National Institute For Nanotechnology

Molecules in Circuits: a New Breed of Microelectronics?

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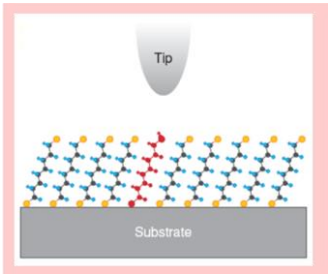
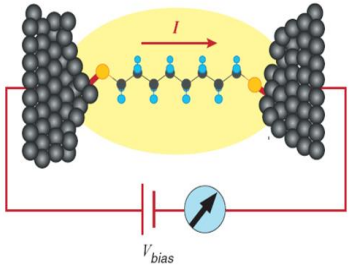
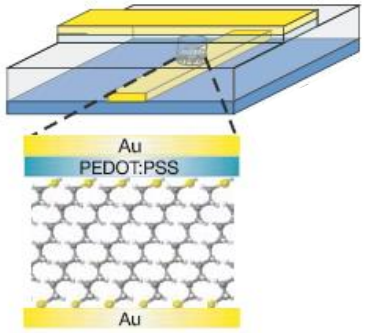
Molecular Electronics:

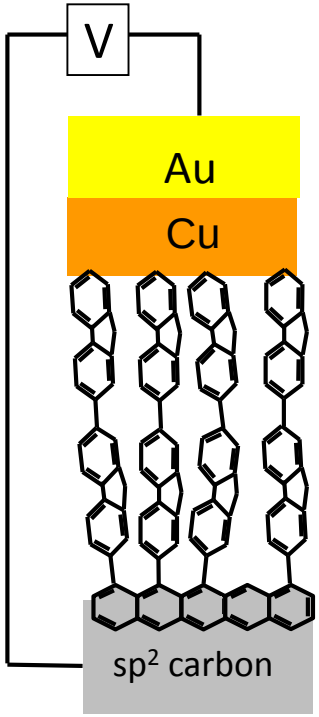


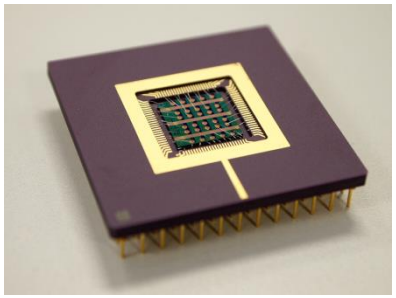


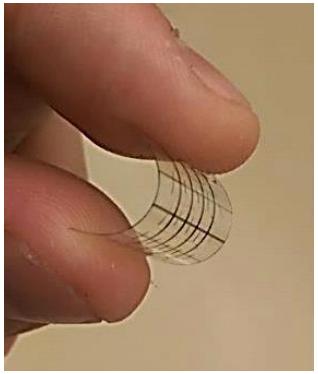


Our approach:

- "Manufacturable" devices tolerant of the real world
- Large area (~10 μm^2 to ~0.1 mm^2) molecular junctions. Nanoscale (1-20 nm) in one dimension.
- Unique junction design based on carbon-carbon bonding between substrate and molecular layer







Two main questions:

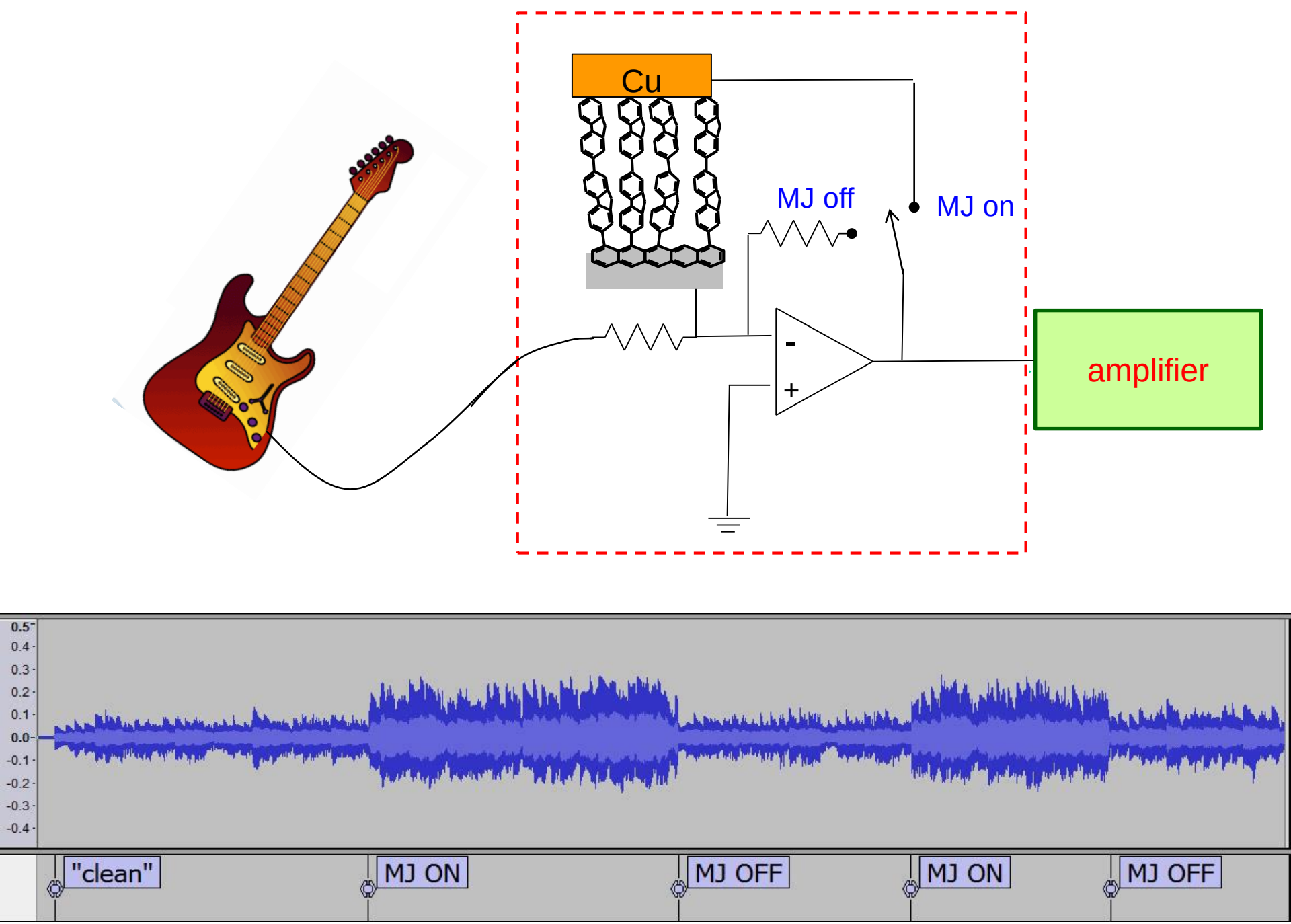
How do molecules behave as circuit elements?

What electronics can we do with molecules that we can't do with silicon?

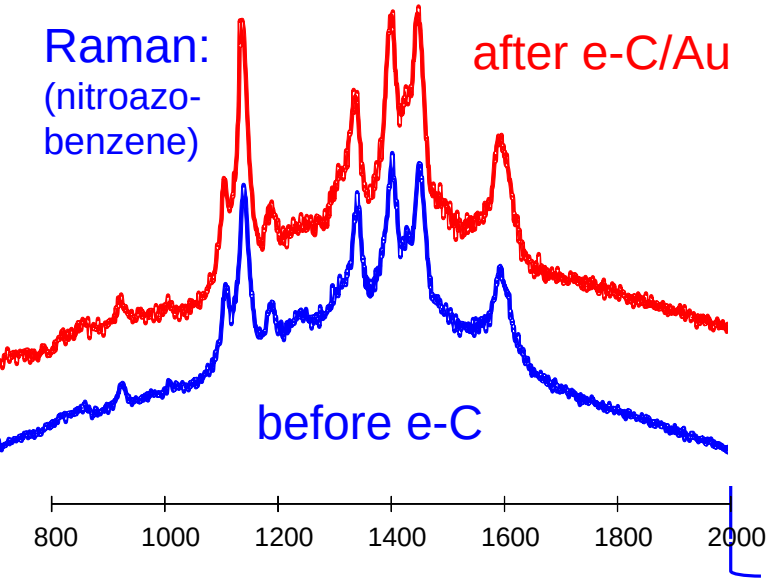
A short outline:

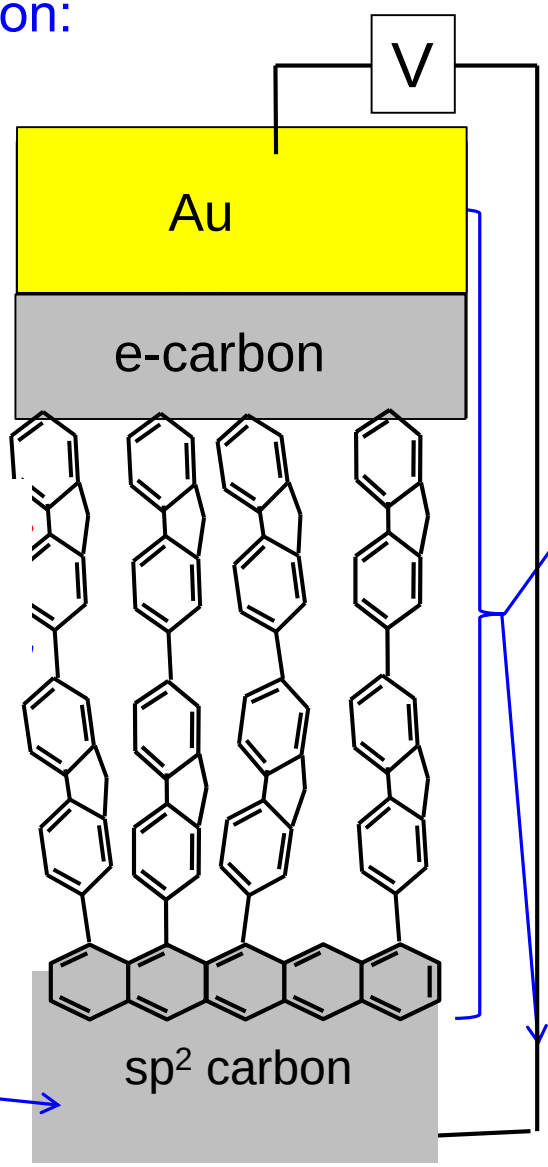
- musical molecules (intro)
- carbon-based molecular junctions
- tunneling & beyond
- light emission
- audio distortion

Start with something you can’t do with silicon…..

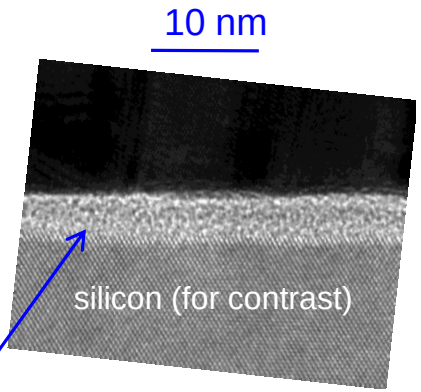

Cu
MJ off
MJ on
amplifier
-
+
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
"clean"
MJ ON
MJ OFF
MJ ON
MJ OFF

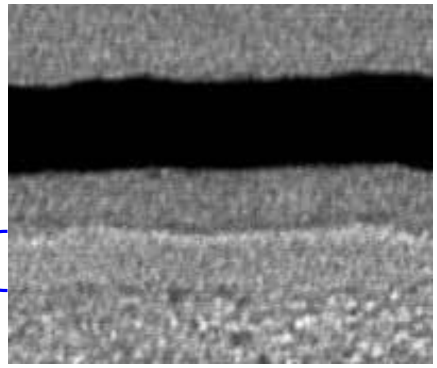
“All carbon” molecular junction:





FIB/TEM:



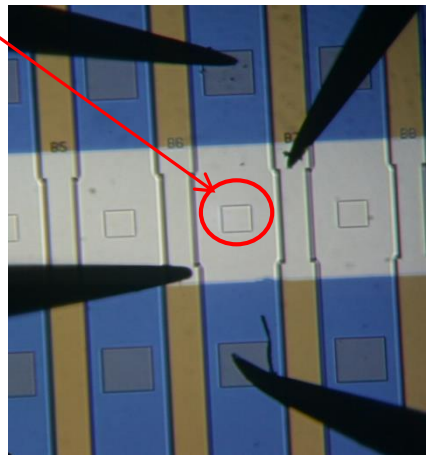


pyrolyzed photoresist film (PPF). Roughness < 0.4 nm rms by AFM

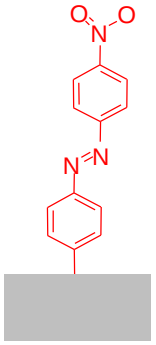
Anariba, Steach, McCreery, J. Phys. Chem. B. ***2005***, 109, 11163

Yan, Bergren, McCreery, J. Am. Chem. Soc. ***2011***, 133, 19168

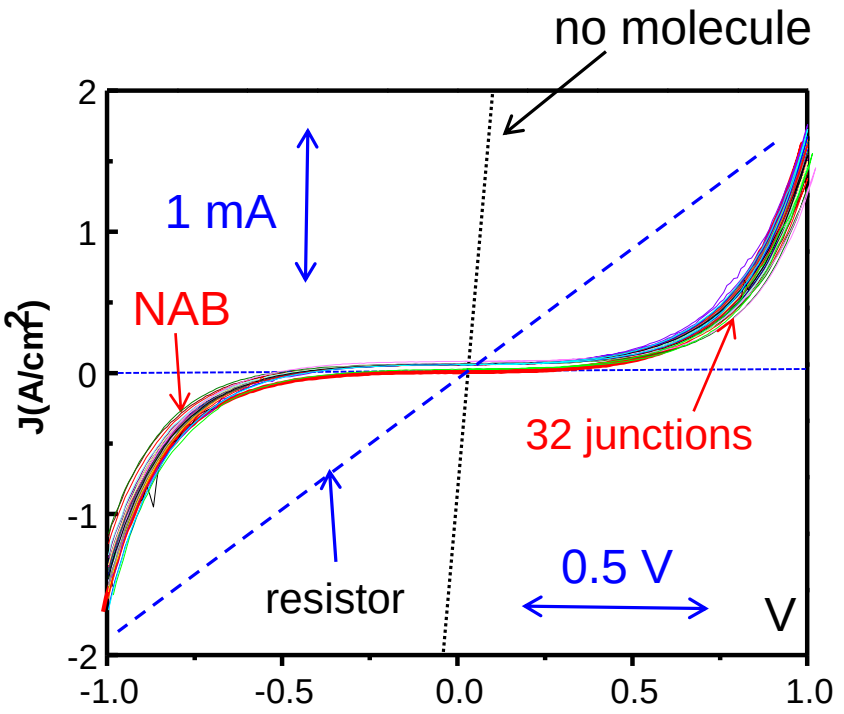
80 x 80
μm junction



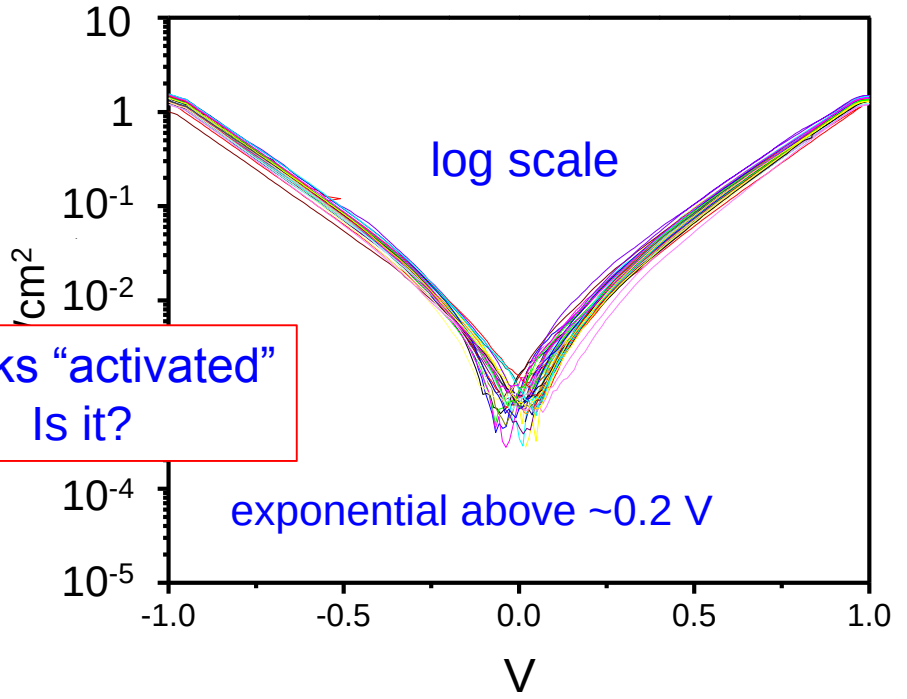
Cu



NAB (nitroazo-benzene, 3.5 nm)

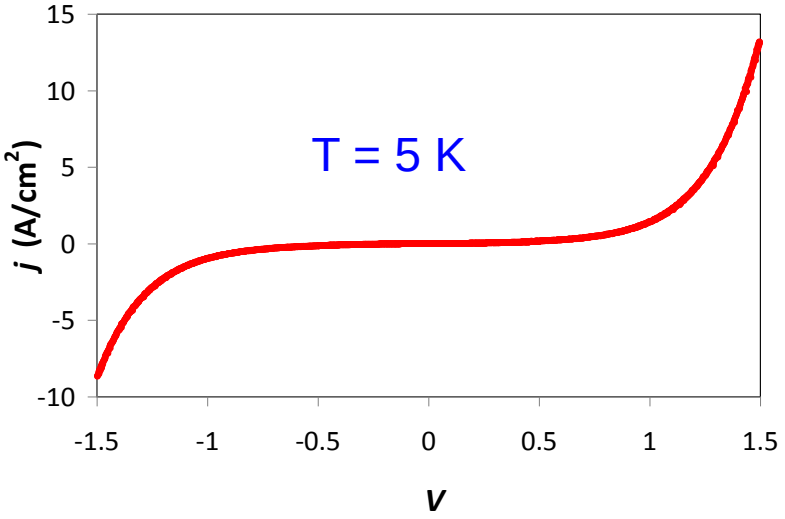


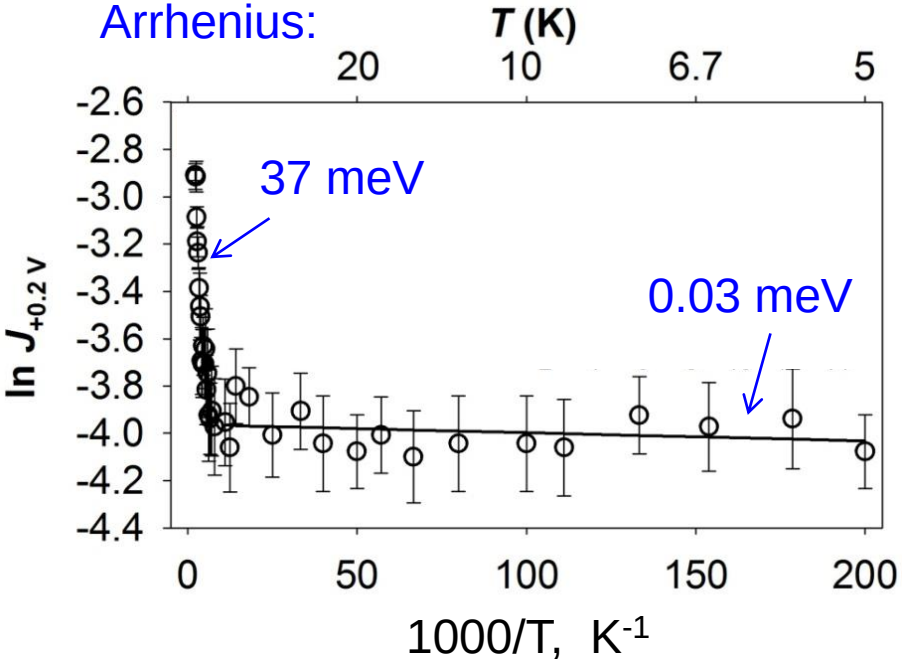
- frequency independent,0.01 to 10^5 Hz
- symmetric
- can scan > 10^9 cycles at 100 °C without change
- survived 150 °C for > 40 hrs
- survived 350 °C for 5 minutes
- shelf life> 7 years

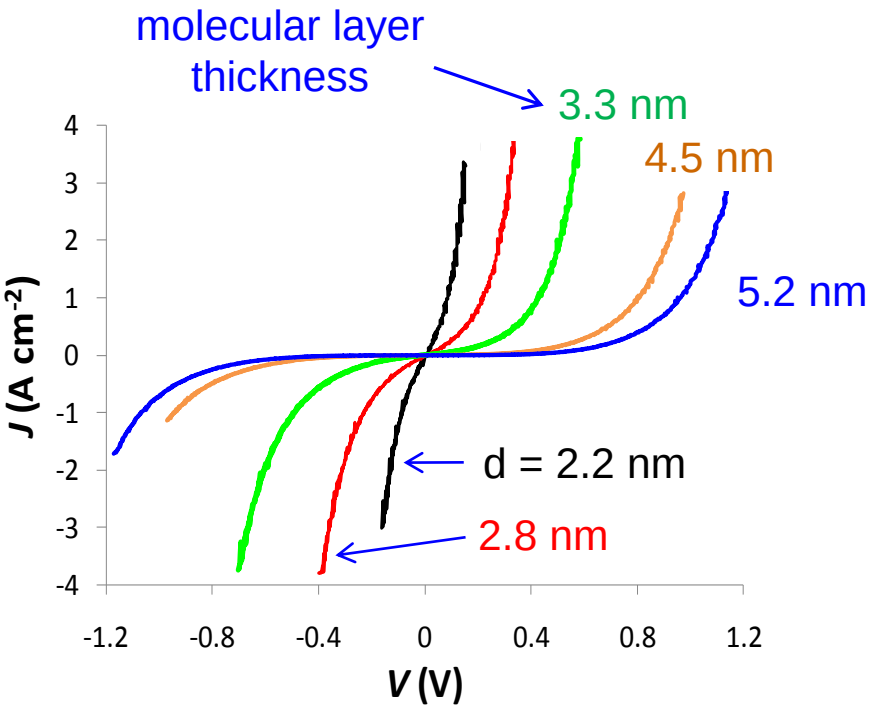


It looks "activated"
Is it?

ACS Applied Materials & Interfaces ***2010,*** 2, 3693

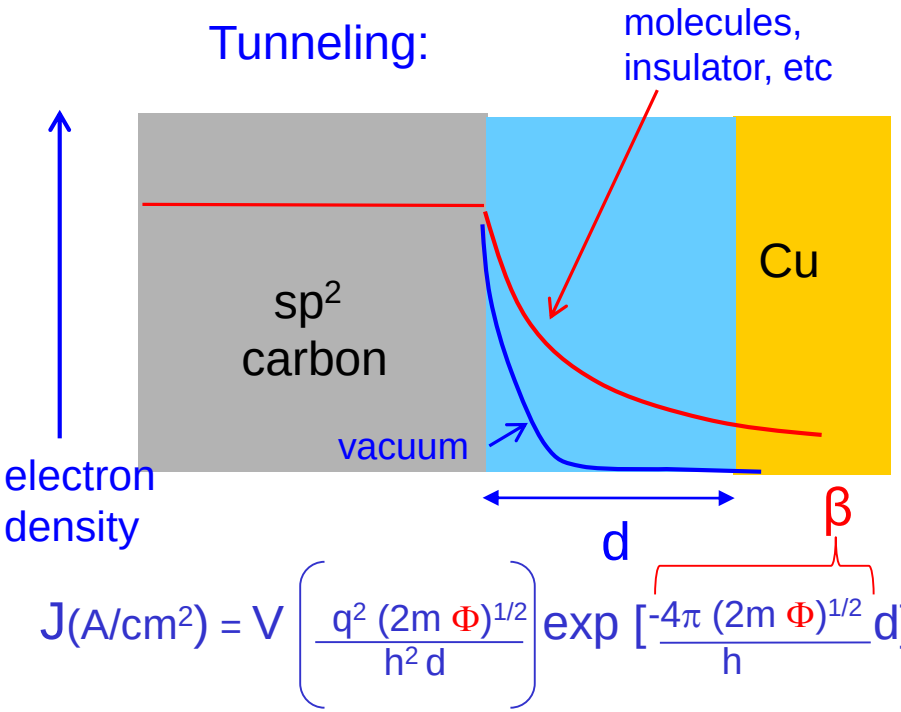




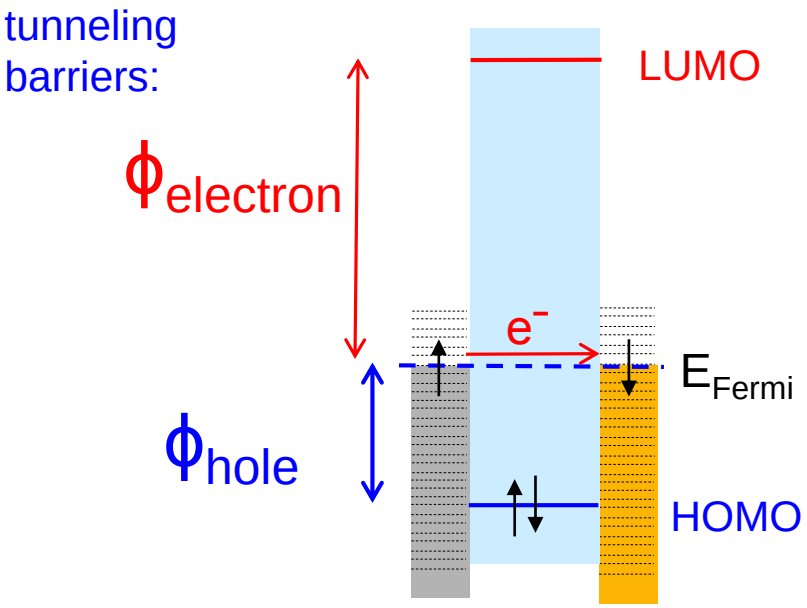


- not activated for T<200 K
- strong thickness dependence
- NOT activated electron transfer, so what is it?

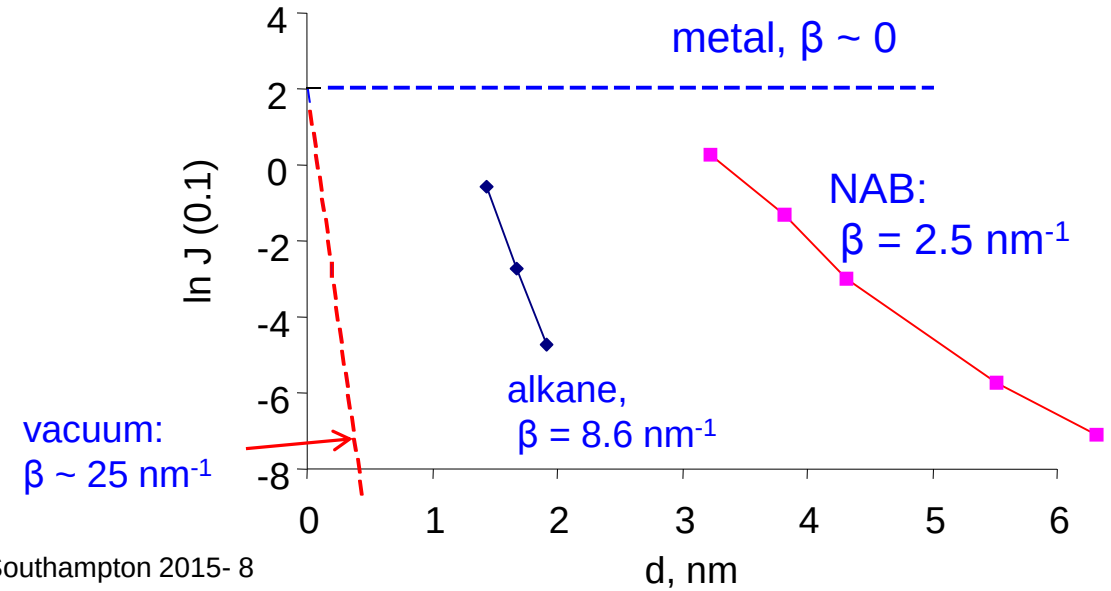
J. Phys. Chem C, **2010**, 114, 15806



$$J(A/cm^2) = V \left(\frac{q^2 (2m\,\Phi)^{1/2}}{h^2\, d} \right) \exp\left[\frac{-4\pi (2m\,\Phi)^{1/2}}{h} d \right]$$



$$J = VA\, e^{-\beta d} \qquad \ln J = \ln(AV) - \beta d$$



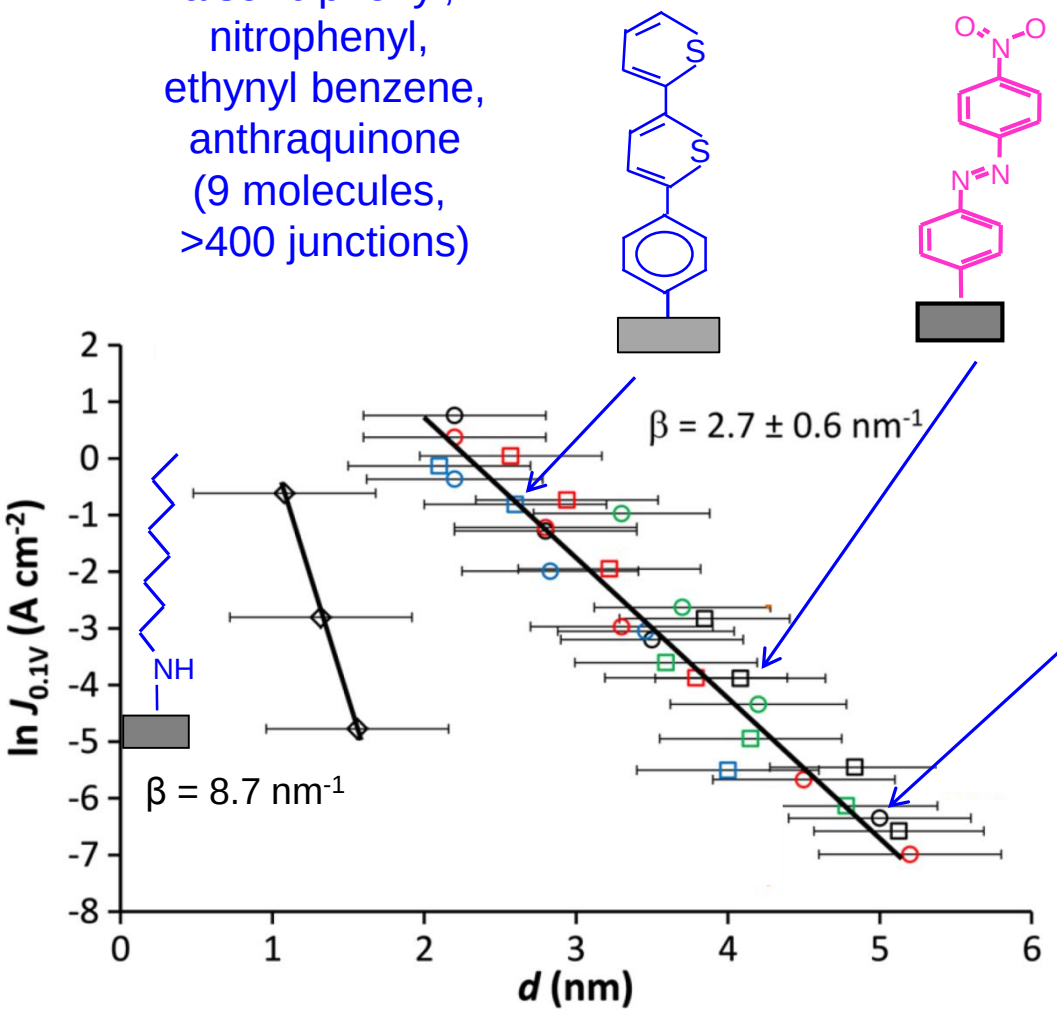
by electrochemistry in solution:

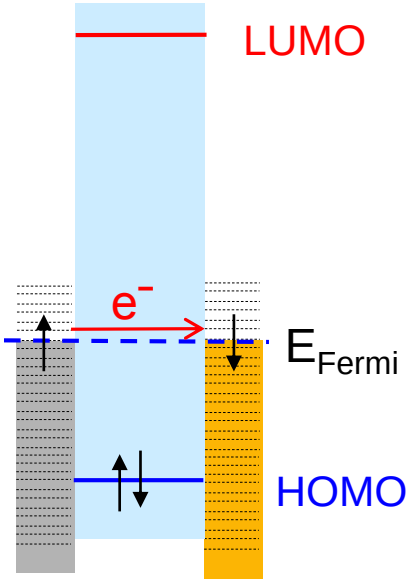
β = 8-9 nm^{-1} (alkanes)

β = 2.2 nm^{-1} (aromatics)

Carbon/molecule/Cu devices:

also: biphenyl,
nitrophenyl,
ethynyl benzene,
anthraquinone
(9 molecules,
>400 junctions)





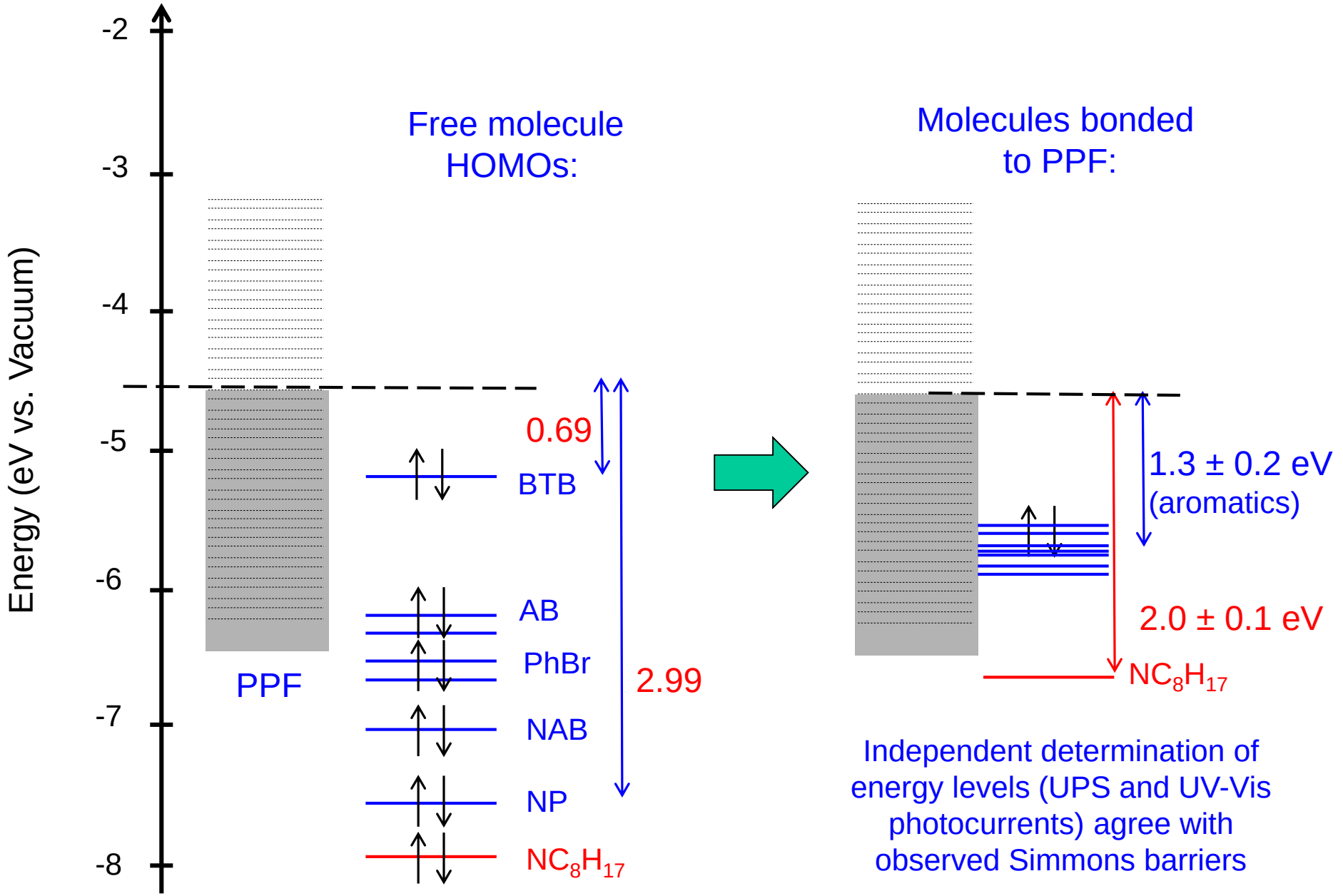
1.3* ± 0.2 eV
(aromatics)

*Independent determination of energy levels (UPS and UV-Vis photocurrents) agree with observed Simmons barriers

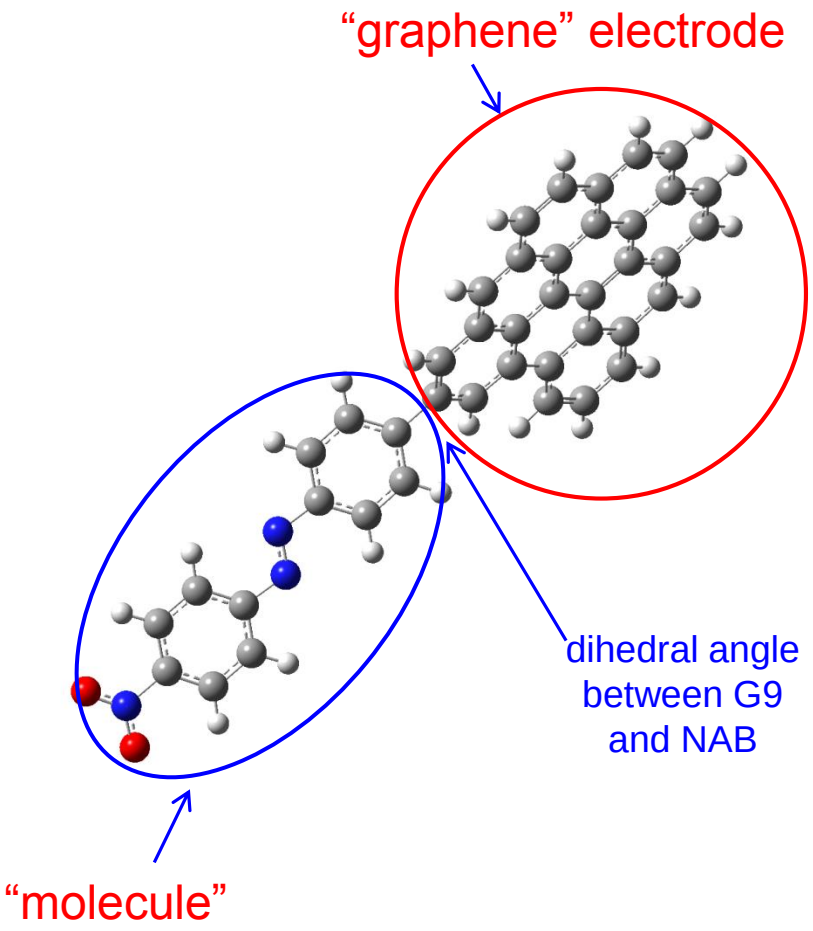
2.4 eV range of HOMOs,
2.3 eV range of LUMOs

small effect!

PNAS (***2012***) *109, 11498*

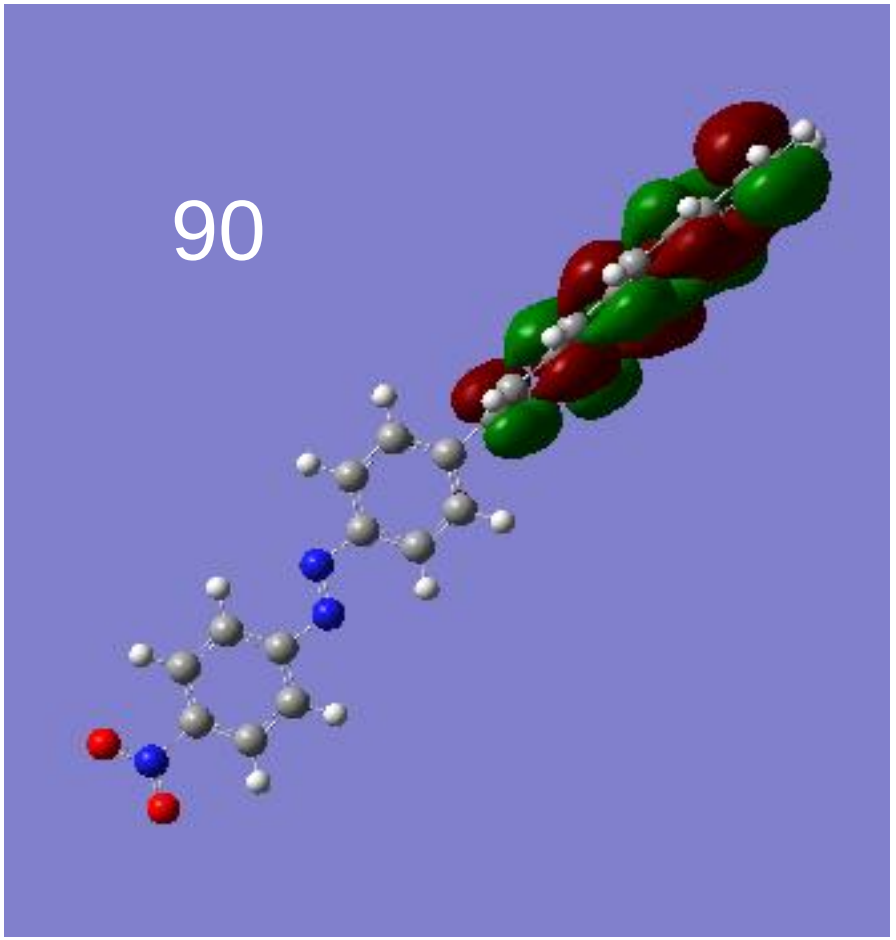


Sayed, Fereiro, Yan, RLM, Bergren, PNAS, 109, 11498 (2012)
Fereiro, McCreery, Bergren, A J. Am. Chem. Soc. 135, 9584 (2013)



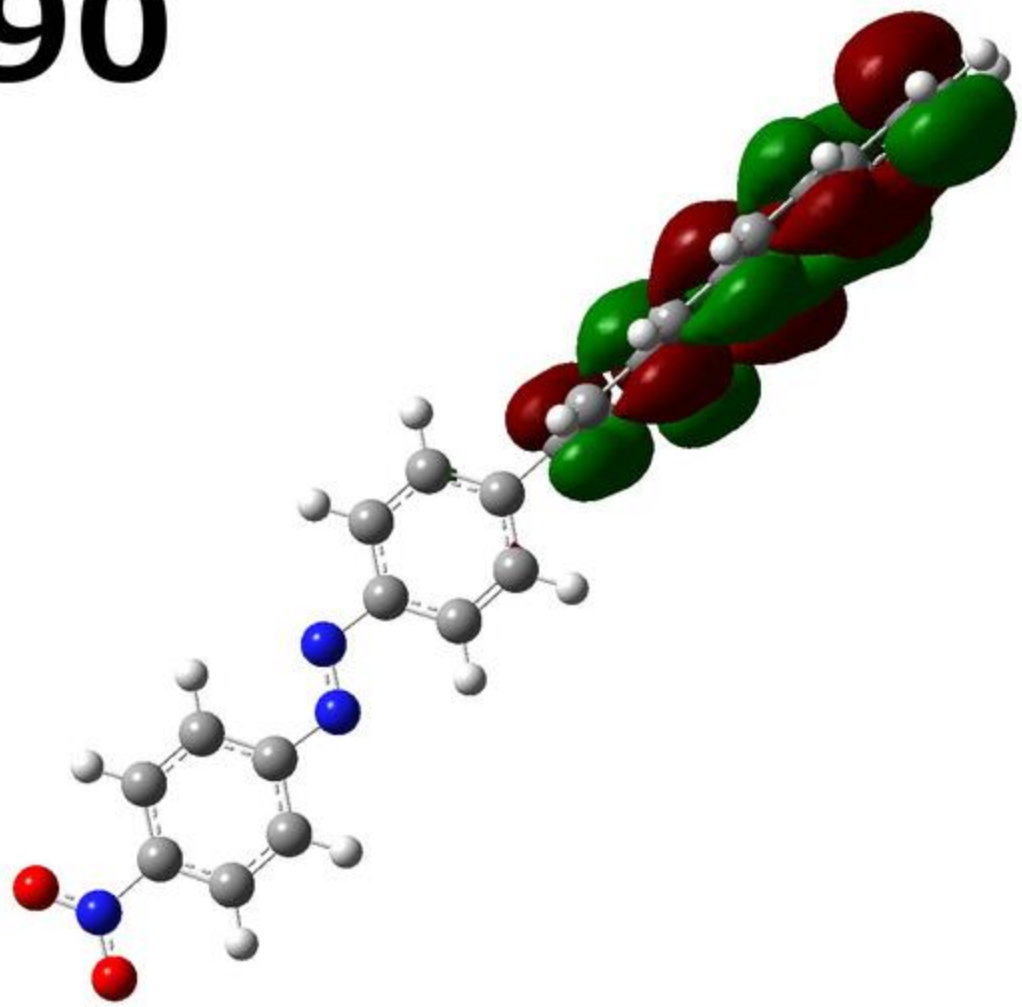
HOMO-1 orbital*

90^{o} dihedral

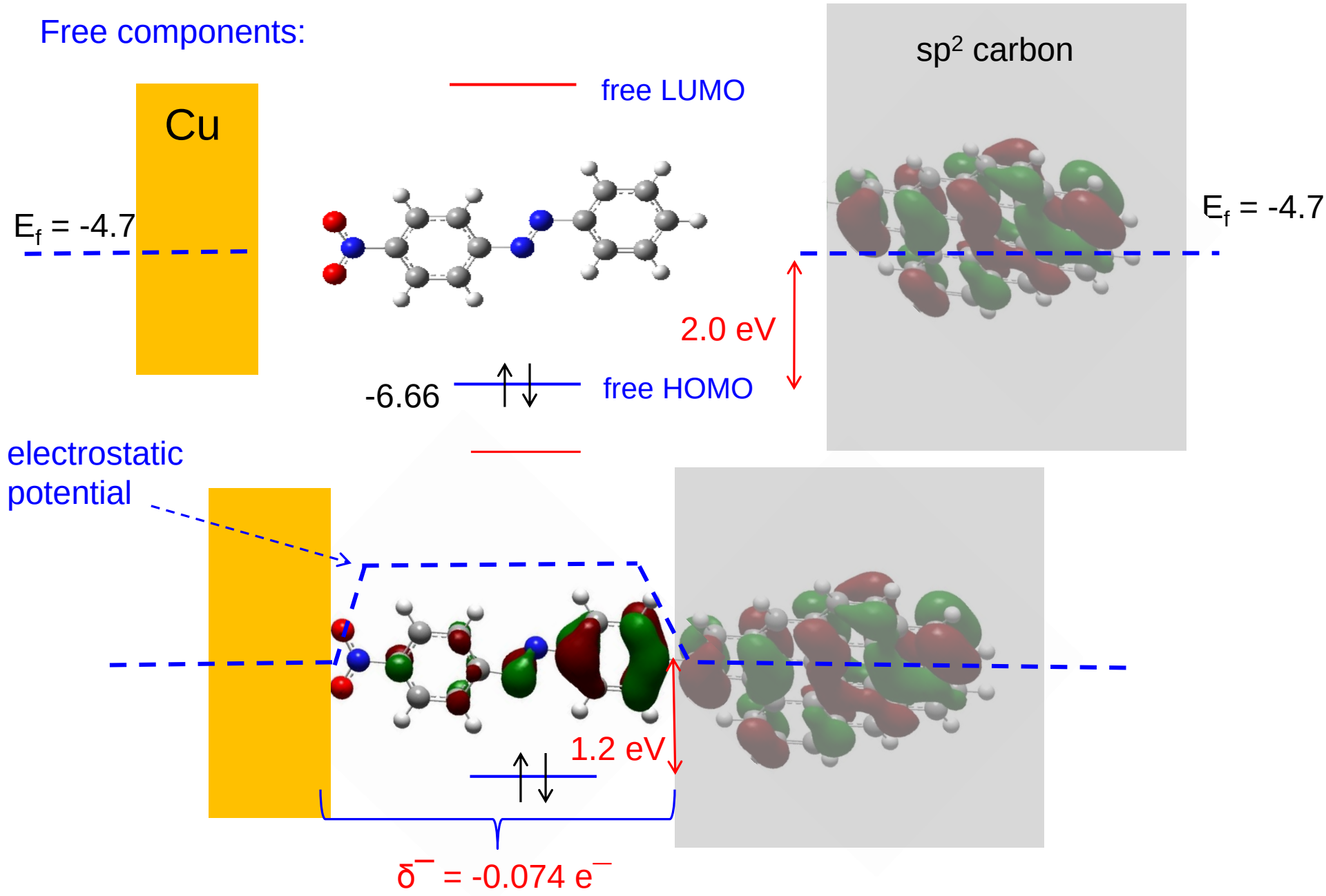


*Gaussian ‘03, B3LYP/6-31G(d)

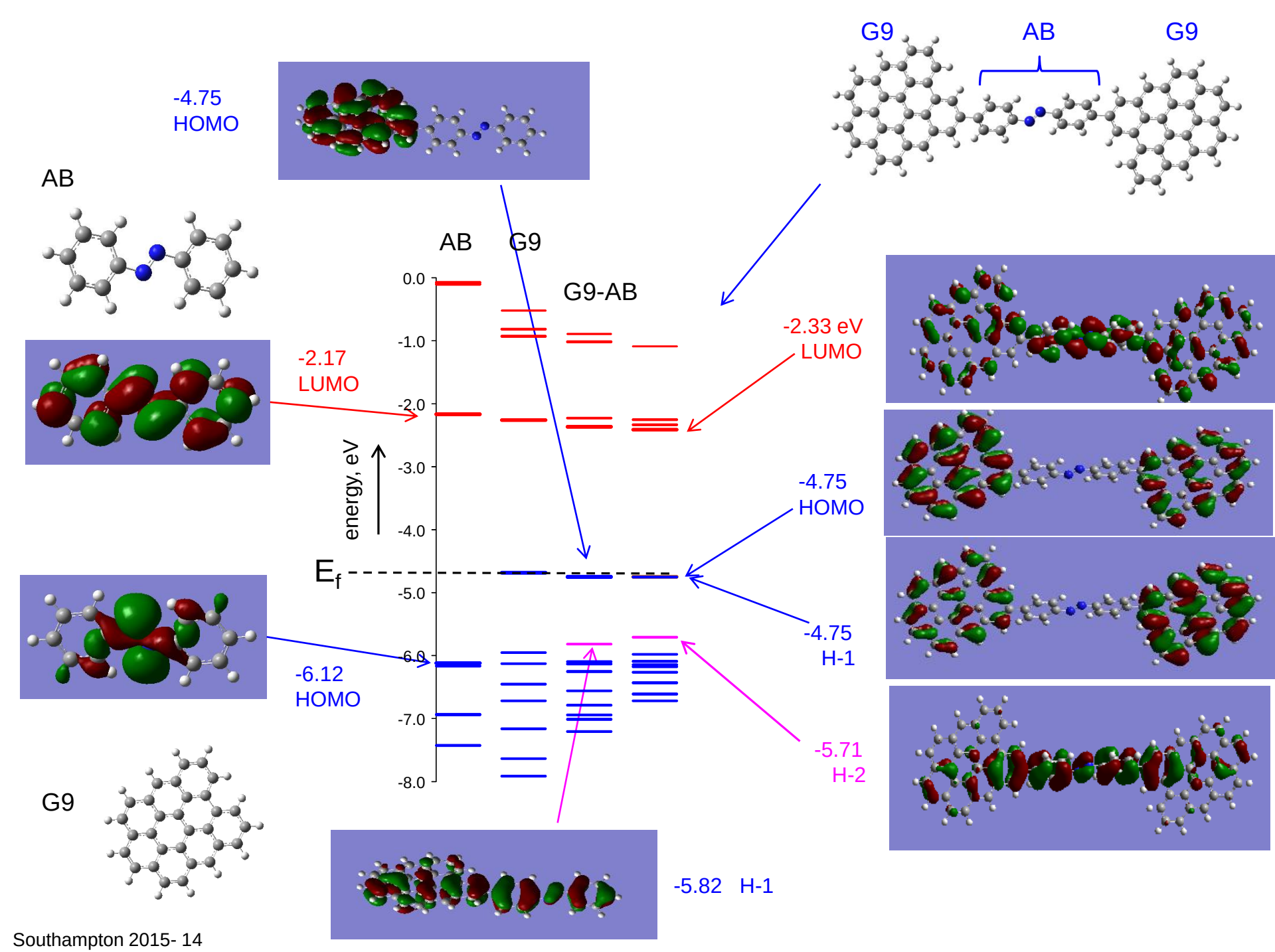
90

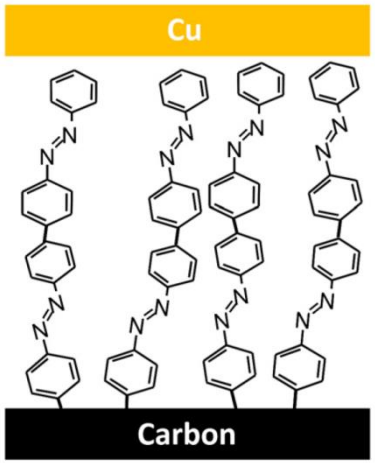


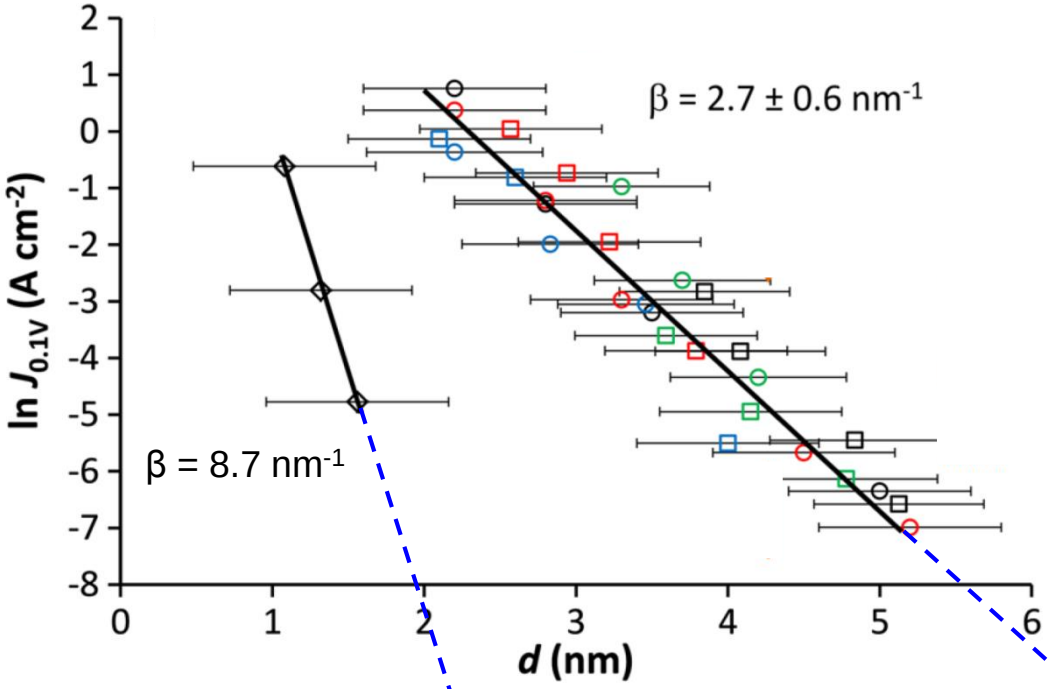
Free components:



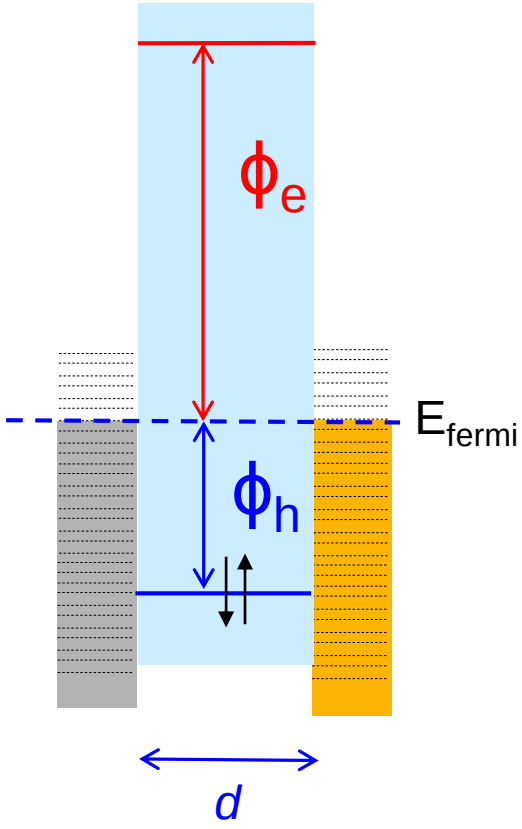
"vacuum level shift": Hwang, J.; Wan, A.; Kahn, A.; *Materials Science and Engineering: R: Reports* ***2009,*** *64, 1-31*
Vilan, A.; Yaffe, O.; Biller, A.; Salomon, A.; Kahn, A.; Cahen, D.; *Adv. Mater.* ***2010, 22, 140-159***


G9
AB
G9
-4.75
HOMO
AB
AB
G9
G9-AB
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
energy, eV
-2.17
LUMO
-2.33 eV
LUMO
-4.75
HOMO
E_f
-4.75
H-1
-6.12
HOMO
-5.71
H-2
G9
-5.82 H-1





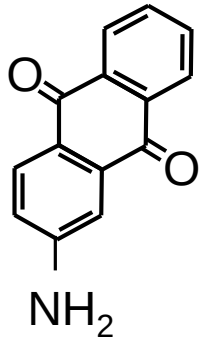
what if ϕ_h (or ϕ_e) approach zero?



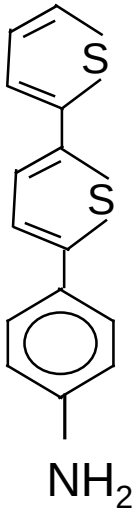
what happens beyond tunnelling?

some different molecules,
and thicker junctions:

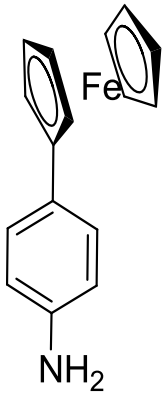
2-AQ (3-11 nm)



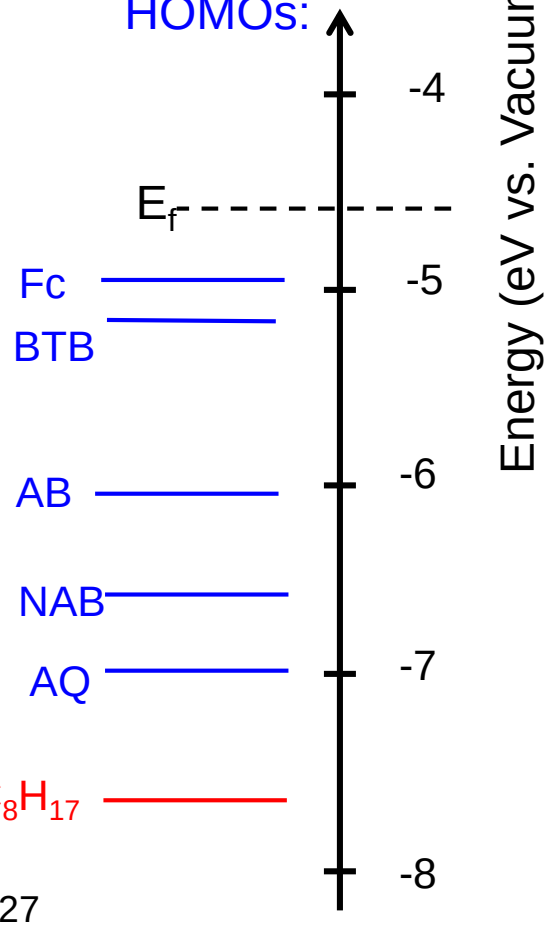
BTB (4-22 nm)*



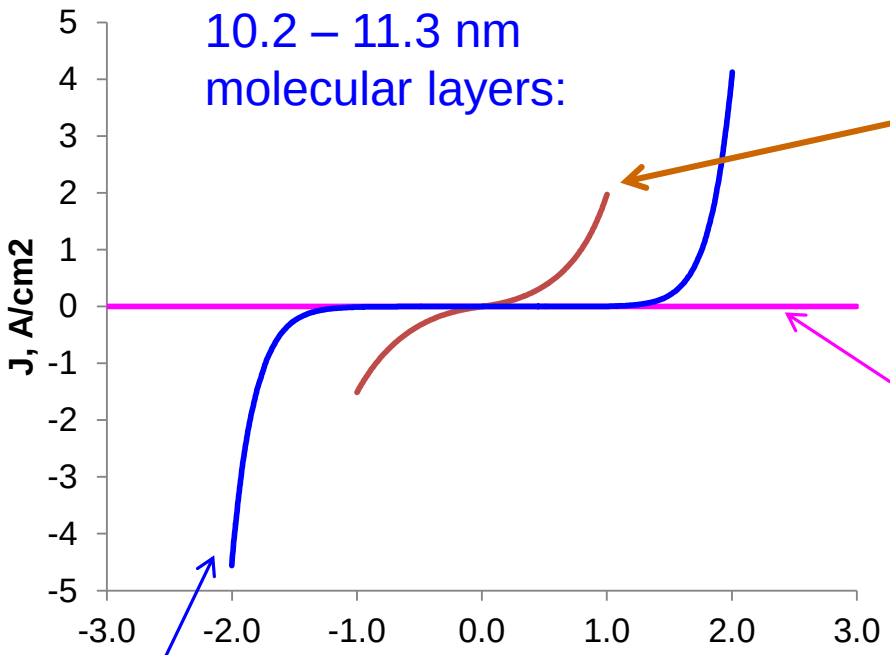
Fc-phen (5-25 nm)

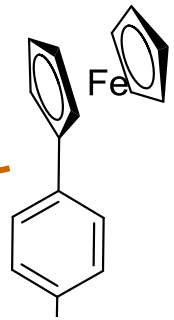


Free molecule
HOMOs:

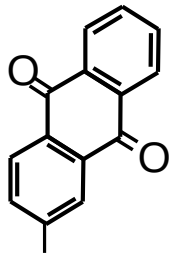


* Lacroix, et al. *J. Am. Chem. Soc.* **2009**, *131*, 14920-14927

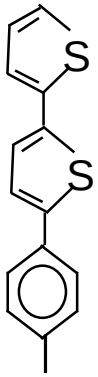




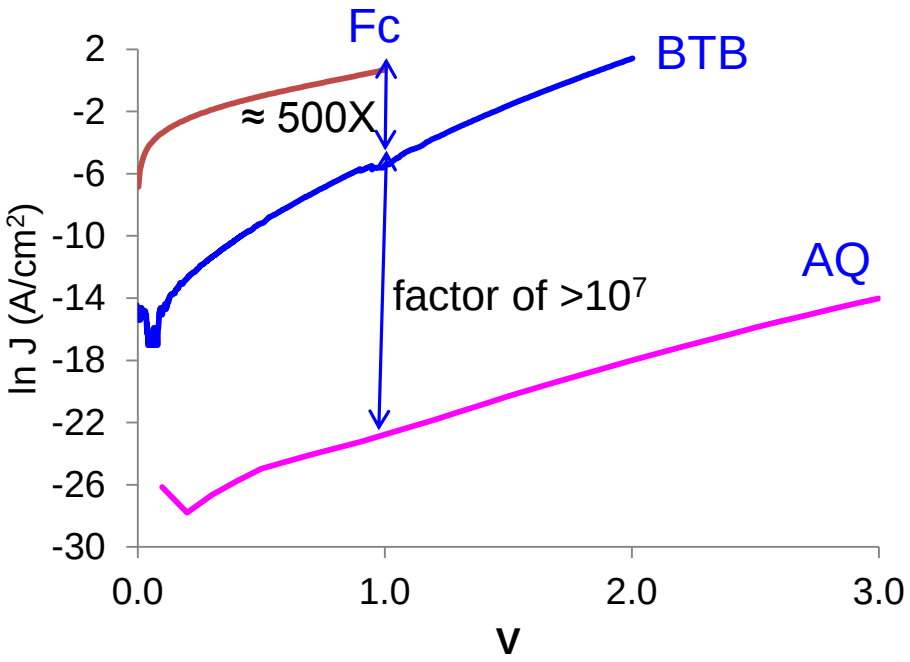
(11.3 nm)

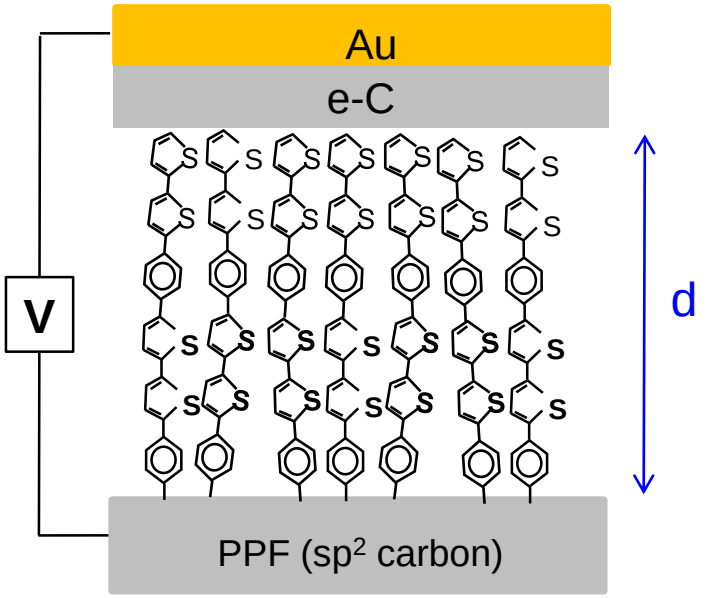


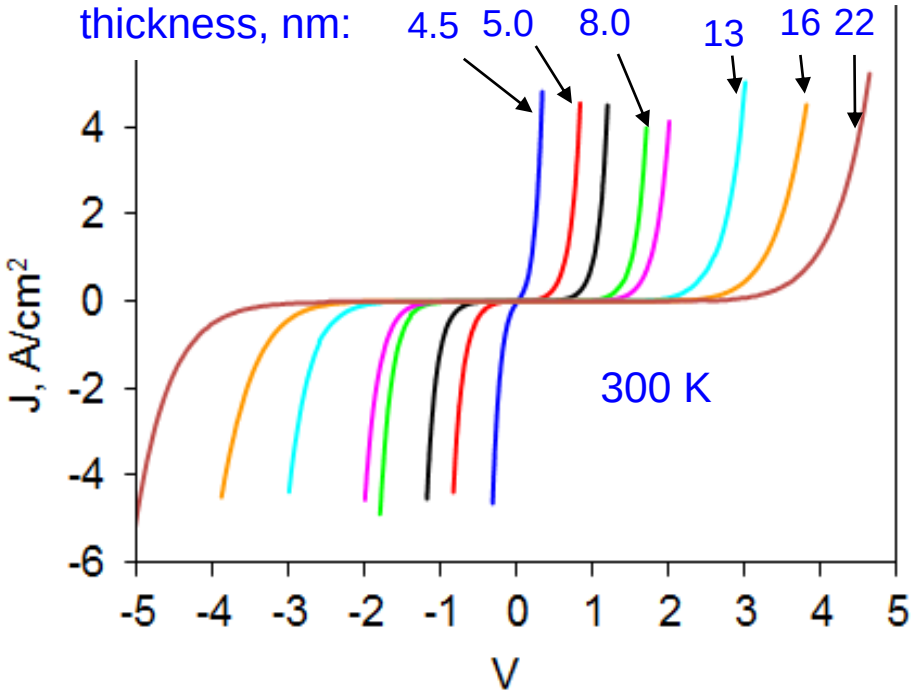
(10.2 nm)

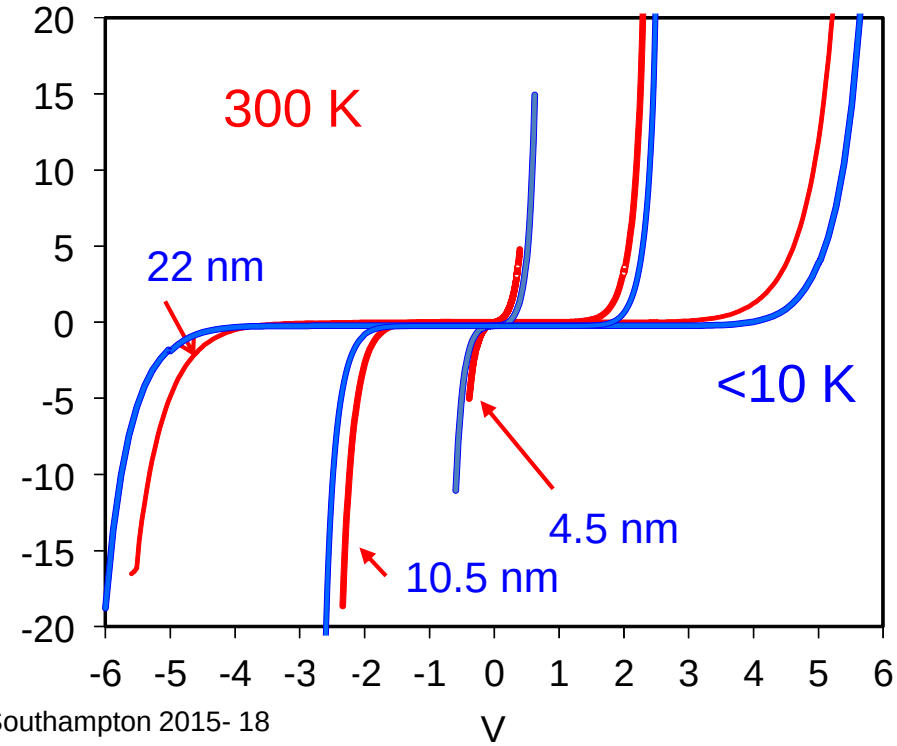


(10.5 nm)



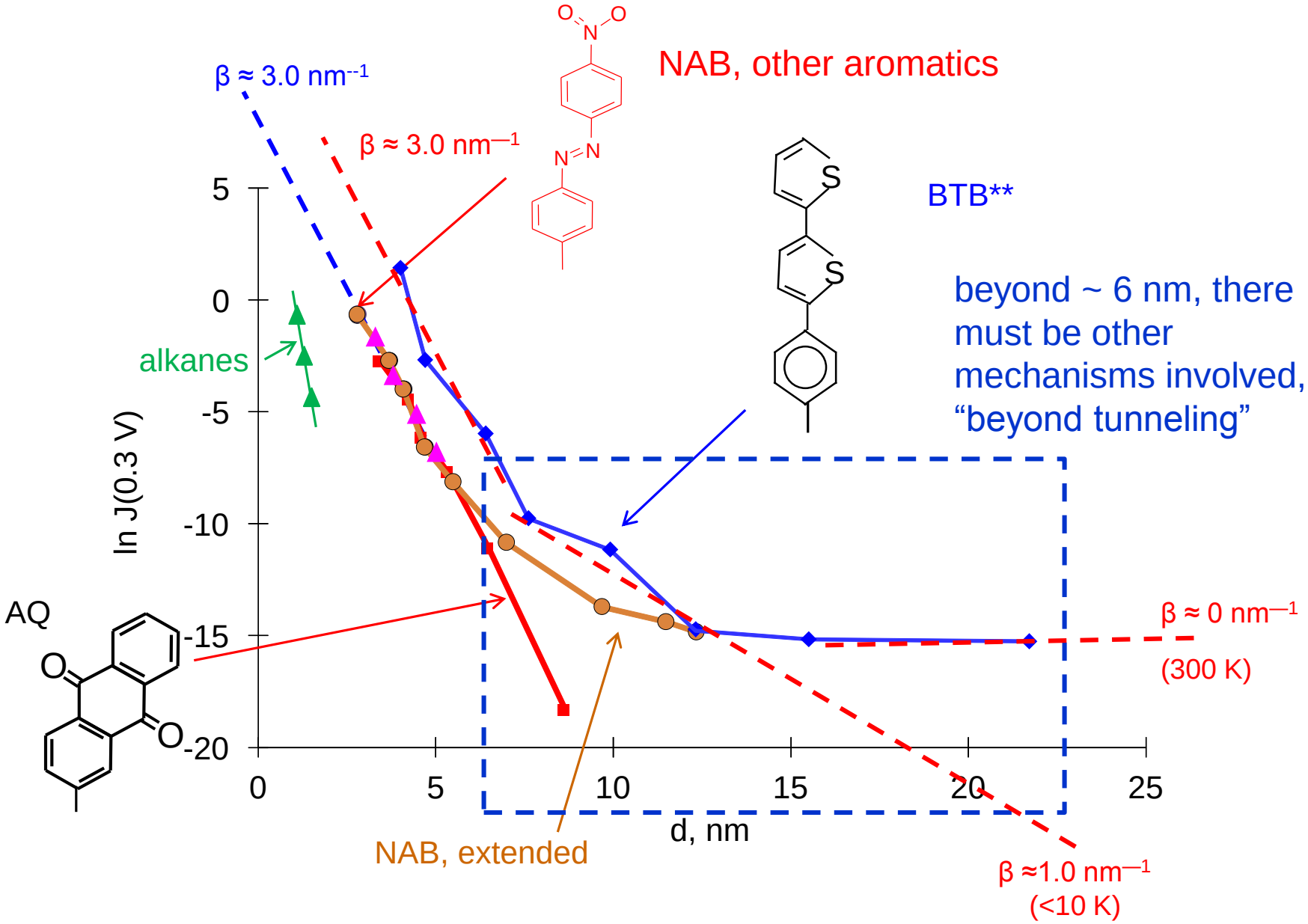






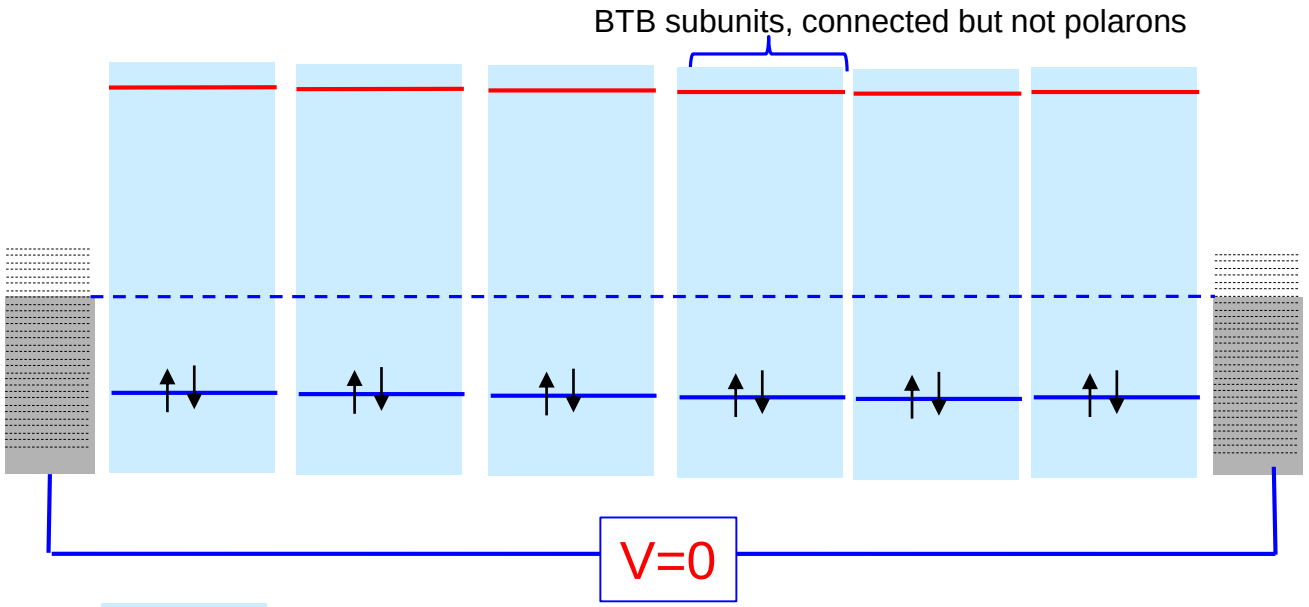
weak temperature dependence

not “hopping” by redox exchange



** Yan, Bergren, McCreery, Della Rocca, Martin, Lafarge, Lacroix, *PNAS* **2013**, *110*, 5326

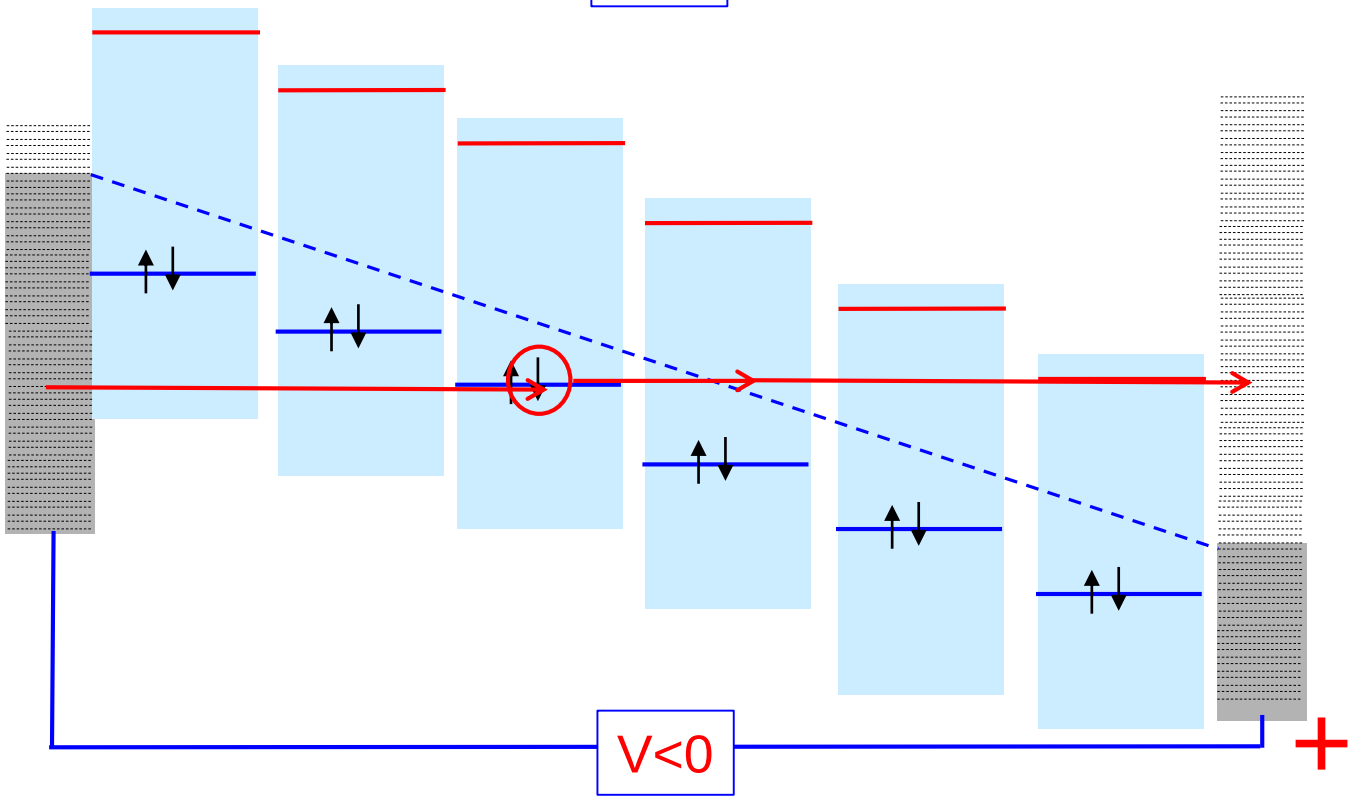
Suppose the HOMO is not too far below the contact Fermi level:

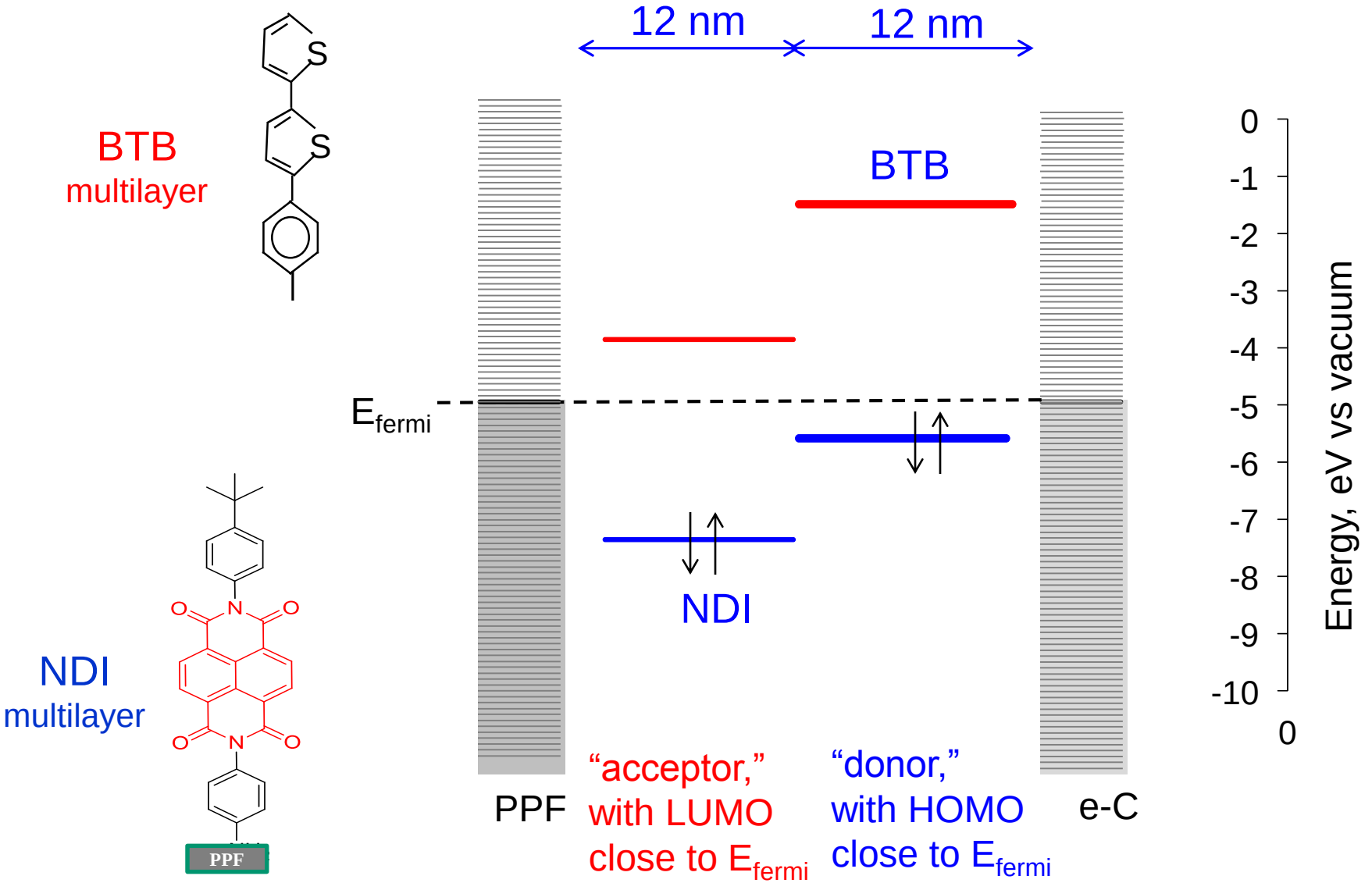


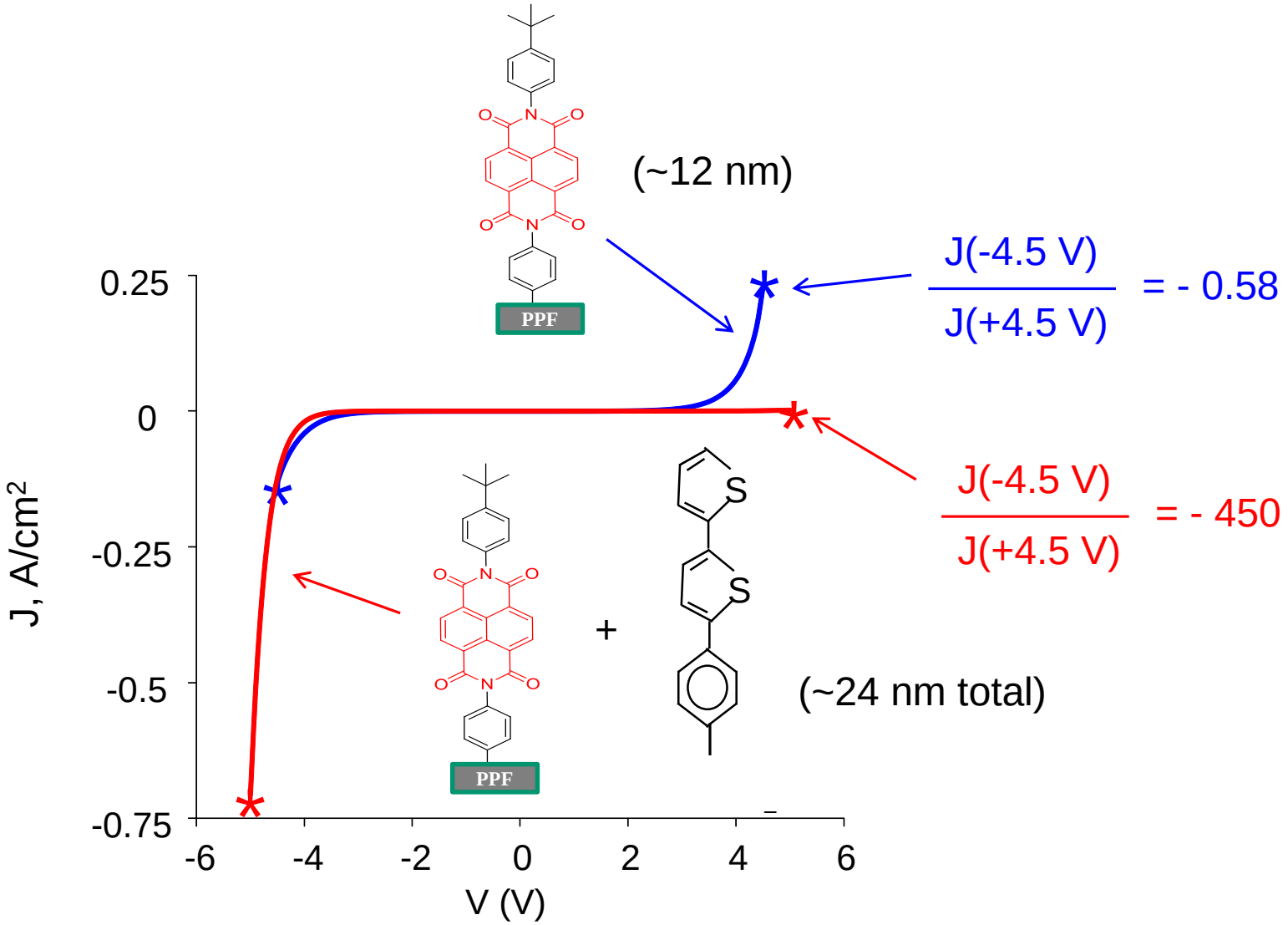
"Molecular field ionization"

Note: field ionization in gas phase occurs at ~10^7 V/cm; our field is ~10^6 V/cm, but barrier is much smaller

Like "oxidation" except reorganization occurs *after* ionization




BTB
multilayer
NDI
multilayer
PPF
12 nm
12 nm
BTB
NDI
E_fermi
PPF
e-C
"acceptor," with LUMO close to E_fermi
"donor," with HOMO close to E_fermi
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
0
Energy, eV vs vacuum

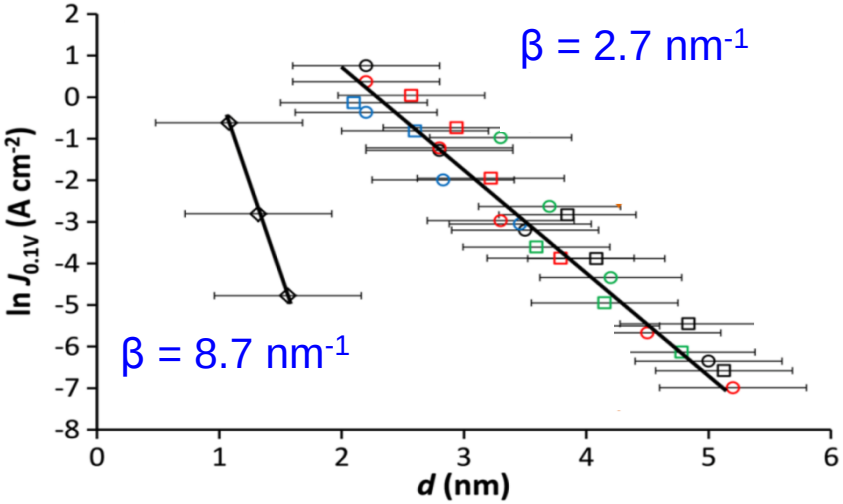


note: 12 nm of thickness should decrease current by a factor of 10^{-16} for $\beta = 3\ nm^{-1}$

certainly not tunneling !

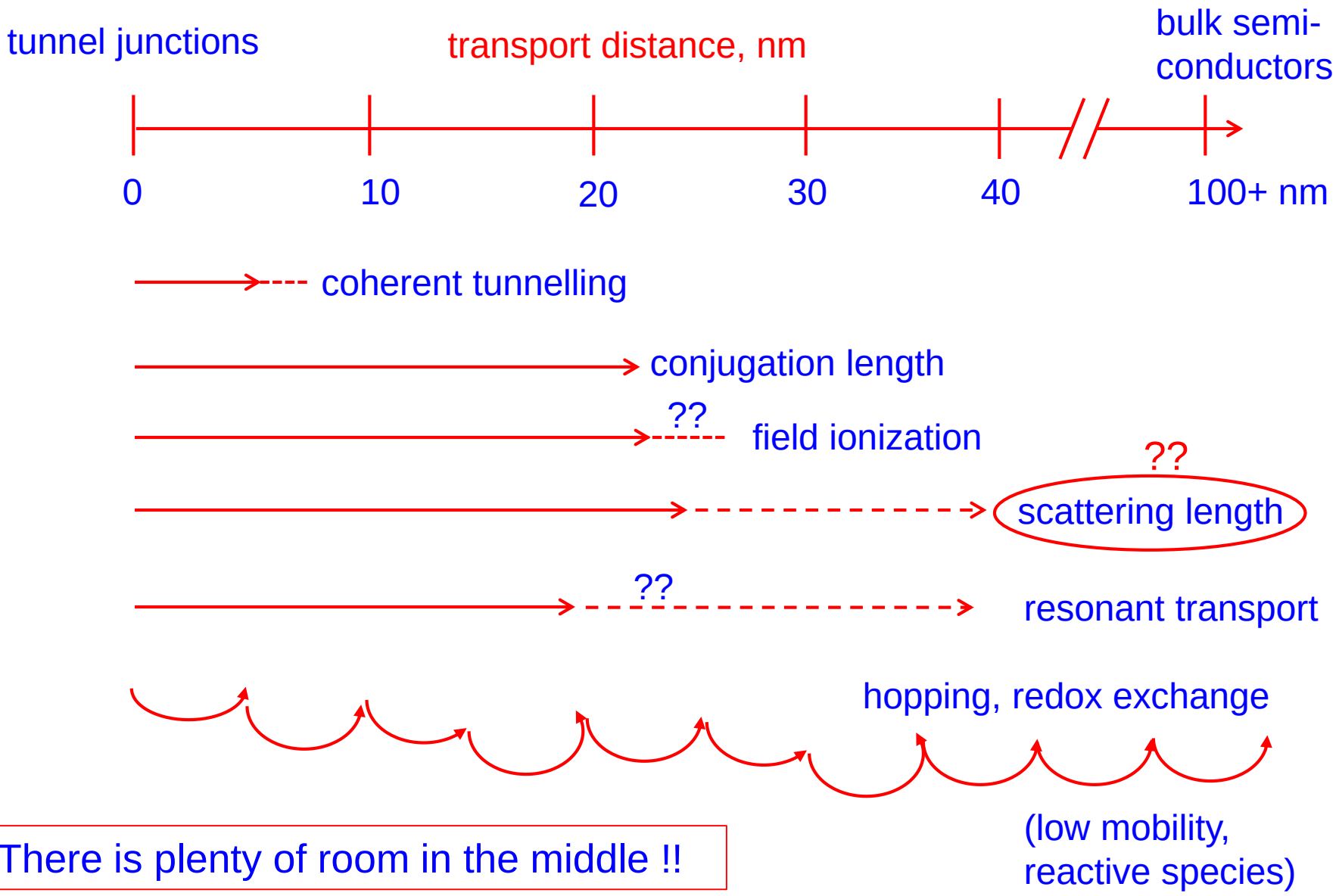
Richard Feynman, 1959

"There's Plenty of Room at the Bottom"



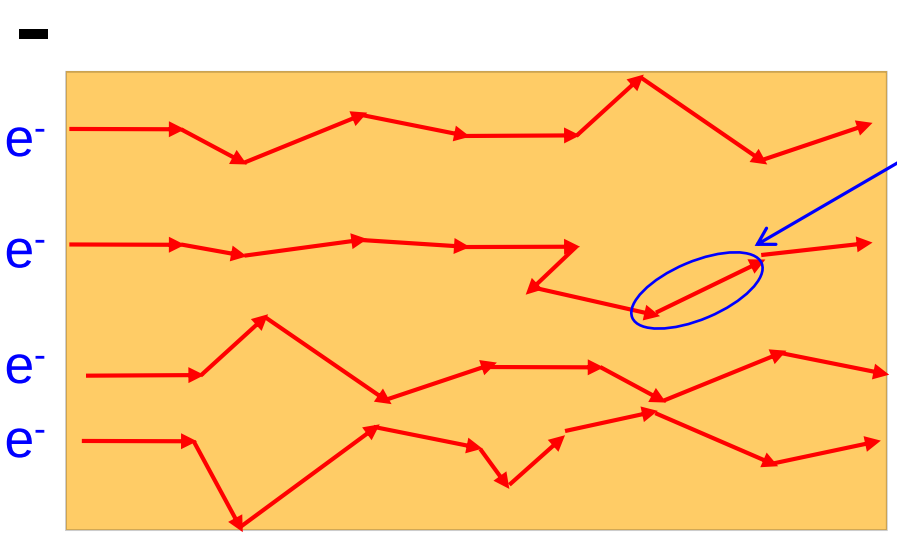
"the bottom" for aromatic molecular junctions ?

"barrier electronics" and not much control over barrier height



Phys. Chem. Chem. Phys., 2013,**15**, 1065

Electronic conduction in metals, carbon, and semiconductors is “diffusive”:



scattering length, or “mean free path (mfp)”

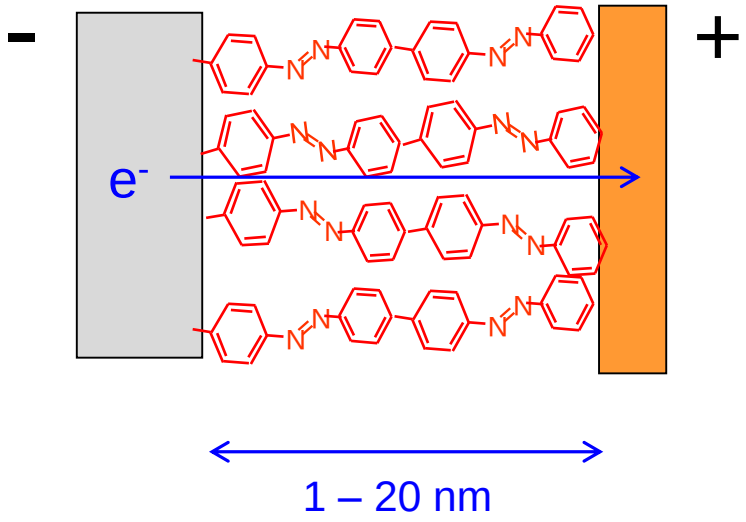
metals: 10 - 40+ nm
insulators: < 1 nm

scattering is the origin of:

1. Ohm’s law and resistance
2. low mobility
3. resistive heating

if transport distance is < mean free path, transport is “ballistic”

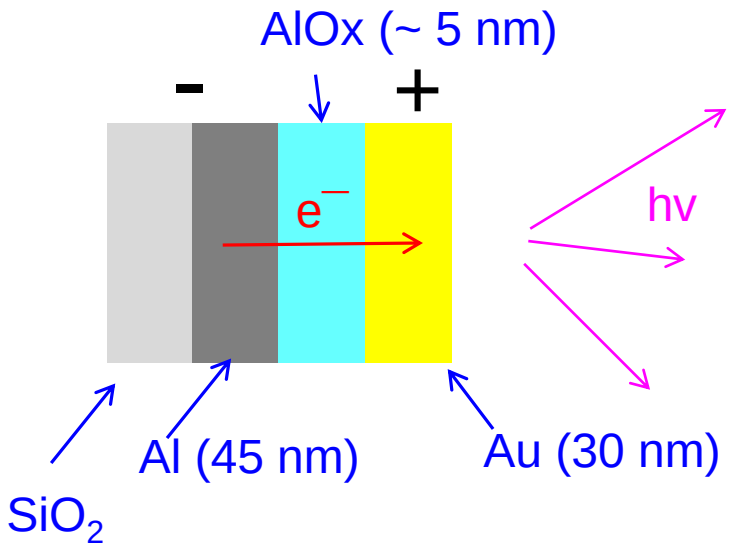
how about molecular junctions?

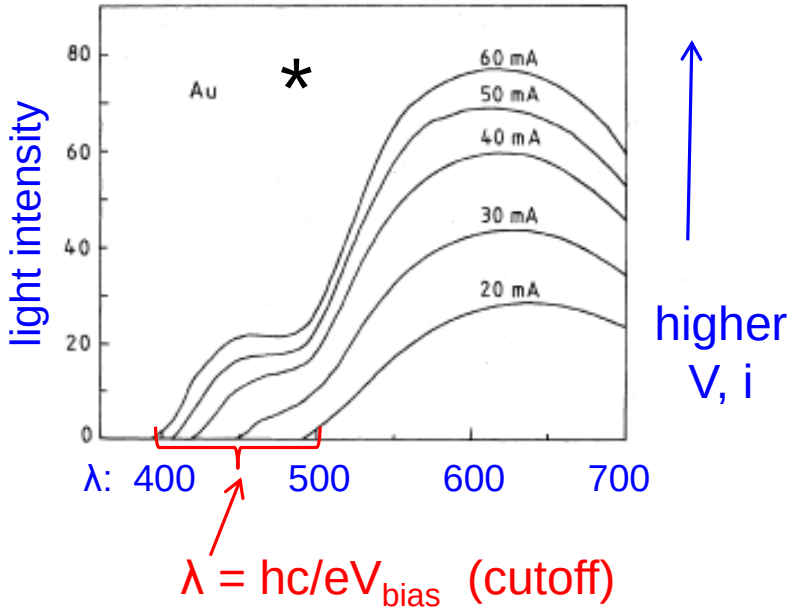


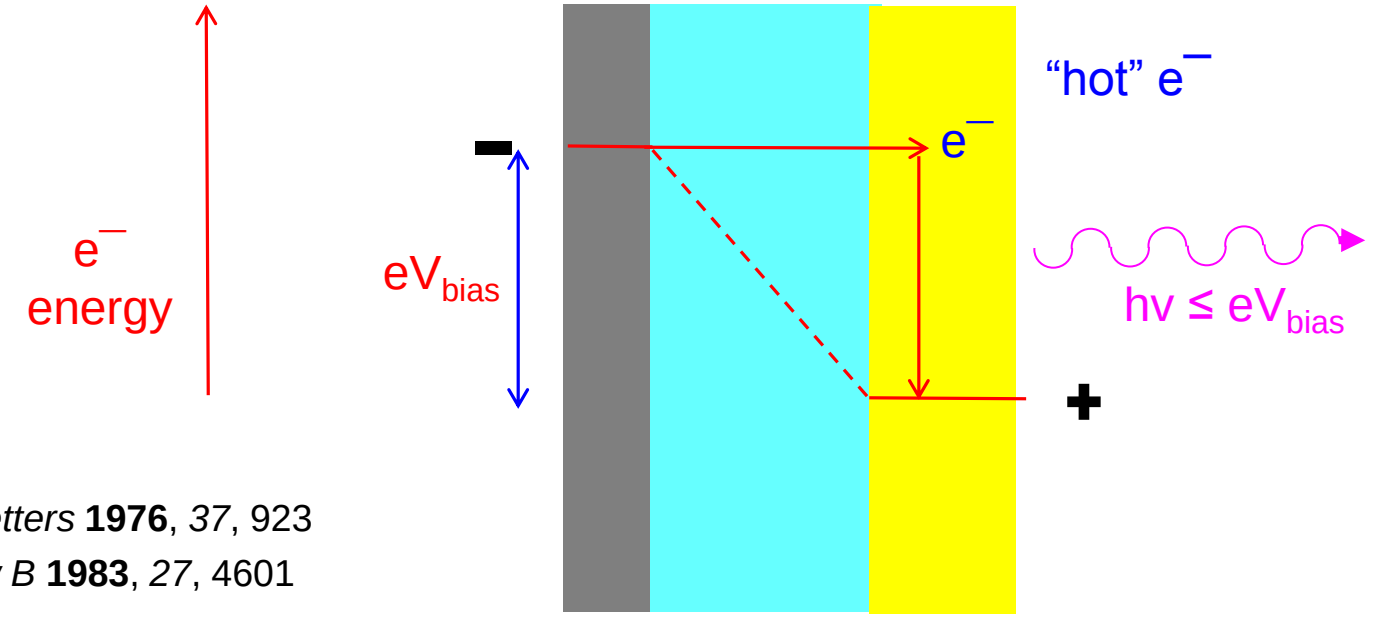
is transport ballistic?

if it is, so what?

Light emitting tunnel junction:

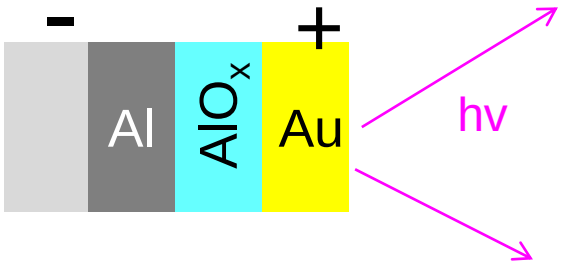


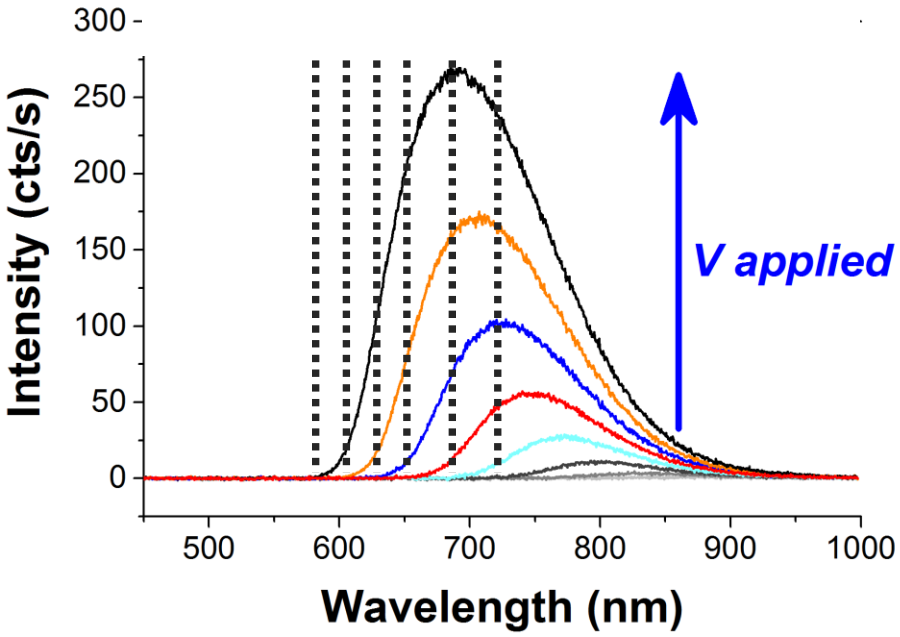


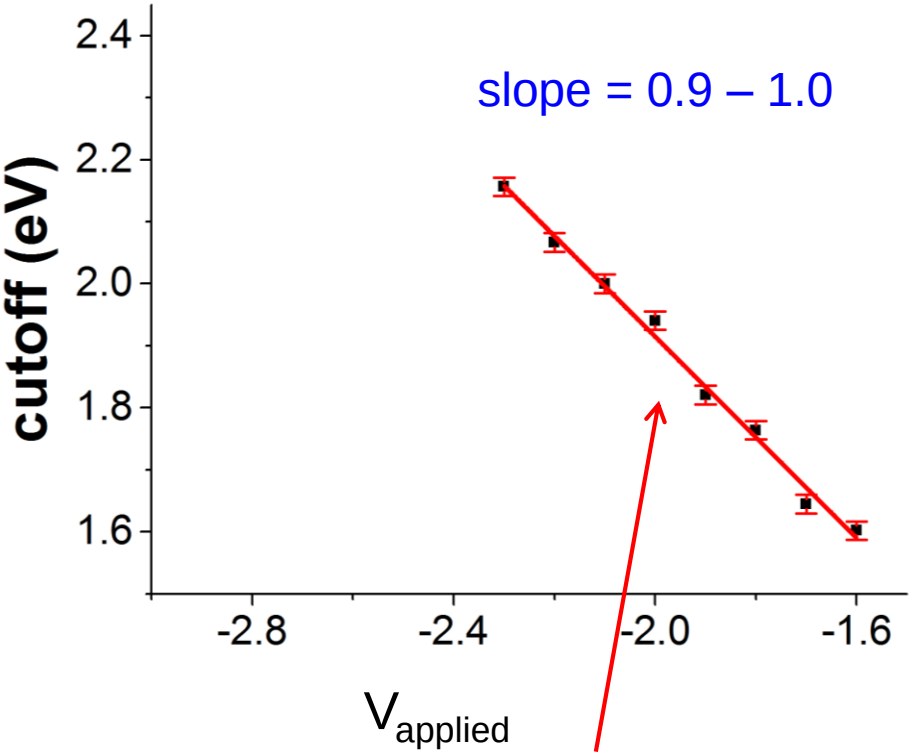


e.g. *Physical Review Letters* **1976**, *37*, 923

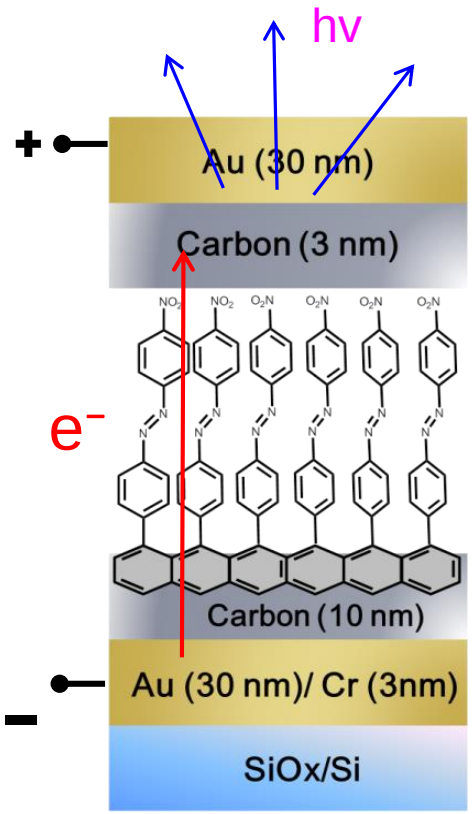
* *Physical Review B* **1983**, *27*, 4601

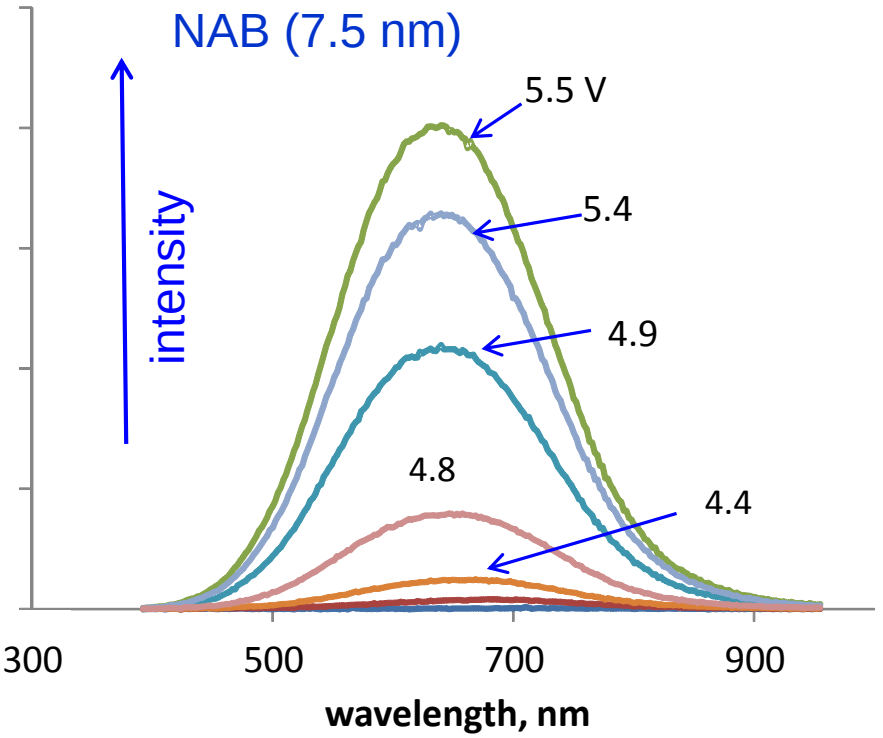




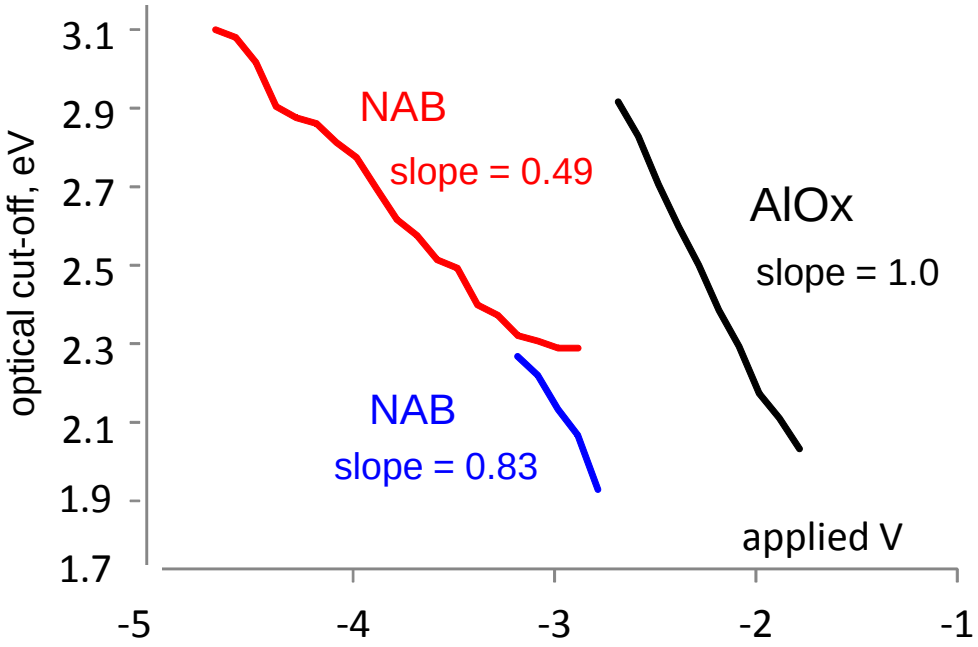


- Maximum energy of photons is a linear function of $V_{applied}$, i.e. $hv_{max} = eV_{applied}$
- Emission is stable for hours (18h of AC bias)
- AC bias allows continuous emission without degradation (useful for molecular junctions)



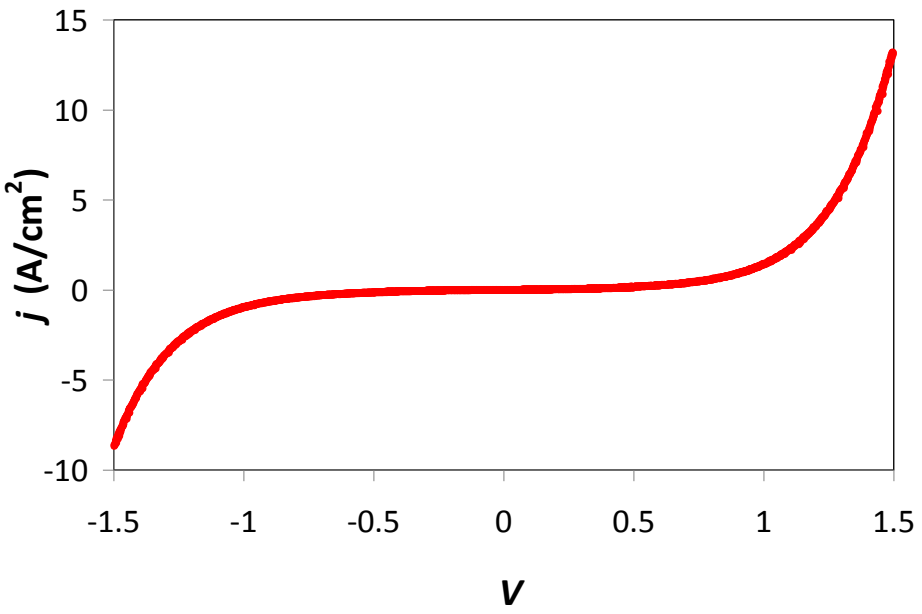


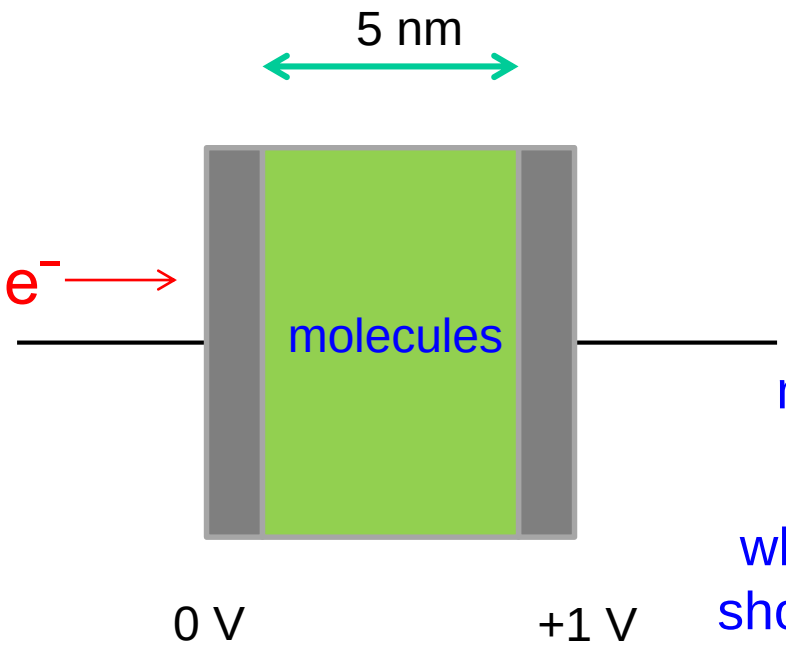
- Intensity and energy cutoff scale with $V_{applied}$, similar to AlOx junctions
- Energetics of light emission are consistent with at least elastic transport for thin (d< 5 nm) molecular layers.



if MJ transport is ballistic, so what?

Something special about ballistic transport:





electron transit time ≈ 15 fsec
(15 x 10^{-15} seconds)

maximum frequency > 10,000 GHz

whatever we can do with ballistic junctions should be VERY fast, with little resistance or heat generation in molecular layer

a little history about audio distortion:

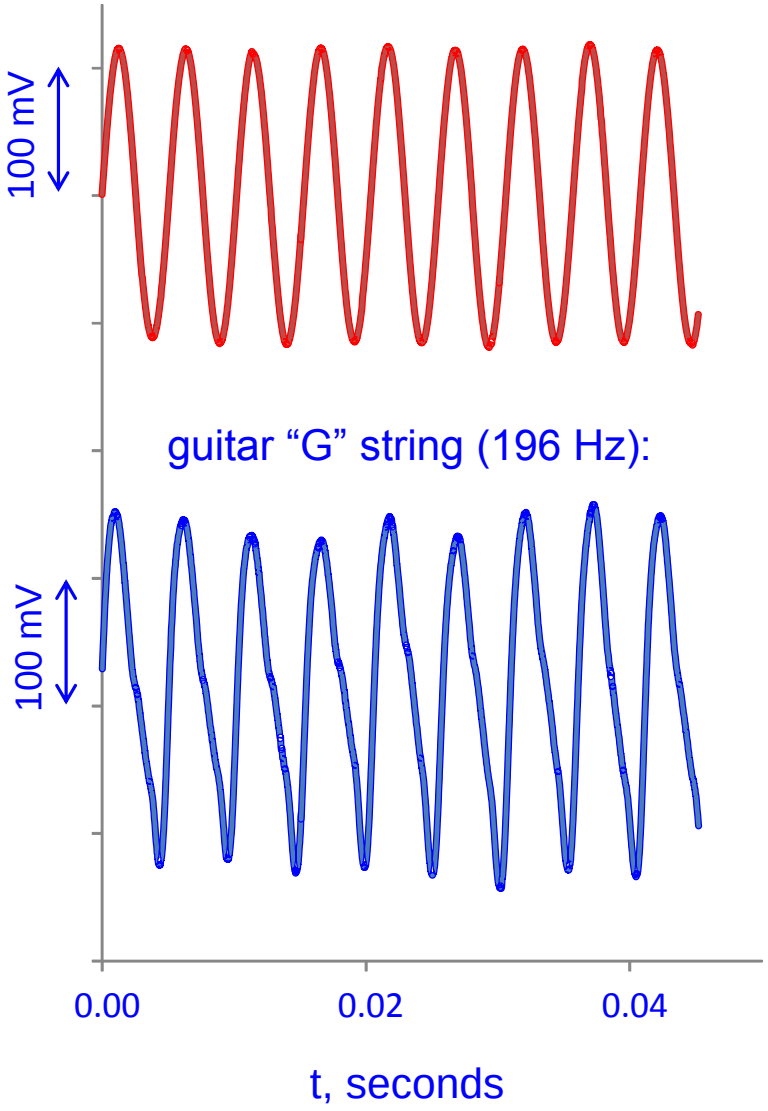
Victoria “5E3”
guitar amplifier

designed by Leo Fender in 1954

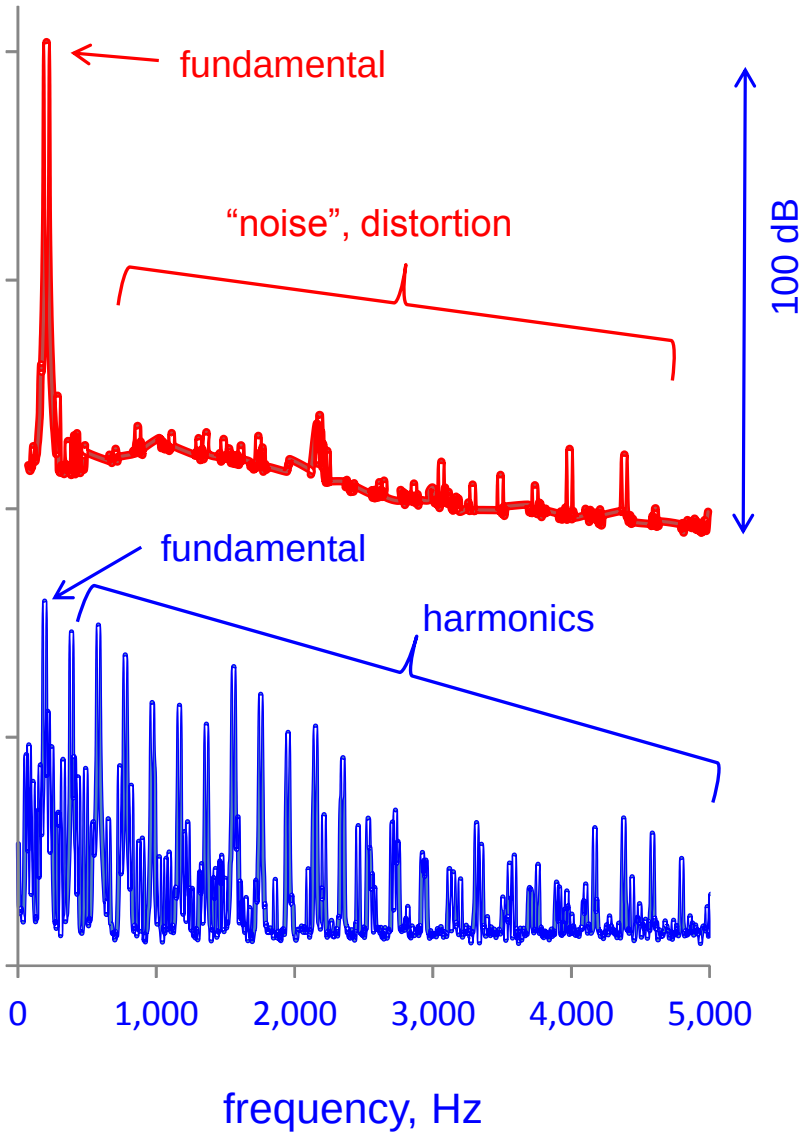
12AX7 preamp tubes (ca. 1946)
6V6GT power tubes (ca. 1940)

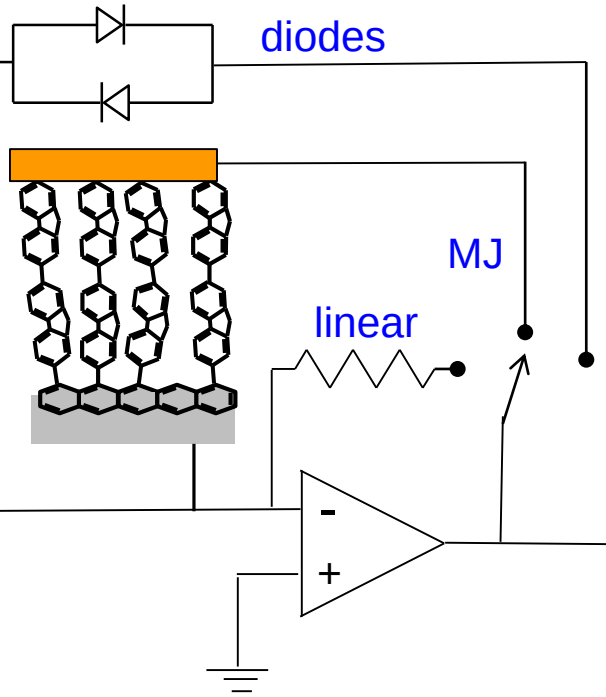
This one was built and
sold in **2007** ($2095);
“clones” currently sold by
30 - 40 builders

196 Hz tone (from function generator):

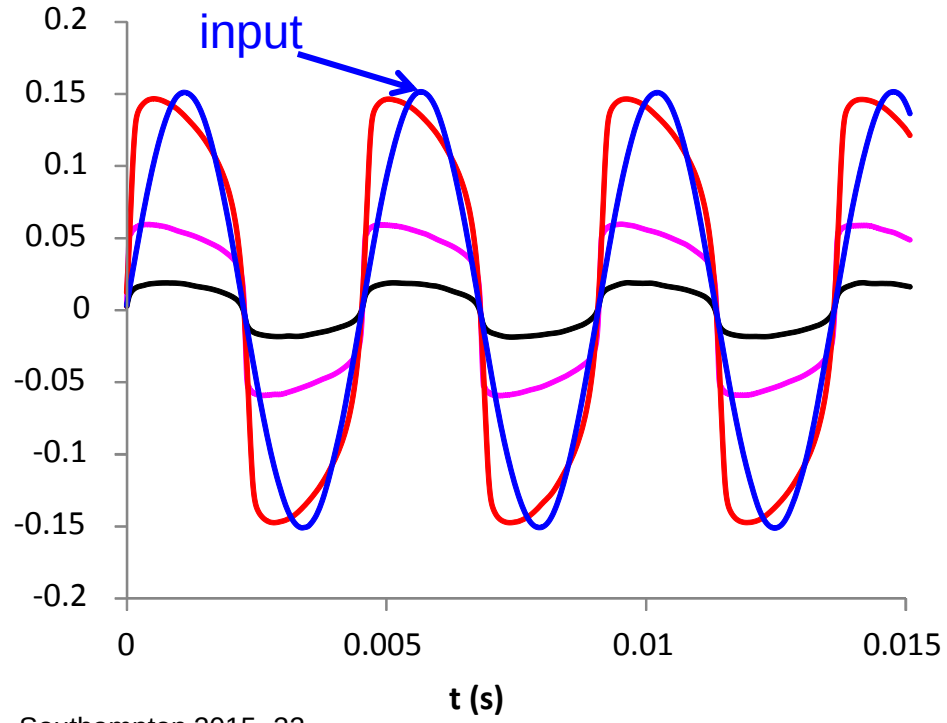


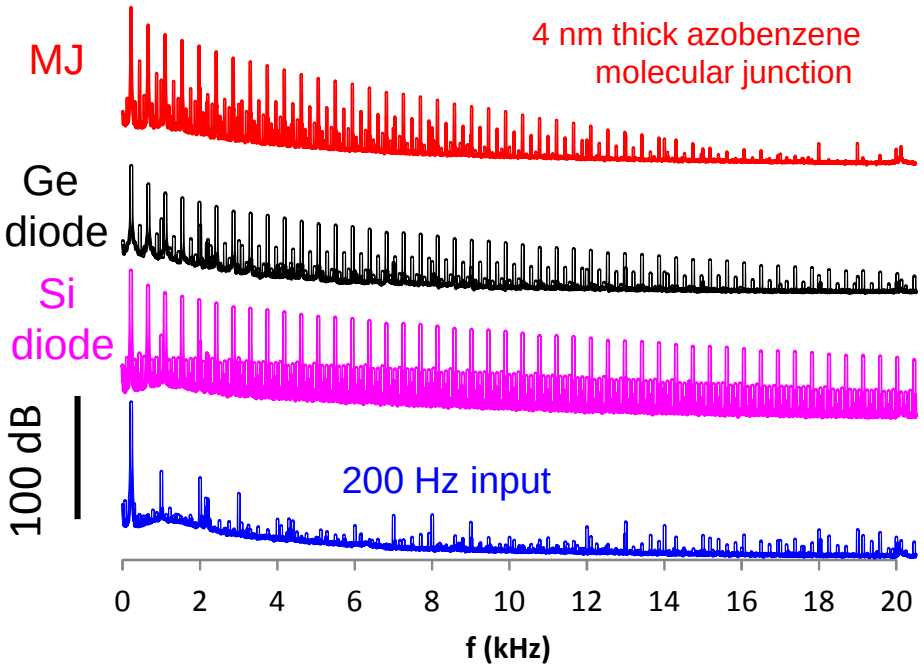
Fourier transform:

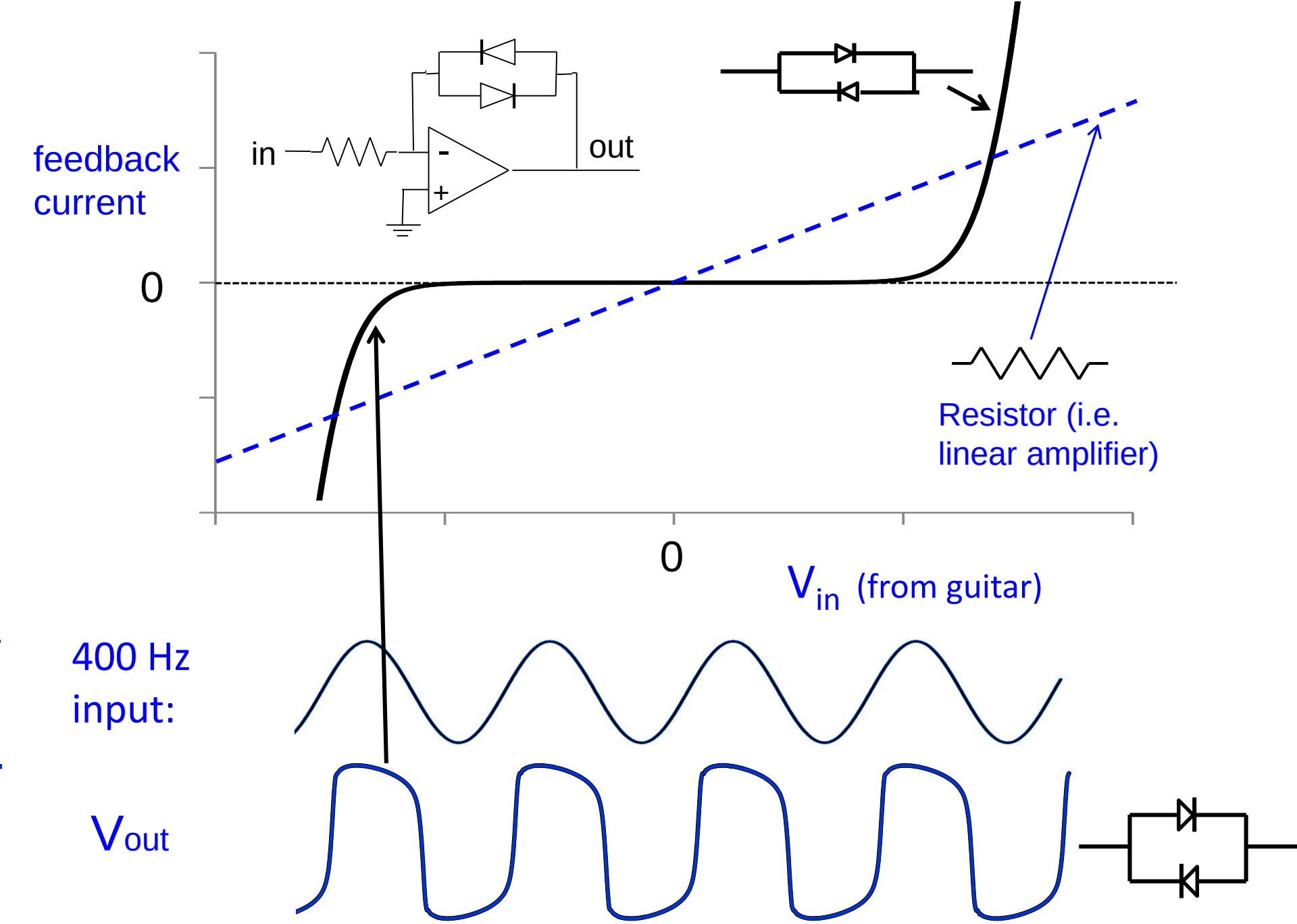


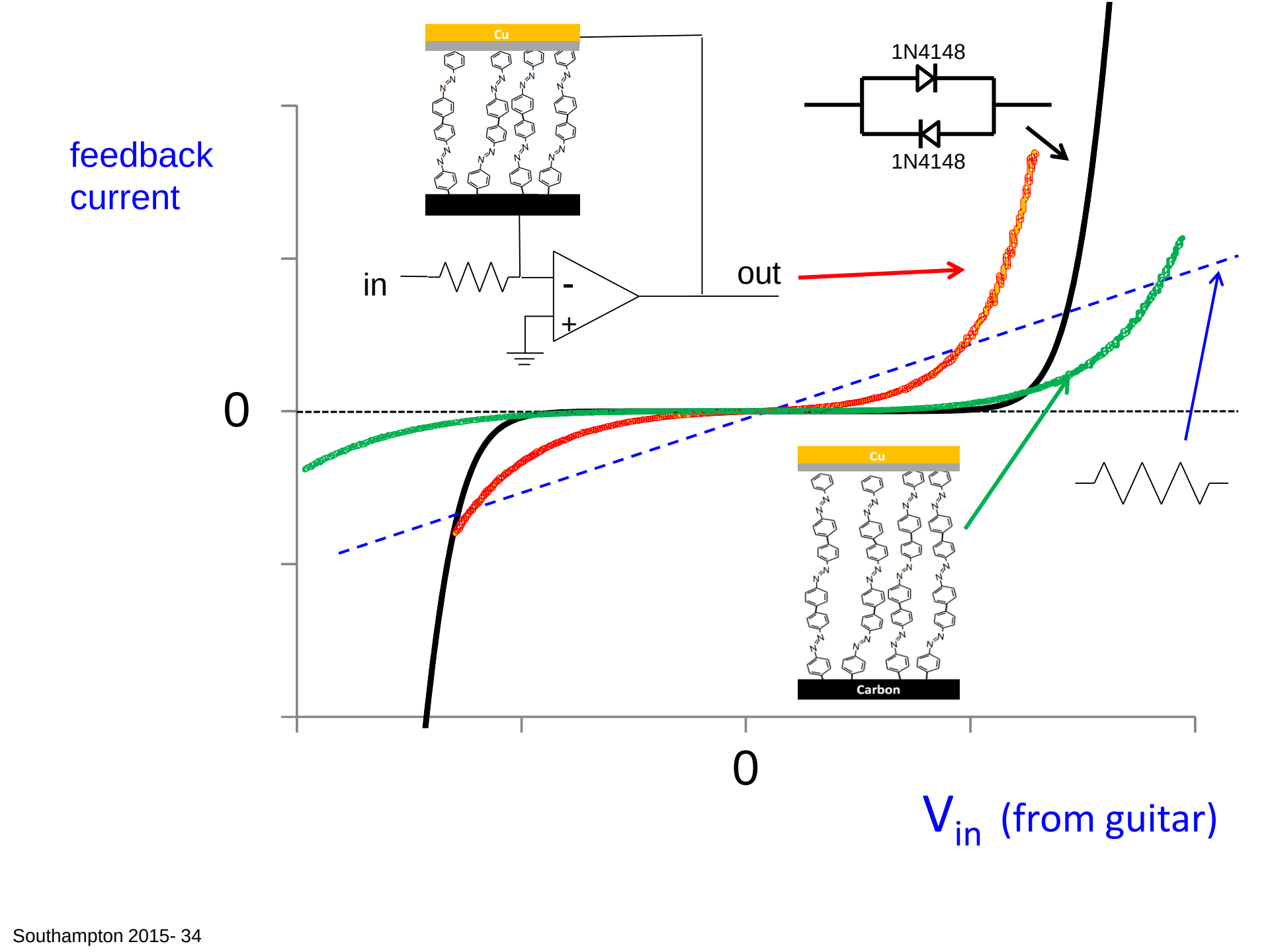


Adam Bergren

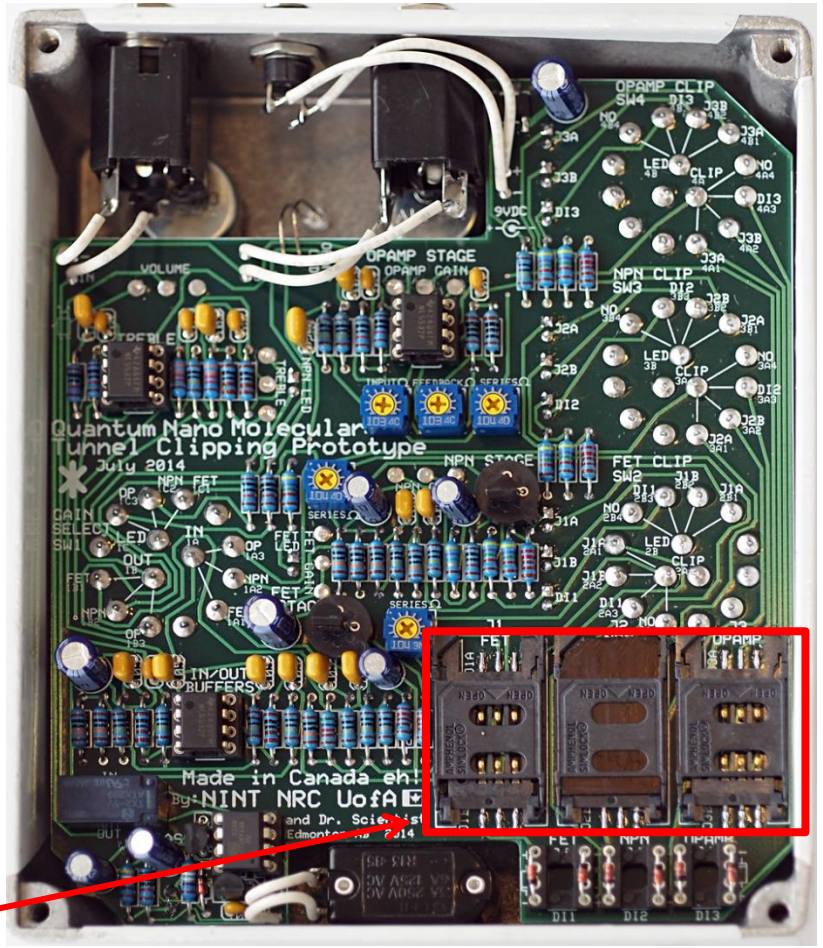


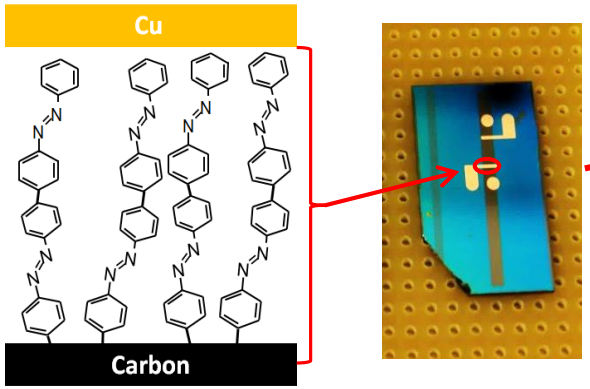



feedback current
0
in
out
-
+
Resistor (i.e. linear amplifier)
0
V_{in} (from guitar)
400 Hz input:
V_{out}


feedback
current
Cu
1N4148
1N4148
in
out
-
+
0
Cu
Carbon
0
V_{in} (from guitar)

NINT “clipping” prototye (Oct. 2014)





selects diodes,
molecular junction,
or “clean”

Nick Jaffe
(http://nickjaffe.com/
or google “NINT prototype”)

video and “hands”:
Becca Barniskis

ON when pedal active

prototype built by Dr. Scientist Sounds with three pairs of MJs (http://www.drscientist.ca/)

Comments about Youtube videos:

"This is so tone junky exciting, I can't stand it. Nano drives. NANO DRIVES!!! Dig this one, Max Planck!!....NANO DRIVES! Hot damn."

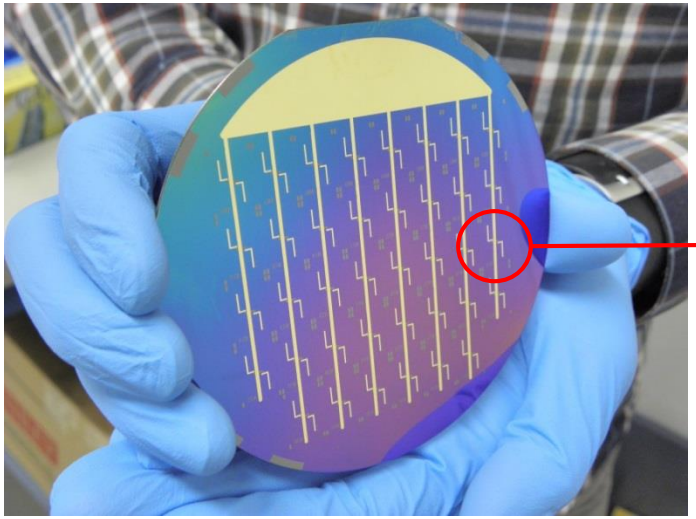
"I can see that the era of [vacuum] tubes is coming to a close."

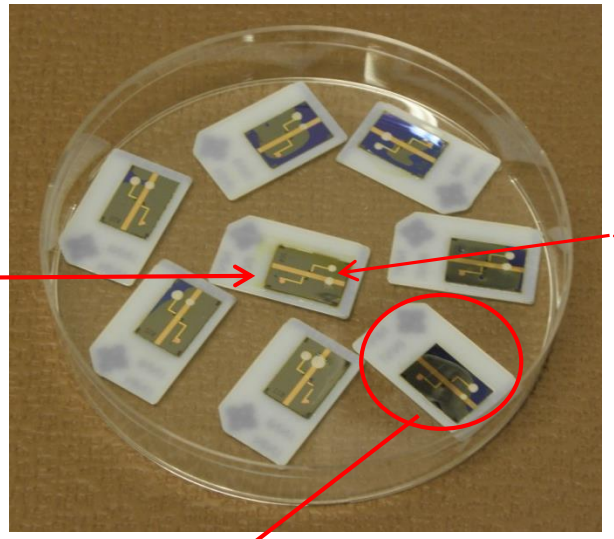
"Is this for real? For really real? If this is, and you said they used an organic in this, can I donate some of my cells? I would make an amazingly sexy fuzz pedal. I'm sure of it!"

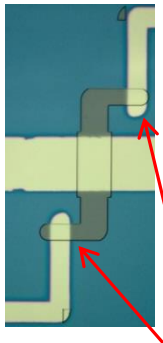
" 1 word to describe the smooth sound of these new fandangled contraptions is GRAILTONE. I don't think I could play this pedal without wearing my sex face, it sounds so good."

…for more, google "NINT prototype"

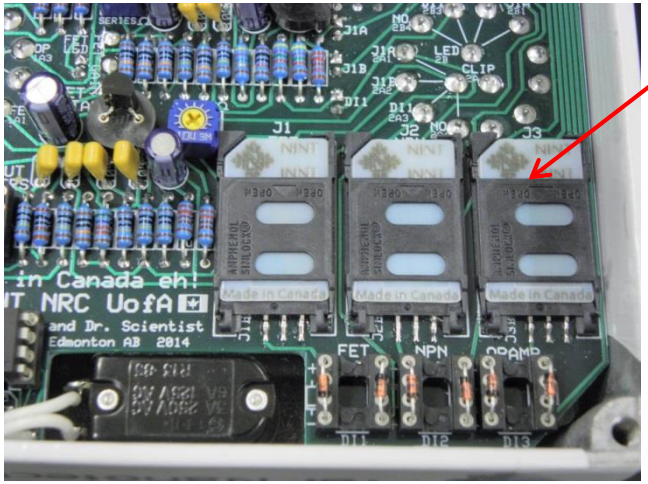
Coming soon…





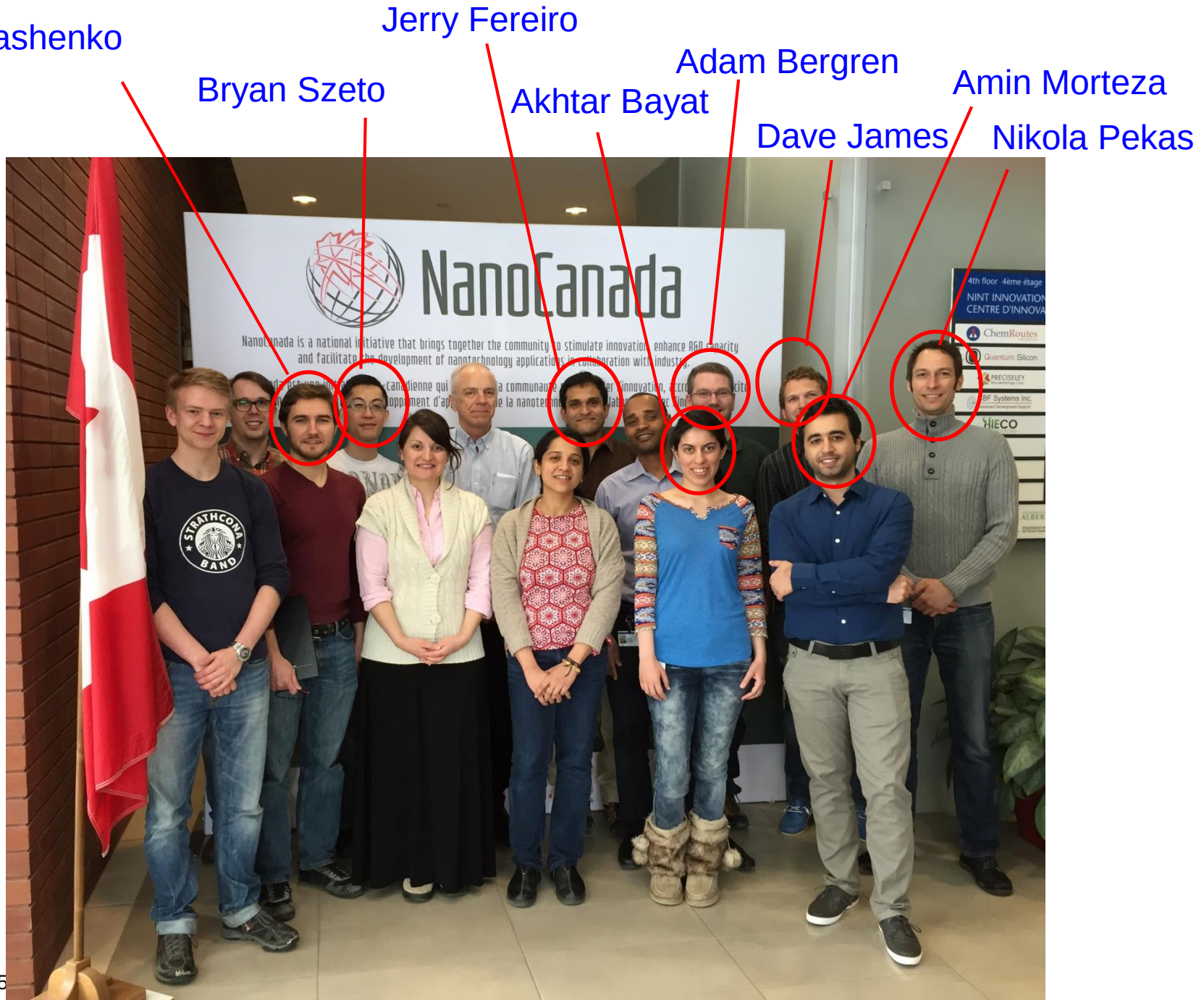


molecular junctions



quote from the web: “you can know whether it's on or how the controls are set, but not both”

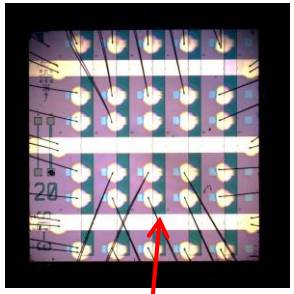
“Heisenberg Nanodrive” (www.drscientist.ca)

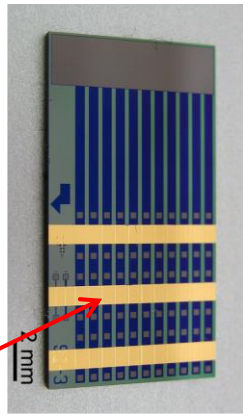

Oleksii Ivashenko
Bryan Szeto
Jerry Fereiro
Akhtar Bayat
Adam Bergren
Dave James
Amin Morteza
Nikola Pekas
NanoCanada
STRATHCONA BAND

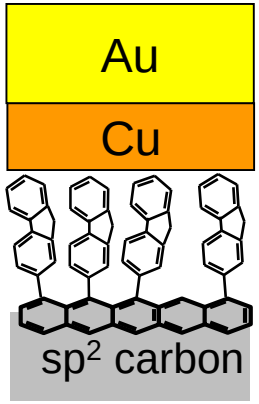
$$$:
University of Alberta
National Research Council
NSERC (Canada)
Alberta Innovates
CFI (Canada)

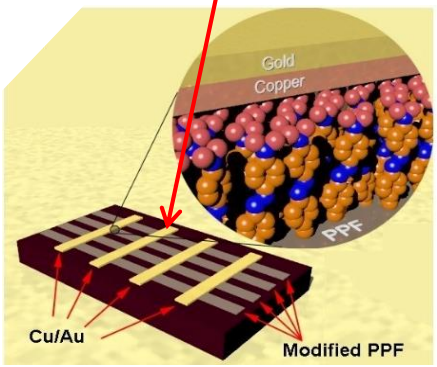
Also:
J. C. Lacroix
Pascal Martin
Maria Luisa Della Roca
Philippe Lararge
Gaelle Trippe-Allard
(U. Paris, Diderot)

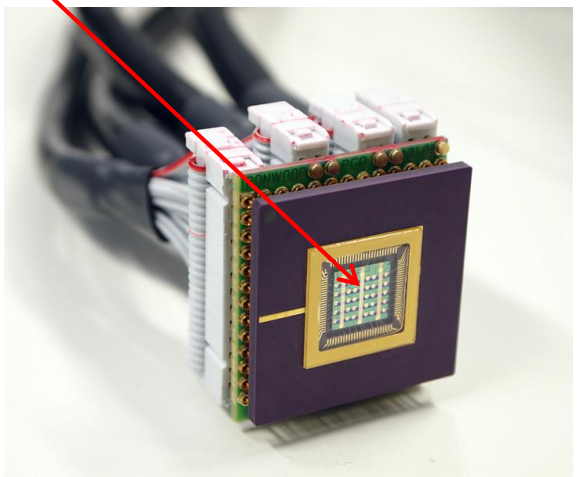
Ryan Clarke
(Dr. Scientist Sounds)

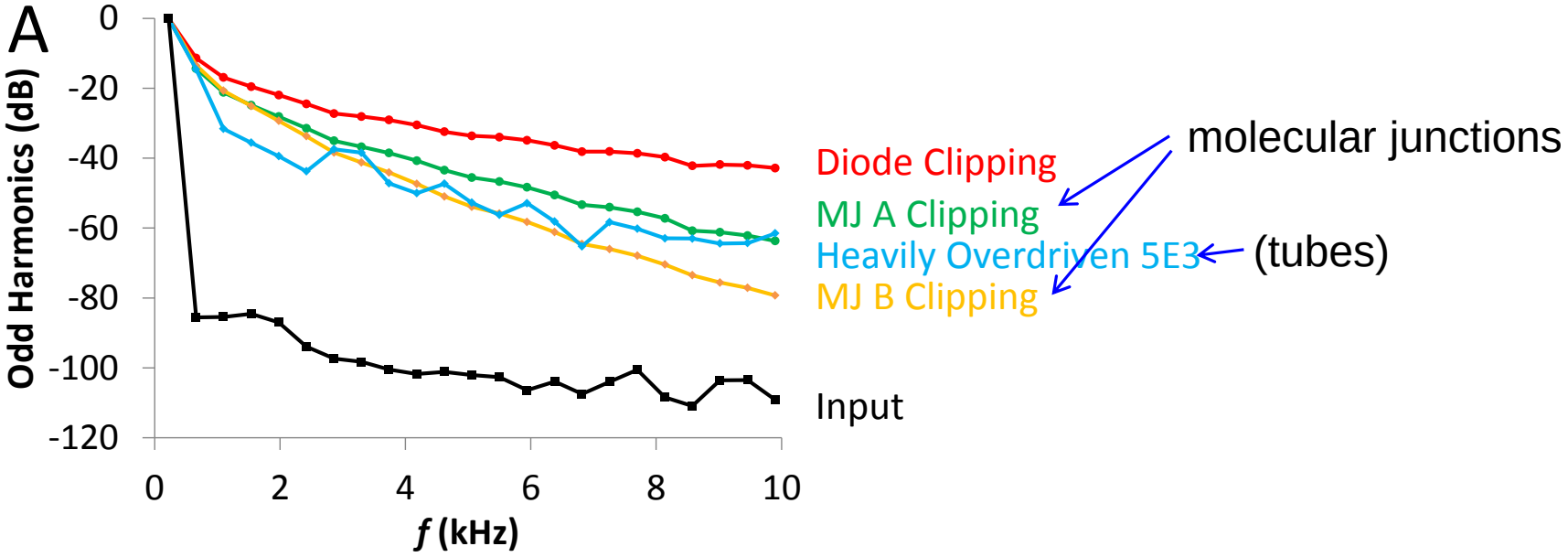


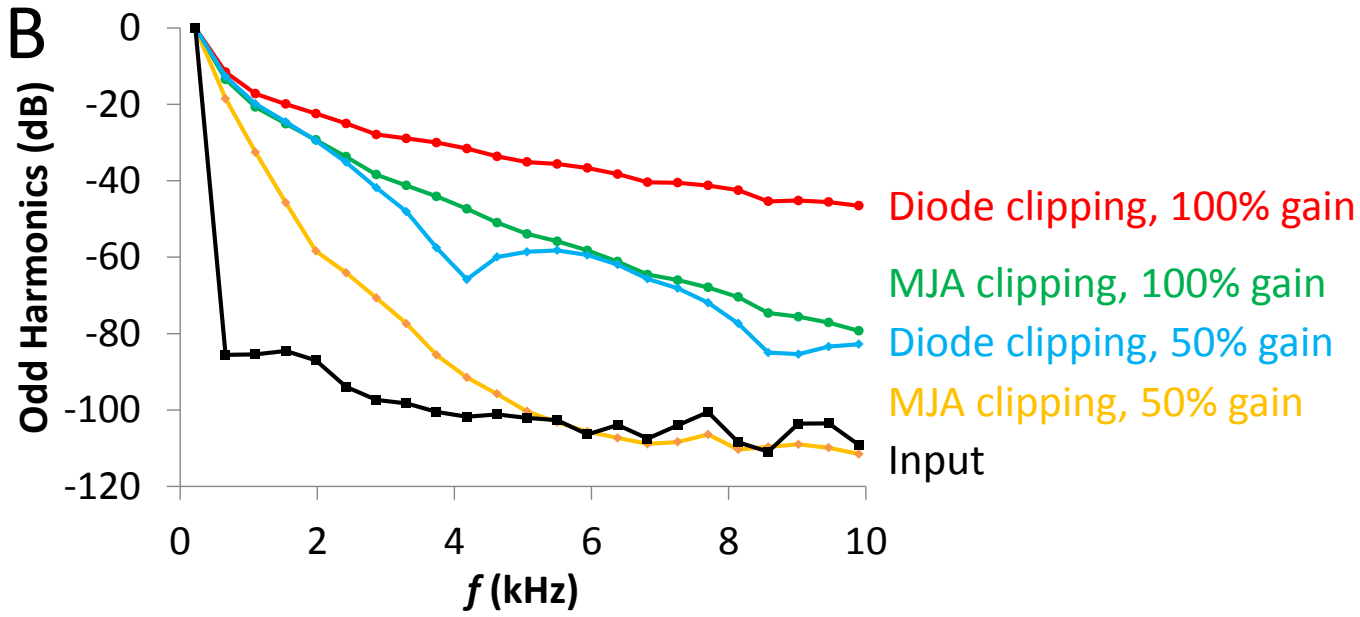




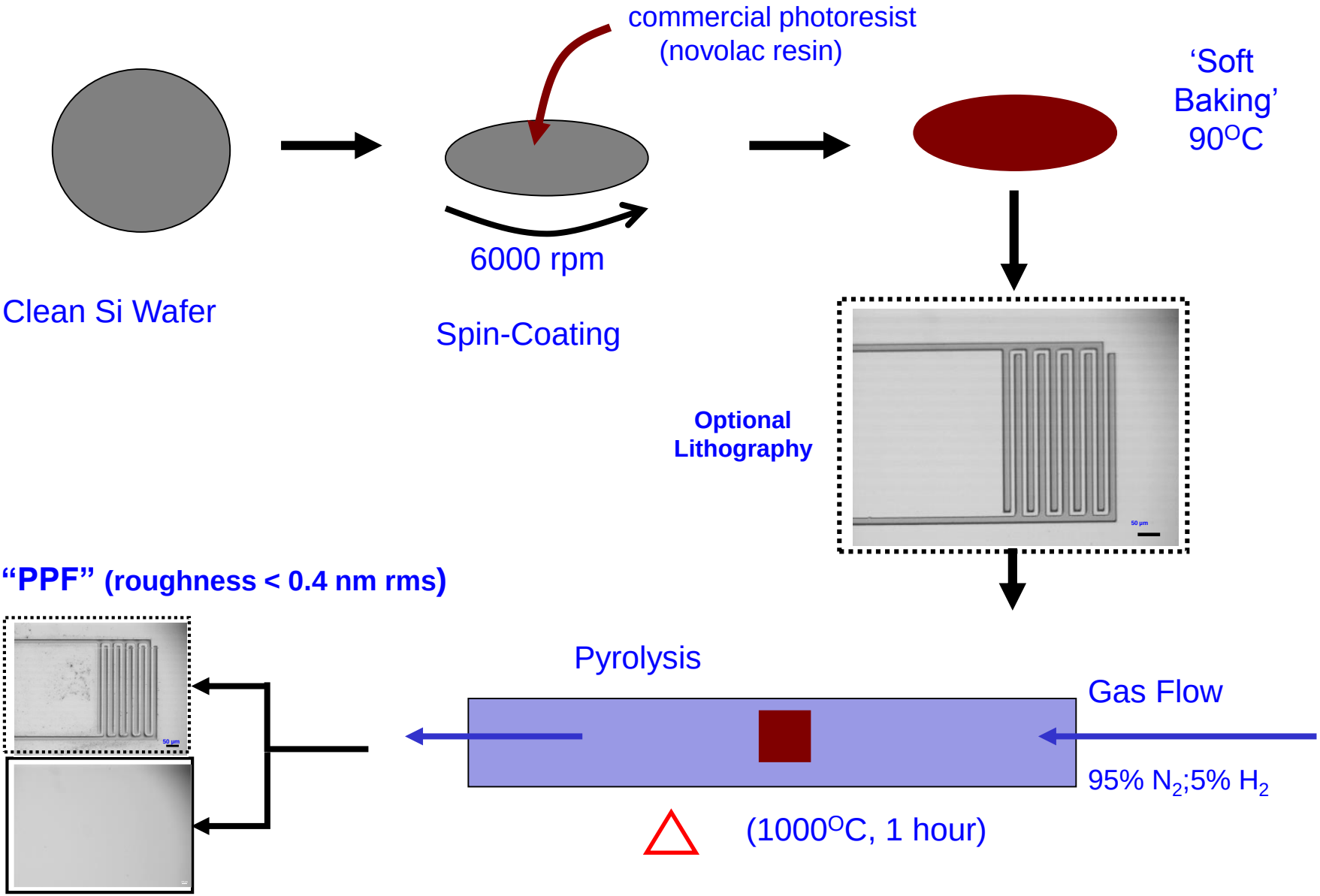





A
Odd Harmonics (dB)
0
-20
-40
-60
-80
-100
-120
0
2
4
6
8
10
f (kHz)
Diode Clipping
MJ A Clipping
Heavily Overdriven 5E3
MJ B Clipping
Input
molecular junctions
(tubes)

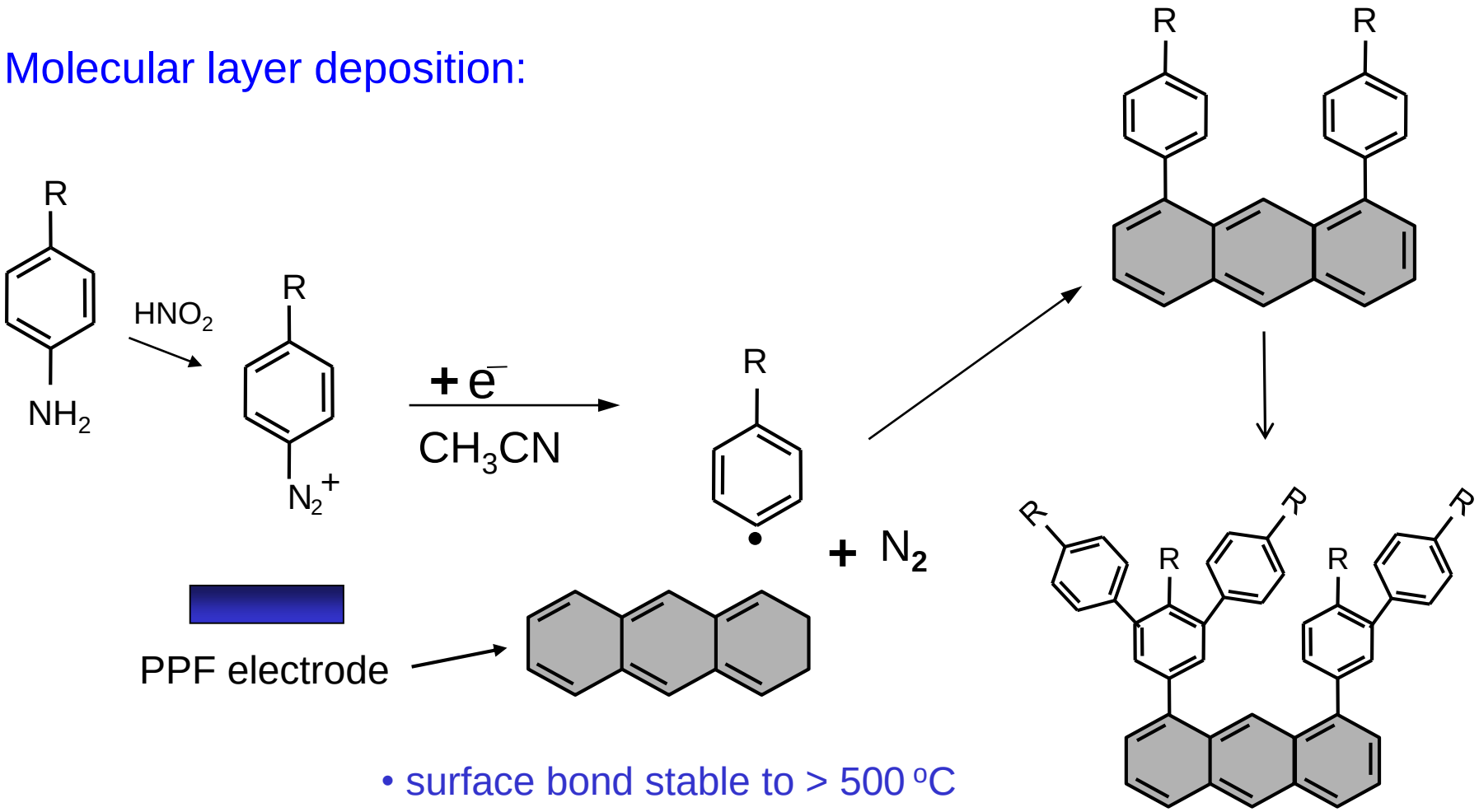

B
Odd Harmonics (dB)
0
-20
-40
-60
-80
-100
-120
0
2
4
6
8
10
f (kHz)
Diode clipping, 100% gain
MJA clipping, 100% gain
Diode clipping, 50% gain
MJA clipping, 50% gain
Input

Our substrate: Pyrolyzed Photoresist Film (PPF)



Kim, Song, Kinoshita, Madou, and White, *J. Electrochem. Soc.*, **1998**, 145, 2315
Ranganathan, McCreery, Majji, and Madou, *J. Electrochem. Soc.*, **2000**. 147, 277–282
Ranganathan, McCreery, *Anal. Chem*, **2001**, *73*, 893-900.

Molecular layer deposition:



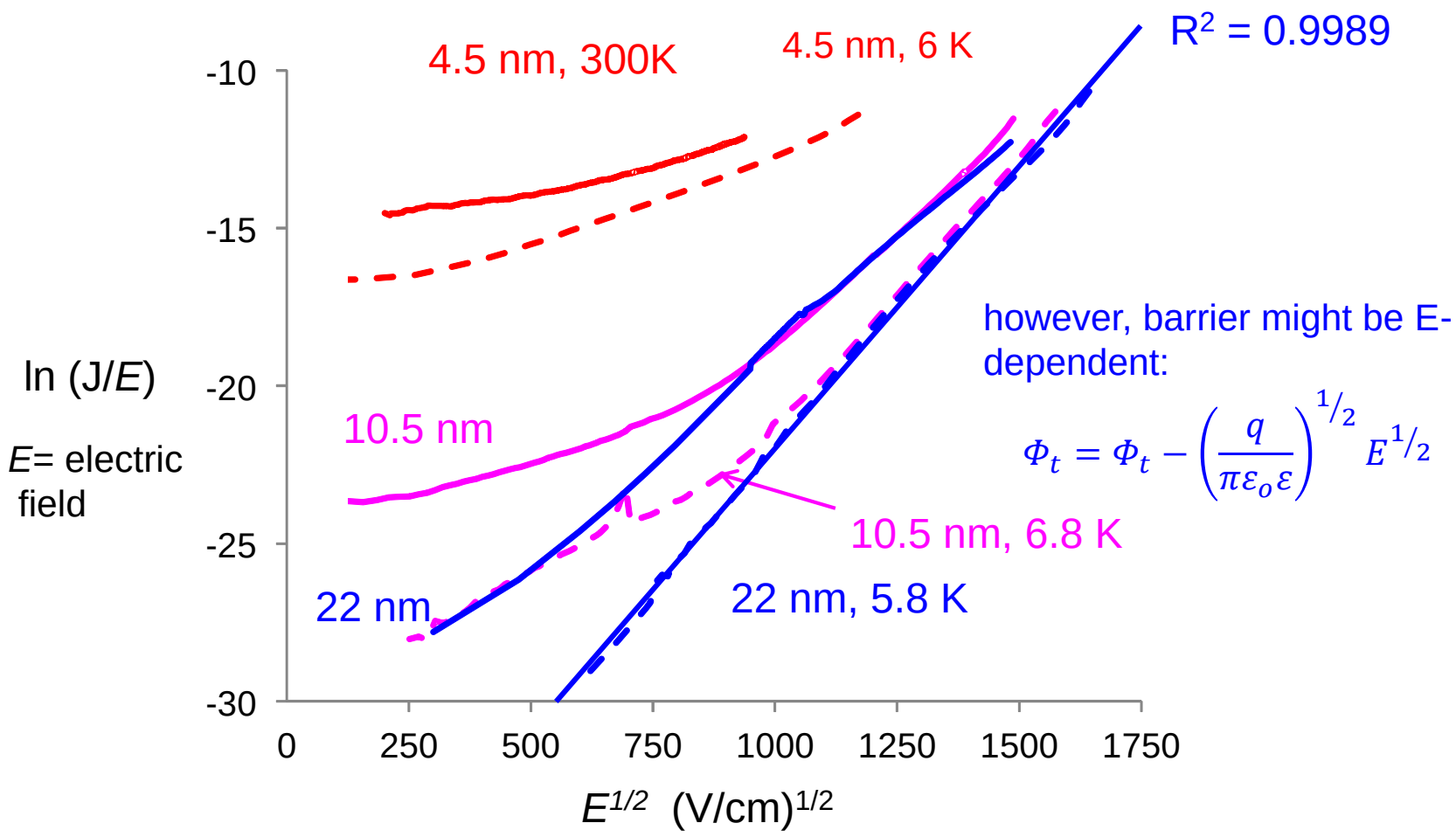
- surface bond stable to > 500 °C
- high coverage
- very low in pinholes
- often forms multilayers
- kinetically favored at edge sites

Delamar, M.; Hitmi, R.; Pinson, J.; Saveant, J. M.; *J. Am. Chem. Soc.* **1992**, *114*, 5883.
Liu, McCreery, *J. Am. Chem. Soc*., **1995**, 117, 11254.
Kariuki, J. K.; McDermott, M. T.; *Langmuir* ***1999, 15, 6534.***

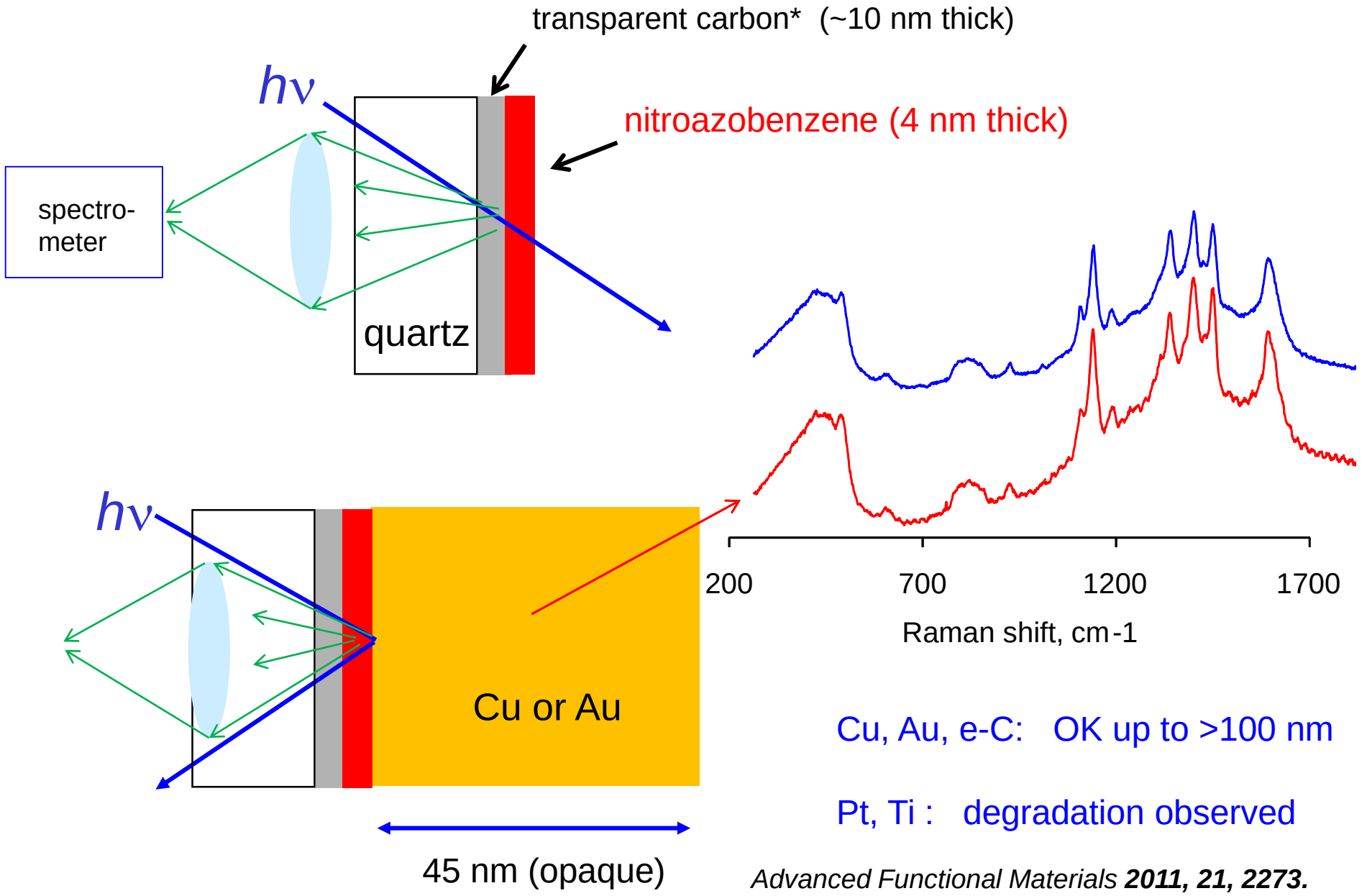
Poole Frenkel transport:

$$J_{PF} = qn_0 \mu E_N \exp[-\frac{q}{kT}(\phi_{trap} - \sqrt{\frac{qE_N}{\pi\varepsilon_N}})]$$

ln (*J*/*E*) linear with $E^{1/2}$



"Backside" Raman:

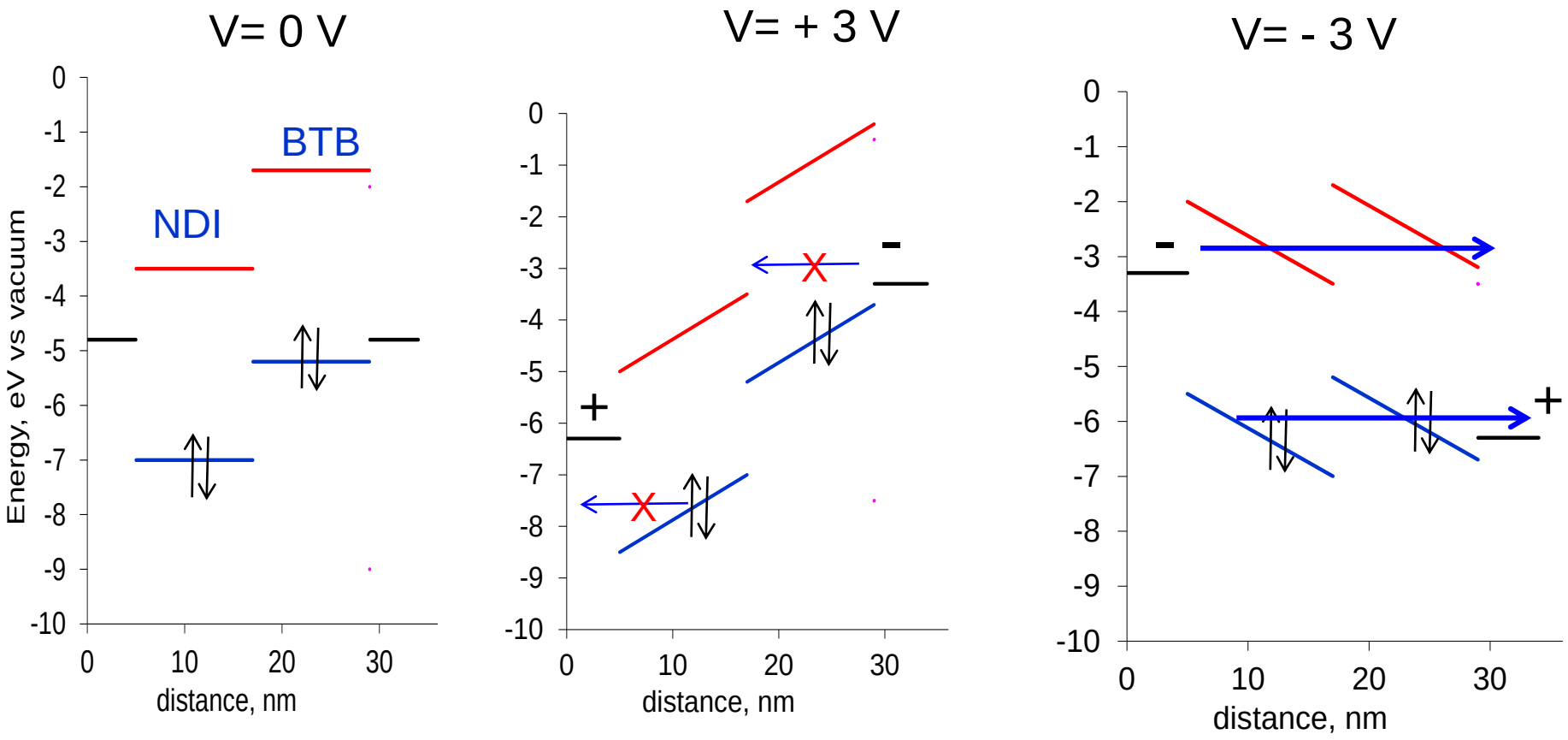


Cu, Au, e-C: OK up to >100 nm

Pt, Ti : degradation observed

Advanced Functional Materials ***2011, 21, 2273.***

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



definitely rectification, mechanism tentative at present