

# Conductance Switching in Fluorene/TiO<sub>2</sub> Molecular Heterojunctions

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**NRC-CNRC**



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ALBERTA



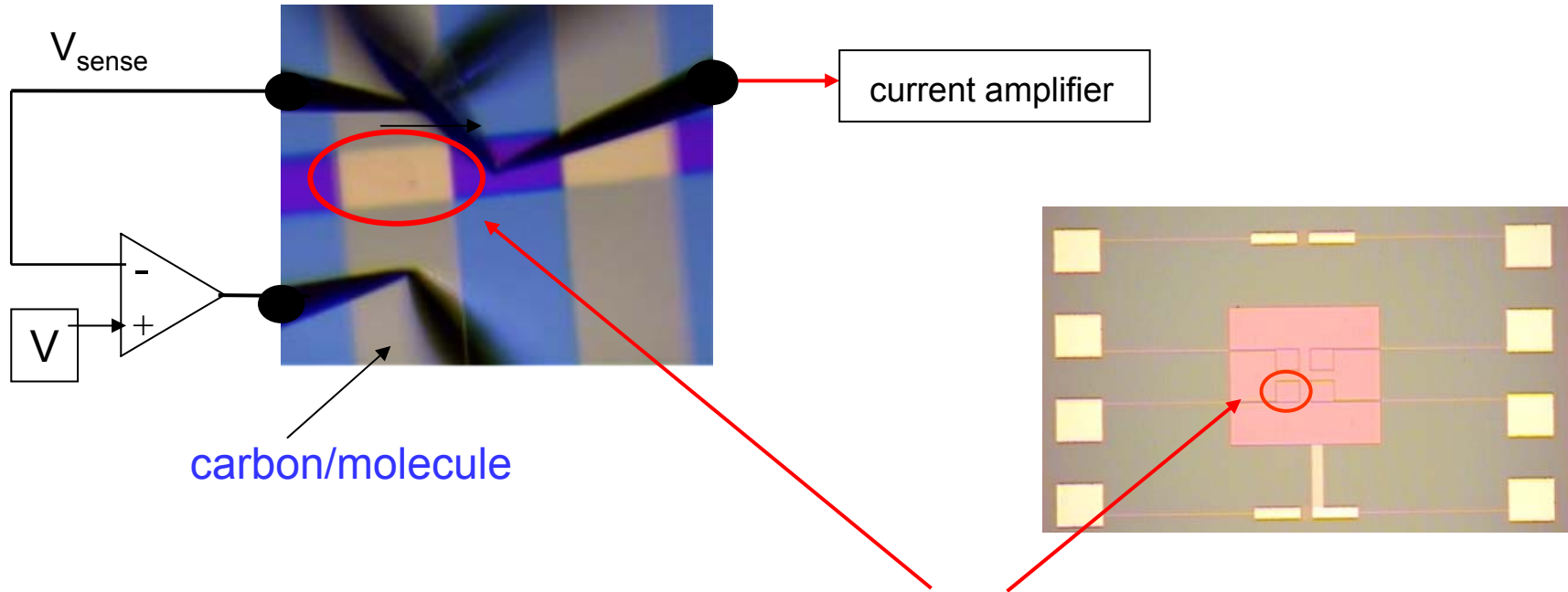
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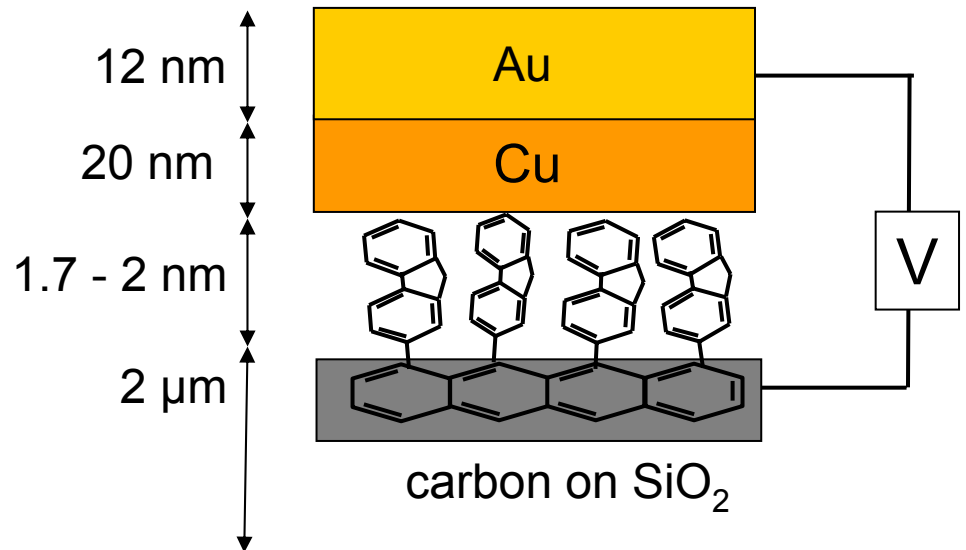
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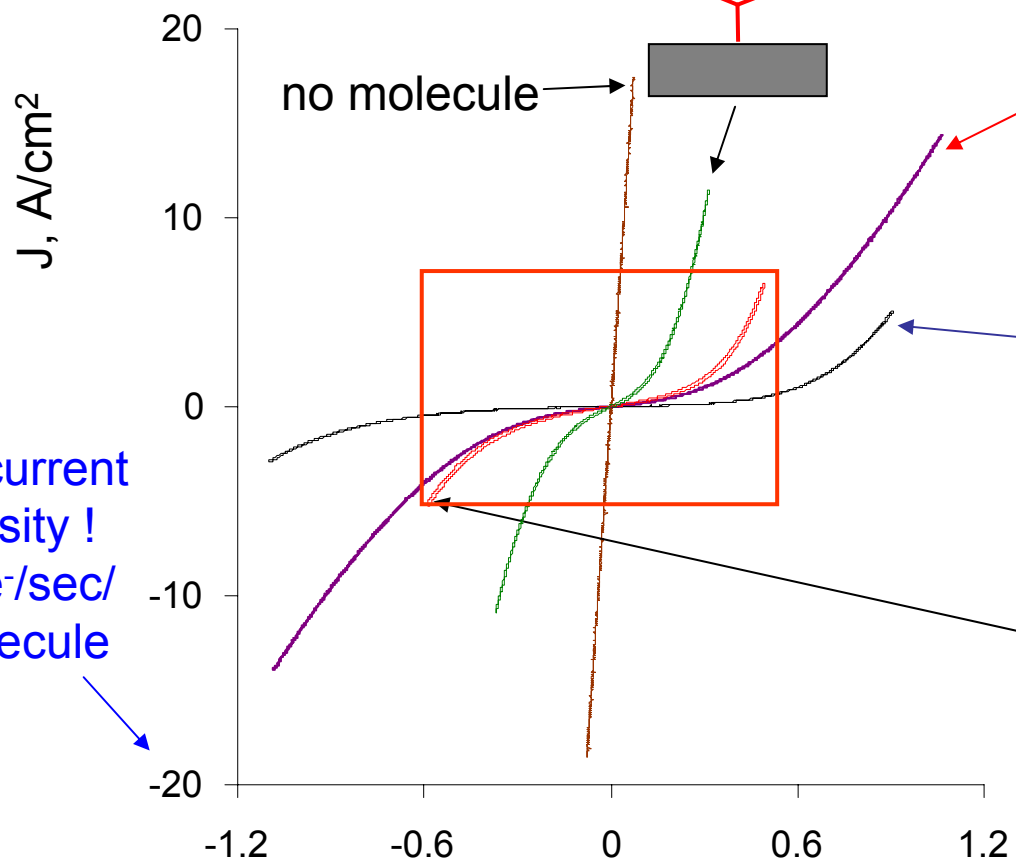
# “Molecular Junction” (Alberta variant):



- strong C-C bond
- strong electronic coupling with substrate
- dense packing,
- thermally stable
- $\sim 10^{10}$  molecules/junction



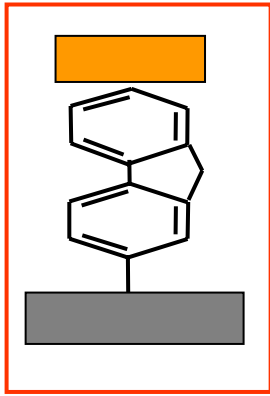
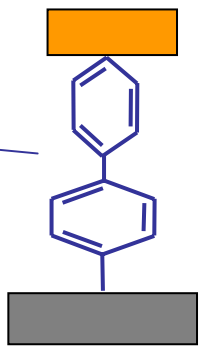
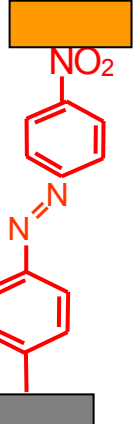
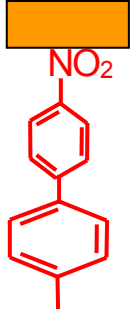
Current/voltage curves  
of molecular monolayers:



Note current density!  
 $\sim 10^5$  e<sup>-</sup>/sec/  
molecule

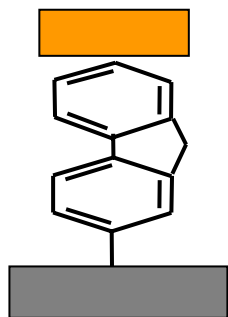
- strong dependence on structure
- invariant for 1 Hz to 100 KHz
- repeatable at least  $10^8$  cycles
- weak T dependence

1000 V/s



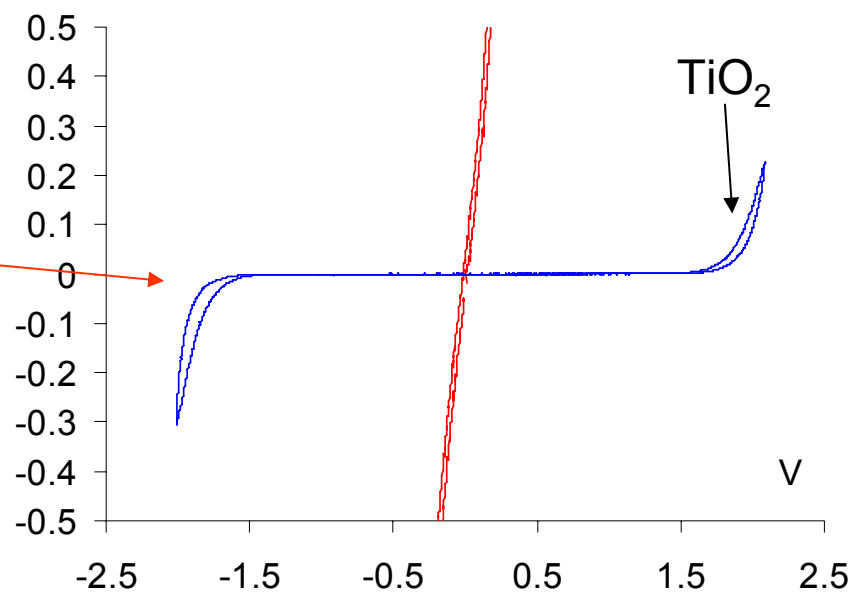
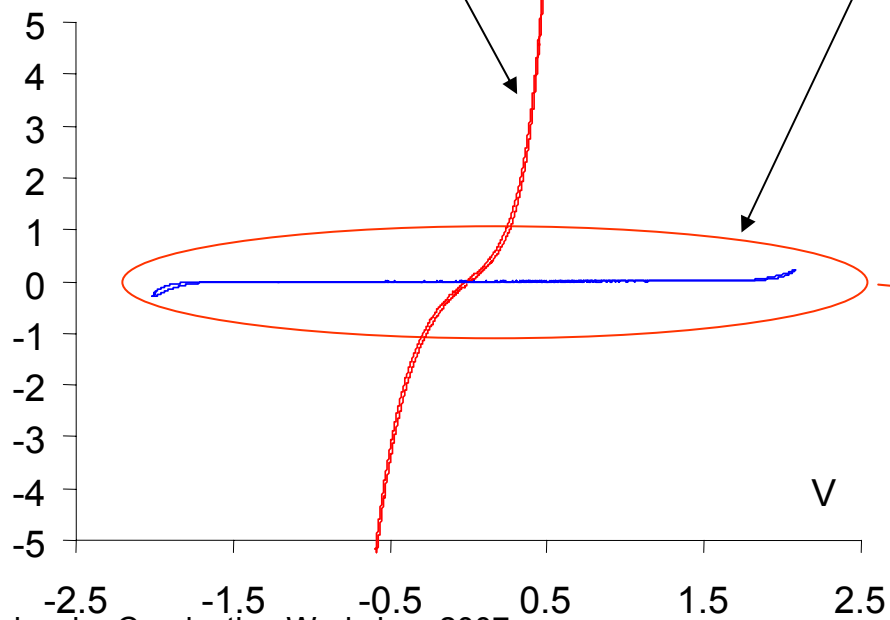
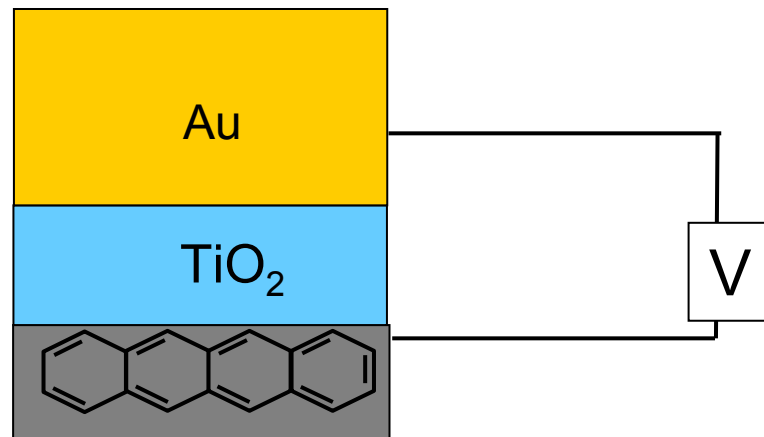
Now, substitute  $\text{TiO}_2$   
for fluorene:

fluorene=

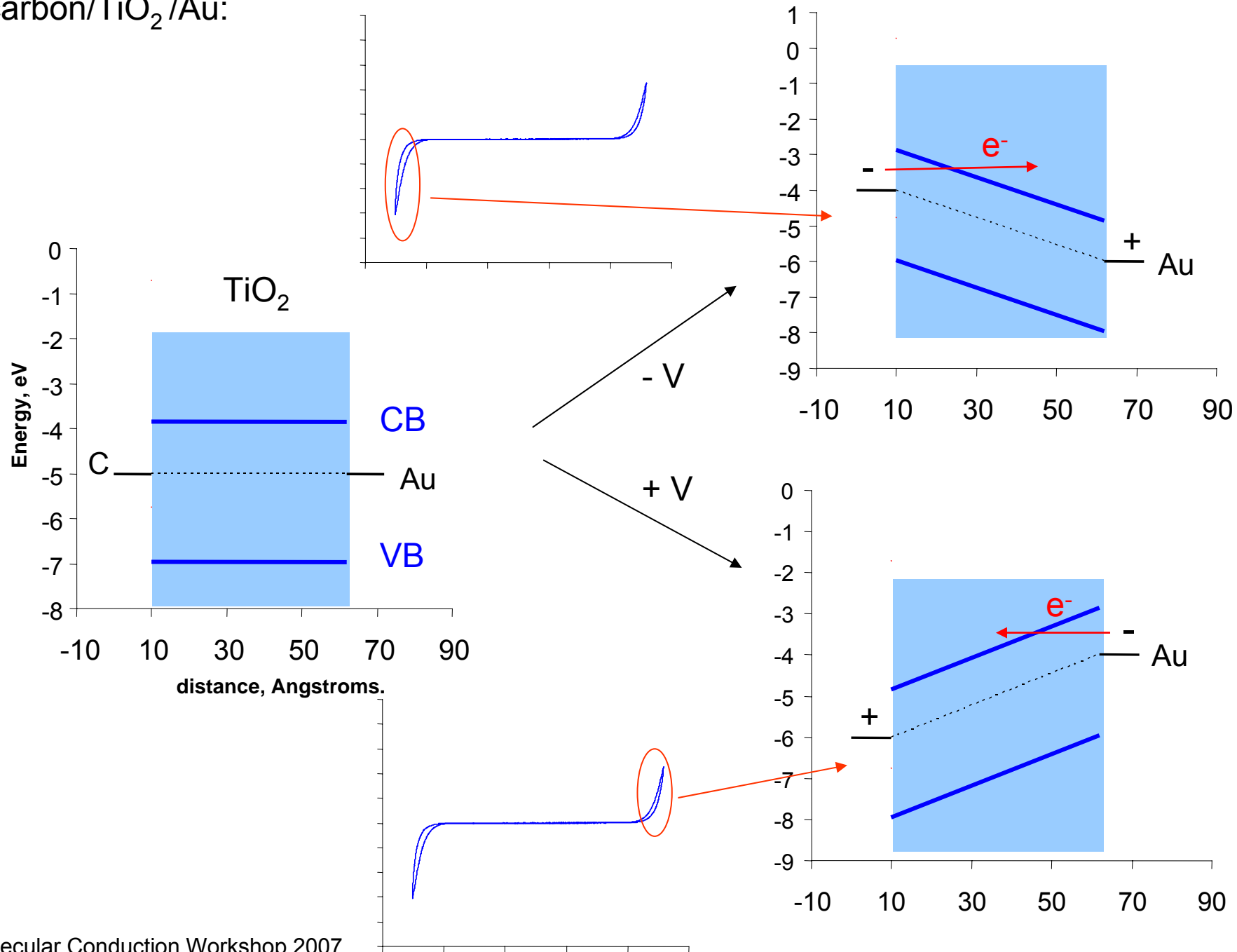


12 nm

5.2 nm

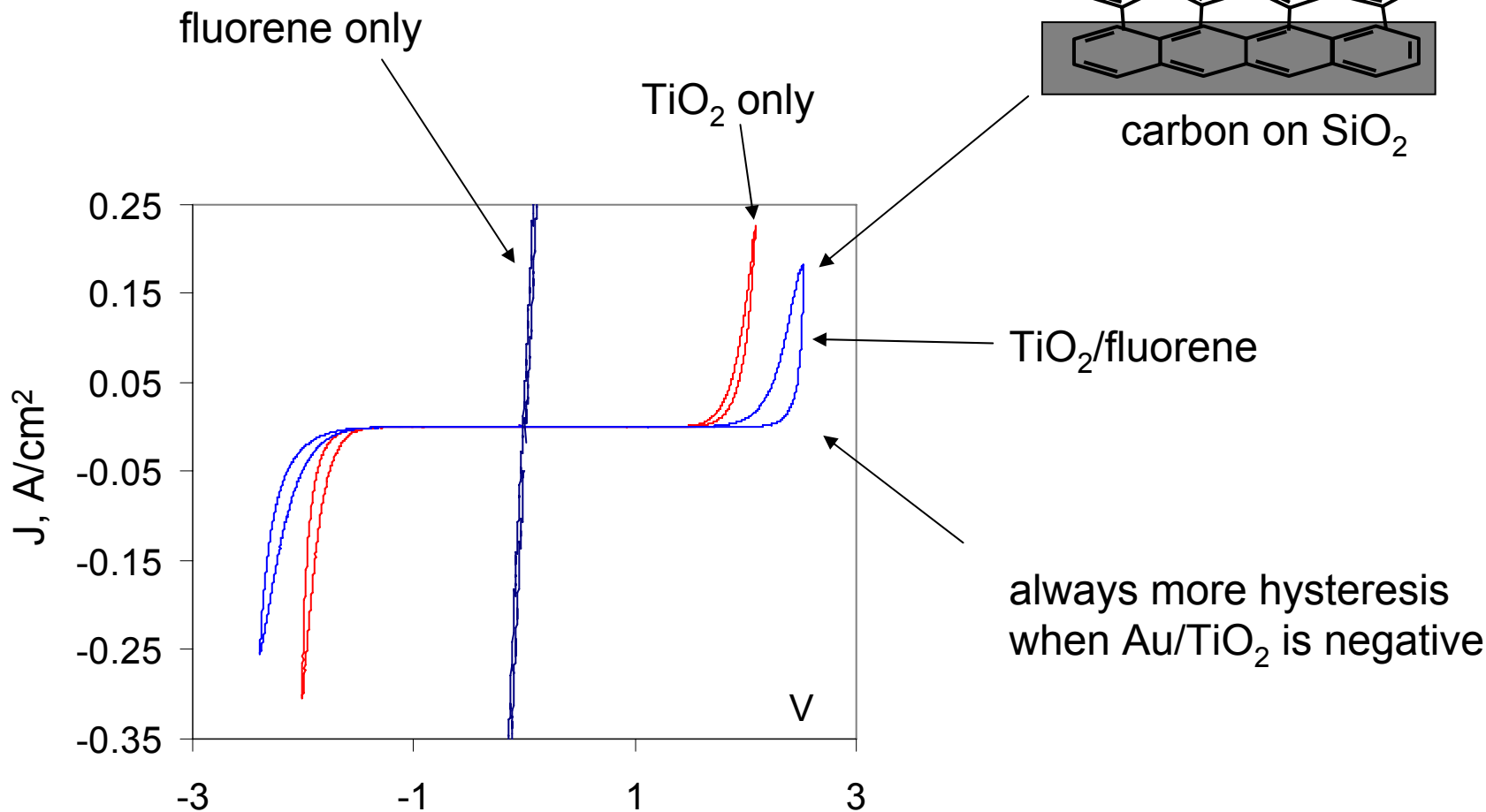
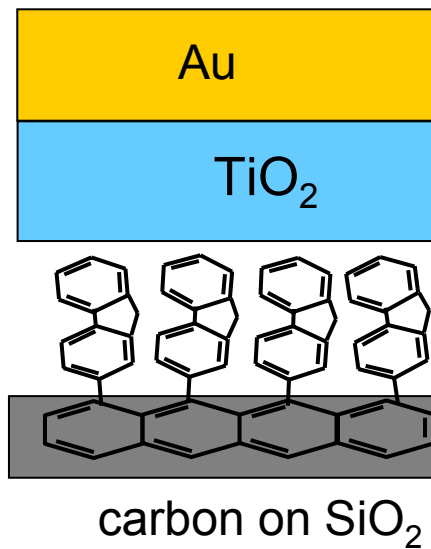


carbon/TiO<sub>2</sub>/Au:

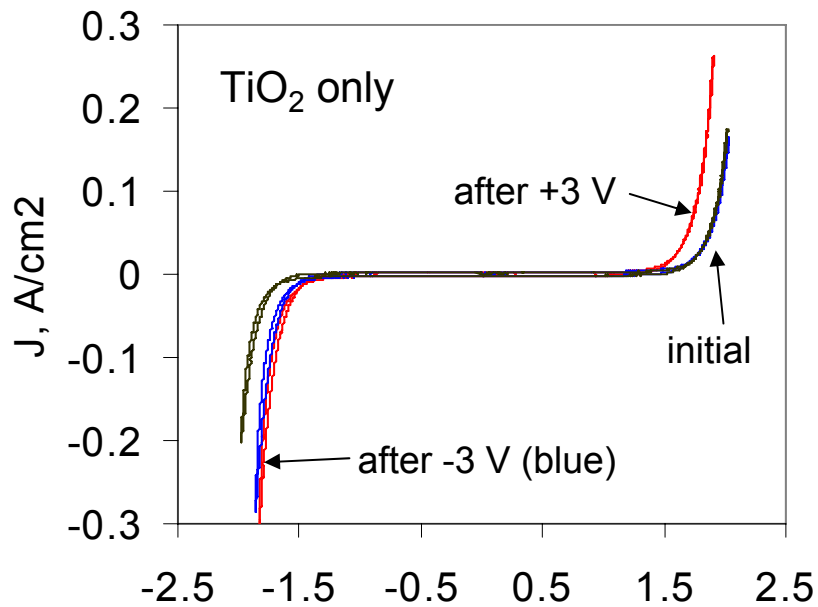
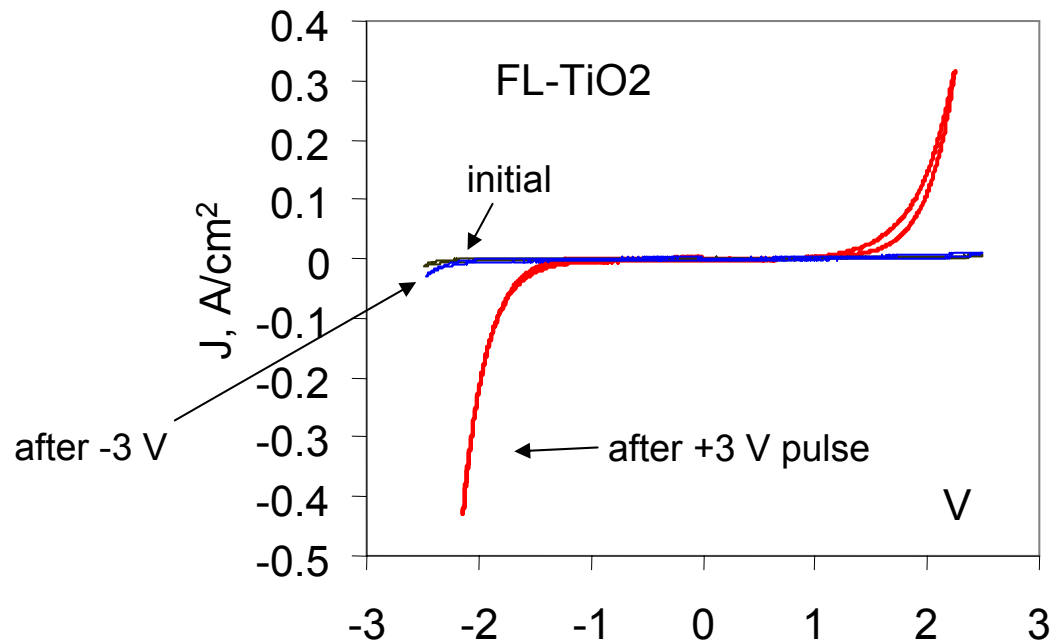


# Molecular "heterojunction"

5.2 nm

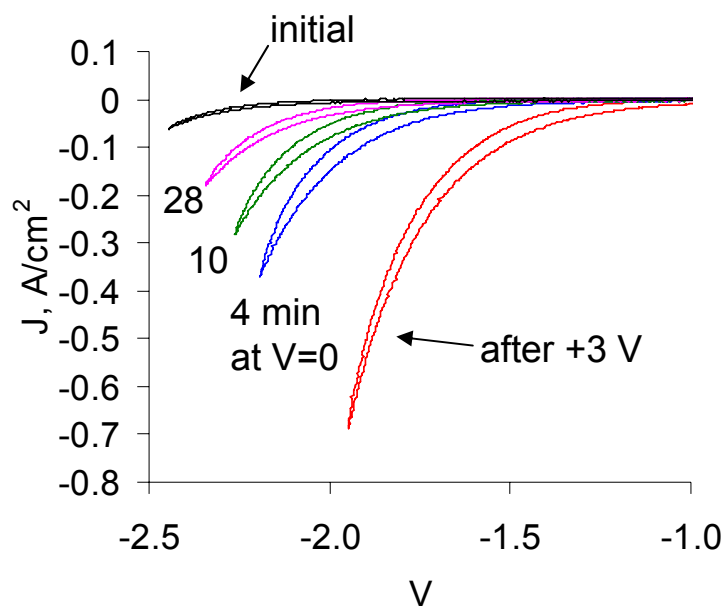
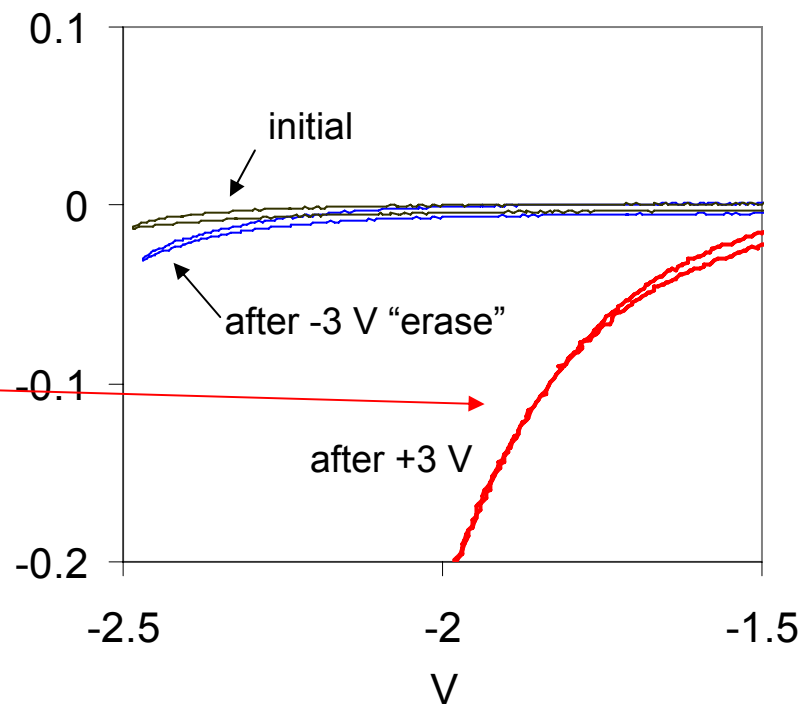
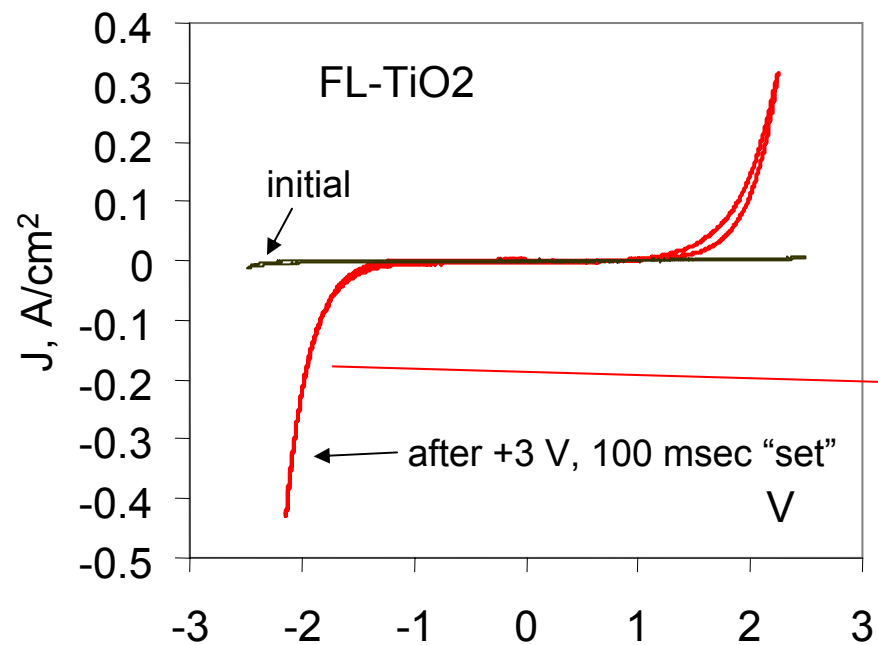


Heterojunction has a strange reaction to voltage pulses (+ or - 3 V, 0.05 -100 msec):



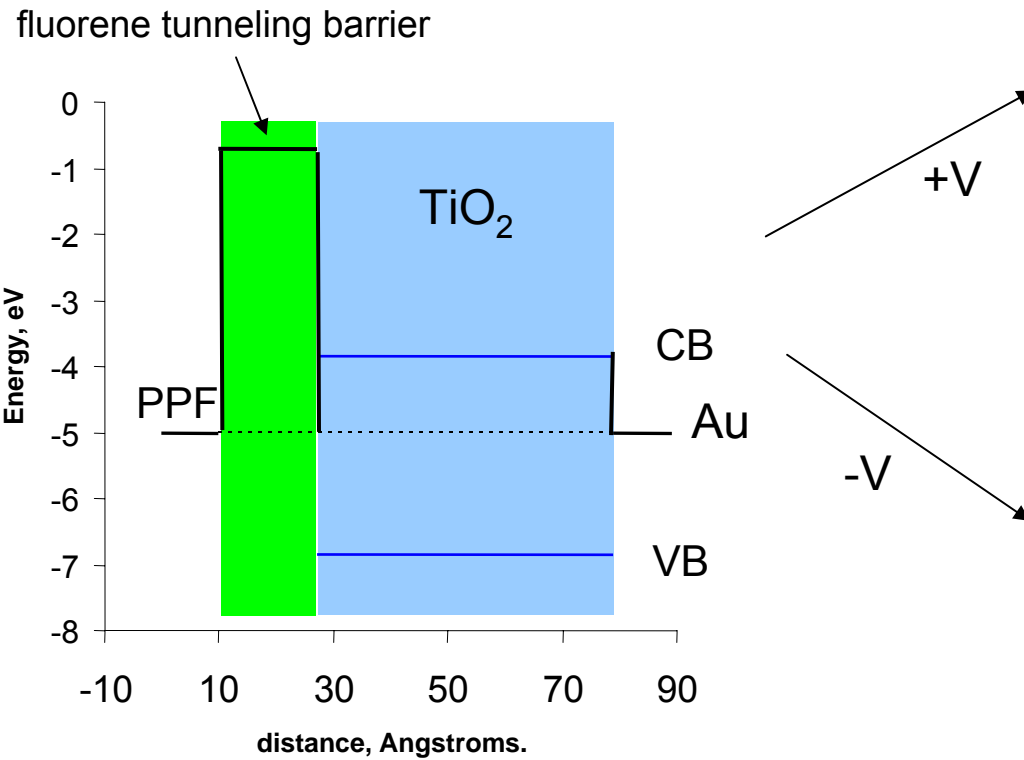
FL-TiO<sub>2</sub> heterojunction is structurally asymmetric, and has “memory” not observed with either TiO<sub>2</sub> or FL alone



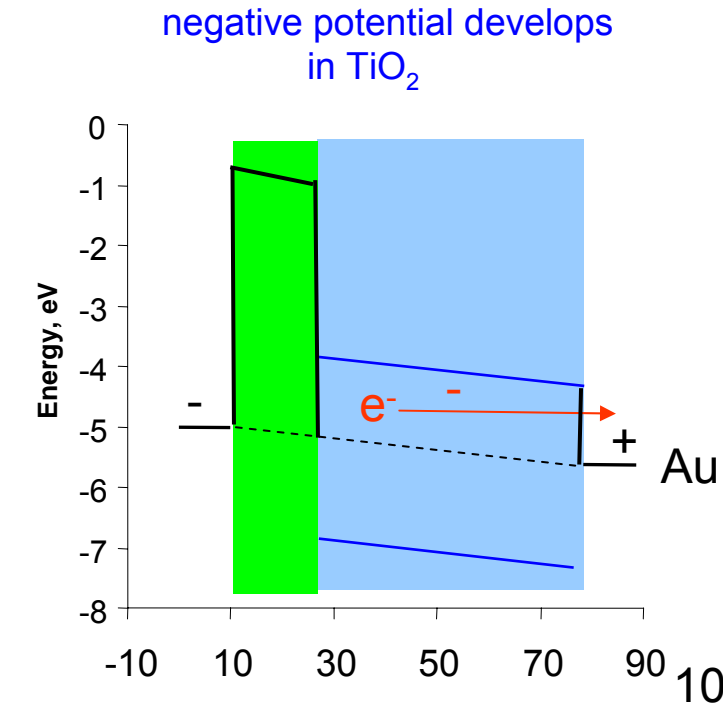
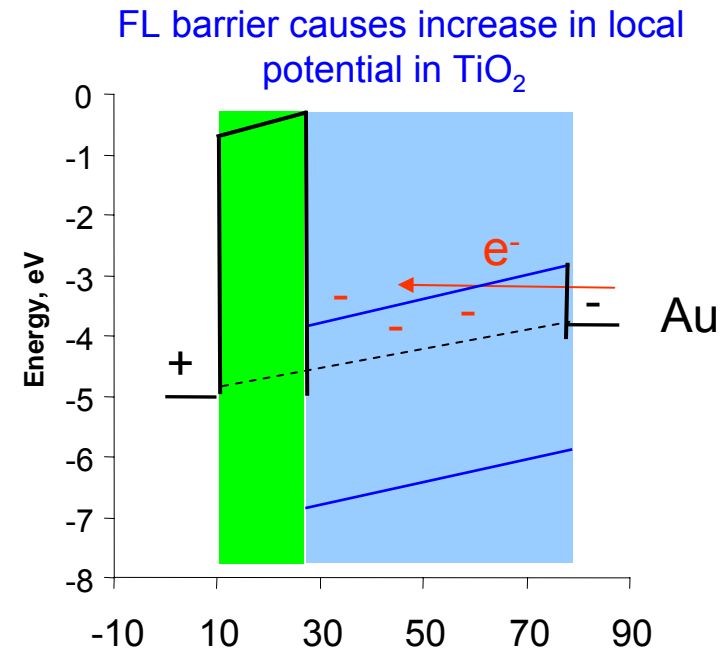


What is causing this persistent change in junction conductivity?

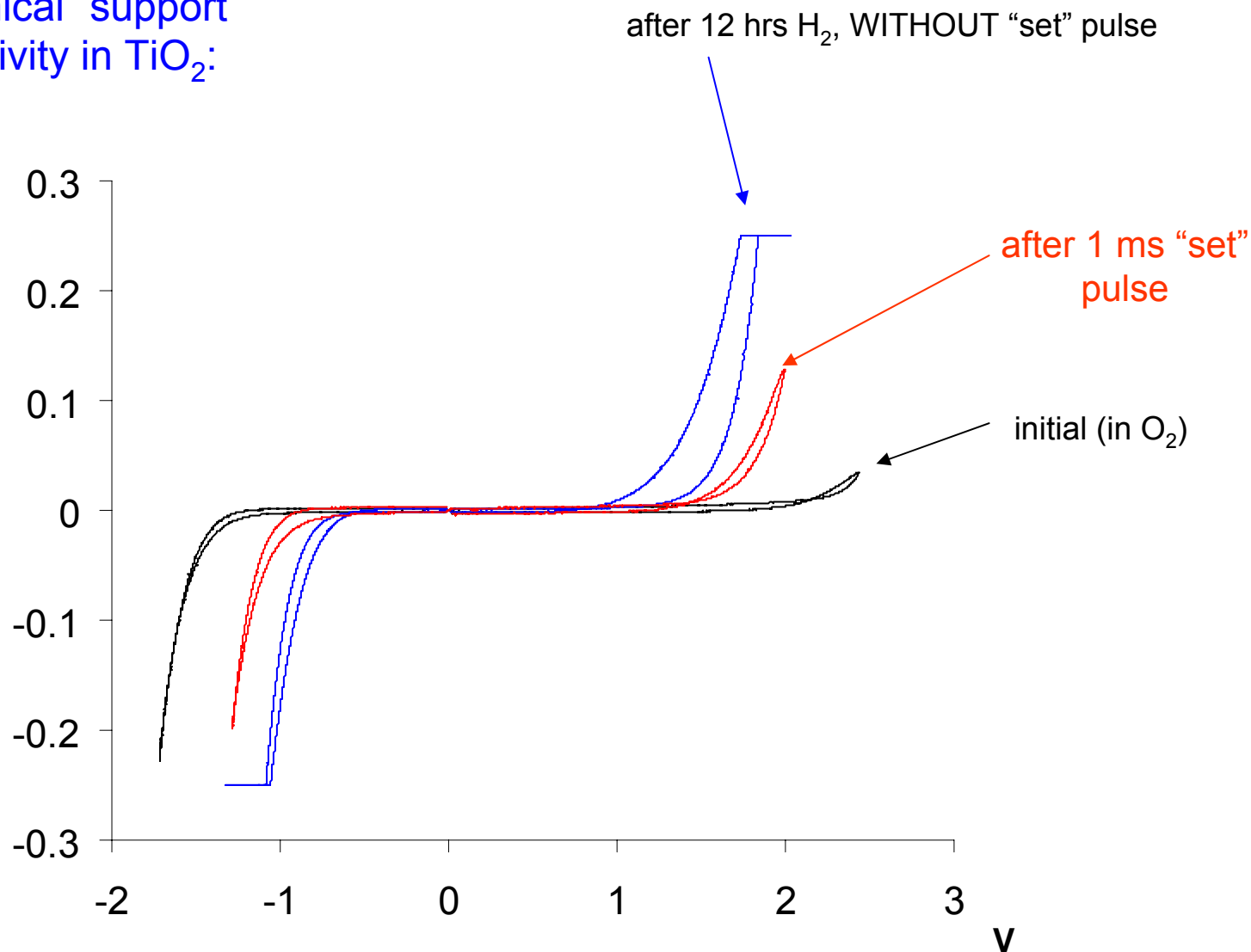
Suppose fluorene is merely a tunneling barrier:



Fluorene barrier results in a space charge in the TiO<sub>2</sub>. When Au is negative, the Fermi level in the TiO<sub>2</sub> shifts to higher energy. Does the TiO<sub>2</sub> then get reduced?



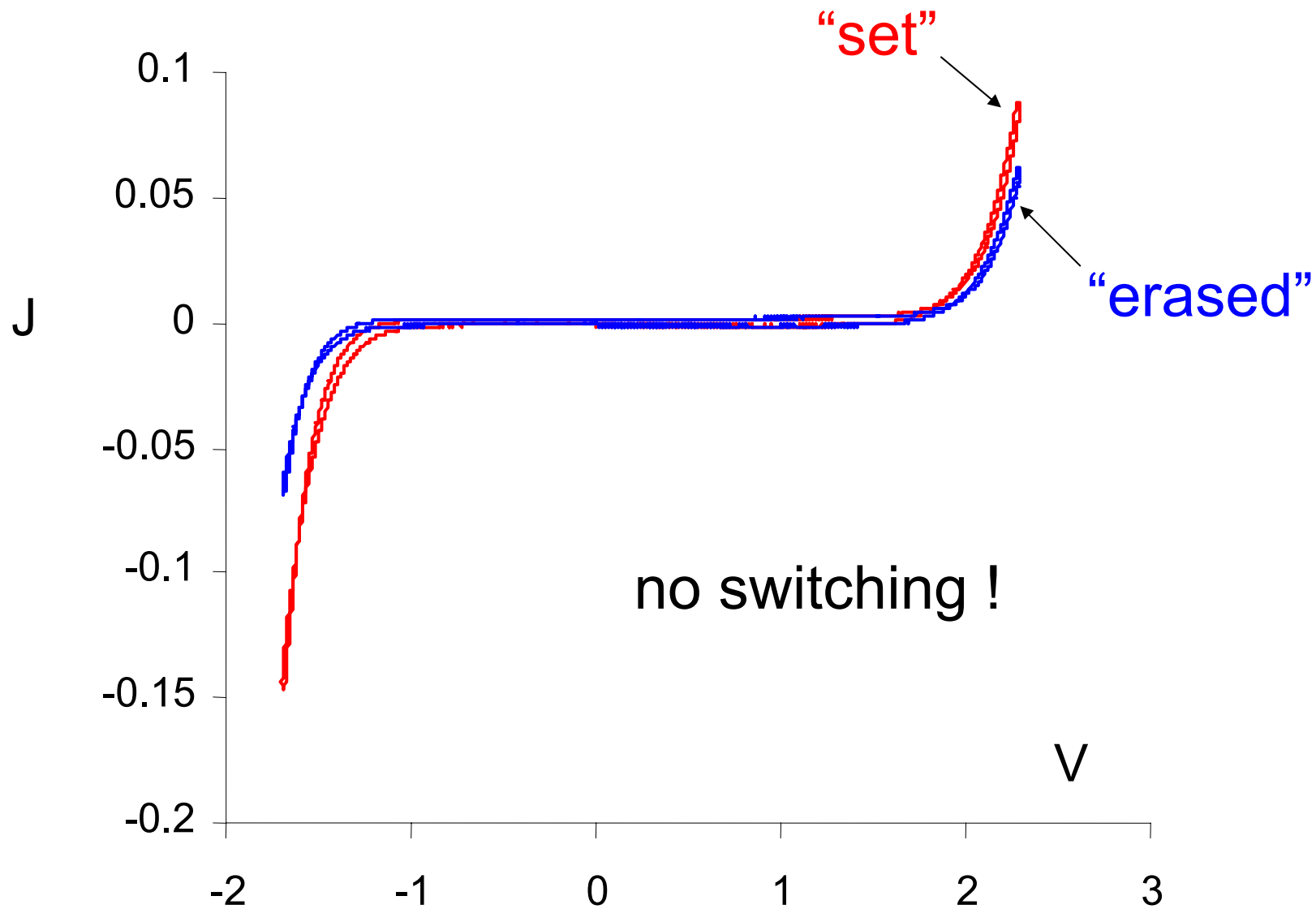
Some “chemical” support  
for redox activity in  $\text{TiO}_2$ :



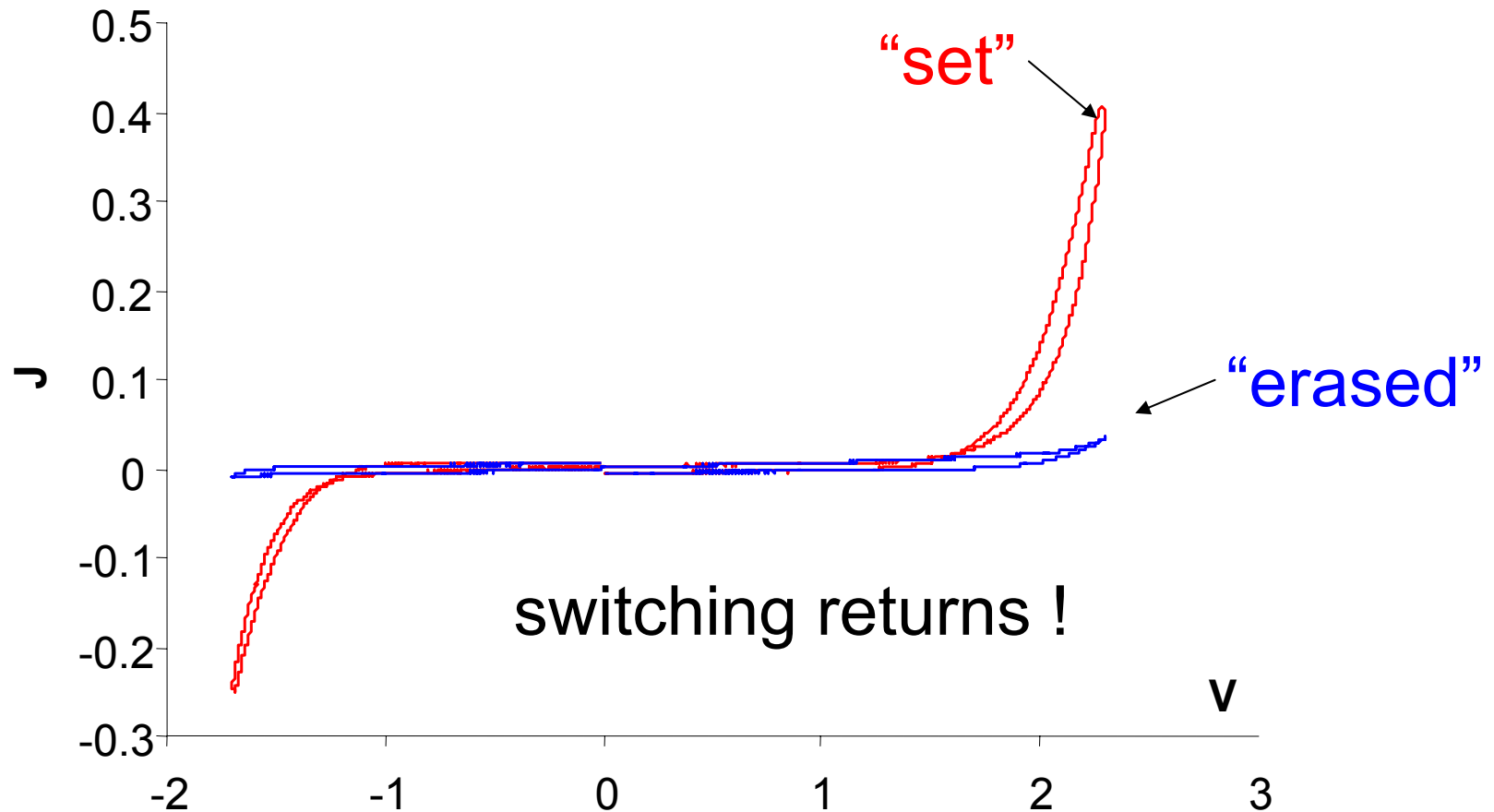
$\text{H}_2$  and  $\text{O}_2$  treatment mimic in ~12 hours what a  
“set” pulse can do in 1 msec

## More “chemistry”:

Junction made in dry conditions, and kept dry:

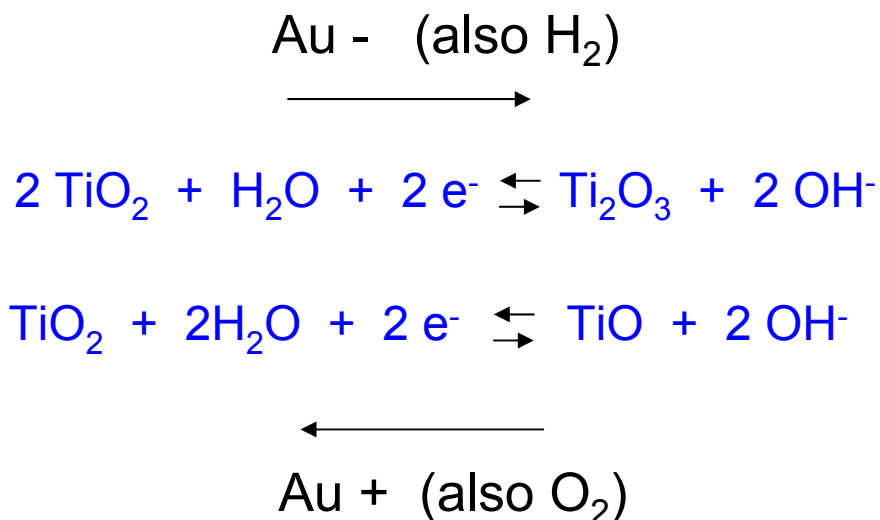


Same junction, exposed to 20 torr H<sub>2</sub>O overnight:



- H<sub>2</sub> and O<sub>2</sub> mimic effect of 1 msec “set” and “erase” pulses
- H<sub>2</sub>O required for conductance switching

Some likely possibilities when Au is negative:



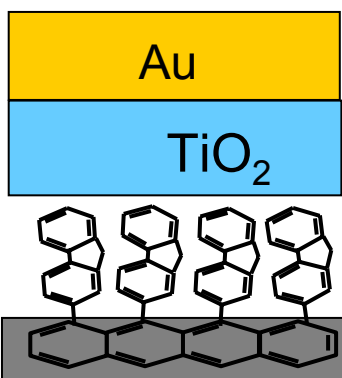
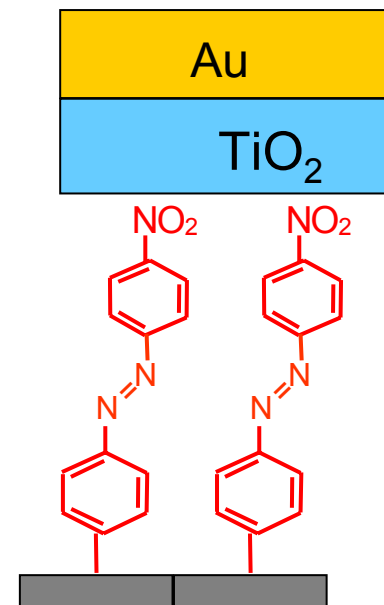
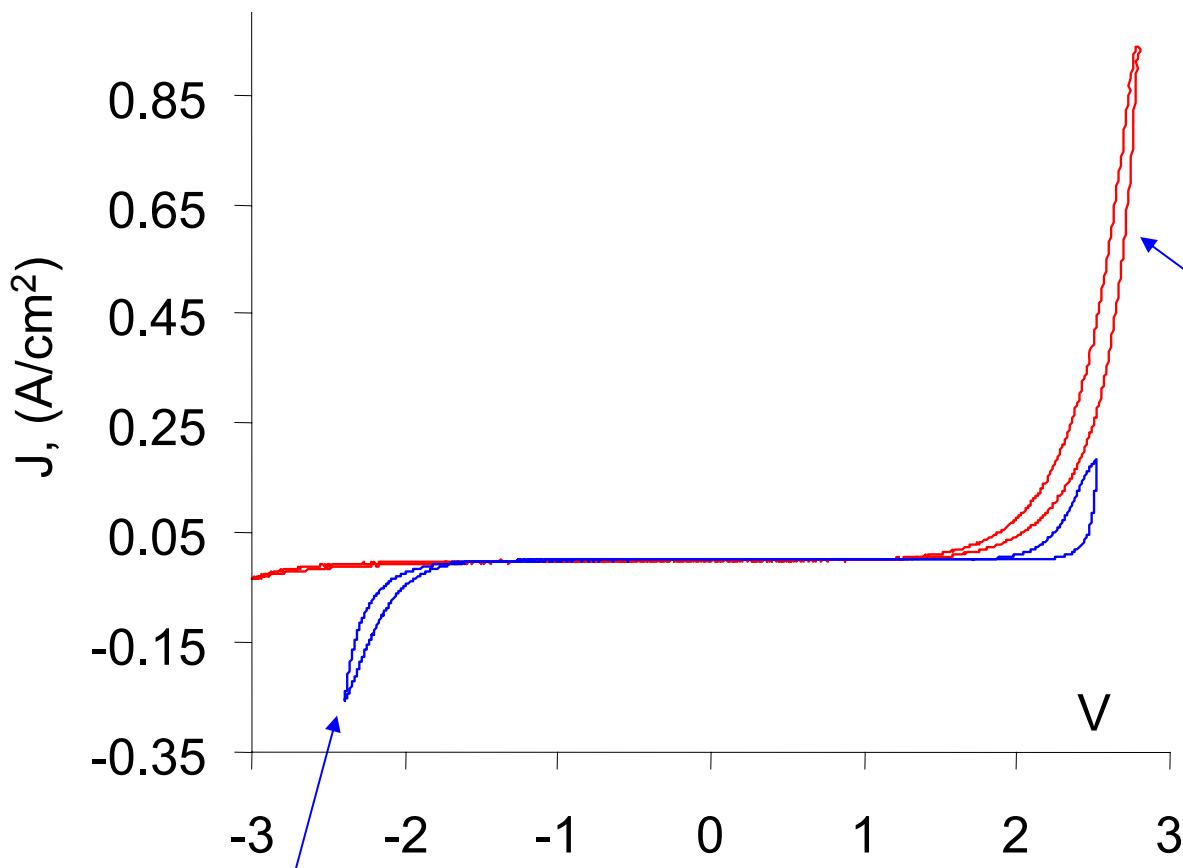
Bias-induced redox  
reactions in a "cell"  
~12 nm thick

Fluorene monolayer causes Fermi level shifts in  $\text{TiO}_2$ , causing its reduction, to make metallic  $\text{TiO}$  and  $\text{Ti}_2\text{O}_3$   
"Dynamic doping" induced by heterojunction asymmetry

resistivities:

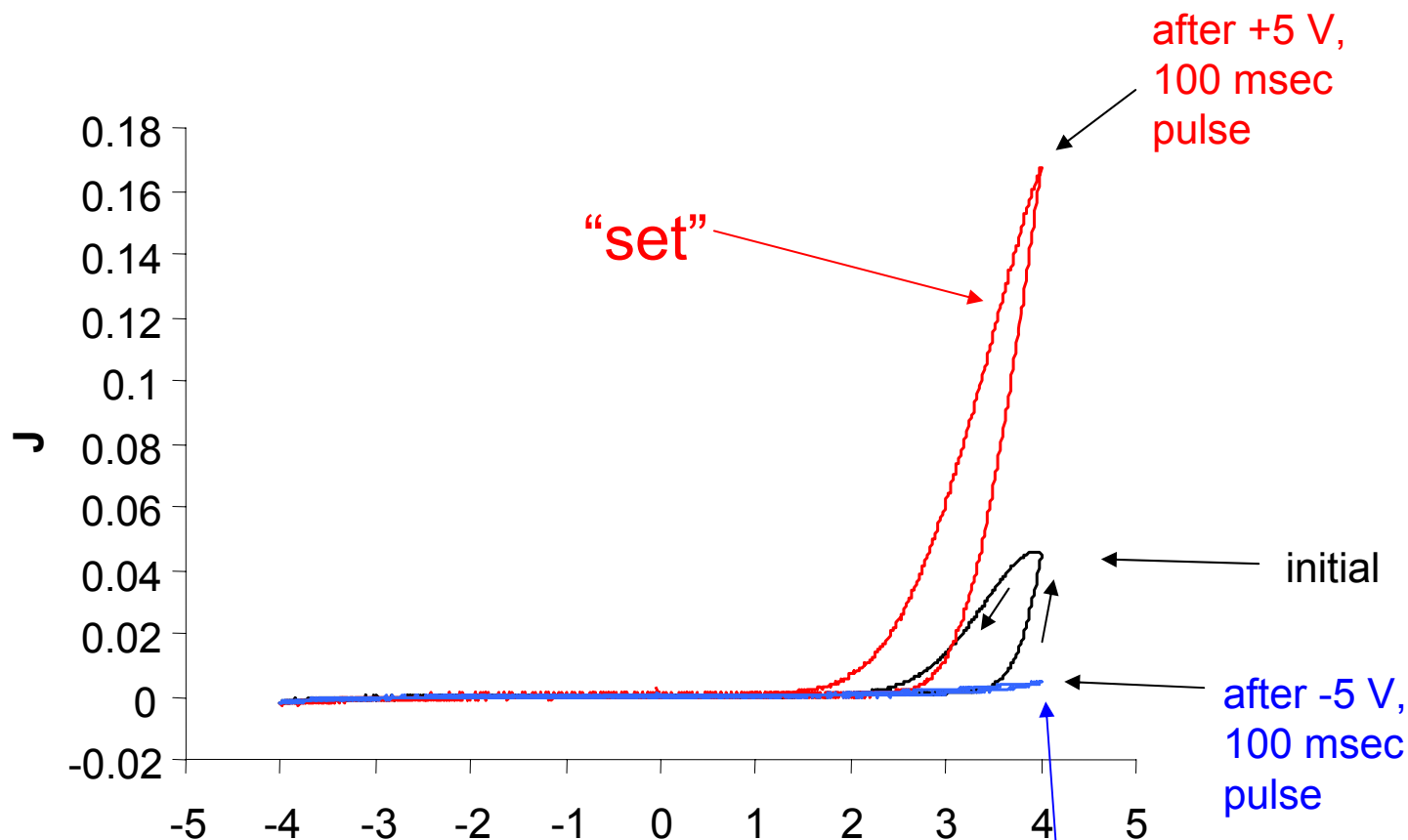
Ti metal:  $42 \mu\Omega\text{-cm}$   
TiO:  $170 \mu\Omega\text{-cm}$   
TiO<sub>2</sub>:  $> 10^{10} \mu\Omega\text{-cm}$

# Is the electronics *molecular*?



NAB/TiO<sub>2</sub> shows rectification,  
Fluorene/TiO<sub>2</sub> does not

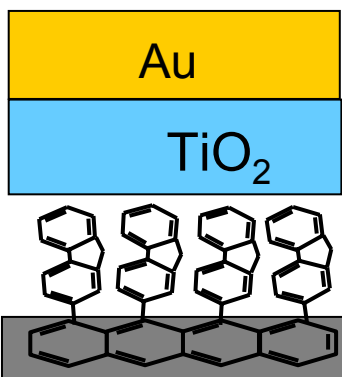
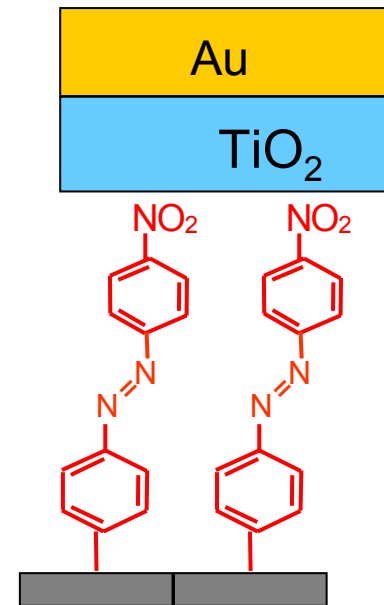
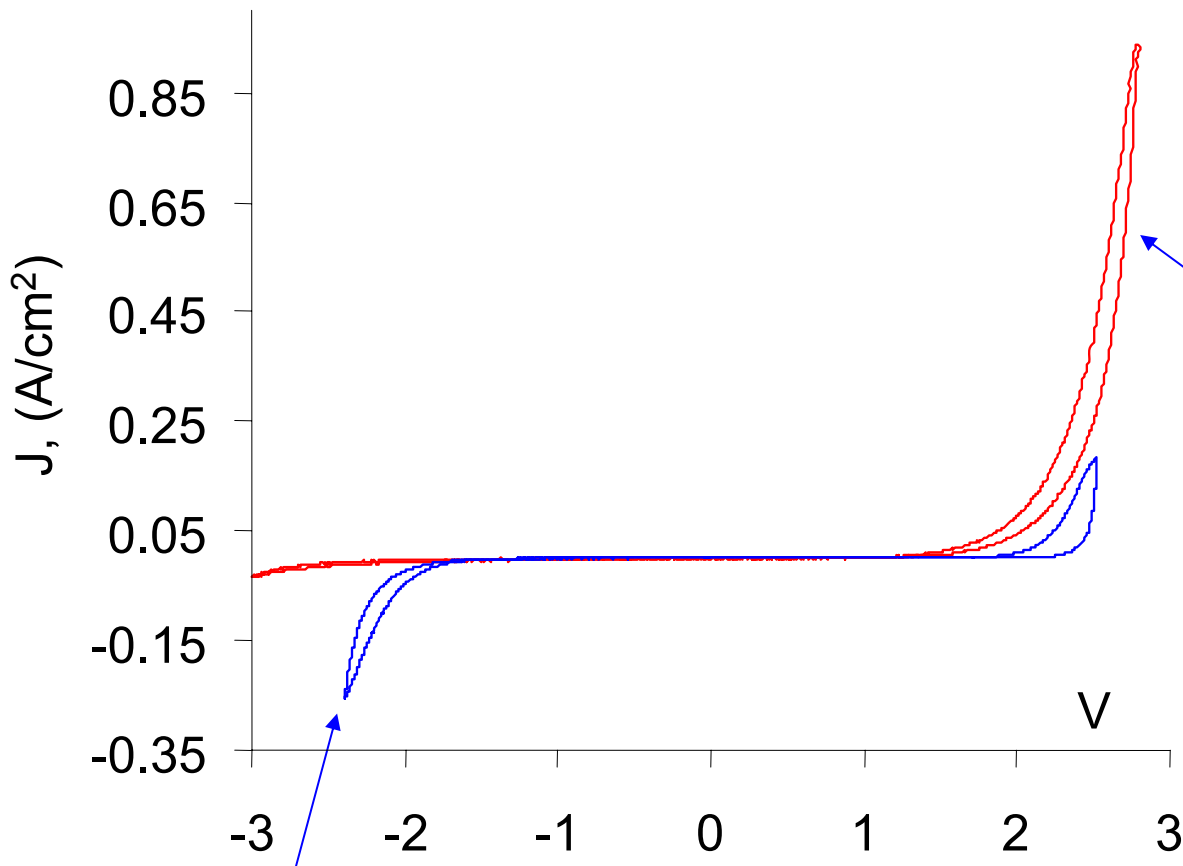
NAB/TiO<sub>2</sub> devices exhibit “memory”, like FL/TiO<sub>2</sub>:



Both show “memory”, but why does NAB rectify and fluorene not?



# Is the electronics *molecular*?



NAB/TiO<sub>2</sub> shows rectification,  
Fluorene/TiO<sub>2</sub> does not

PPF/NAB/TiO<sub>2</sub>/Au

-V

Coulomb barrier !

current

+V

fast

slow

fast

slow

X

Au

NAB  
HOMO

TiO<sub>2</sub> VB

- PPF

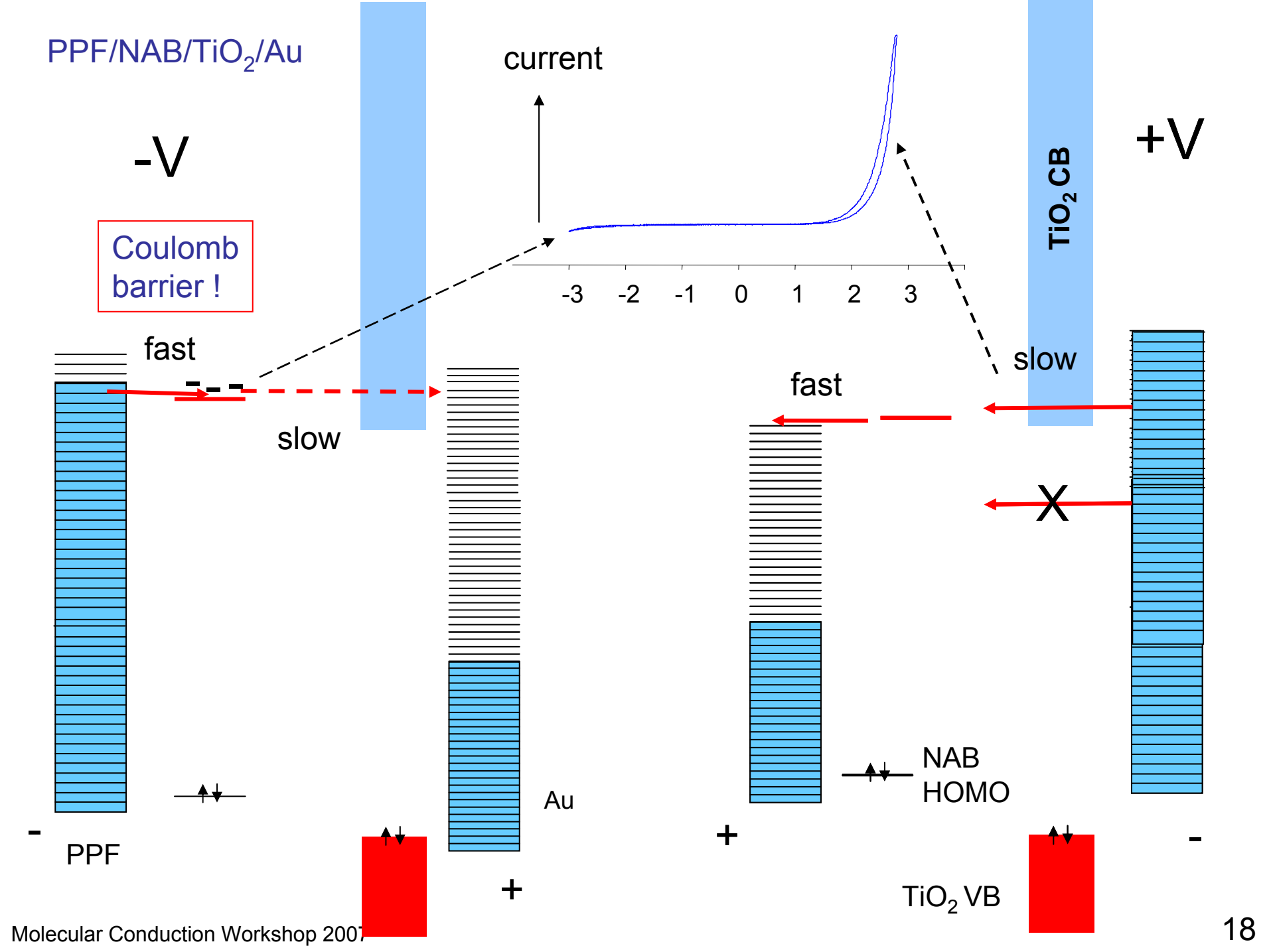
+

+

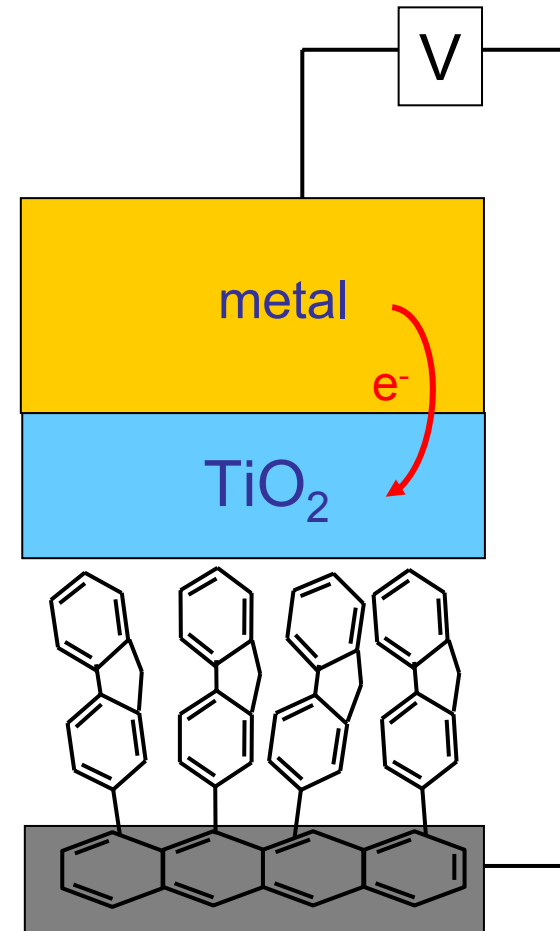
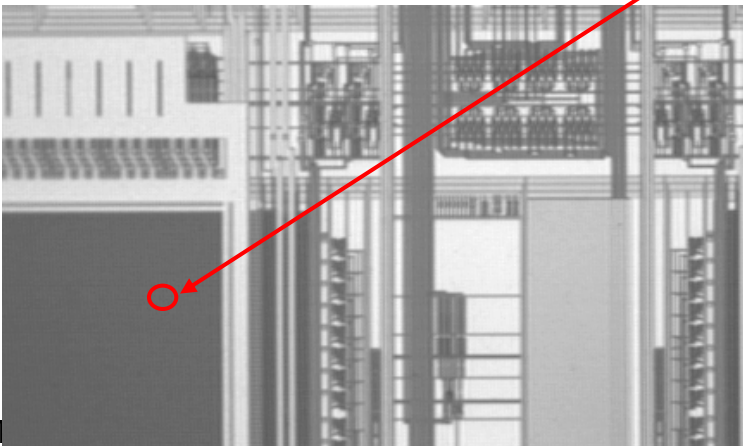
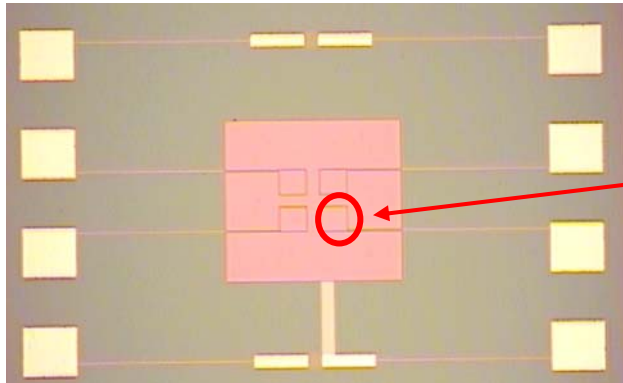
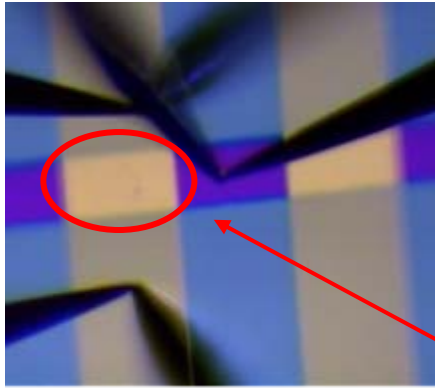
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-3 -2 -1 0 1 2 3

TiO<sub>2</sub> CB



# Integration with CMOS:



ZettaCore prototype molecular memory chip

