UNIVERSITY OF ALBERTA

Photoeffects as Probes of Transport in all-Carbon Molecular Junctions

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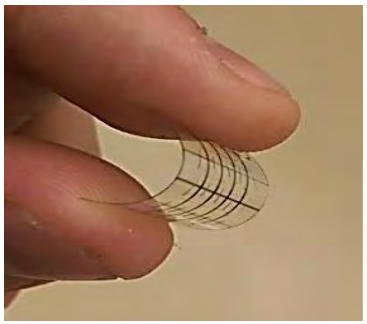
ALBERTA INNOVATES

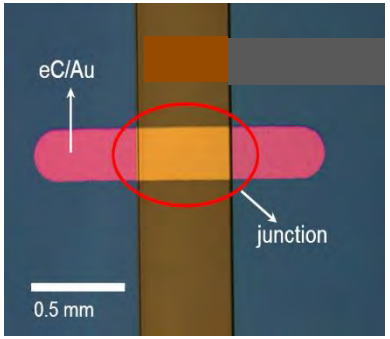
NSERC CRSNG

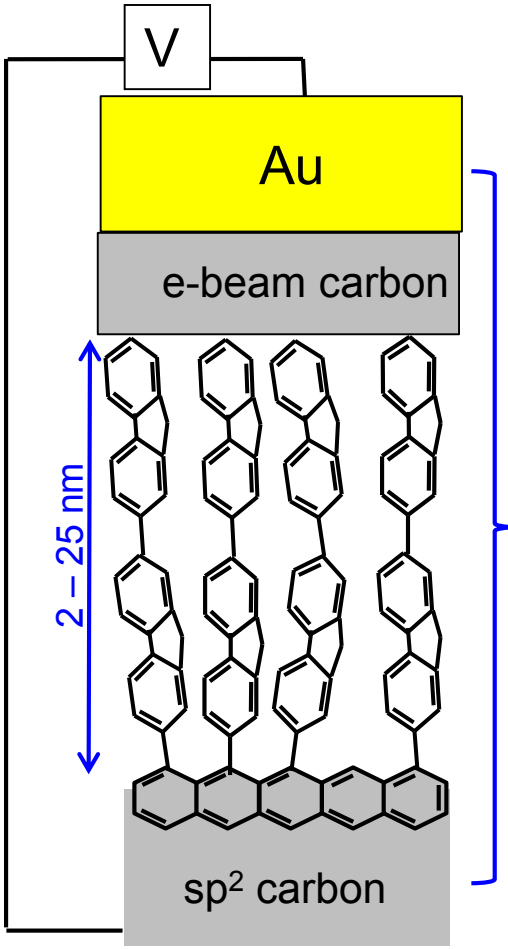
Canada Foundation for Innovation

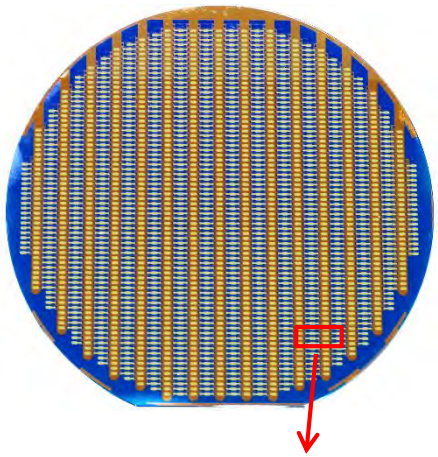
“All carbon” molecular junction:

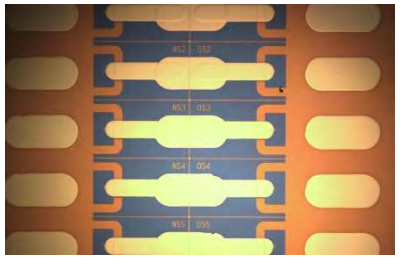
Large area (0.001 cm^2, $>10^{11}$ molecules)
2 - 25 subunit oligomers
covalent throughout (nearly)



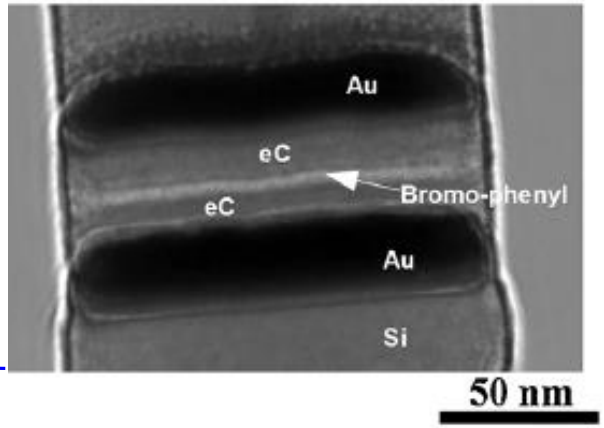








FIB/TEM

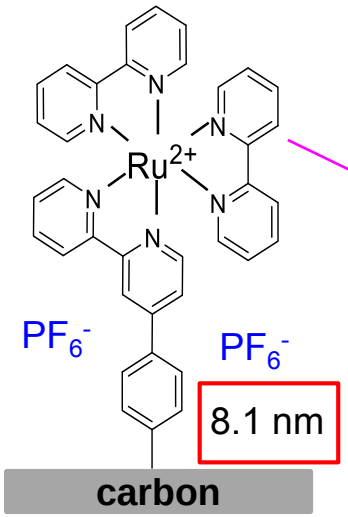


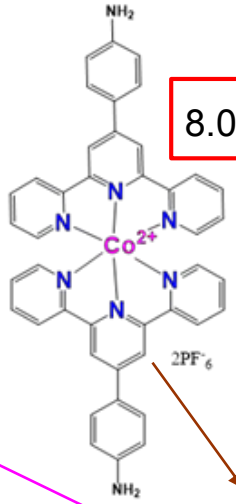
Two main questions:

How do molecules behave as circuit elements?

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

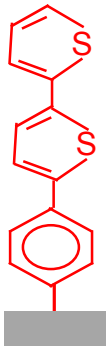
Is the electronics *molecular?*

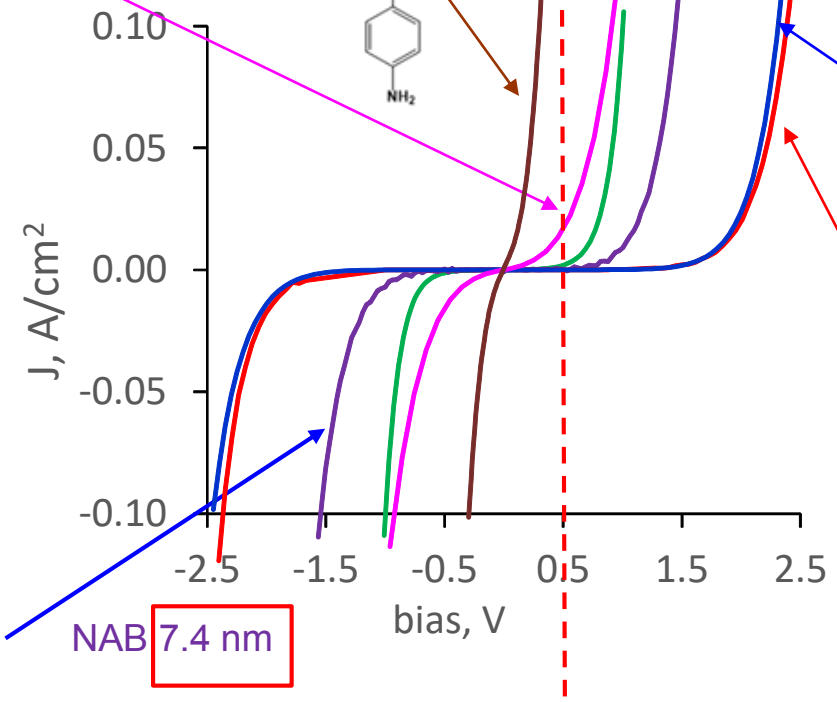




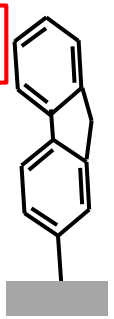
8.0 nm

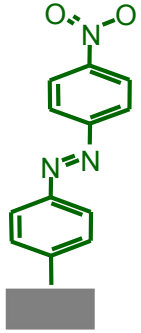
BTB 8.1 nm





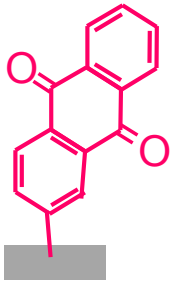
FL 8.0 nm





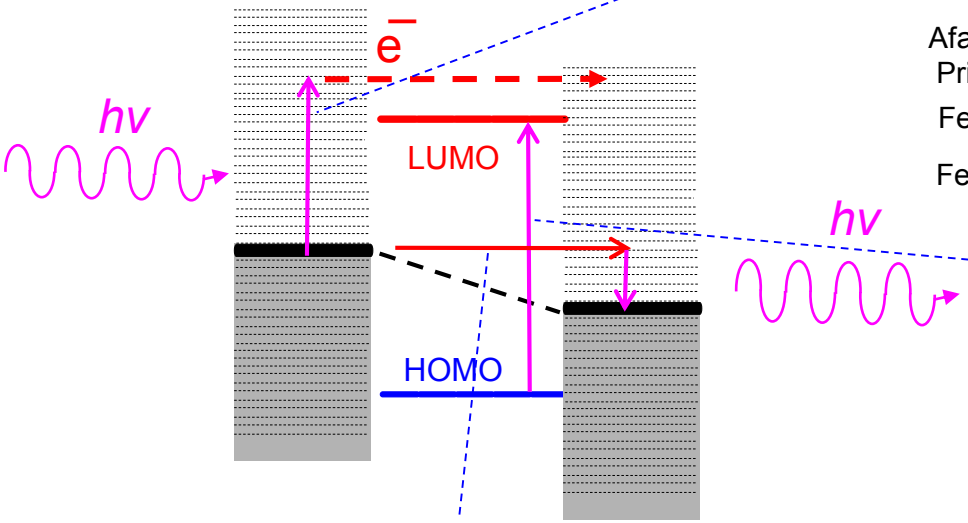
NAB 7.4 nm

> 6 orders of magnitude
for *d*=8 nm, *V*=0.5 V



AQ 8.0 nm

Some observed photoeffects in molecular junctions:



- internal photoemission (IPE)
  absorption by contacts

Afanas'ev, V. V. Internal Photoemission Spectroscopy: Principles and Applications; Elsevier: Amsterdam, 2008

Fereiro..RLM, *JACS* **2015**, *137*, 1296.

Fereiro..RLM, *JACS* **2013,** *135*, 9584

- optical gap transition
  (aka photon assisted transport)
  absorption by molecule

Galperin, Nitzan, *PCCP* **2012**, *14*, 9421

Viljas, Cuevas, *Phys. Rev B* **2008**, *77*, 155119

Morteza, RLM *ACS nano* **2019**, *13*, 867-877

Morteza, RLM, Galperin, *J. Phys. Chem. Lett.* **2019,** *10*, 1550

Morteza, RLM, *JACS* **2019**, *140*, 1900

- hot electron/plasmon emission

Ivashenko, RLM,*JACS.* **2016,** *138*, 722

Wang, Nijhuis, *Nat. Photon.* **2016,** *10*, 274

Ivashenko, RLM, *Adv. Electr. Mat.* **2016,** *2*, 1600351

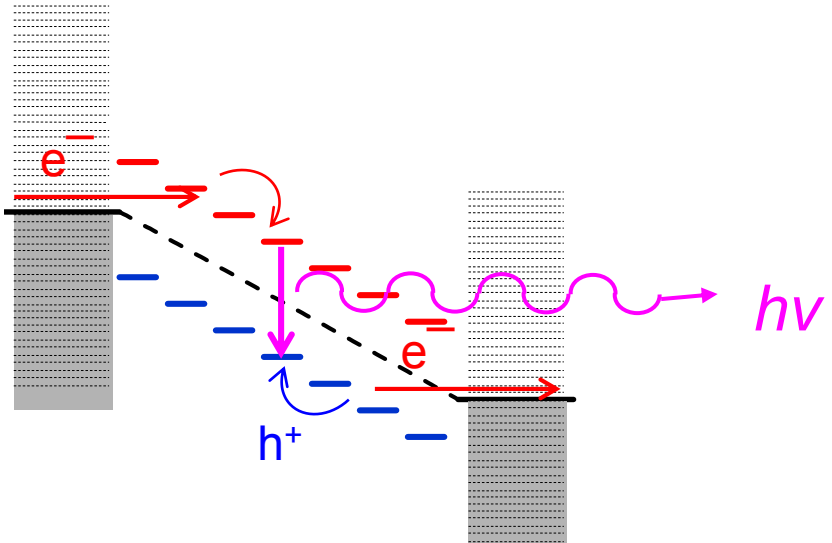
Galperin, Nitzan, *Phys. Rev. Lett.* **2005,** *95*, 206802

Lambe, McCarthy, *Phys. Rev. Lett*. **1976**, 37, 923 (AlOx)

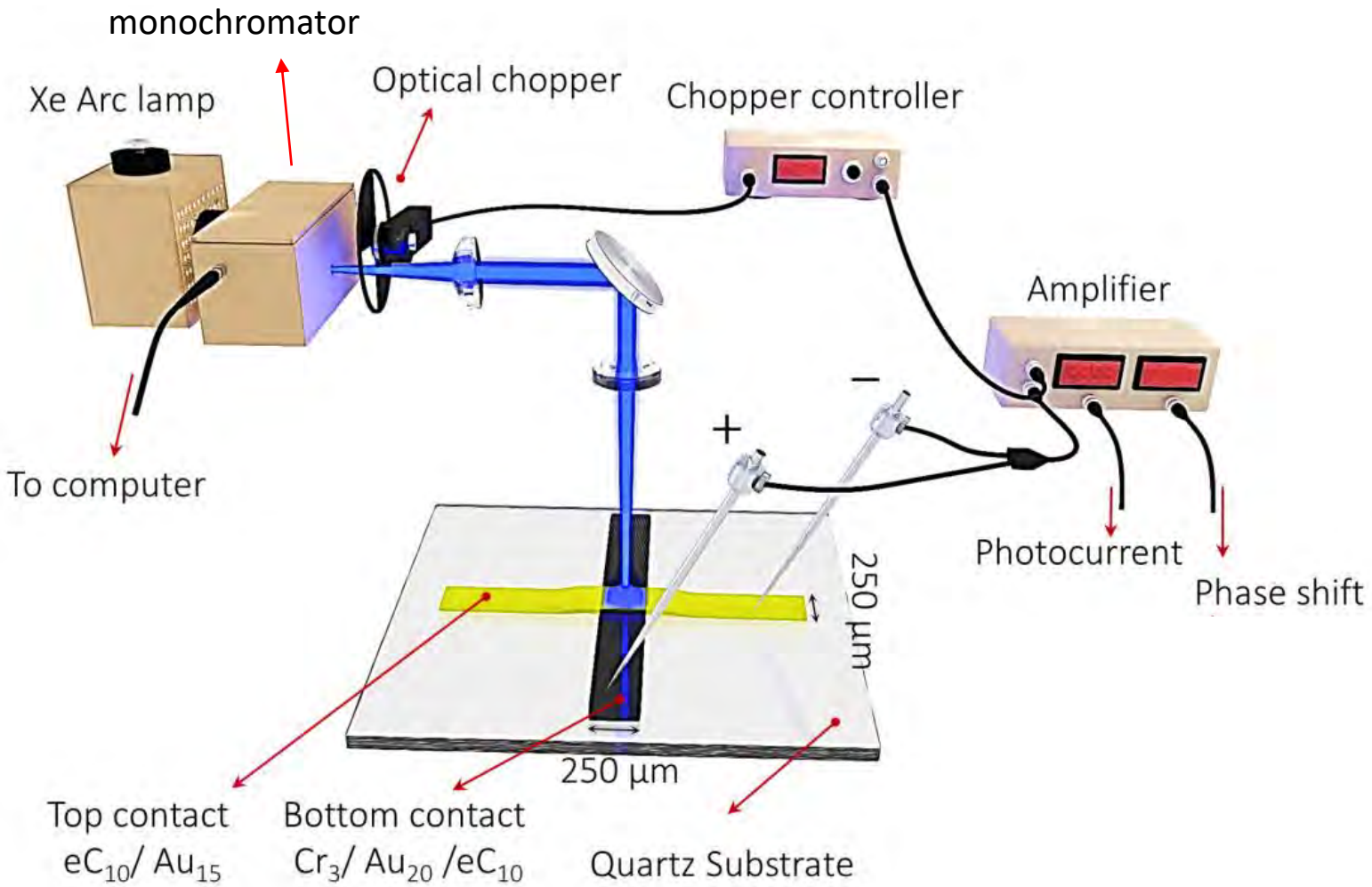
Berndt, et al., *Science* **1993**, 262, 1425 (STM)

- bipolar injection and light emission

Tefashe, Lacroix, RLM, *JACS* **2017,** *139*, 7436

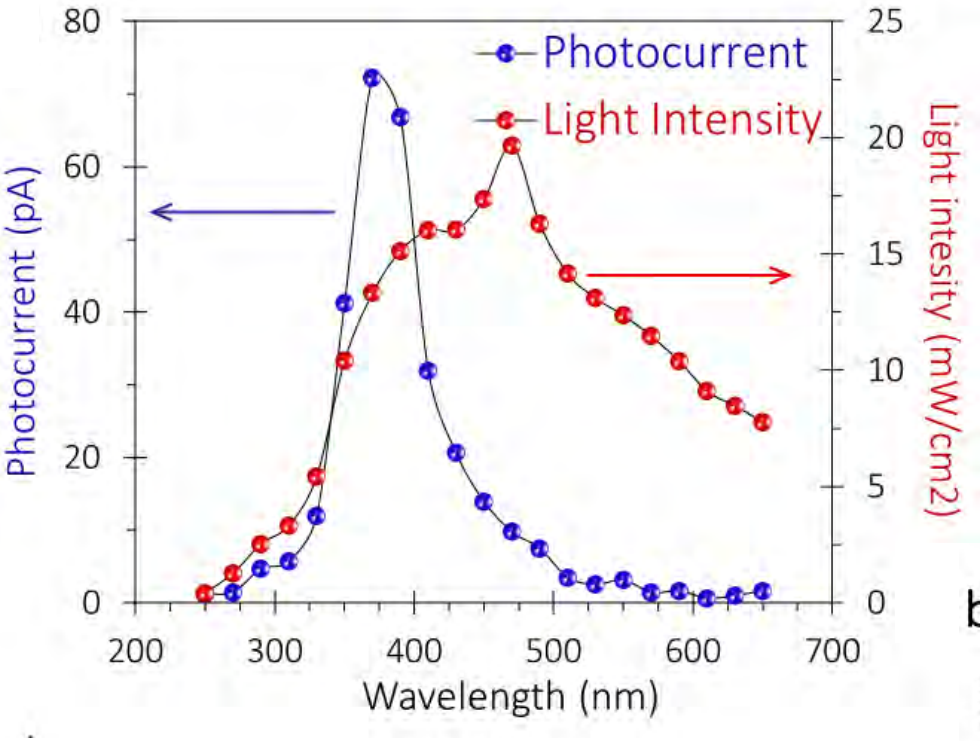


Measuring photocurrents:



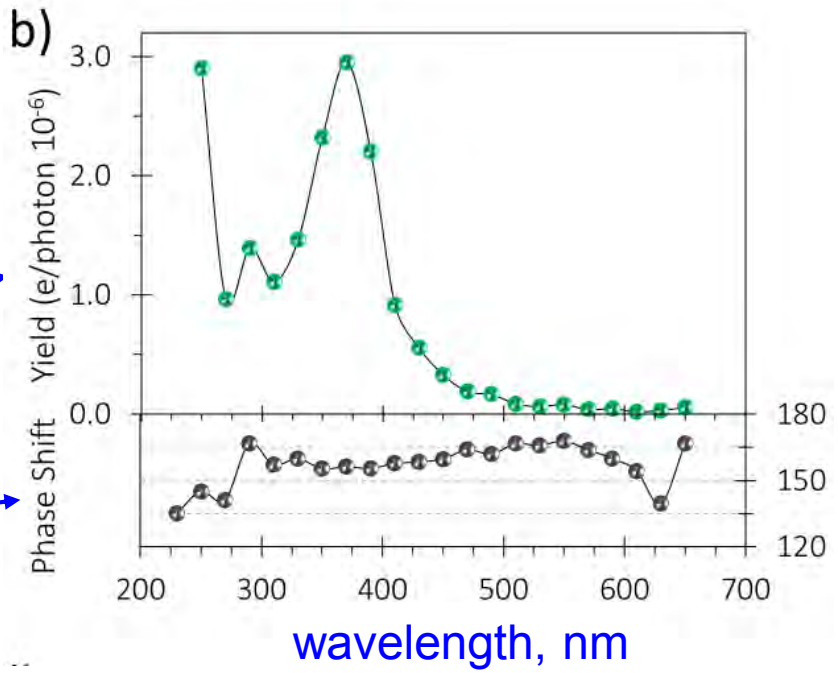
Morteza-Najarian, RLM, JACS **2018,** *140*, 1900-1909.

Photocurrents at zero bias:

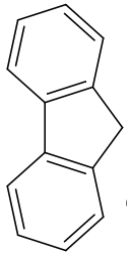


photoelectrons per incident photon
("external quantum efficiency, EQE")

phase indicates photocurrent
sign (i.e direction of $\bar{e}$ flow)

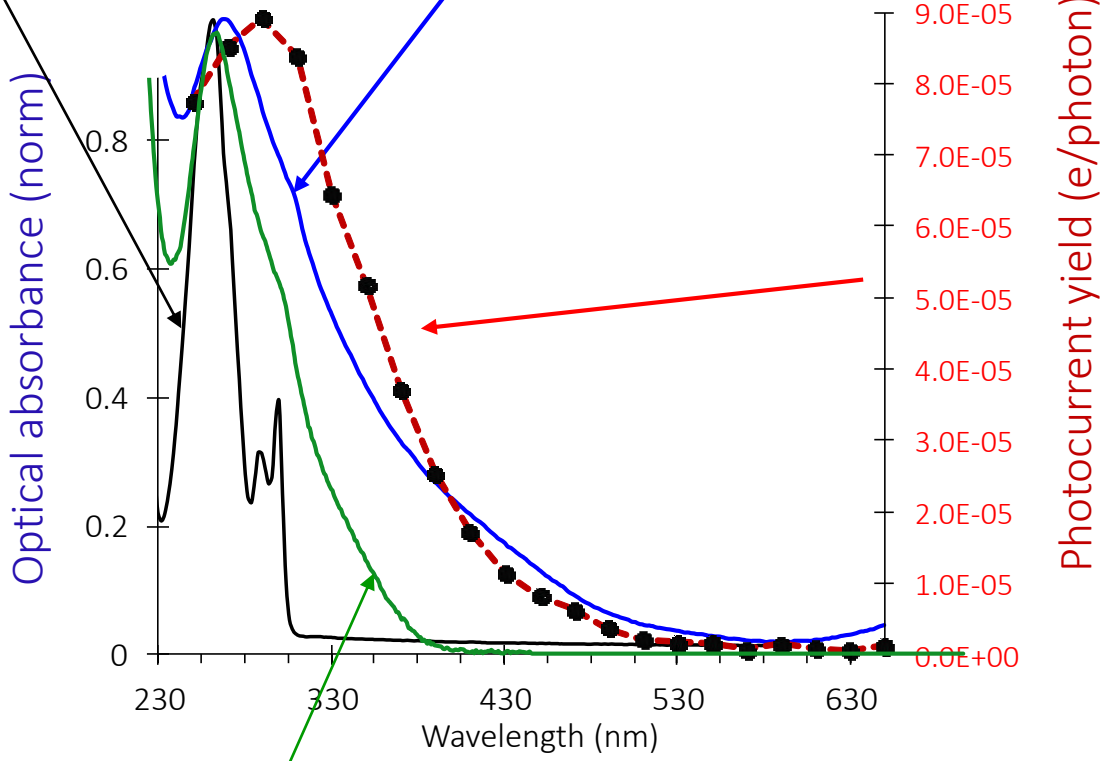


FL

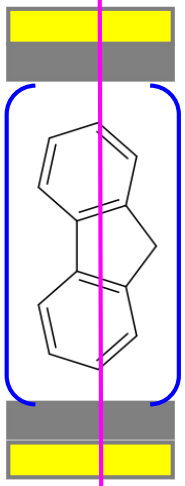


in CH_3CN

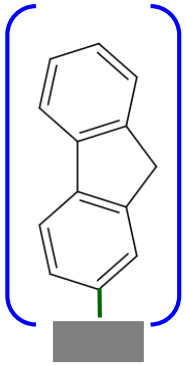
Au/eC/FL/eC/Au (full MJ)
(Au/eC/eC/Au subtracted)



hv



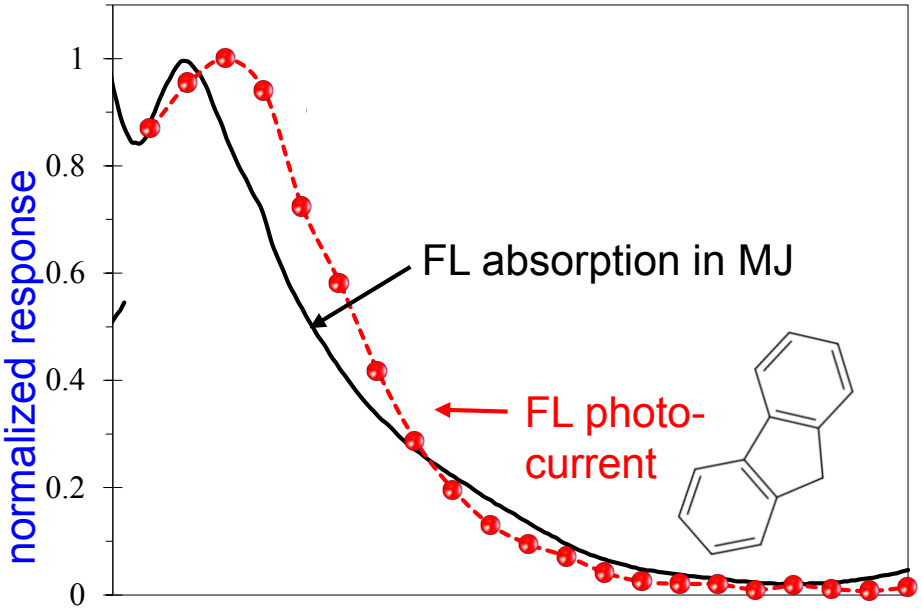
n~5

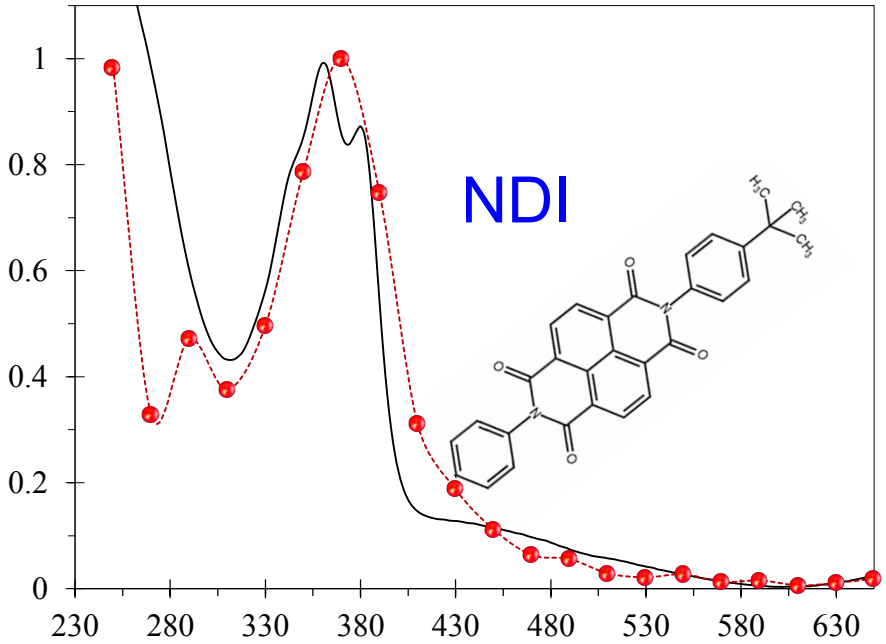


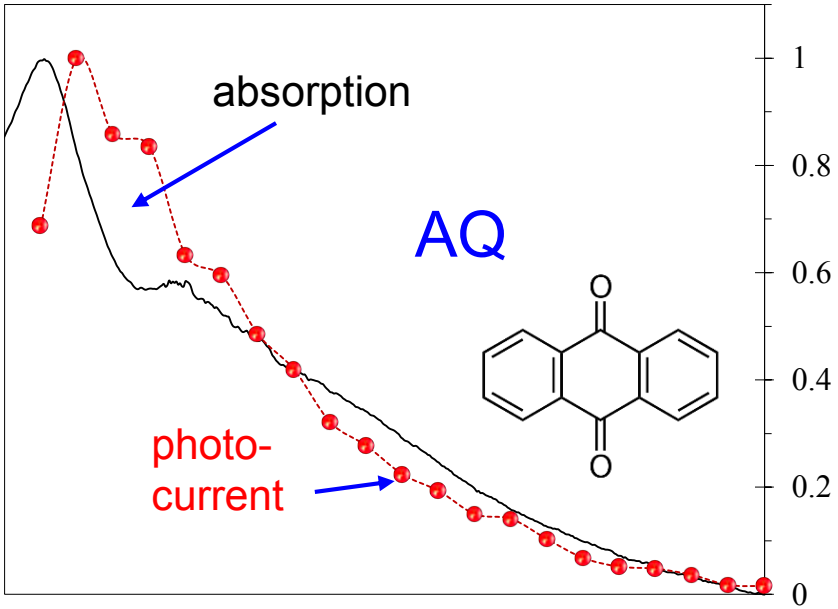
n~5

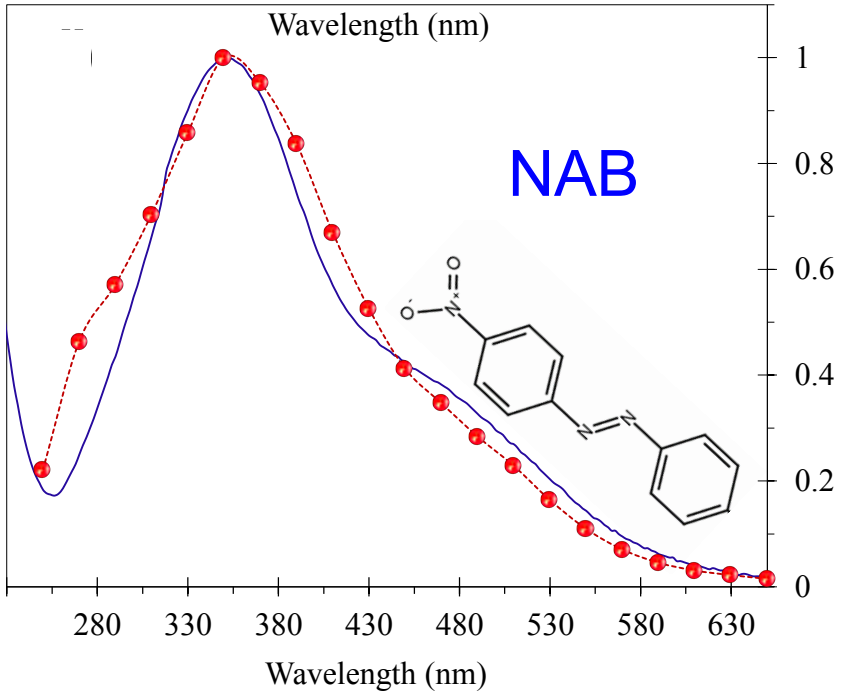
Au/eC/FL
(Au/eC subtracted)

Morteza, Bayat, RLM, *JACS* **2018**, *140*, 1900



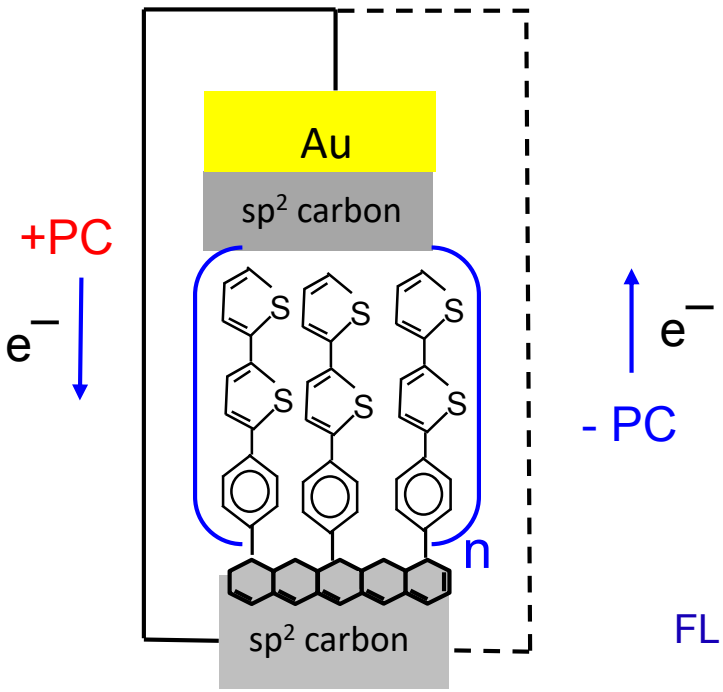


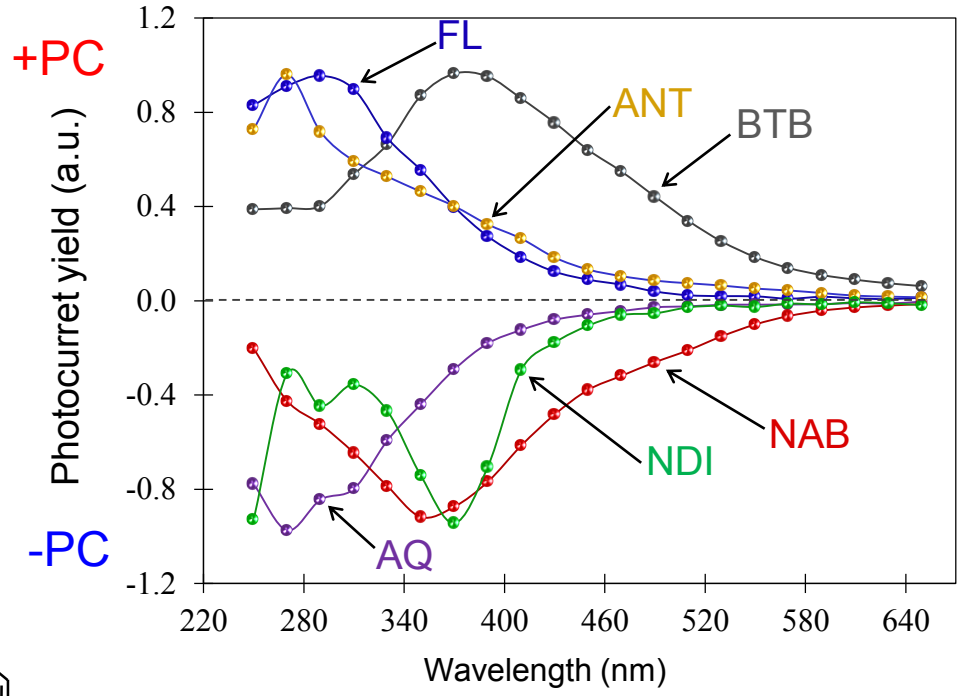




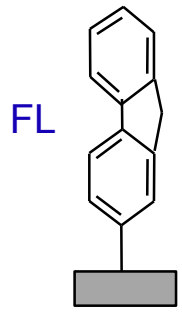
Morteza, Bayat, RLM, *JACS* **2018**, *140*, 1900

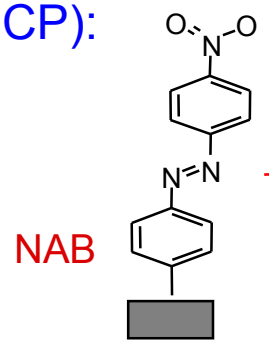
Photocurrent sign:

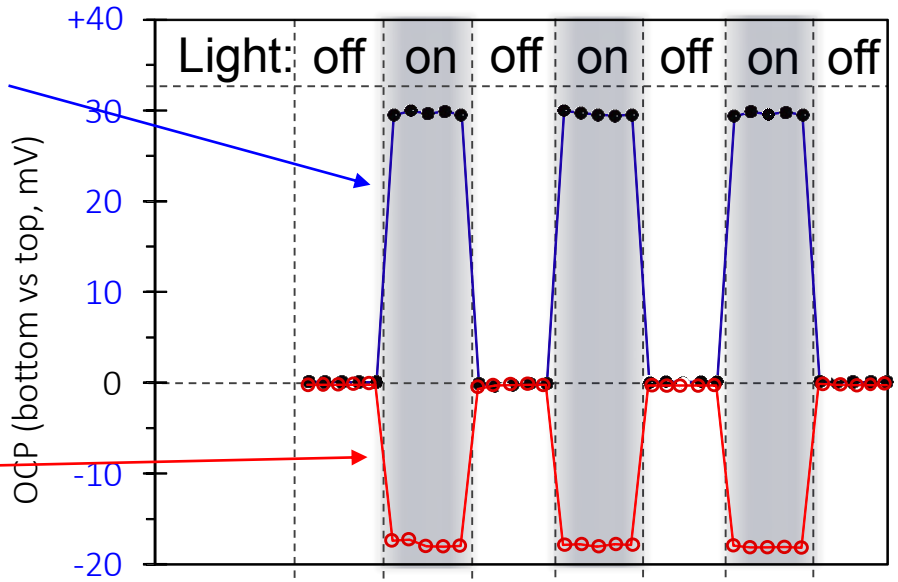


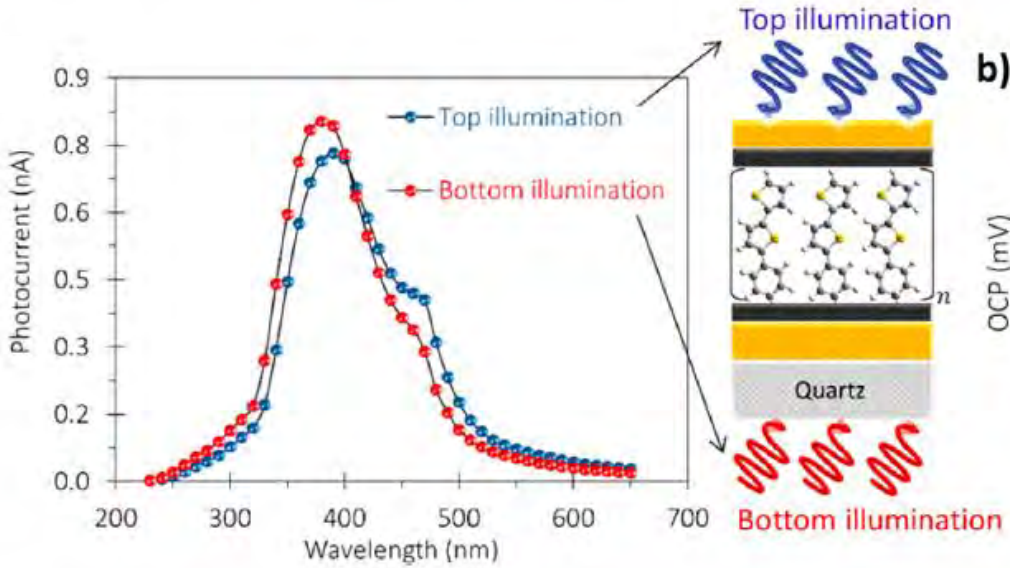


Photovoltage (OCP):

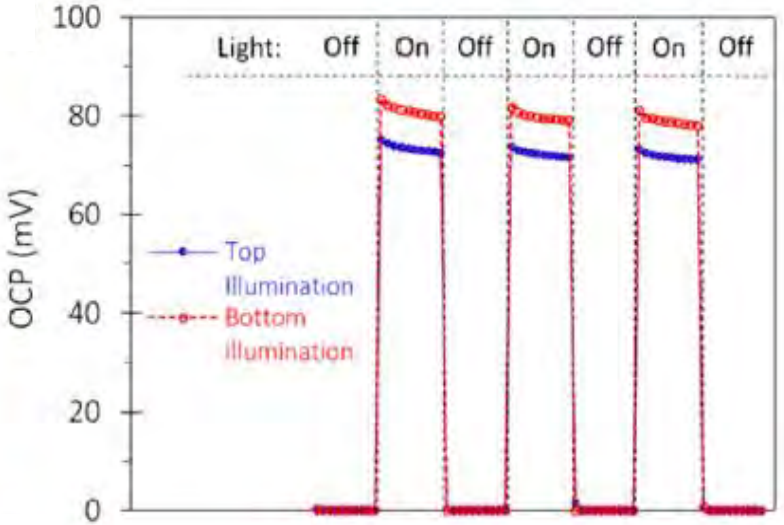


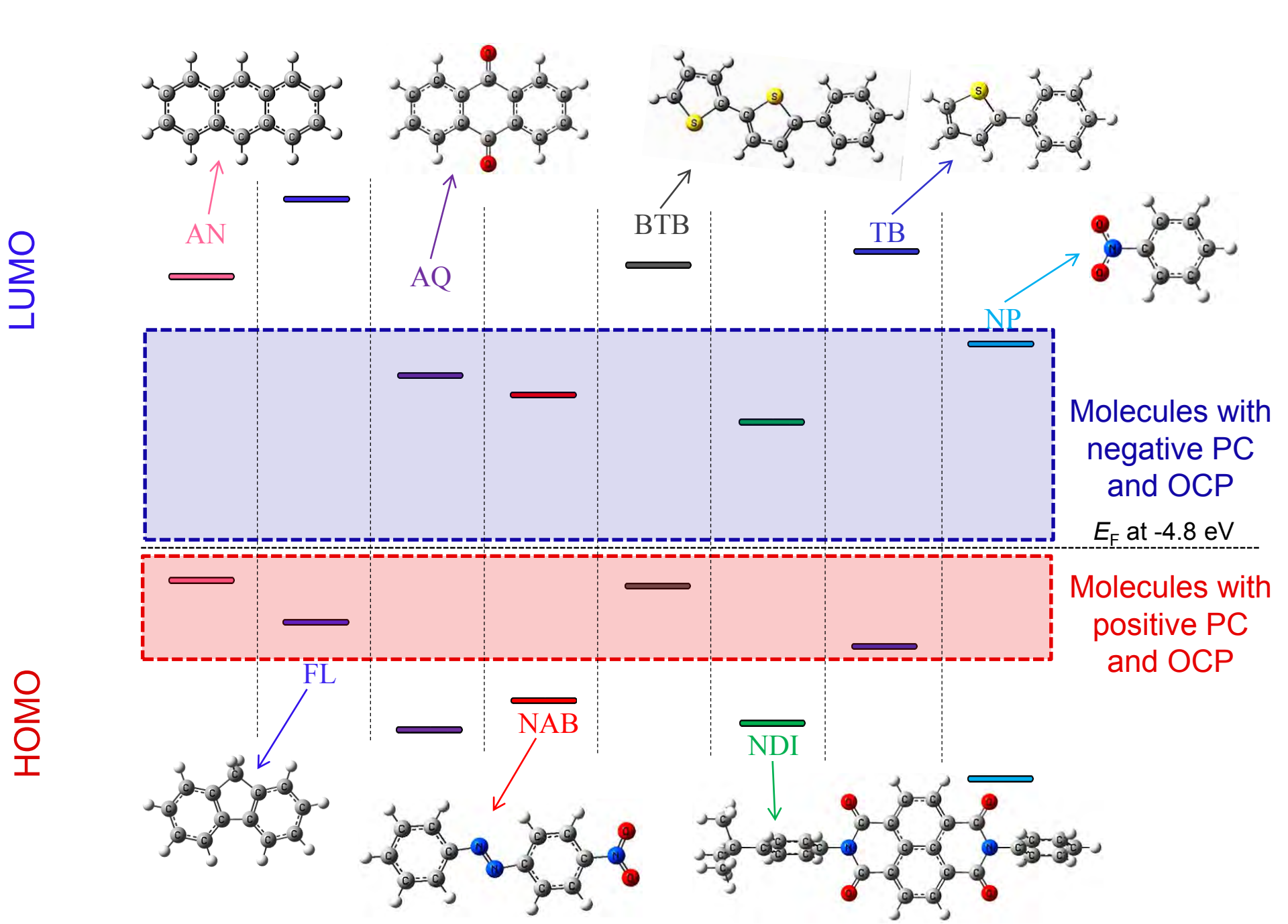






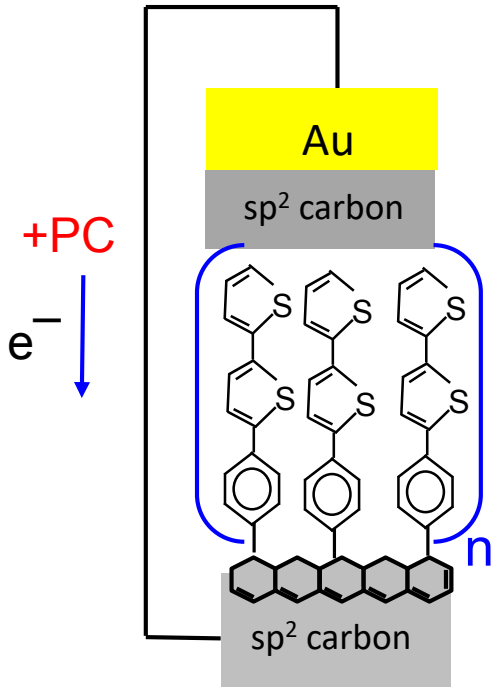
direction of illumination does not change PC or photovoltage sign




LUMO
HOMO
AN
AQ
BTB
TB
NP
FL
NAB
NDI
Molecules with negative PC and OCP
E_F at -4.8 eV
Molecules with positive PC and OCP

Photocurrents at *V*=0 in carbon/molecule/carbon molecular junctions:

- PC polarity depends on the molecule
- OCP and PC polarity consistent across 8 molecular structures
- PC spectrum tracks molecular absorption spectrum
- PC and OCP polarity independent of illumination direction
- "Donors" yield positive PC, "Acceptors" yield negative PC.



But why is there photocurrent at all for zero bias in a symmetric device??

An important guide from theory:

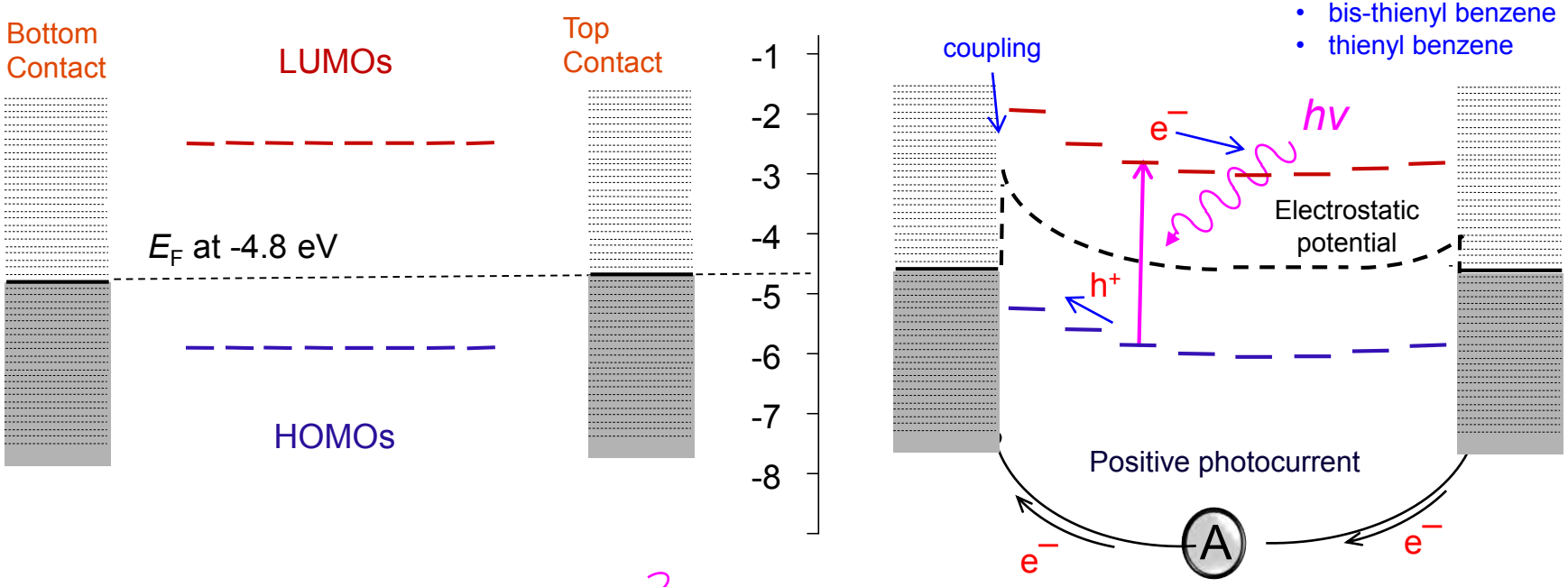
Galperin, M.; Nitzan, A.; *Phys. Rev. Lett.* **2005**, *95*, 206802

isolated “donor” molecules:

in C/C junction:

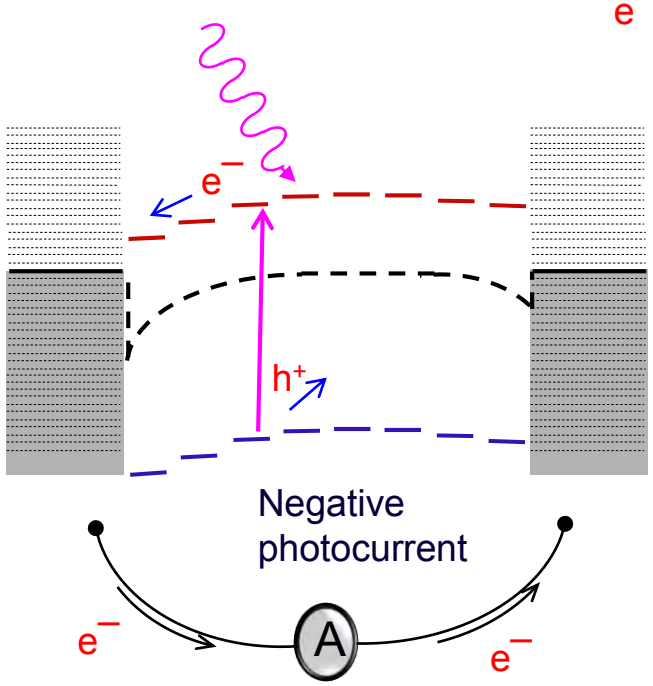
“donors”

- anthracene
- fluorene
- bis-thienyl benzene
- thienyl benzene



“acceptors”

- anthraquinone
- nitrobenzene
- nitroazobenzene
- naphthalene di-imide

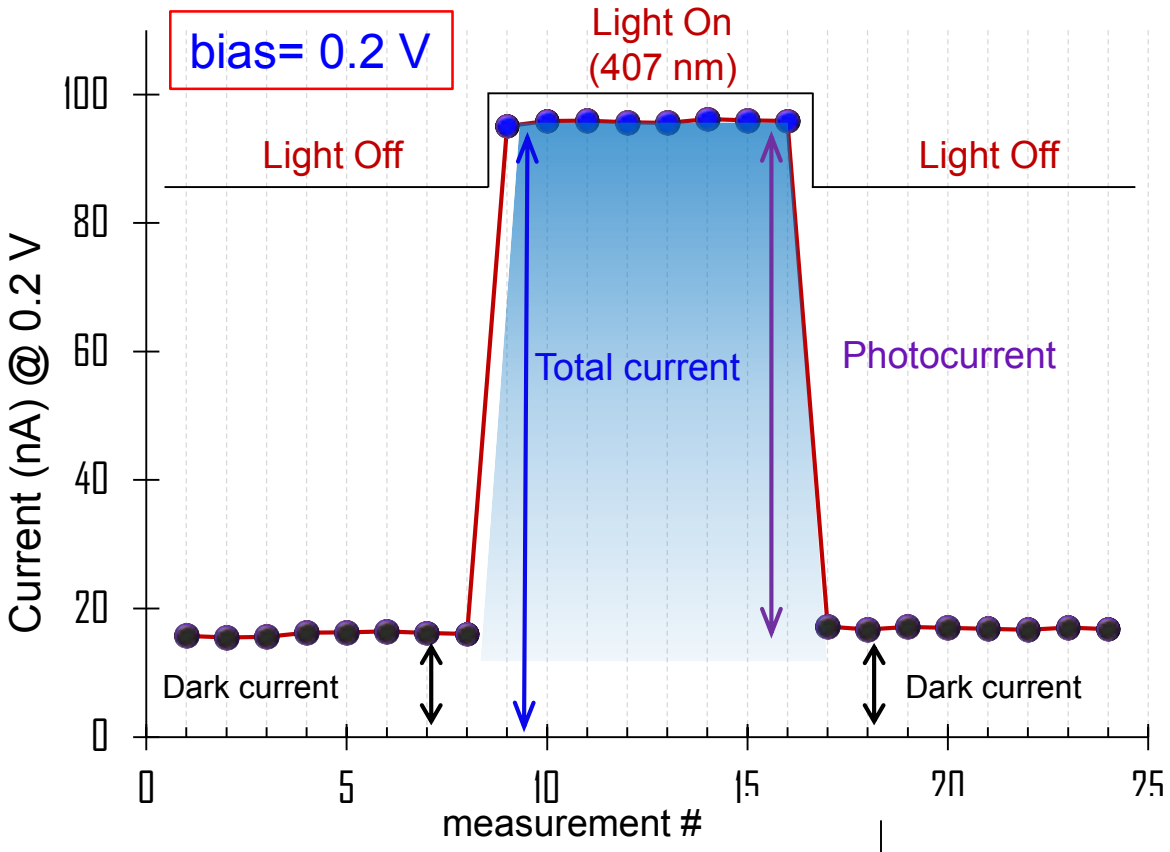


sign of photocurrent indicates with whether HOMO or LUMO is closer to electrode Fermi level

This picture applies for zero bias, with charge transfer dependent on the internal electric field.

What happens with non-zero bias??

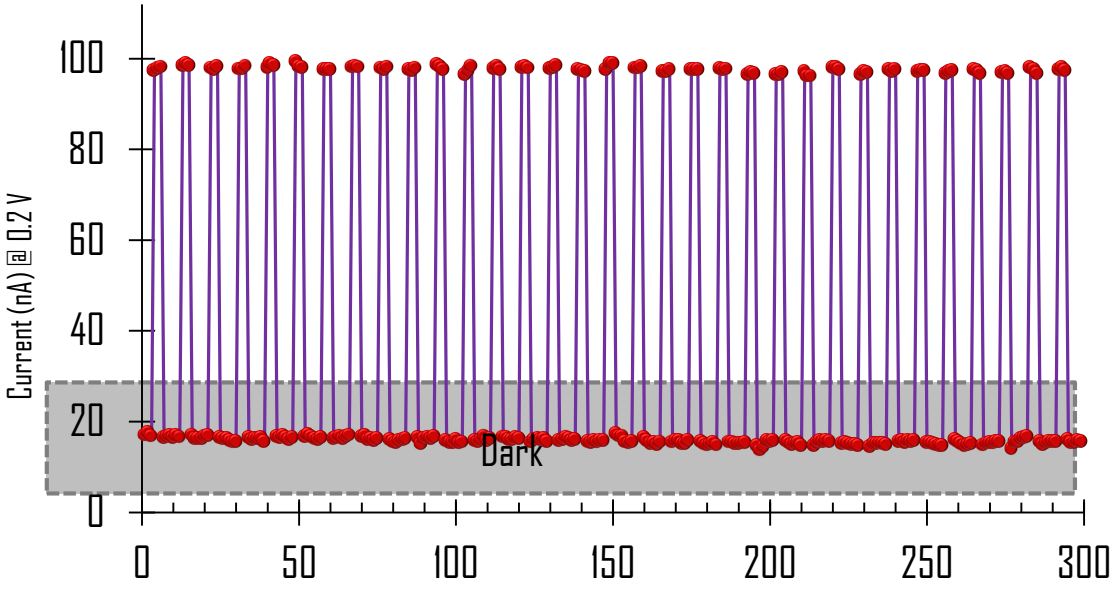
Morteza, RLM, *JACS* **2018**, *140*, 1900



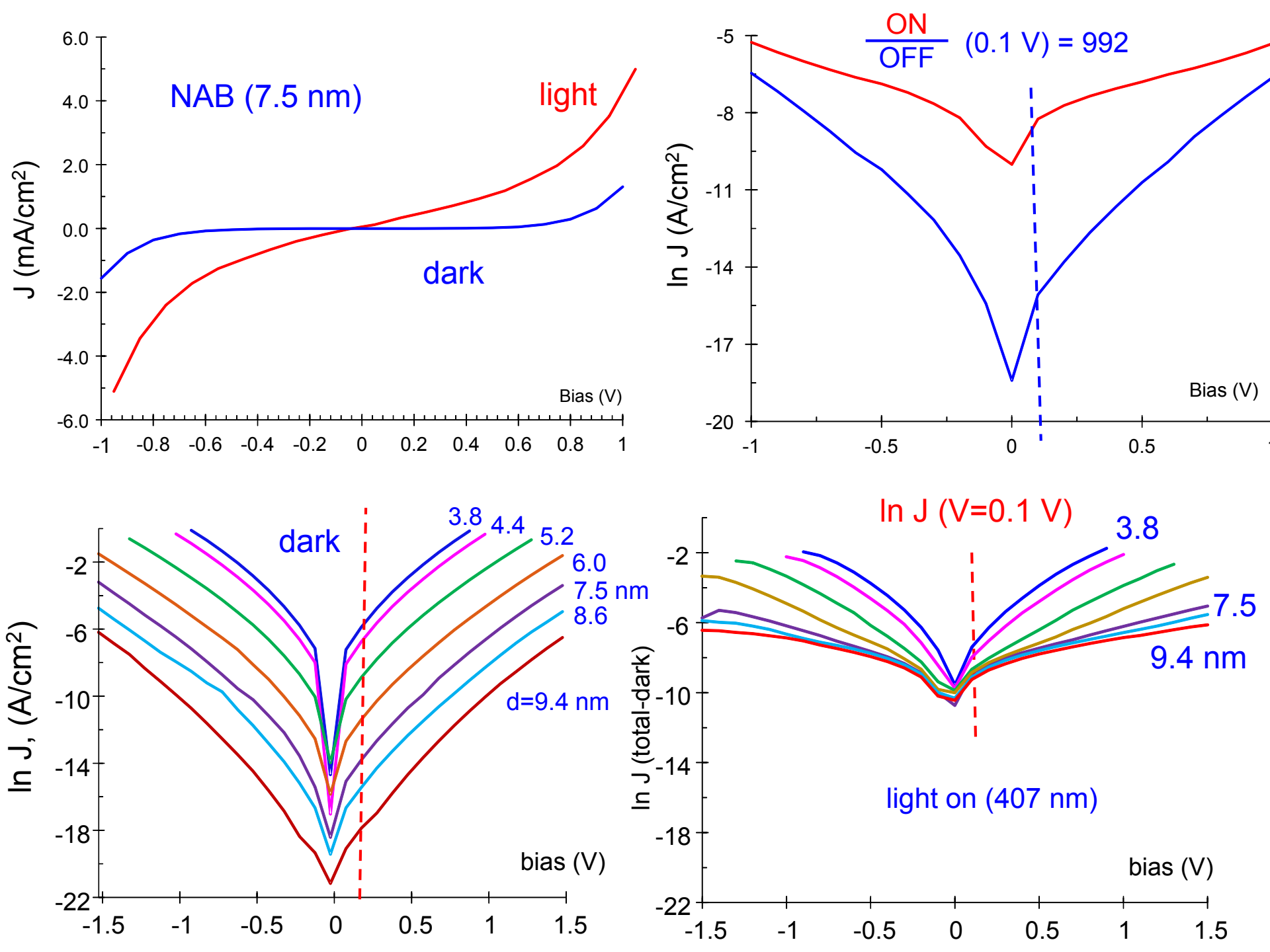
75 nA photocurrent
for V=0.2 V

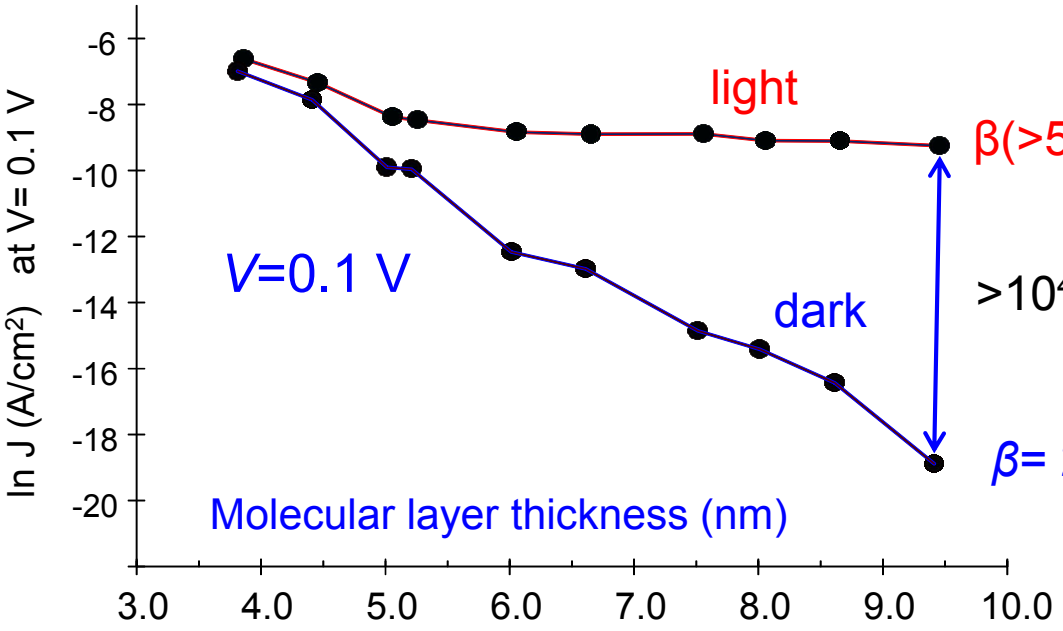
(0.23 nA @ V=0)

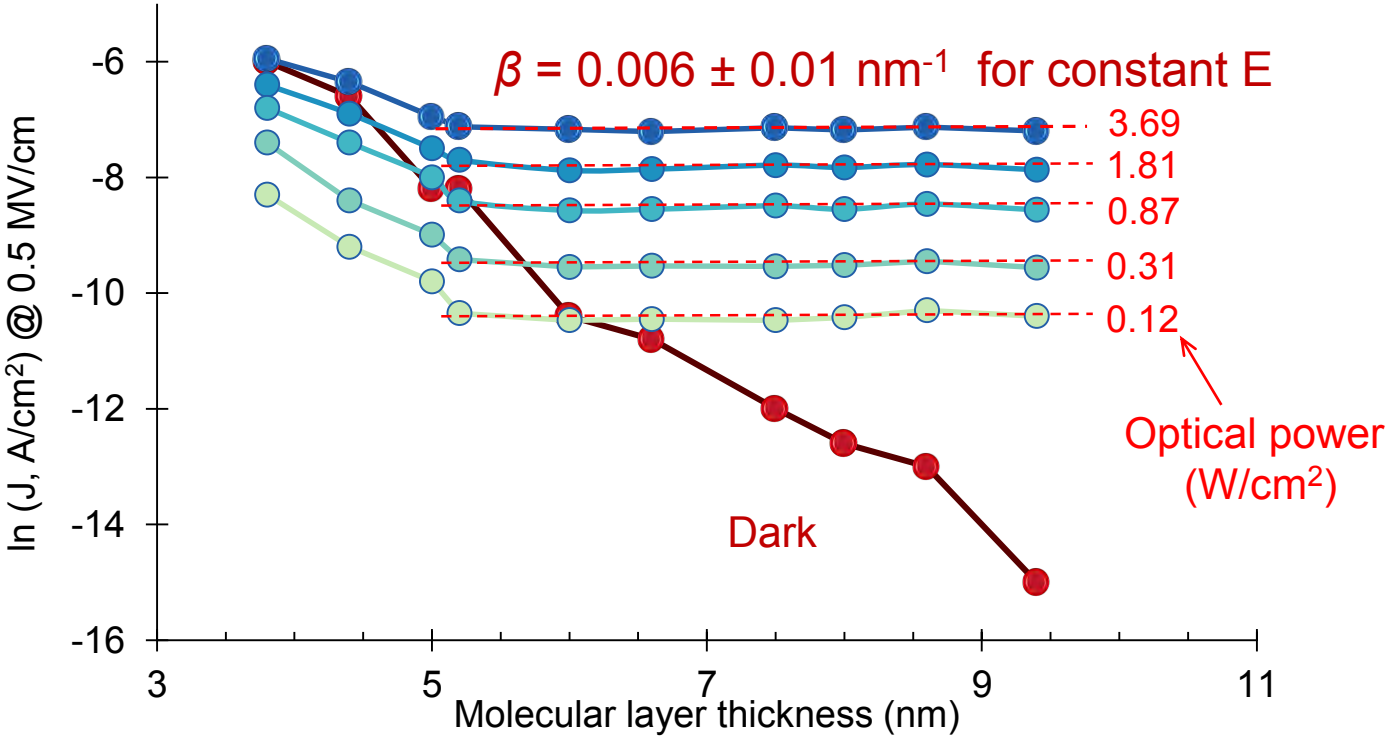
repetitive switching
between “dark” and
“illuminated” for
V=0.2 V



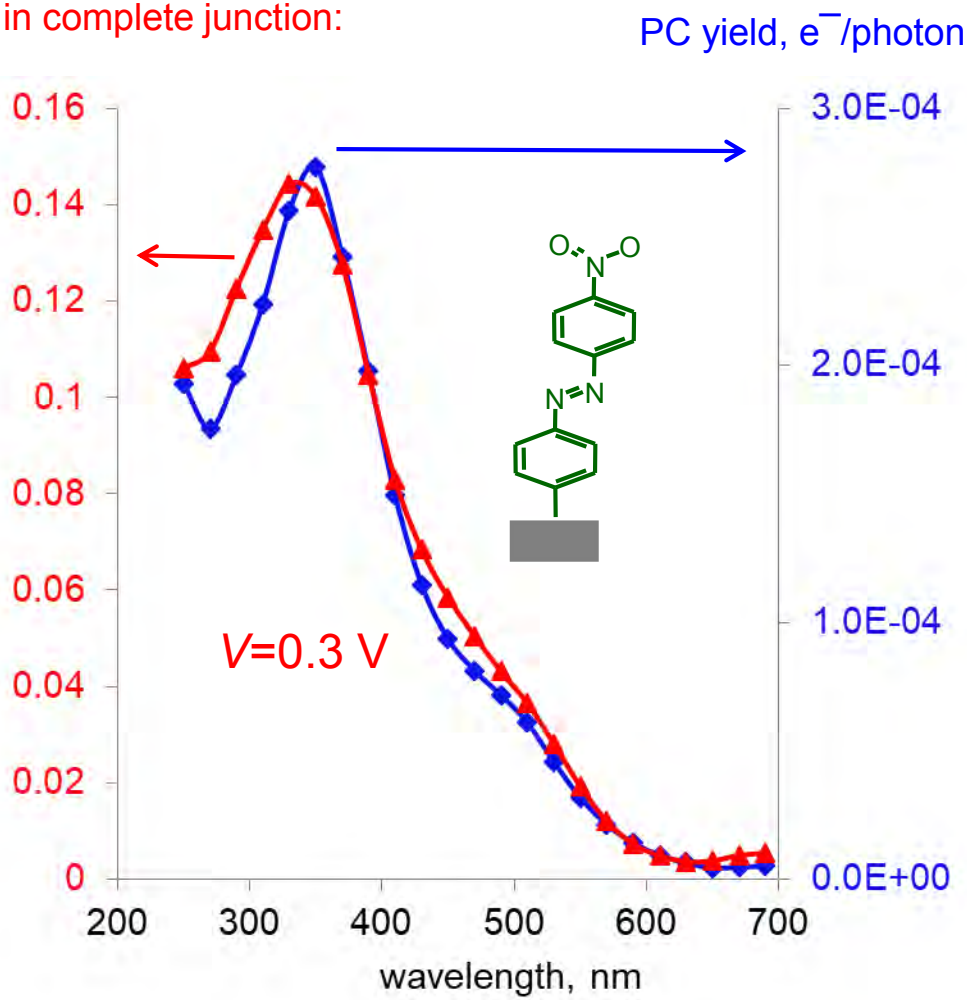
Morteza, RLM *ACS nano* **2019**, *13*, 867-877

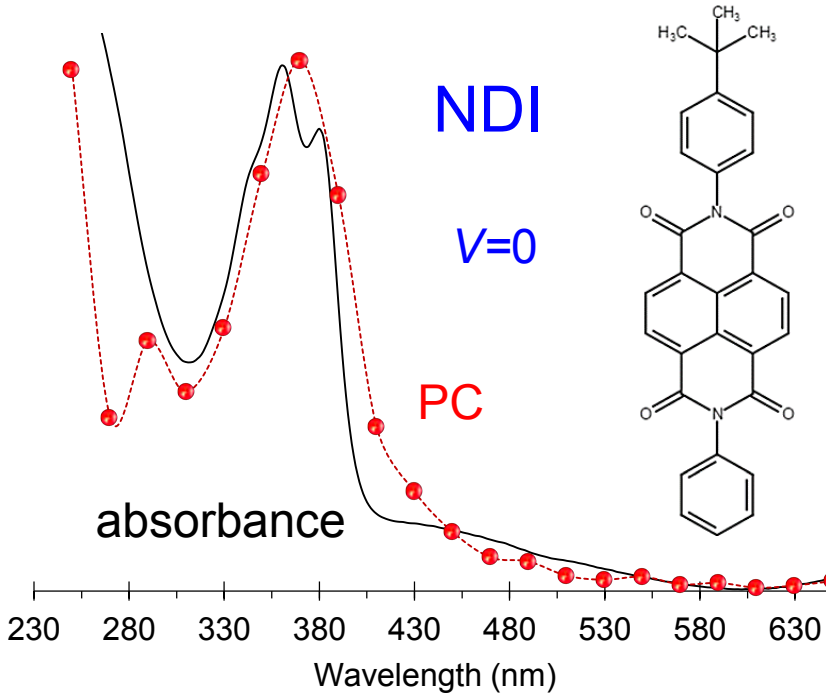

NAB (7.5 nm)
light
dark
J (mA/cm²)
Bias (V)
ON
OFF
(0.1 V) = 992
ln J (A/cm²)
Bias (V)
dark
3.8
4.4
5.2
6.0
7.5 nm
8.6
d=9.4 nm
ln J, (A/cm²)
bias (V)
ln J (V=0.1 V)
3.8
7.5
9.4 nm
ln J (total-dark)
light on (407 nm)
bias (V)

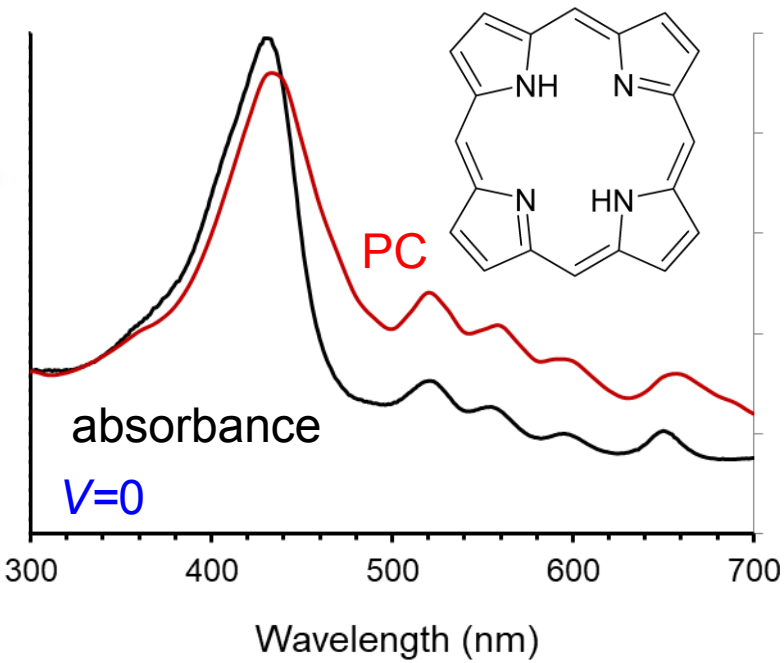

ln J (A/cm²) at V= 0.1 V
-6
-8
-10
-12
-14
-16
-18
-20
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Molecular layer thickness (nm)
light
dark
V=0.1 V
β(>5nm)= 0.13 nm⁻¹ (14%/nm)
>10⁴ increase
β= 2.1 nm⁻¹ (~8x per nm)


E=0.5 MV/cm
ln (J, A/cm²) @ 0.5 MV/cm
-6
-8
-10
-12
-14
-16
3
5
7
9
11
Molecular layer thickness (nm)
β = 0.006 ± 0.01 nm⁻¹ for constant E
3.69
1.81
0.87
0.31
0.12
Optical power (W/cm²)
Dark

Absorbance of 8.6 nm NAB
in complete junction:



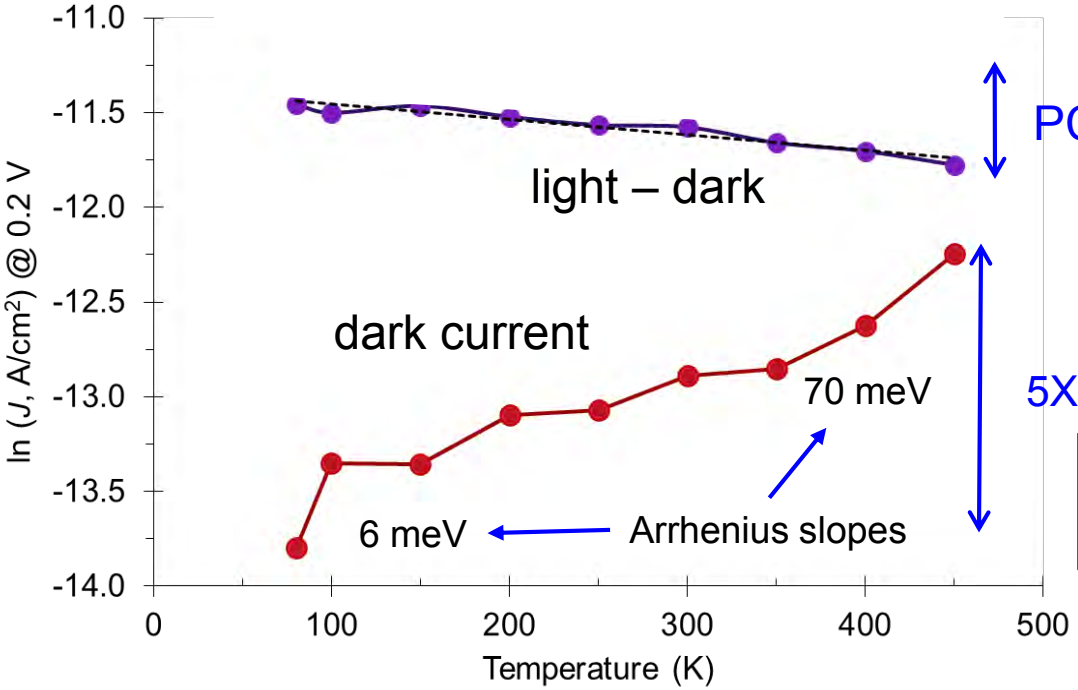




photocurrent tracks in-situ absorbance spectrum, independent of bias for ±0.3 V

Temperature Dependence, V= 0.2 V

Nitroazobenzene, d=7.4 nm

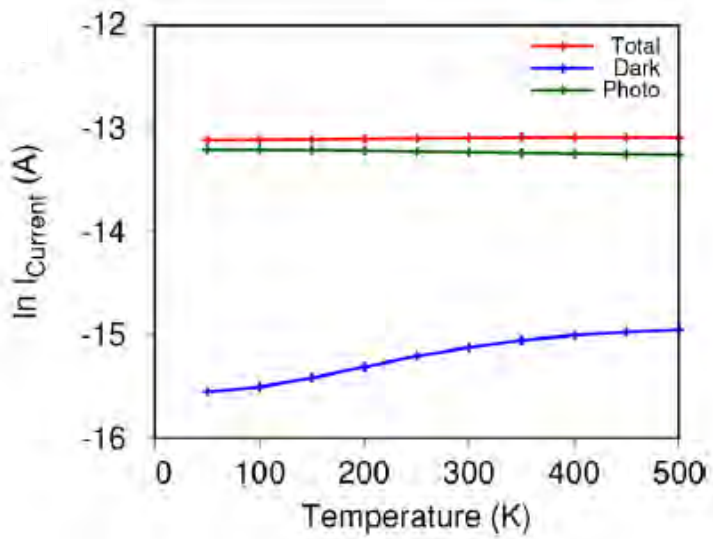


PC *decreases* by 30% for 80 – 450 K

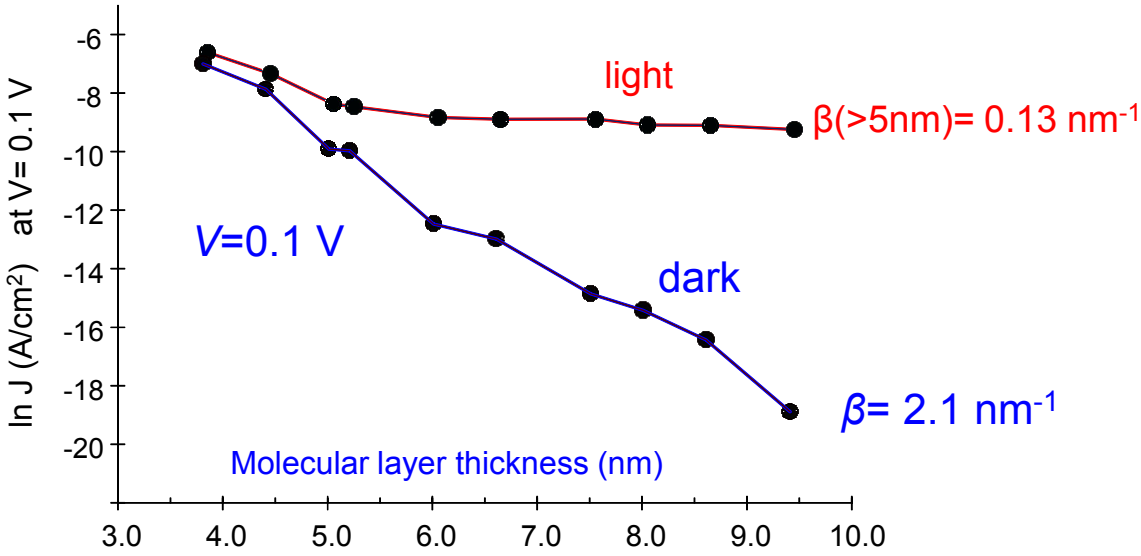
5X for 80 - 450 K

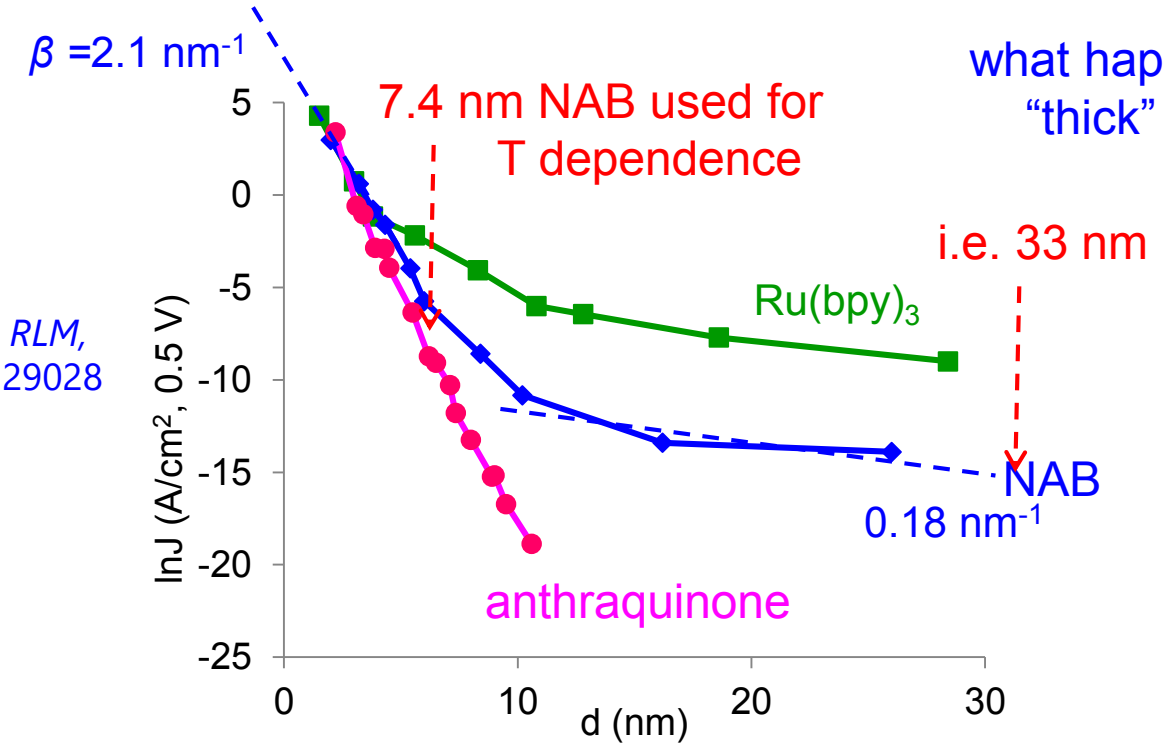
inverse Arrhenius behavior for photocurrent

Theory: Miwa, Morteza, RLM, Galperin: JPC letters **2019**, *10*, 1550

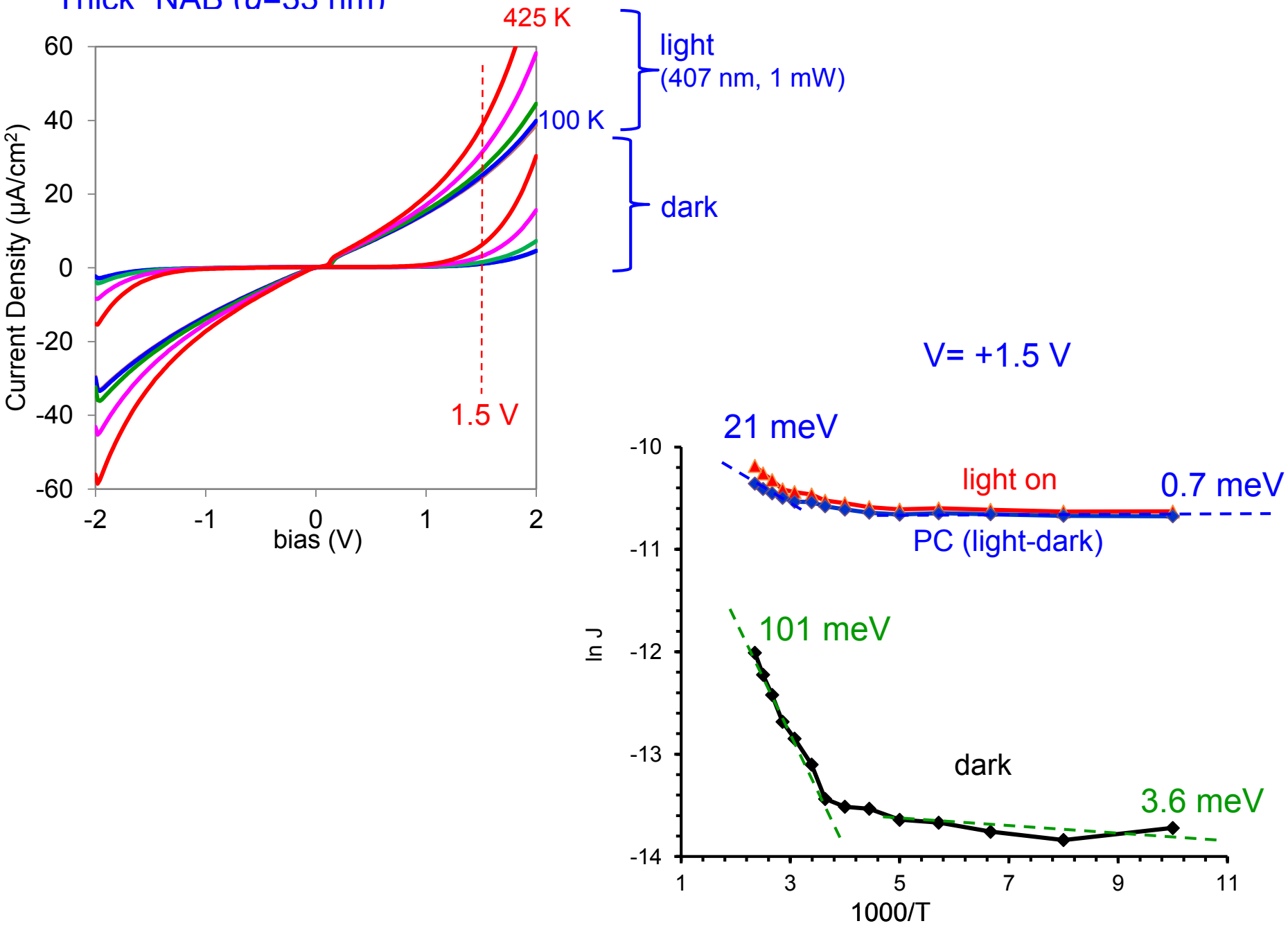


recall β plot:



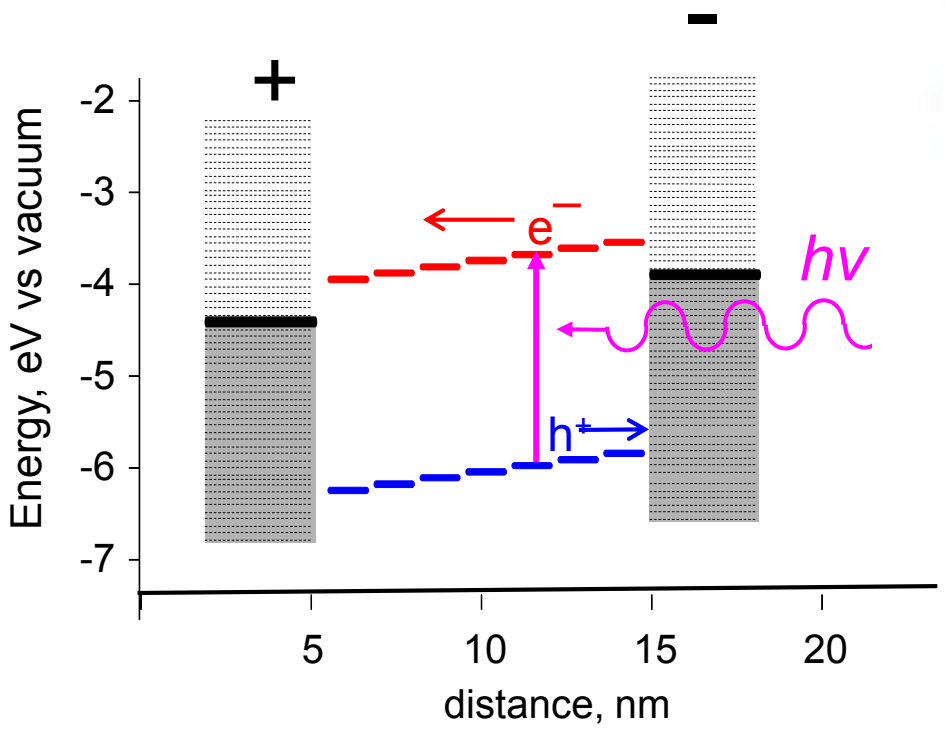


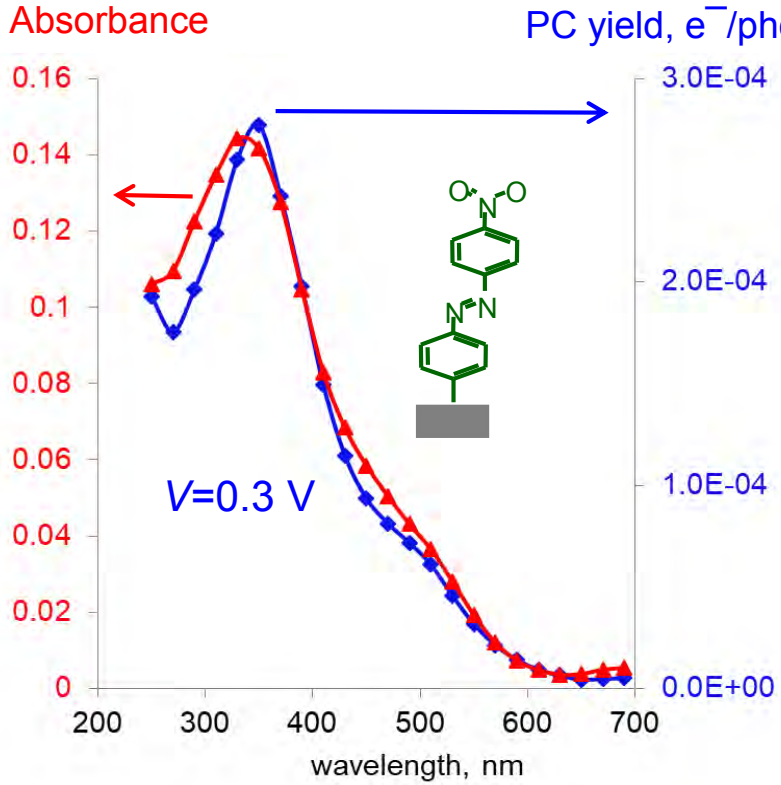
Tefashe,... Lacroix, RLM, JPC-C **2018**, *122*, 29028

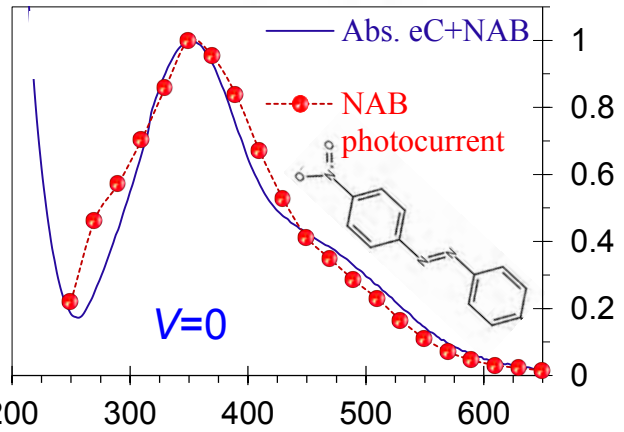

"Thick" NAB (d=33 nm)
425 K
100 K
light
(407 nm, 1 mW)
dark
Current Density (μA/cm²)
bias (V)
1.5 V
V= +1.5 V
21 meV
light on
0.7 meV
PC (light-dark)
101 meV
dark
3.6 meV
ln J
1000/T

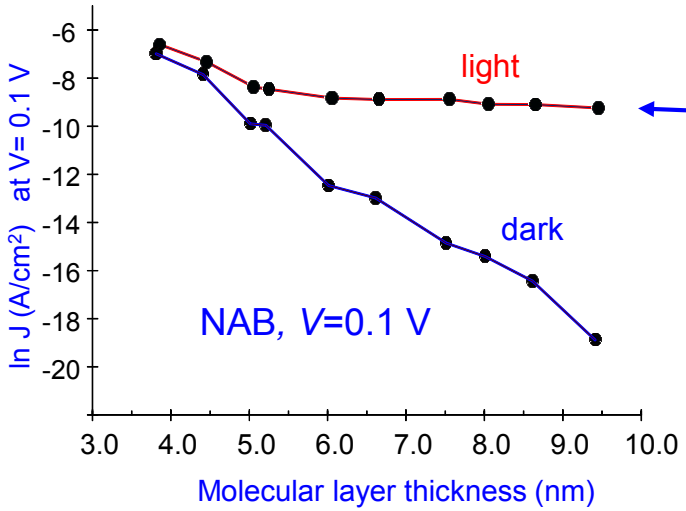
Interim conclusions:

- similarity of absorption and photocurrent spectra indicates optical excitation across H-L gap. (i.e. “band gap spectroscopy”)

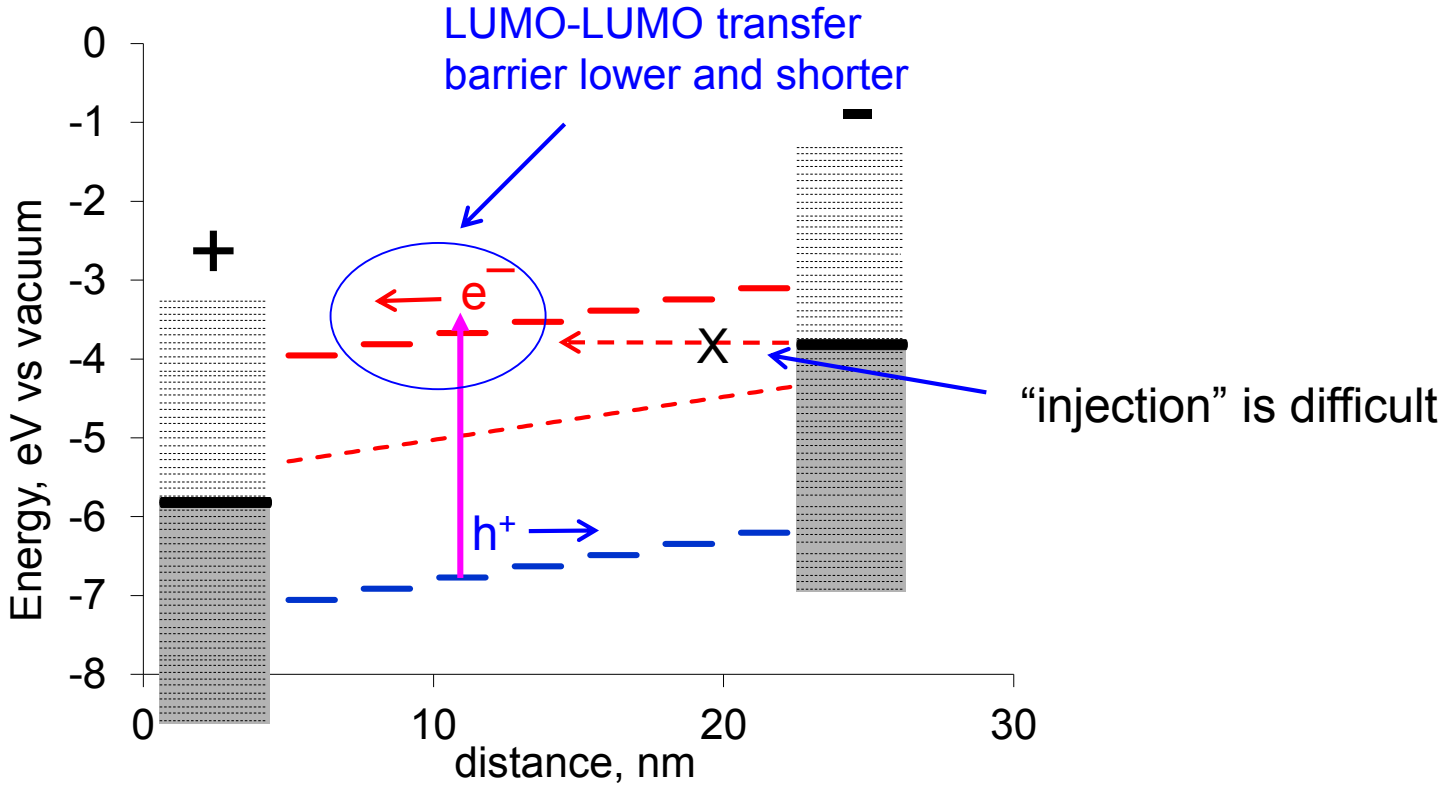




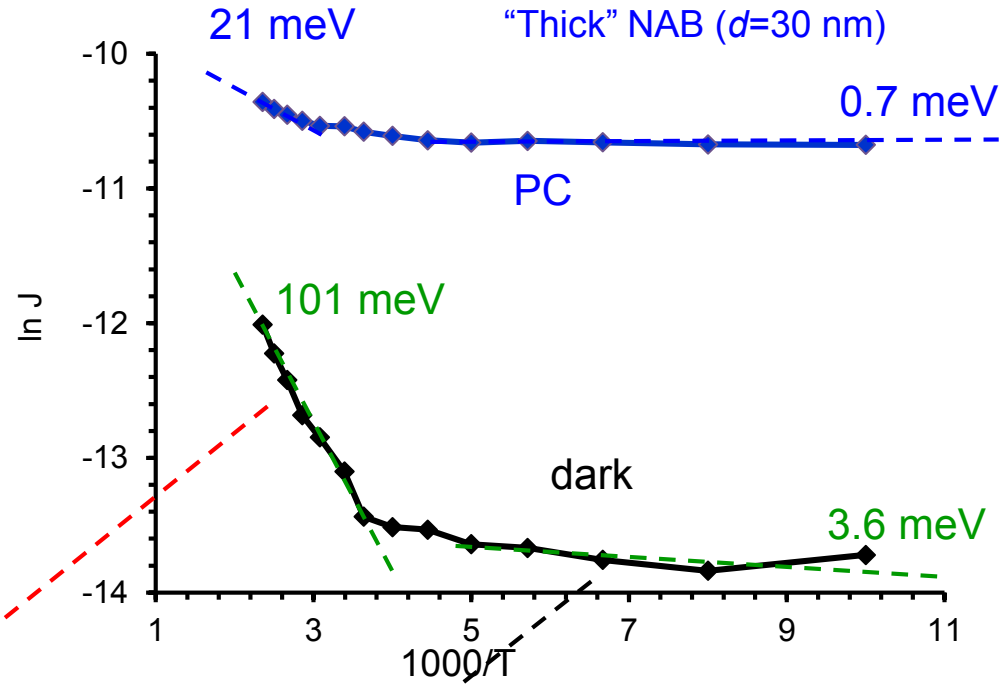


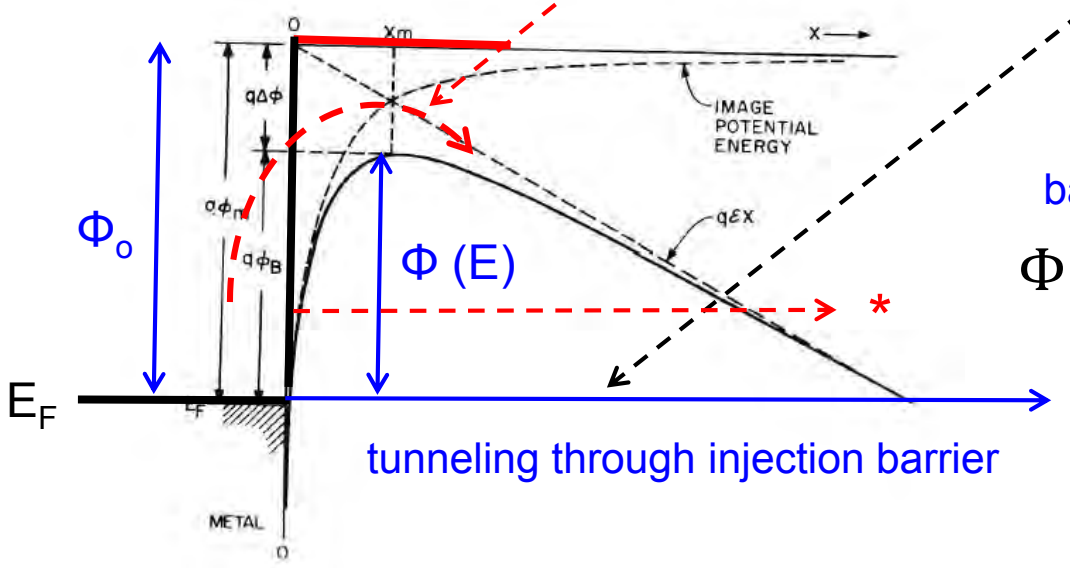


- once the carriers are in the molecular layer, there is minimal attenuation with distance.
- transport is close to "resonant" between LUMOs



- Activation at higher T likely due to thermally assisted tunneling or Schottky-like injection.





barrier lowering by electric field (E)

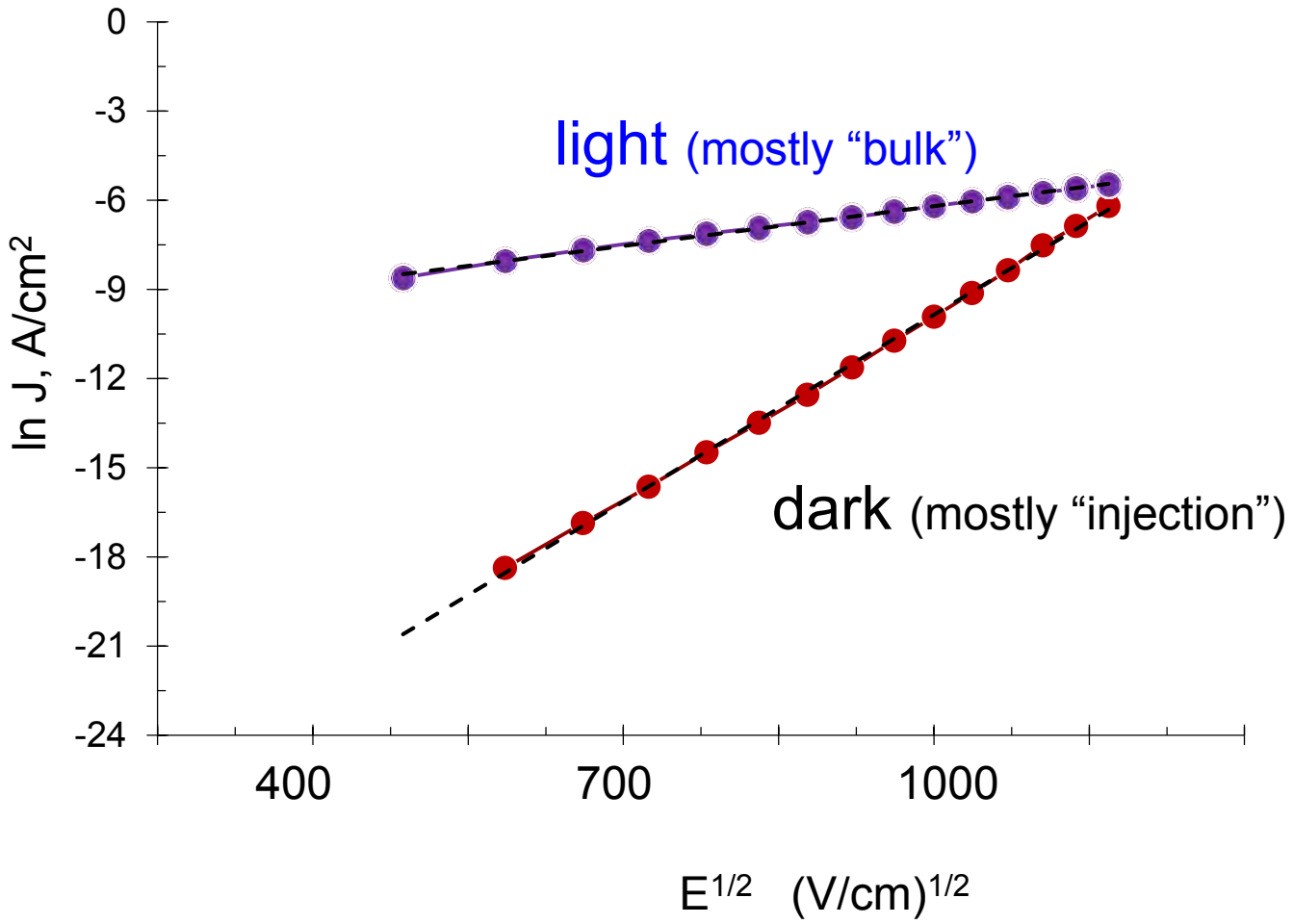
$$\Phi(E) = \Phi_o - \frac{q^{1/2}}{(4\pi\varepsilon\varepsilon_o)^{1/2}} E^{1/2}$$

* "thermally assisted tunneling"

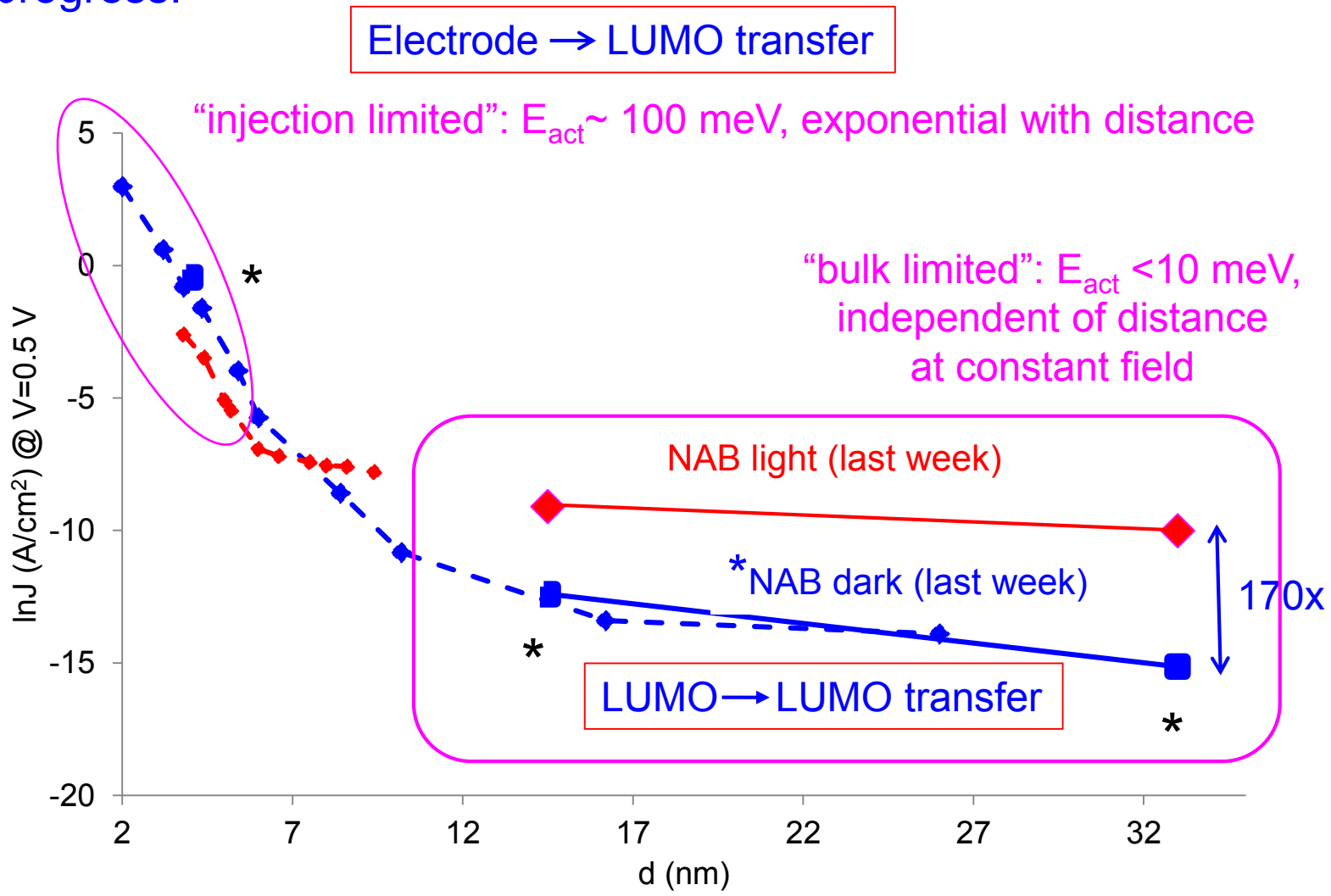
Sze, p. 250

$$\Phi(E) = \Phi_o - \frac{q^{1/2}}{(4\pi\varepsilon\varepsilon_o)^{1/2}} E^{1/2}$$

- since barrier height is linear with $E^{1/2}$, we expect ln J to be linear with $E^{1/2}$:



Plot in progress:



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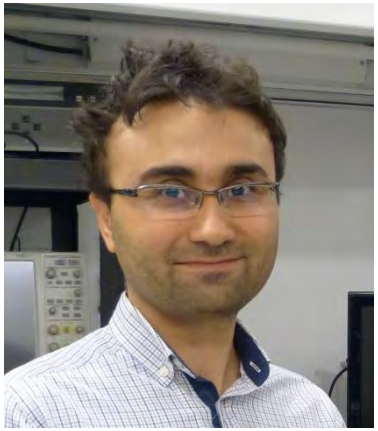

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