Electrophoretic length fractionation

Rajan, Strano, Heller, Hertel, Schulten, JPCB (in press)

Determining the exciton size



Phase space filling model

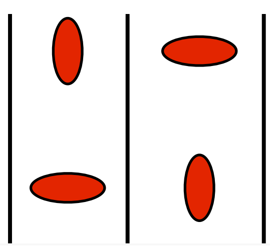
Schmitt-Rink, Chelma, Miller, PRB **32**, 6601 (1985)

$$f_e(k) = f_h(k) = \frac{\Delta \tilde{n}}{2} |\Psi_x(k)|^2$$

$$\Delta k \Delta x \approx \hbar/2$$

delocalized exciton — saturates easily

localized exciton — saturates later

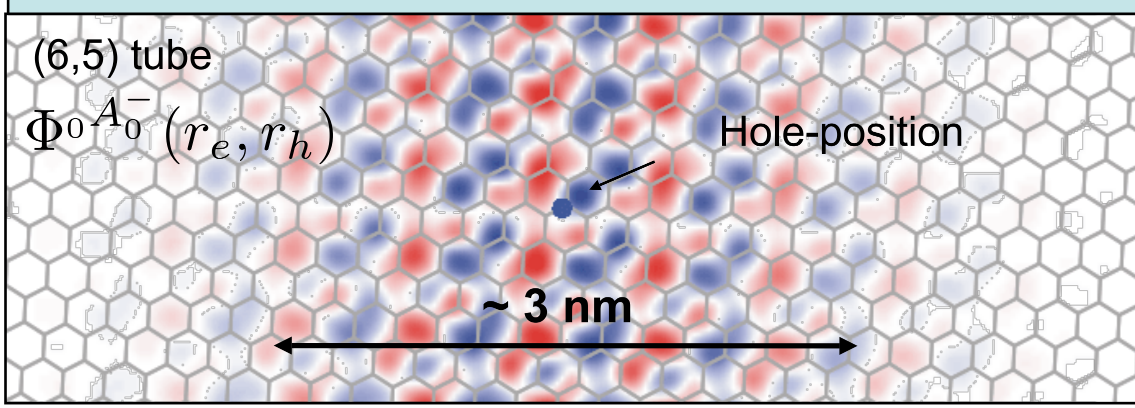


Exciton size is about 5x the tube diameter

- Nonlinear-response $\Delta T/T = -\Delta\tilde{n}/\tilde{n}_s$

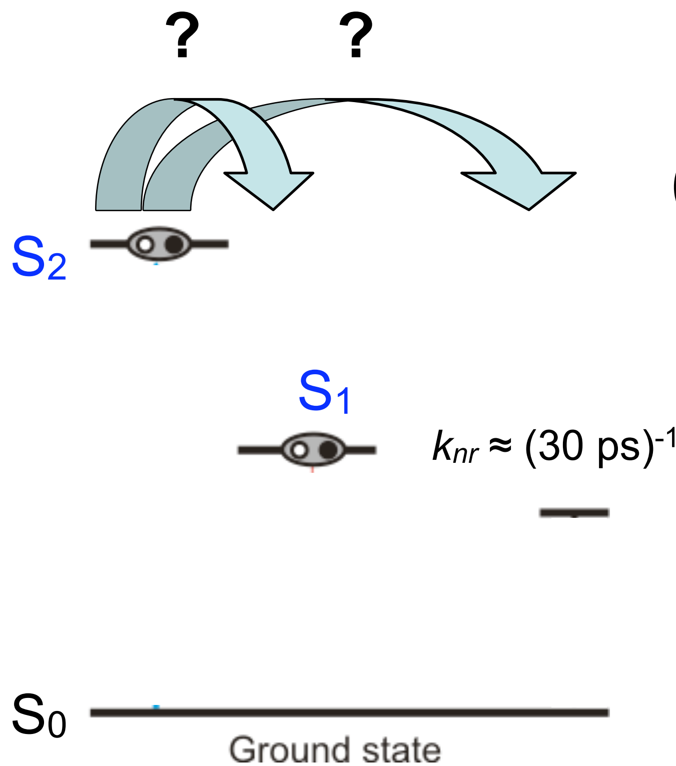
$\tilde{n}_s$ - Saturation density

$\Delta\tilde{n}$ - Electron-hole density



Lüer, Hoseinkhani, Crochet, Hertel, Lanzani, (submitted)

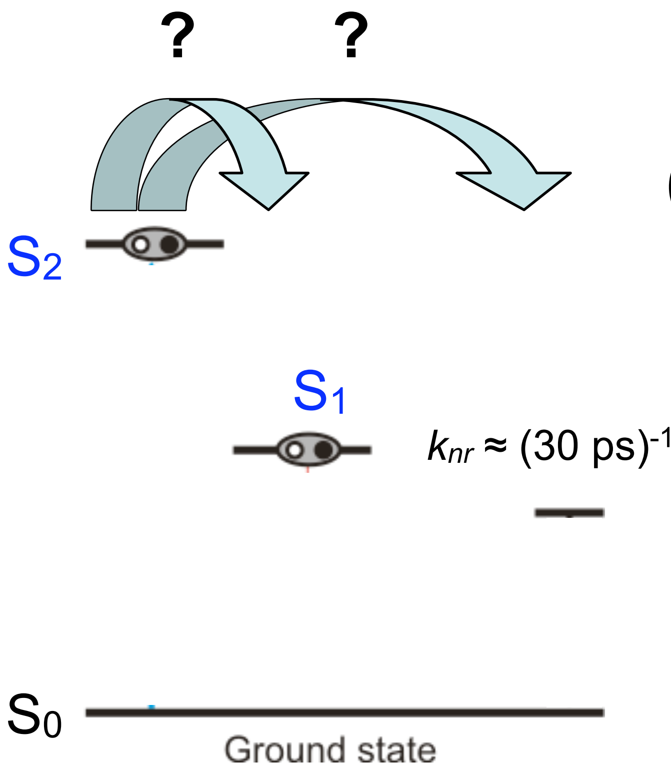
Radiative and non-radiative decay



Now, do we know the radiative lifetime?

$$\eta = \frac{N_{PL}}{N_{abs}} + \eta = \frac{\tau_{PL}}{\tau_{rad}} \Rightarrow k_{rad} = 1/\tau_{rad}\ ?$$

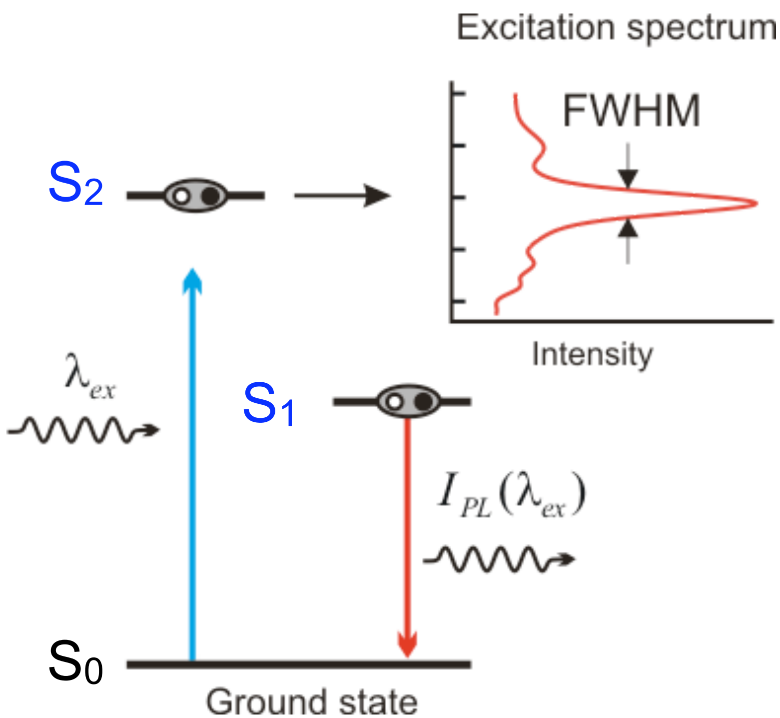
Radiative and non-radiative decay

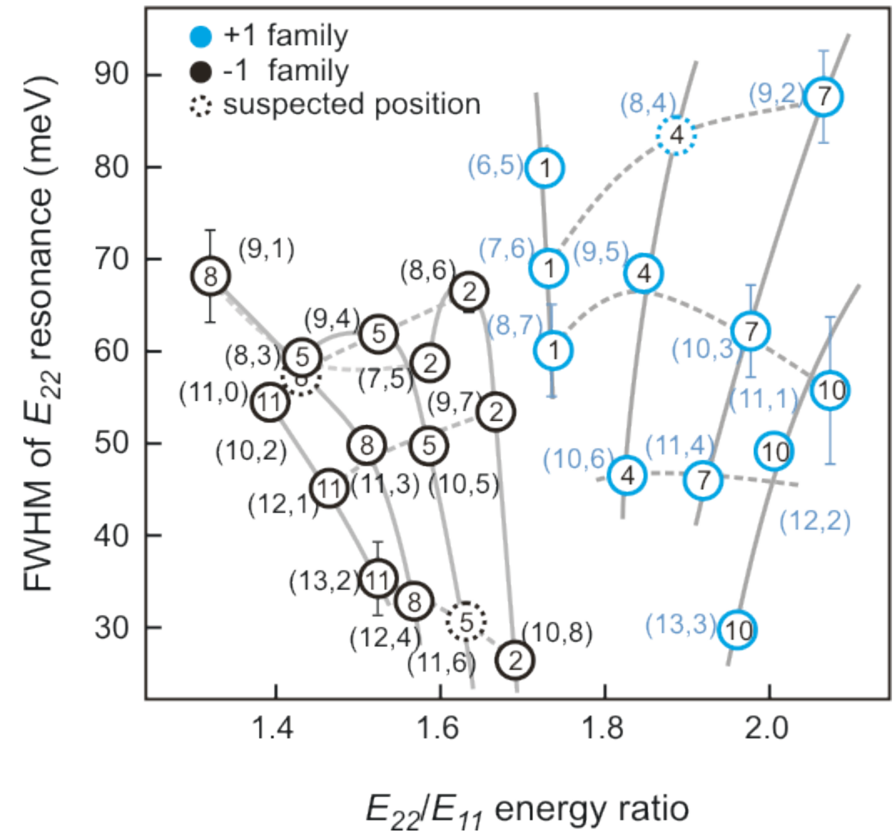


Now, do we know the radiative lifetime?

No!

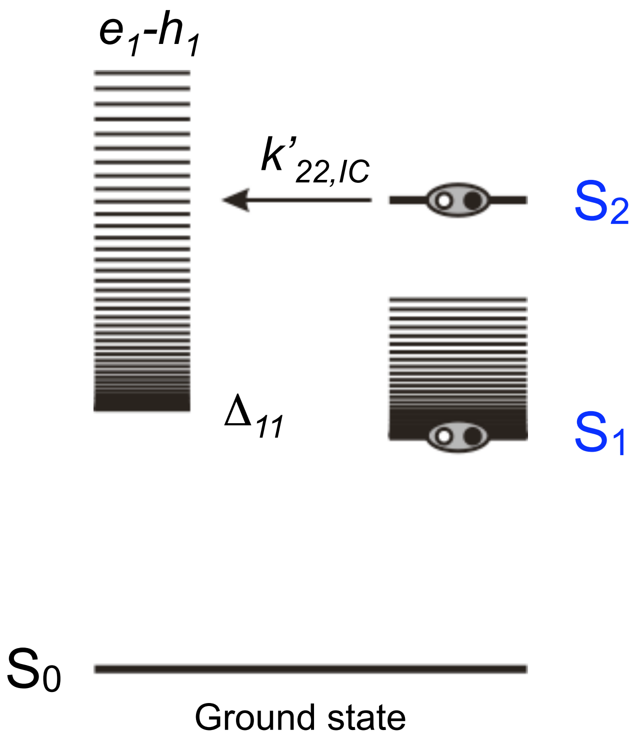
The S_2 resonance is short lived





Hertel, Crochet, Perebeinos, Arnold, Kappes and Avouris,
(Nano Lett. **8**, 87 (2008))

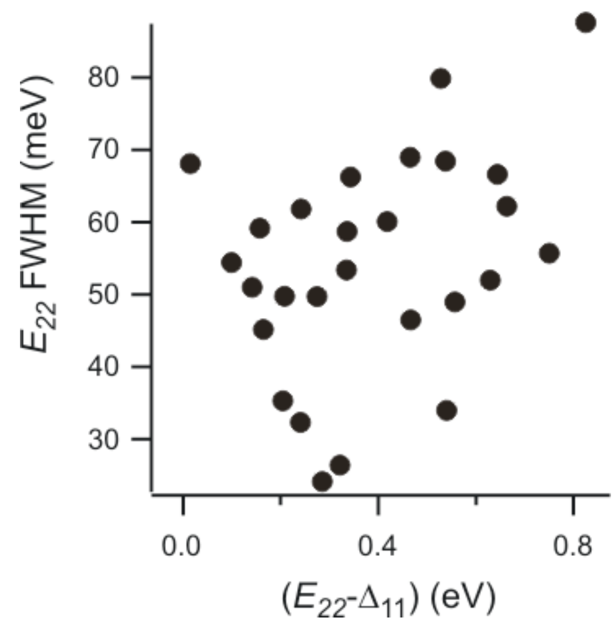
No S_2 decay into the e_1-h_1 continuum



Perturbation theory

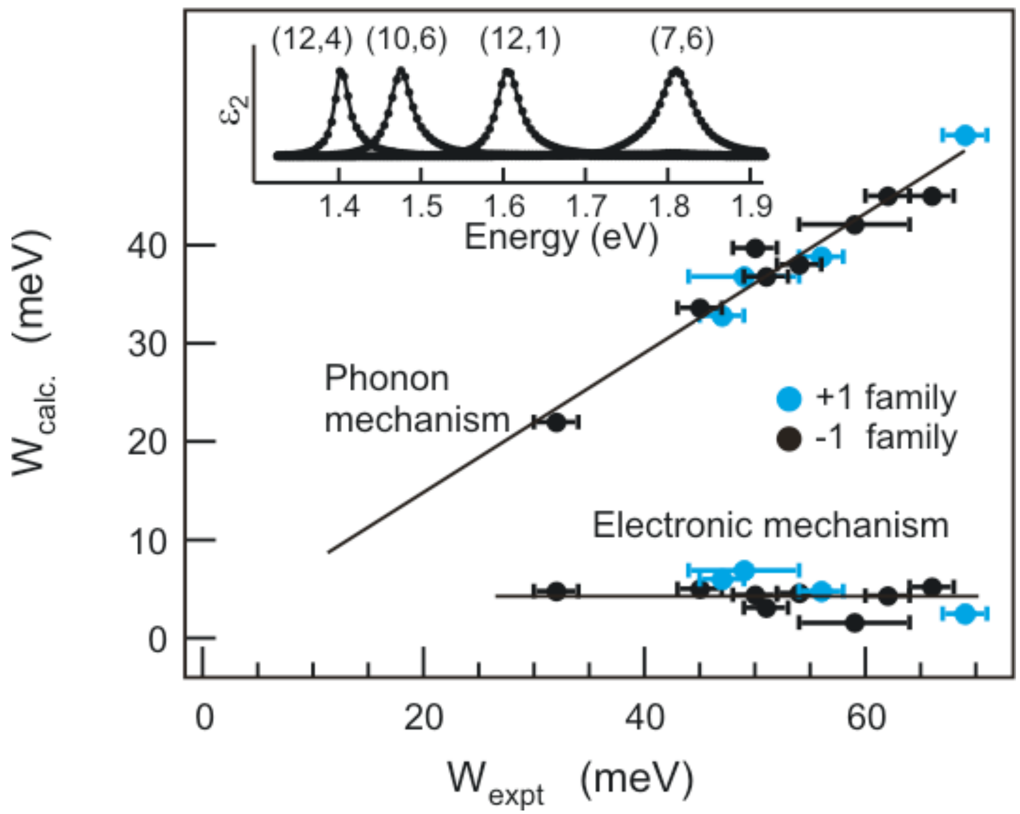
$$W_{22} \propto \left|\langle \psi_{22} | V | \psi_{e-h} \rangle\right|^2 \rho_{e-h}(E_{22})$$

Rate should scale with DOS in final state



Hertel, Crochet, Perebeinos, Arnold, Kappes and Avouris, (Nano Lett. **8**, 87 (2008))

Phonons scatter S_2 into higher S_1 states



Using Su-Schrieffer-Heeger model with matrix element:

$$t = t_0 - g\,\delta R_{C-C}$$

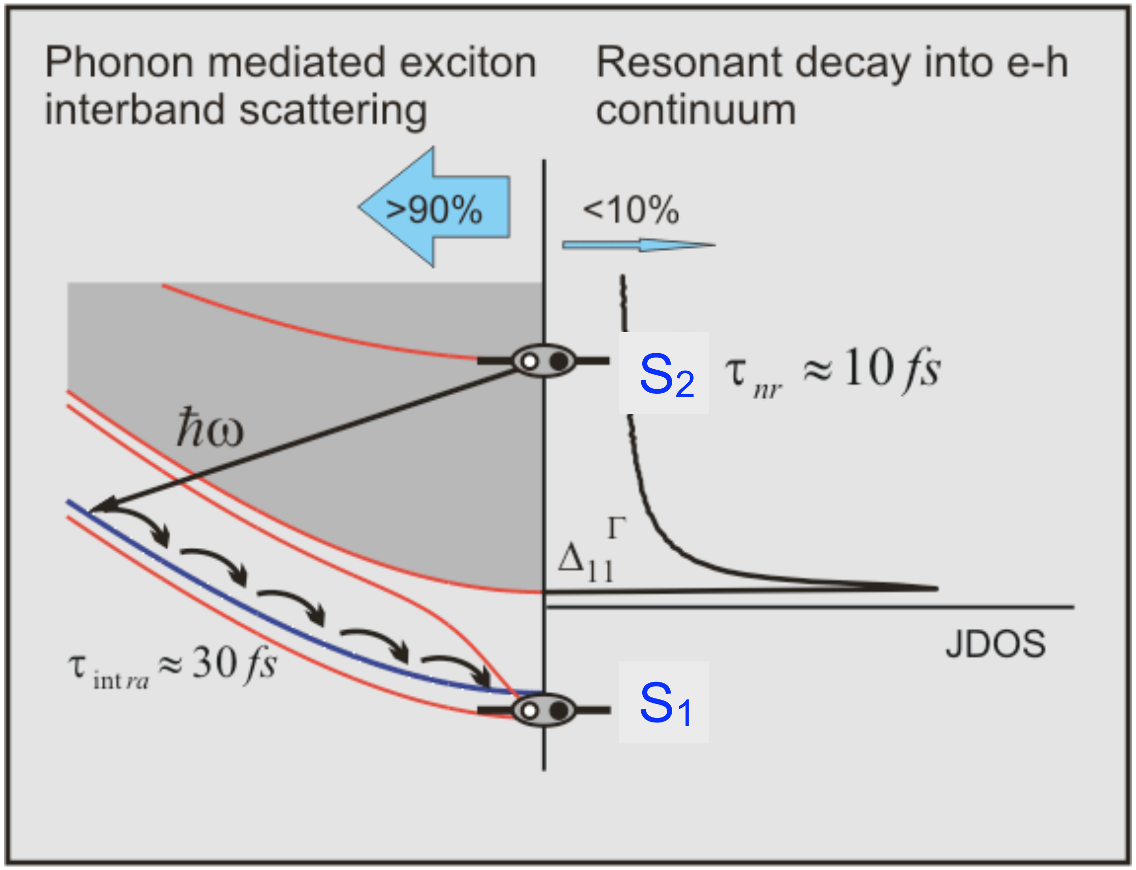
$$g = 5.3\,eV / A$$

→ phonon coupling to dark S_1 exciton via zone-boundary optical phonon.

Su et al., PRL **42** (1980) 1698.

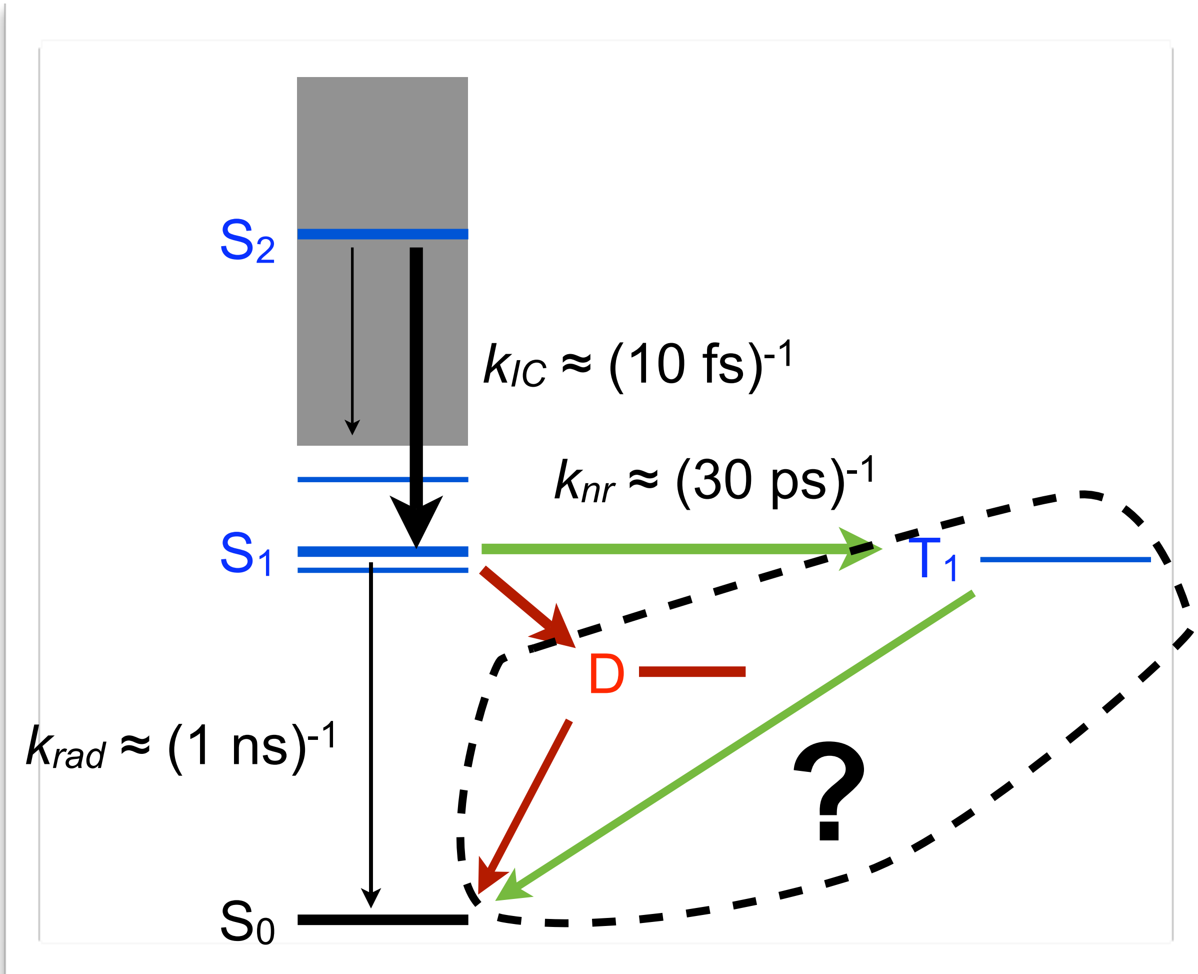
Hertel, Crochet, Perebeinos, Arnold, Kappes and Avouris,
(Nano Lett. **8**, 87 (2008))

S_2 relaxation summary

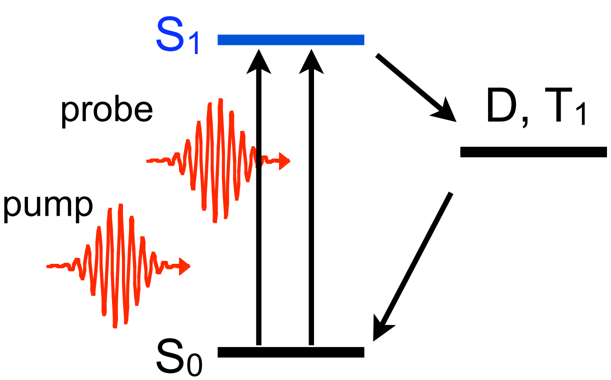


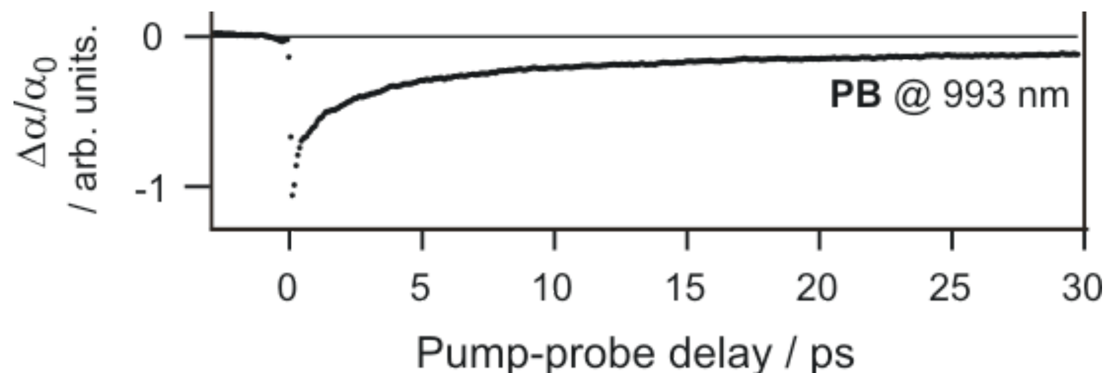
Hertel, Crochet, Perebeinos, Arnold, Kappes and Avouris,
(Nano Lett. **8**, 87 (2008))

so far


S2
$k_{IC} \approx (10\ fs)^{-1}$
$k_{nr} \approx (30\ ps)^{-1}$
S1
T1
D
$k_{rad} \approx (1\ ns)^{-1}$
?
S0

Pump-probe spectroscopy: (6,5) DGU material





Extinction coefficient:

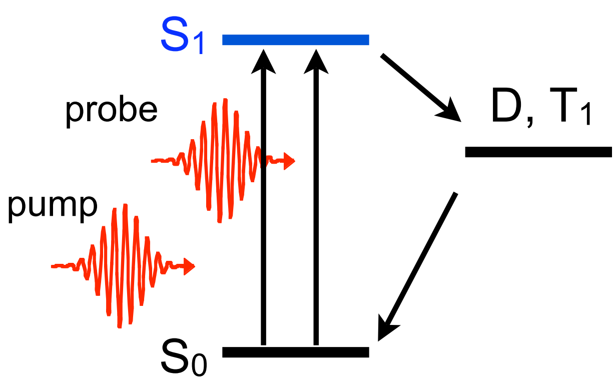
$$\Delta\alpha_{S_0\rightarrow S_1} \propto \Delta\rho_{S_0} - \Delta\rho_{S_1}$$

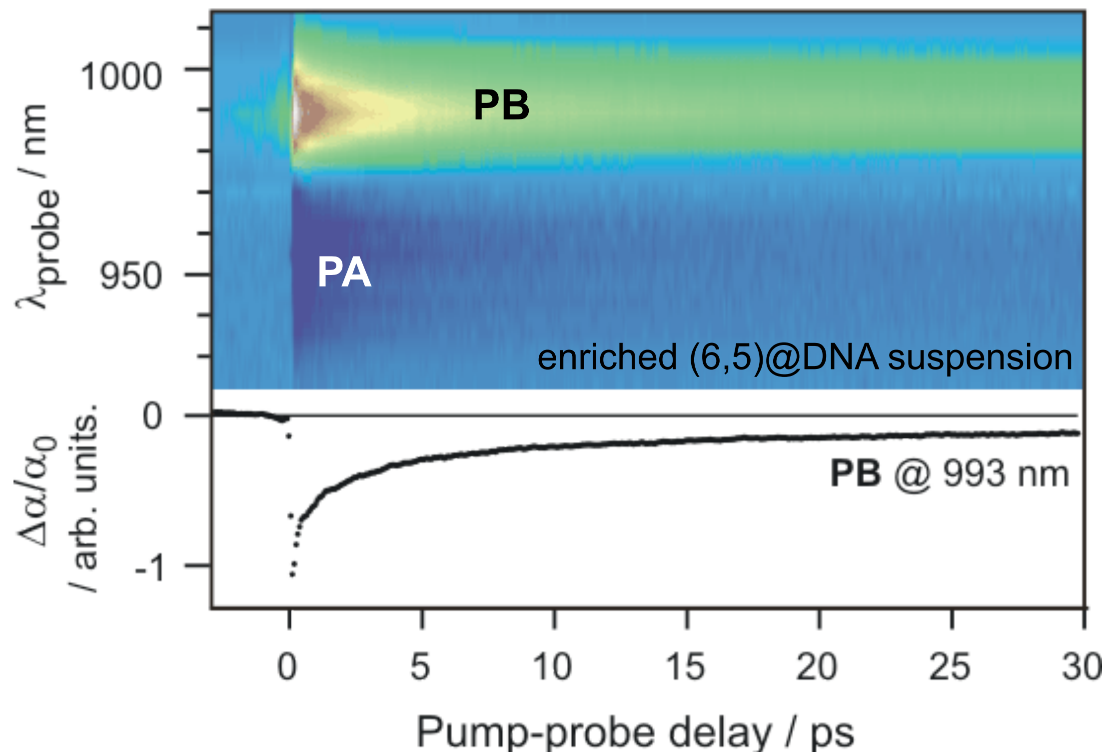
α first decreases (photobleach, PB)

then α recovers because of decay of the S_1 state

Zhu, Crochet, Resasco, Arnold, Hersam, and Hertel, J. Phys. Chem. C **111**, 3831 (2007)

Pump-probe spectroscopy: (6,5) DGU material





Extinction coefficient:

$$\Delta\alpha_{S_0 \to S_1} \propto \Delta\rho_{S_0} - \Delta\rho_{S_1}$$

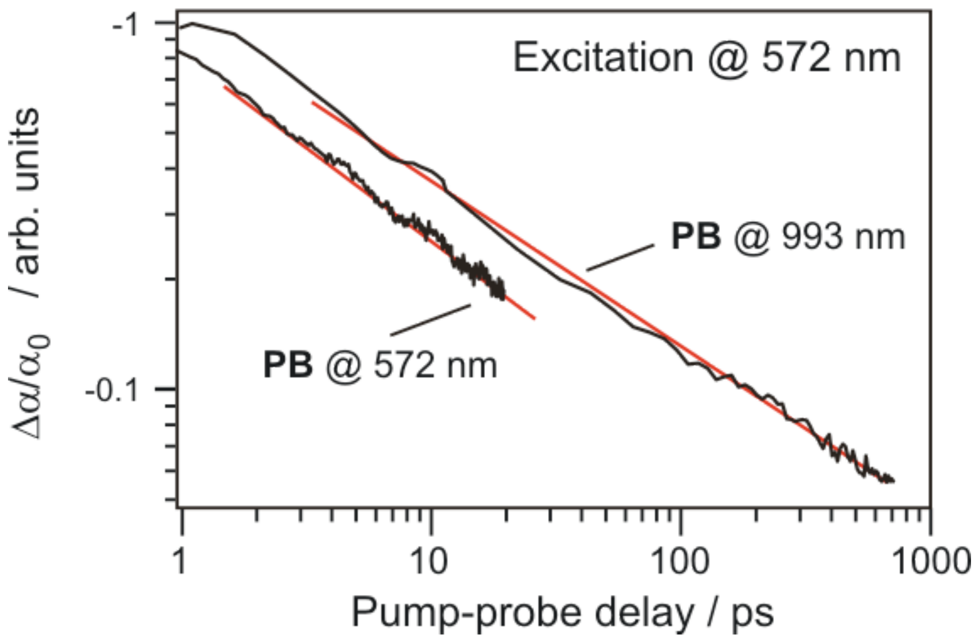
α first decreases (photobleach, PB)

then α recovers because of decay of the S_1 state

Zhu, Crochet, Resasco, Arnold, Hersam, and Hertel, J. Phys. Chem. C **111**, 3831 (2007)

Ground state recovery is diffusion limited

Optical transients

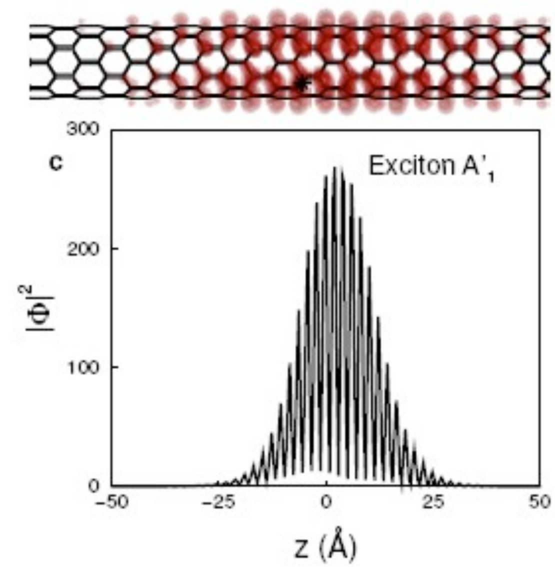


Survival probability scales like power law in time

$$[\mathrm{A}] \propto t^{-\gamma}$$

Zhu, Crochet, Resasco, Arnold, Hersam, and Hertel,
J. Phys. Chem. C **111**, 3831 (2007)

Exciton wavefunctions



Spataru et al. PRL 92, 77402 (2004)
Luer et al. (submitted)

Exciton diffusion should be 1-dimensional.

diffusion limited reactions in 1D

Educt-survival probabilities scale with time:

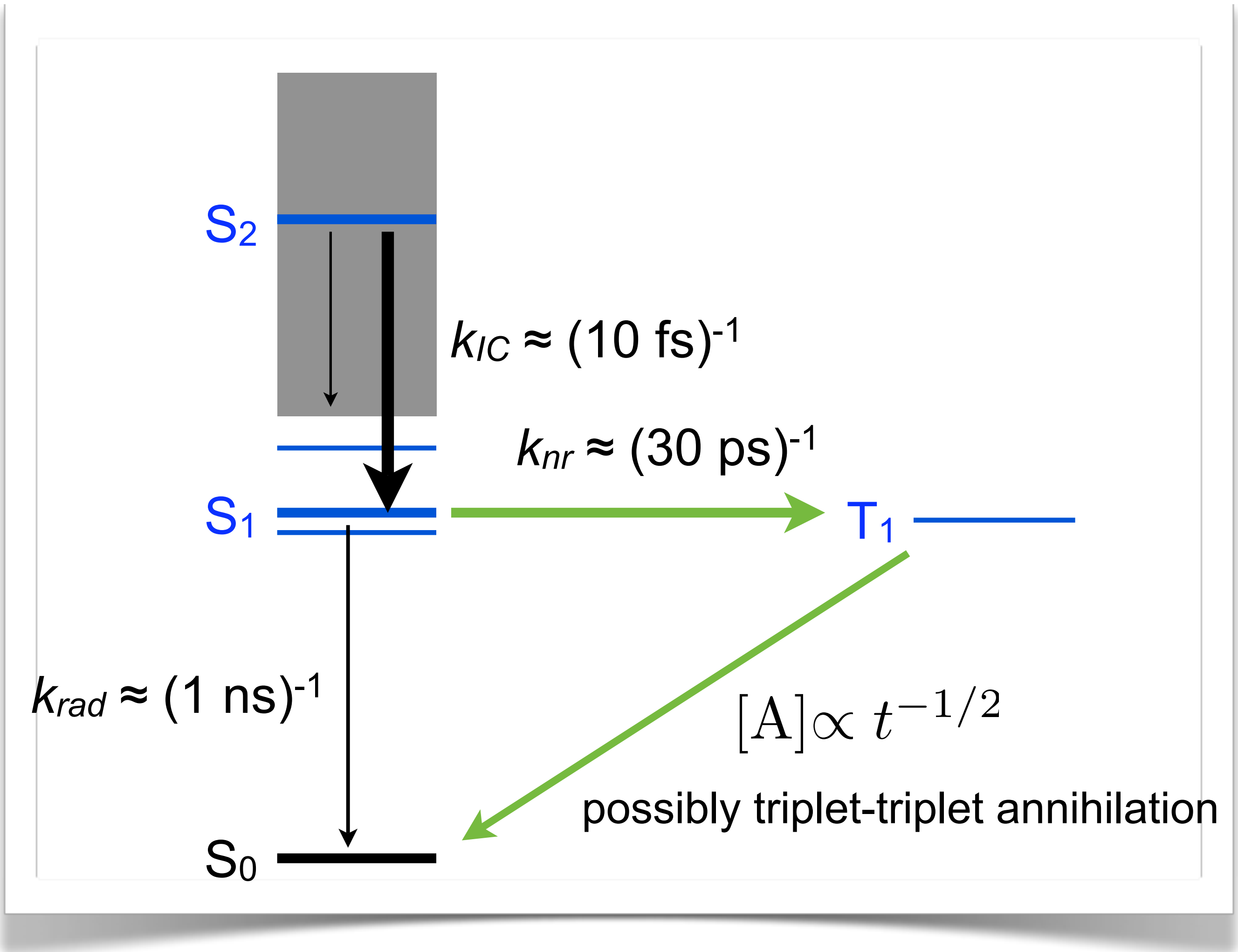
$$[\mathrm{A}] \propto t^{-\gamma}$$

Reaction type		**exponent γ**
Bimolecular reaction	$A + A \rightarrow B$	¼
Particle-antiparticle annihilation	$A + \overline{A} \rightarrow B$	½
Trapping by defects	$A + D \rightarrow D^*$	1

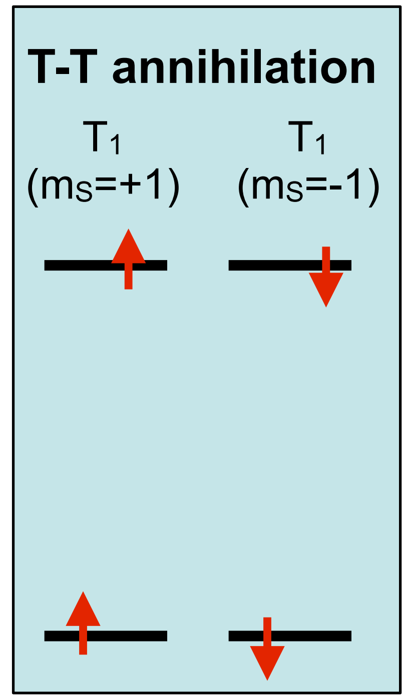
experiment: 0.45±0.03

Toussaint et al., JCP **78**, 2642 (1983); Havlin, Adv. Phys. **36**, p695 (1987); Yuste et al. Physica A **336**, p334 (2004)

Overview

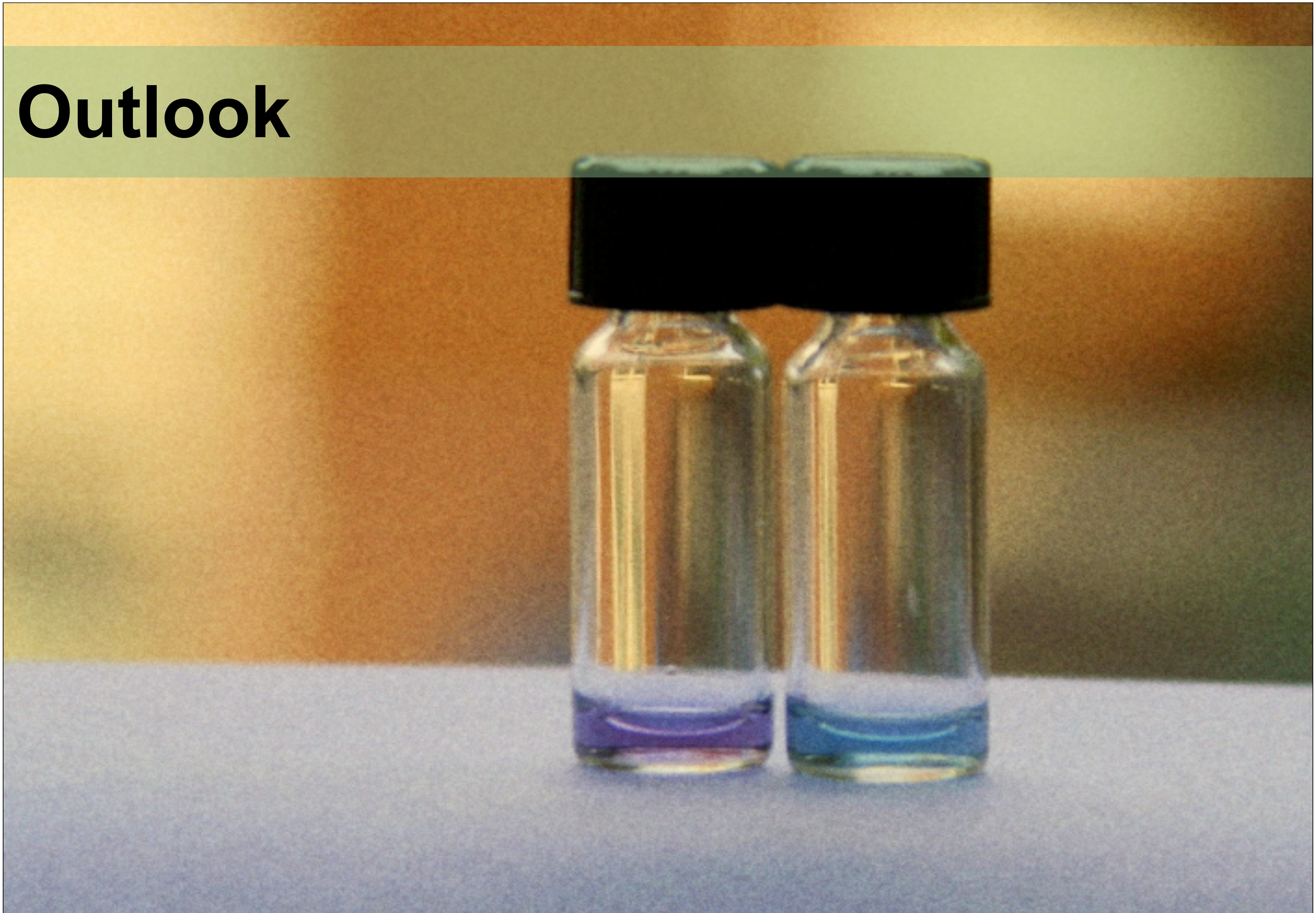


S2
$k_{IC} \approx (10\ \text{fs})^{-1}$
$k_{nr} \approx (30\ \text{ps})^{-1}$
S1
T1
$k_{rad} \approx (1\ \text{ns})^{-1}$
$[\mathrm{A}] \propto t^{-1/2}$
possibly triplet-triplet annihilation
S0



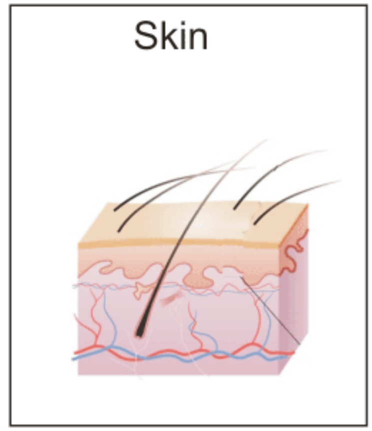
T-T annihilation
T1 (mS=+1)
T1 (mS=-1)

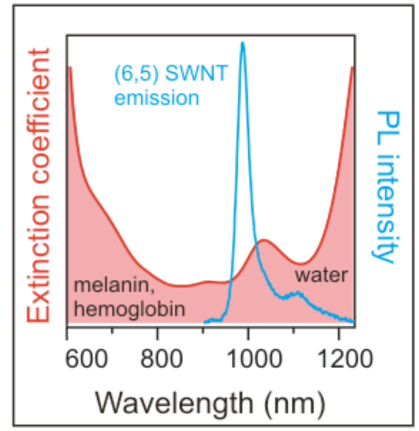
Outlook

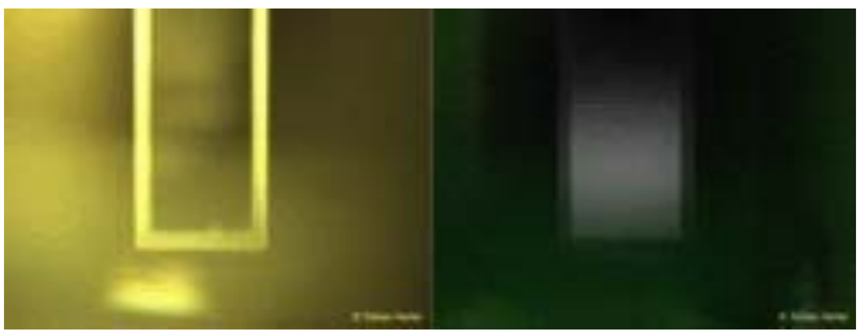


Imaging with Si-detectors

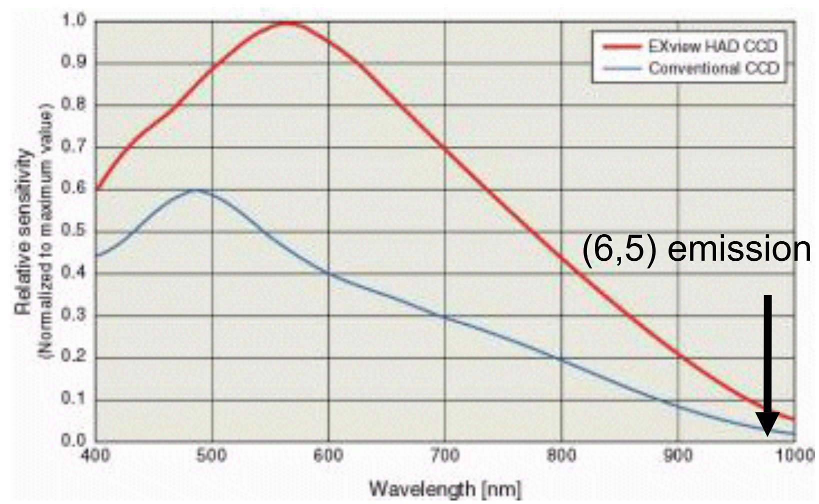
- DGU purification of (6,5) suspension
  - PL QY ~ 1%
  - Emission at 980 nm







PL image (right) of SWNT suspension recorded with Si hole accumulation diode (HAD) CCD array.



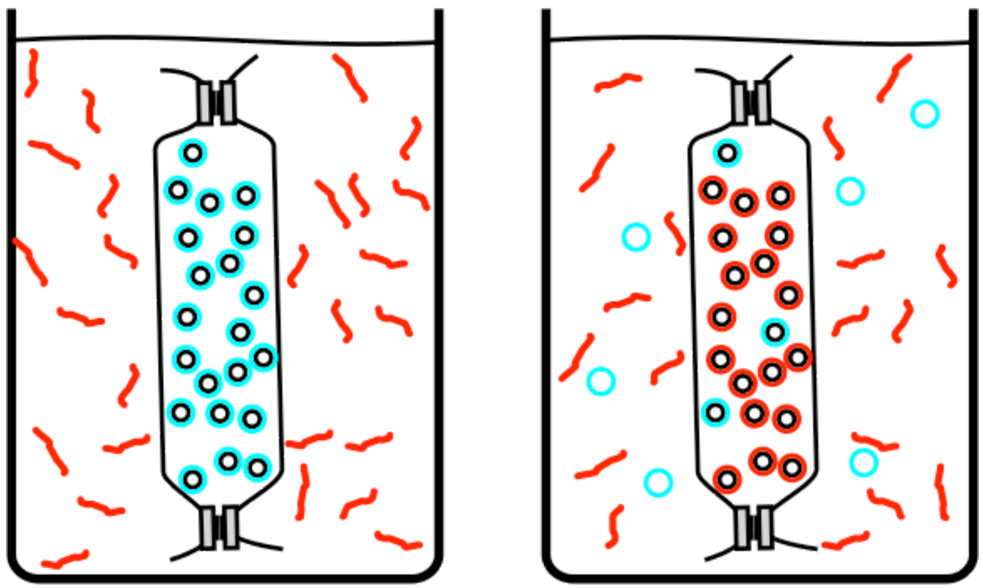
Si hole accumulation diode (HAD) CCD sensitivity

Soft functionalization

Replacement of surfactants with single stranded DNA by dialysis

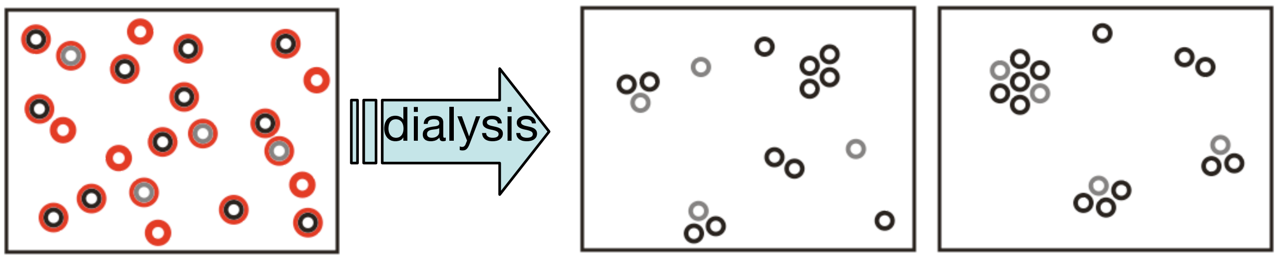
○ Na-cholate

▬ Nucleotide sequence



thermal stability of DNA-CNT hybrids ~ oligomer length

Re-Aggregation



Engineering of crystallites

- Lateral exciton delocalization

- Metallic impurities

- Semiconducting impurities

Funding

- NSF
- American Chemical Society
- Max-Kade Foundation
- VINSE

THANKS

Thanks

Current and recent

F. Bonnacorso
(summer student)
DGU, aggregates

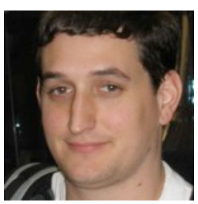
K. Müller
(summer student)
DGU

M. Clemens
(graduate student)
TCSPC

S. Novikov
(summer student)
DGU, solvatochromism

D. Stich
(graduate student)
nonlinear dynamics

J. Thompson
(graduate student)
outreach



J. Crochet
(graduate student)
nonlinear-optics

Z. Zhu
(graduate student)
nonlinear-optics

Collaborations

- **University of Oklahoma**
  Resasco
- **Northwestern University**
  Arnold, Hersam
- **Polytechnical Univ. de Milano**
  Lanzani, Lüer
- **Technische Universität München**
  Hartschuh
- **Universität Karlsruhe**
  Kappes, Richert
- **MIT**
  Strano, Heller
- **IBM Yorktown Heights**
  Avouris, Perebeinos

Interested to join?

people.vanderbilt.edu/~tobias.hertel

tobias.hertel@vanderbilt.edu