

Conductance Switching in Fluorene/TiO₂ Molecular Heterojunctions

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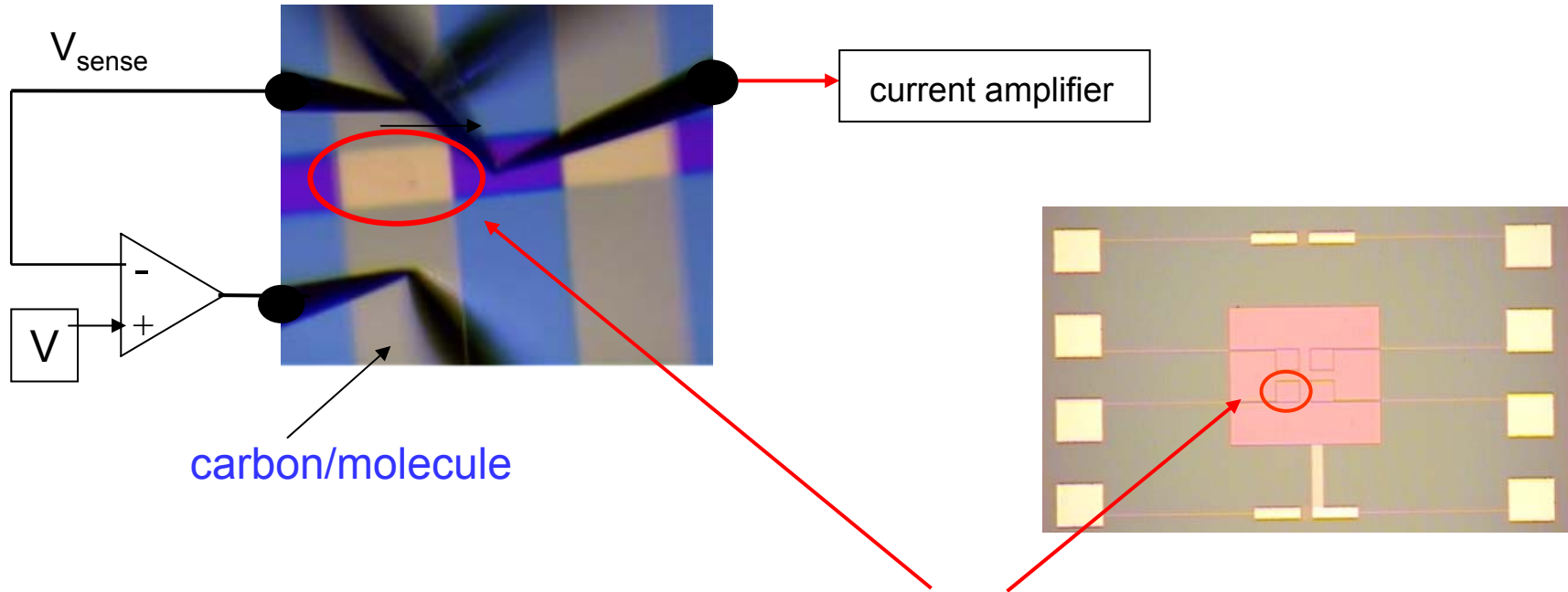
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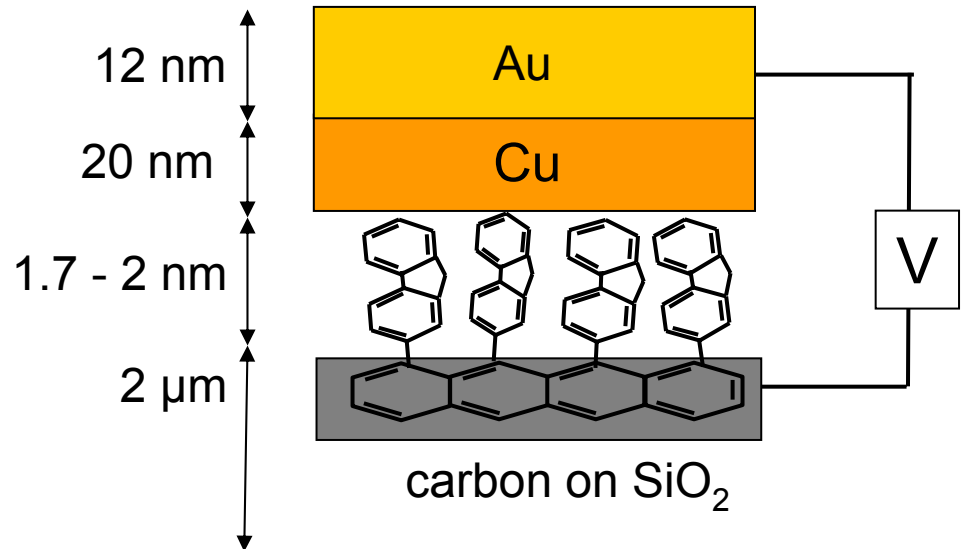


“Molecular Junction” (Alberta variant):

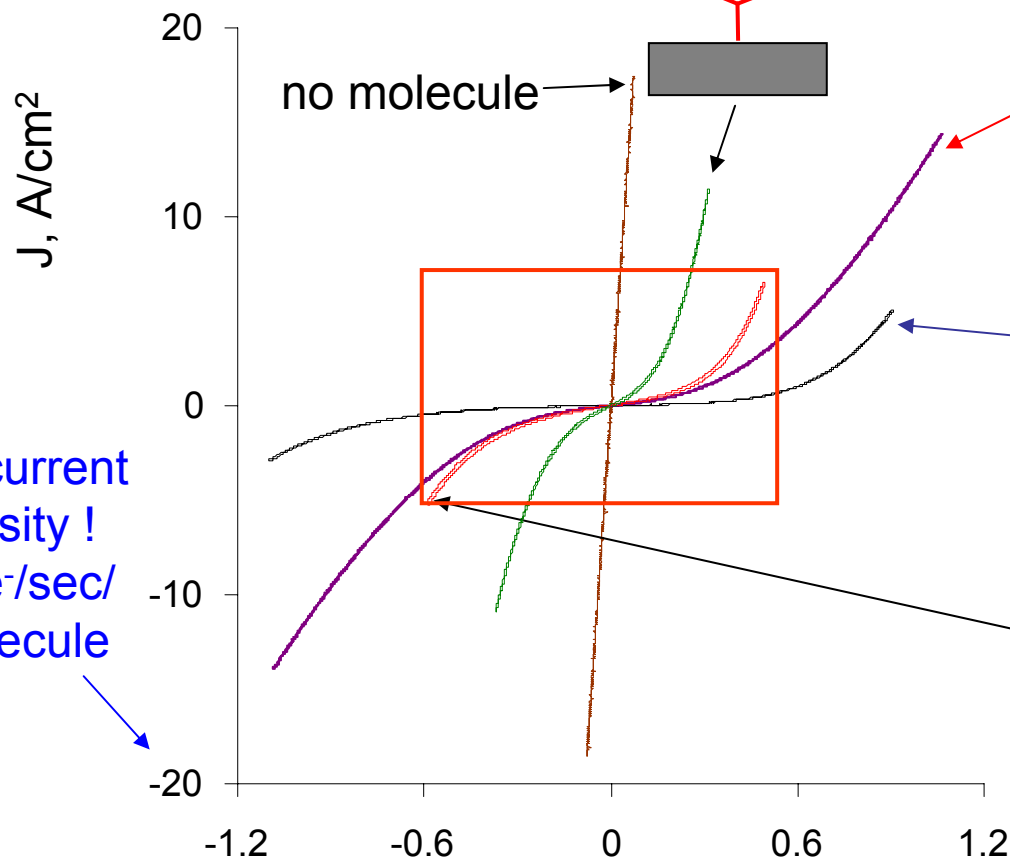


carbon/molecule

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

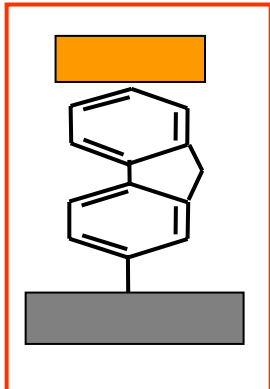
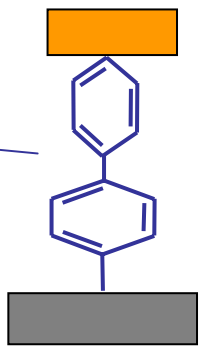
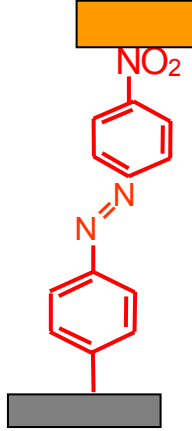
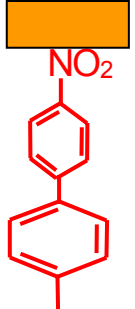


Current/voltage curves
of molecular monolayers:



Note current density!
 $\sim 10^5$ e⁻/sec/
molecule

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

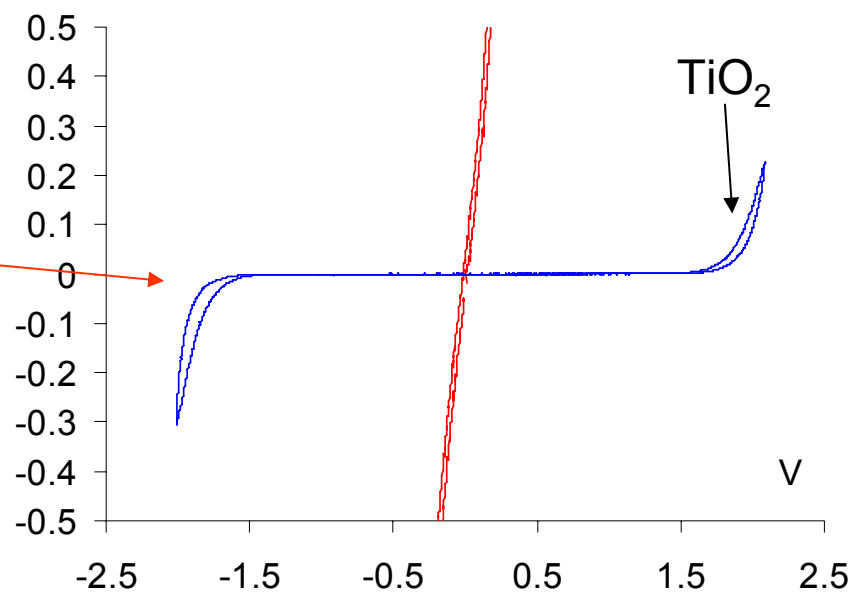
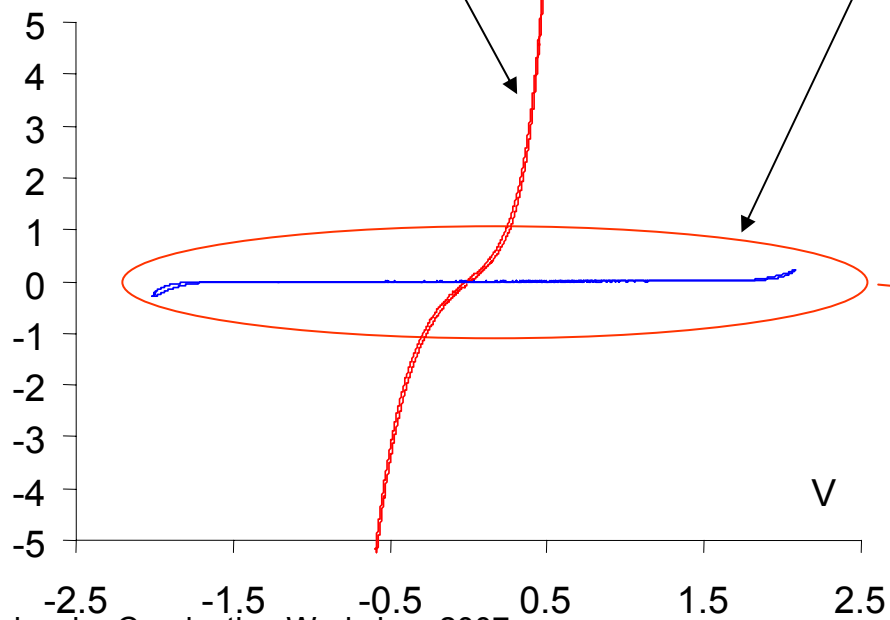
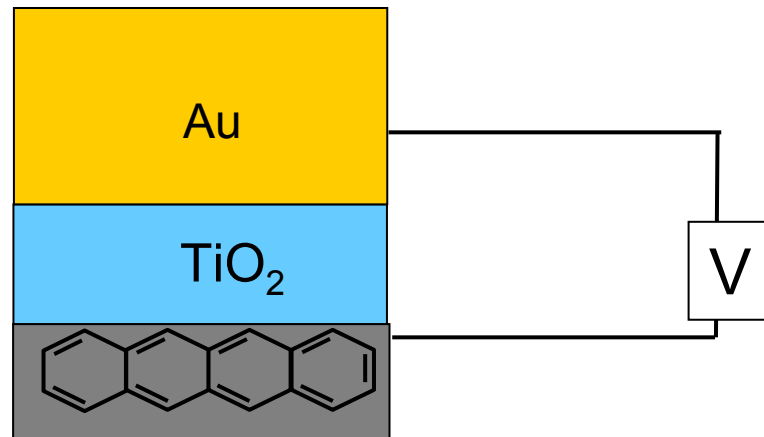
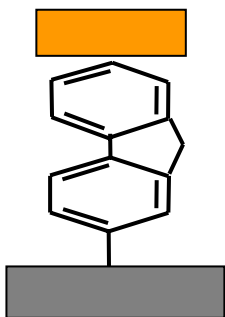


Now, substitute TiO_2
for fluorene:

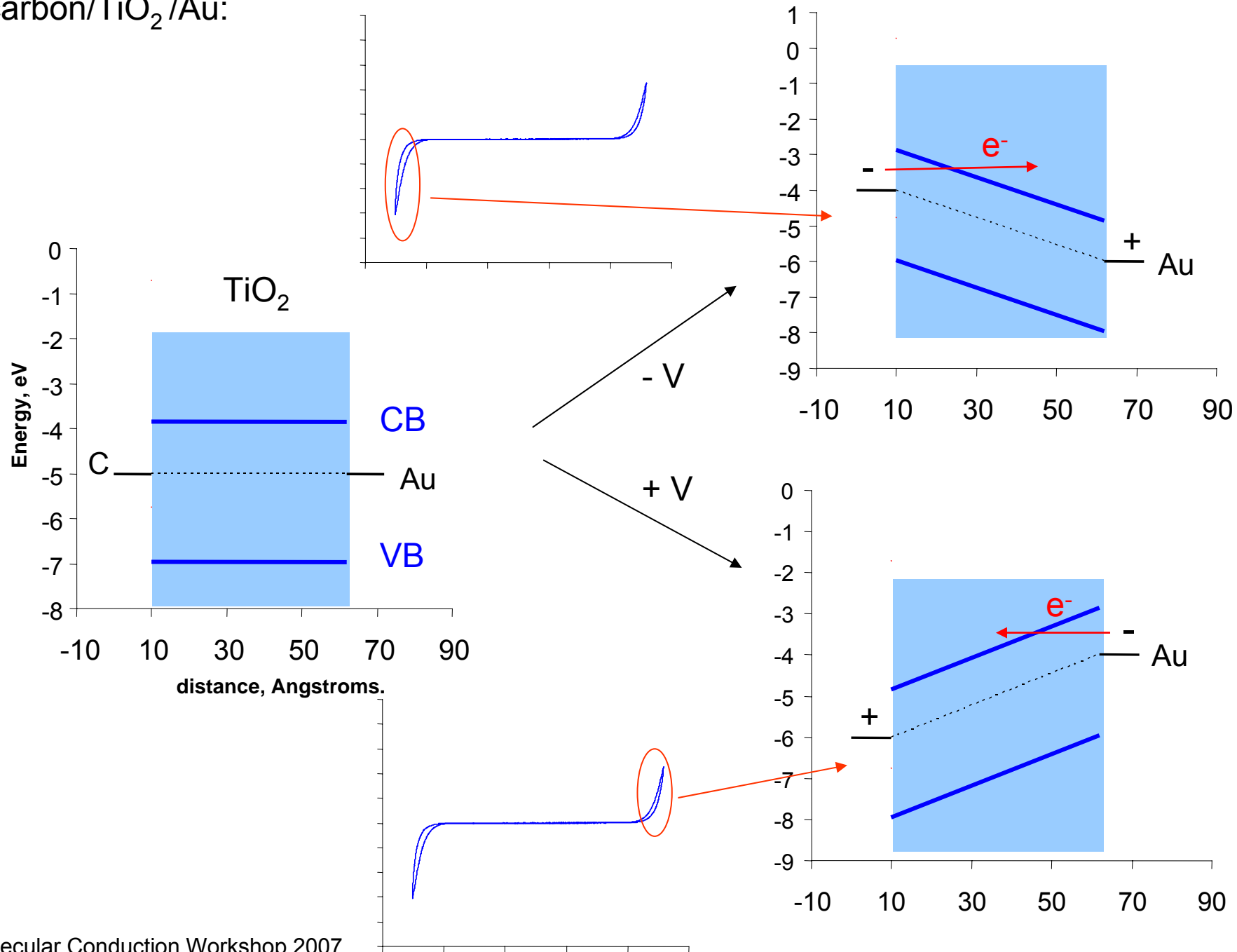
12 nm

5.2 nm

fluorene=

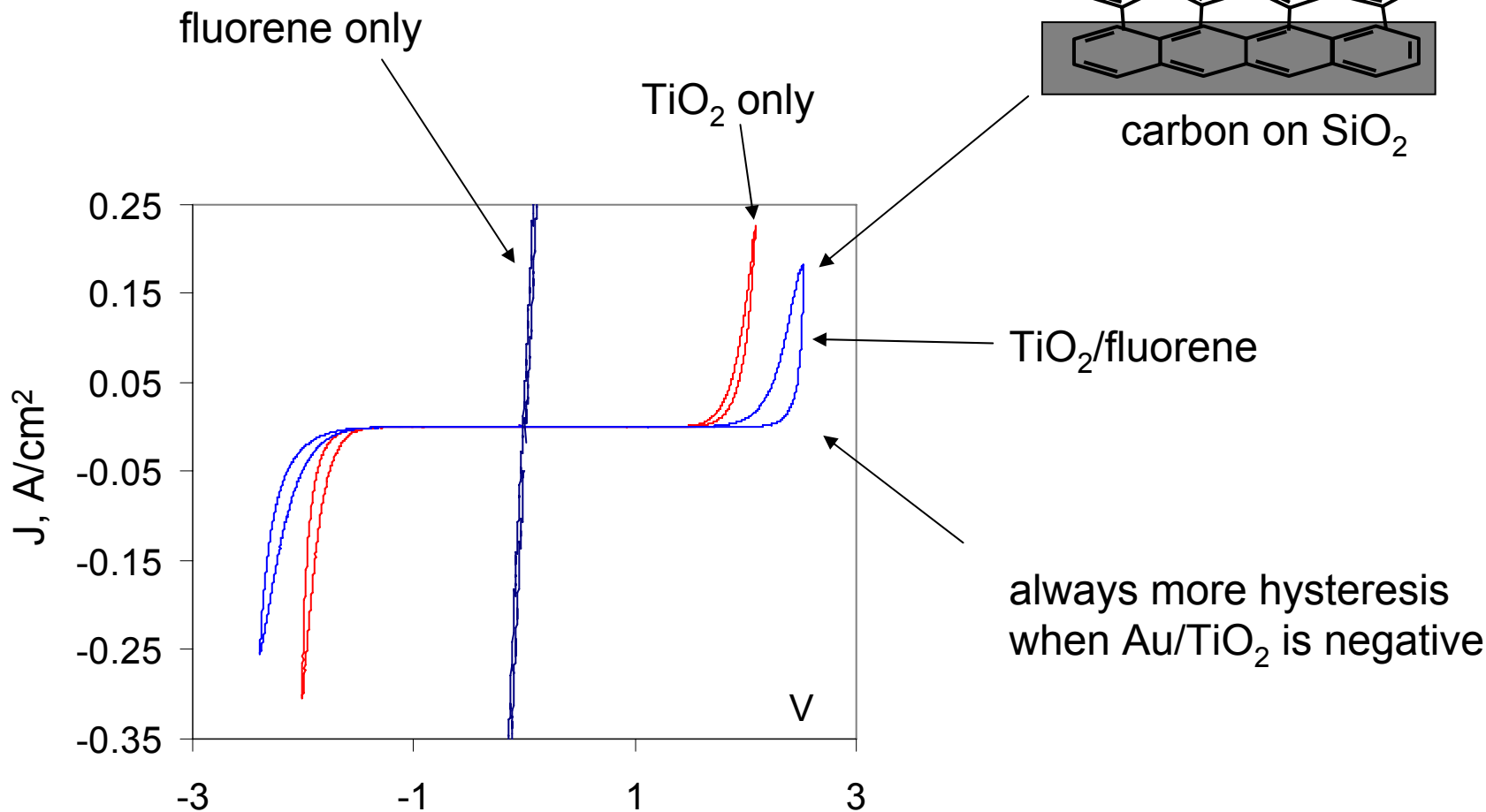
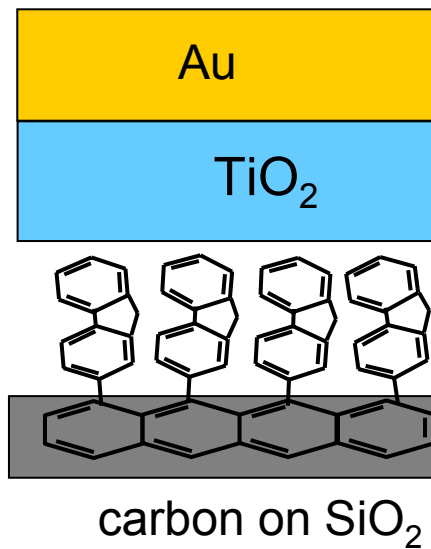


carbon/TiO₂/Au:

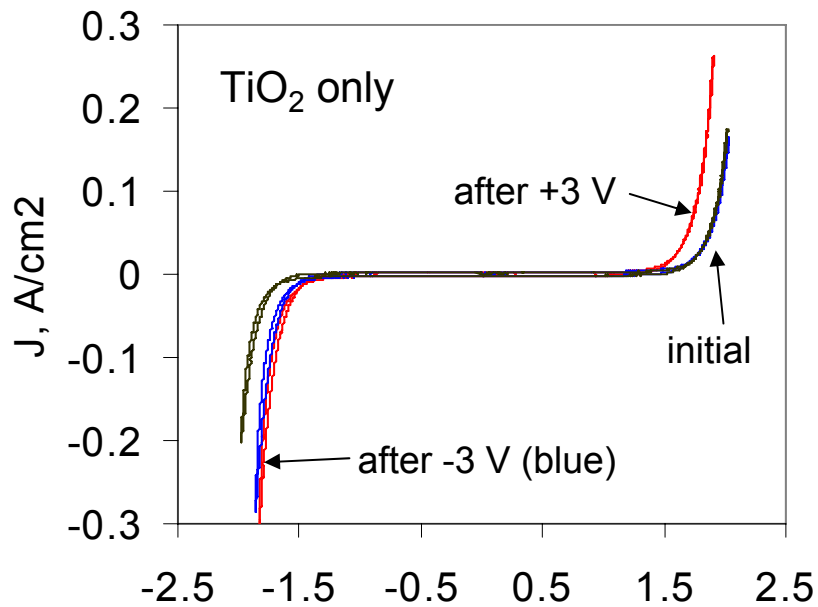
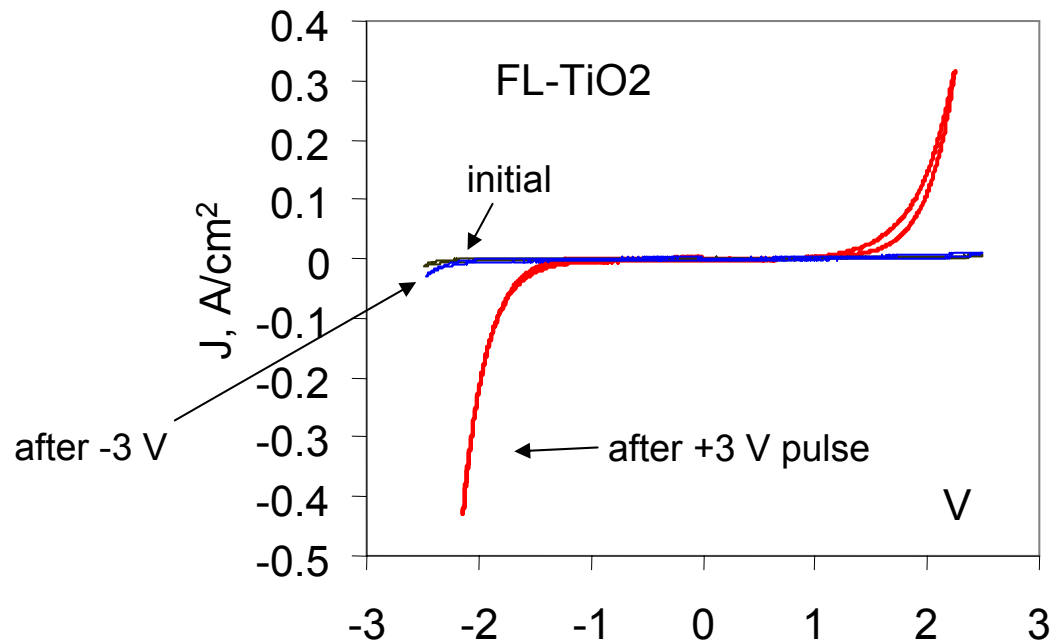


Molecular "heterojunction"

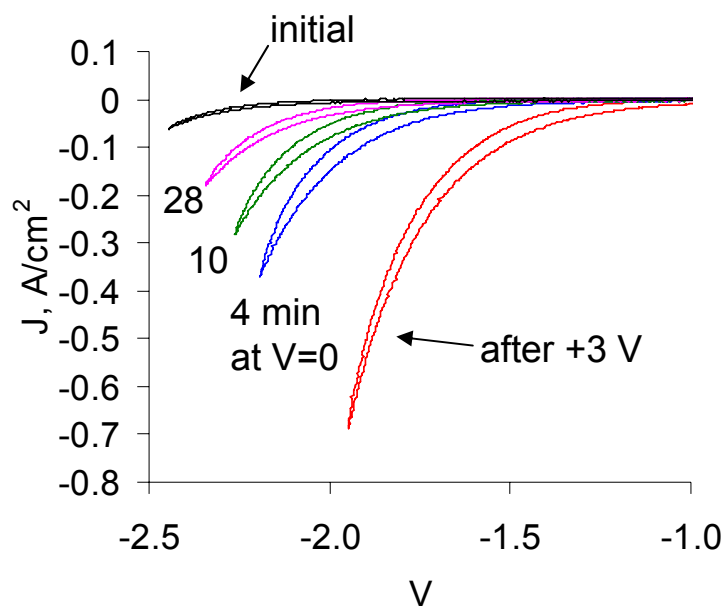
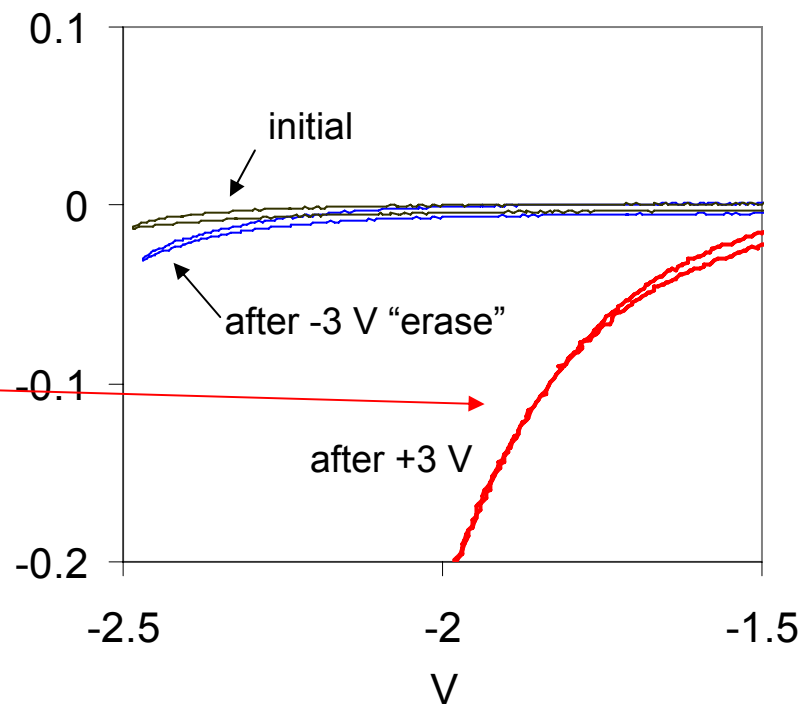
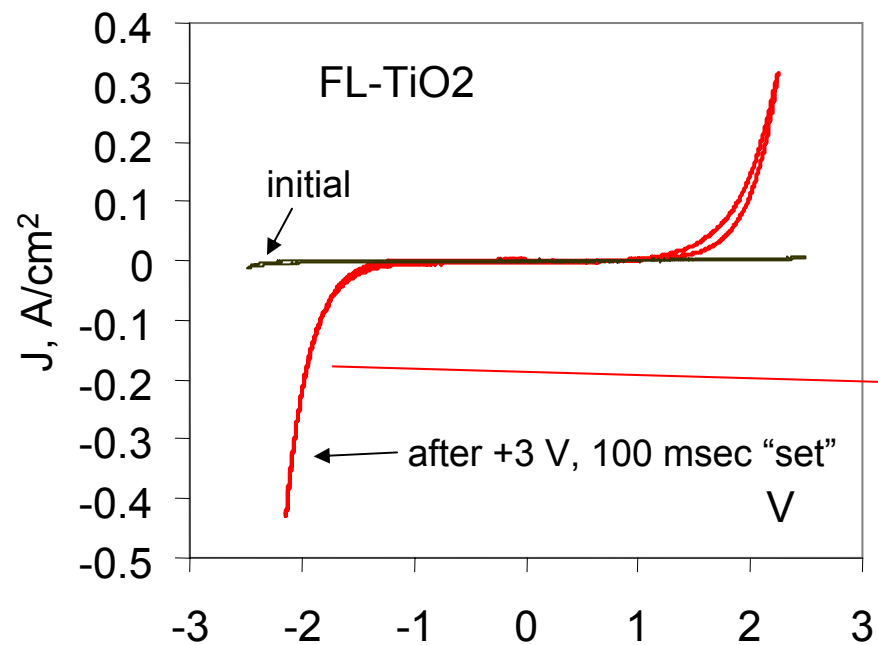
5.2 nm



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

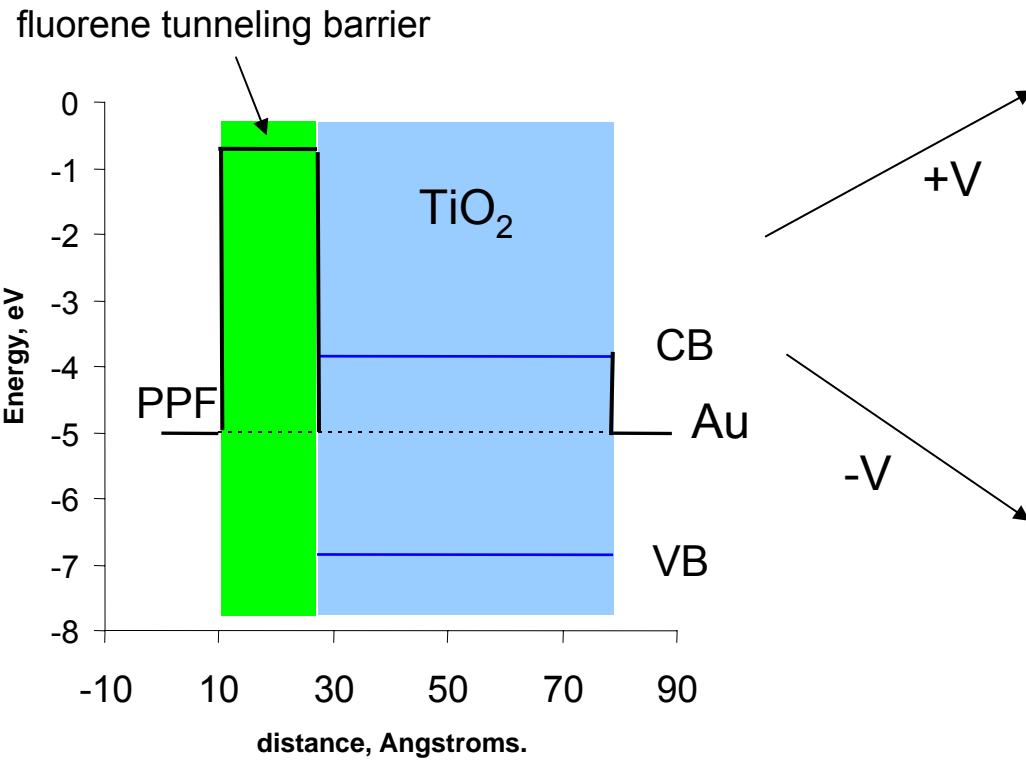


FL-TiO₂ heterojunction is structurally asymmetric, and has “memory” not observed with either TiO₂ or FL alone

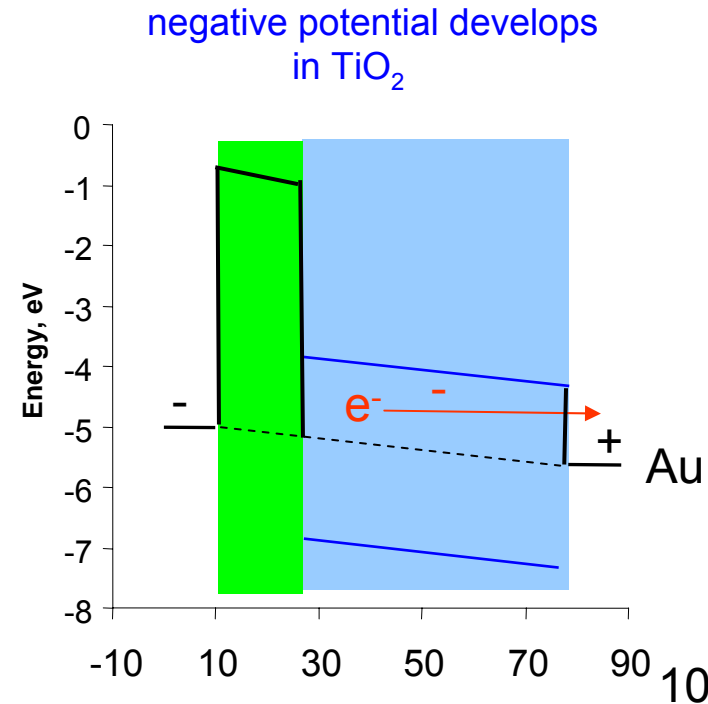
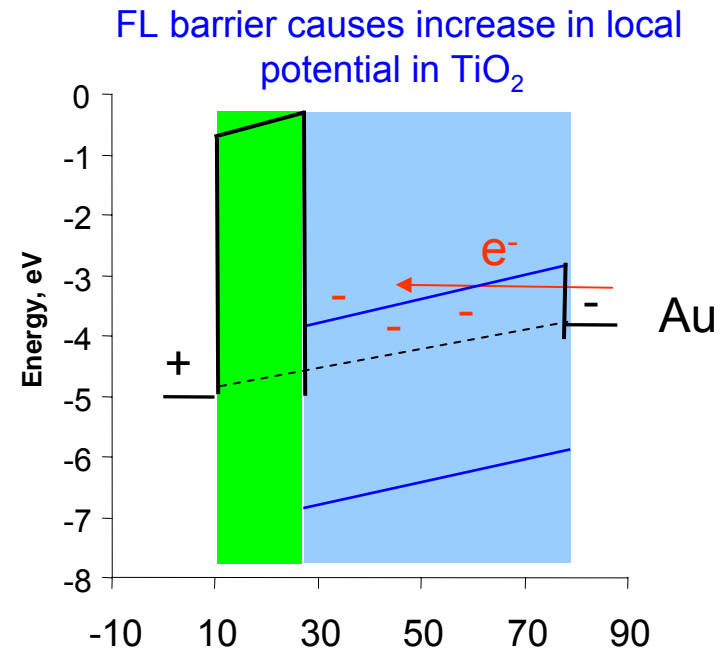


What is causing this persistent change in junction conductivity?

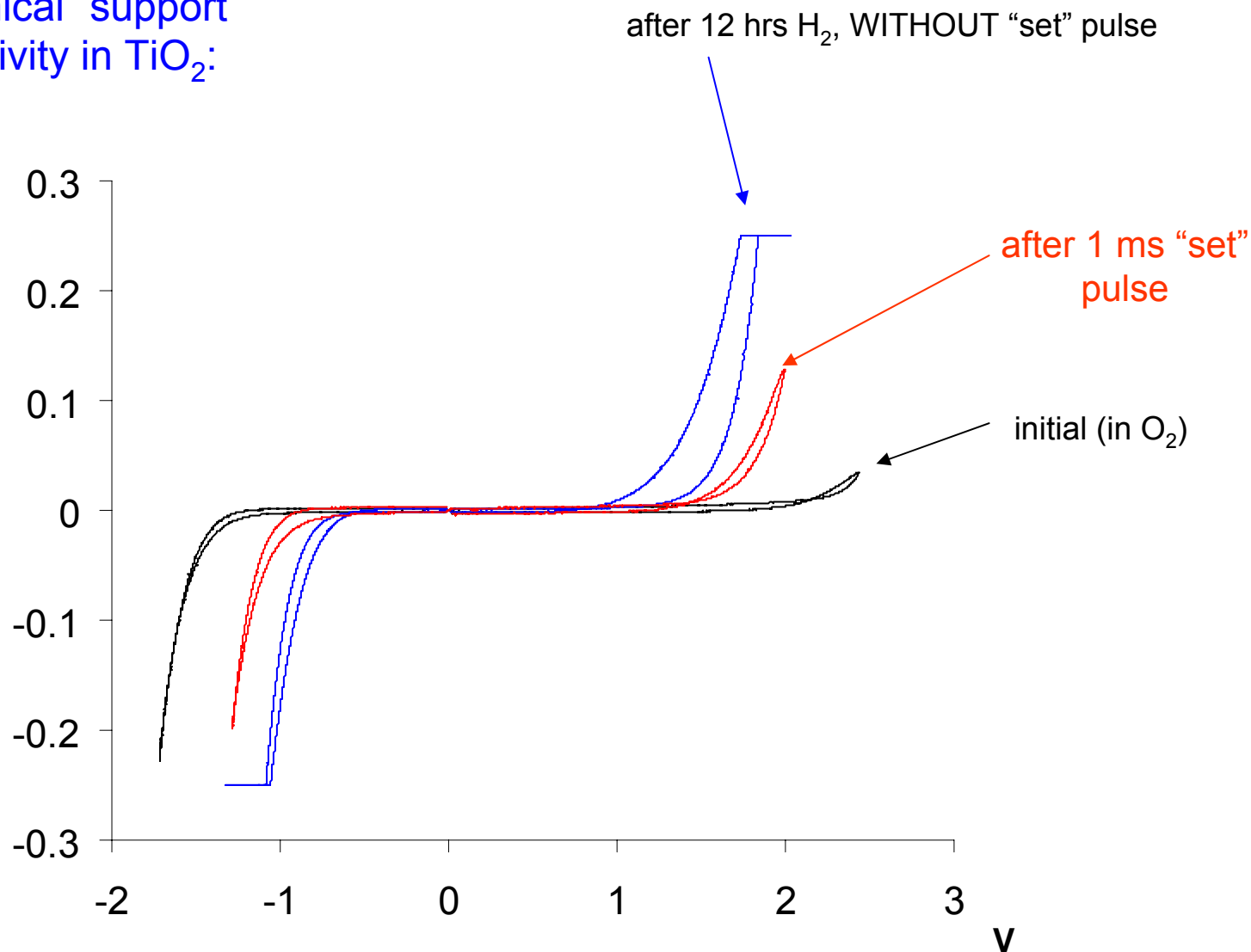
Suppose fluorene is merely a tunneling barrier:



Fluorene barrier results in a space charge in the TiO₂. When Au is negative, the Fermi level in the TiO₂ shifts to higher energy. Does the TiO₂ then get reduced?



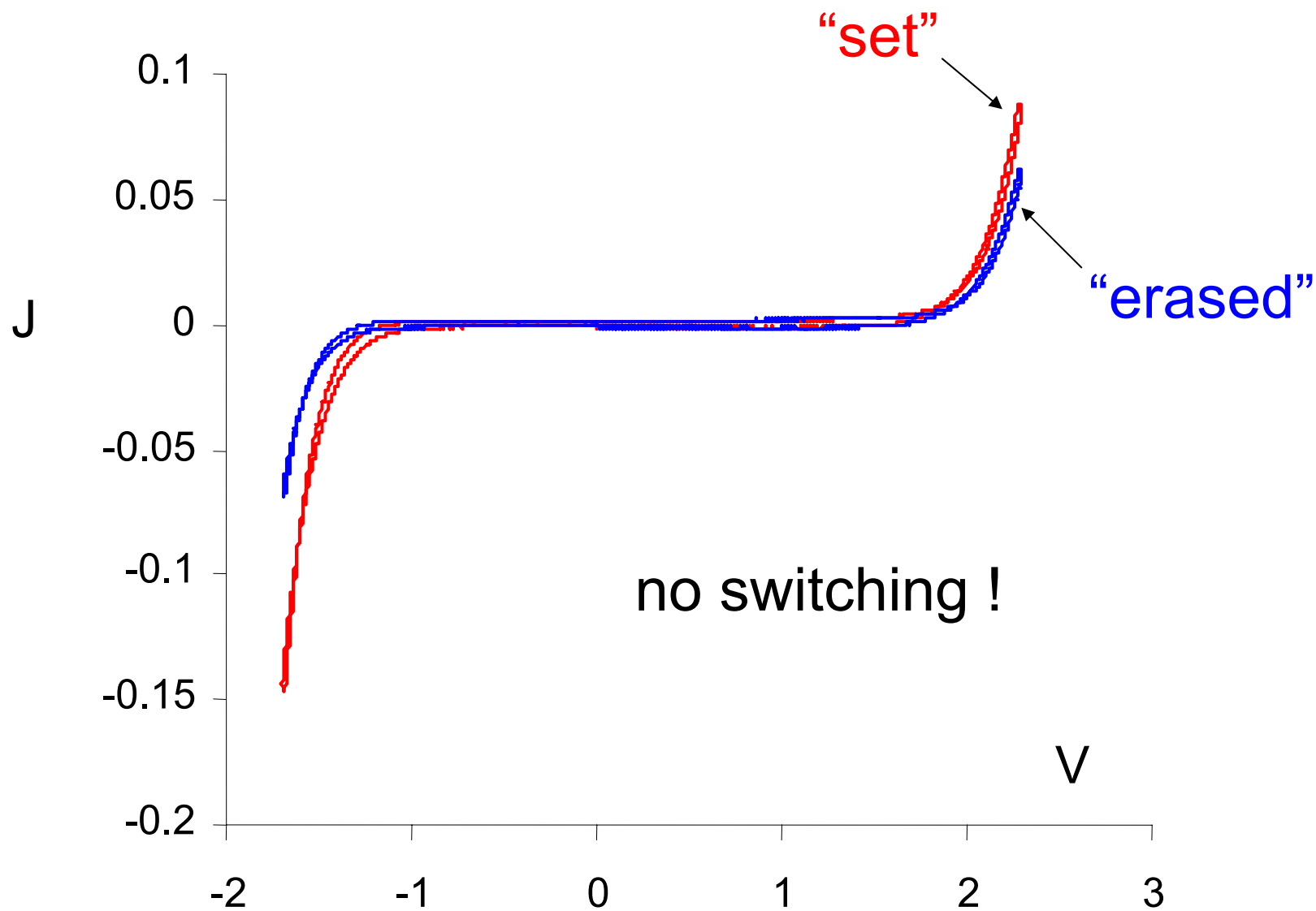
Some “chemical” support
for redox activity in TiO_2 :



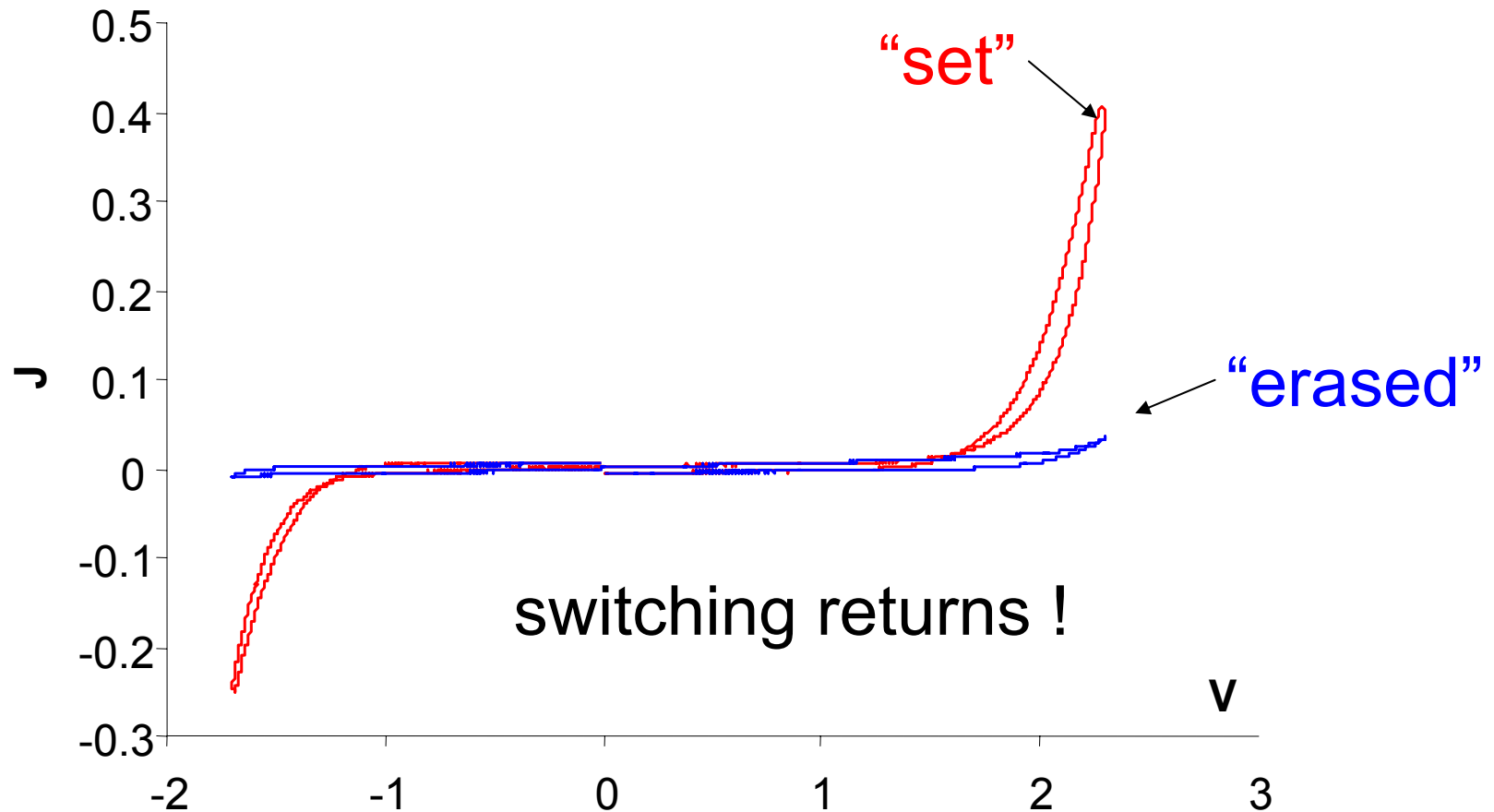
H_2 and O_2 treatment mimic in ~12 hours what a
“set” pulse can do in 1 msec

More “chemistry”:

Junction made in dry conditions, and kept dry:

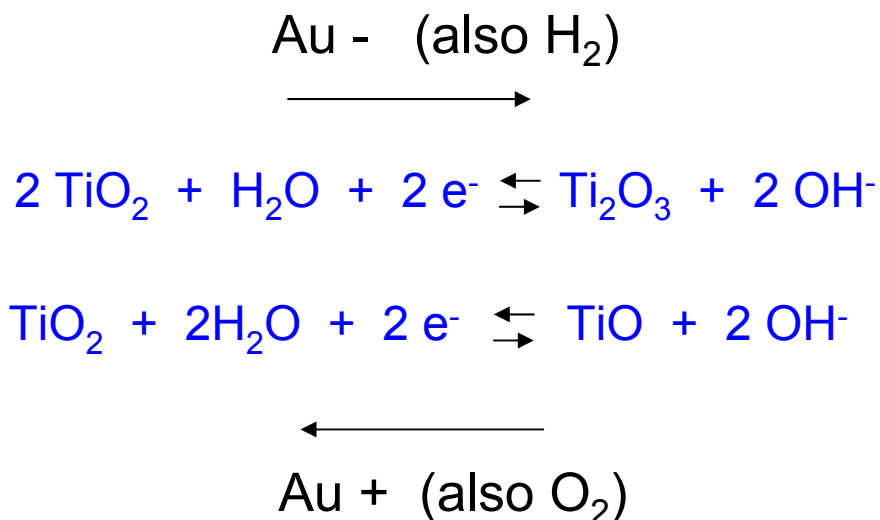


Same junction, exposed to 20 torr H₂O overnight:



- H₂ and O₂ mimic effect of 1 msec "set" and "erase" pulses
- H₂O required for conductance switching

Some likely possibilities when Au is negative:



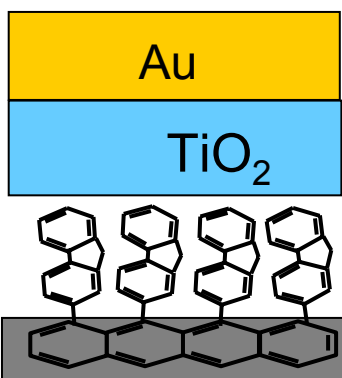
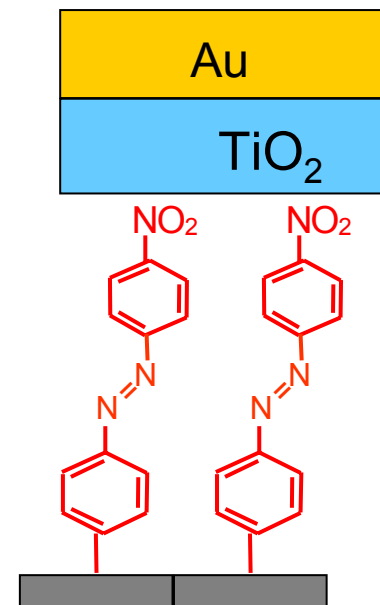
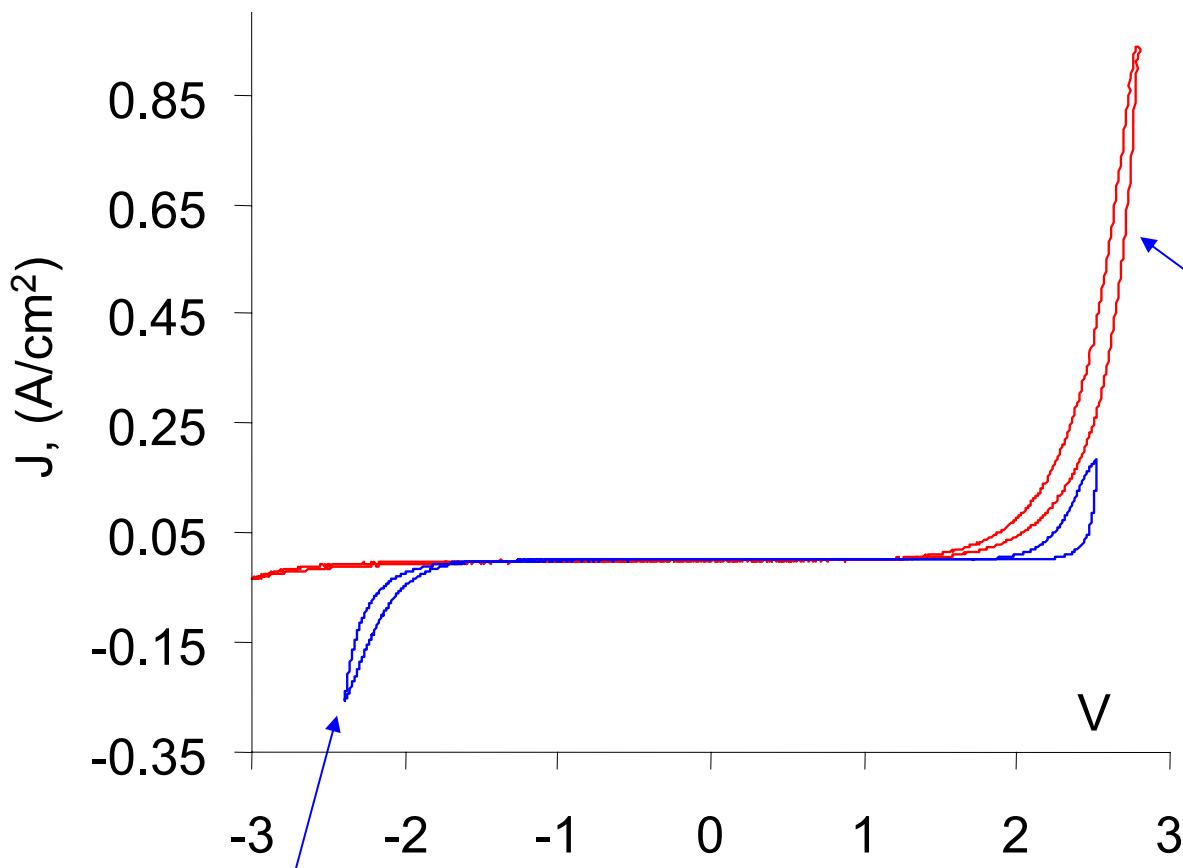
Bias-induced redox
reactions in a "cell"
~12 nm thick

Fluorene monolayer causes Fermi level shifts in TiO_2 , causing its reduction, to make metallic TiO and Ti_2O_3
"Dynamic doping" induced by heterojunction asymmetry

resistivities:

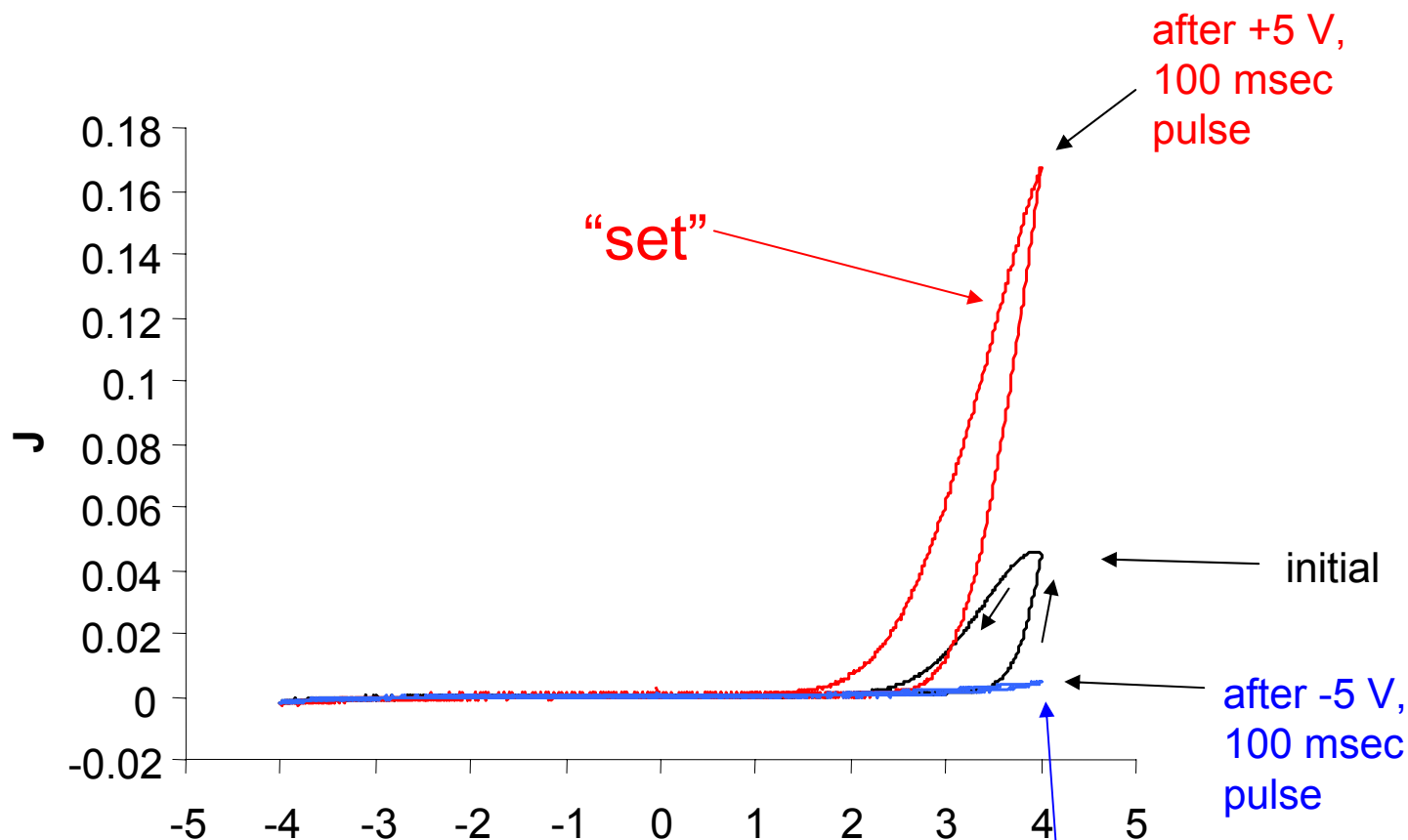
Ti metal: $42 \mu\Omega\text{-cm}$
TiO: $170 \mu\Omega\text{-cm}$
TiO₂: $> 10^{10} \mu\Omega\text{-cm}$

Is the electronics *molecular*?



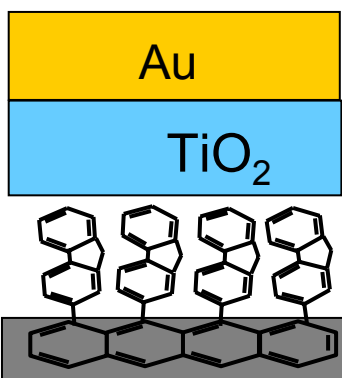
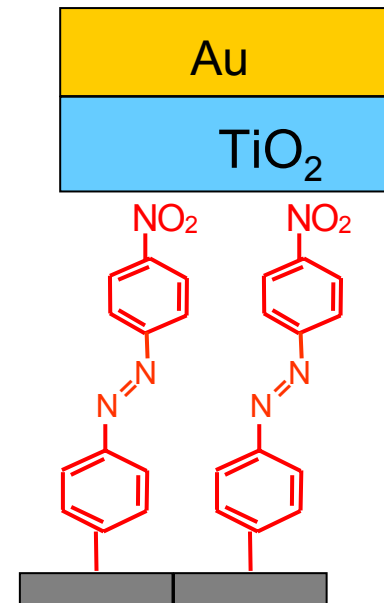
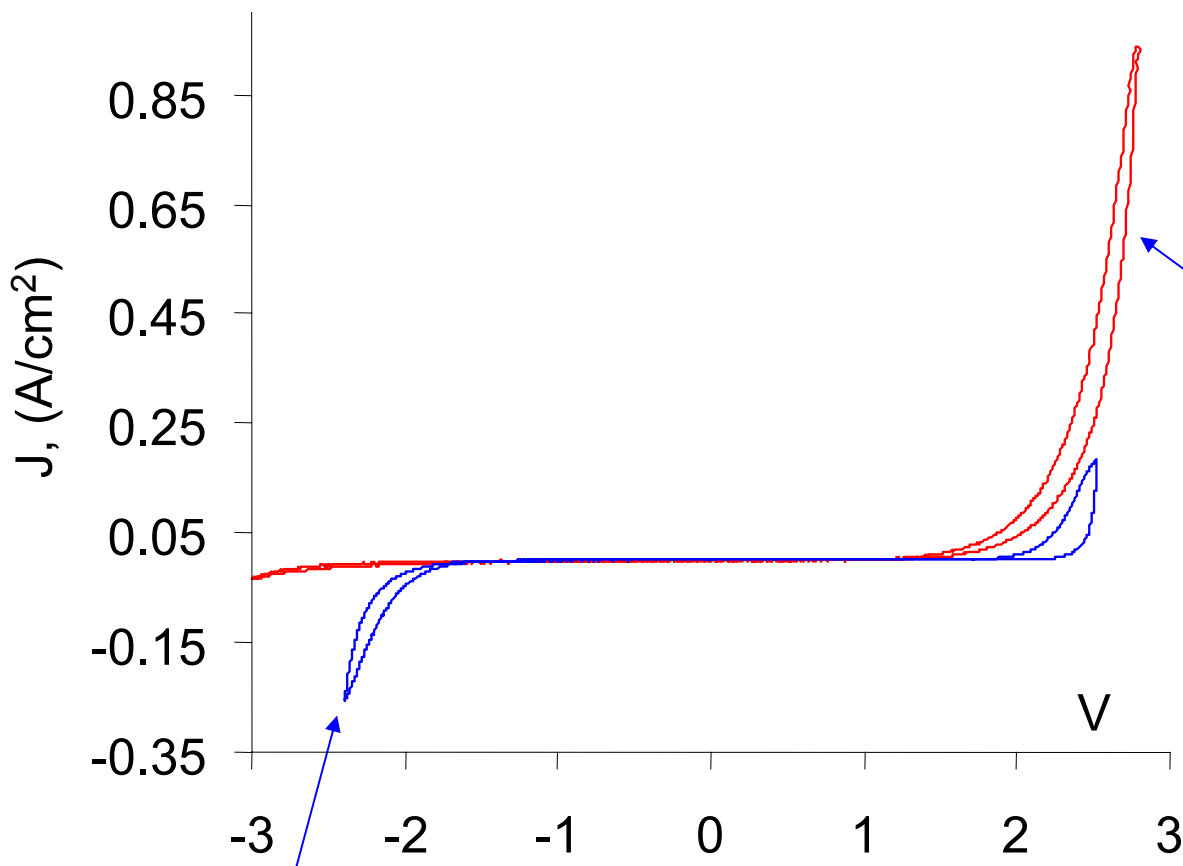
NAB/TiO₂ shows rectification,
Fluorene/TiO₂ does not

NAB/TiO₂ devices exhibit “memory”, like FL/TiO₂:



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

Is the electronics *molecular*?



NAB/TiO₂ shows rectification,
Fluorene/TiO₂ does not

PPF/NAB/TiO₂/Au

-V

Coulomb barrier !

current

+V

fast

slow

fast

slow

X

Au

NAB
HOMO

TiO₂ VB

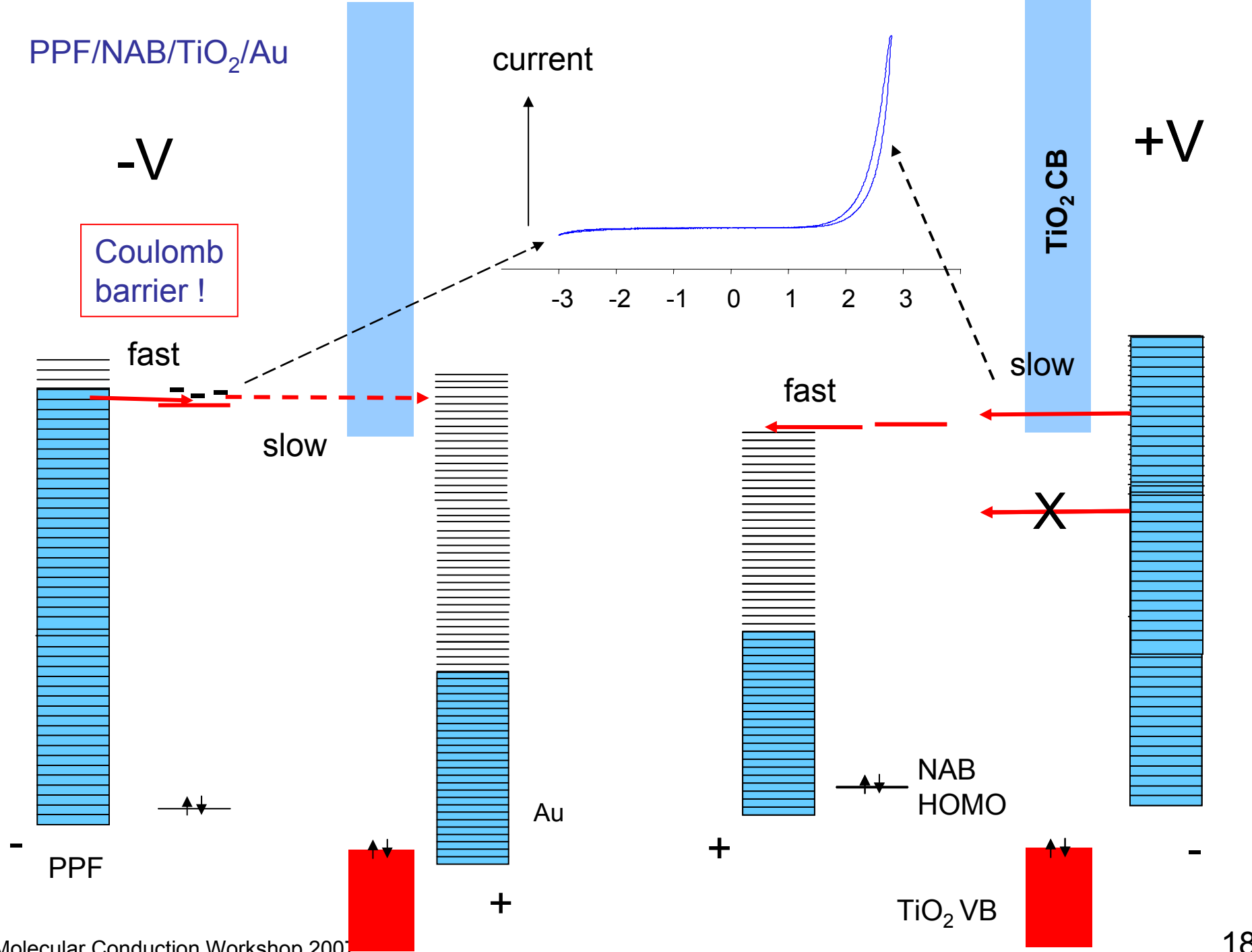
TiO₂ CB

- PPF

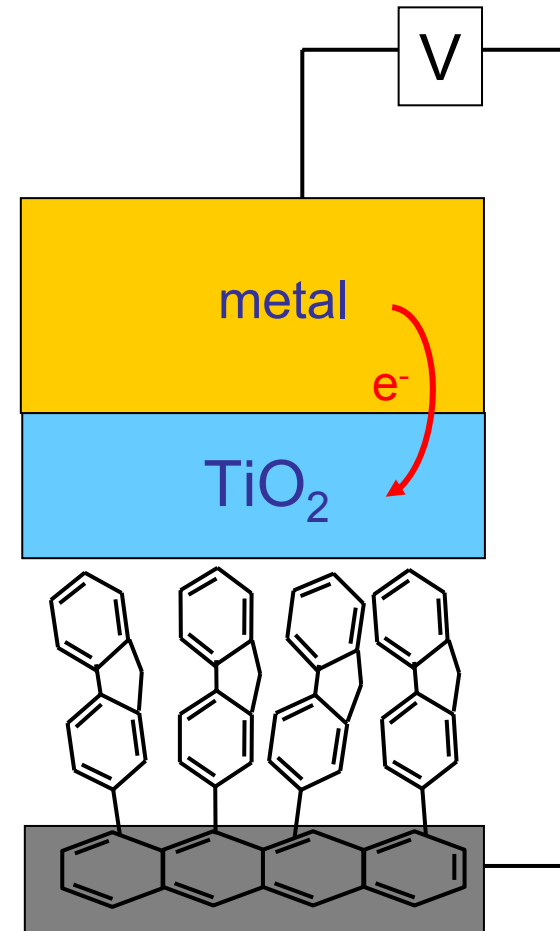
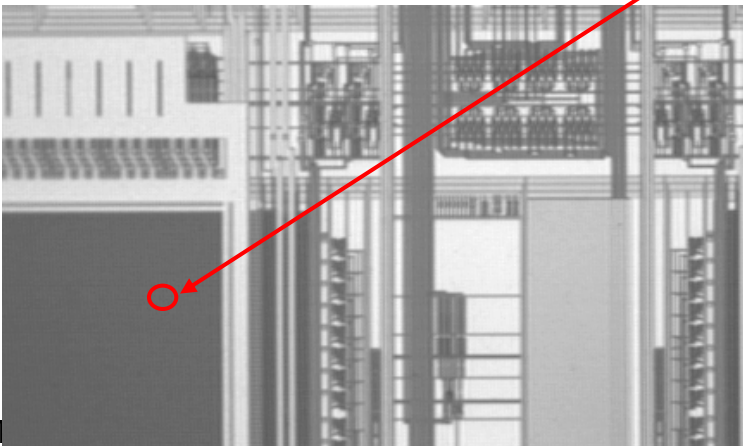
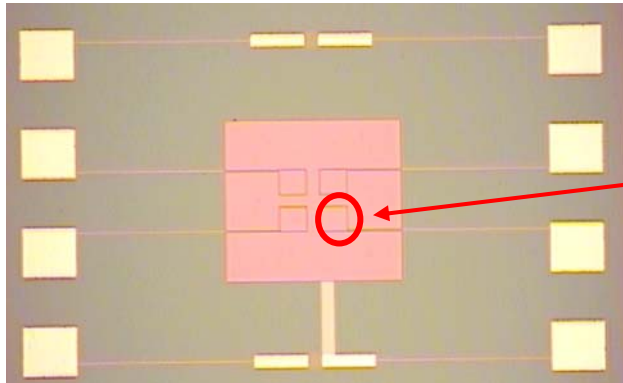
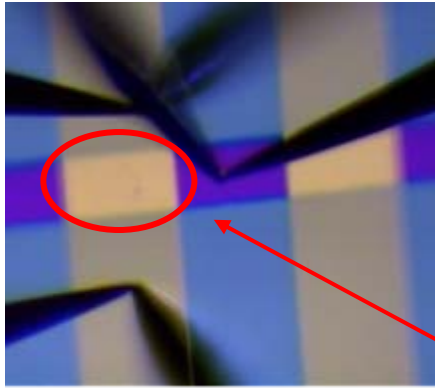
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Integration with CMOS:



ZettaCore prototype molecular memory chip

