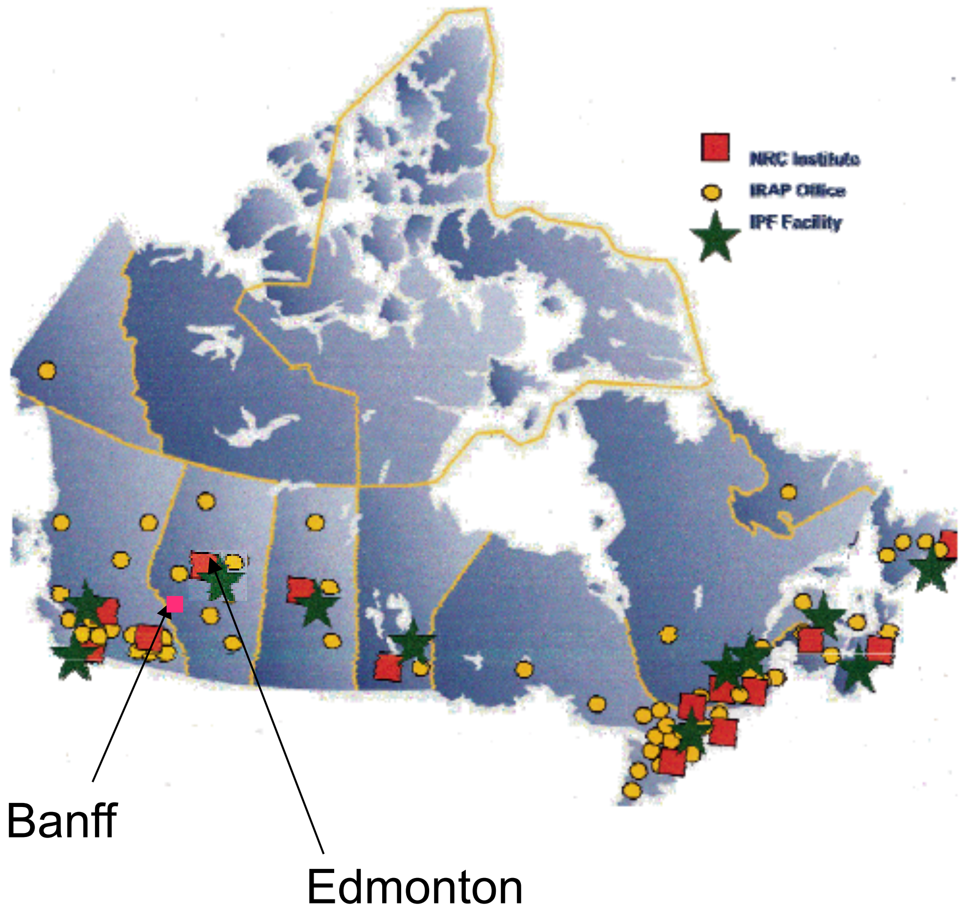
Canada : National Research Council



- National organization, federal government agency
- Provides essential elements of national S&T infrastructure
- 4,200 employees
- 1,500 visiting workers
- Labs and facilities across the country
- 20 Research Institutes
- Total expenditures $750M

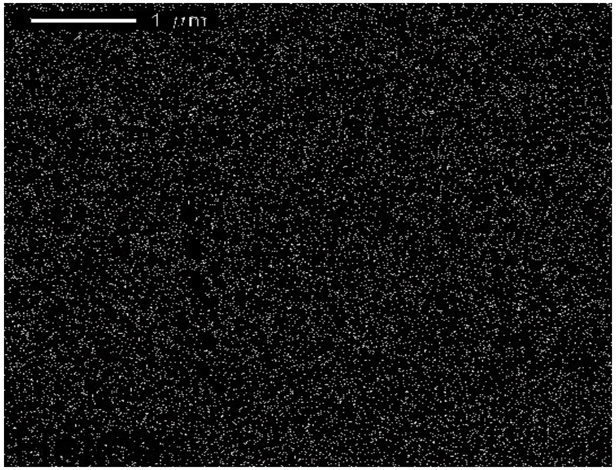
National Institute for
Nanotechnology
University of Alberta,
Edmonton, Alberta,
Canada

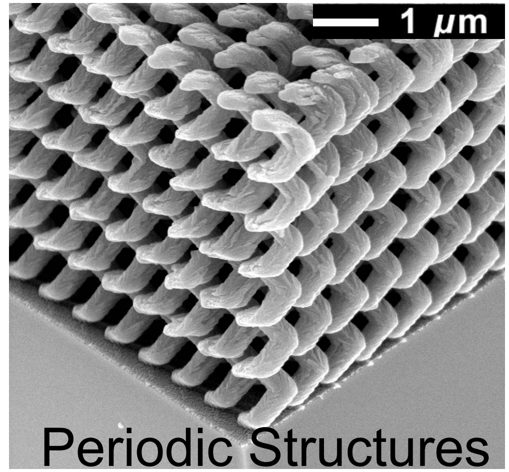
Founded 2002
Building opened
June, 2006

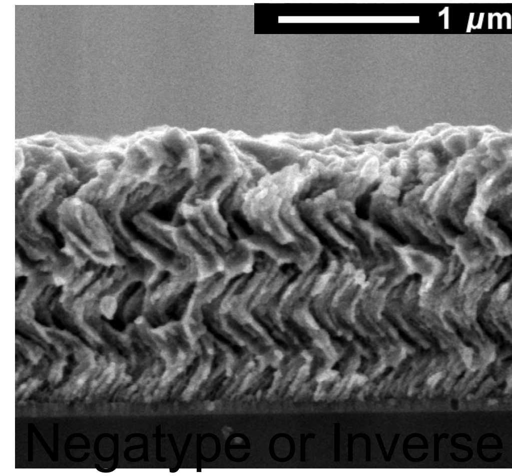
15,000 m^2 on five floors
500 m^2 class 1000 clean room

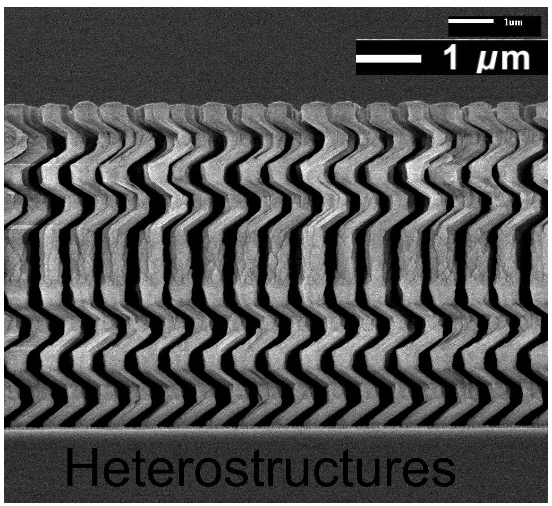
~ 160 people + ~100 grad. students
~$24 million CAD/year
~40% NRC funding

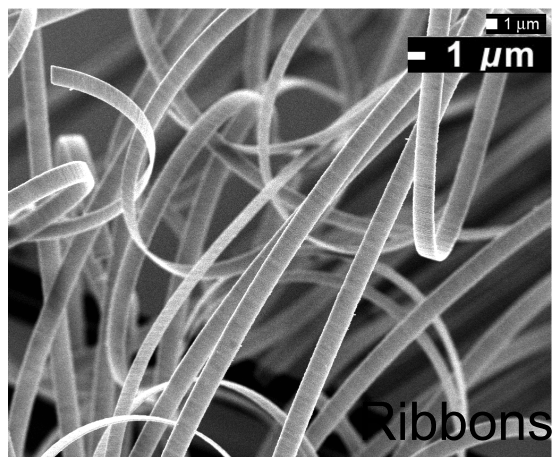
Michael Brett: Device applications of sub-μm architectures fabricated by Glancing Angle Deposition (GLAD)

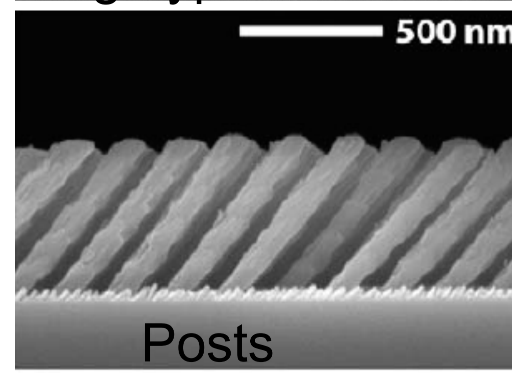


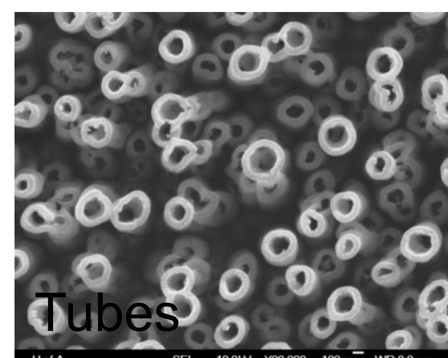








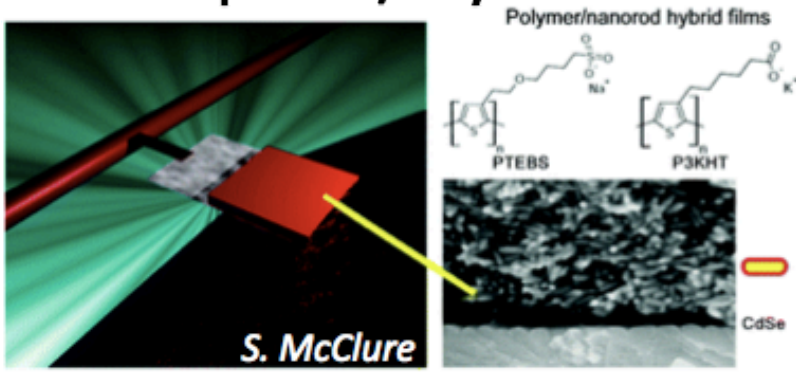




GLAD overview: M. Hawkeye and M. Brett, *Science* **319**, 1192 (2008).

Jillian Buriak/ Mike Brett: organic photovoltaic devices:

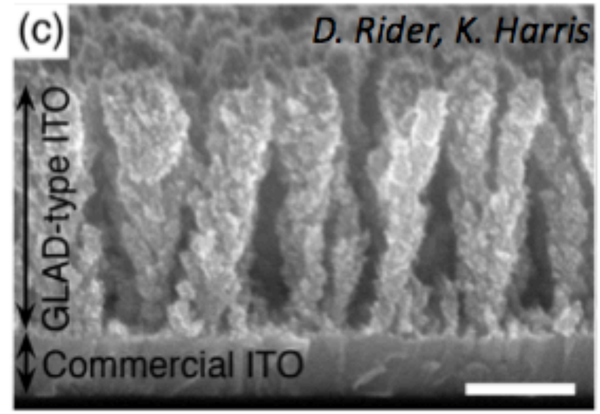
Nanoparticle/Polymer OPVs

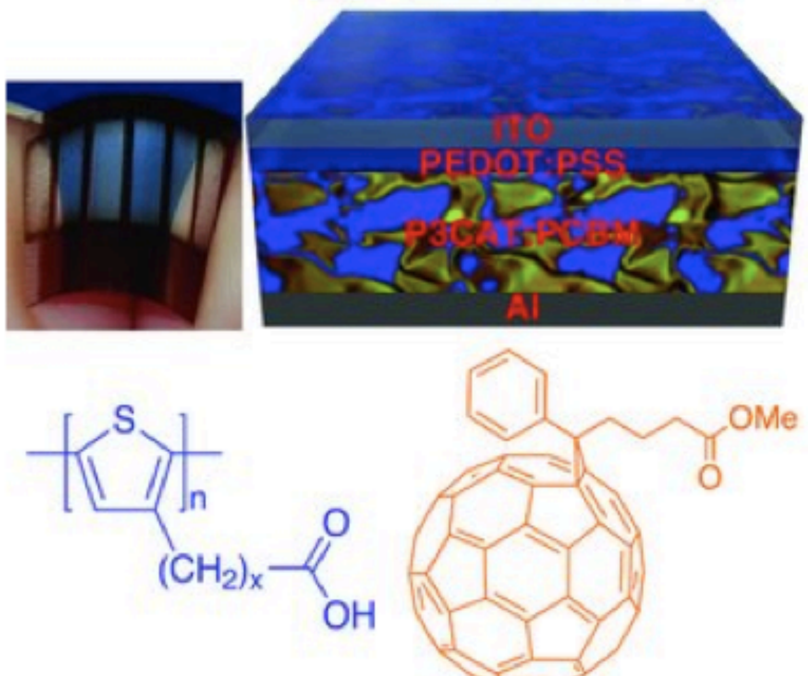


ACS Appl. Mater. Interfaces, 2010

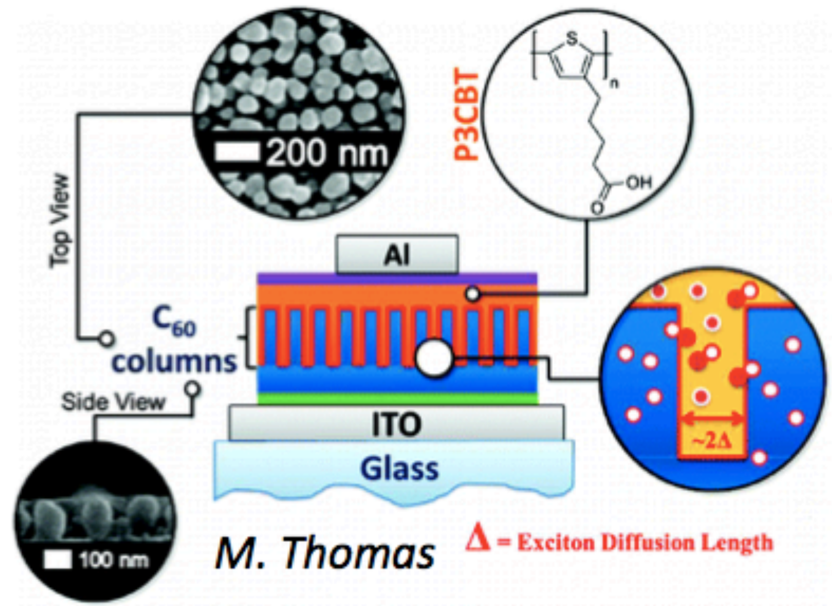
** Most read paper of 2010*

GLAD ITO OPVs



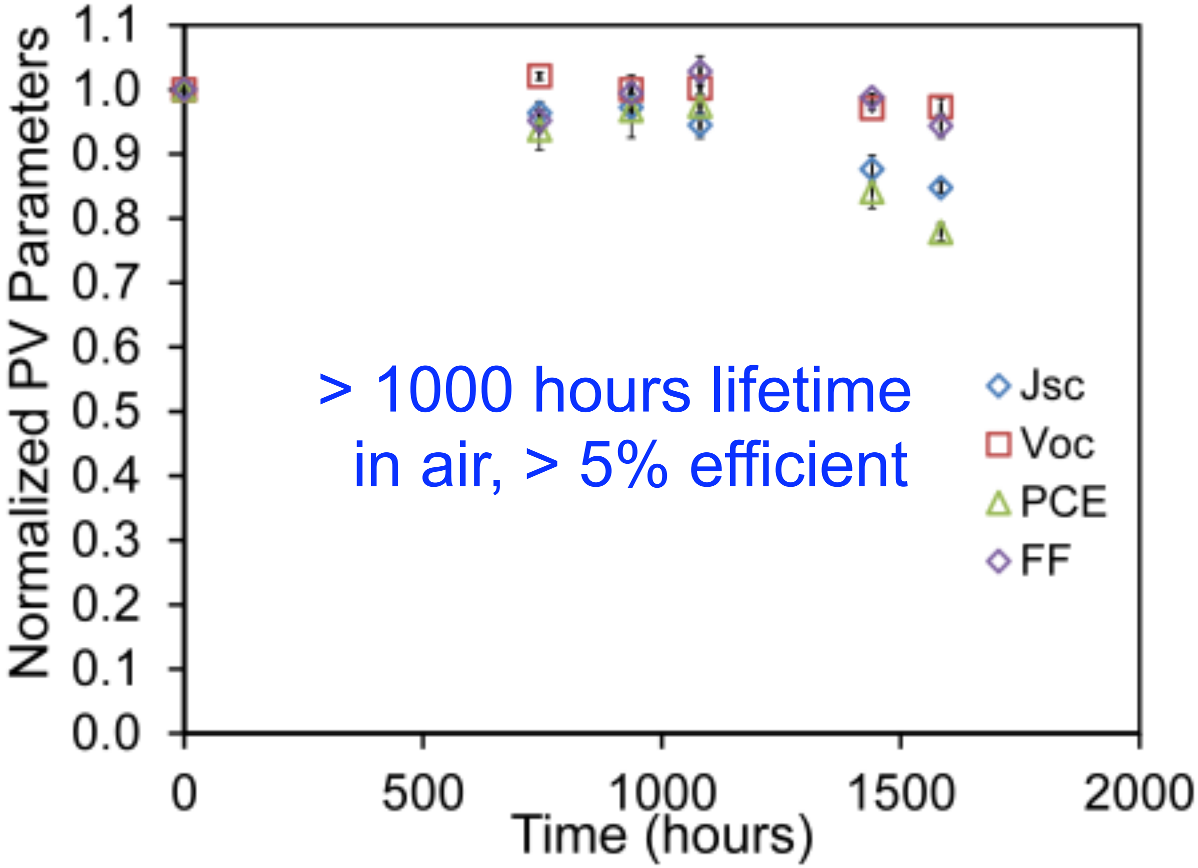


Adv. Funct. Mater. *ASAP*



ACS Appl. Mater. Interfaces, *ASAP*

Long-lived, air stable OPV devices based on our new interfacial chemistry, and a low band gap polymer from Mario Leclerc's group (Laval)



Buriak/Brett et al.

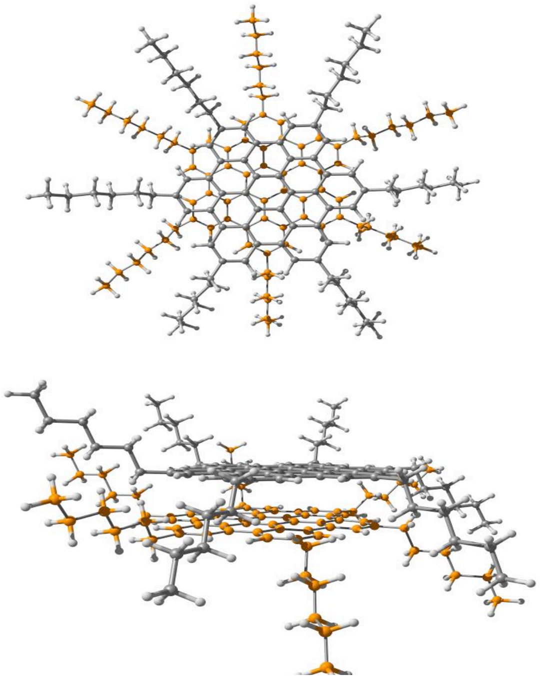
Development and Application of Density-Functional Theory Methods to Model Non-Covalent Interactions

Gino.DiLabio@nrc.ca

Non-covalent interactions drive important processes like self-assembly and electron transport, and are also responsible for coupling between molecules in nanostructured materials.

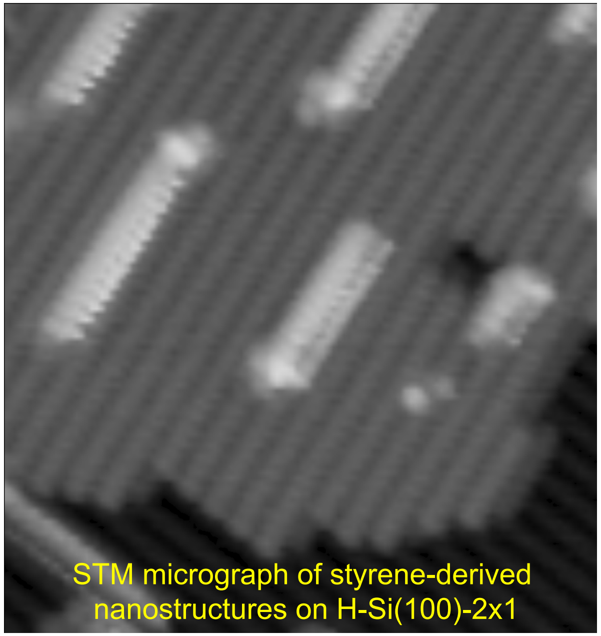
We are actively developing and applying new DFT methods that allow for the accurate computational modeling of nanosystems in which non-covalent interactions are important.

Discotic liquid Crystals



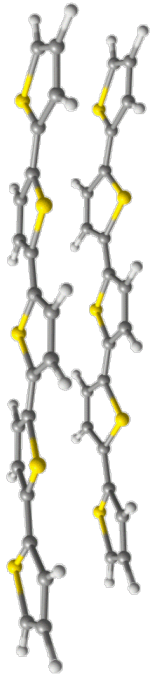
2 x Hexyl-hexabenzacoronene:
Non-covalent binding energy > 2 eV

Ordered molecular structures on semiconducting silicon



STM micrograph of styrene-derived nanostructures on H-Si(100)-2x1

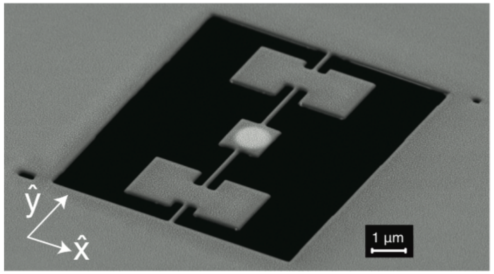
Organic electronic materials

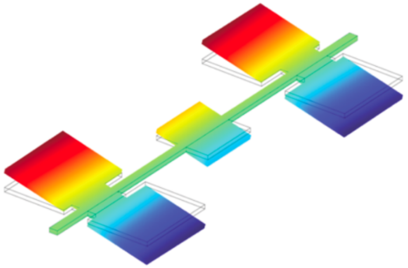


Coupling in oligothioohene is too low by 50% with conventional DFTs

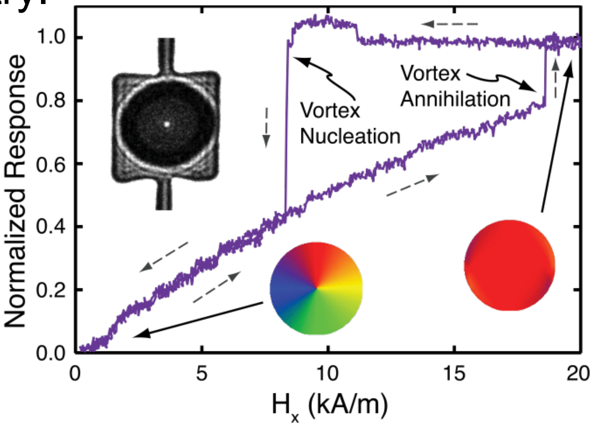
Mark Freeman et al. : Integrated Nano-Optomechanical Platform for Applications in Magnetic Memory/Logic and Molecular Sensing

Currently: Using traditional optics to measure the motion of a nanomechanical device yields state-of-the-art vortex magnetometry.



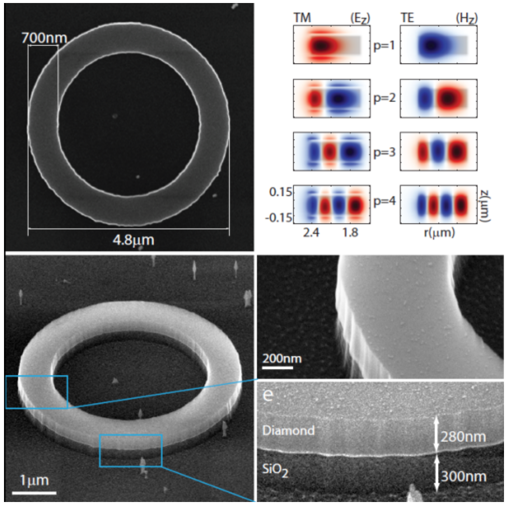


Davis *et al.*, New Journal of Physics 12, 093033 (2010).



If our sensitivity to nanomechanical motion was improved by 100-fold we would "revolutionize" ultra-sensitive magnetometry for

- Nanomagnetic devices for logic and memory
- Nanoscale superconductors
- Nitrogen-vacancies for quantum information storage



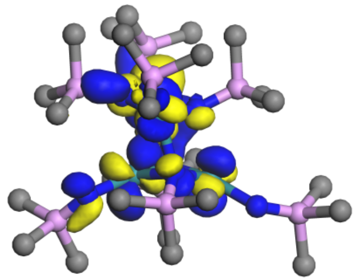
Faraon, Barclay, *et al.*, accepted to Nature Photonics.

Quantum Chemical Modeling of Nanosystems

ANDRIY KOVALENKO
Theory and Modeling Group
www.cein.ualberta.ca / research / kovalenko

Molecule (supramolecule)

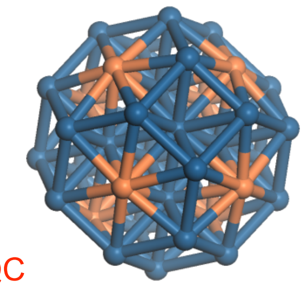
- Geometry
- Charges
- Electronic structure analysis
- Spectroscopy



QC, Semiempirical, QM/MM, ReaxFF

Nanoparticle

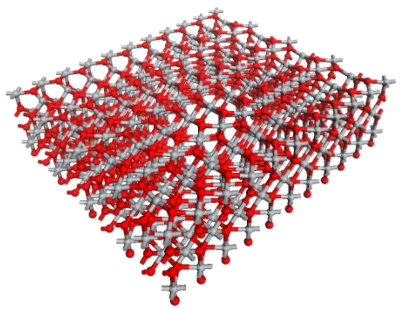
- Structural changes
- Diffusion
- Stability
- Activity



MD, QM/MM, Semiempirical, QC

Surface

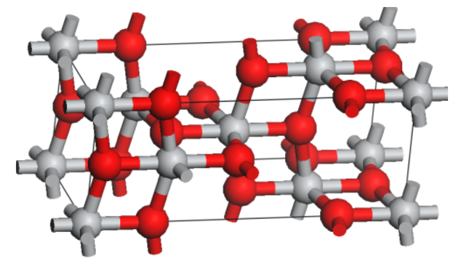
- Adsorption
- Catalyst-Support interaction
- Conductivity
- Porosity
- Formation/Cohesive energy



QC, PBC, QM/MM, ReaxFF

Bulk: crystals, lyquids, amorphous phase

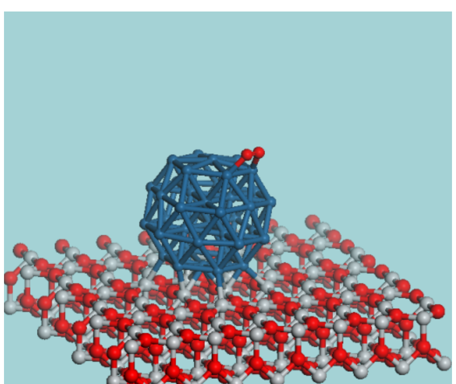
- Crystal structure
- Doping
- Defects
- DOS
- Conductivity



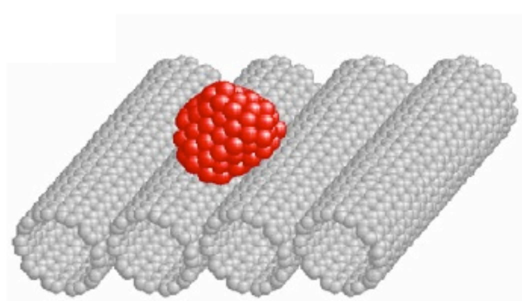
QC, PBC, Semiempirical

Multiscale systems

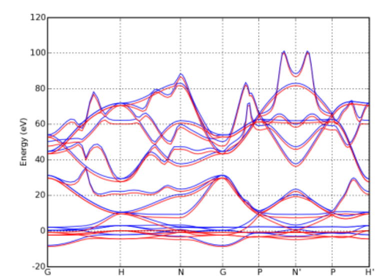
Reaction at a nanoparticle adsorbed on a surface in solution



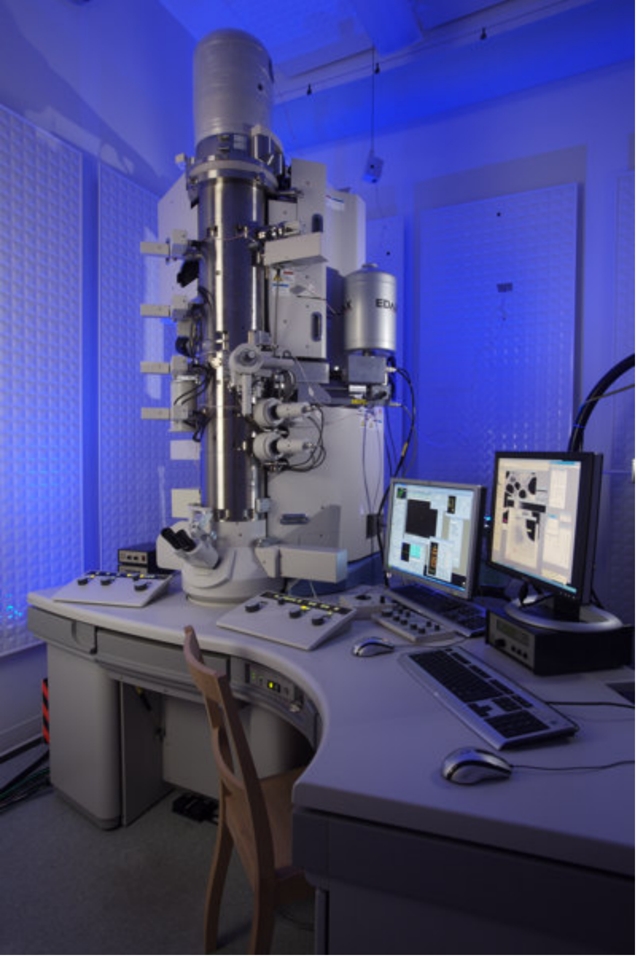
Motion and deformation of a nanoparticle on CNT



- Adsorption
- Solvation
- Diffusion
- Surface reactions
- Stability
- Dynamics
- Heat transfer



QM/MM, PBC, ReaxFF, MD, 3D-RISM-KH



Hitachi HF3300
Materials Science TEM

300 kV
0.2 nm probe size
EELS
Electron Holography
EDX

Electron Microscopy

Marek Malac
(director)

Also:

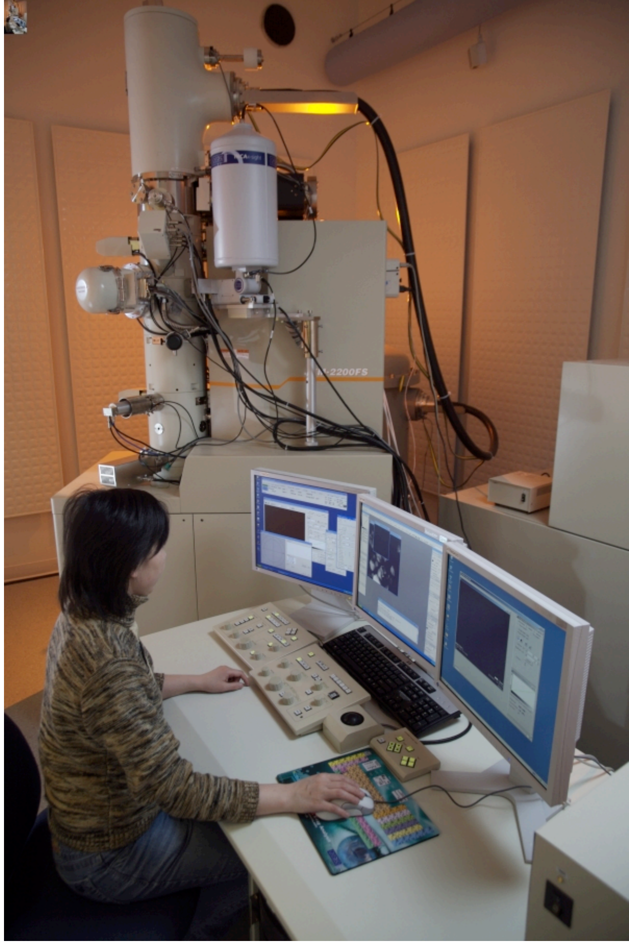
Focused ion beam (2)

Hitachi S4800 high resolution SEM

Environmental TEM

lots more, see:

http://www.nrc-cnrc.gc.ca/eng/facilities/nint/electron-microscope.html



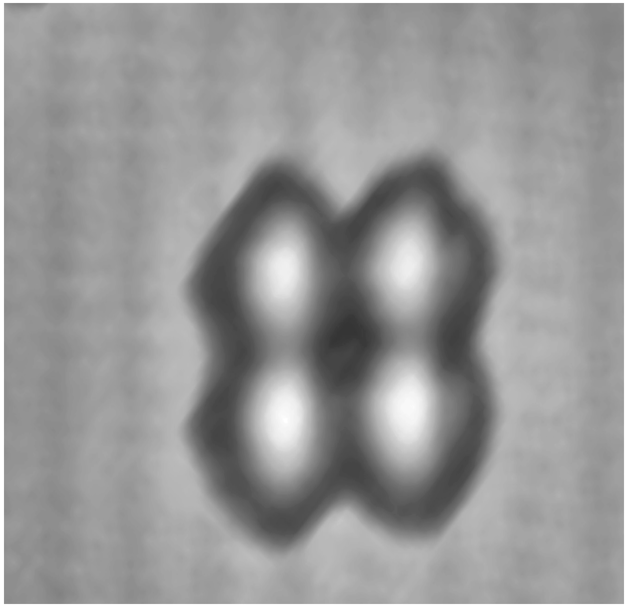
JEOL 2200 FS soft materials TEM

200 kV, field emission
EELS
electron diffraction

Robert Wolkow: Molecular Scale Devices Group

- Atom level silicon surface chemistry and physics and electronics
- STM, quantum chem. theory, cond. mat. theory, Field ion microscopy, high resolution electron energy loss spectroscopy
- Commercial ambitions: ion microscope, e-microscope development, atomic electronics
- Atomic electronics also has quantum computing ramifications

4-atom,
2-electron cell:



~2 nm between atoms

Bridging the Gap between Single Molecule and "Large Area" Molecular Electronic Junctions

Adam Bergren, Andrew Bonifas*, Nikola Pekas, Jie Ru
Bryan Szeto, Haijun Yan
Richard McCreery

University of Alberta
*Ohio State University
National Institute for Nanotechnology

NRC · CNRC

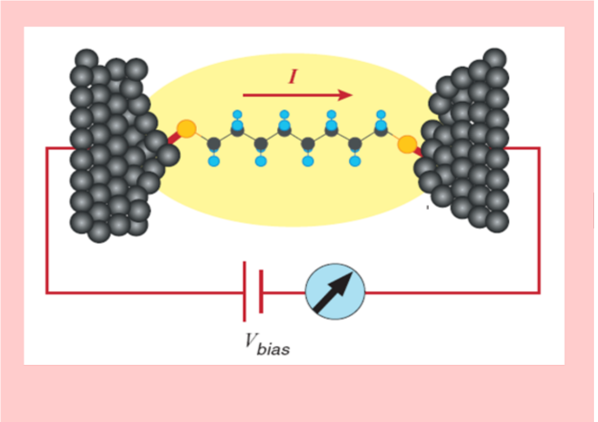
ALBERTA INGENUITY FUND

UNIVERSITY OF ALBERTA

NSERC CRSNG

Canada Foundation for Innovation

Single molecule electronics:



single molecule FET
STM, CP-AFM
single molecule memory cell

Transport:
- distance < 2 nm
- T-dependent ?
- tunneling ??, hopping ??

Today's question: what happens when organic electronics is extended to the nanoscale?

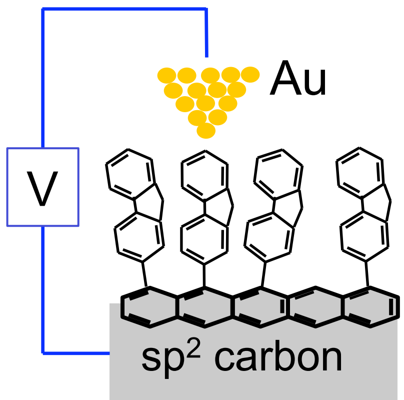
Organic electronics:

Sony OLED display

organic semiconductors
redox polymers
conducting polymers
O-FET, O-LED

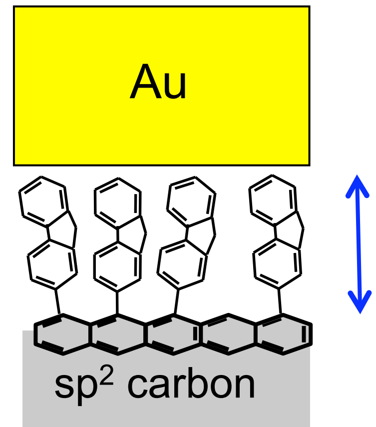
Transport:
- distance > 100 nm
- T-dependent, i.e. "activated"
- "hopping", redox exchange

The main question: How do electrons move through molecules?

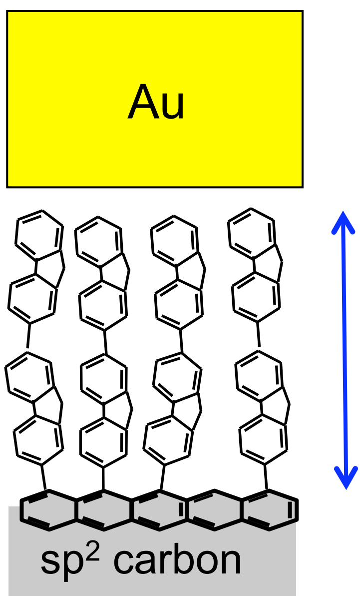


single molecule "junction"

connected one molecule at a time

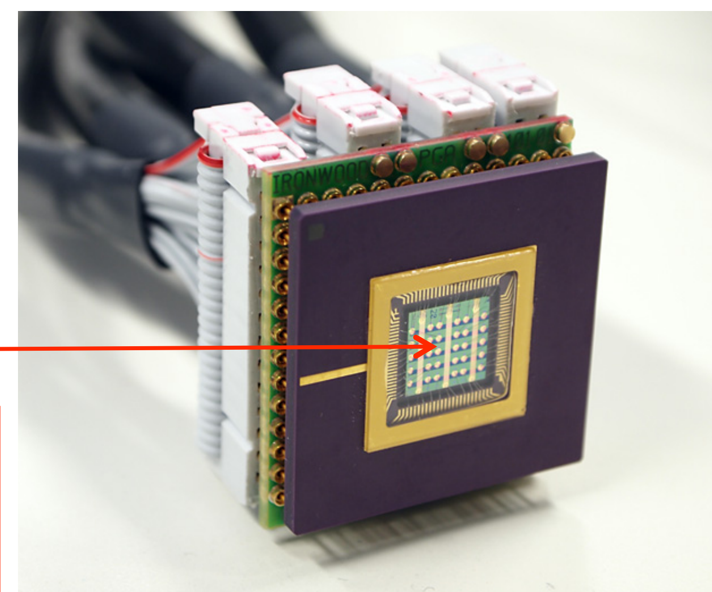


< 1 nm monolayer



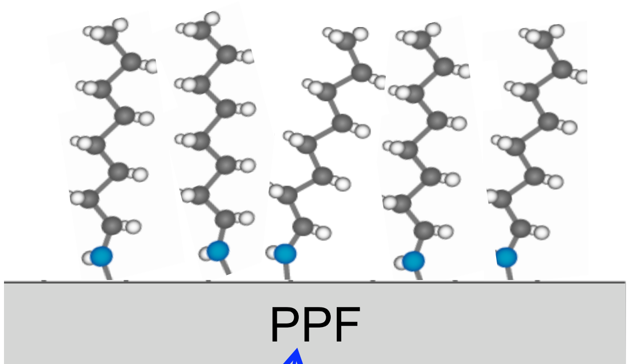
1-5 nm multilayer

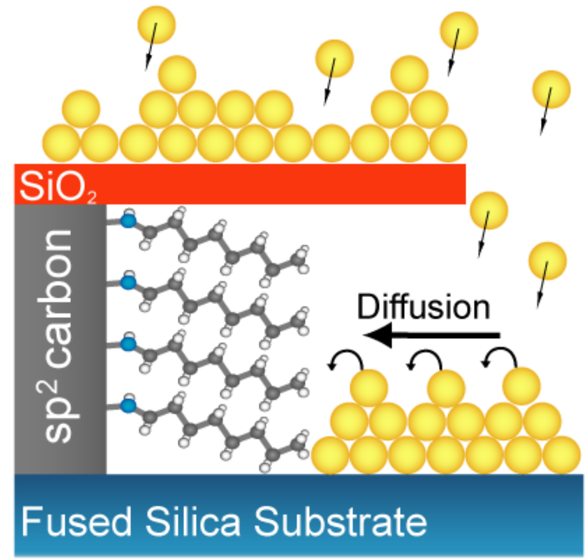
Transport:
- distance 1 – 5 nm
- T-dependent ??
- mechanism ??

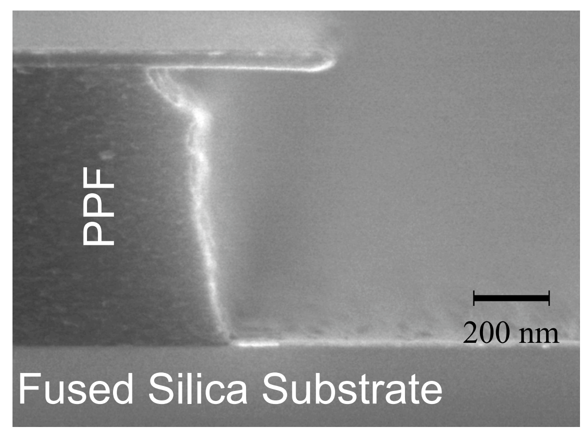


Making molecular junctions one molecule at a time:

bonded by amine oxidation

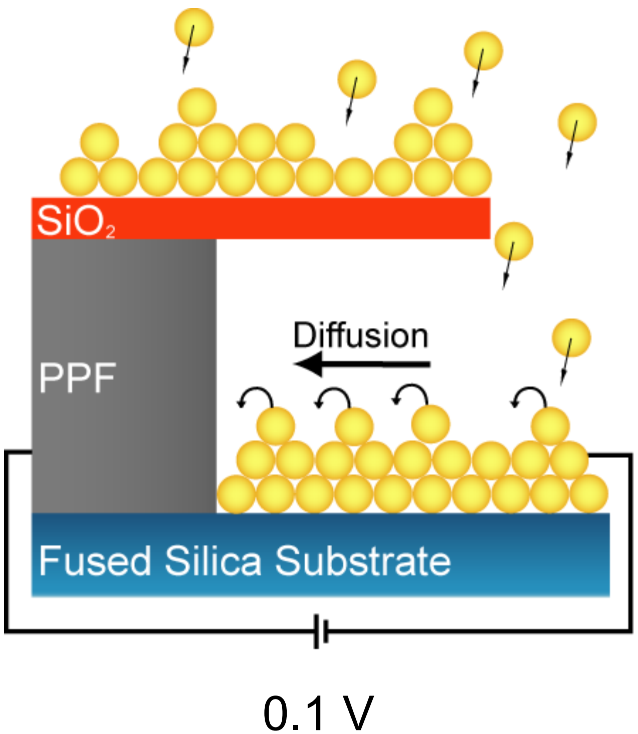


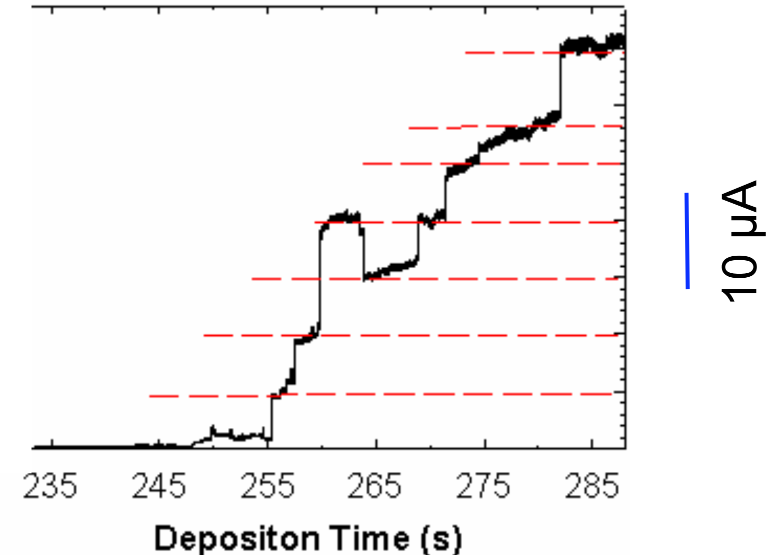


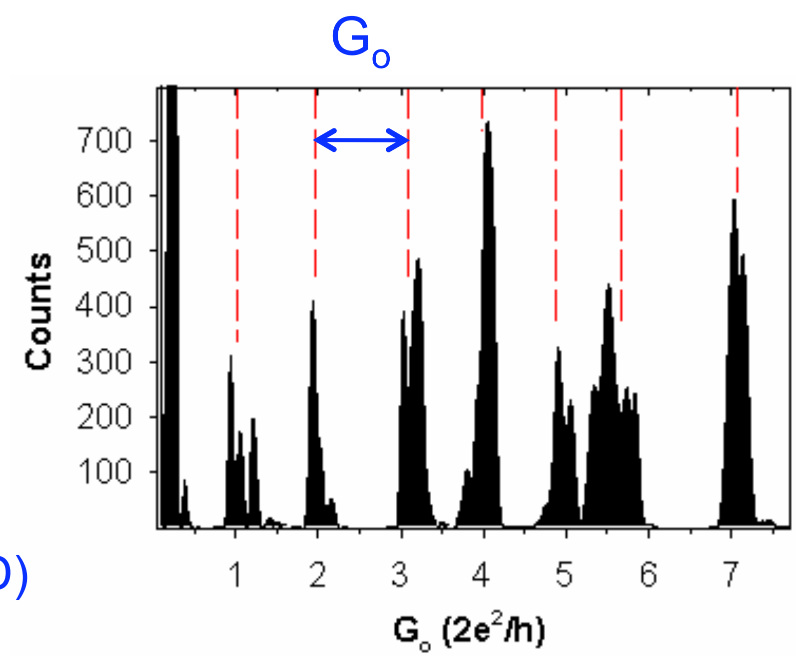


- only “cold” Au atoms touch molecules
- molecules are “contacted” one at a time
- conductance may be monitored during formation

Bonifas, A.P., McCreery, R.L. Nature Nanotech. **5**, 612 (2010) “control” with no molecule present, monitored in-situ

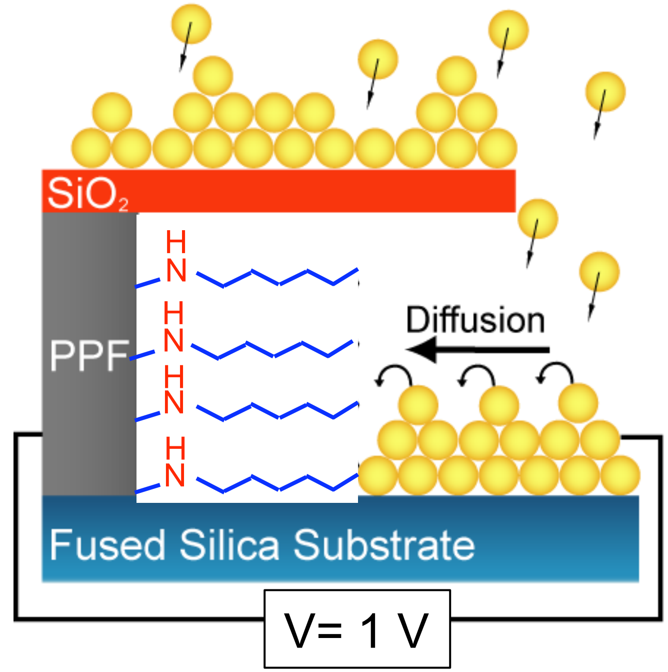






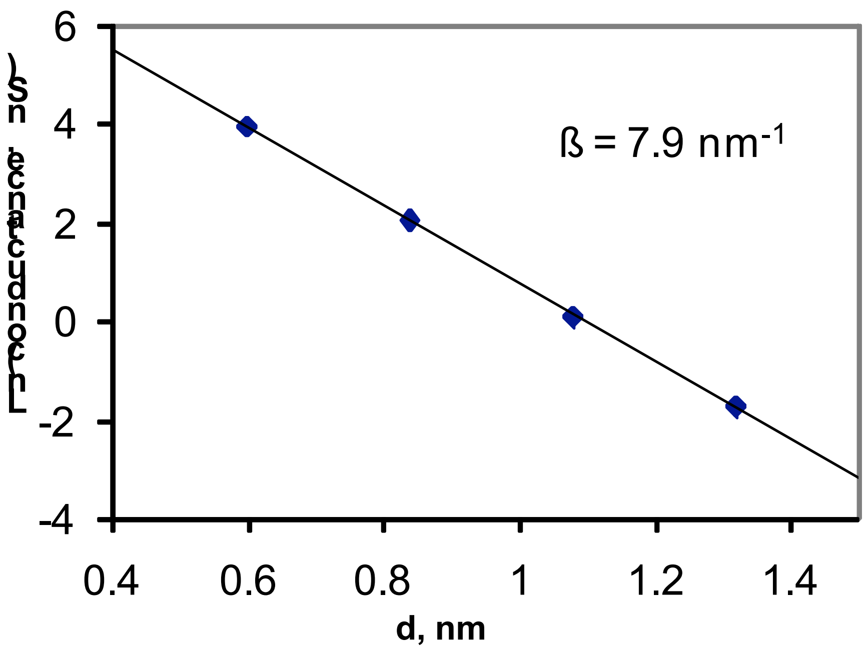
Surface diffusion mediated deposition (SDMD)

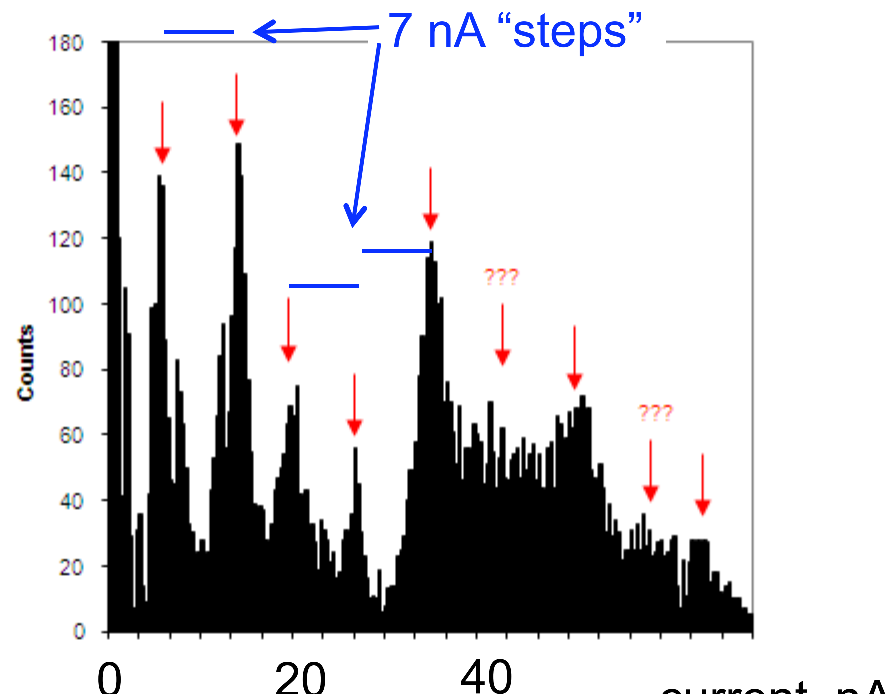
Alkane molecules present
(n-hexyl amine):



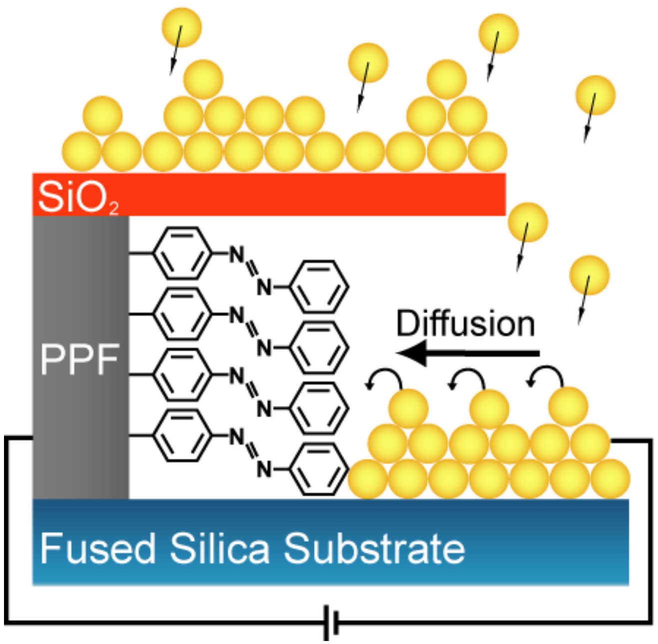
current decreases by 1/e
for each 0.13 nm of length
(about 1/e for each CH_2 group)

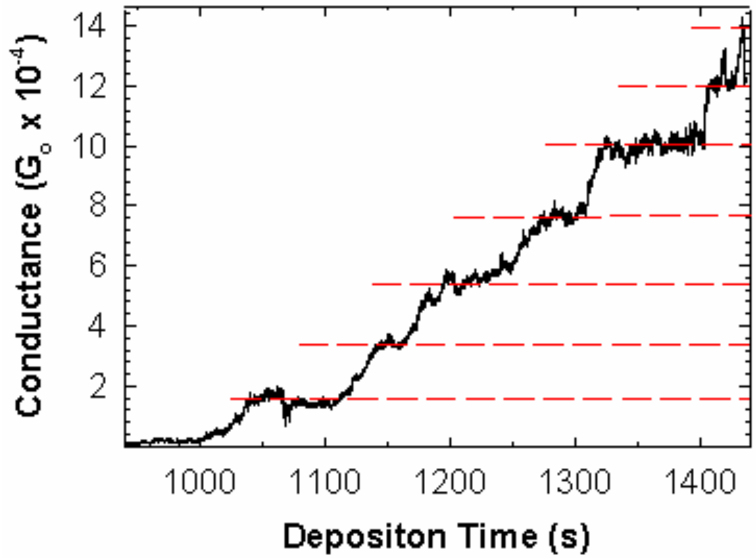
$C_4 - C_8$ alkyl amines:

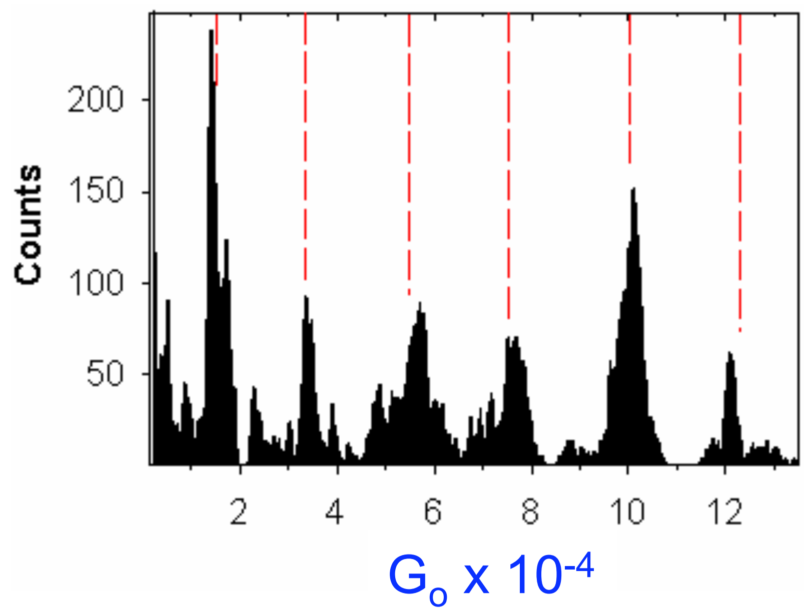




Aromatic molecules:

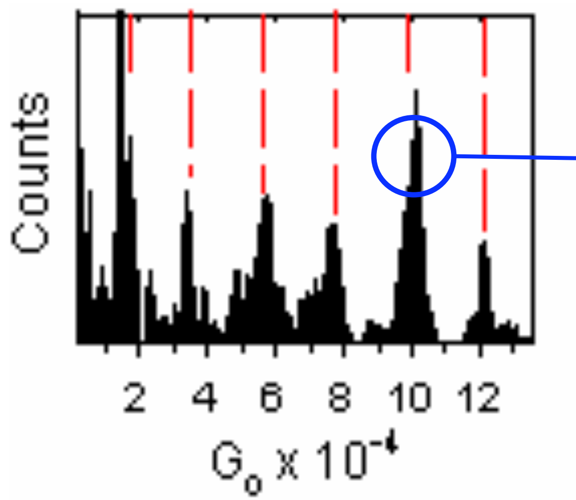


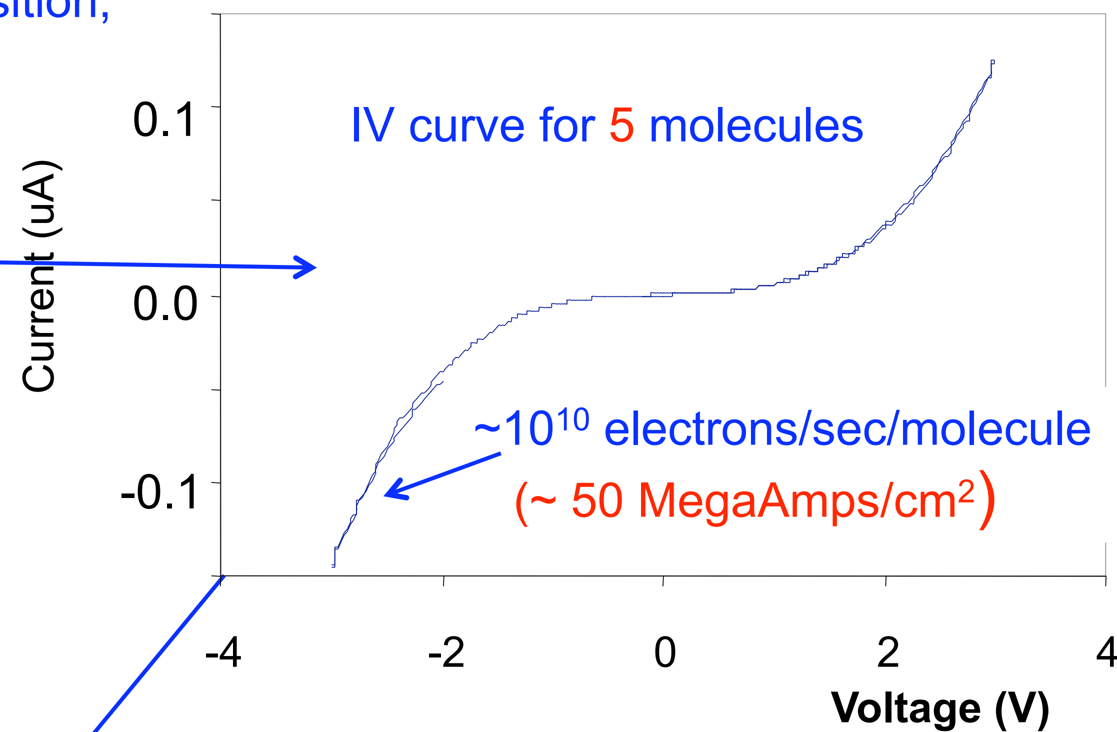




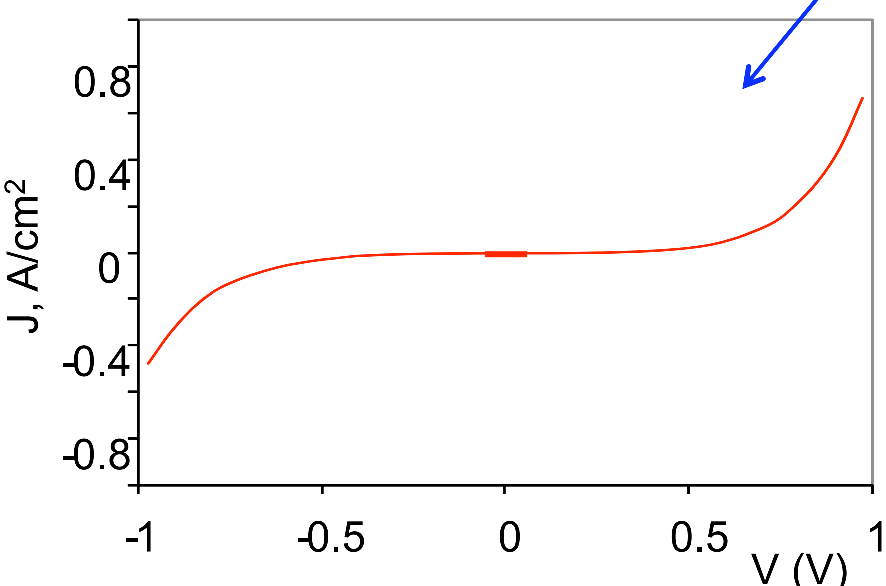
Each azobenzene molecule "conducts" about 10^{-4} as well as a single Au/C contact

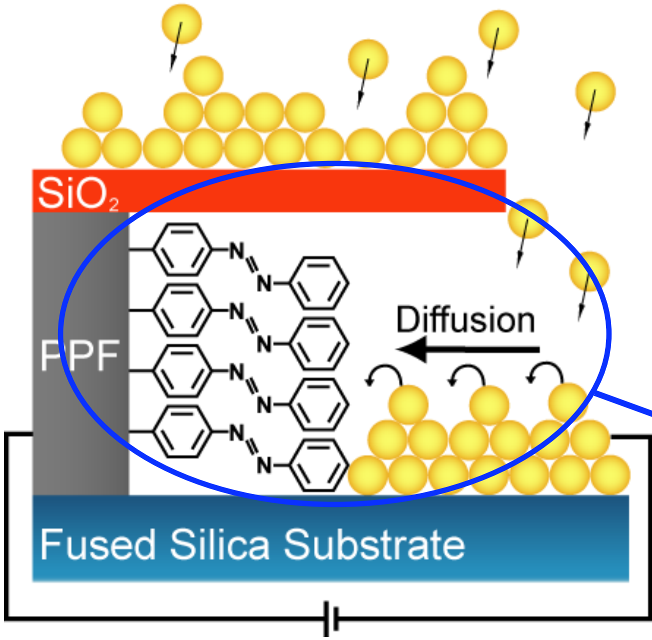
We can stop deposition, then scan voltage:

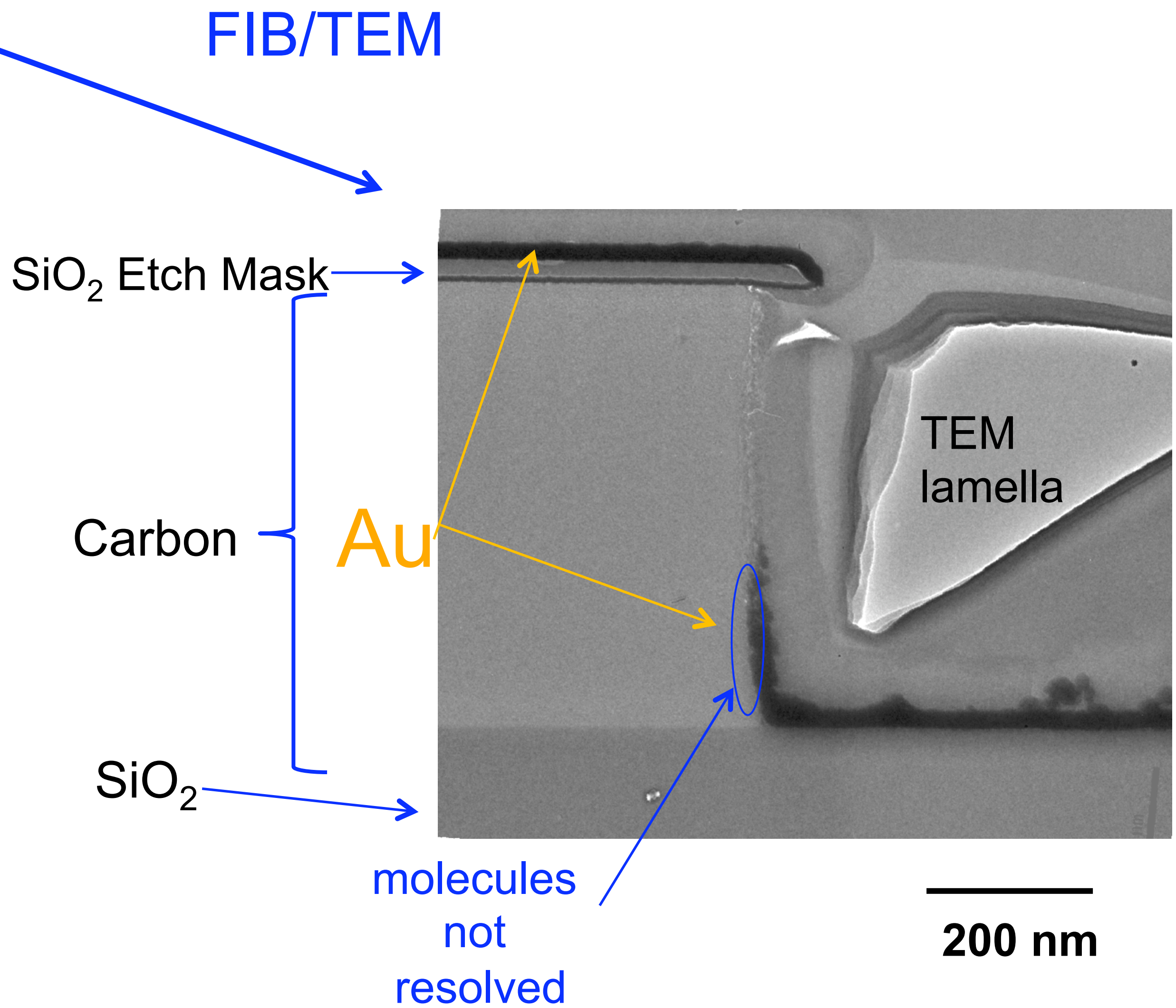




Continue deposition
to ~ 1 um^2 area
(~10^6 molecules)





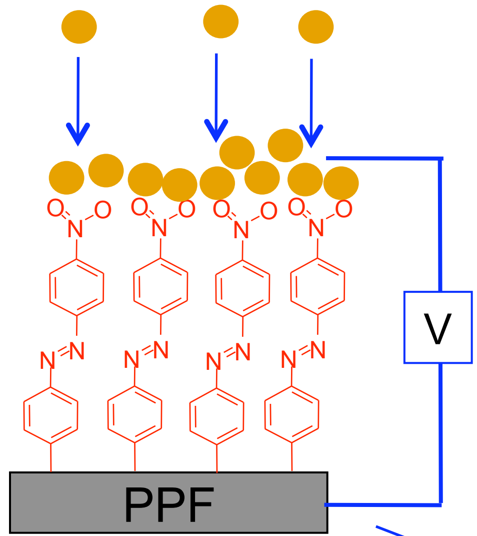


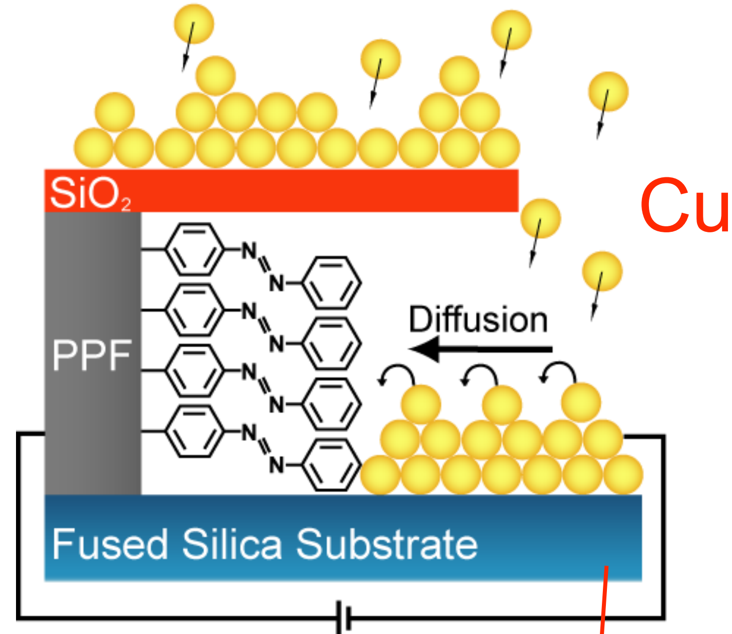
Peng Li

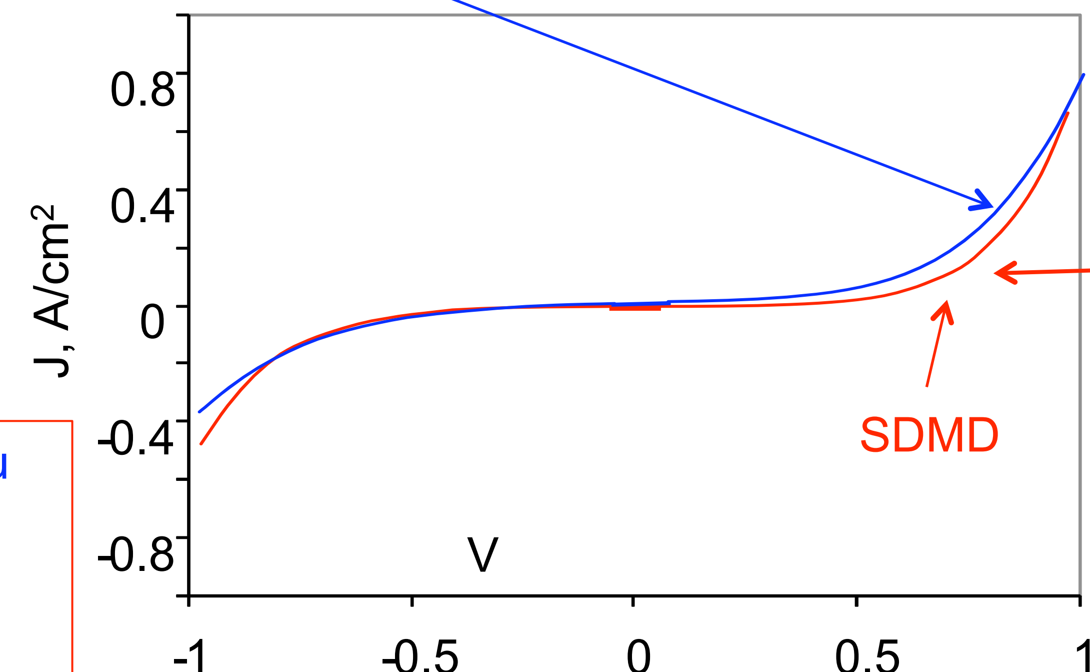
Marek Malac

NINT EM group

"Direct" deposition of 25 nm Cu (by e-beam):

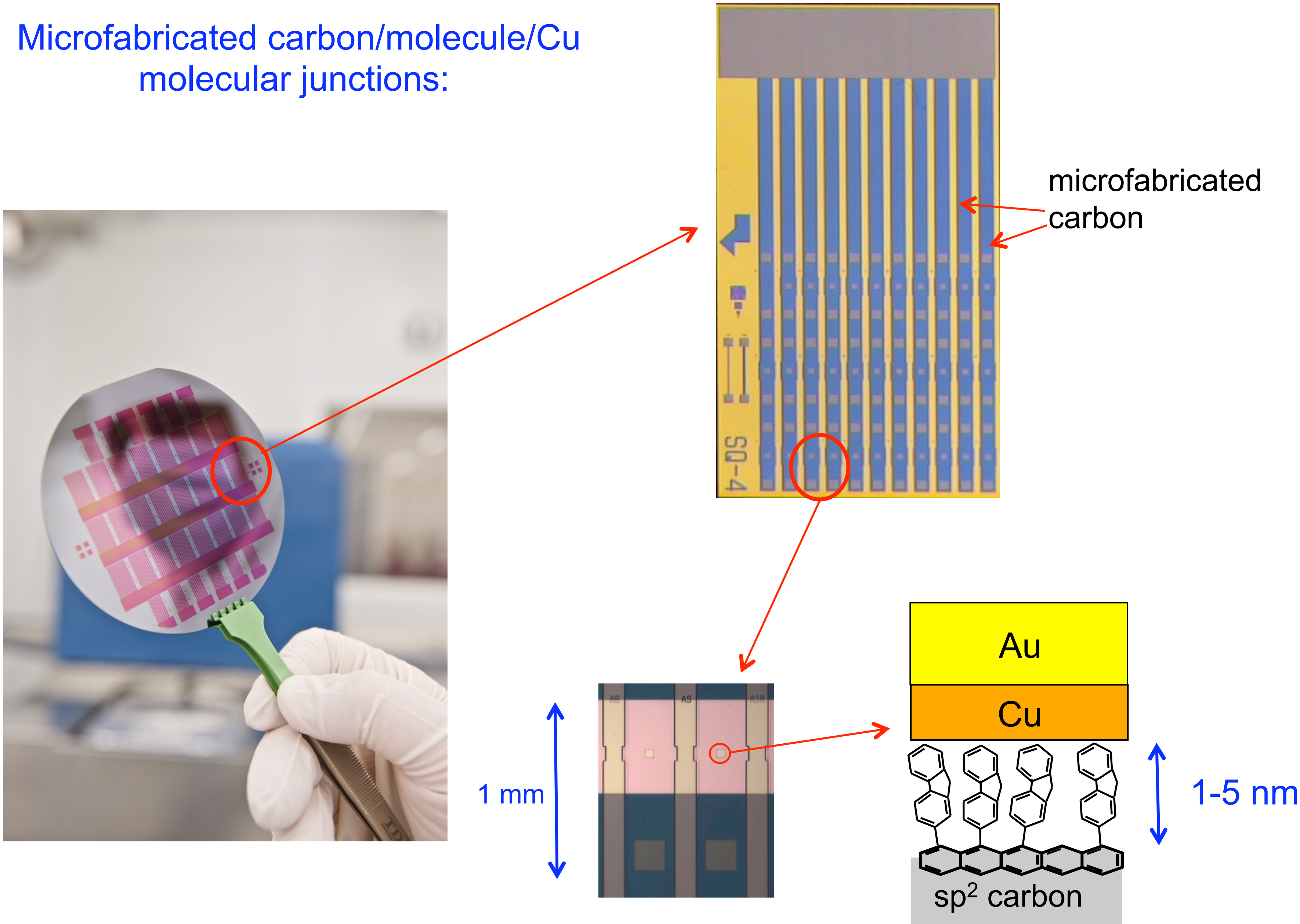




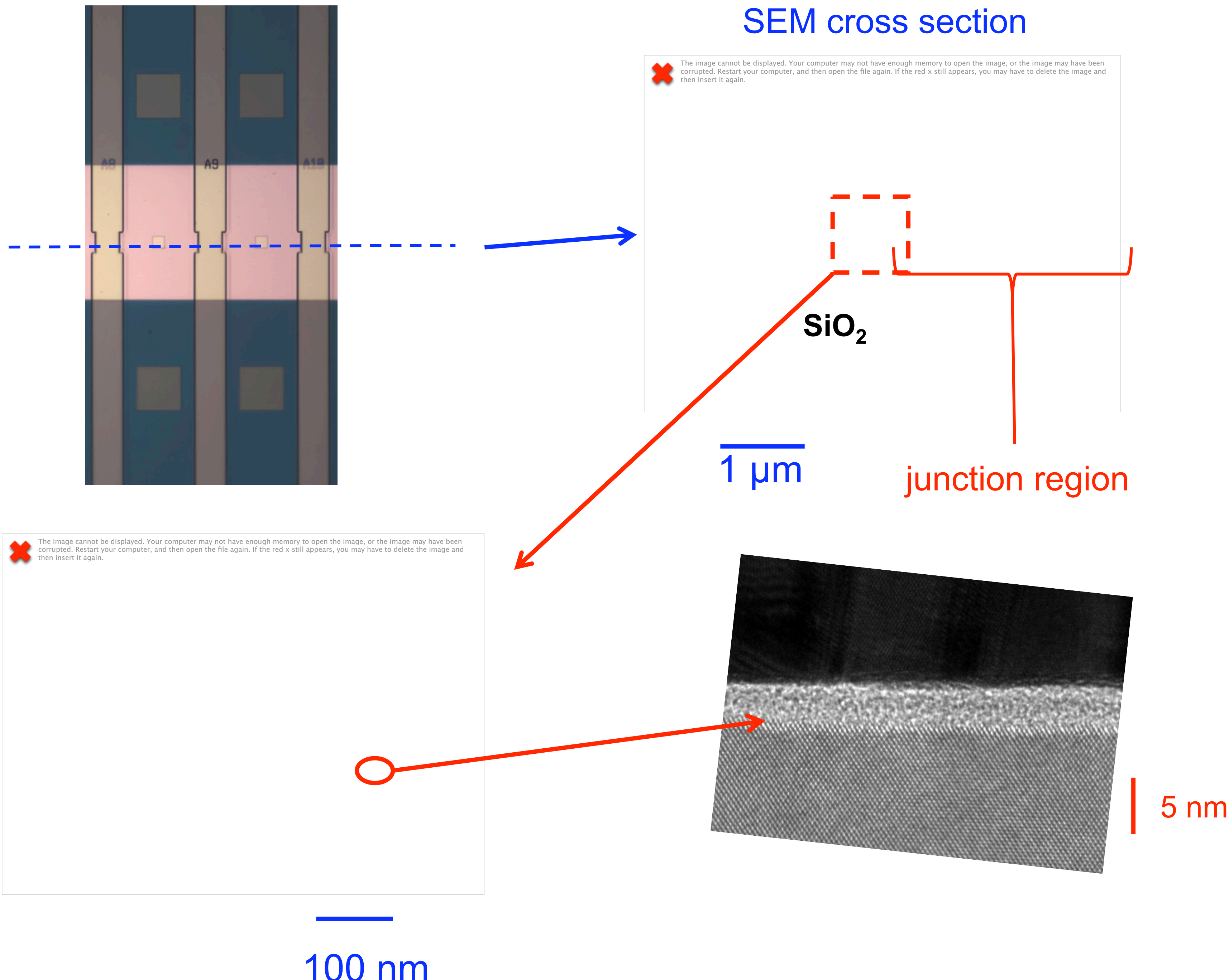


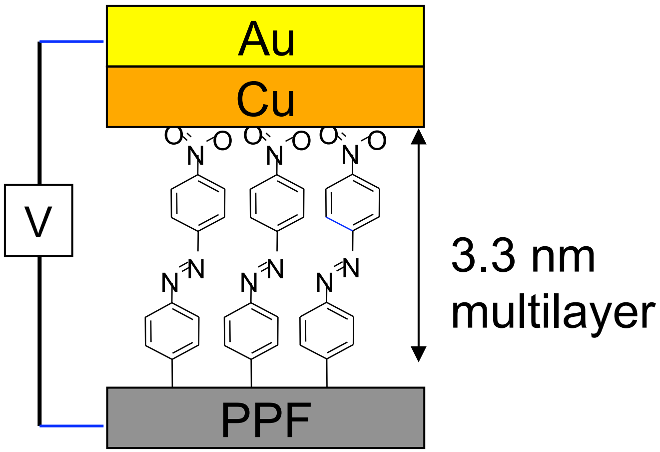
Success of direct Cu deposition enables massively parallel fabrication with conventional equipment

Microfabricated carbon/molecule/Cu molecular junctions:



Ru, Szeto, Bonifas, RLM, ACS Applied Materials & Interfaces ***2010,*** 2, 3693.

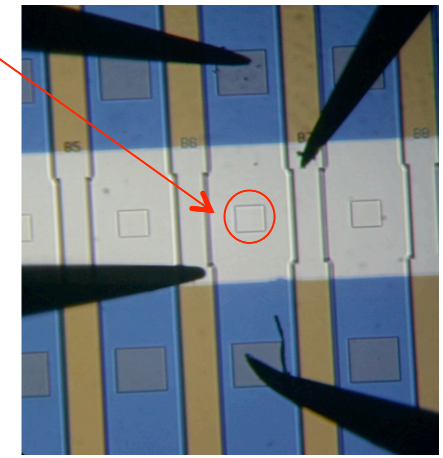

A9
A9
A10
SEM cross section
The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.
SiO_2
1 μm
junction region
The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.
5 nm
100 nm

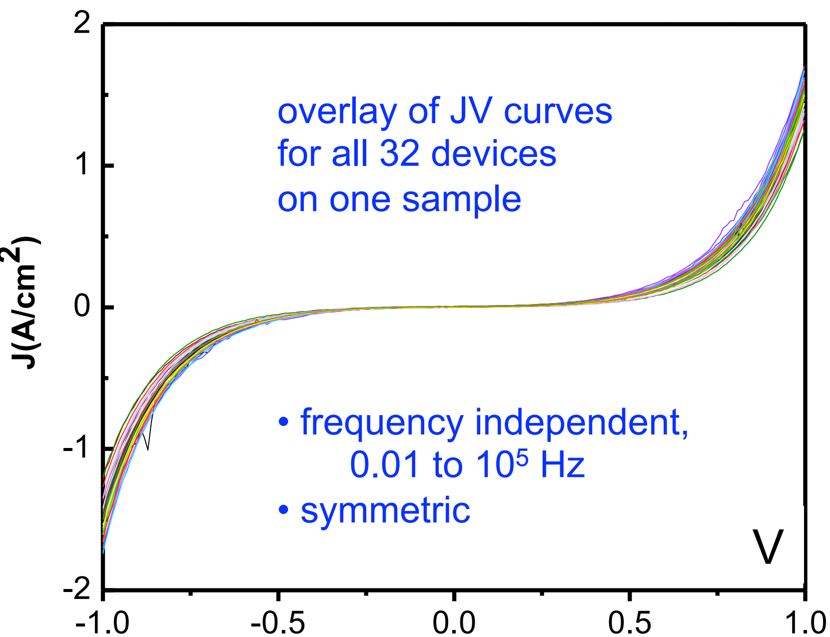


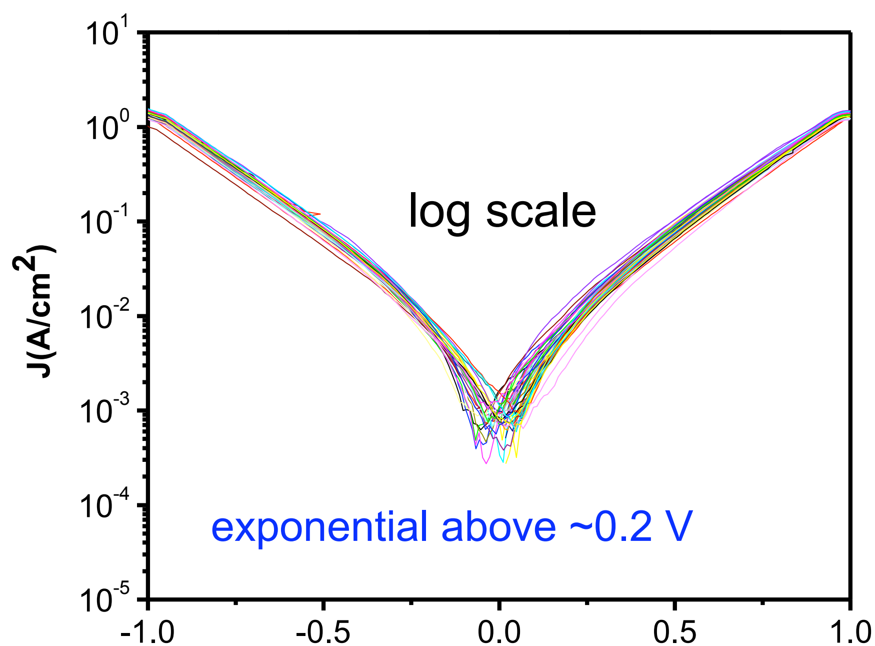
yield: 32/32

RSD (J at 0.5V)= 15.8%

80 x 80
µm junction

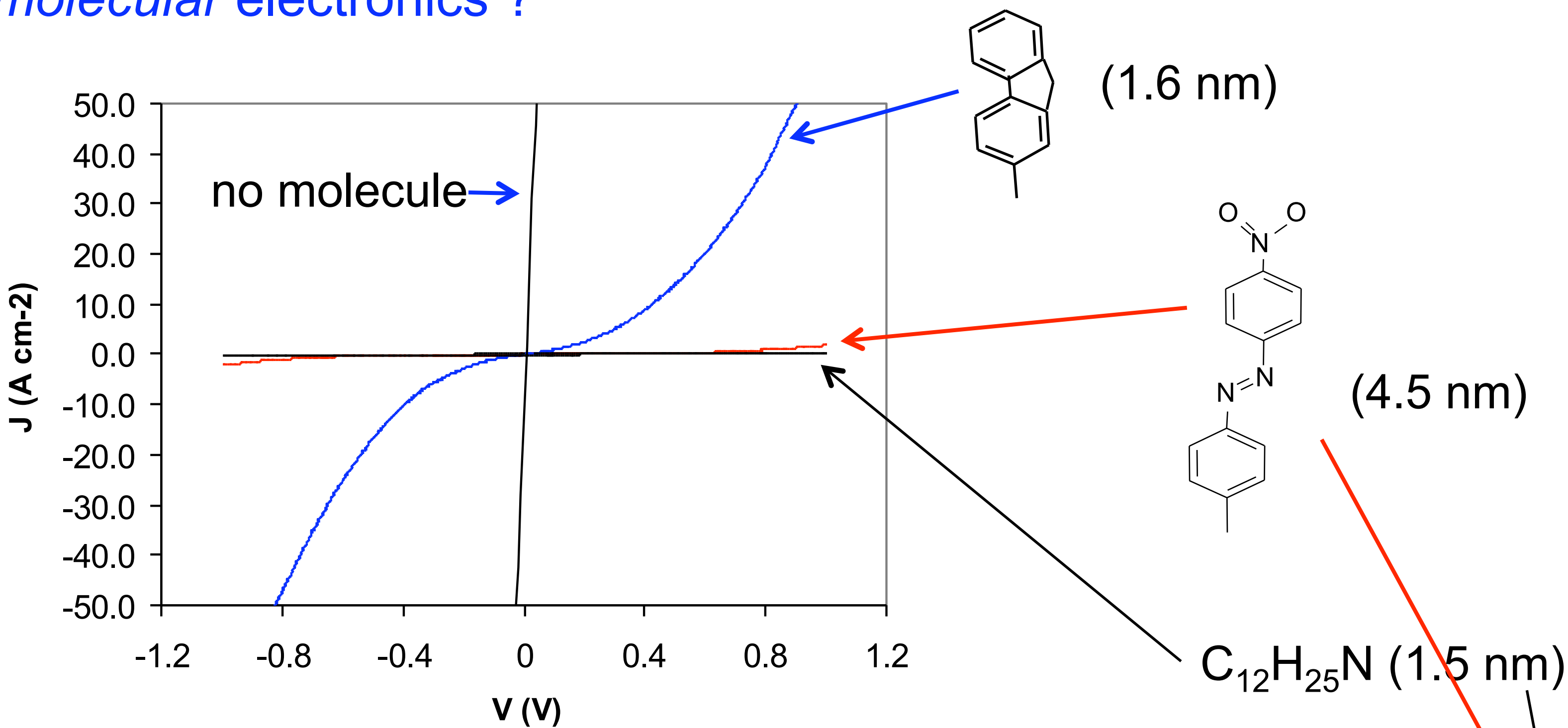


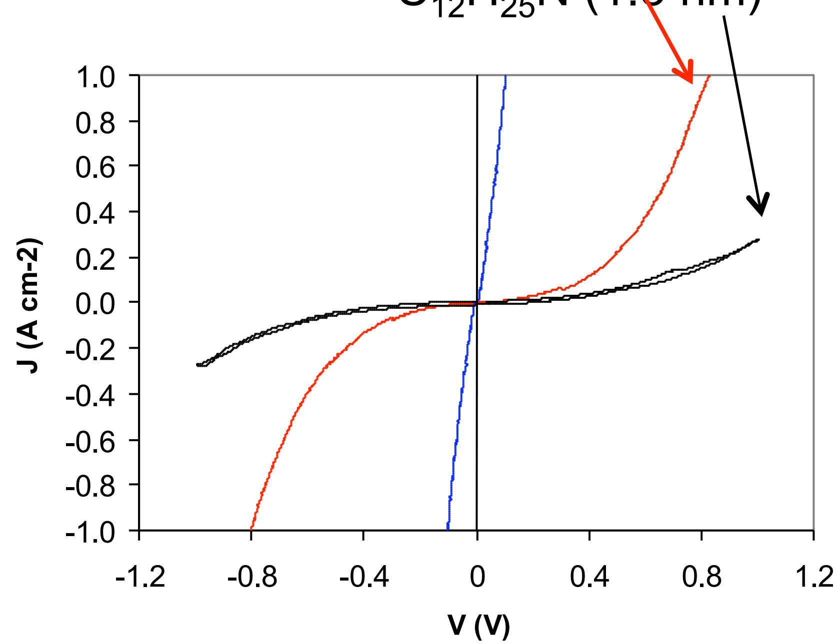




Ru, Szeto, Bonifas, McCreery, *ACS Applied Materials & Interfaces* ***2010,*** 2, 3693

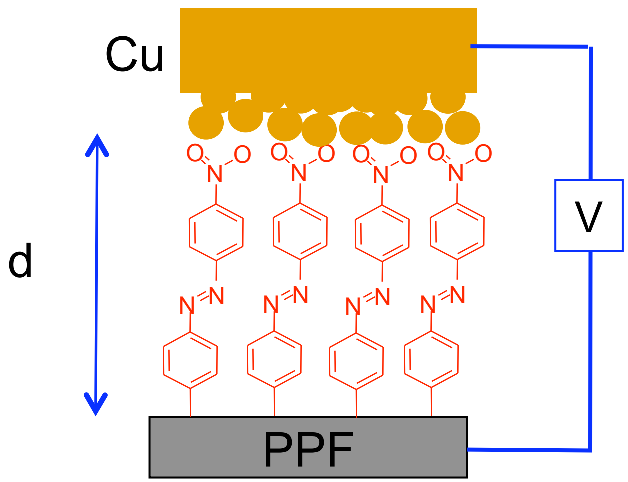
Is this *molecular* electronics ?

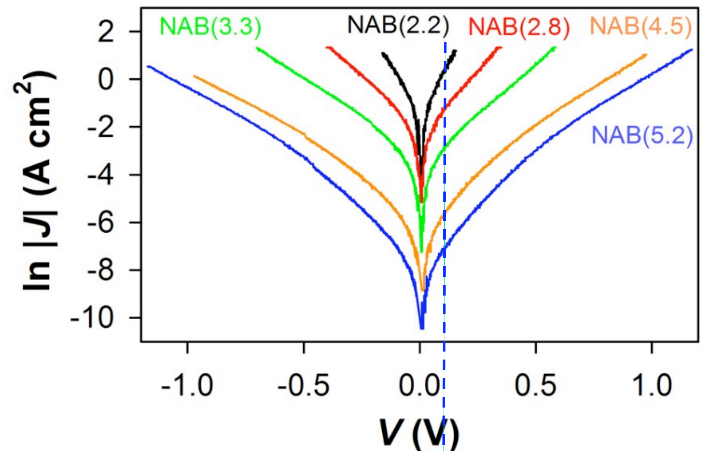


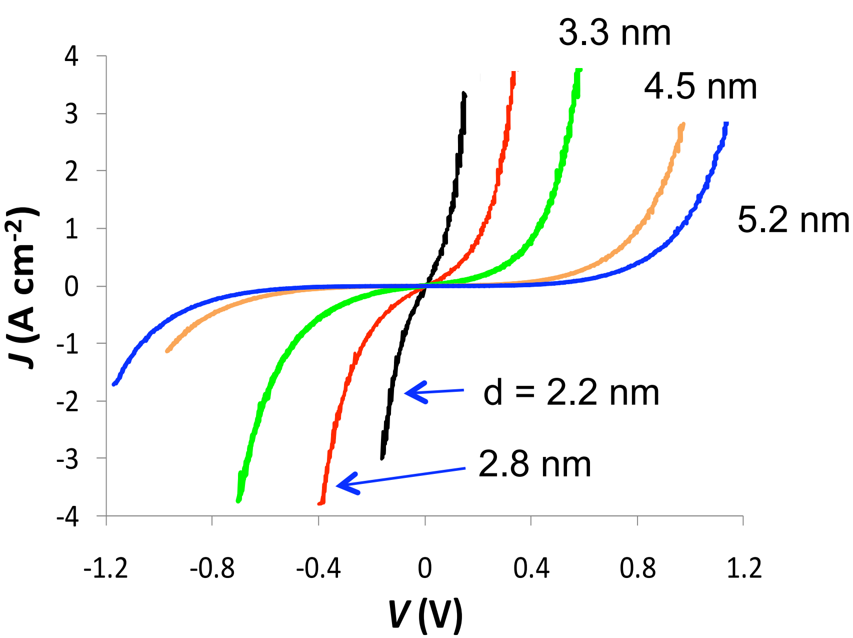


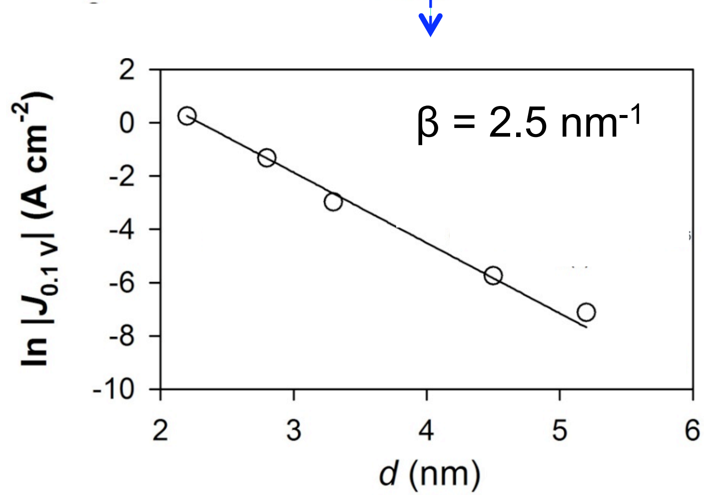
Junction conductance is a strong function of structure and thickness

Back to the main question: how do electrons travel through molecules?
Consider thickness and temperature dependence:



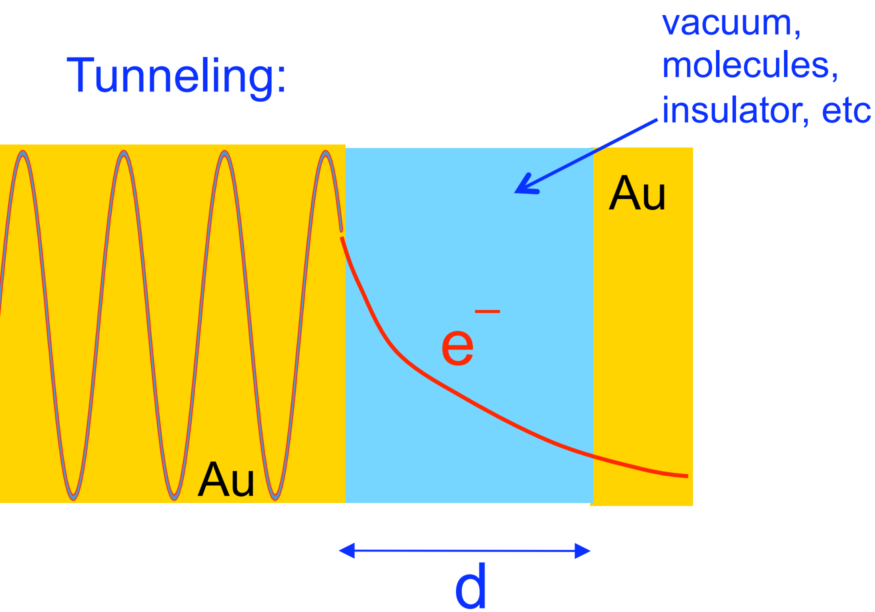






Bergren, McCreery, Stoyanov, Gusarov, Kovalenko, J. Phys. Chem C, **2010**, 114, 15806

Tunneling:



Literature: β

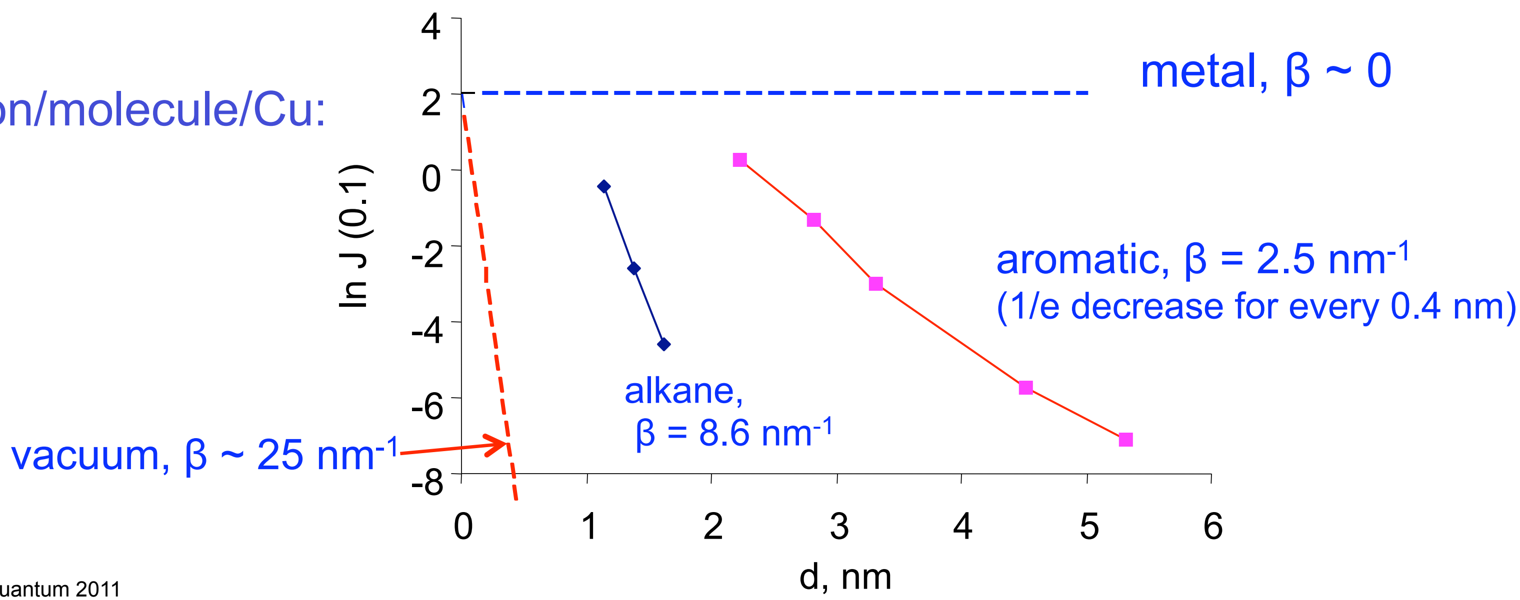
- alkanes (echem or junctions) 8-9 nm^{-1}
- aromatic (echem, 1999) 2.2
- conjugated (echem, SAM) 3 to 6

Single (or few) molecules:

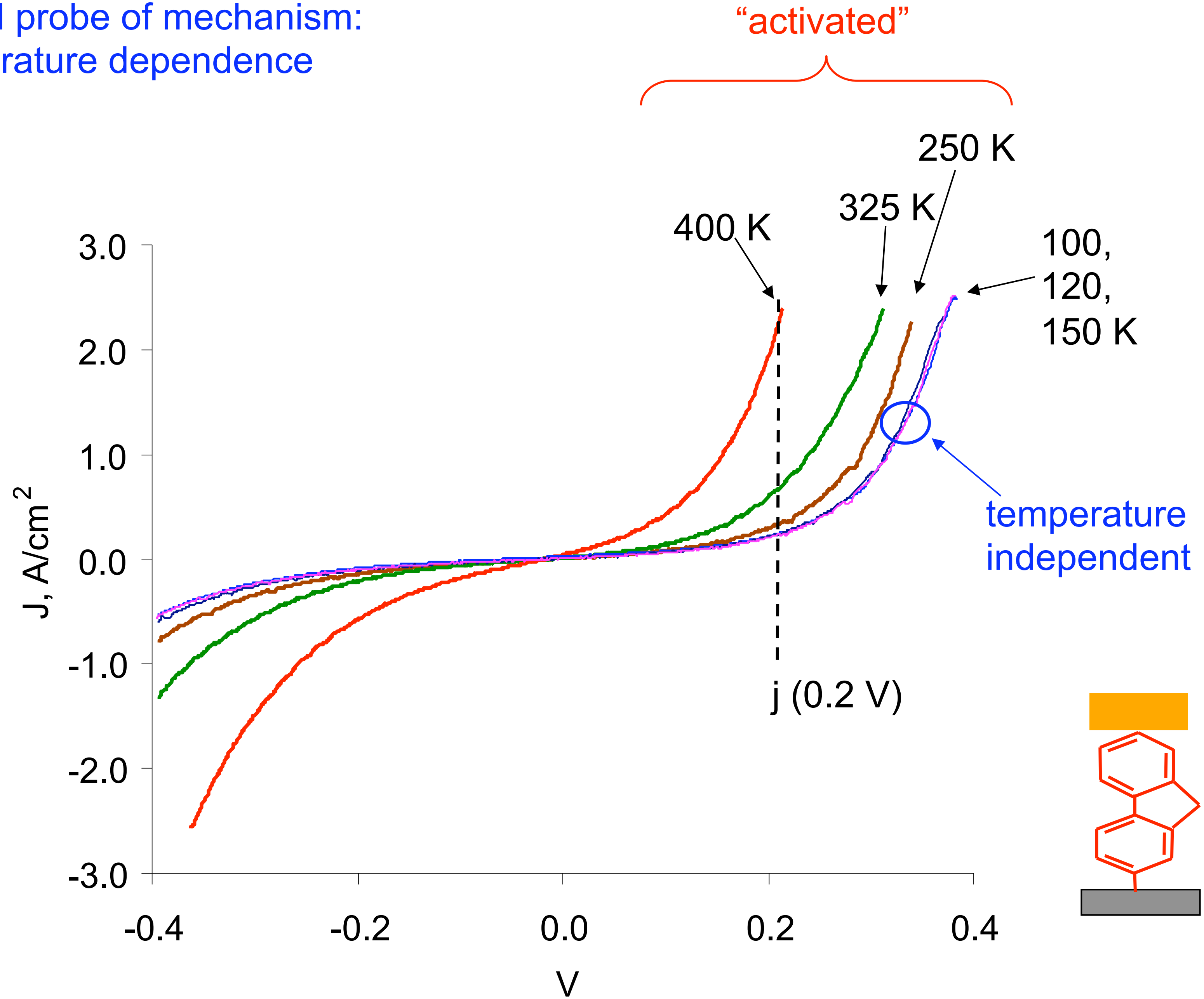
- polyene (2005) 2.2 nm^{-1}
- oligoporphyrin (2008) 0.4
- oligophenyleneimine (2008) 3.0

$$J\ (A/cm^2) = K \exp(-\beta d)$$

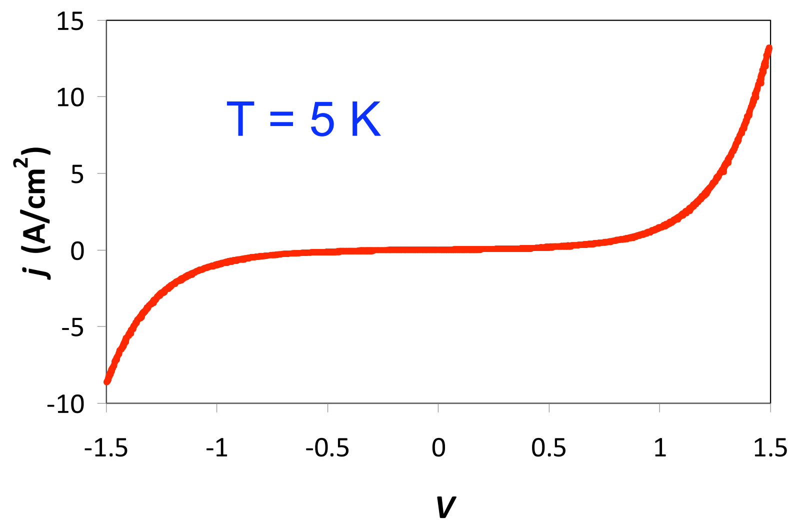
Carbon/molecule/Cu:

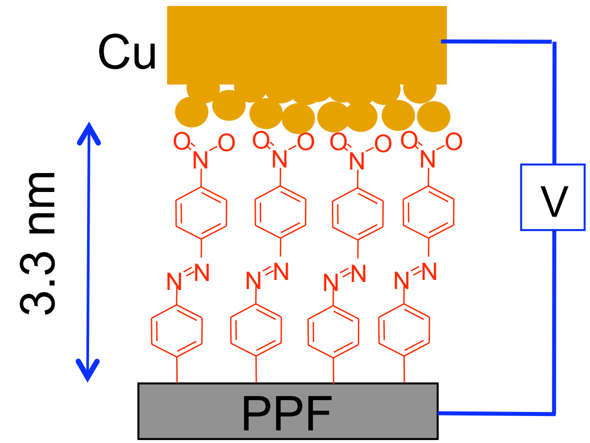


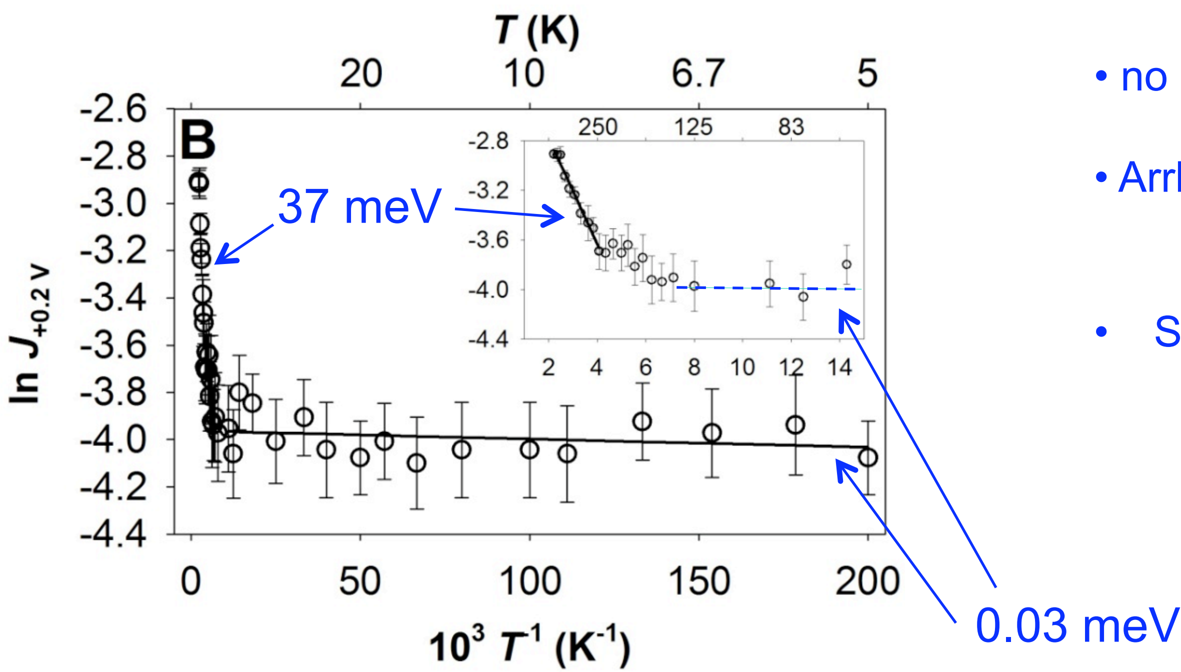
A good probe of mechanism:
Temperature dependence



J. Phys. Cond. Matter, 20, 374117 (2008)



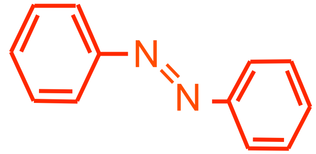


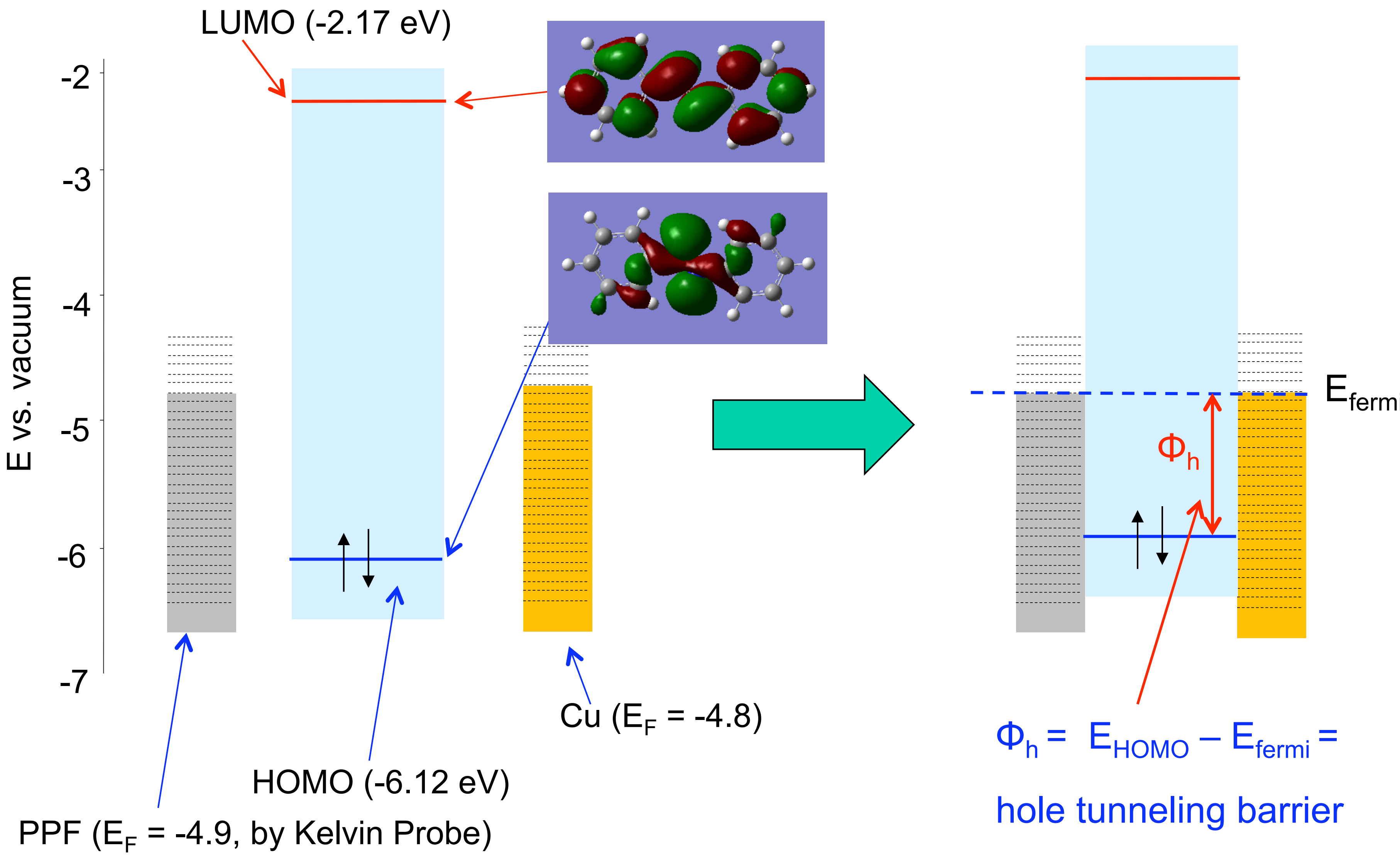


- no "activation" below 200 K
- Arrhenius slope above 200K too small for most "chemistry"
- Slope above 200 K due to Fermi function broadening

Adam Bergren, NINT

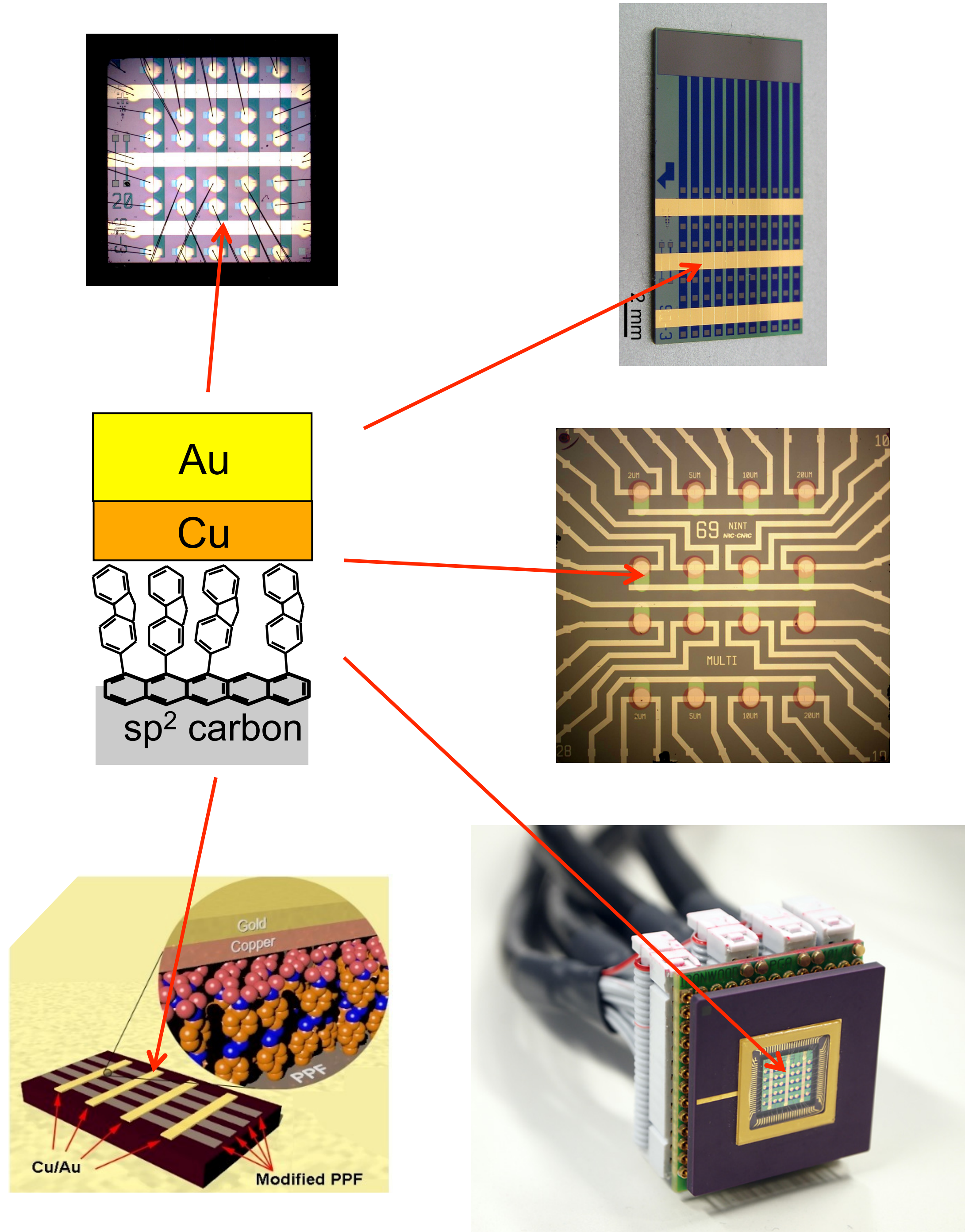
Consider Azobenzene:

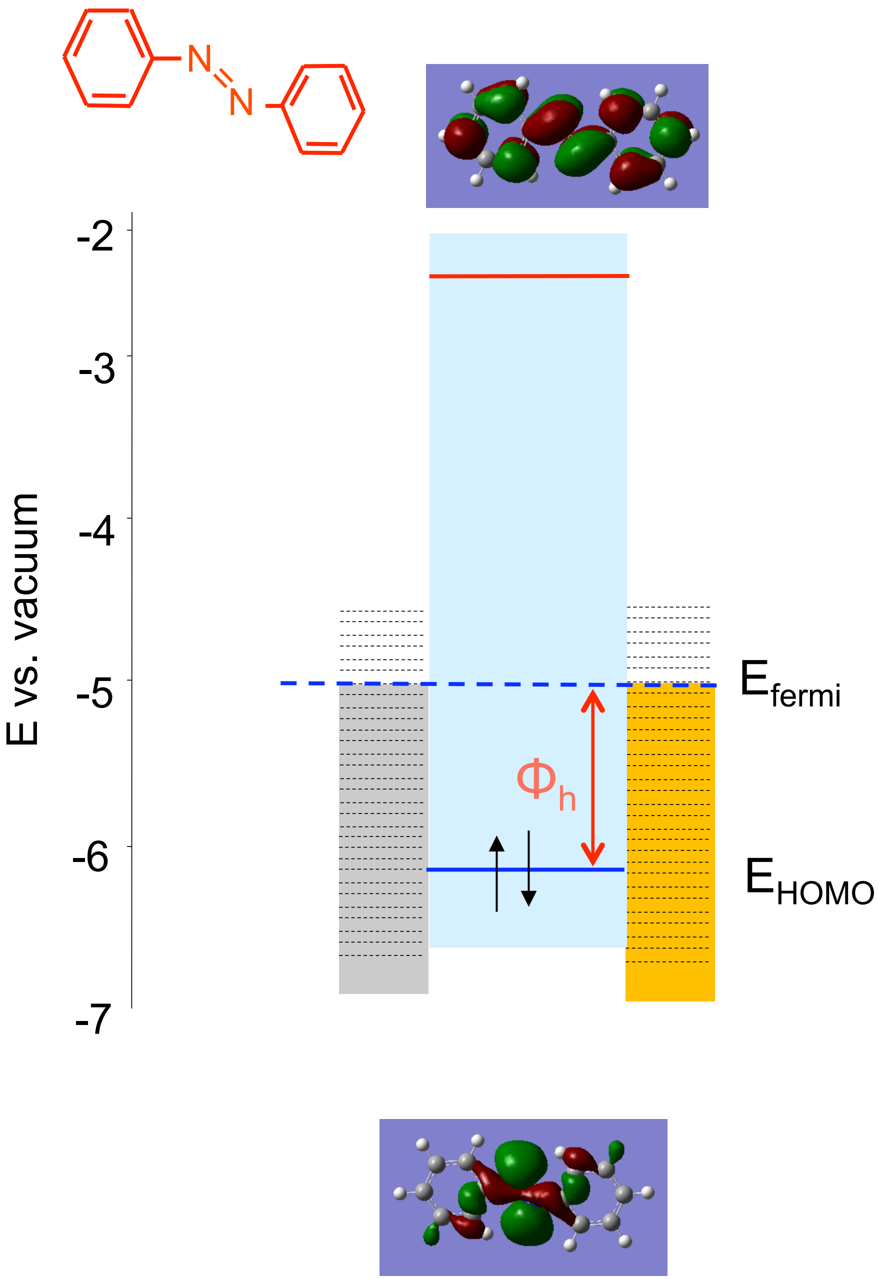




Take-home messages:

- tunneling effective <1.5 nm in alkanes, > 5 nm in aromatics.
- not "activated" over 5 K- 400 K unlike "organic" electronics
- tunneling barrier is usually E_{fermi} (contacts) - E_{HOMO}
- tunneling is very fast, non-dissipative
- "off-resonant" so far, resonant transport should exhibit new and distinct phenomena



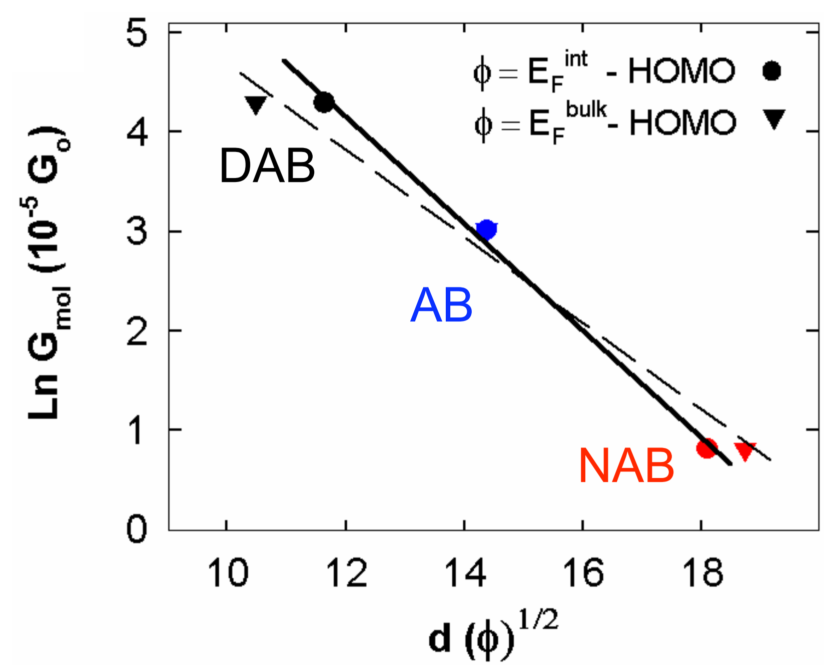


$$J\ (\mathrm{A/cm^2}) = K \exp(-\beta d)$$

$$J\ (\mathrm{A/cm^2}) = K \exp(-C\, d\Phi_h^{1/2})$$

$$\Phi_h = E_{fermi} - E_{HOMO}$$

ln G should be proportional to $d\Phi_h^{1/2}$



Adam Bergren, Haijun Yan
(transport)

Andrew Bonifas (SDMD)

Nikola Pekas, Jie Ru, Bryan Szeto (microfabrication)

Peng Li, Marek Malac (TEM)

Andriy Kovalenko, Stan Stoyanov, Sergey Gusarov (theory)

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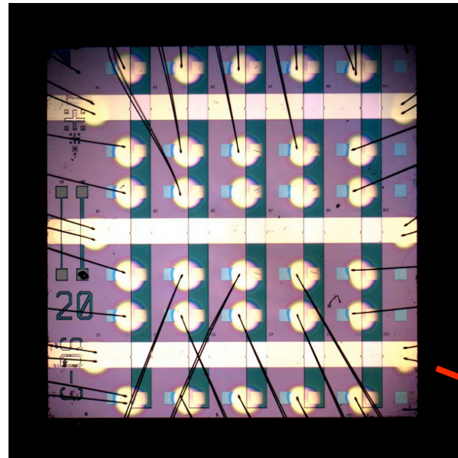
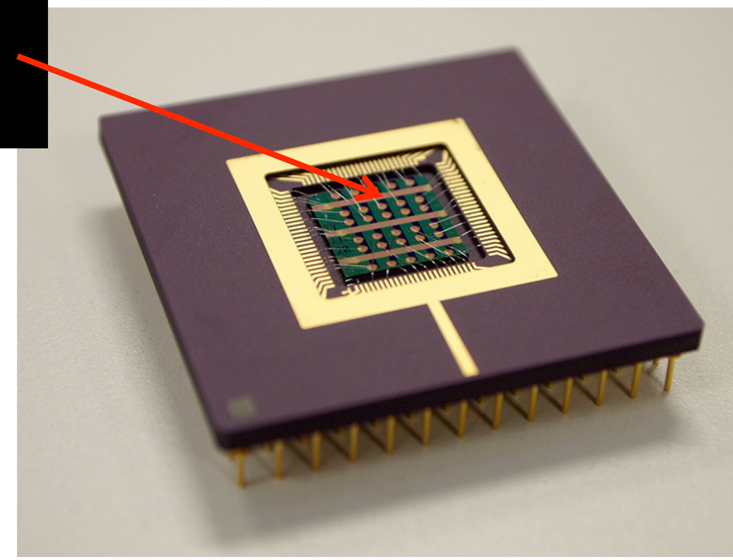
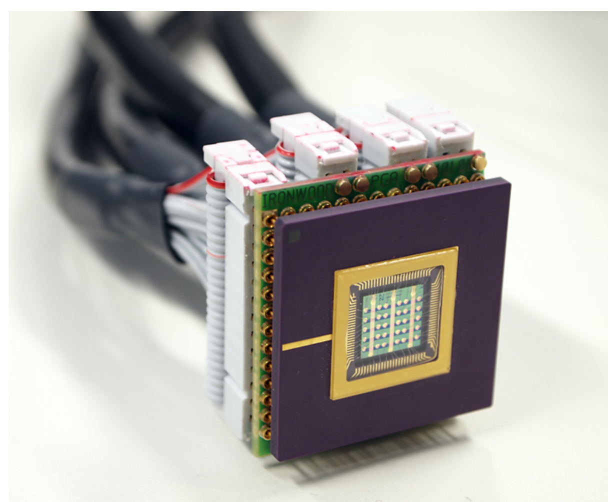






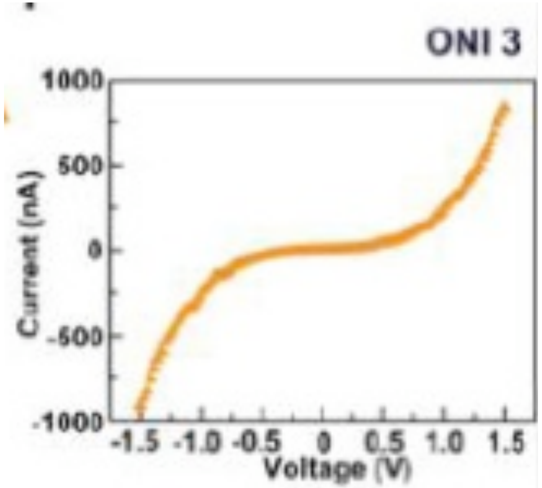
Some big remaining questions:

1. what happens if $E_{fermi} = E_{HOMO}$?

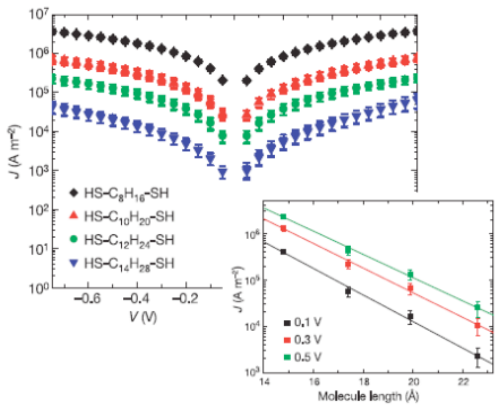
2. can molecules undergo redox reactions during transport ?
(more in next lecture)

3. How far can electrons go in molecules without “activation” ?

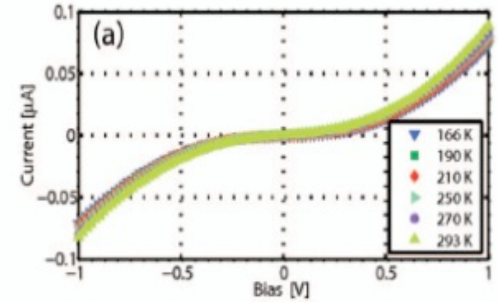
4. Is off-resonant tunneling “ballistic” ?



Frisbie, et al, *JACS* 132, 4358, Au-S-aromatic/Au(CP-AFM tip)

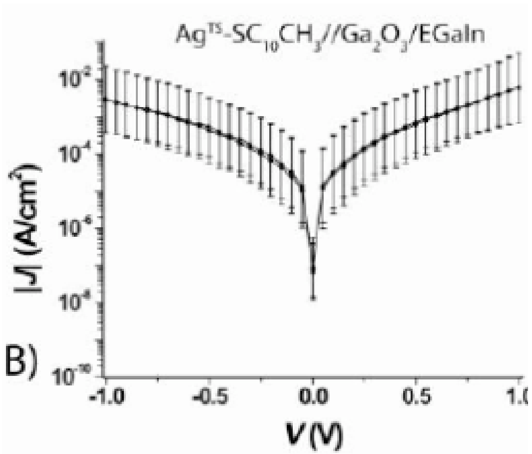


Akkerman, et al., *Nature* **2006**, *441*, 69, Au-S-alkane-SH/PEDOT:PSS

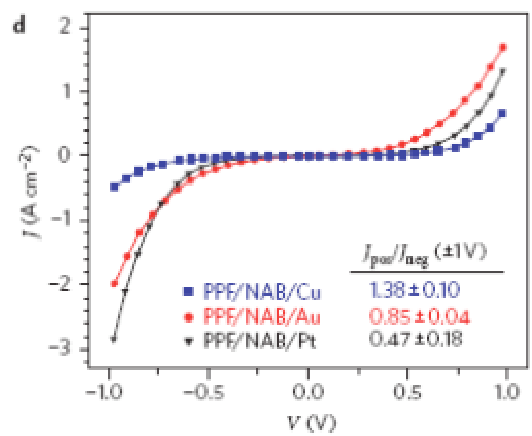


Melosh, et al. *Appl. Phys. Lett.* **2008**, *92*, 213301

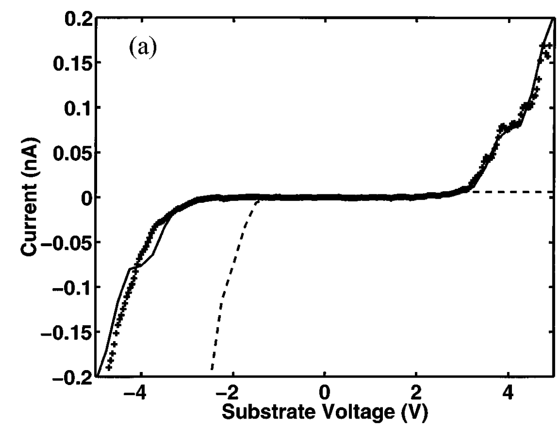
Au-S-C_8H_{16}-COOH-Al_2O_3(ALD)/Au



Whitesides, et al. *JACS* **2009**, *131*, 17814

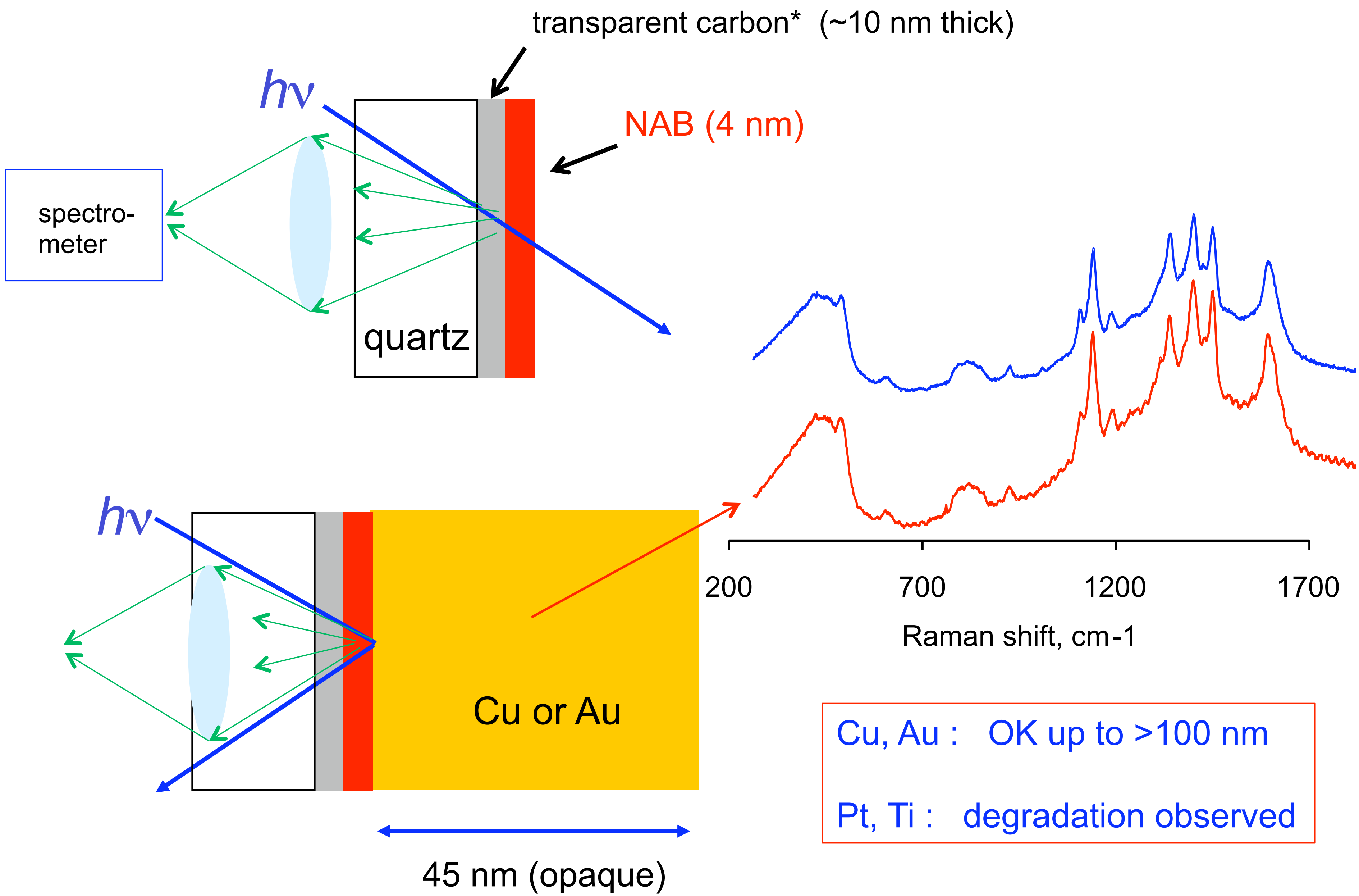


Bonifas et al., Nature Nano 5, 612, carbon-nitroazobenzene-metal



Datta et al., Phys. Rev. Let. 1997, Au-a,a'-xylyl dithiol/ Au STM tip

“Backside” Raman:



Cu, Au : OK up to >100 nm

Pt, Ti : degradation observed

*Donner, Li, Yeung, Porter, Anal. Chem. 78, 2816 (2006).

Non-comprehensive list of NINT projects:

- nanofabrication, both “top down” and “bottom up” (Wolkow, Freeman, McDermott, Evoy, Bosnick)
- surface modification (McCreery, Wolkow, Buriak, Brett, McDermott)
- nanoelectromechanical systems (NEMS): resonators, detectors (Heibert, Evoy, Freeman)
- nanostructured separation devices (Harrison, Brett)
- nanoscale electronic and magnetic structures (Wolkow, Freeman, McCreery, McDermott, Stoyanov, DiLabio)
- nanostructures for energy conversion and storage (Buriak, Kovalenko, Brett)
- theory and modeling of nanoscale phenomena (DiLabio, Kovalenko, Stepanova, Gusarov, Stoyanov)