Scanning Probe Microscopy on Active Polymer Solar Cells

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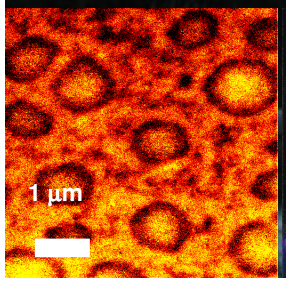

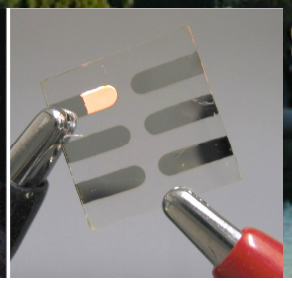

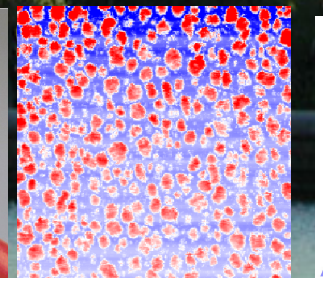

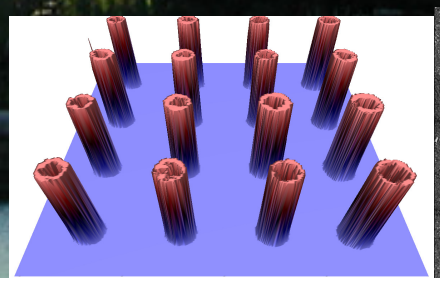

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Group Members:
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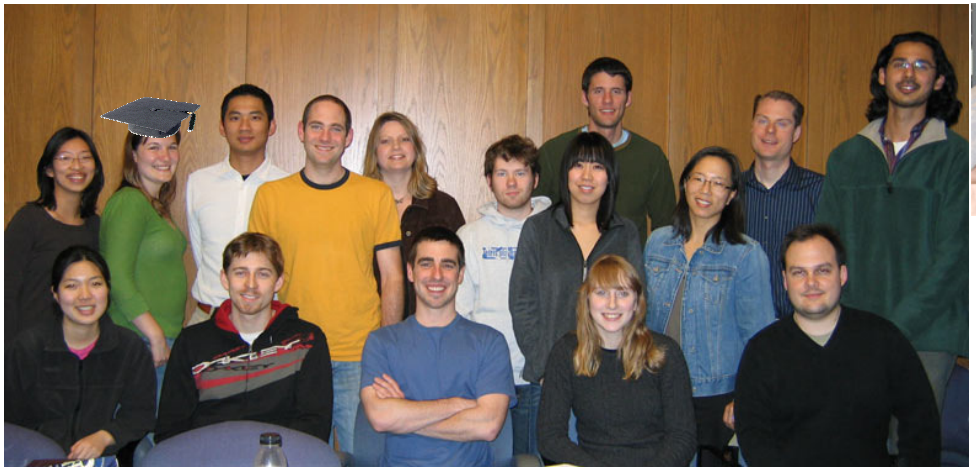

Undergrads Co-Authoring Papers:
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Ilan Jen-La Plante (to Berkeley PhD)
Jessica Smith (to Berkeley PhD)
Marsha Ng (to UW MS)

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Christine Luscombe, Mehmet Sarikaya, Dan Schwartz, Francois Baneyx, Sam Jenekhe, Guozhong Cao, Daniel Gamelin, Lee Park (Williams College)

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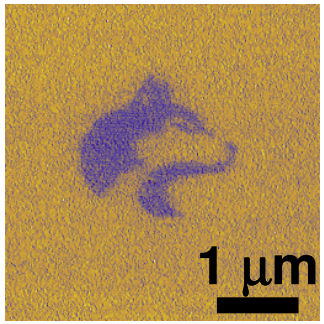
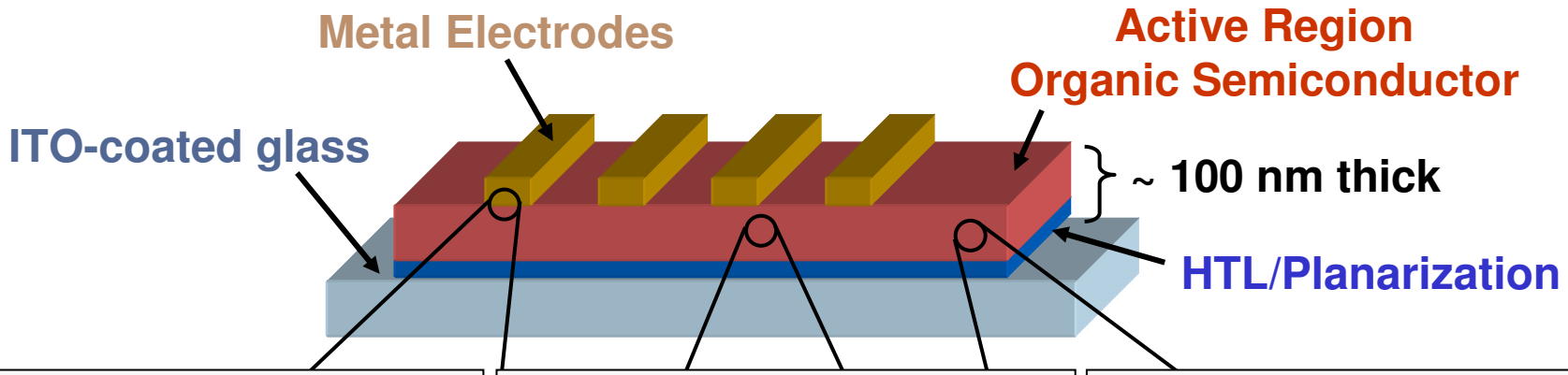
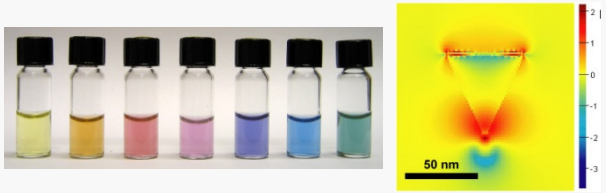
NSF UW MRSEC/"GEMSEC"



Physical Chemistry of Organic Electronics



optical processes near metals



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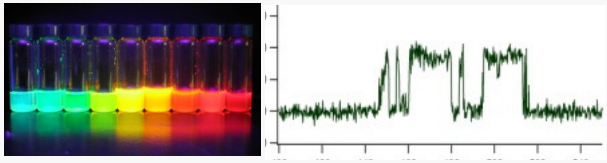
quantum dot chromophores



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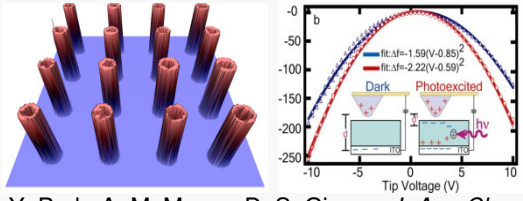
film morphology



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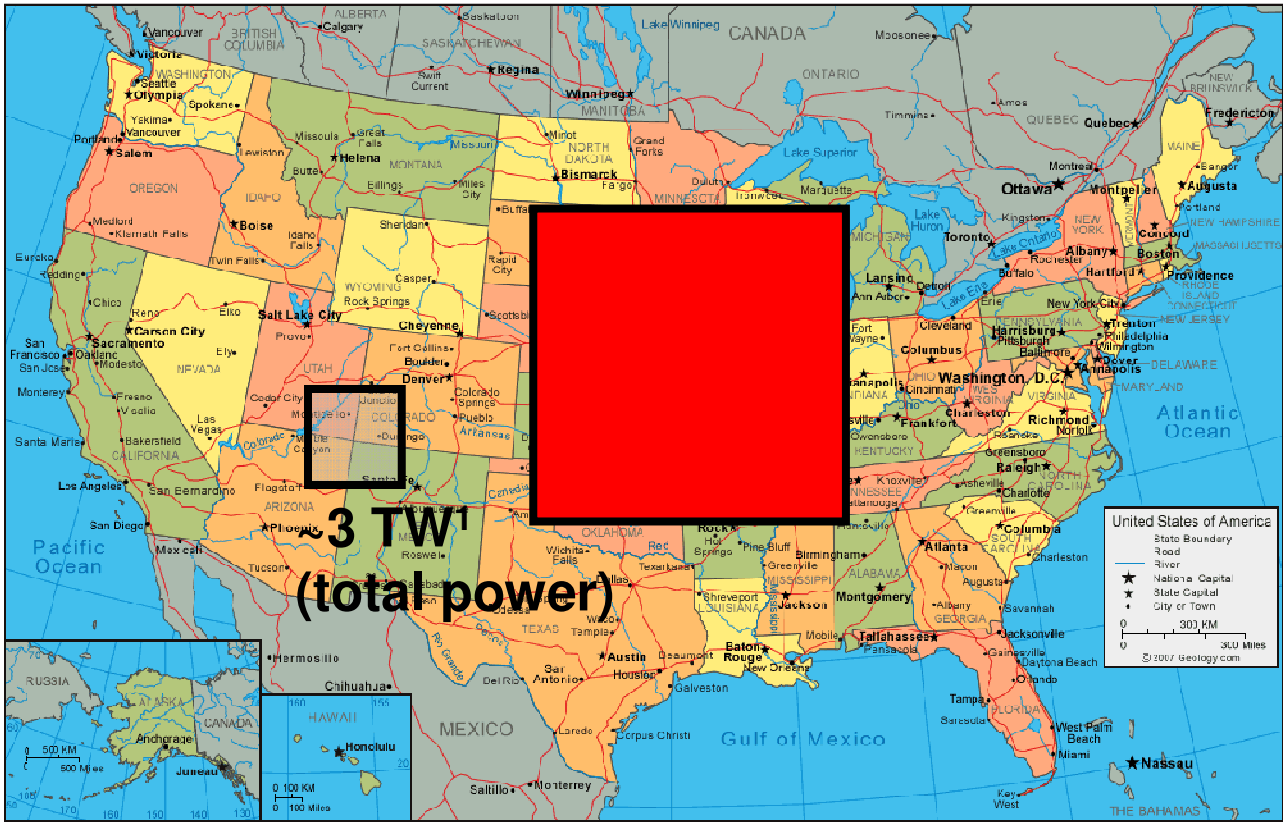
Perspective on Scale

We need **Really Big** Solar Cells



North American polyethylene capacity[4] could cover Arizona with >4 layers of plastic wrap every year[5]

~300 days of newspape

Cell Area ~ 10^{11} m^2

US Roadway:[3] ~ 10^{10}-10^{11} m^2

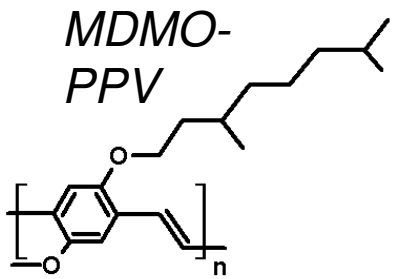
rooftop capacity: 540 GW (18% of total energy)[2]

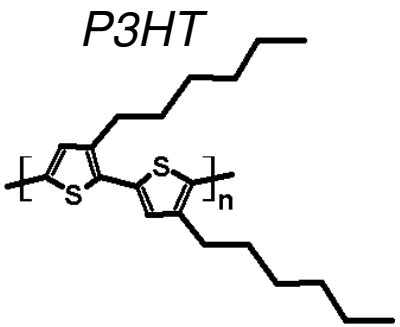
25% of highway area = 100% of electricity[2]

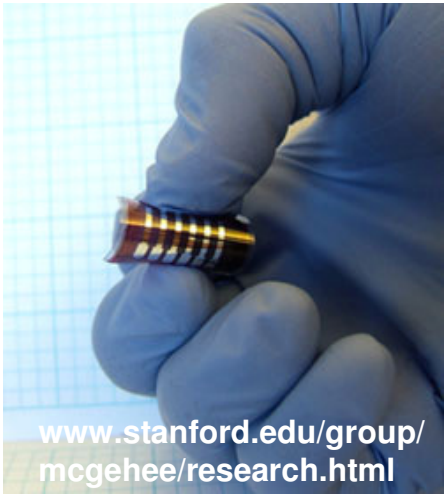
1: http://www.ipcc.ch/pdf/assessment-report/ar4/wg3/ar4-wg3-chapter4.pdf
2: http://www1.eere.energy.gov/solar/pdfs/set_myp_2007-2011_proof_1.pdf
3: https://www.cia.gov/library/publications/the-world-factbook/print/us.html
4: 30 billion pounds: http://www.the-innovation-group.com/ChemProfiles/Polyethylene-HD.htm Note: Polyethylene is NOT a semiconductor
5: given 0.5 mil thickness of "Glad wrap" = ~12.5 microns thick = http://www.glad.com/faqs/plasticwrap.php
6: circulation data USA today

Plastic Semiconductors are Printable

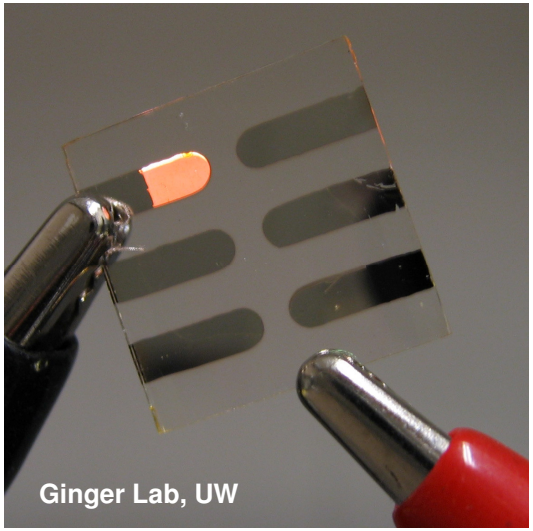
C&EN / Konarka





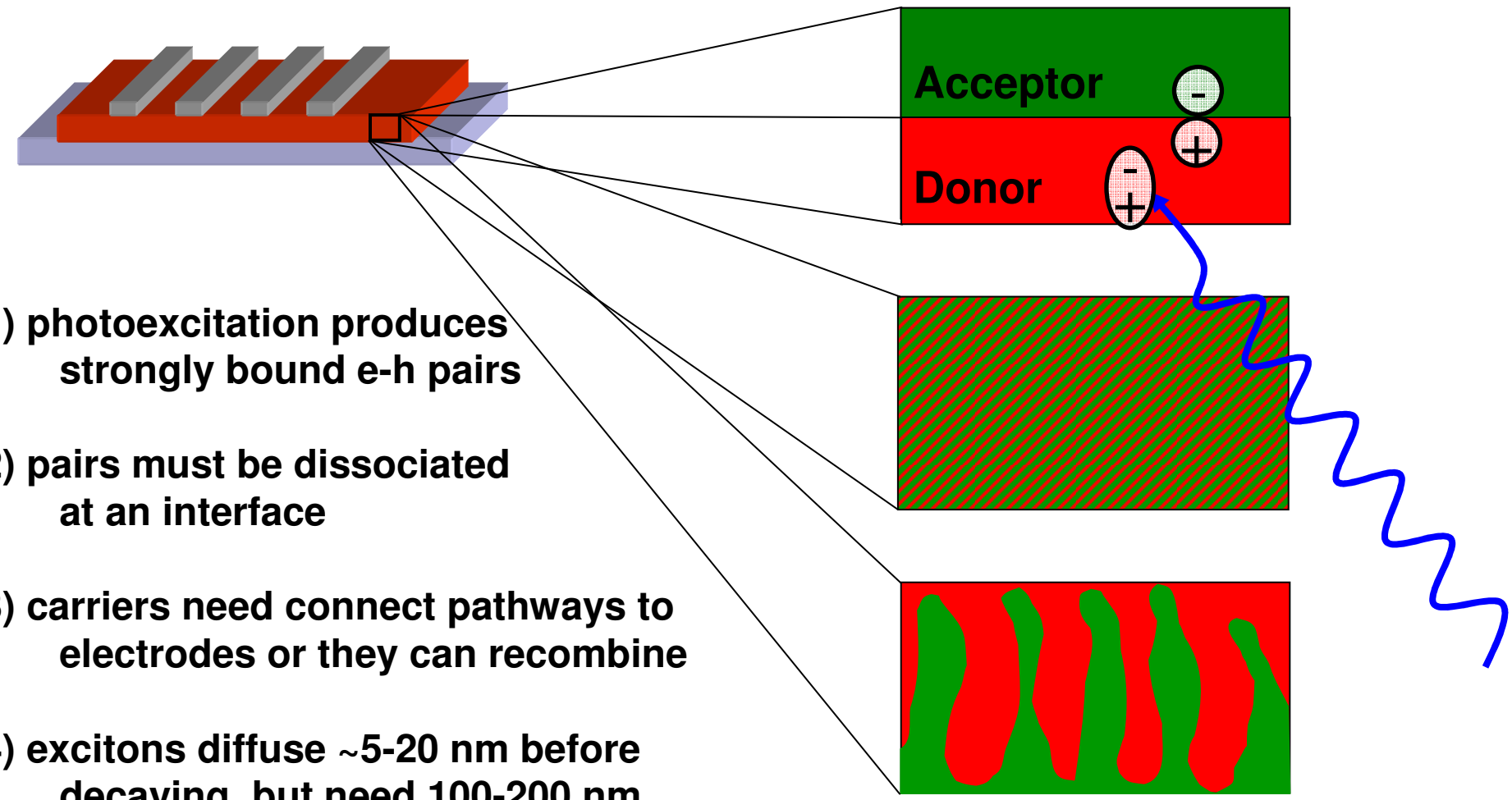


ink jet printed flat panel TV



Polymer Cells are Excitonic Solar Cells

film morphology critical to polymer photovoltaic performance



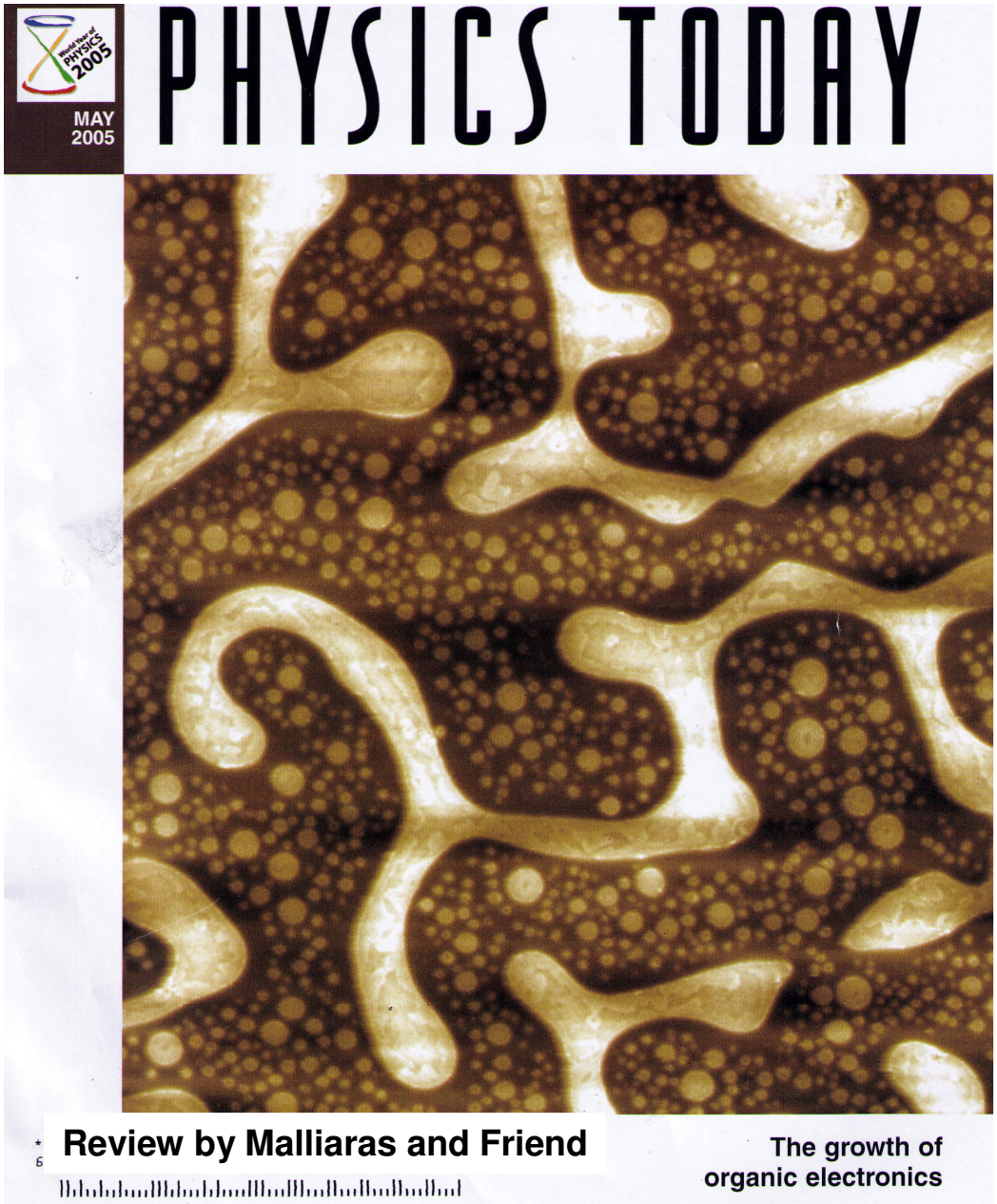
1) photoexcitation produces strongly bound e-h pairs

2) pairs must be dissociated at an interface

3) carriers need connect pathways to electrodes or they can recombine

4) excitons diffuse ~5-20 nm before decaying, but need 100-200 nm thick film to absorb incident light

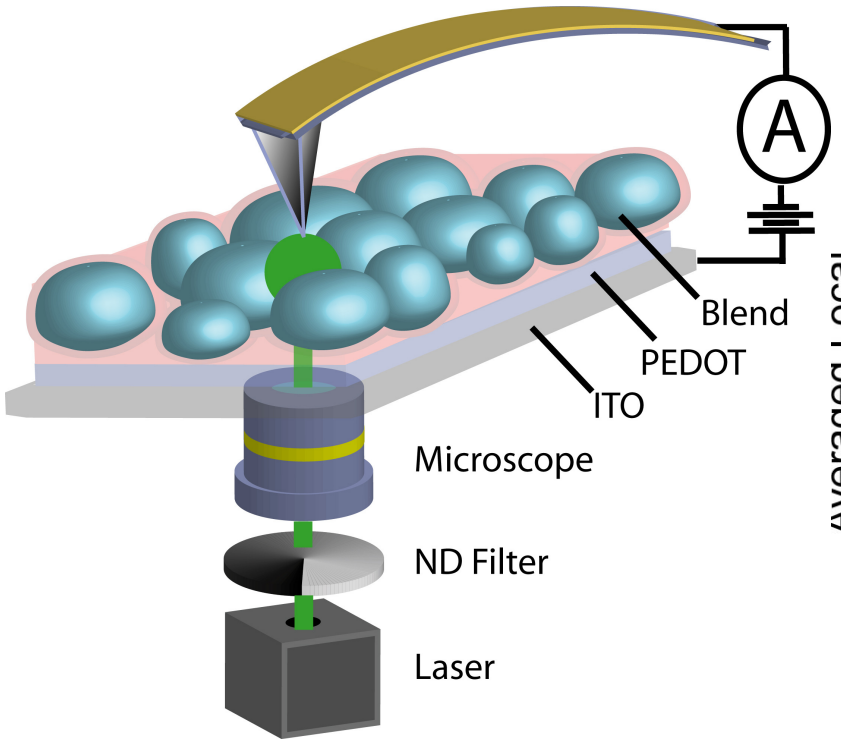
Morphology is a critical challenge

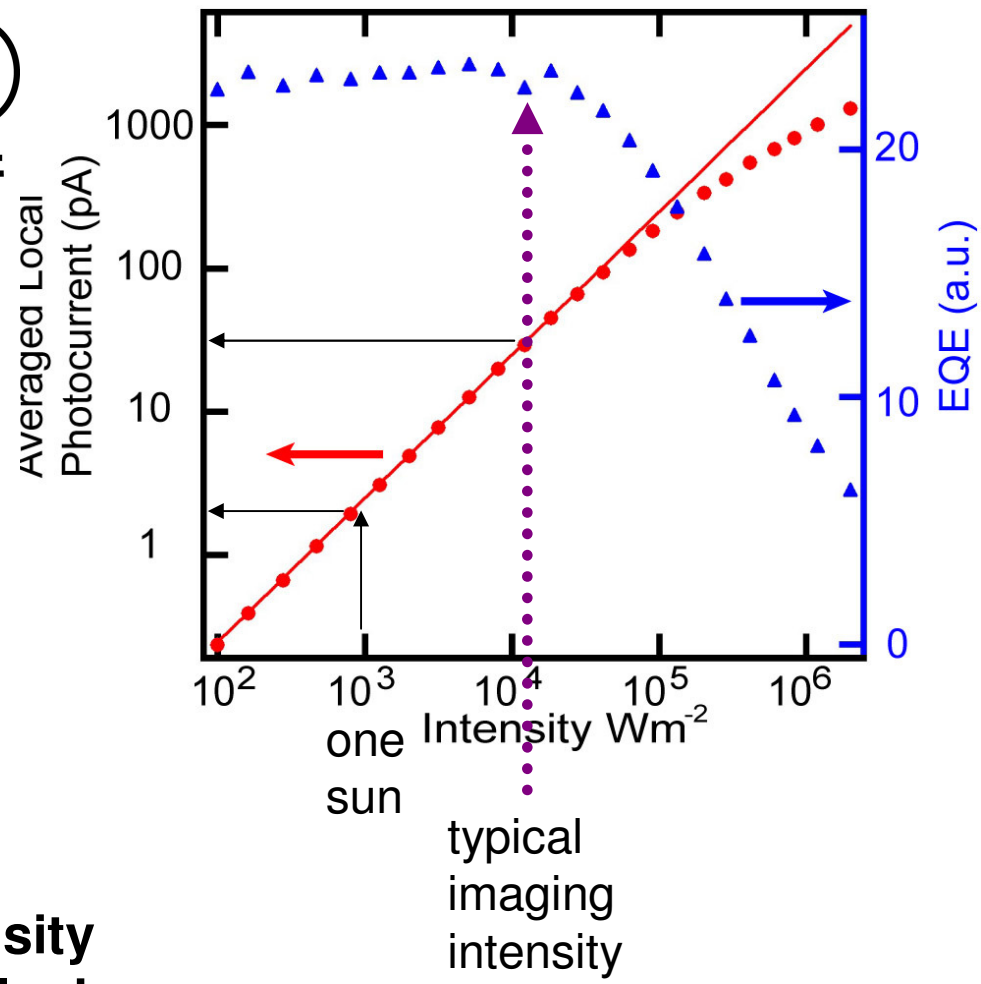


1) Can we develop tools to measure electronic properties (photocurrents, trapping rates, etc.)

2) Can we control film morphology (texture?)

Photoconductive AFM



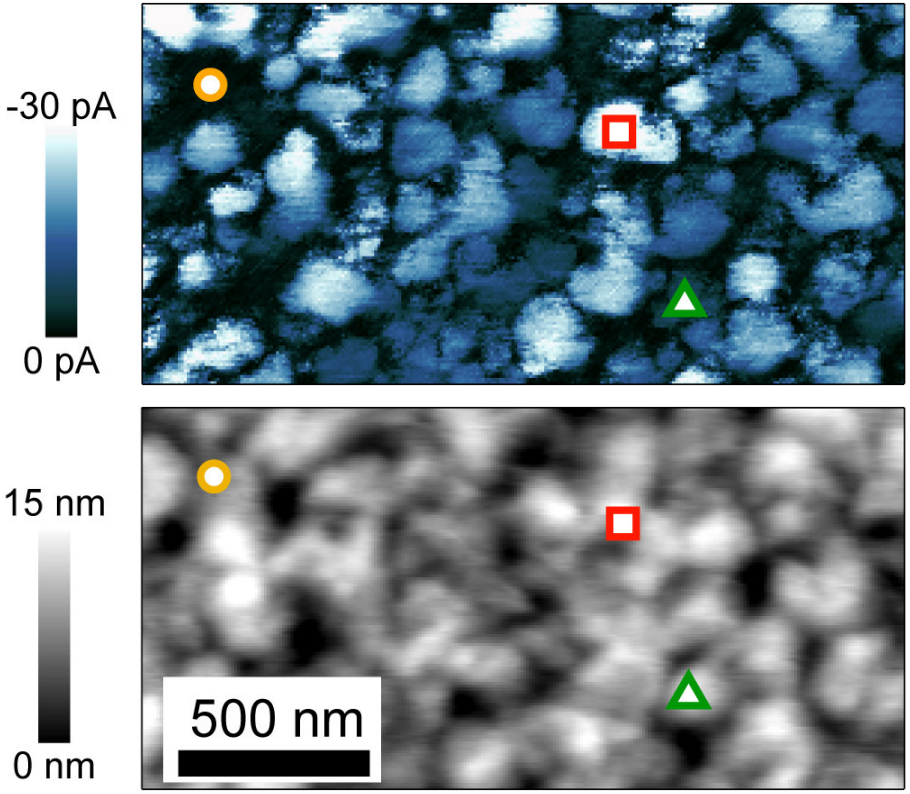


D.C. Coffey, O.G. Reid, D.B. Rodovsky, G. P. Bartholomew, D.S. Ginger, *Nano Letters* 7 p738 (2007)

Small focus allows: 1) high intensity
2) less sample damage

MDMO-PPV/PCBM

Results: Photocurrent Variation



spin-coated from xylenes

Current

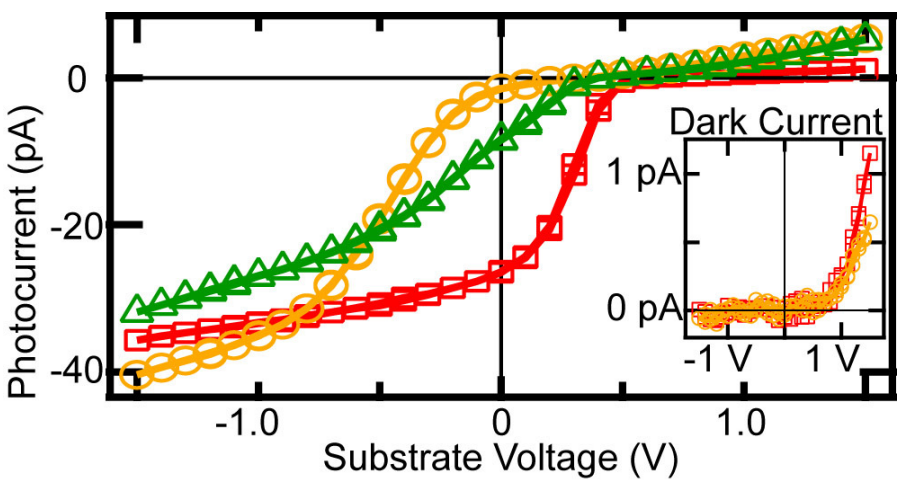
J_{SC}

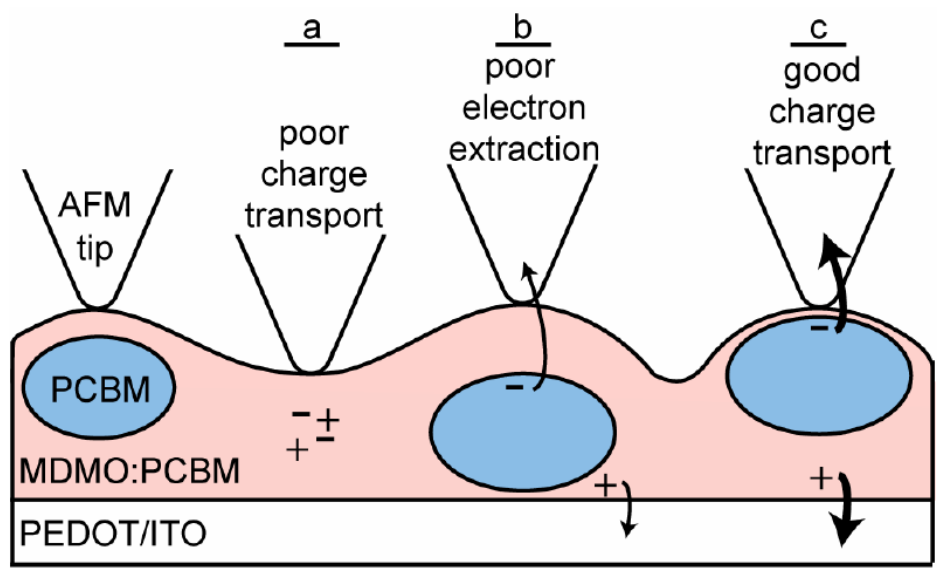
FF

V_{OC}

all vary with location

Height

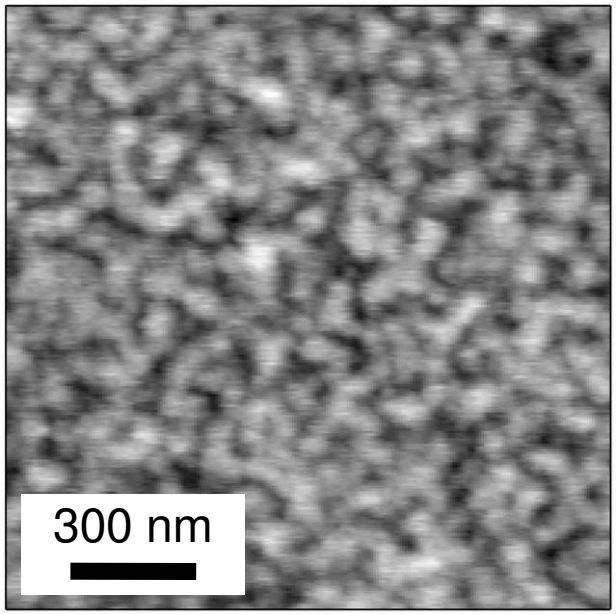




Variation in Chlorobenzene Blends

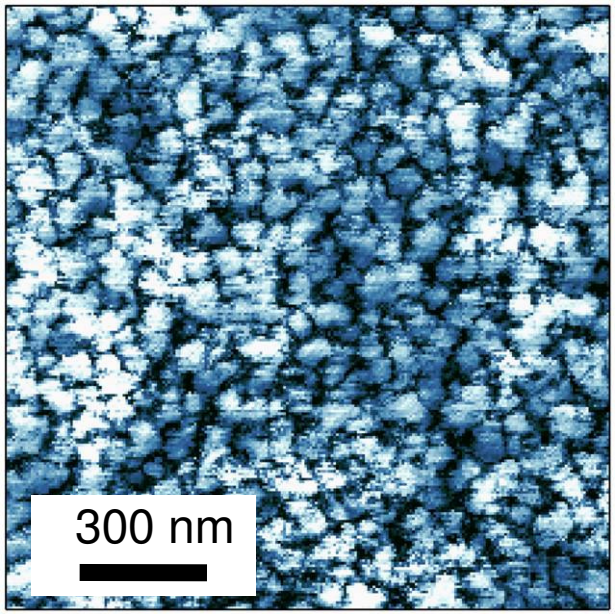
Current fluctuations on 2 length scales

Height



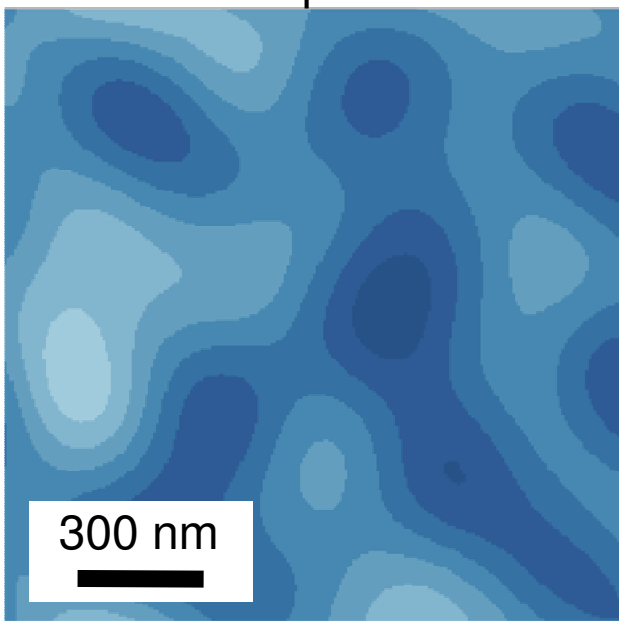
0 nm 10 nm

Photocurrent



0 pA -14 pA

Photocurrent after FFT low pass filter

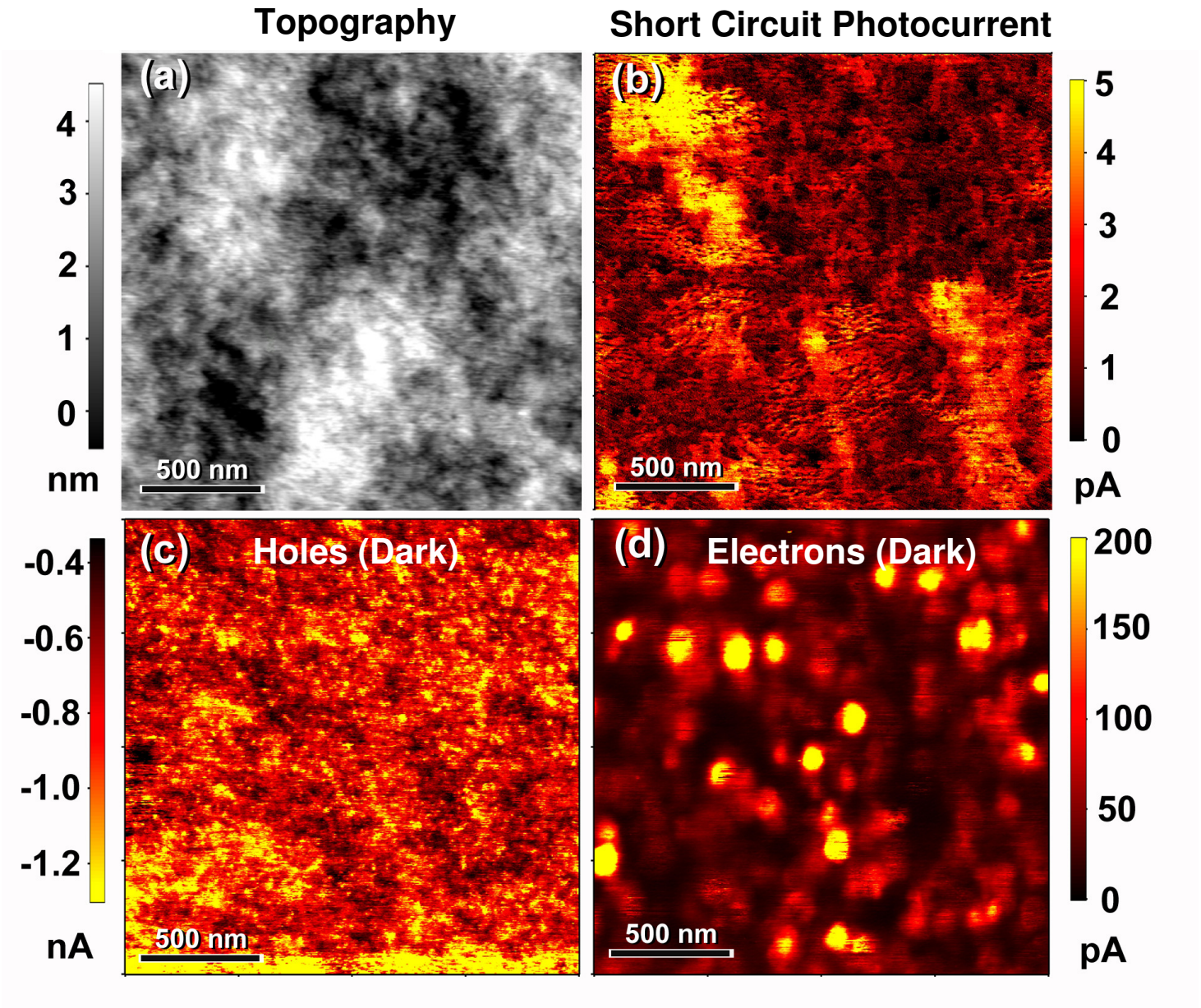


0 pA -14 pA

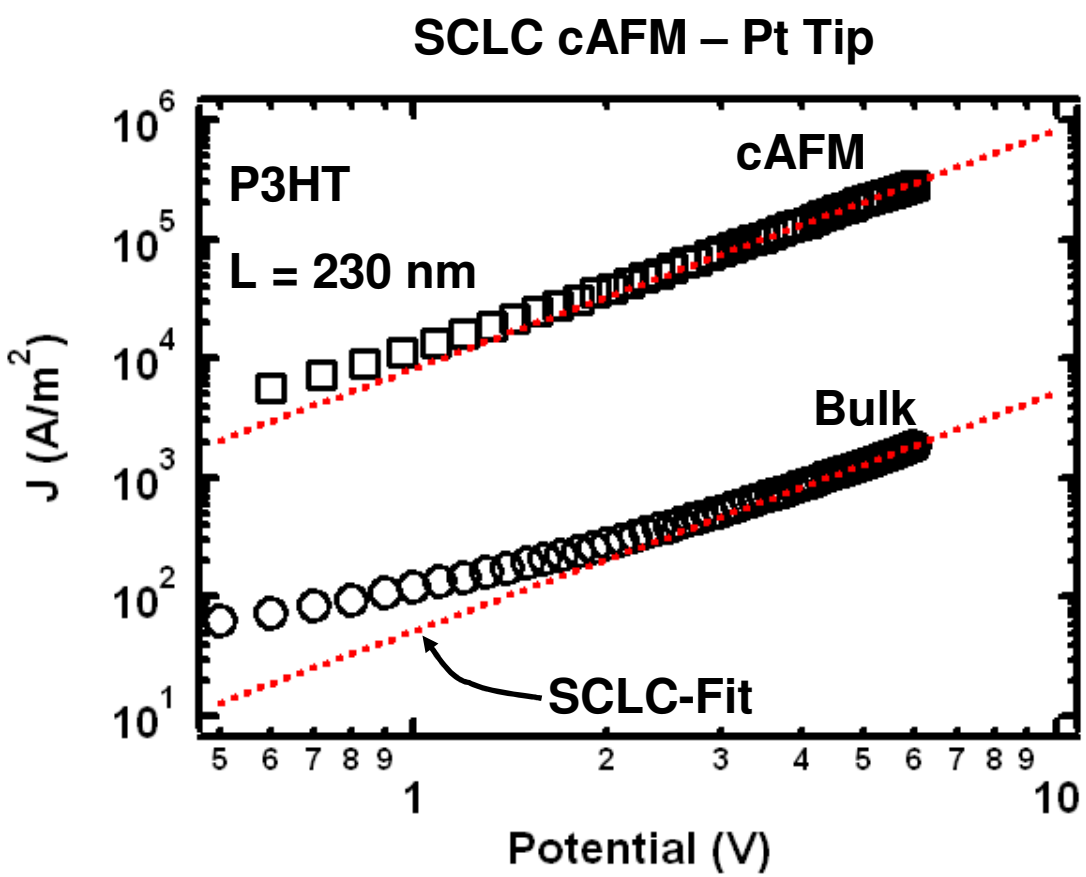
$$\sigma_I = 0.57 < I >$$

Good news: there is room to improve these devices with existing materials
However, source of large-scale variation unknown…suspect bottom contact ITO, PEDOT?

Annealed P3HT/PCBM Blends



Looking at Local Charge Transport



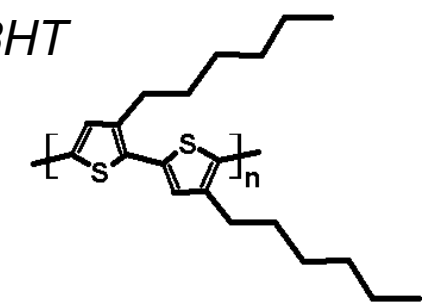
Mott-Gurney Law gives WRONG mobility in cAFM measurements (but is widely used!)

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{L^3}$$

Space Charge Limited Currents

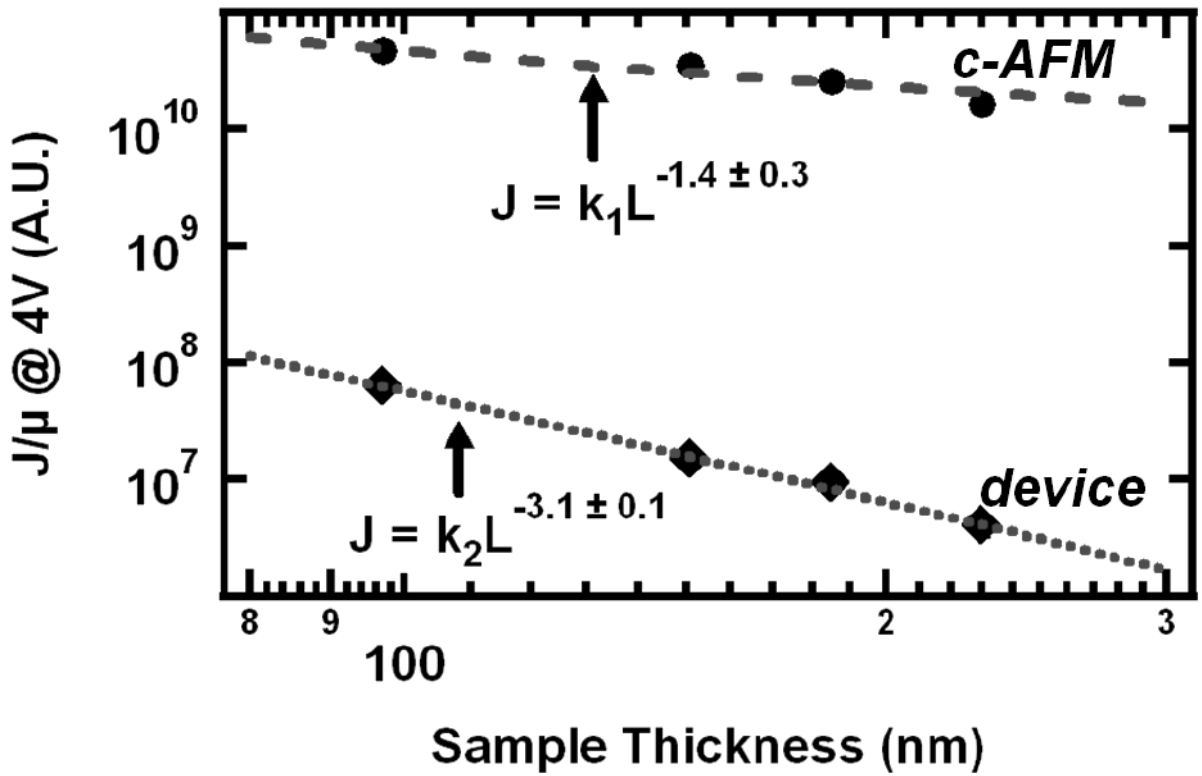
$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu_0 e^{0.89\gamma\sqrt{\frac{V}{L}}}\frac{V^2}{L^3}$$

P3HT



O. G. Reid, K. Munechika, D. S. Ginger *Nano Lett.* 8(6): 1602-1609 (2008).

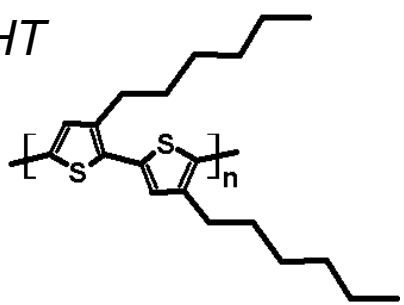
cAFM and Mott-Gurney Law



$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{L^3}$$

Clear deviation from distance dependence of Mott-Gurney law in cAFM

P3HT



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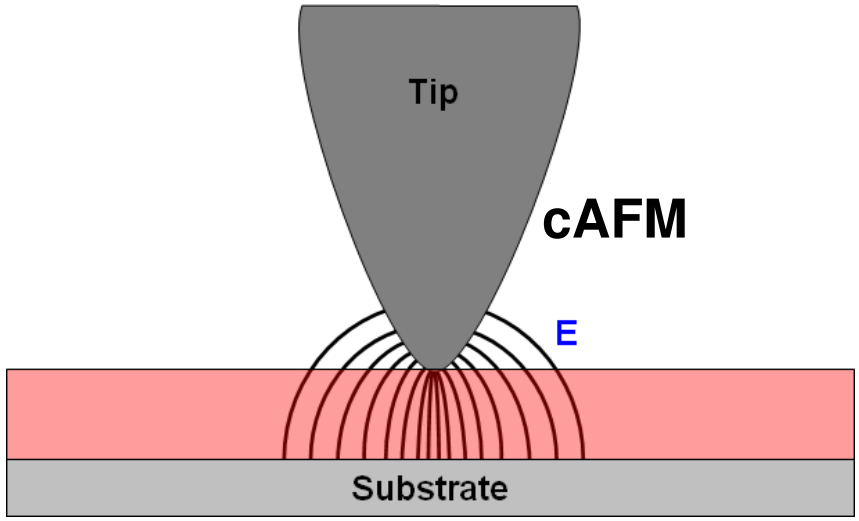
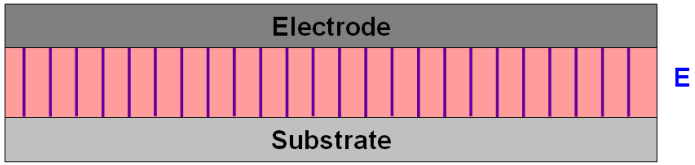
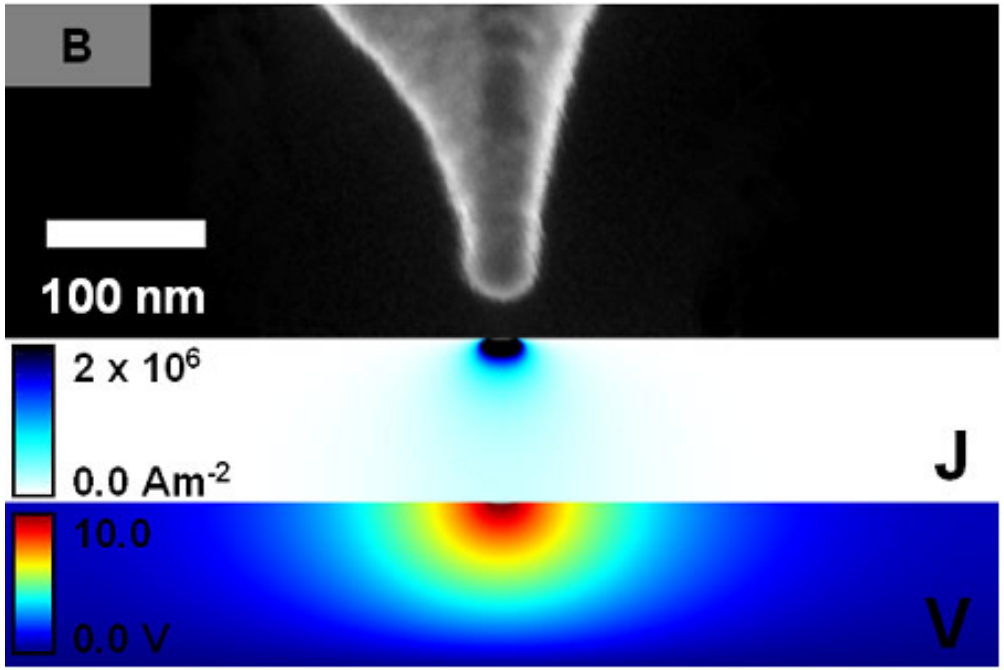
cAFM and Mott-Gurney Law



Device



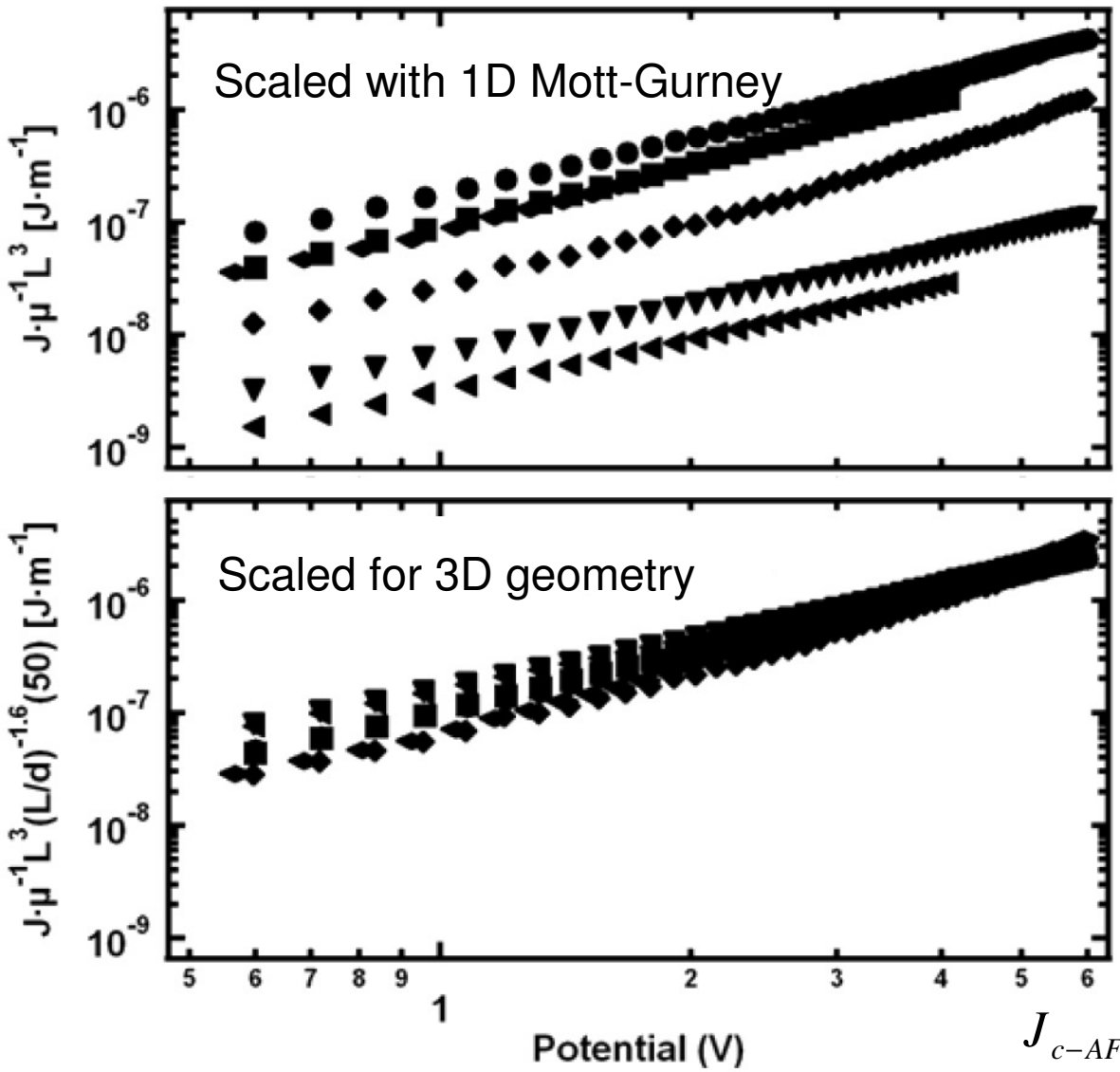


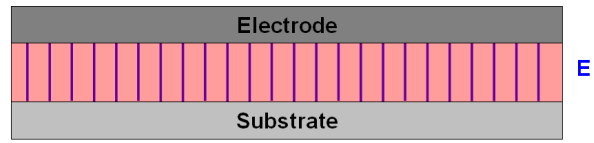
Numerically solve:

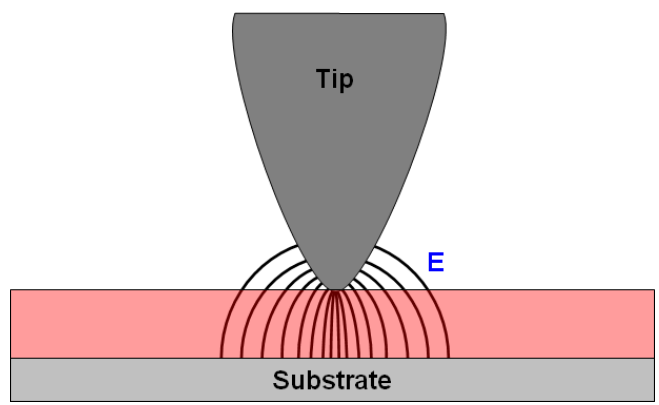
$$\frac{-d\rho}{dt} = \nabla \cdot \left(\mu\rho\nabla V + D\nabla\rho\right)$$

$$-\nabla^2 V = \frac{\rho}{\varepsilon}$$

Geometry Accounts for Deviation



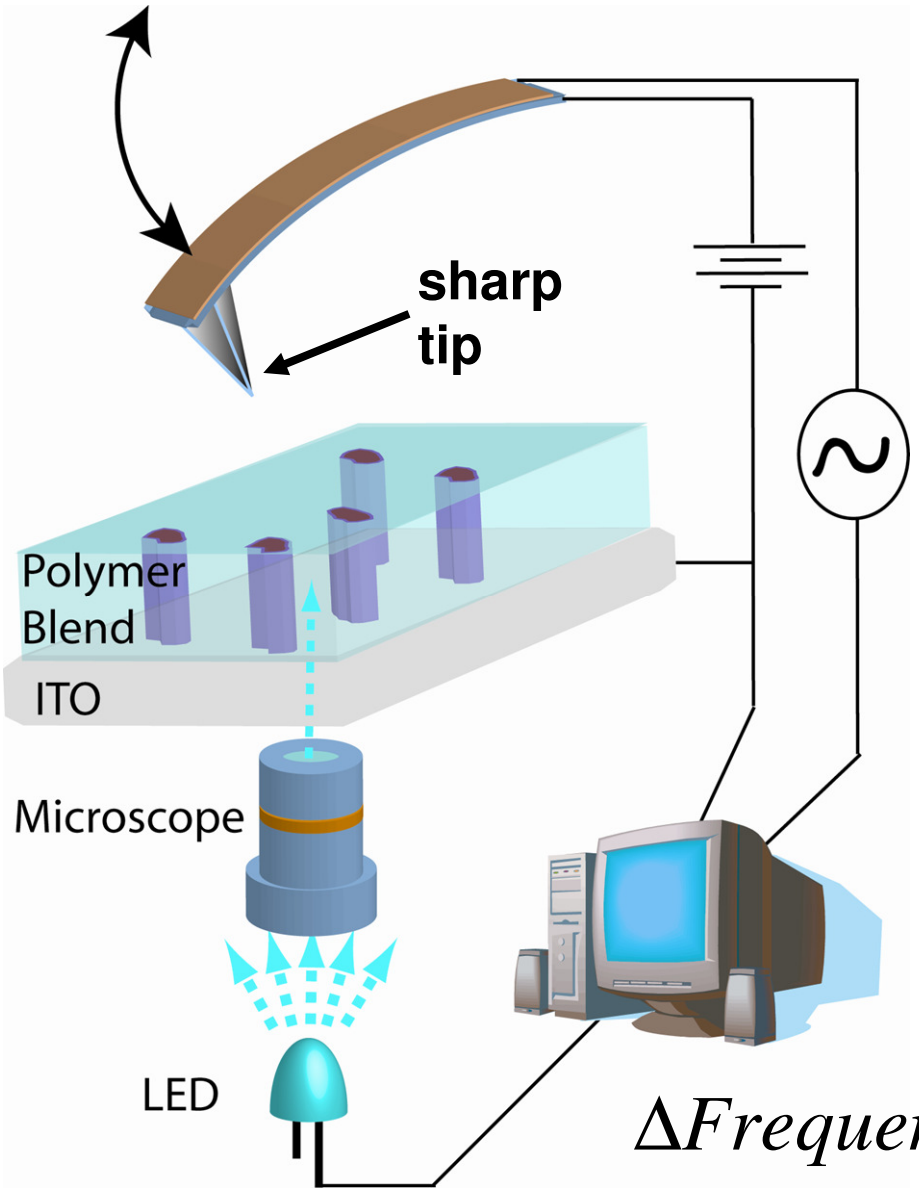




$$J_{c-AFM} = \alpha\mu_0 e^{0.89\gamma\sqrt{\frac{V}{L}}} \varepsilon\varepsilon_0 \frac{V^2}{L^3} \delta\left(\frac{L}{d}\right)^{1.6\pm0.1}$$

O. G. Reid, K. Munechika, D. S. Ginger *Nano Lett.* 8(6): 1602-1609 (2008).

Electrostatic Force Microscopy (EFM)



An AC mode AFM technique:

$$\Delta\omega_{resonant} = -\frac{\omega_o}{2k}\frac{\partial Force}{\partial z}$$

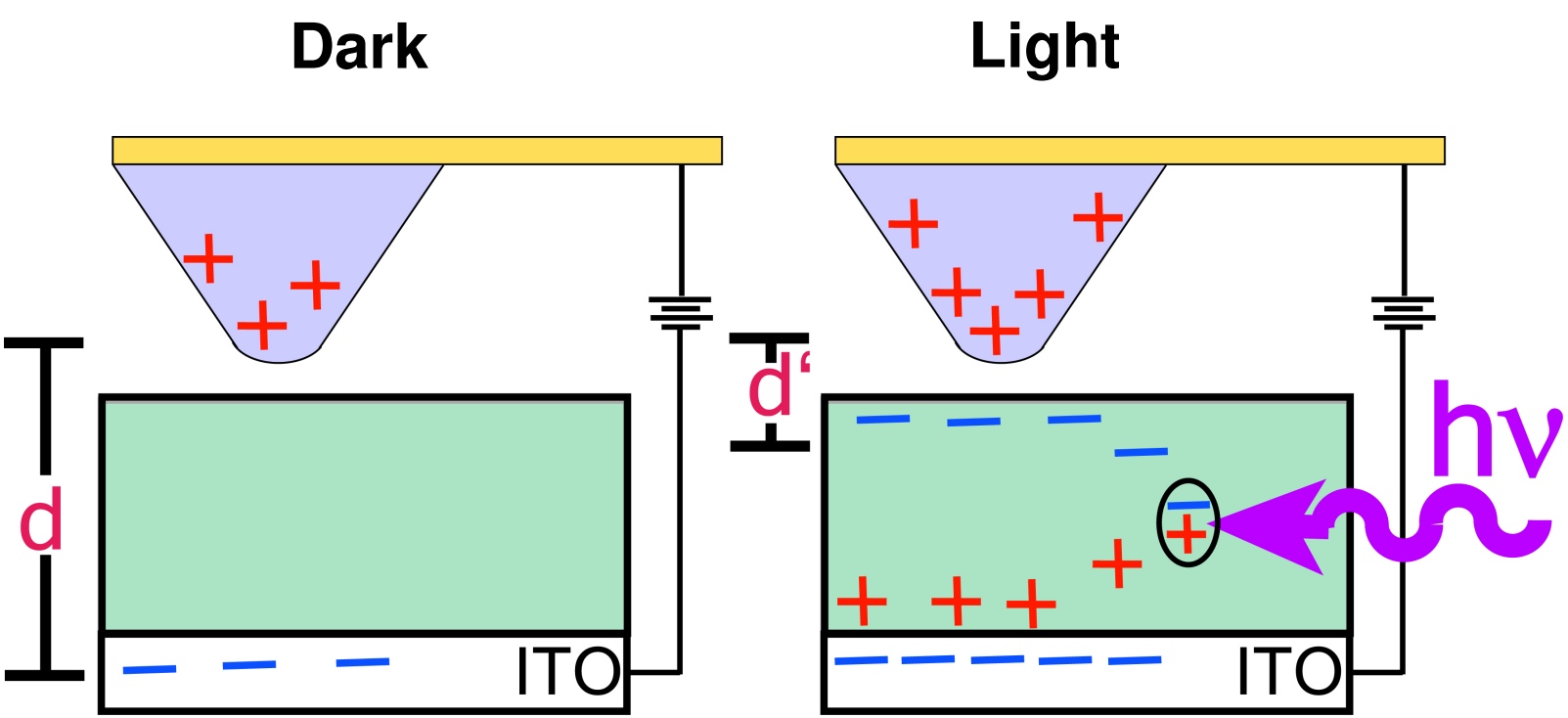
$$Force = \frac{1}{2}\frac{\partial C}{\partial z}\left(V_{tip} - V_{surface}\right)^2$$

Charge distribution and dielectric

Surface Potential

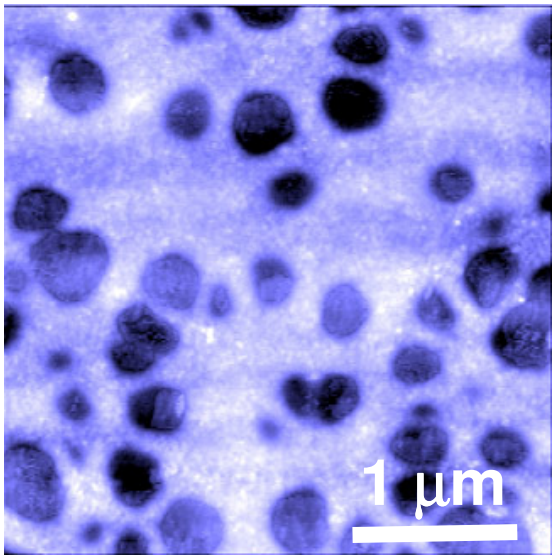
$$\Delta Frequency = -\frac{\omega_o}{4k}\frac{\partial^2 C}{\partial z^2}\left(V_{tip} - V'_{surface}\right)^2$$

Carriers Change V_{surf} and d^2C/dz^2



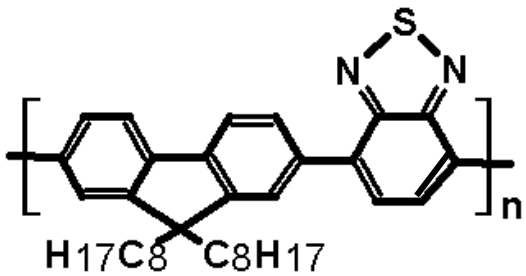
$$\Delta Frequency = -\frac{\omega_o}{4k}\frac{\partial^2 C}{\partial z^2}\left(V_{tip} - V'_{surface}\right)^2$$

Where does the photocurrent come from?

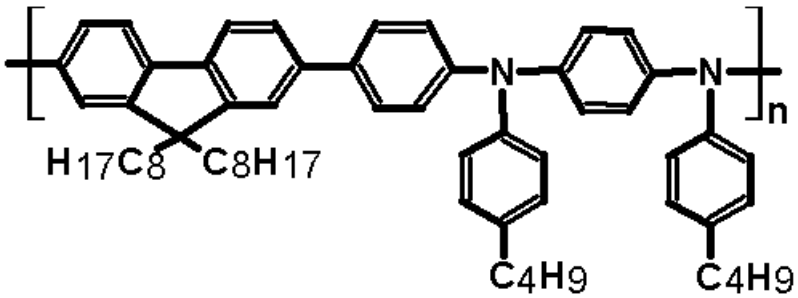


"We observe a linear trend, giving substantial evidence that the external quantum efficiency scales with the interfacial area between the mesoscale phase separated regions." Snaith et al. *Nano Lett.* p1353-1357 (2002)

"…measurements show that current is generated within the bulk and not at the boundaries of the micron-sized phase segregated features" McNeill et al., *Nano Lett*. p2503-2507 (2004)



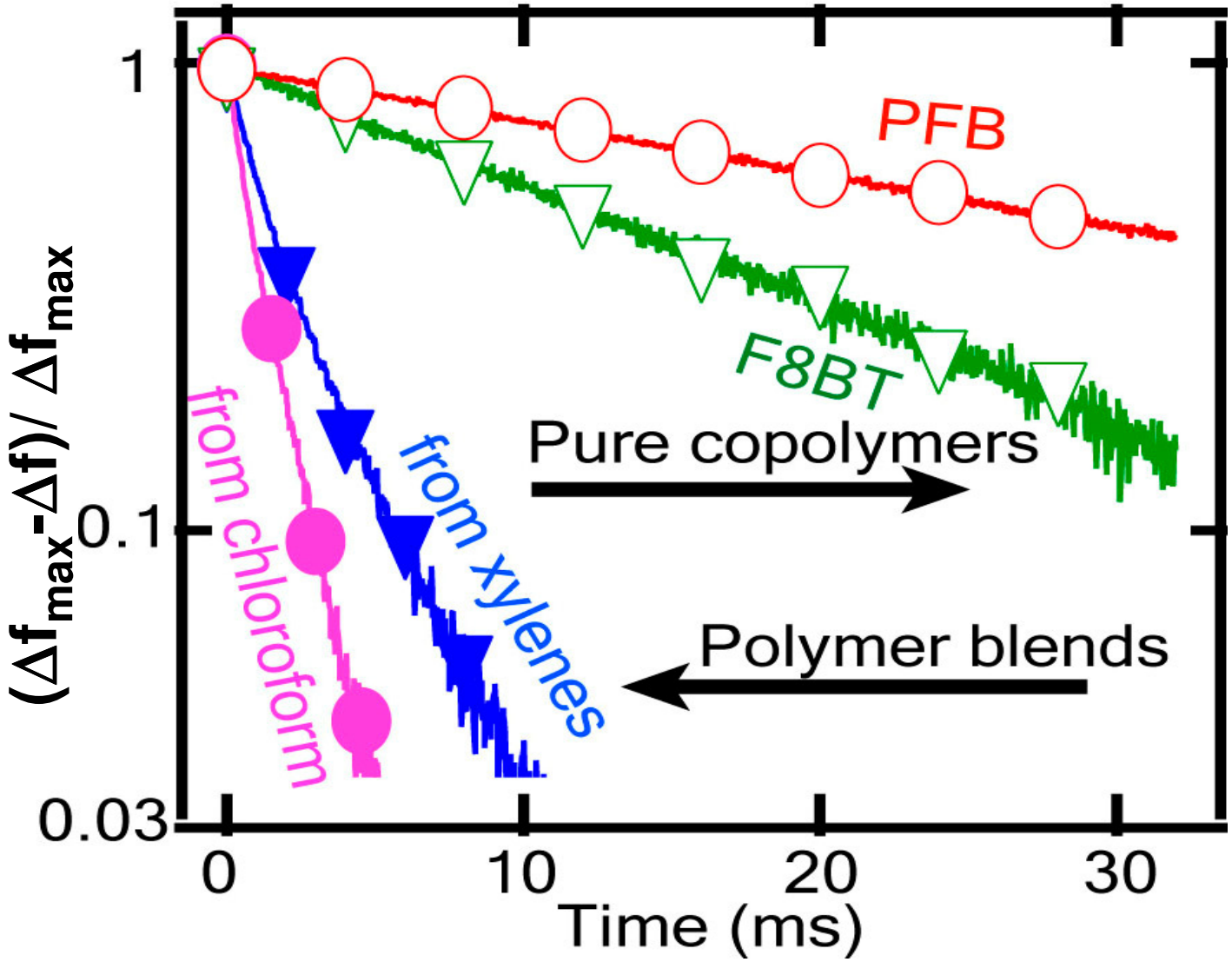
"F8BT"



"PFB"

Friend
Dastoor
Arias
Silva
Snaith
et al.

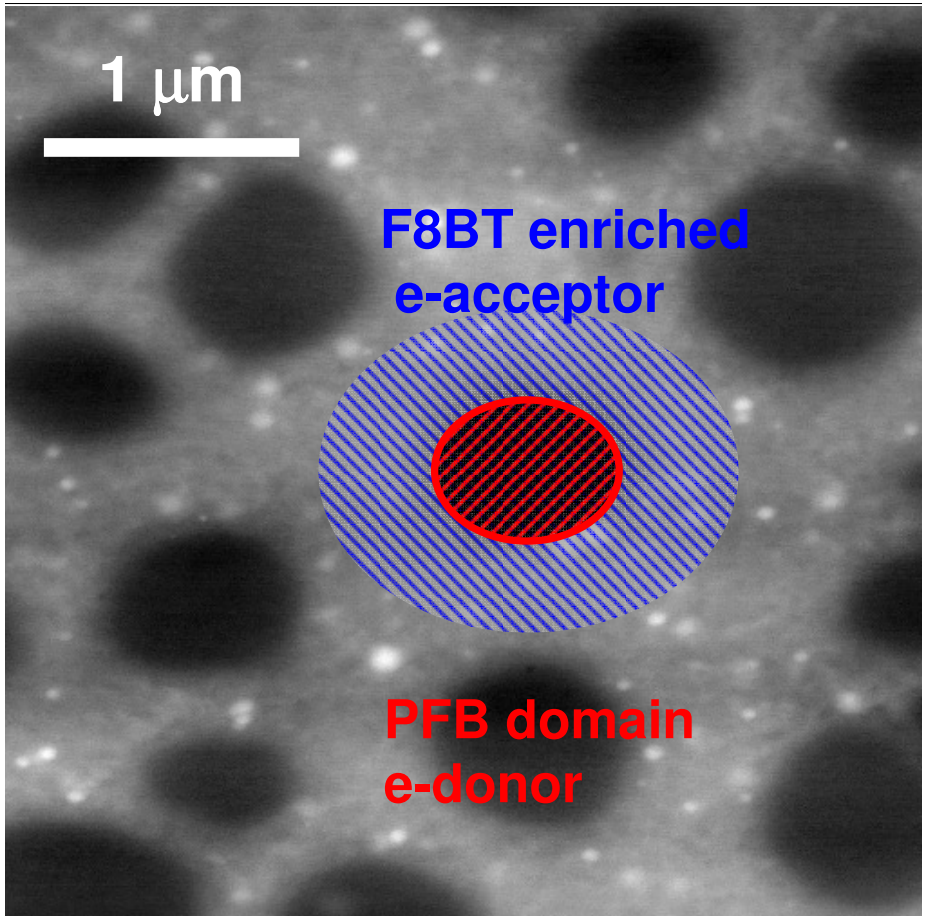
More Efficient Blends Create Charge Faster



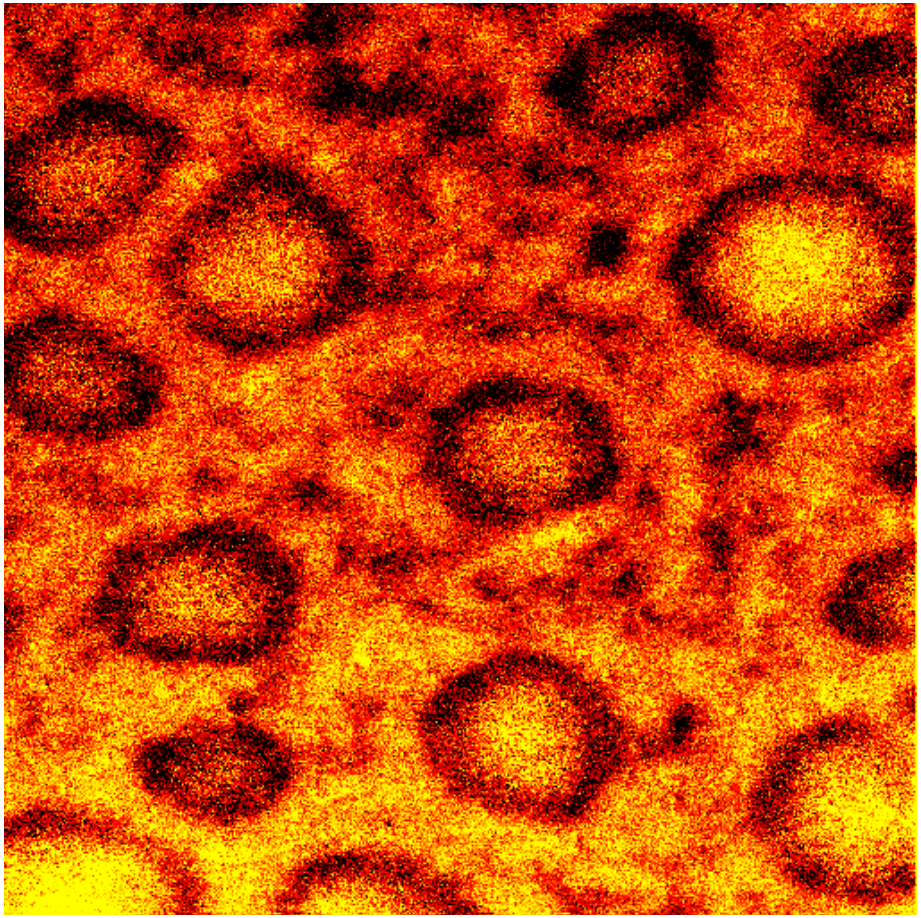
These are all *single-point* measurements: **we can create a map!**

Mapping Carrier Generation

Height



Charging Rate



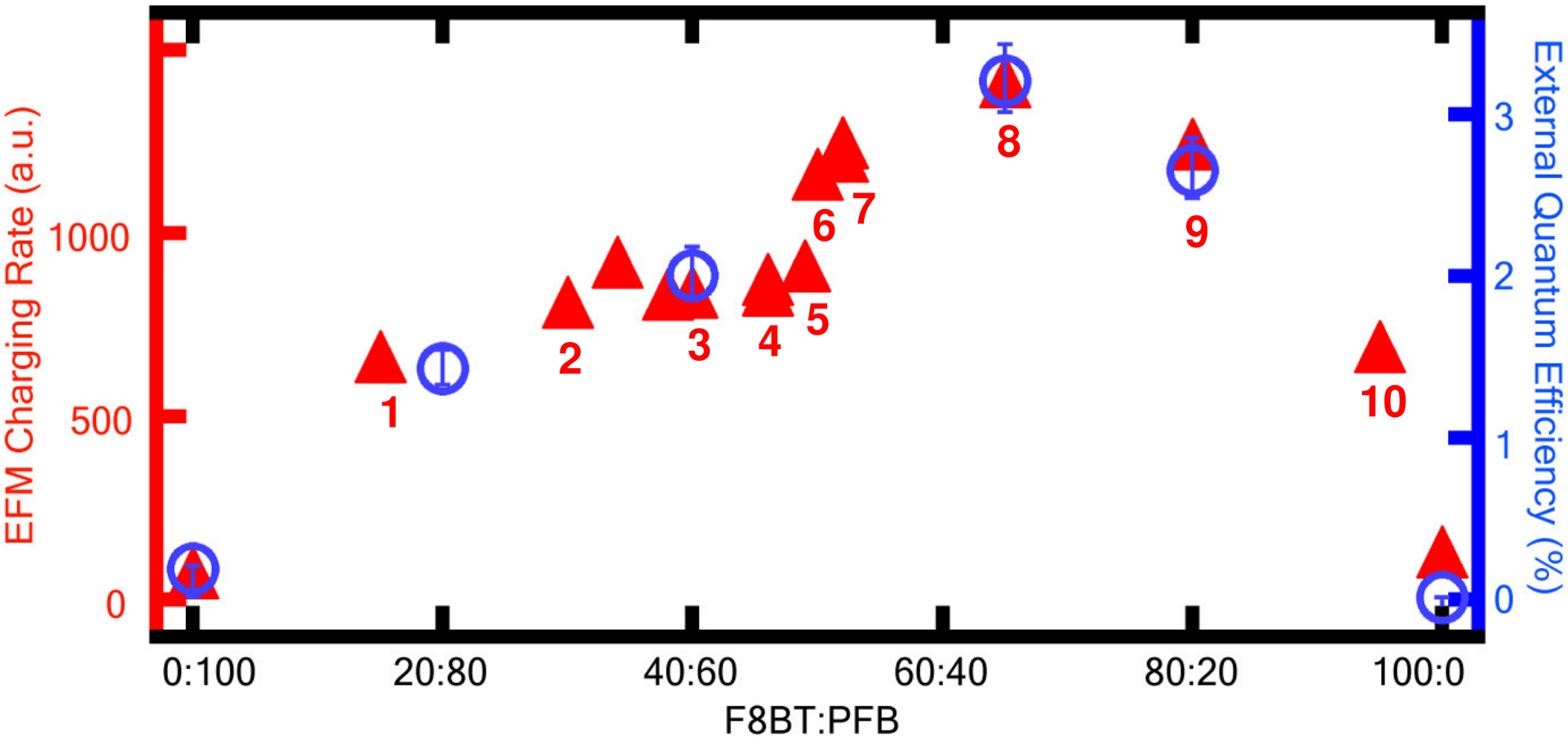
Faster **Slower**

arb. units

(spin-coated from xylene)

D. C. Coffey and D. S. Ginger, *Nature Materials* 5, pp. 735-740, (2006)

EFM Measurements Predict Device Efficiency



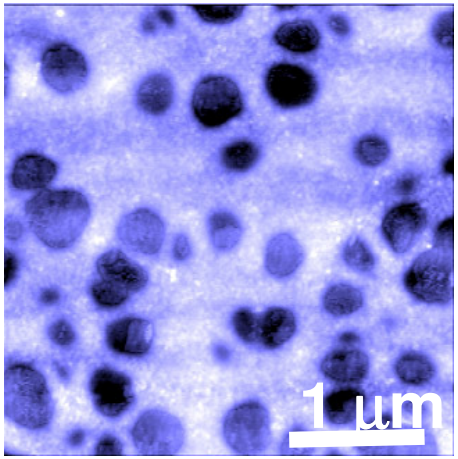
What is happening as the films become more efficient?

D. C. Coffey and D. S. Ginger, *Nature Materials* 5, pp. 735-740, (2006)

trEFM on polyfluorenes summary

Where does the photocurrent come from?

"We observe a linear trend, giving substantial evidence that the external quantum efficiency scales with the interfacial area between the mesoscale phase separated regions." Snaith et al. *Nano Lett.* p1353-1357 (2002)



PFB/F8BT

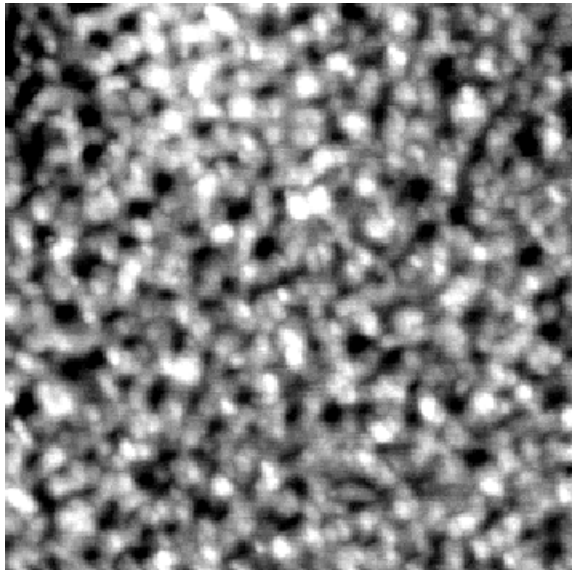
"…measurements show that current is generated within the bulk and not at the boundaries of the micron-sized phase segregated features" McNeill et al, *Nano Lett*. p2503-2507 (2004)

Local composition is most important in PF blends

D. C. Coffey and D. S. Ginger, *Nature Materials* 5, pp. 735-740, (2006)

trEFM is Superior to SKPM

Topography

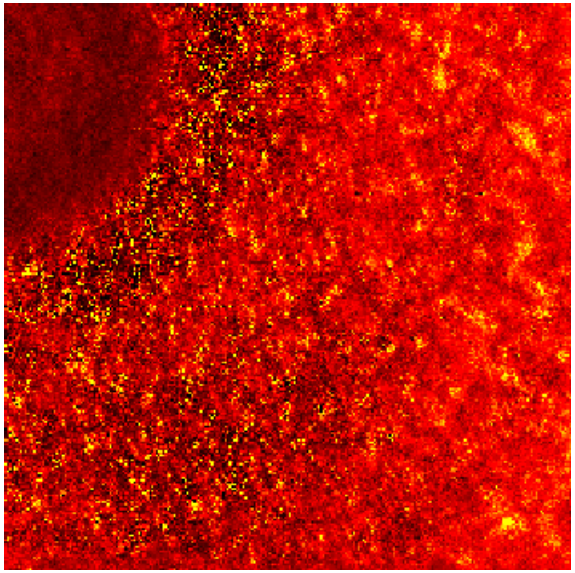


17

nm

0.0

Charging Rate



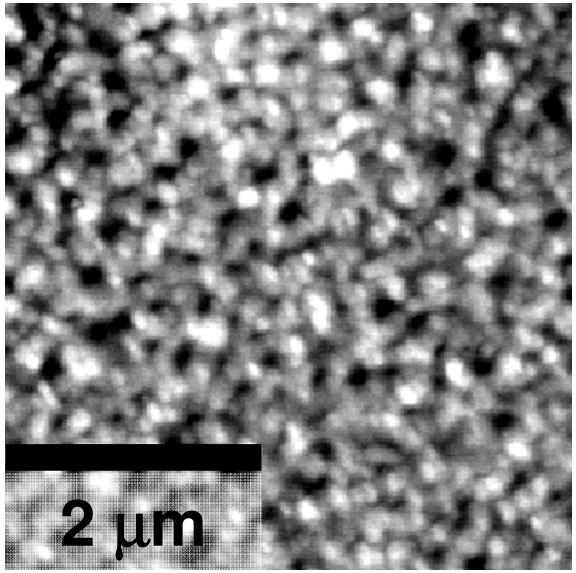
2.0

kHz

0.00

simple SKPM can give wrong answer

Topography

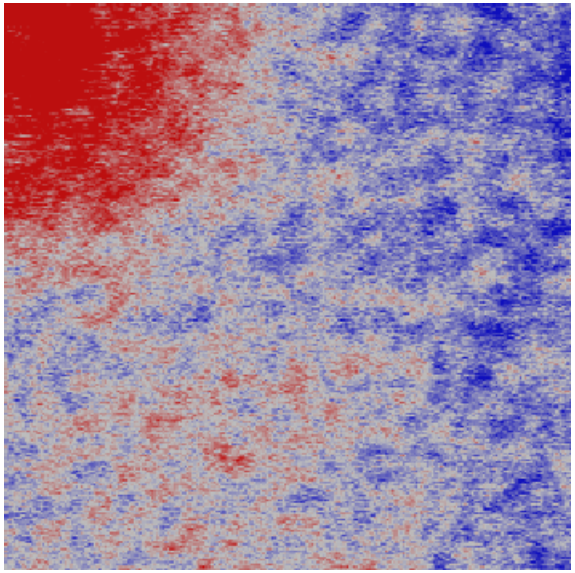


17

nm

0.0

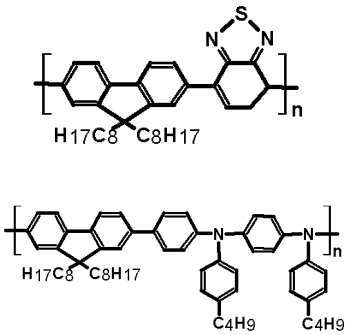
Surface Potential



-200

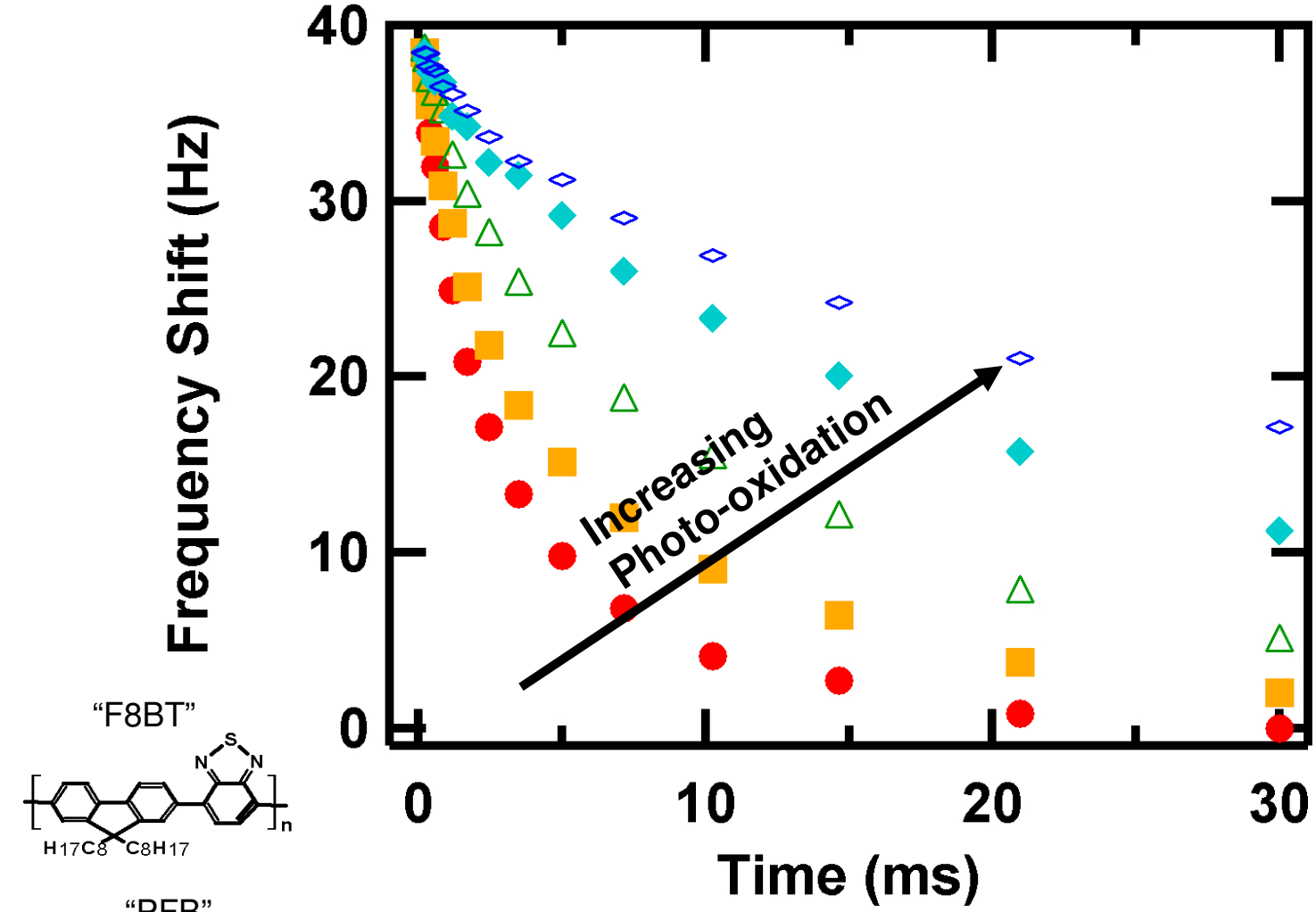
mV

-400



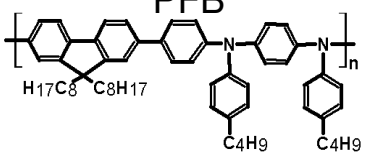
unpublished

Can watch charges leak out of traps



"F8BT"

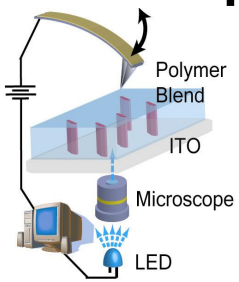
"PFB"

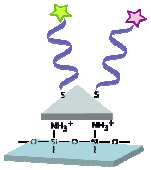


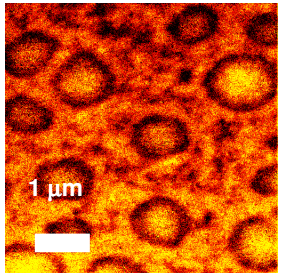
(also decrease in total Δf)

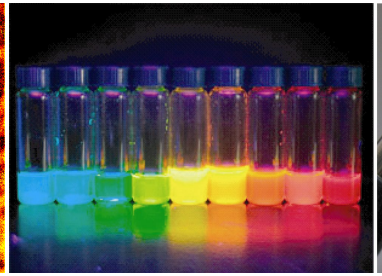
Summary

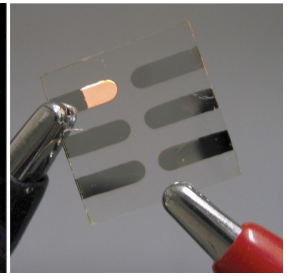
- Scanning probe techniques help reveal microscopic workings of organic photodiodes
- Should think about polymer cells as consisting of many different nanoscale diodes in parallel
- Improved morphological control and anode/contact interface are promising targets for improving efficiencies with many materials
- Distribution of currents will be critical for design of multi-layer cells
- Surface chemistry promising for controlling lateral (and vertical?) morphology

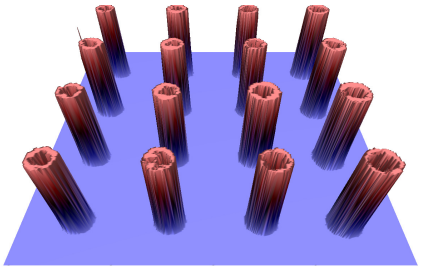












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