

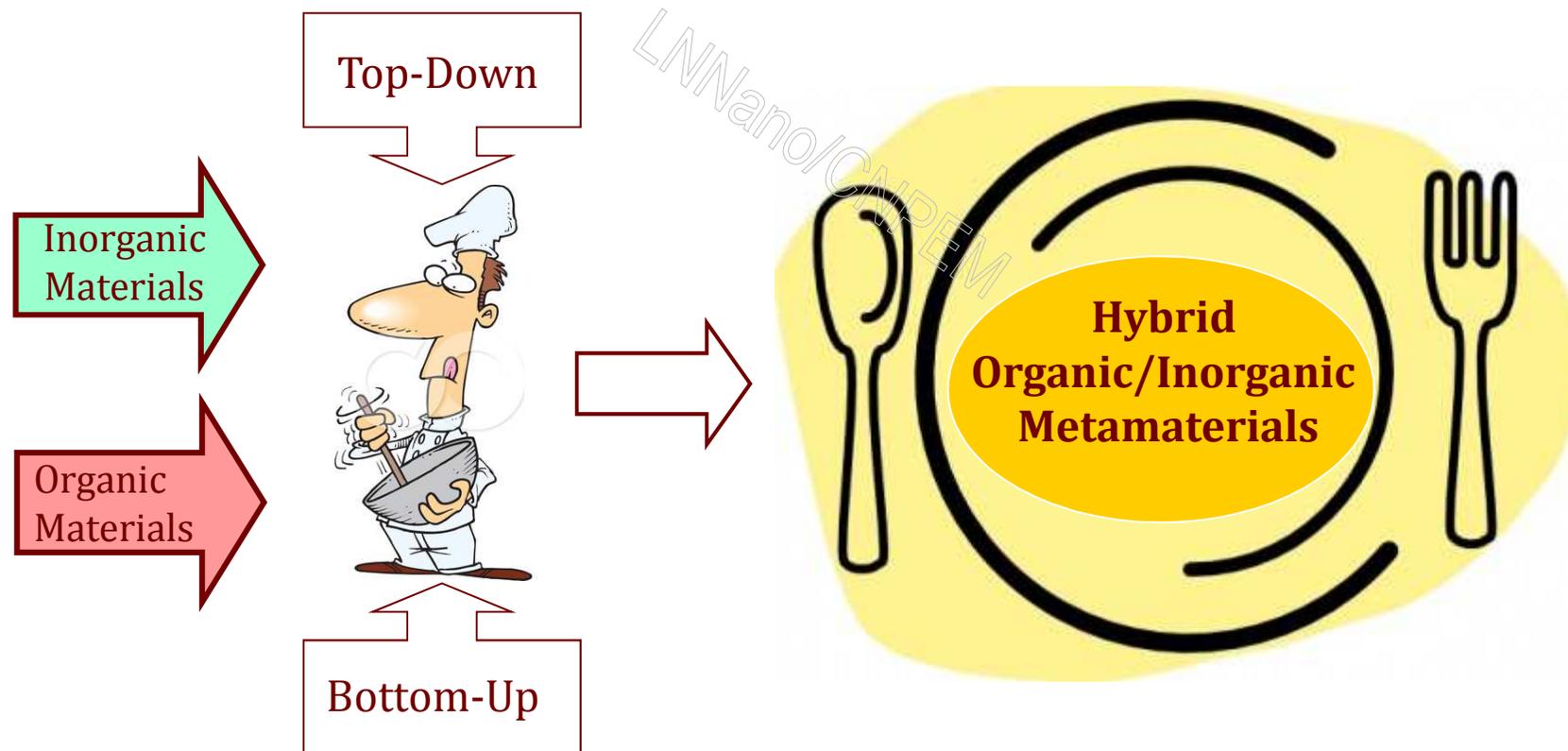
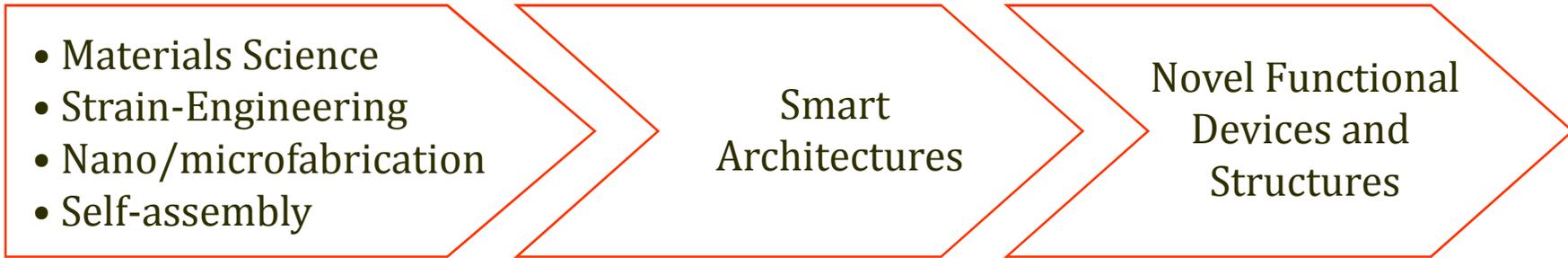


Dispositivos baseados em nanomembranas híbridas: um caso onde o micro e o nano se complementam através da auto-organização

Carlos César Bof Bufon

Grupo de pesquisa em Dispositivos e Sistema Funcionais

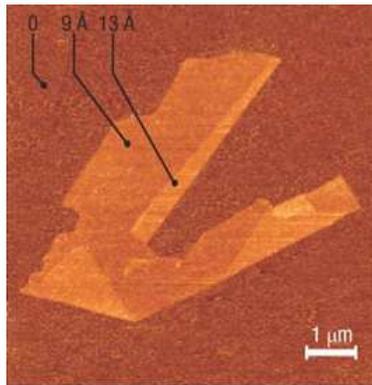
Research scope



Nanomembranes: Third wave of works on nanomaterials

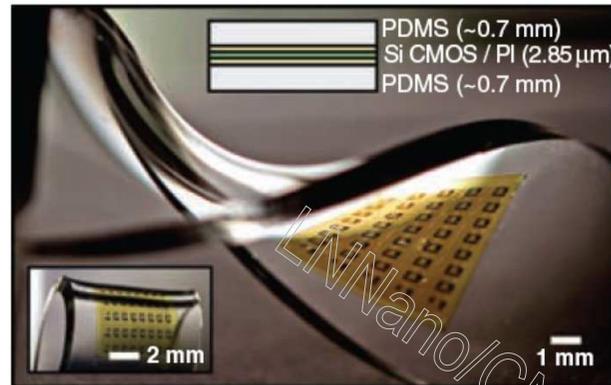
Nanomembranes are structures with *thicknesses of less than a few hundred nanometers* and with minimum *lateral dimensions at least two orders of magnitude larger than the thickness.*

Thin



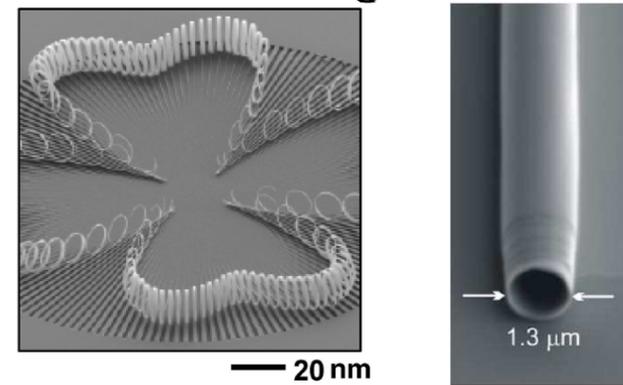
Geim, *Nat. Mater.* 2007

Flexible



Kim, *Science* 2008

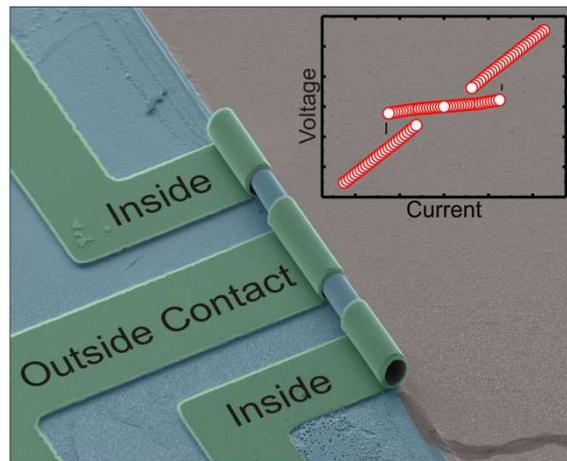
Strain engineered



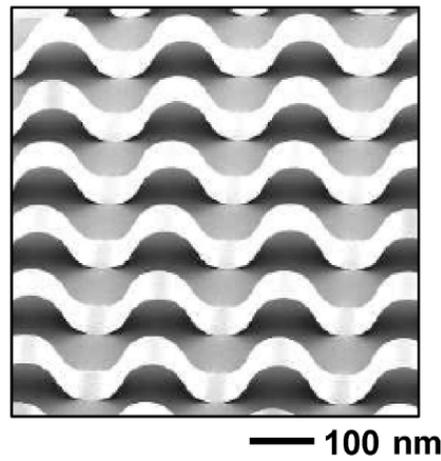
Zhang, *Nano Lett.* 2006

Deneke, *Appl. Phys. Lett.* 2007

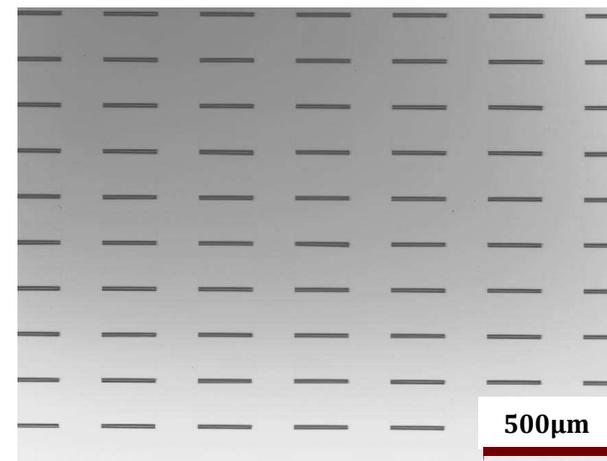
Patternable



Thurmer, *Nano Lett.* 2010



Sun, *Nat. Nanotechnol.* 2006



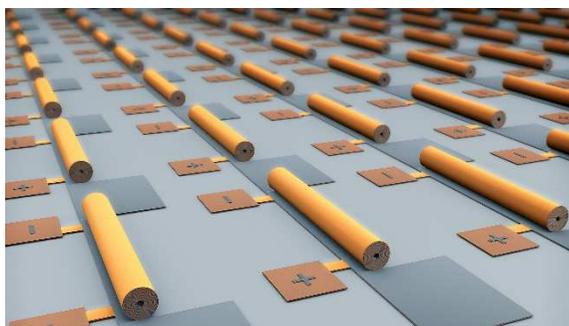
Bof Bufon ; IIN Chemnitz, 2010

Applications of nanomembranes

- ultra-compact functional devices;
- μ -containers and μ -fluidic elements;
- 3D electronics.

NANO LETTERS

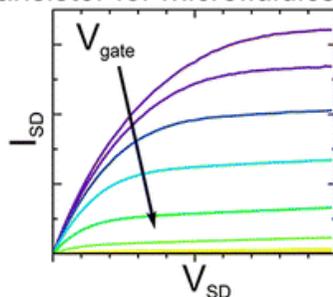
Self-Assembled Ultra-Compact Energy Storage Elements Based on Hybrid Nanomembranes



NANO LETTERS

Rolled-up nanomembranes as compact 3D architectures for field effect transistors and fluidic sensing applications

Rolled-up nanomembrane transistor for microfluidics



Angewandte Chemie International Edition

Light Off

Light On



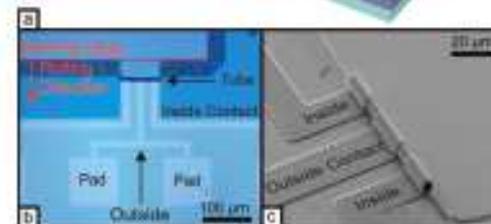
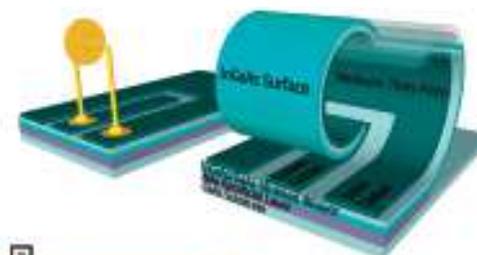
Microengine On

Microengine Off

Light-Controlled Propulsion of Catalytic Microengines

NANO LETTERS

Nanomembrane-Based Mesoscopic Superconducting Hybrid Junctions

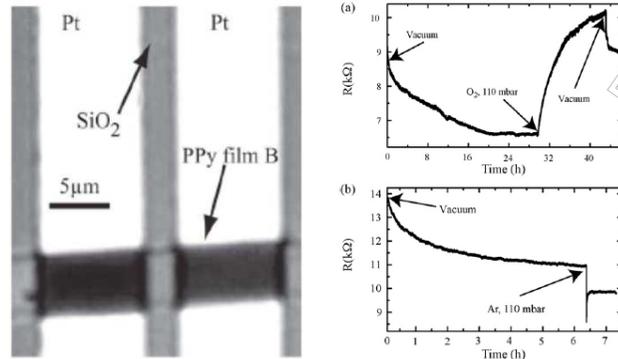


Hybrid organic – inorganic heterojunctions based on nanomembranes

- Molecular heterojunctions;
- Hybrid sensors;
- 3D ultra-compact organic devices;



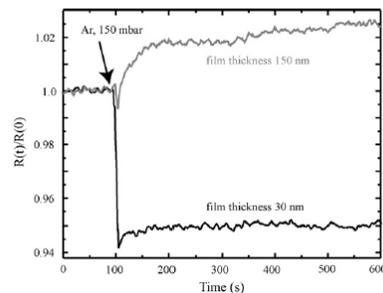
Polypyrrole thin-film field-effect transistor



Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

Piezoresistance in chemically synthesized polypyrrole thin films

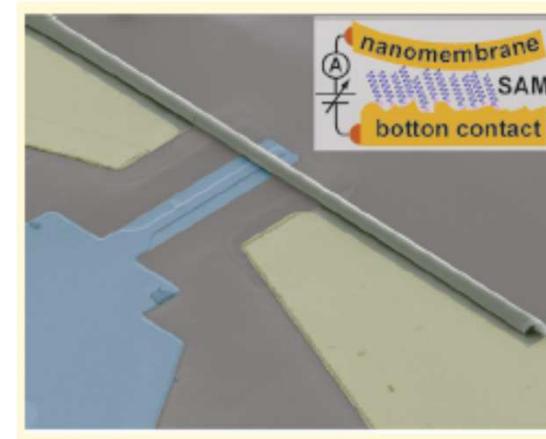


NANO LETTERS

LETTER

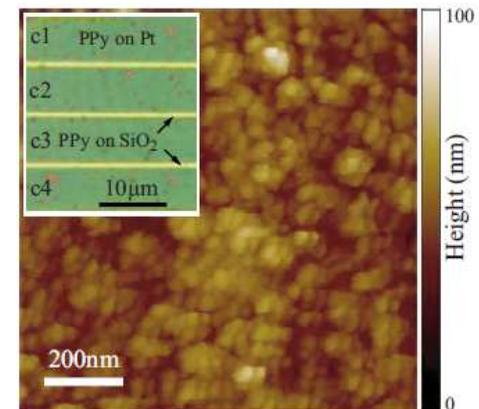
pubs.acs.org/NanoLett

Hybrid Organic/Inorganic Molecular Heterojunctions Based on Strained Nanomembranes



PHYSICAL REVIEW B 76, 245206 (2007)

Transport properties of chemically synthesized polypyrrole thin films



Self-releasing in everyday life

The Tension of Metallic Films deposited by Electrolysis.

By G. GERALD STONEY.

(Communicated by the Hon. C. A. Parsons, C.B., V.-P.R.S. Received January 16,
—Read February 4, 1909.)

It is well known that metallic films deposited electrolytically are in many cases liable to peel off if deposited to any considerable thickness. This is the case with nickel which, when deposited over a certain thickness, will curl up into beautiful close rolls, especially if it does not adhere very tightly to the body on which it is deposited. For example, if a piece of glass is



Basics on strained nanomembranes

From nano to micro:
the art of shaping nanomembranes
(a research field by itself)

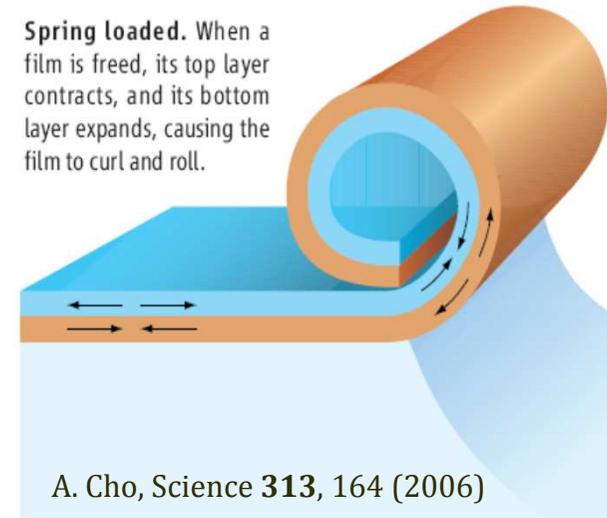
“Deterministic” Self-assembly

Substrate: glass, Si/SiO₂, Si, GaAs ...

Sacrificial layer: photoresist, GeO₂, AlAs, Ge ...

Strained layer: metals, oxides and semiconductors

Spring loaded. When a film is freed, its top layer contracts, and its bottom layer expands, causing the film to curl and roll.



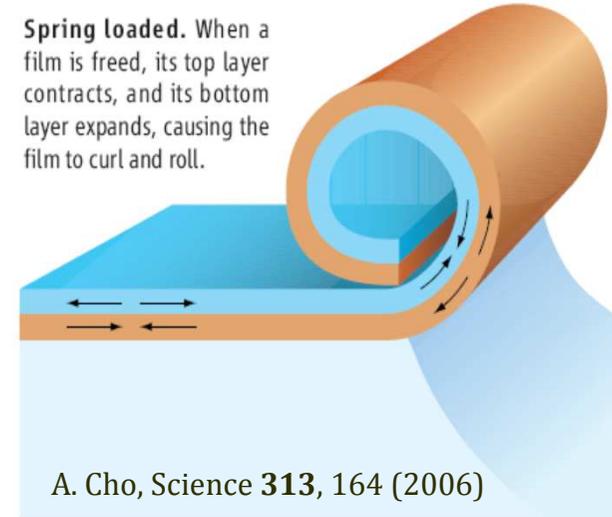
LNNano/CNPEM

“Deterministic” Self-assembly

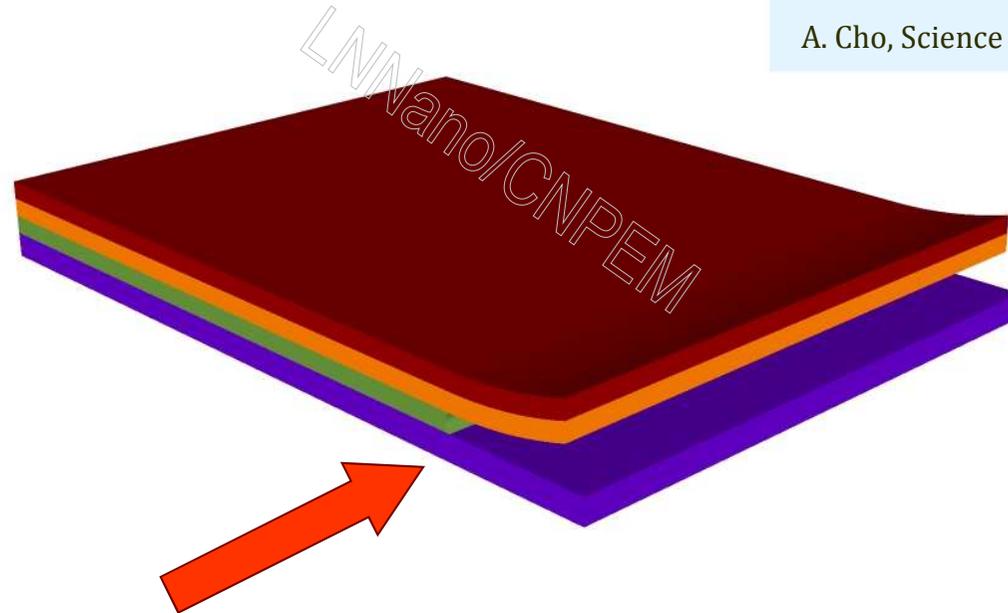
Selective removal of the sacrificial layer:

- $\text{H}_2\text{O} + \text{H}_2\text{O}_2$ (0% to 3%)
- $\text{H}_2\text{O} + \text{HF}$ (0.5% to 2%)
- Acetone

Spring loaded. When a film is freed, its top layer contracts, and its bottom layer expands, causing the film to curl and roll.

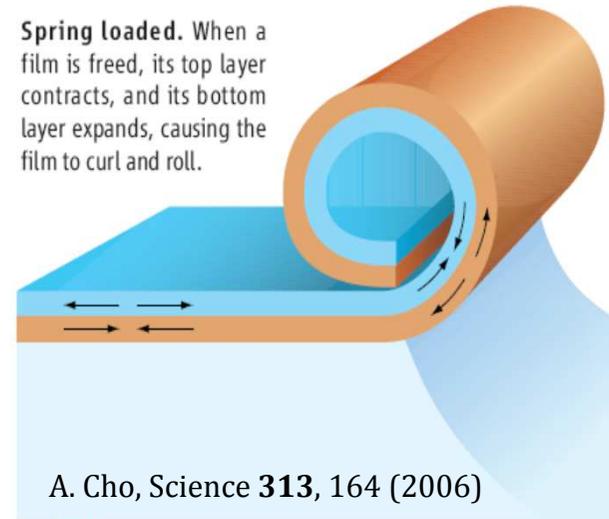


A. Cho, Science **313**, 164 (2006)

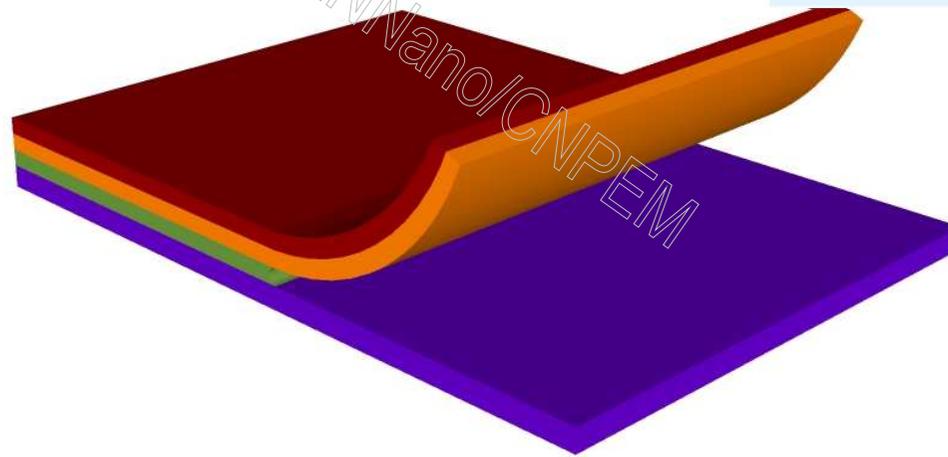


“Deterministic” Self-assembly

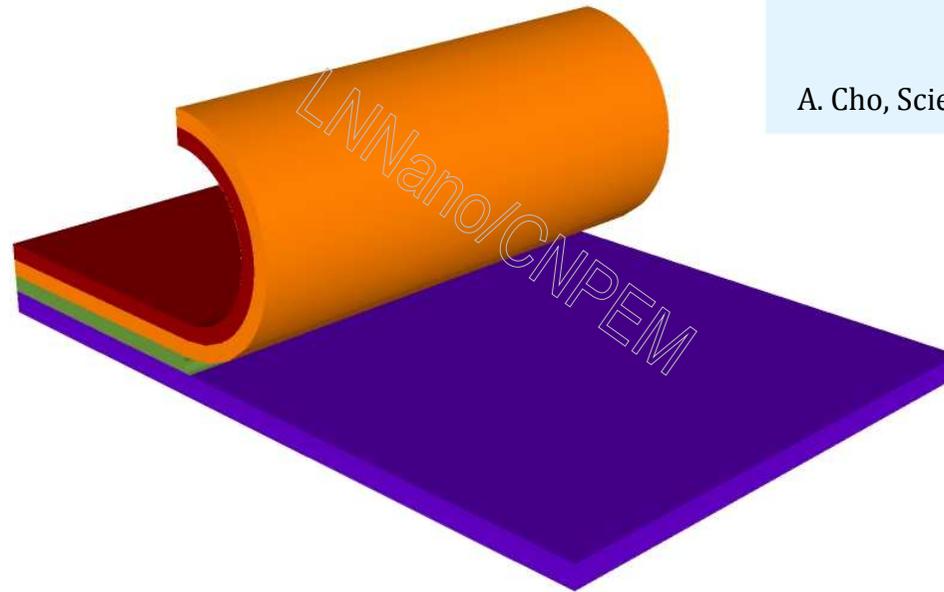
Spring loaded. When a film is freed, its top layer contracts, and its bottom layer expands, causing the film to curl and roll.



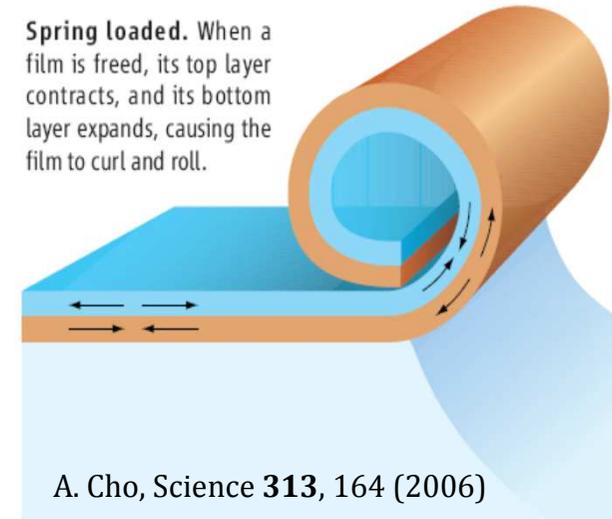
A. Cho, Science **313**, 164 (2006)



“Deterministic” Self-assembly



Spring loaded. When a film is freed, its top layer contracts, and its bottom layer expands, causing the film to curl and roll.

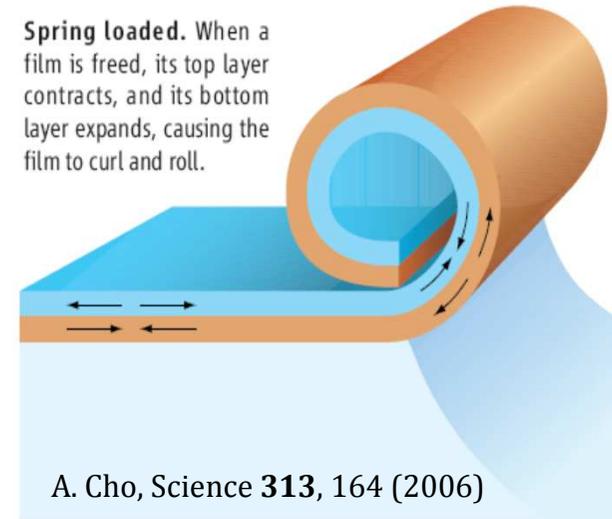


A. Cho, Science **313**, 164 (2006)

“Deterministic” Self-assembly



Spring loaded. When a film is freed, its top layer contracts, and its bottom layer expands, causing the film to curl and roll.

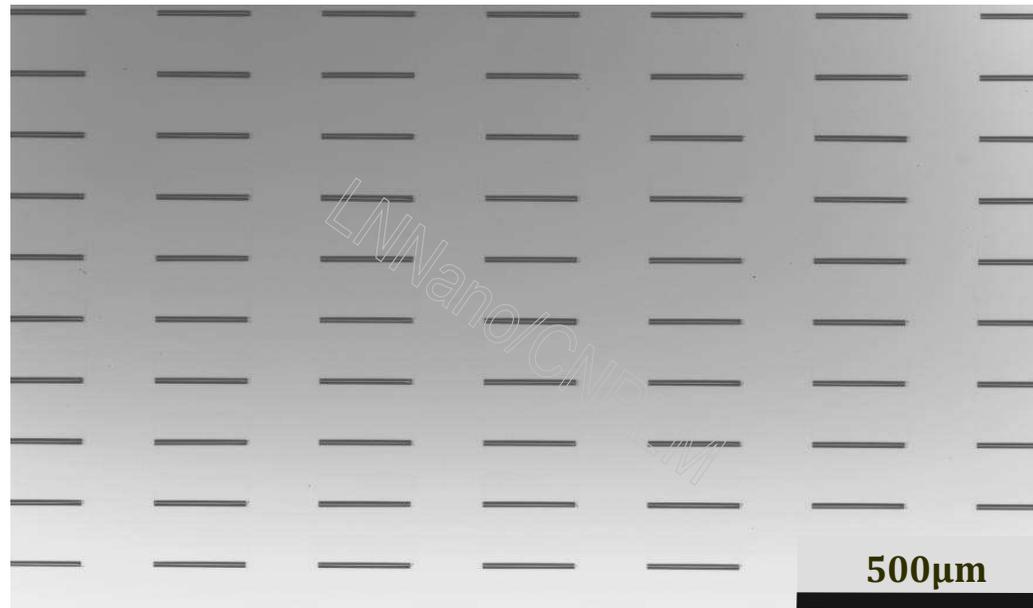


A. Cho, Science **313**, 164 (2006)

Patterning of regular arrays

Strained bilayer: Ti/Cr (15/20nm)
Sacrificial layer: GeO₂ (~20nm)
Substrate: Si/SiO₂

Rolling in H₂O

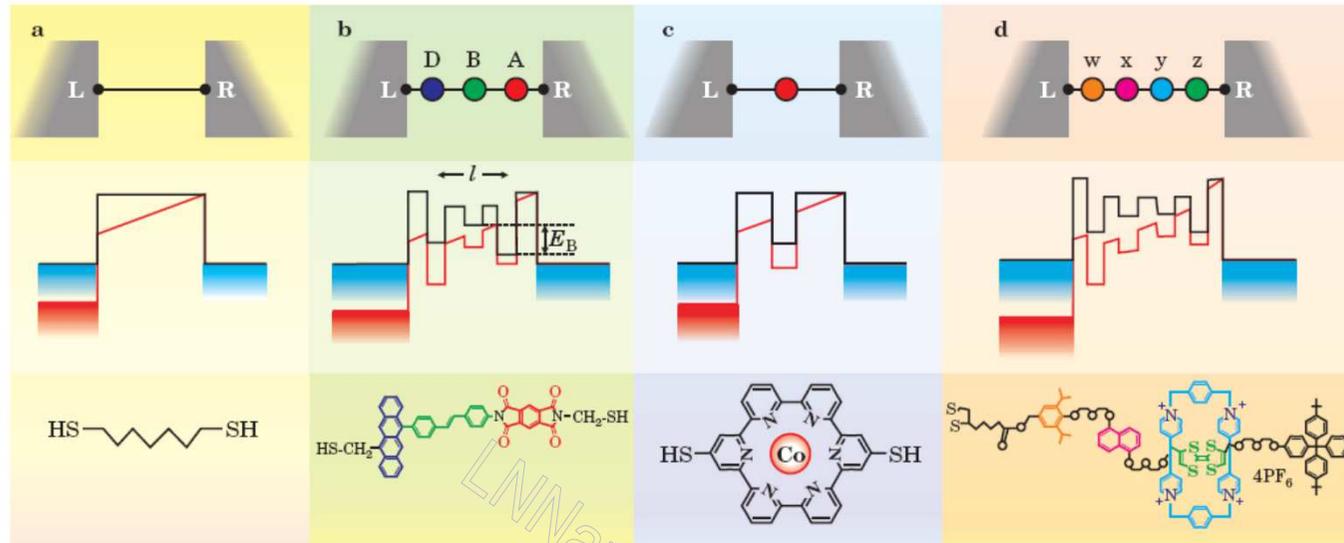


$$\Phi = 1\mu\text{m}-100\mu\text{m}$$

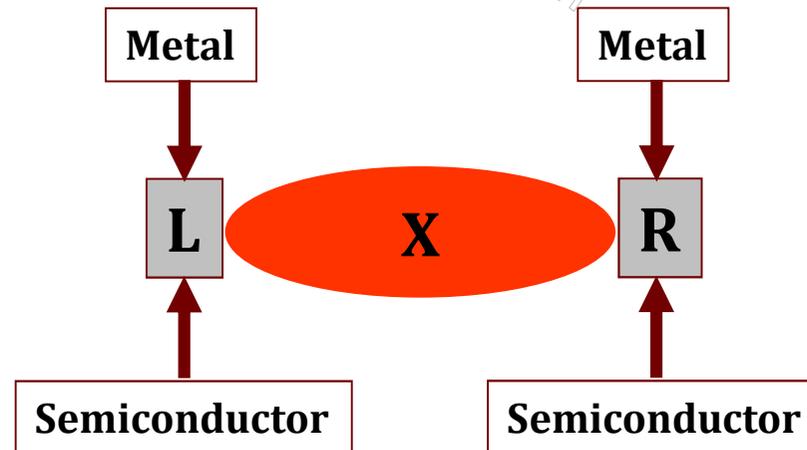
Schadewald and Bof Bufon; IIN Chemnitz, 2010

Hybrid Organic/Inorganic Heterojunctions

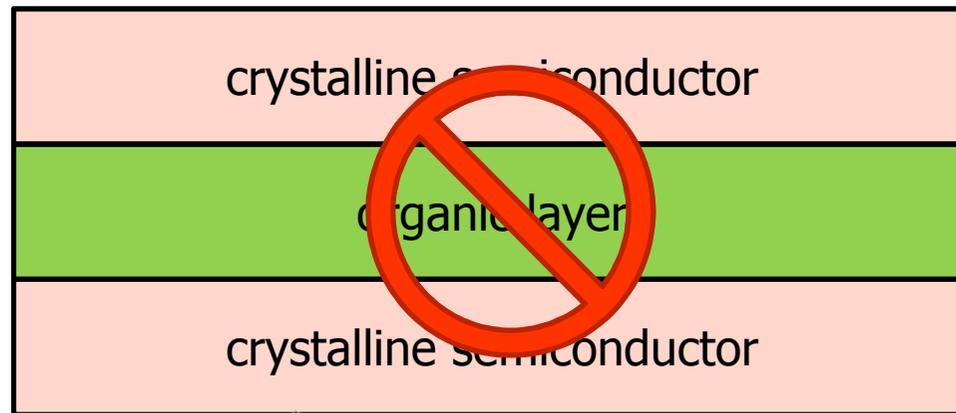
Molecular (hetero)-junctions



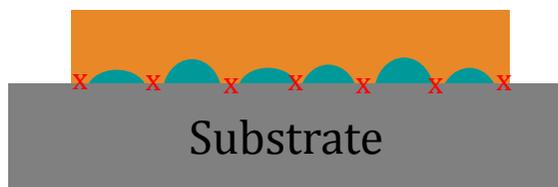
James R. Heath and Mark A. Ratner, *Physics Today* 2003



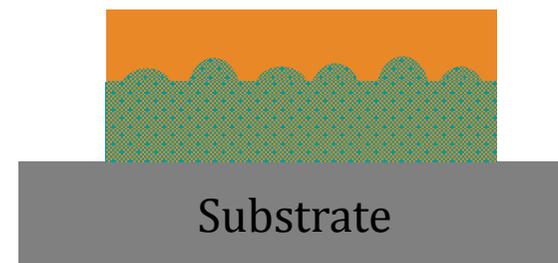
Technological challenges



High temperature damages



Short-circuit via pinholes



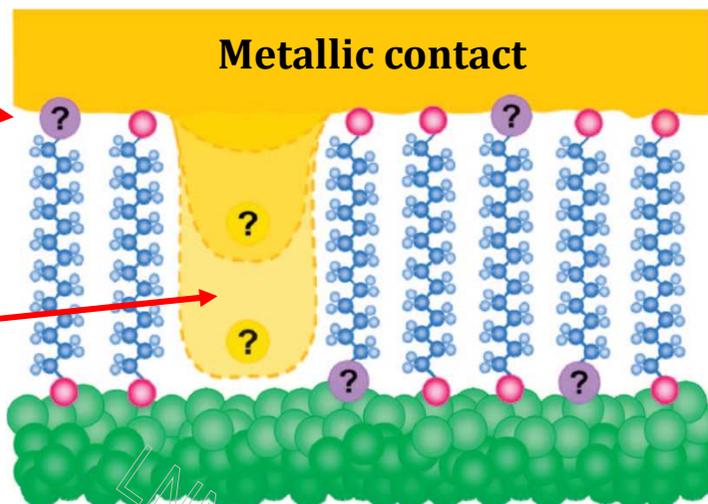
Metal interdiffusion.

Delicate materials require new contacting methods

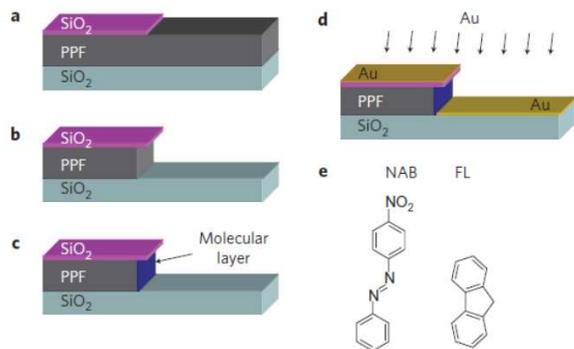
Contacting molecular layers: challenges

bonding damage
(charge localization)

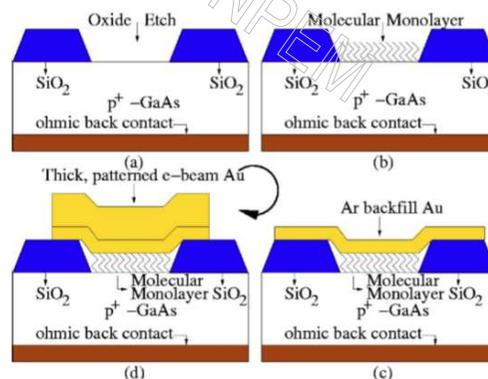
pinholes
(short circuit)



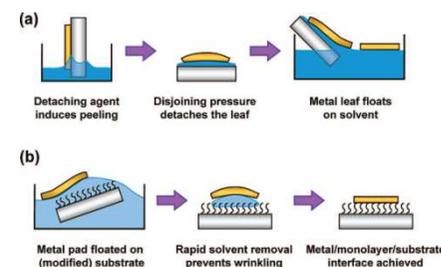
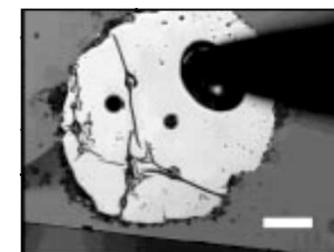
Haick and Cahen, *Acc. Chem. Res.* 41, 359 (2008)



Evaporation of contacts
Bonifas and MacCreery, *Nat. Nanotech.* 2010

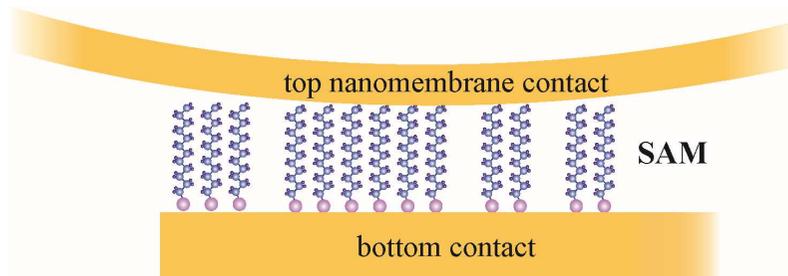


Evaporation of contacts
Lodha et al, *J. Appl. Phys.* 2006



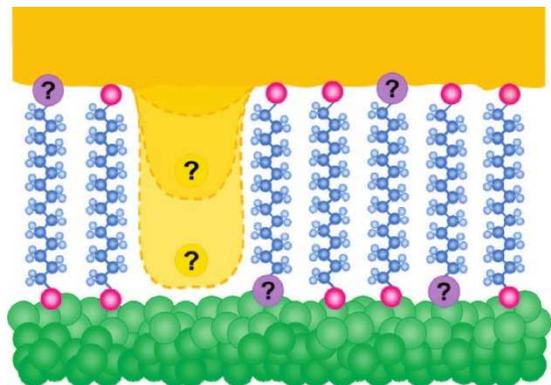
Lift-off Float-off
Cahen et al, *Nature* 2000
Haick and Cahen, *Acc. Chem. Res.* 2008

Hybrid junctions based on nanomembranes



- Pinhole-proof;
- Soft contact: low damage to the MoLa;
- “Large scale” production and integration;
- Versatile material composition;
- Self-adjusting gap.

Soft mechanical contacting method: Self-adjusting contacts.



Haick et al., Acc. Chem. Res. **41**, 359 (2008)



Combination of metal and semiconductor contacts

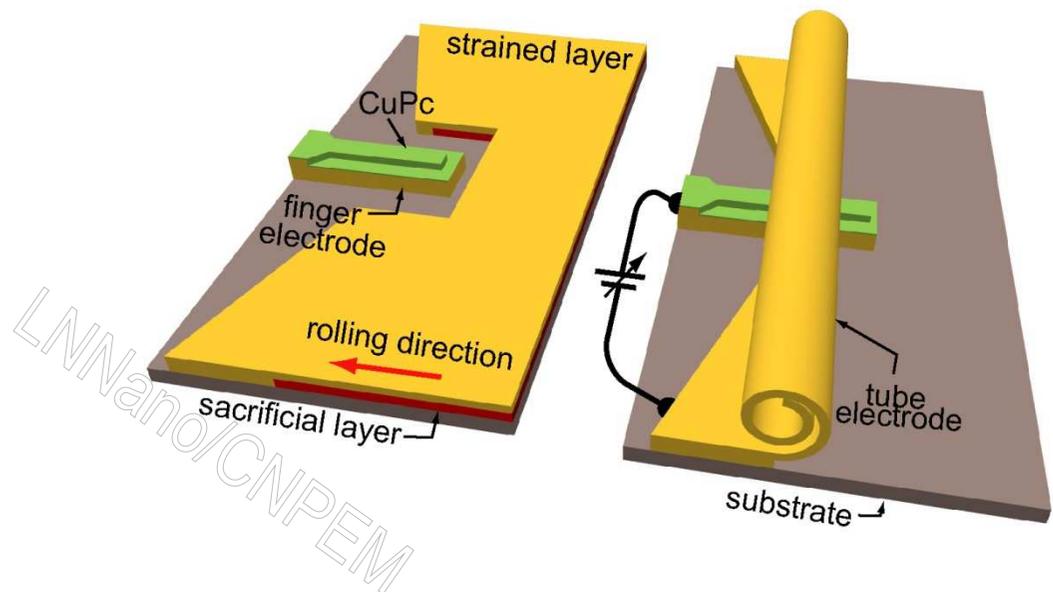
Nanomembrane based top metallic contact



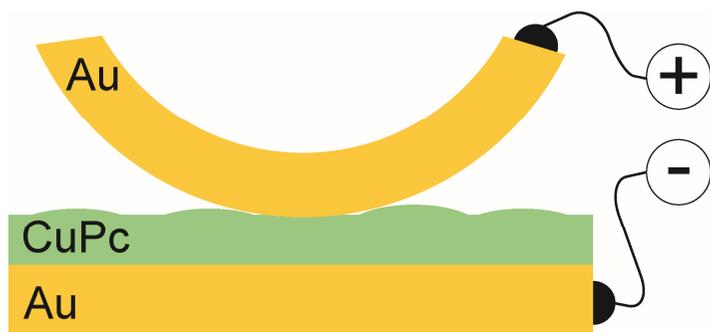
Nanomembrane based top semiconducting contact



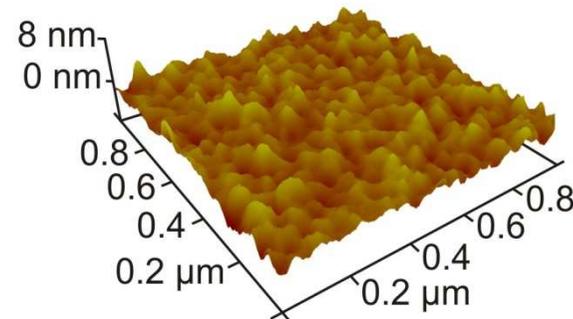
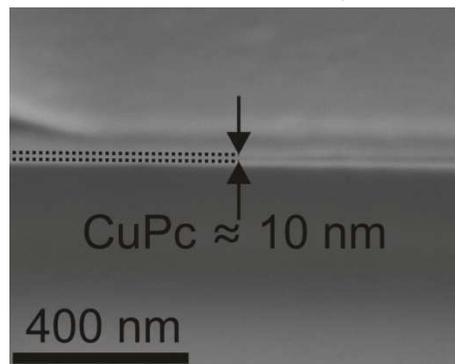
Contacting CuPc thin films (Au/CuPc/Au)



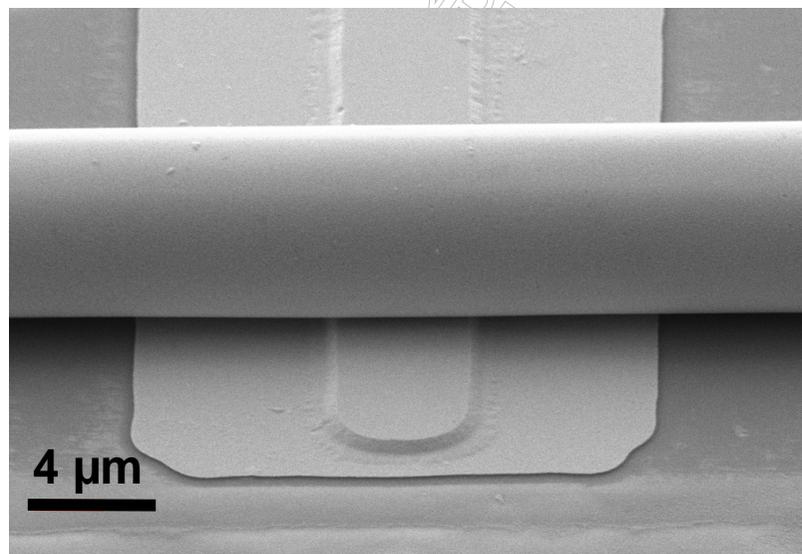
LNNano/CNPEM



Electrode gap ~ 6.5 nm



Submittend to JPC-C

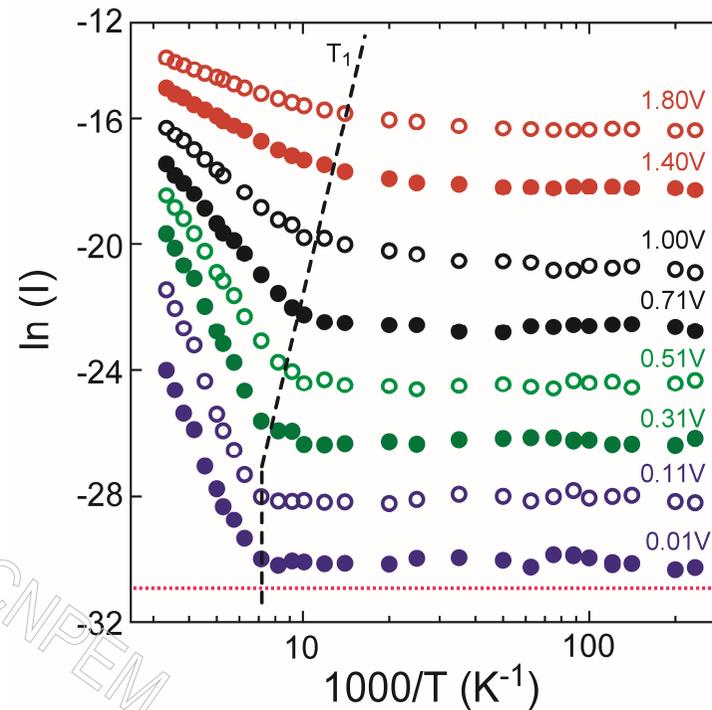
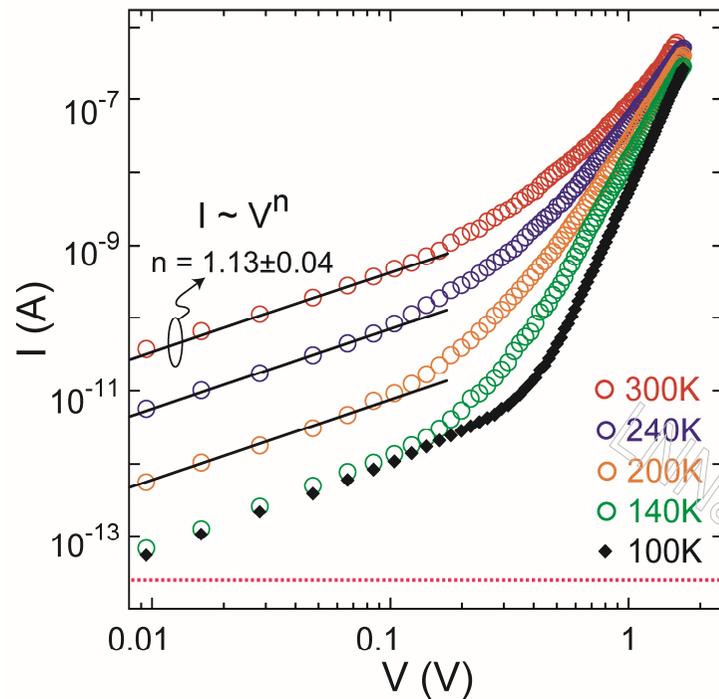


Submittend to JPC-C

C. C. Bof Bufon

IFSC-USP, November 2013

Transport properties of CuPc thin films: IV and IT traces



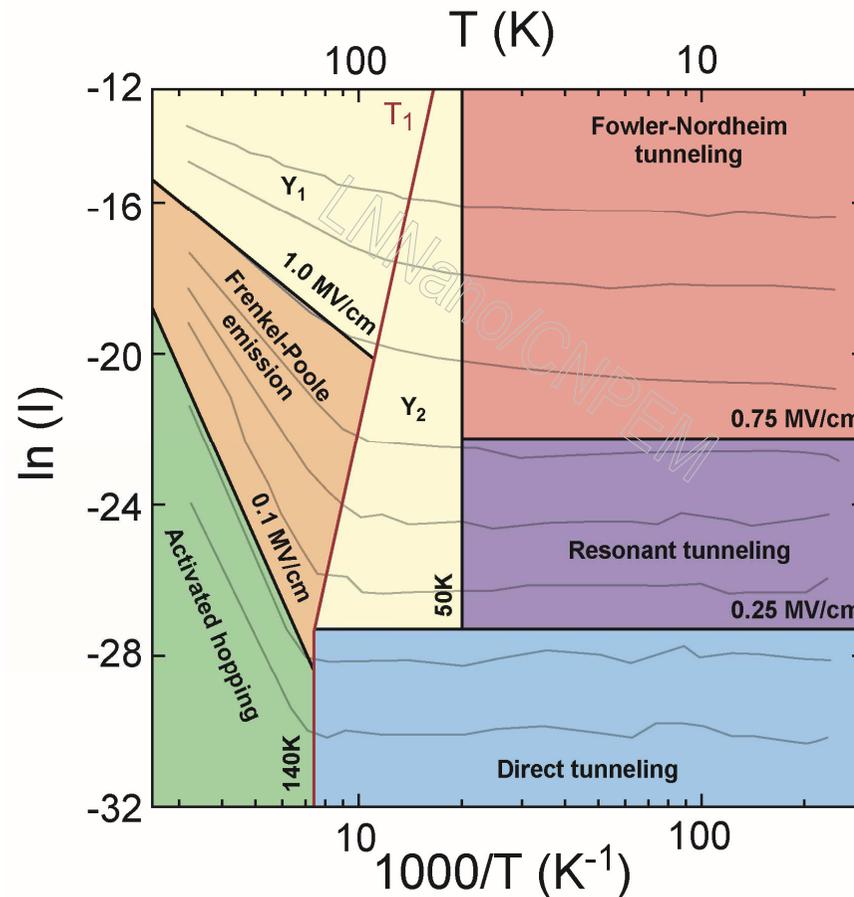
- For $V < 0.15\text{V}$ and $T > 100 - 140\text{ K}$, hopping conduction dominates;
- At $T = T_1$: transition from thermally activated transport to tunneling;
- Strong temperature dependence for $T > T_1$ associated to impurity/defect (ID) sites;
- For $T > T_1$:

$$I \propto V \exp\left(-\frac{E_a}{kT}\right)$$

Submittend to JPC-C

Au/CuPc/Au

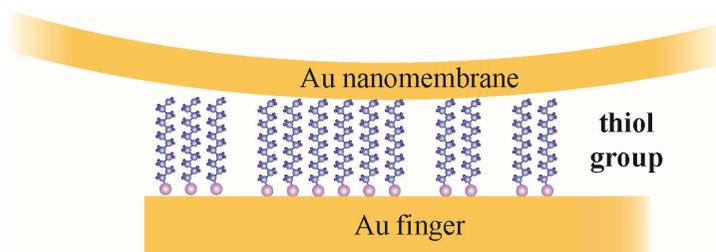
- Rolled-up nanomembranes can gently contact ultra-thin organic semiconducting layers from the top;
- No interdiffusion of metallic atoms was detected.



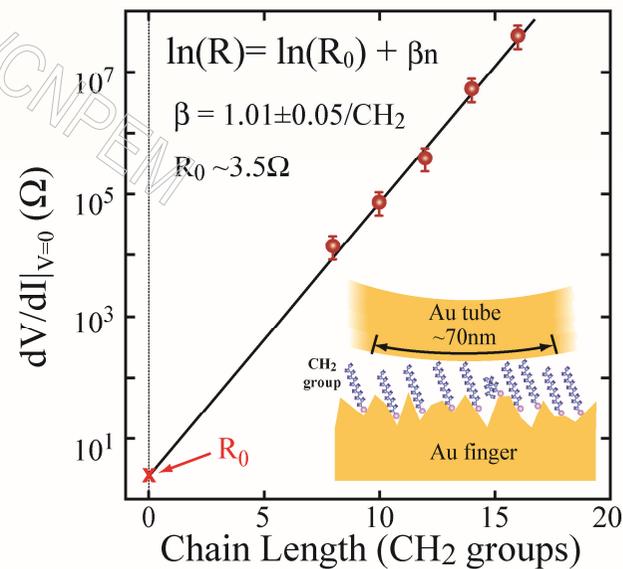
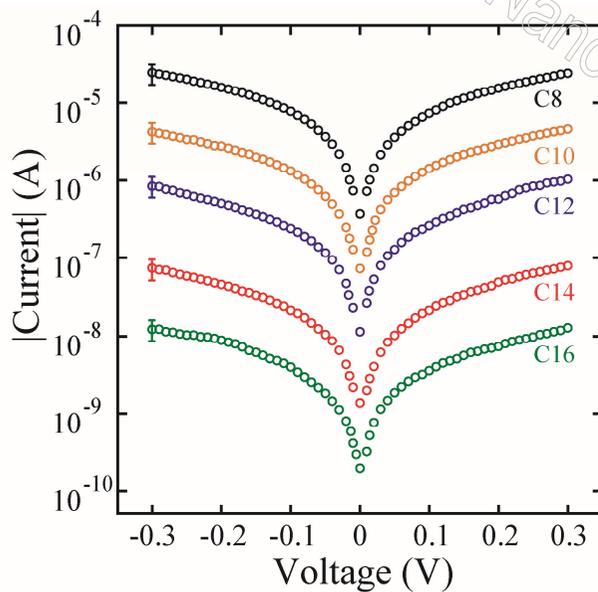
Submittend to JPC-C

Au/SAM/Au heterojunctions

Contacting sulfur terminated alkanes



Non-resonant tunneling transport

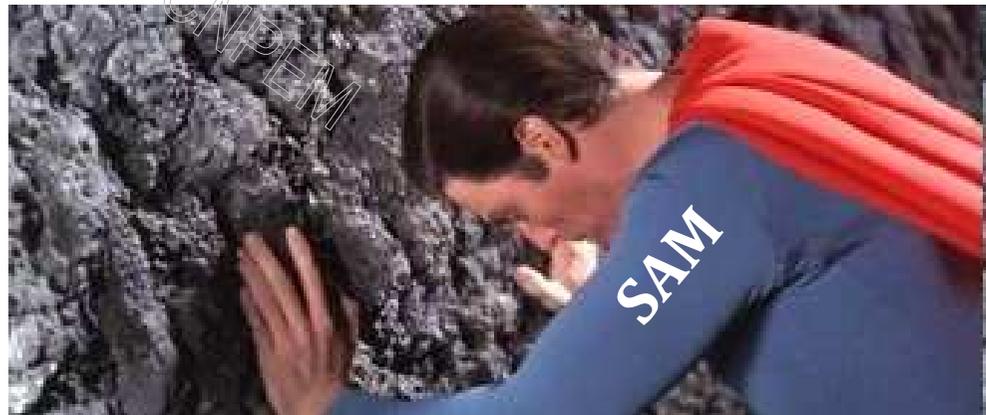
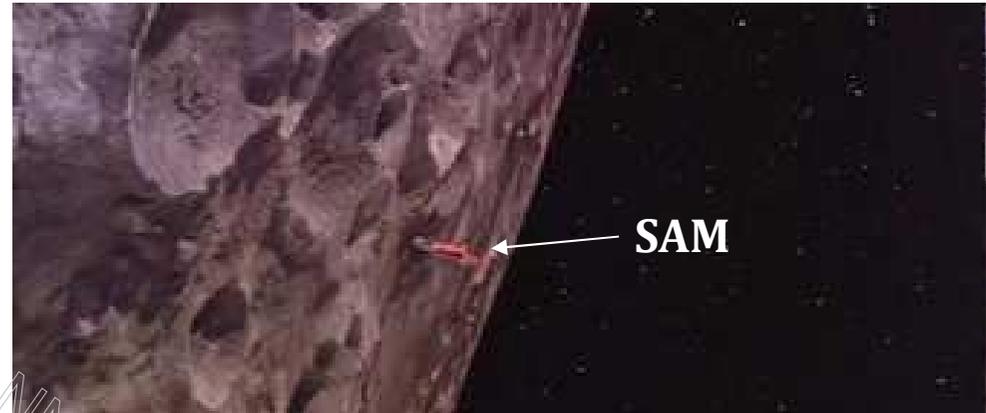


C.C. Bof Bufon et al., *Nano Lett.* 11, 3727 (2011)

Question of perspective

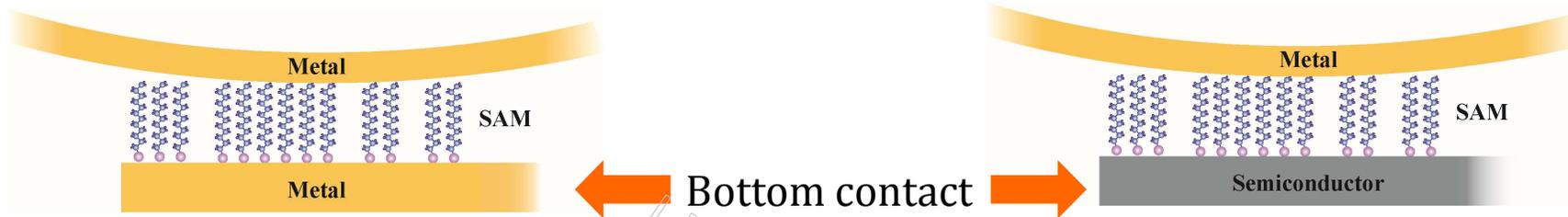
Tube \emptyset
 $\sim 5-10\mu\text{m}$

Chain Length
(C6-C18 thiol)
 $\sim 0.7-2.3\text{nm}$

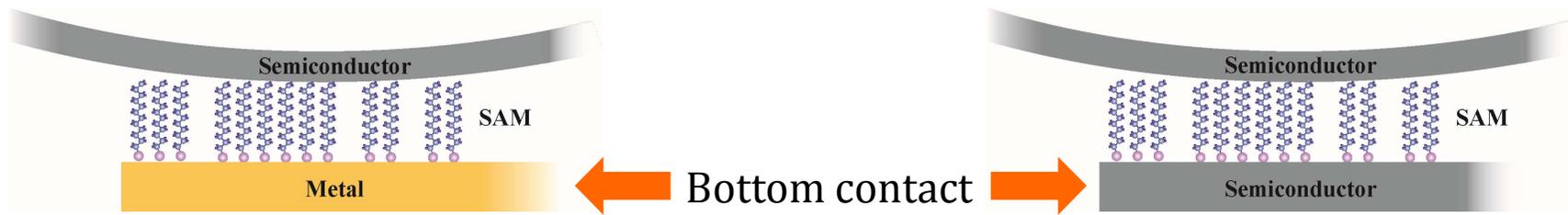


Combination of metal and semiconductor contacts

Nanomembrane based top metallic contact



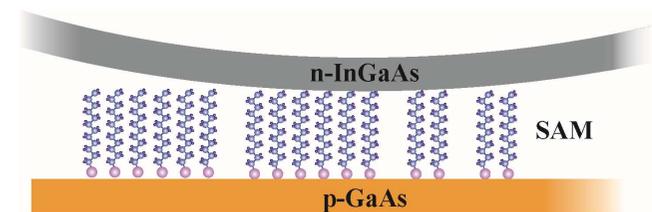
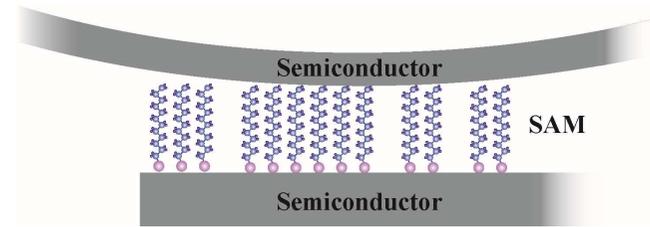
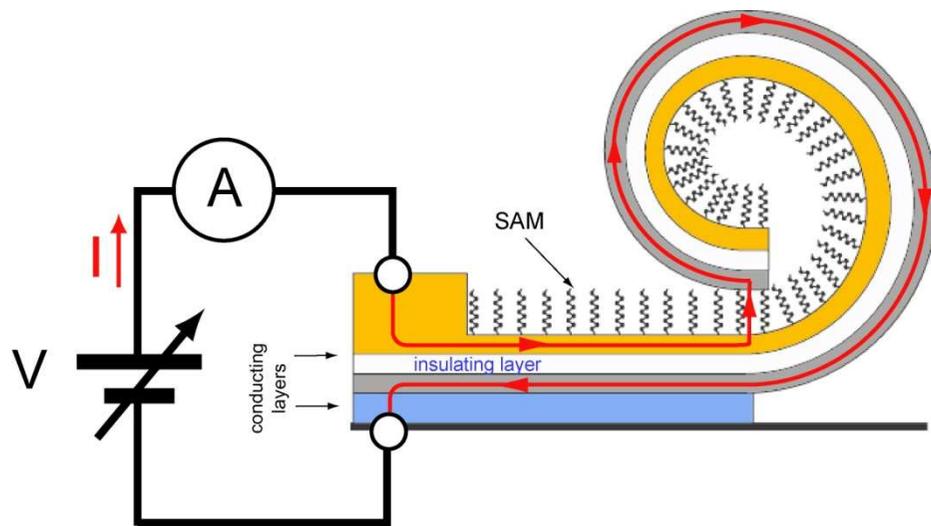
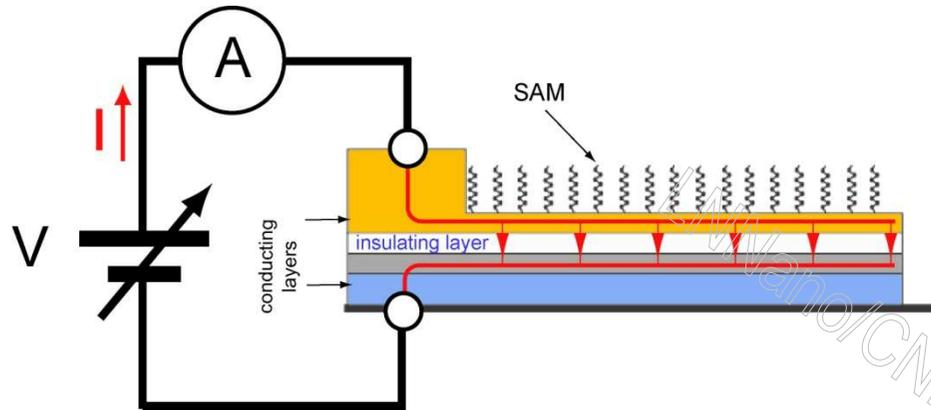
Nanomembrane based top semiconducting contact



Semiconductor/SAM/semiconductor heterojunctions

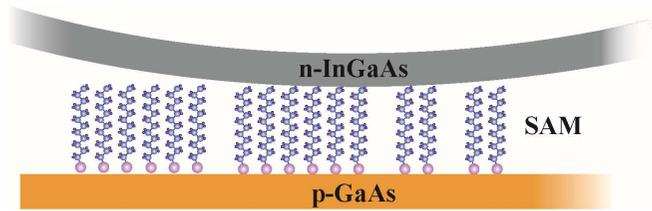
Contacting molecules on semiconducting fingers with semiconducting tubes

Concept of radial injection and tangential

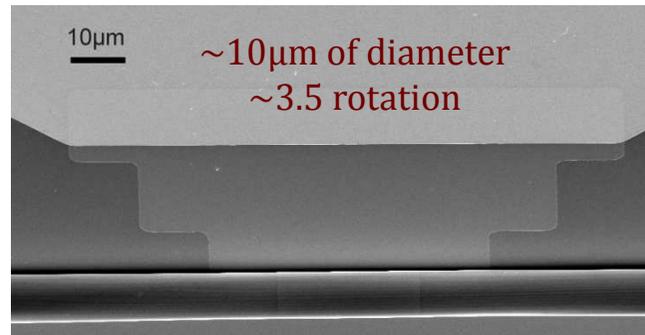
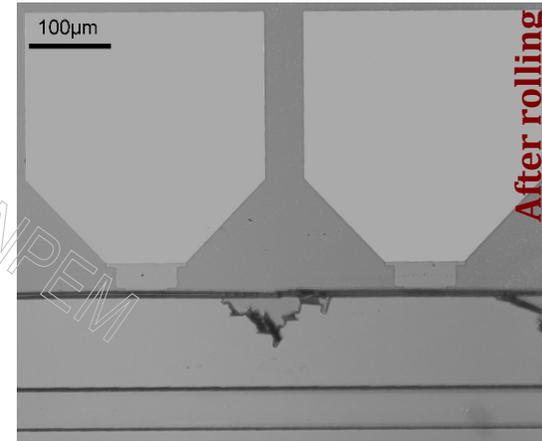
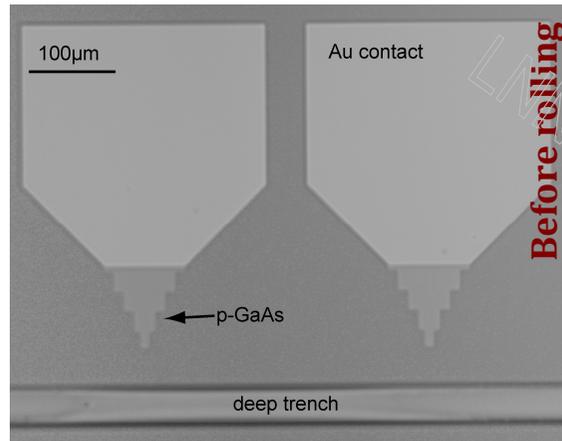
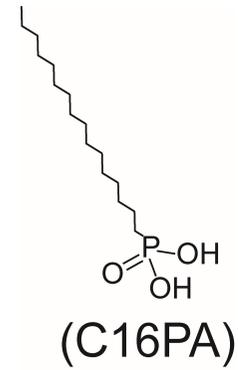


C.C.Bof Bufon *et al.*, *Nano Lett.* 11, 3727 (2011)

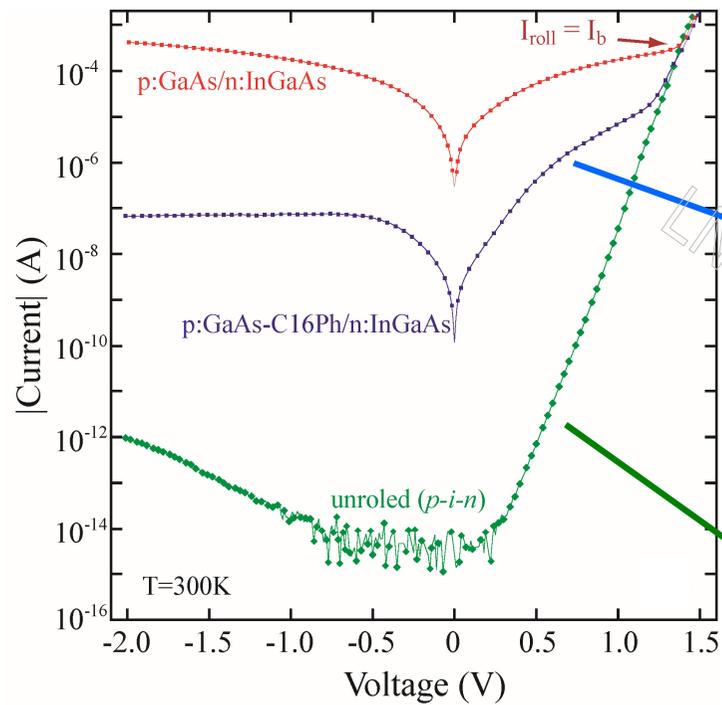
pGaAs-C16PA/nInGaAs



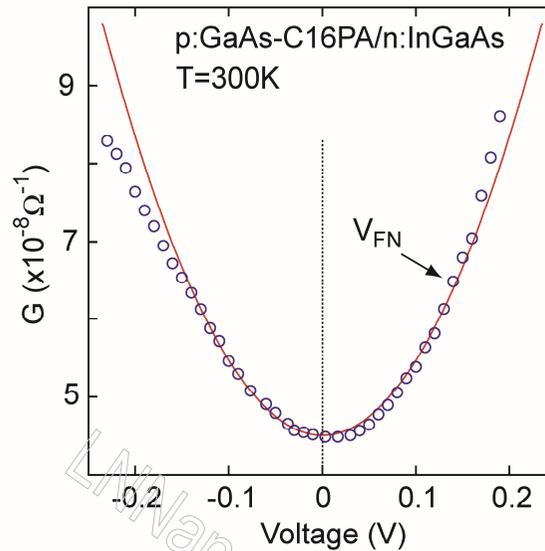
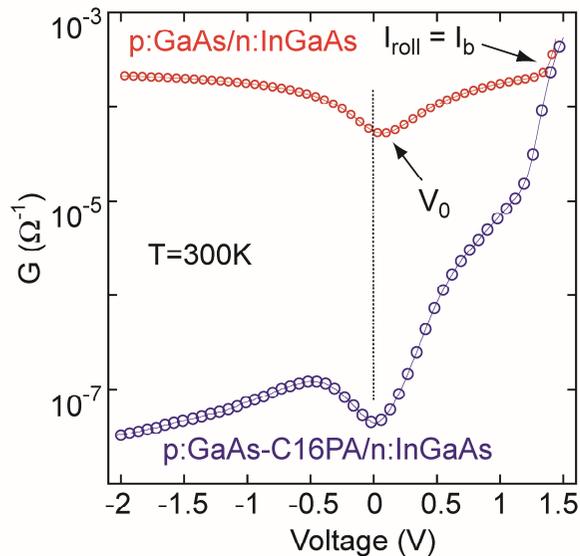
SAM = hexadecylphosphonic acid



Transport across the hybrid junctions

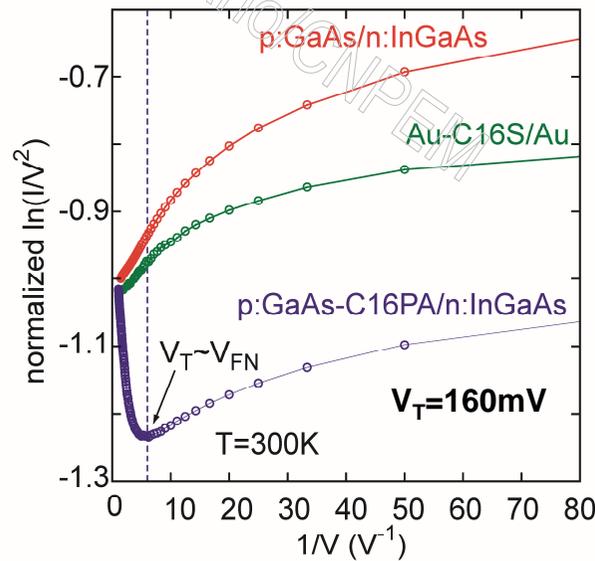
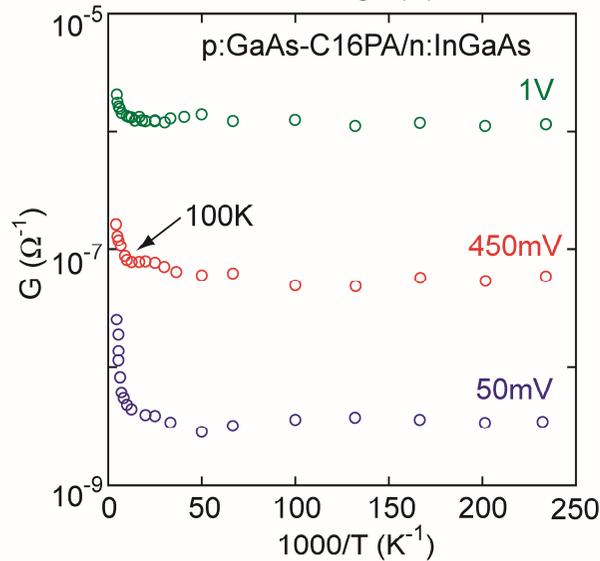


Transport across the hybrid junctions



Simmons model for conductance [1]:

$$G \cong G_0(1 + CV^2)$$



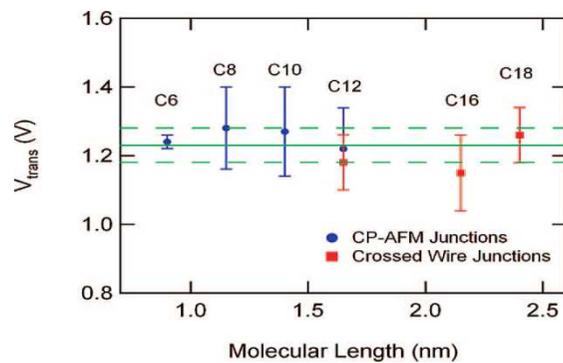
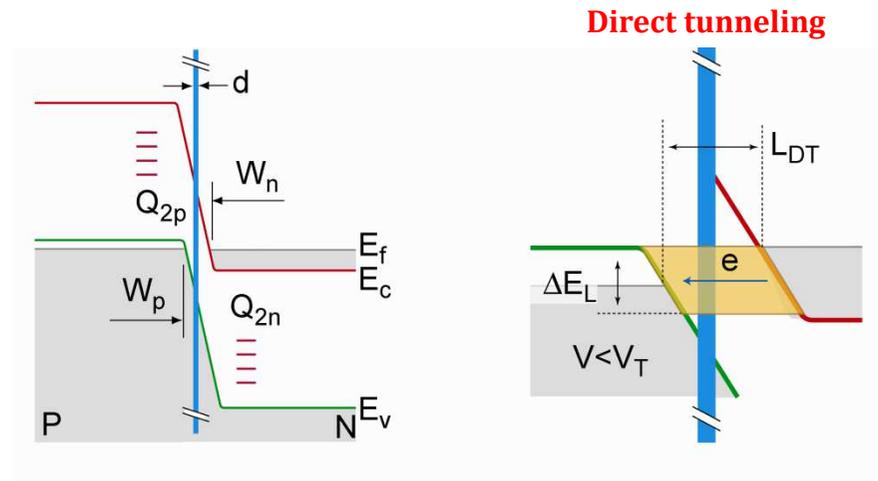
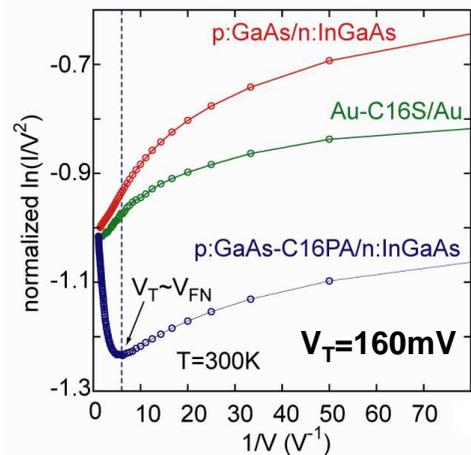
Field-emission [2]:

$$I \propto V^2 \exp\left(-\frac{4W\sqrt{2m_e}\Phi^3}{3\hbar qV}\right)$$

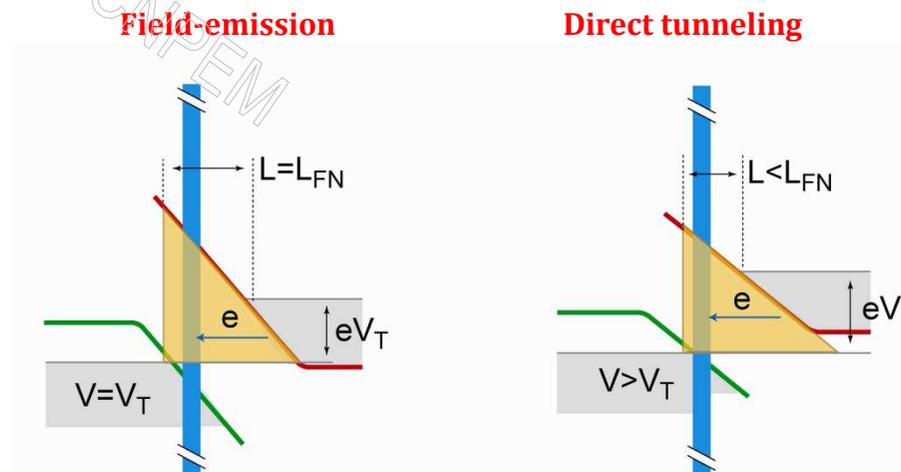
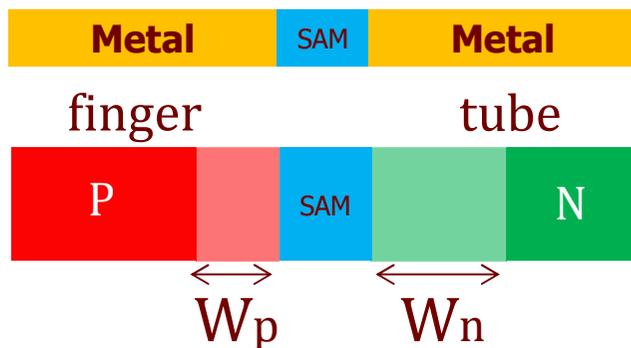
[1] Simmons, J. G. *Journal of Applied Physics* 1963, 34, (1), 238-239.

[2] Gadzuk, J. W.; Plummer, E. W. *Reviews of Modern Physics* 1973, 45, (3), 487-548.

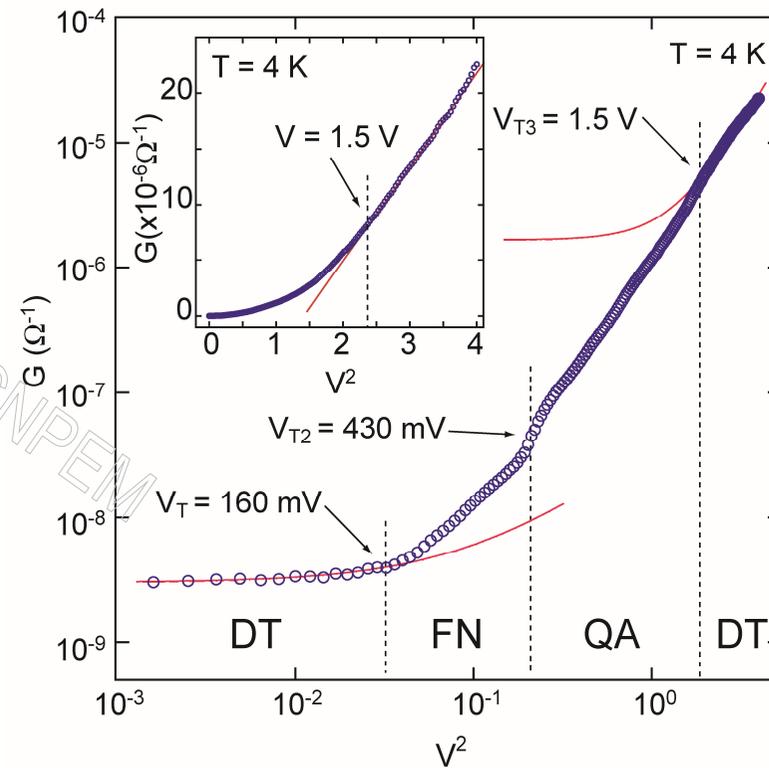
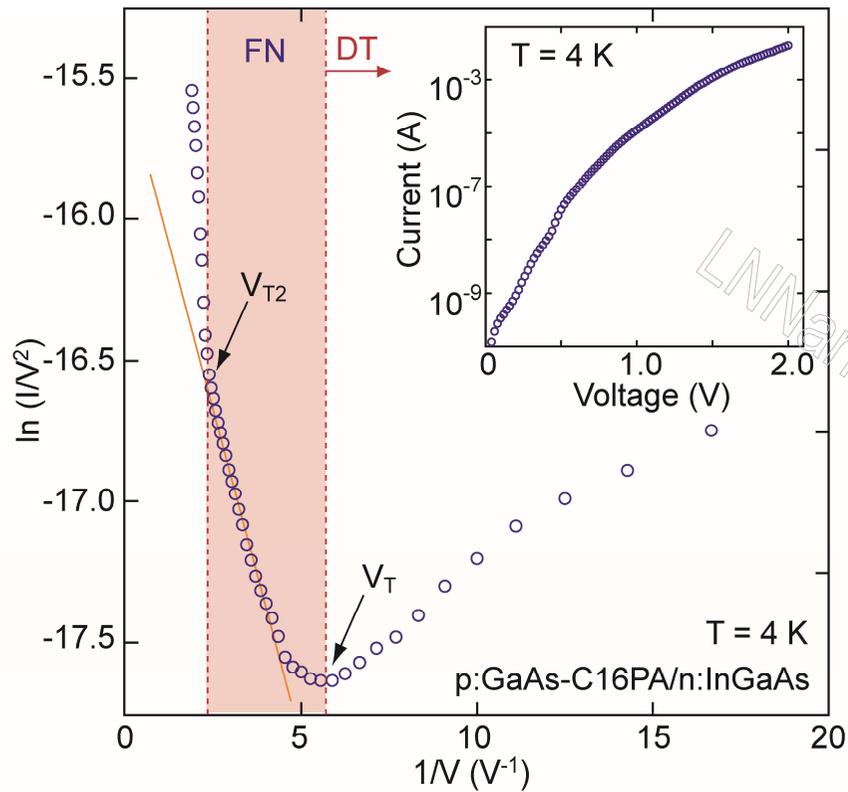
Transport across the hybrid junctions



Beebe et al. ACS Nano 2008

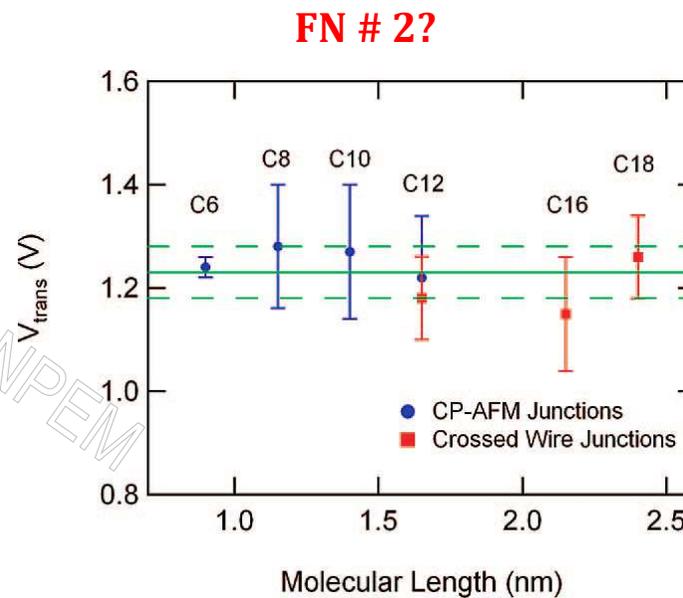
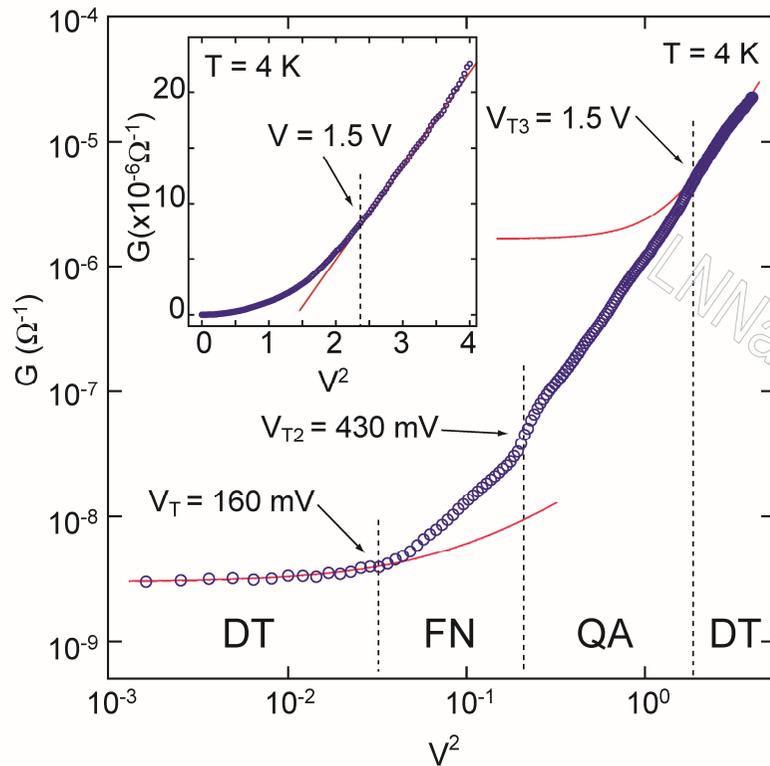


Transport across the hybrid junctions



C.C.Bof Bufon *et al.*, *Nano Lett.* 11, 3727 (2011)

Transport across the hybrid junctions



Beebe et al. ACS Nano 2008

C.C. Bof Bufon *et al.*, *Nano Lett.* 11, 3727 (2011)

Curly contacts

Christian Martin

Nature Materials **10**, 724 (2011) doi:10.1038/nmat3135

Published online 23 September 2011

Applying reliable electrical contacts to self-assembled molecular monolayers poses a persistent challenge in molecular electronics. Evaporated metal top electrodes can cause short circuits at monolayer defects, and solution-processed conducting polymer electrodes may show temperature-dependent electrical characteristics that disguise the physics of molecular charge transport. Carlos Cesar Bof Bufon and colleagues have now developed a process that allows them to contact molecular monolayers using predefined metal and inorganic semiconductor lay...



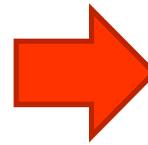
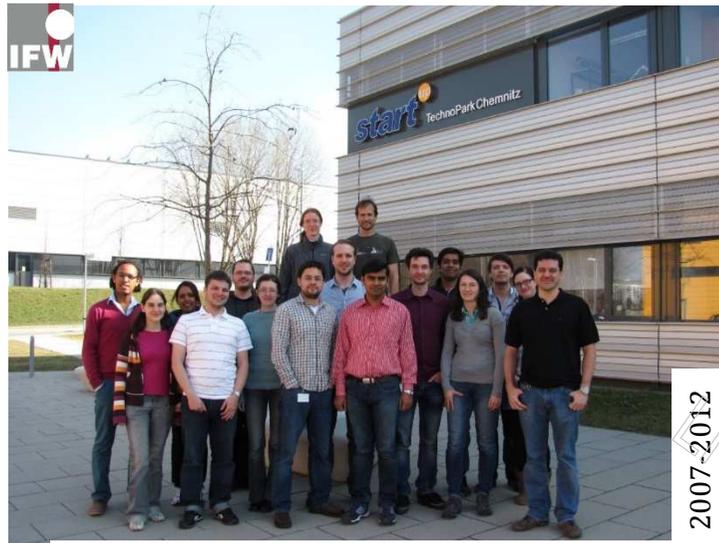
Conclusion

“The interesting fundamental science, the diverse possibilities for creative engineering and the strong potential for broadly influential outcomes make this field of nanomembranes research a fertile one for future investigation.”

J. A. Rogers, M. G. Lagally & R. G. Nuzzo
Nature 477, 45, 2011

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