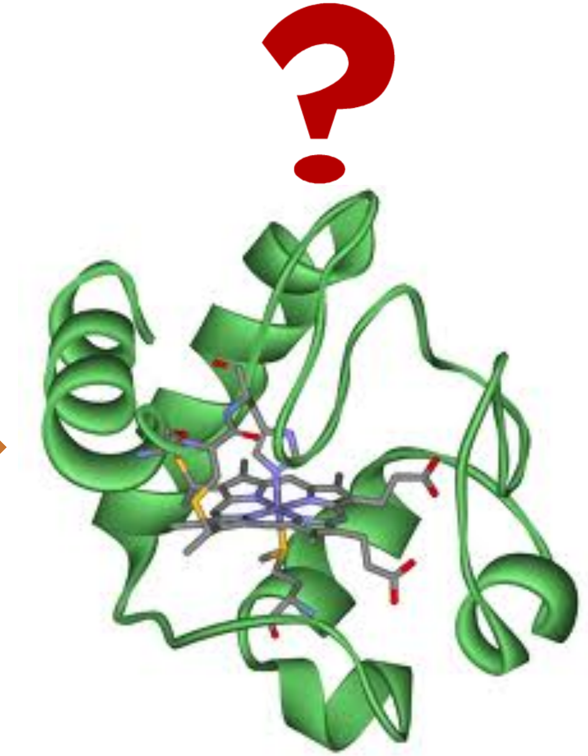
Technion-IIT, 1-2014

e⁻



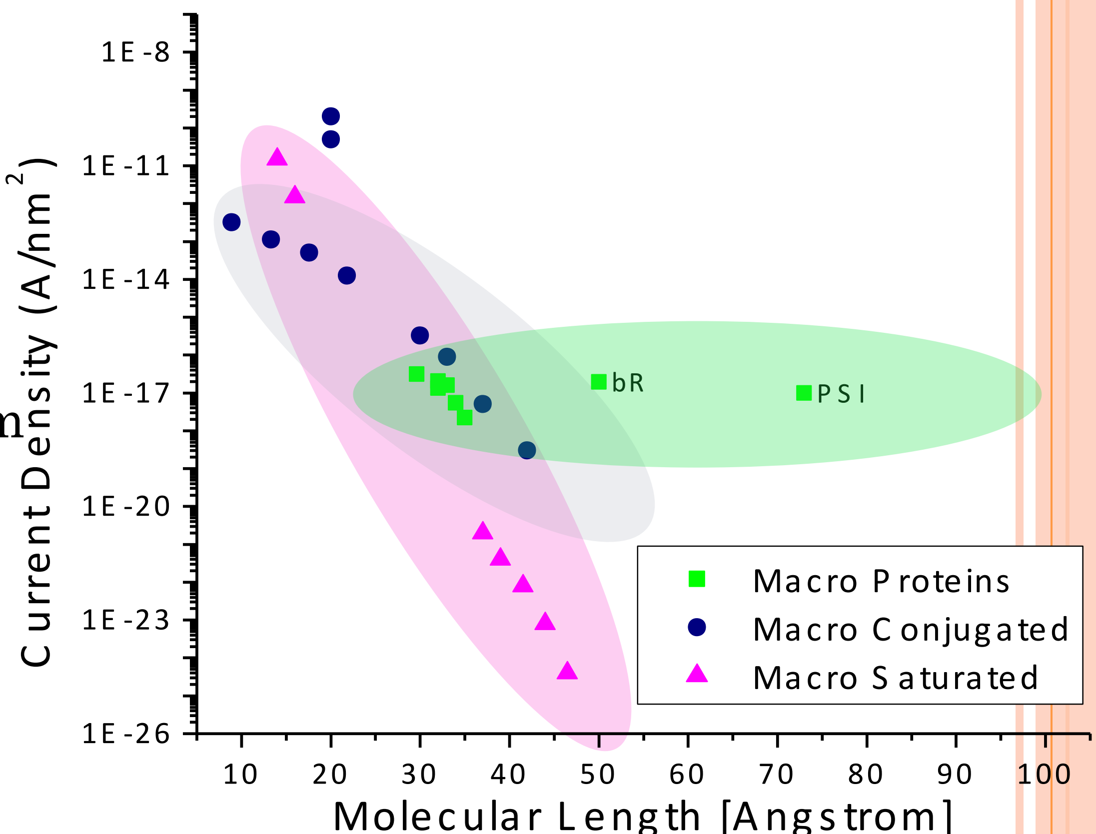
PROTEINS: "DOPABLE" SOLID-STATE ELECTRONIC TRANSPORT MATERIALS TOWARDS *REAL* BIOELECTRONICS?

From electron transfer (ET) to "solid-state" electron transport (ETp)

Proteins survive partial Dehydration → Suitable…

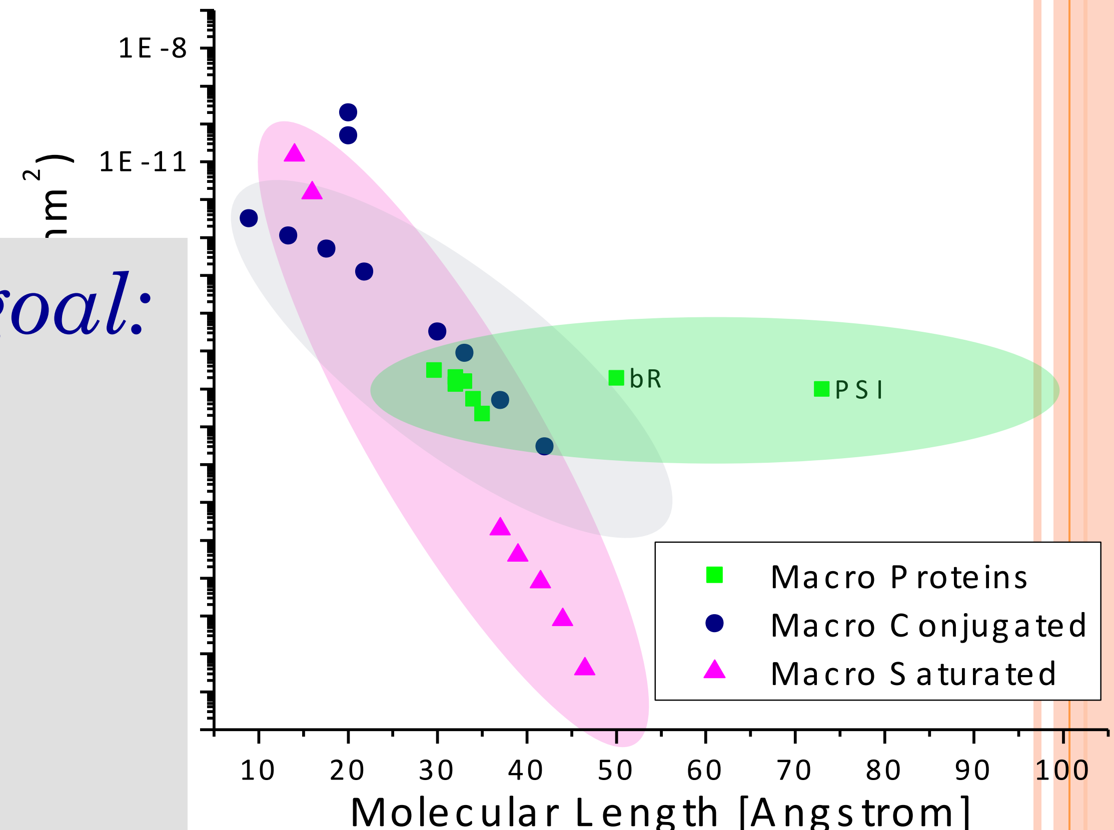
I will show:

- Proteins are quite efficient solid-state transport medium
- Co-factor is central → proteins can be doped
- Amide backbone maybe involved in *elastic* transport
- **Functional and dopable → ★★★**



From electron transfer (ET) to "solid-state" electron transport (ETp)

Proteins survive partial Dehydration → Suitable…



Ultimate scientific goal:

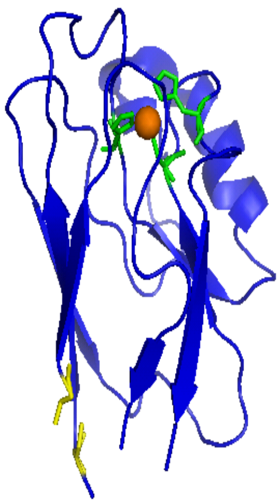
Control & predict electron transport across proteins (& peptides)

- **Functional and dopable → ★★★**

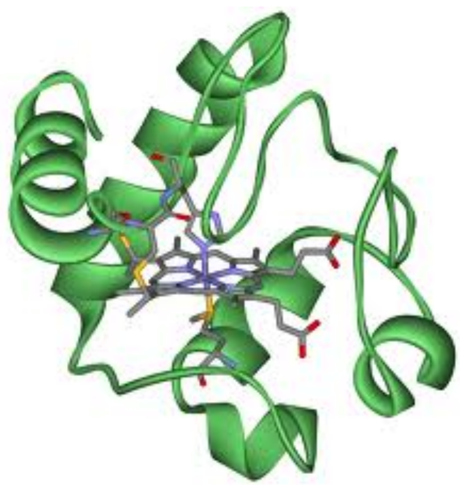
Proteins on Today's Menu

Natural electron transfer proteins

Not an electron transfer protein



Azurin

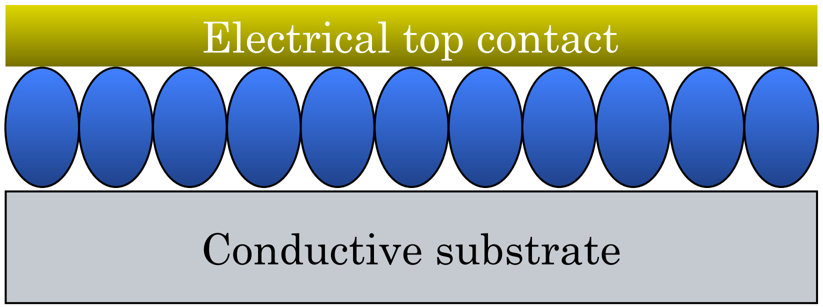


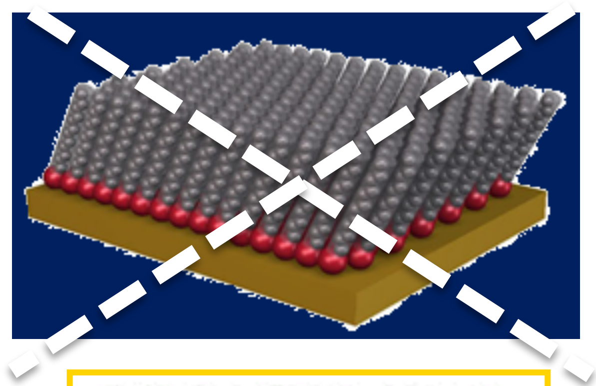
Cytochrome C

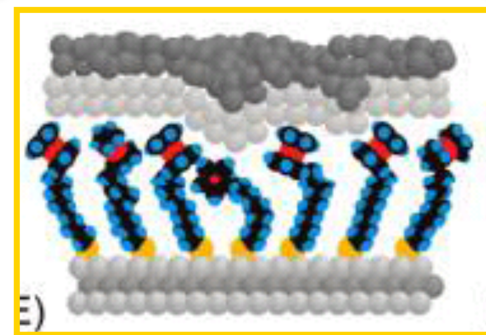
Serum Albumin

Our main experimental approach

Idealized Cartoon!

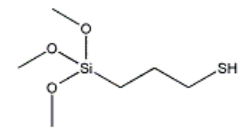




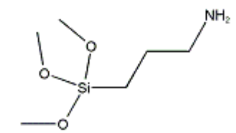


- Substrate – Smooth!
- Protein layer – Dense, usually linked by a short linker
- Top electrode – Suitable to contact soft matter

SUBSTRATE

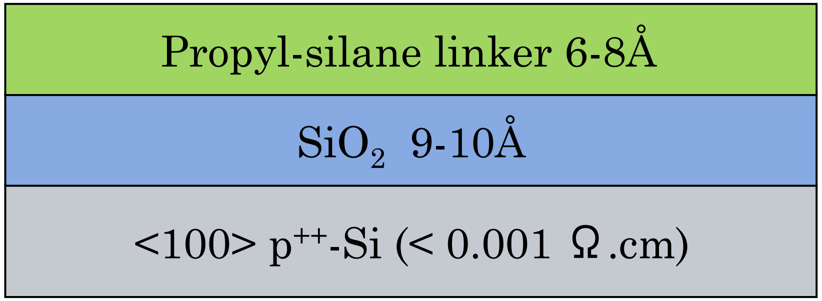


MPTMS

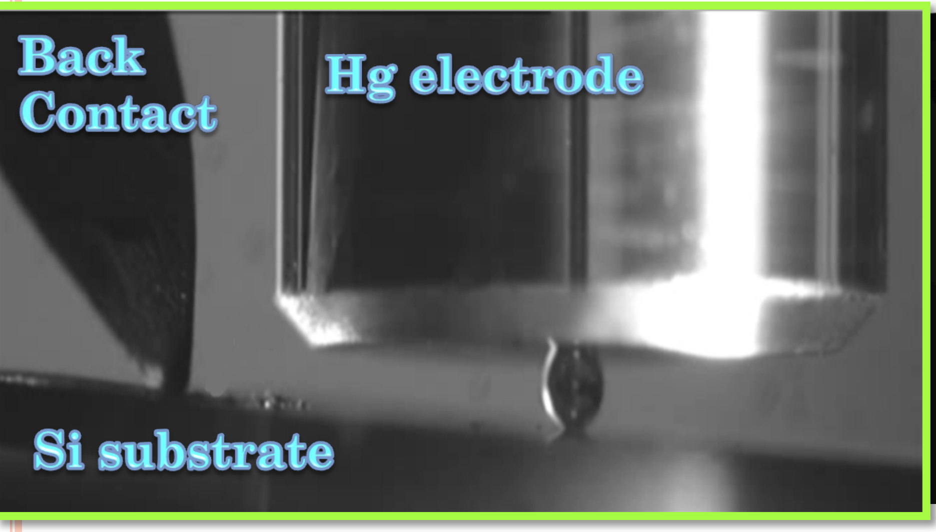


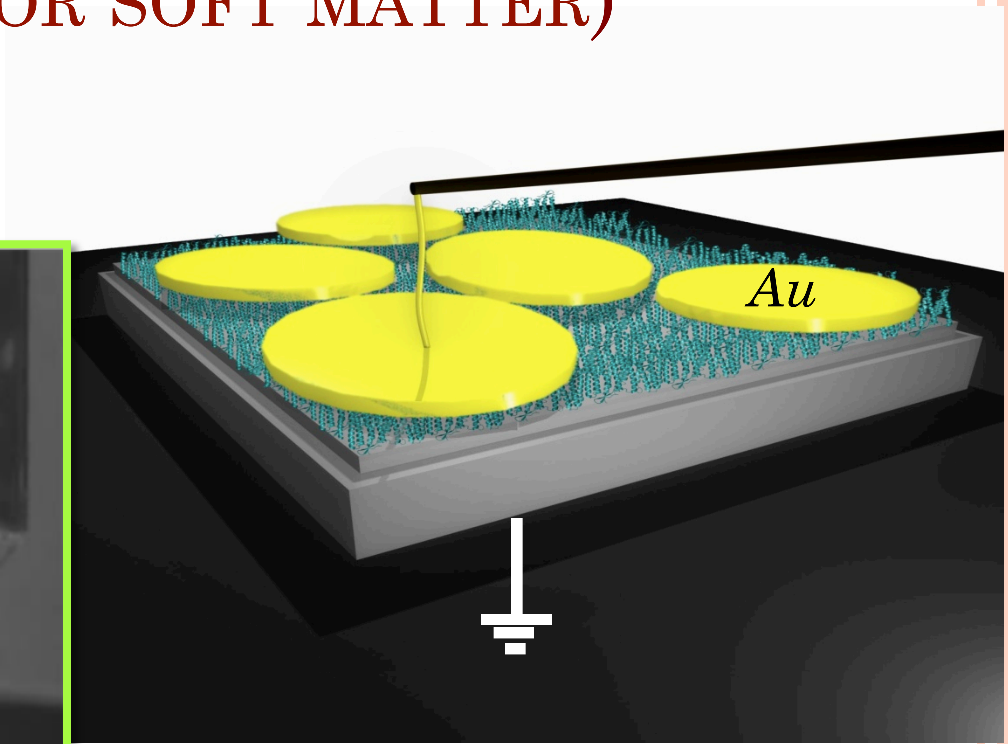
APTMS

- **Highly doped Si**, Al(ox), Au, HOPG
- For Si: Grow thin oxide layer of controlled width
- For Si and Al(ox): add linker layer ("glue")



Top Electrode (for soft matter)



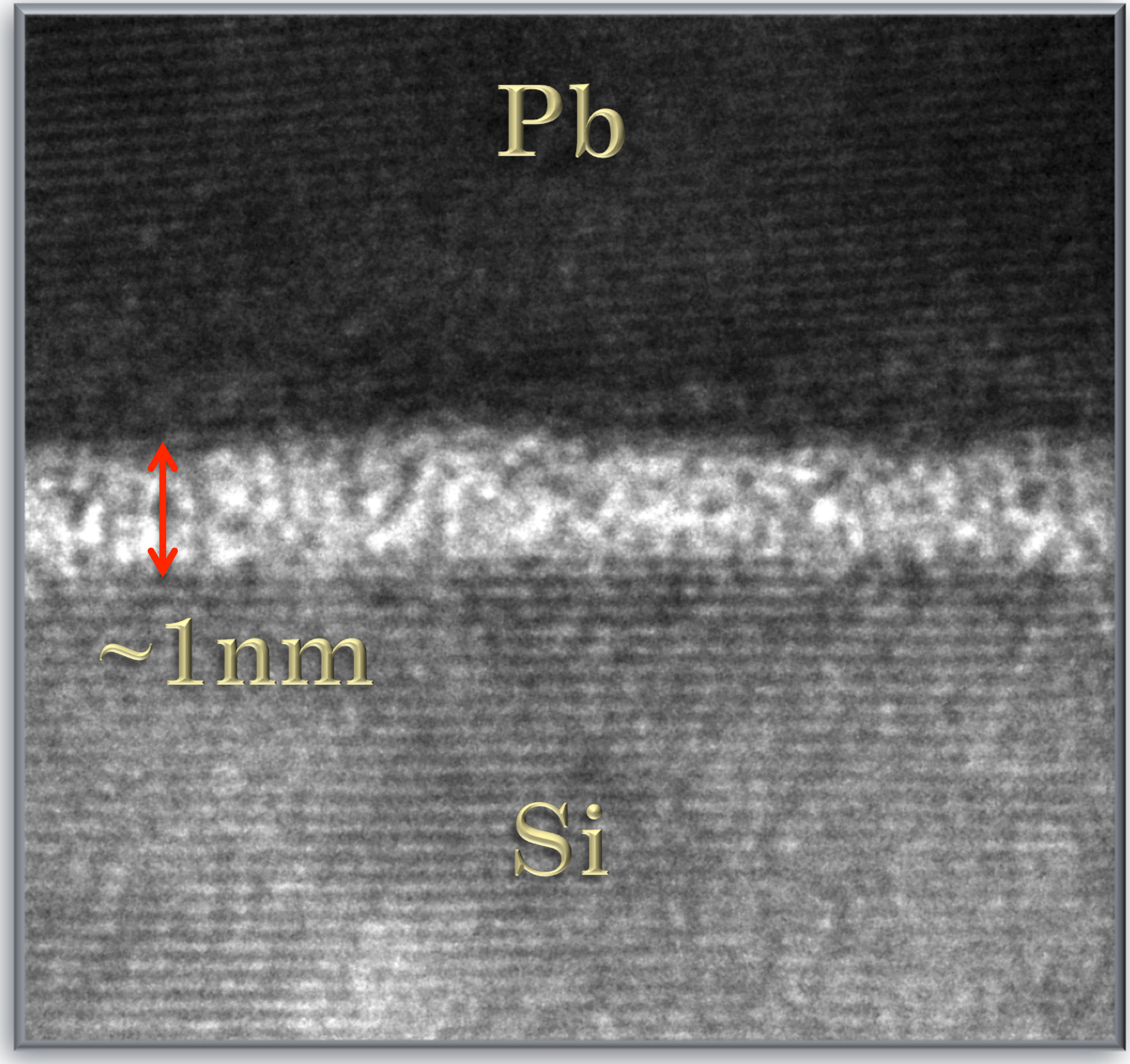


Hanging Hg drop

Lift off float on (LOFO) - Au

0.2 mm^2 → ~10^7-10^9 proteins/contact

Top Electrode (for soft matter)

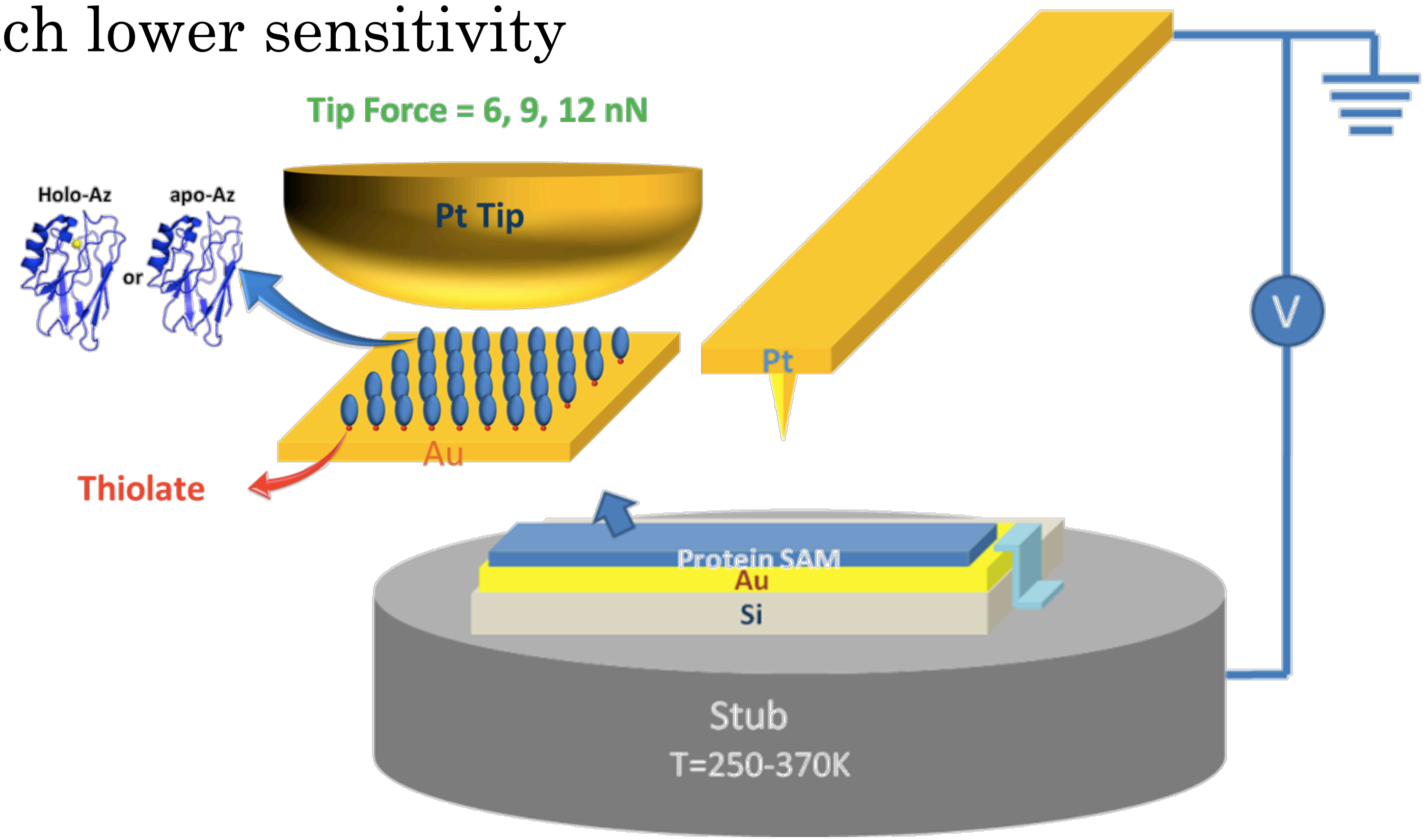


TOP ELECTRODE (FOR SOFT MATTER)

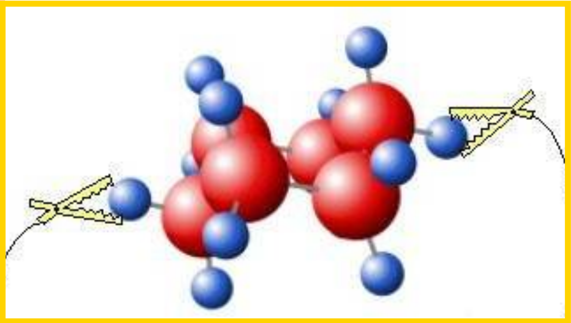
CONDUCTIVE PROBE AFM

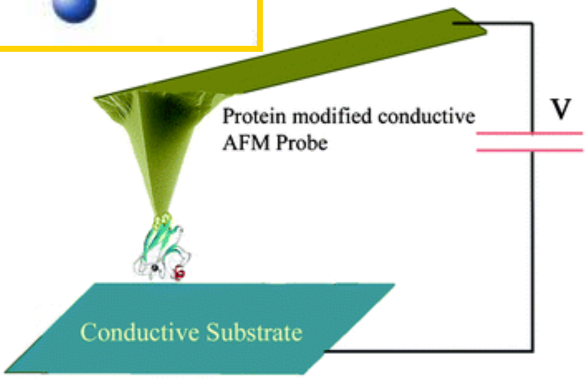
- Less defects
- Force variation
- Much lower sensitivity

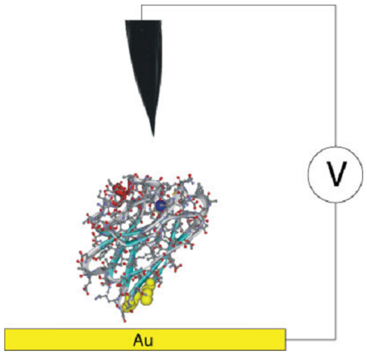
~~10^2 proteins/contact



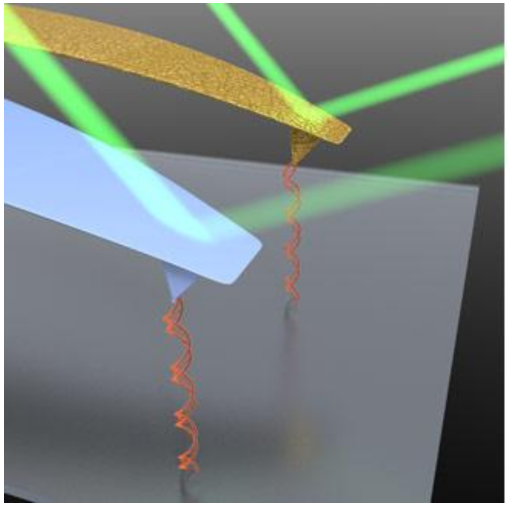
What does a nanoscale experiment look like?

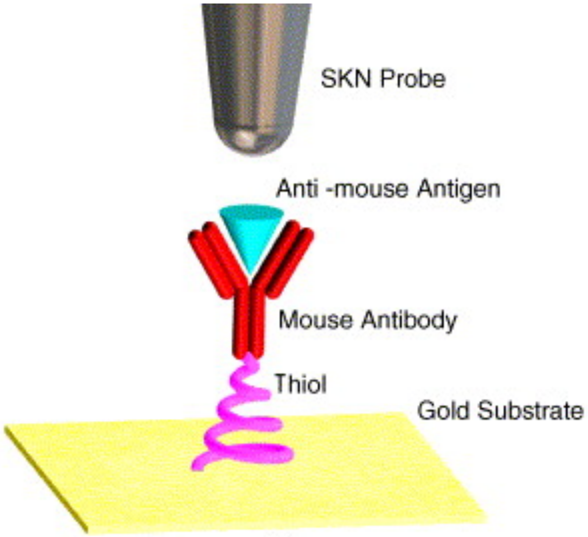






Idealized Cartoons!





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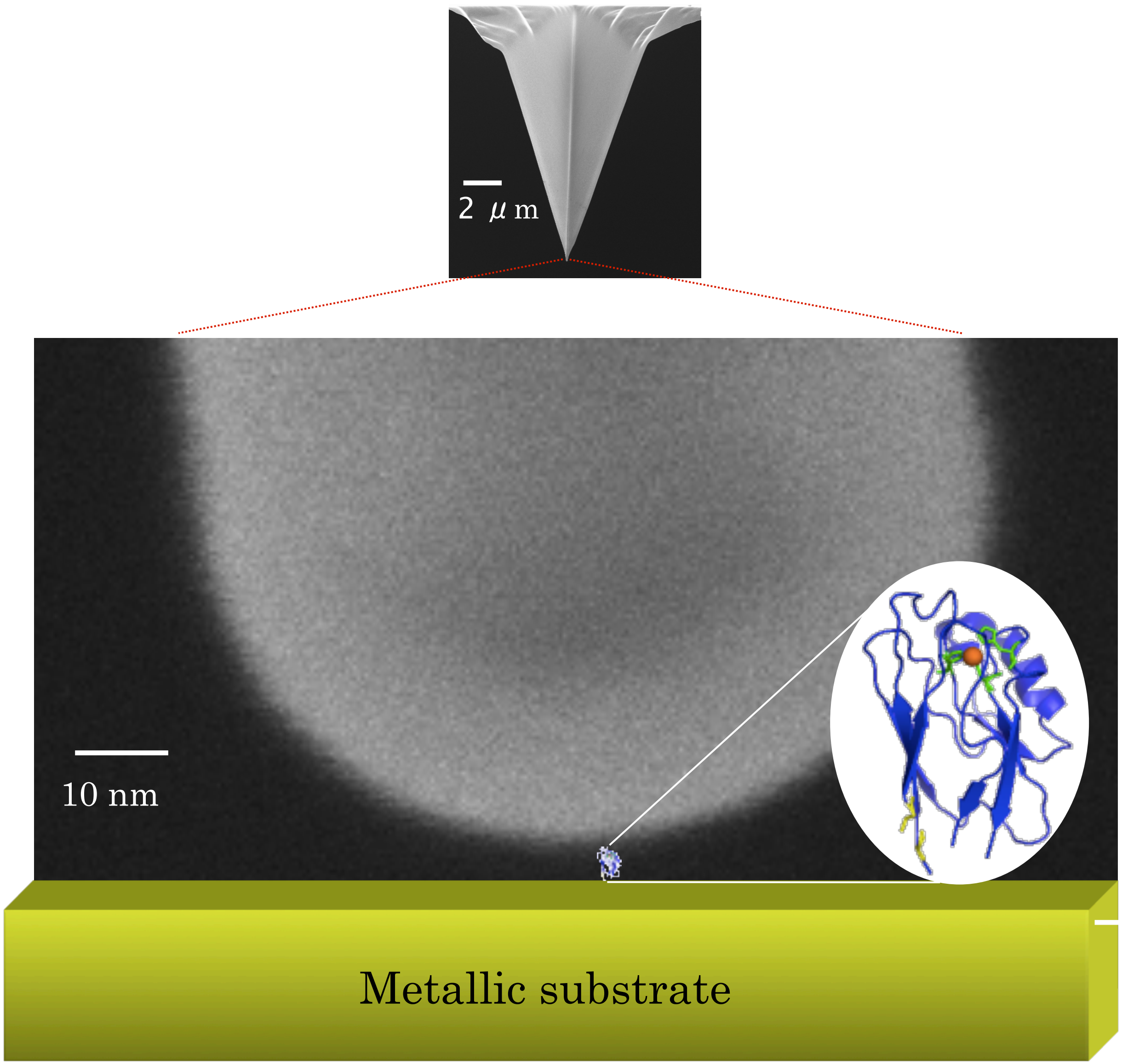
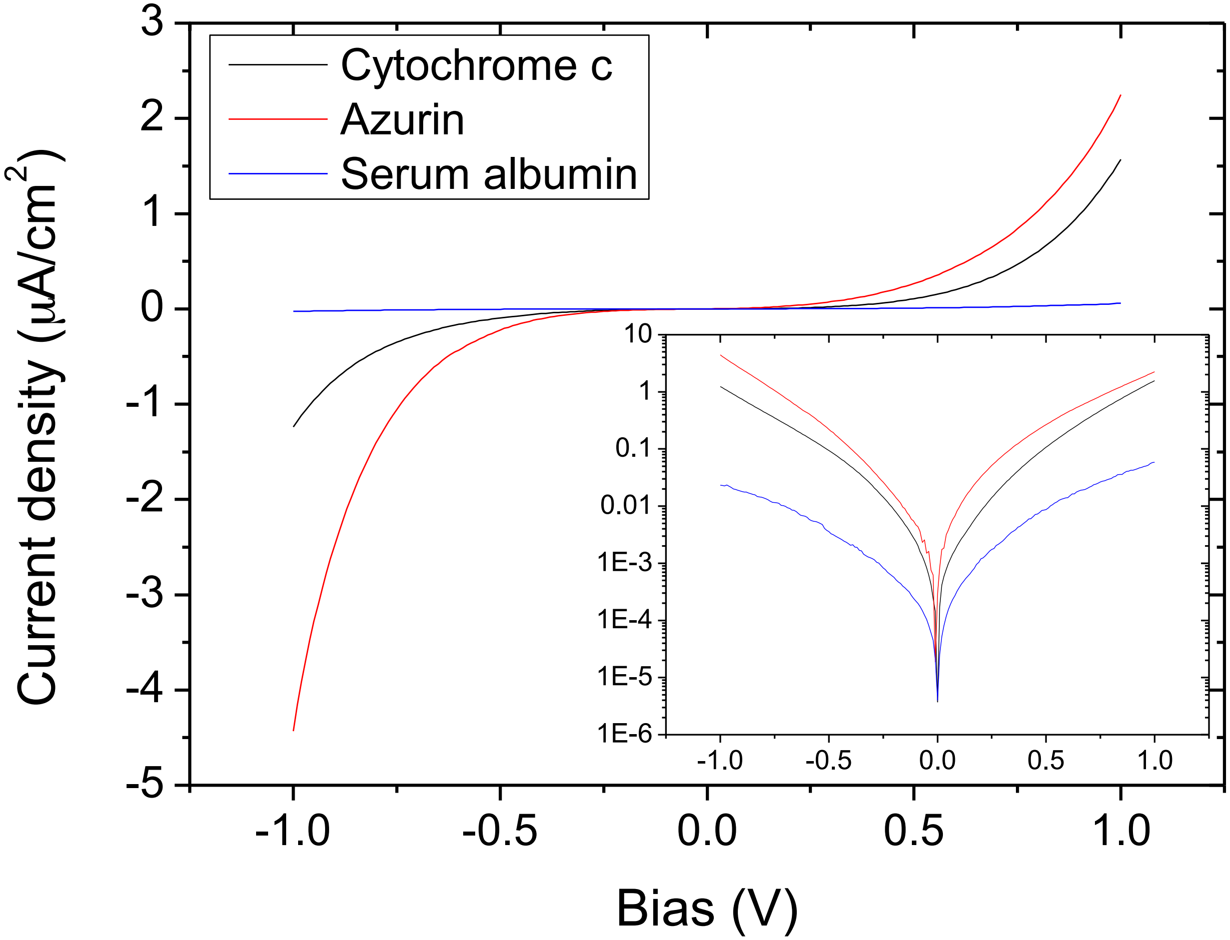
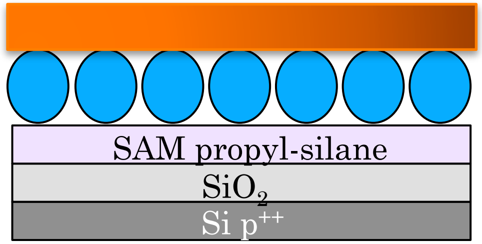


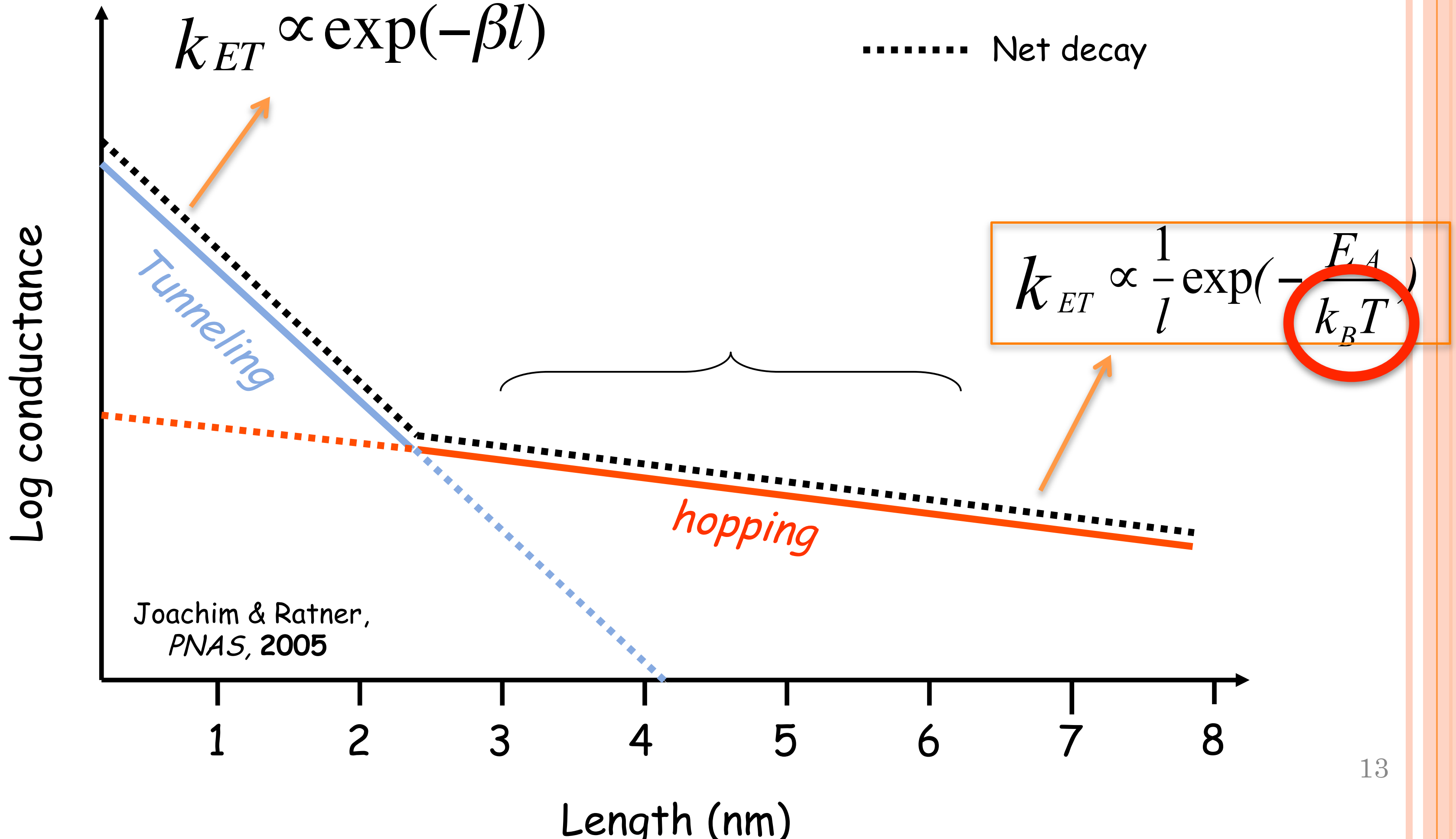
Current-voltage Characteristics of the different proteins



- Same configuration
- Same temperature

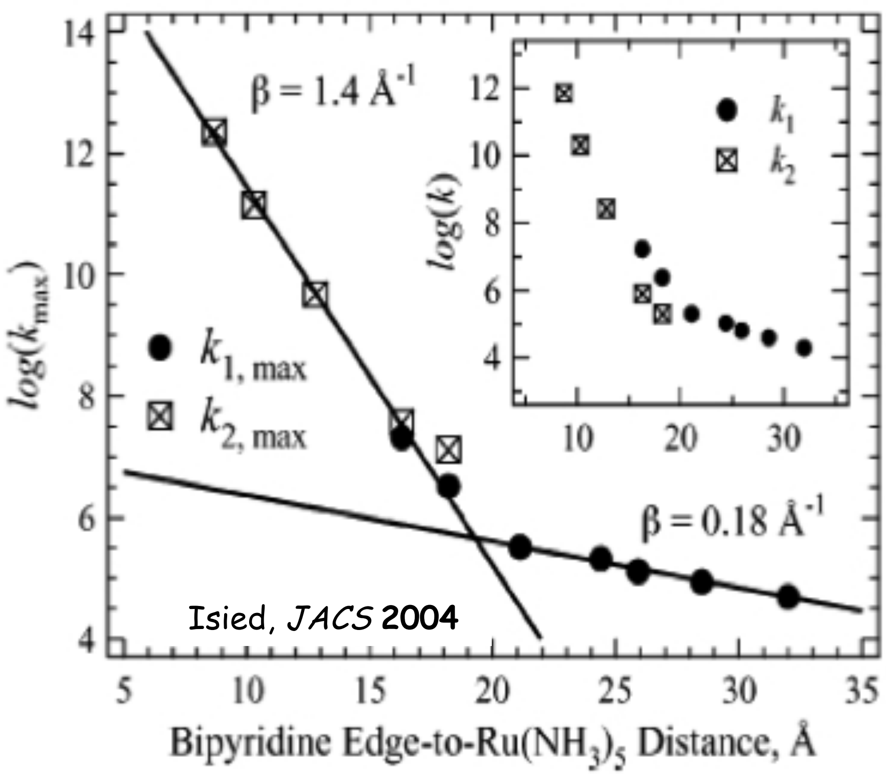


WHAT IS THE ETP MECHANISM?



WHAT IS THE ETP MECHANISM?

$$k_{ET} \propto \exp(-\beta l)$$



$$\boxed{k_{ET} \propto \frac{1}{l}\exp\left(-\frac{E_A}{k_B T}\right)}$$

WHAT IS THE ETP MECHANISM?

- Hopping ………………
- Super-exchange ……..
  - 2-step tunneling ?

- Thermally activated

$$\exp(-\frac{E_A}{k_B T})$$

- Temperature-independent

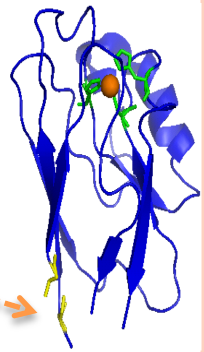
$$\exp(-\beta l)$$

  - but … lower β values than for "natural ET" in solution

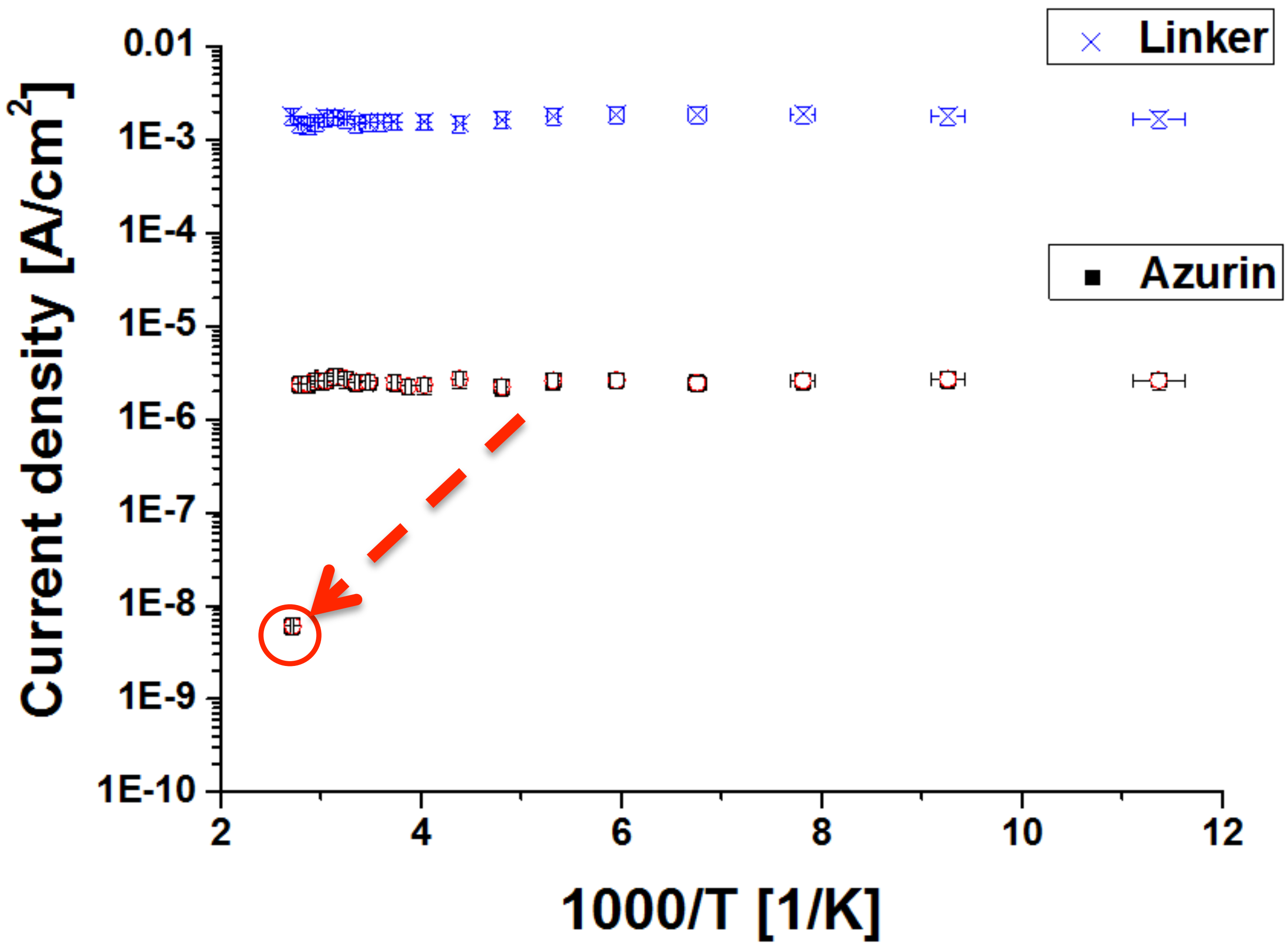
How can we study the ETp mechanism ?

- 1. Vary temperature
- 2. Modify protein:
  - Remove the cofactor (redox)
  - Replace the cofactor
  - Add the cofactor
  - Change binding (to electrode)
  - Change orientation of protein

TEMPERATURE DEPENDENCE *I-V* - *AZURIN*

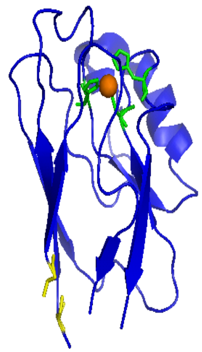


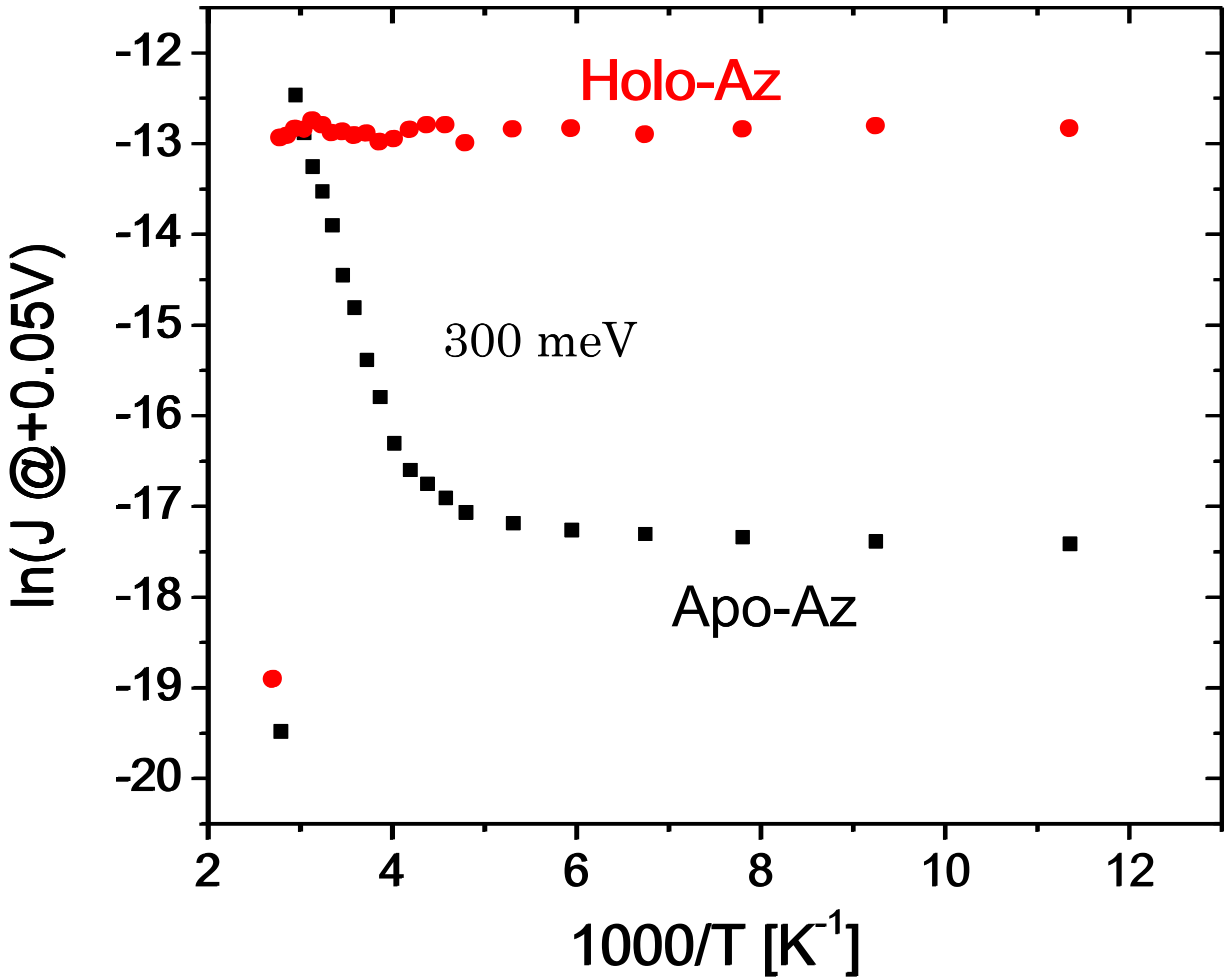
Azurin covalently bound to the surface
(via linker)



Sepunaru et al., JACS 2011

Cu ion removal

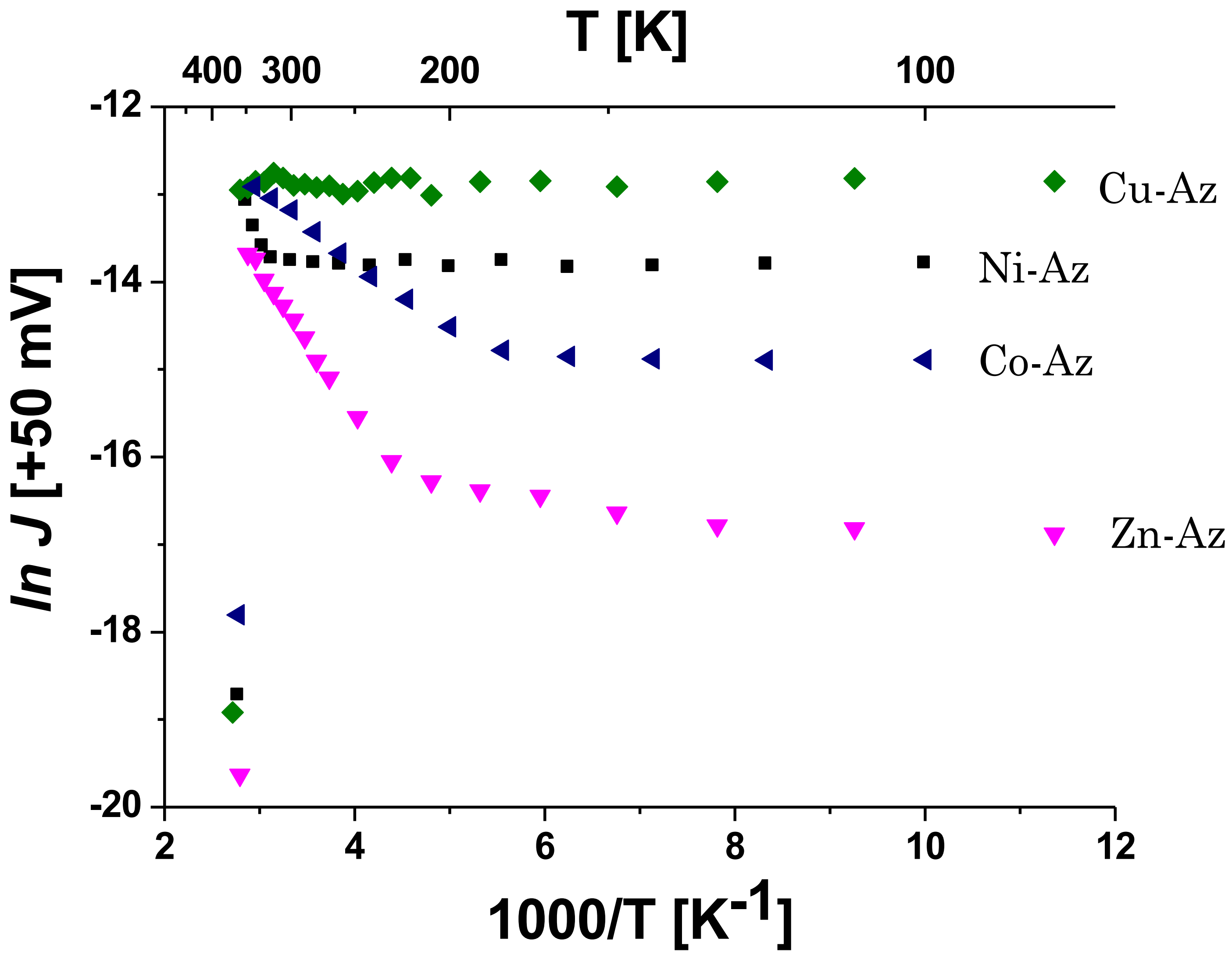




$$I \propto Ae^{-(\frac{E_A}{k_b T})}$$

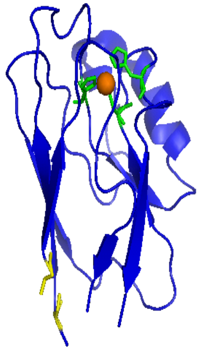
 Sepunaru et al., JACS 2011

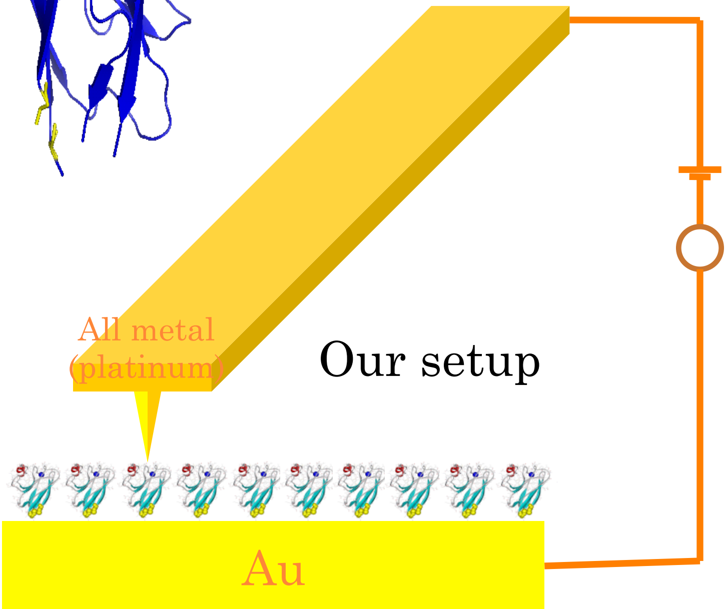
Cu ion replacement

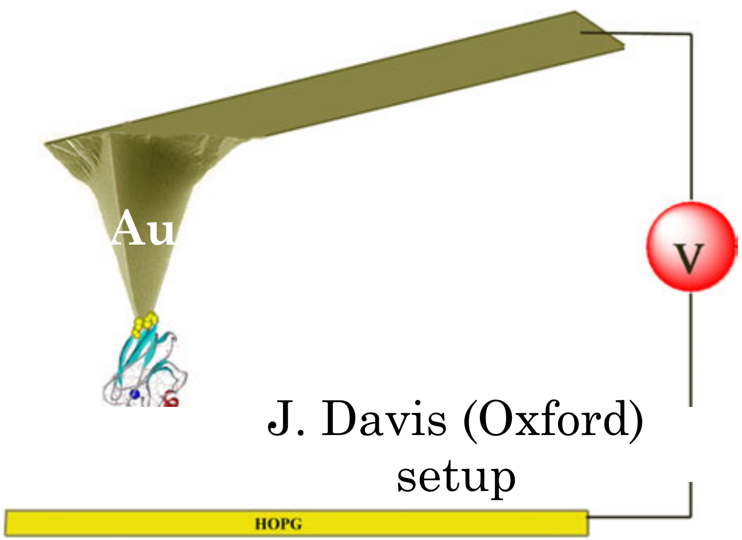


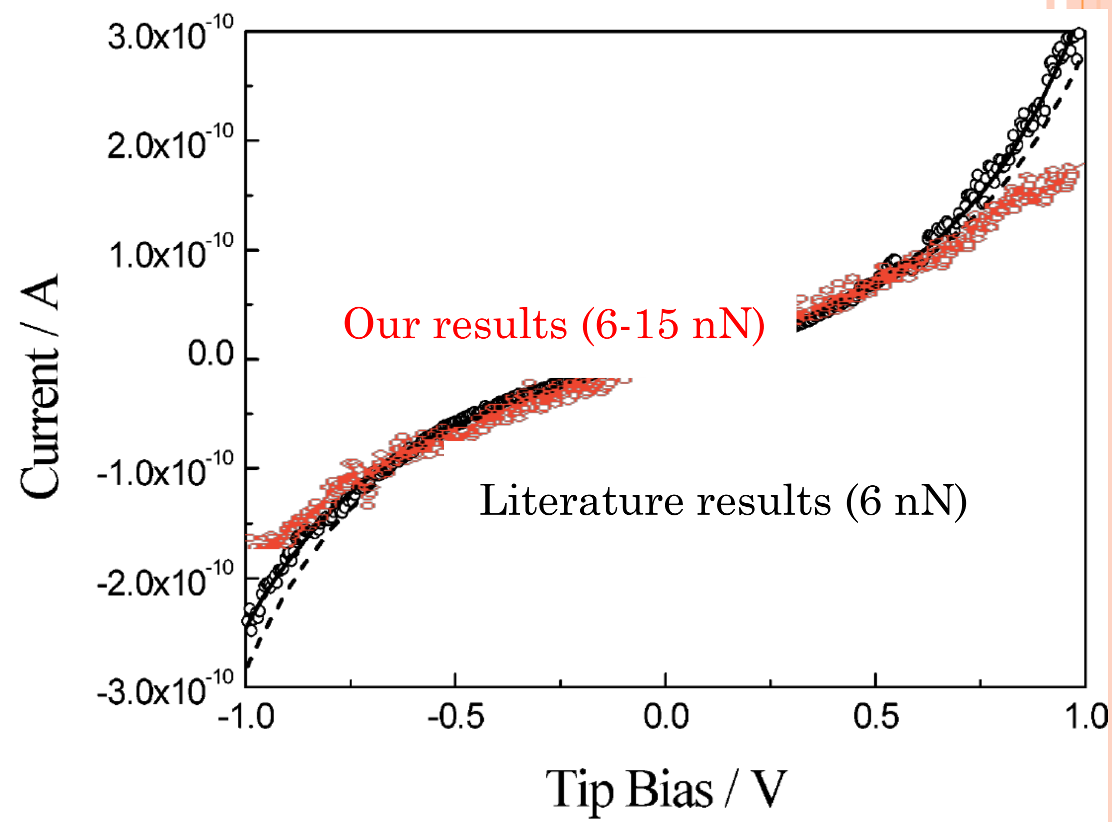
 Unpublished Results

Connect to literature data: Conducting Probe AFM studies on Az



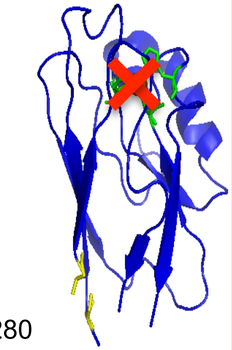


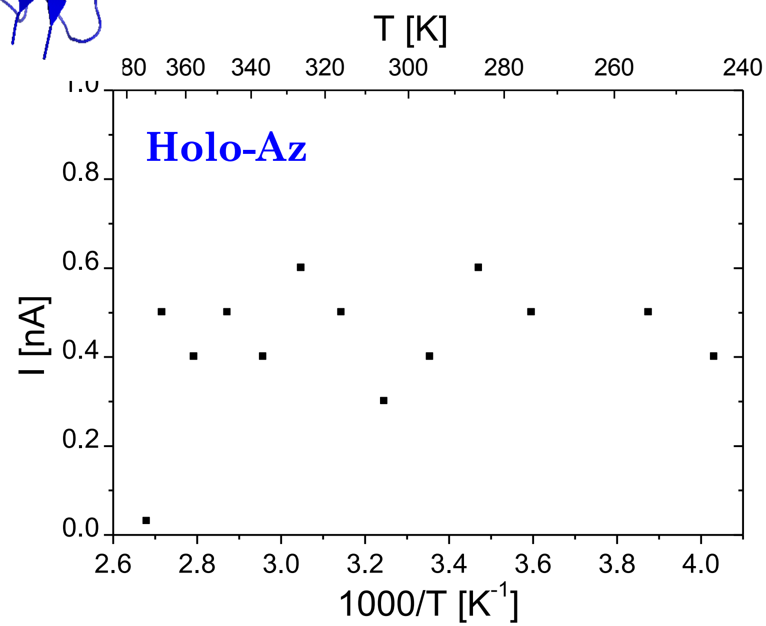


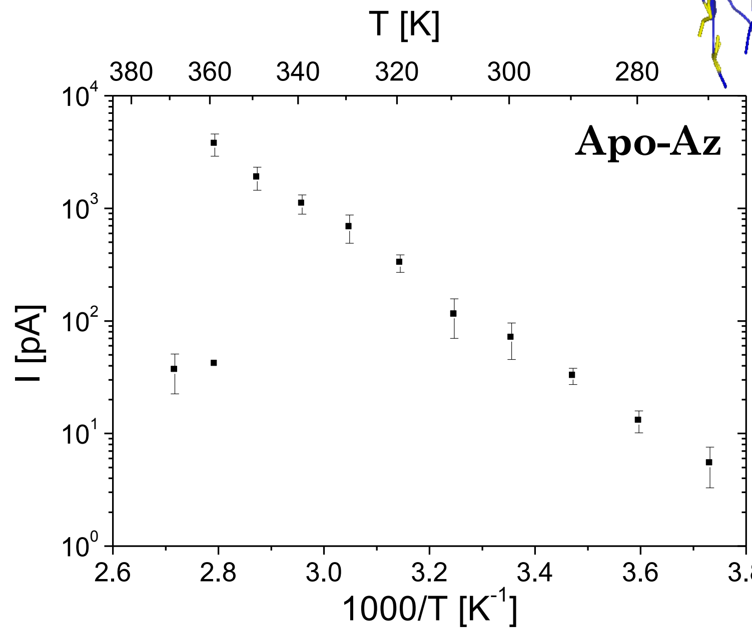


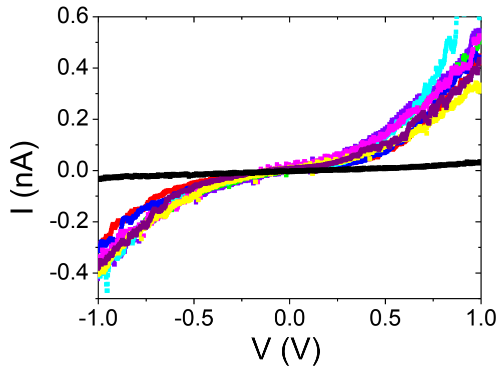
Li et al., ACS Nano 2012

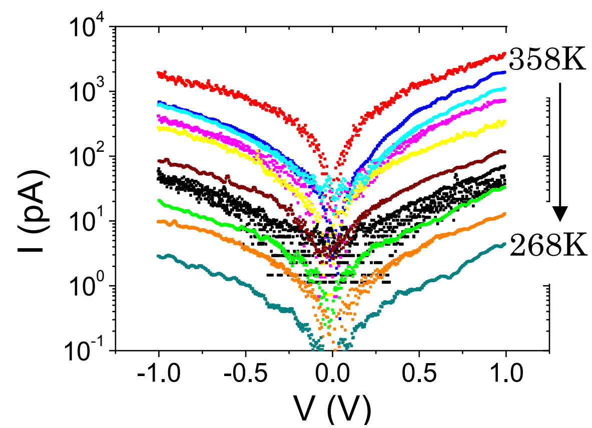
Temperature-dependent conductive probe AFM





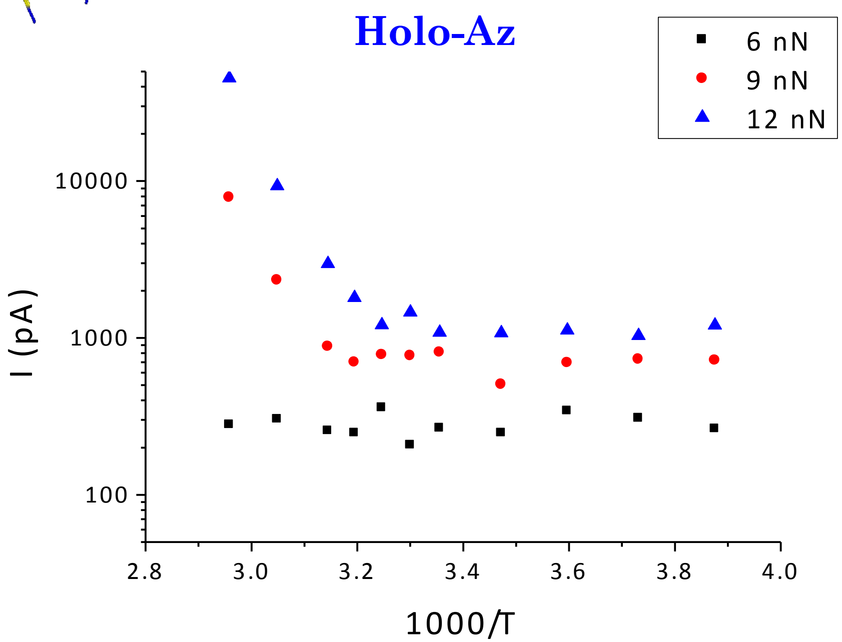






 Li et al., ACS Nano 2012

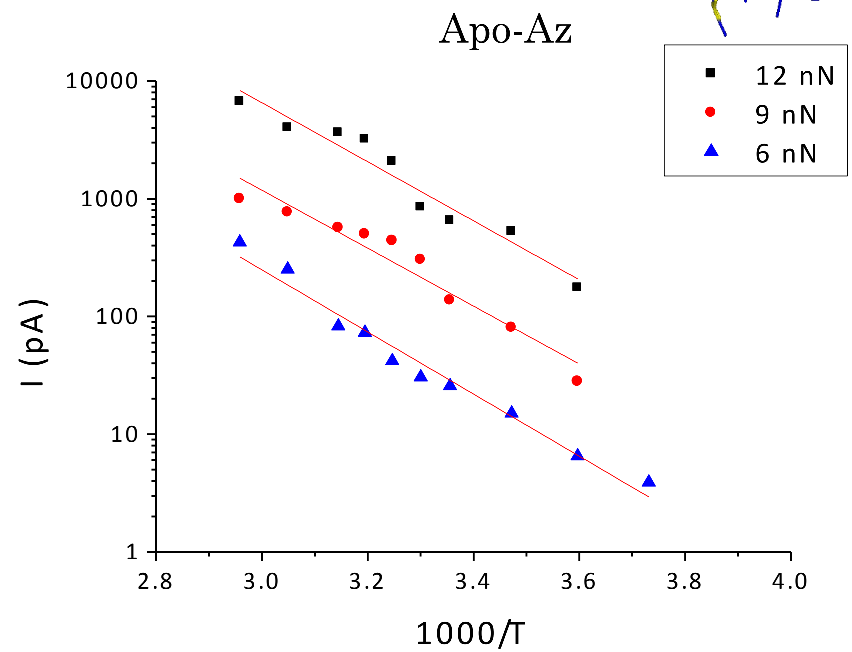
Force-dependent measurements



Increased force

↓

DIFFERENT ETp mechanism



Increased force

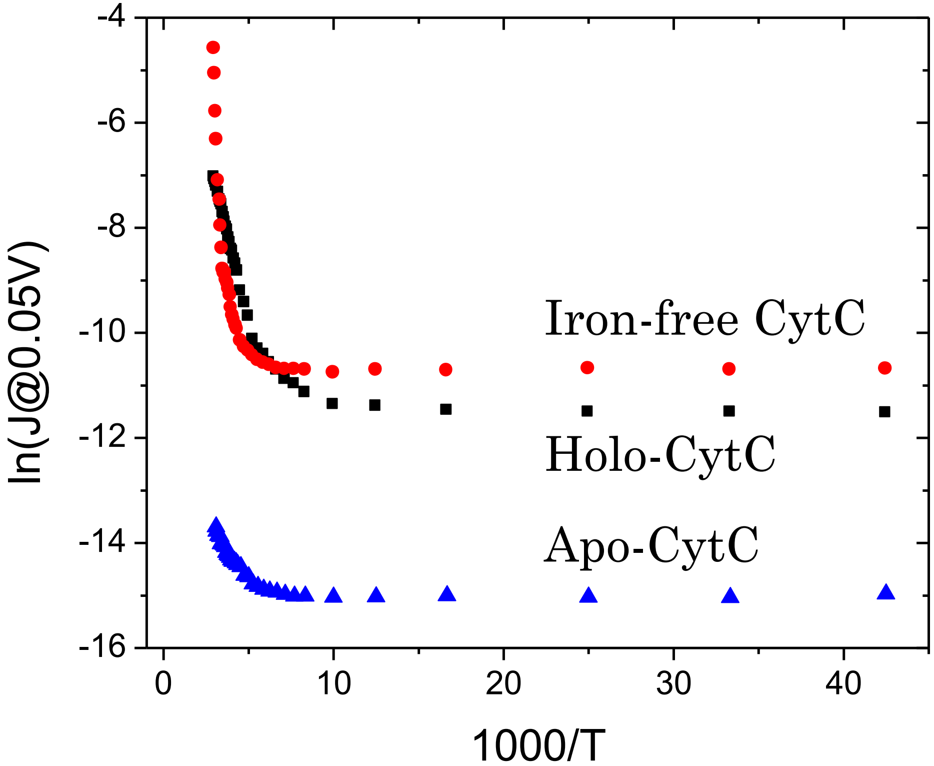
↓

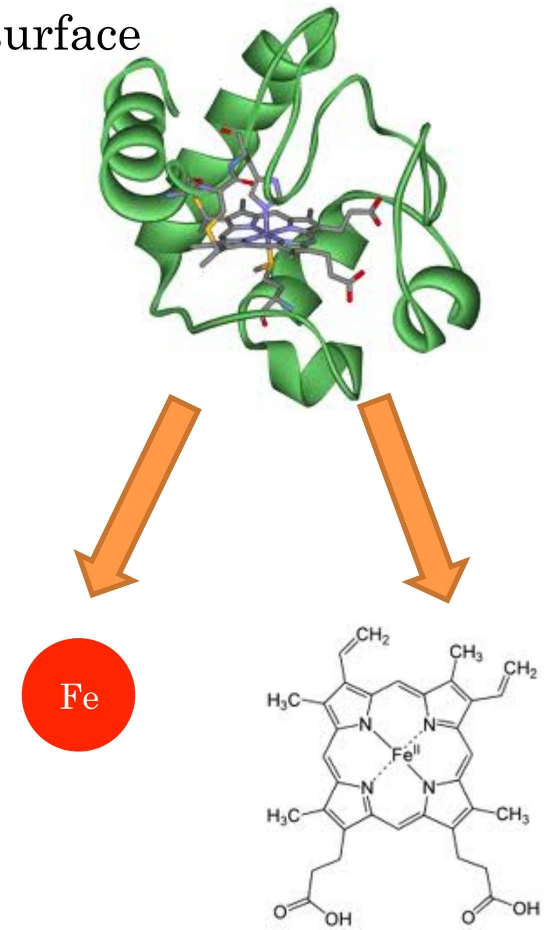
Increased currents
Same ETp mechanism

Li et al., ACS Nano 2012

TEMPERATURE DEPENDENT *I-V WITH CYT C*

Cyt C bound **electrostatically** (physisorbed) to surface





WHAT IS THE ETP MEDIATOR?

 Amdursky et al., JACS 2013

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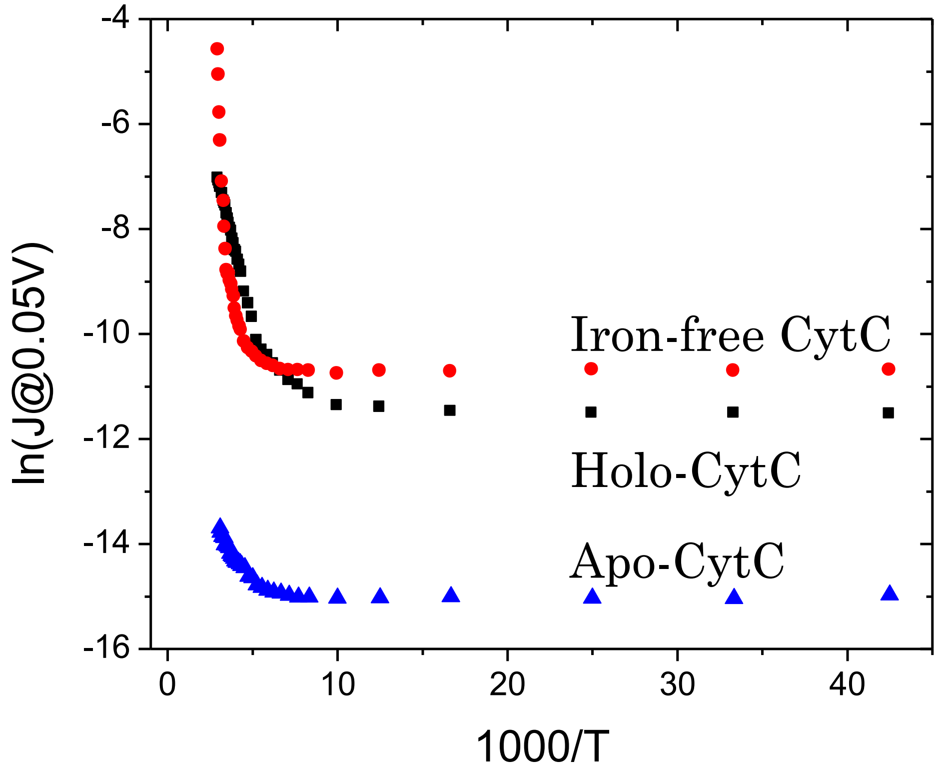
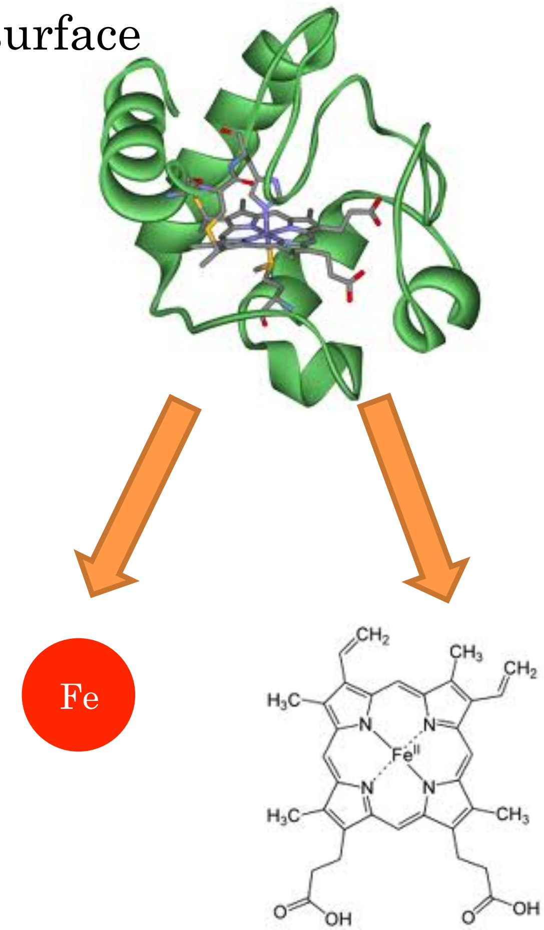


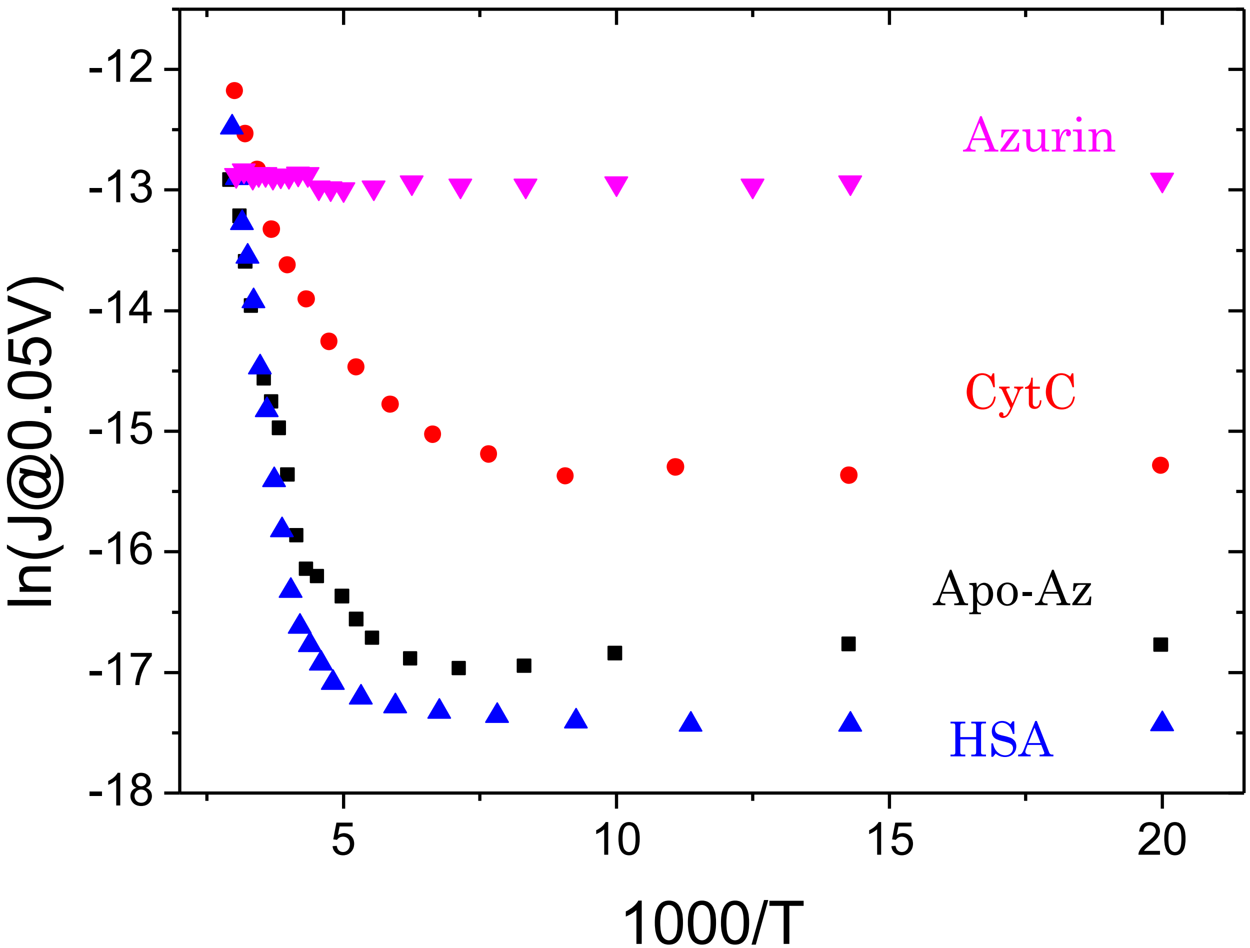


WHAT IS THE ETP MEDIATOR?

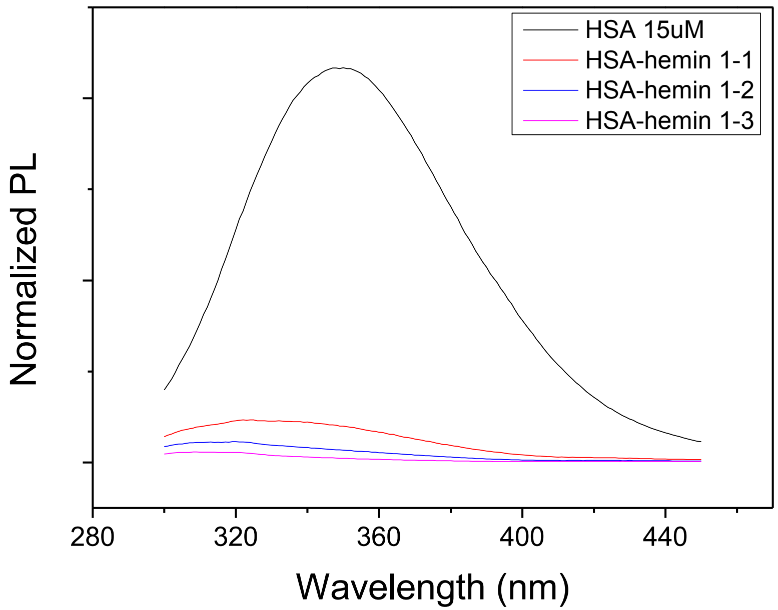
Amdursky et al., JACS 2013

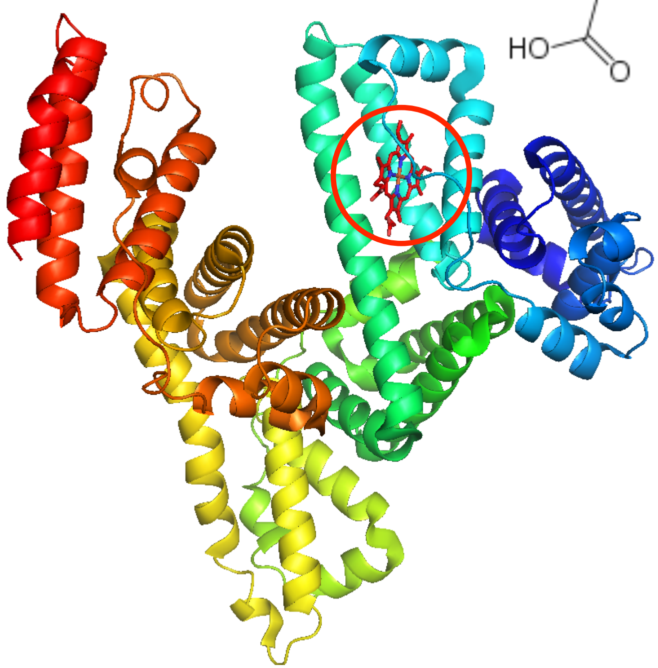
What is the ETp mediator?

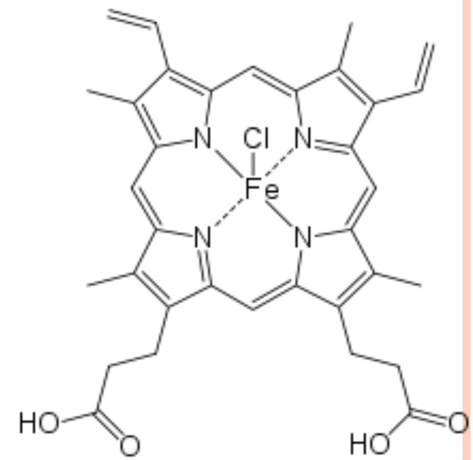
use 'Doping' to find out



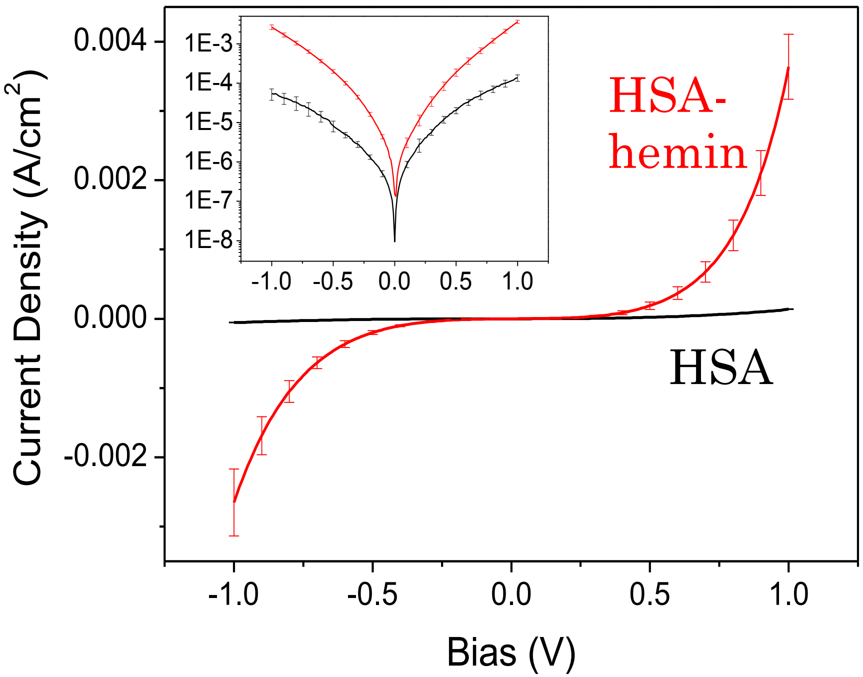
'DOPING' SERUM ALBUMIN WITH **HEMIN**

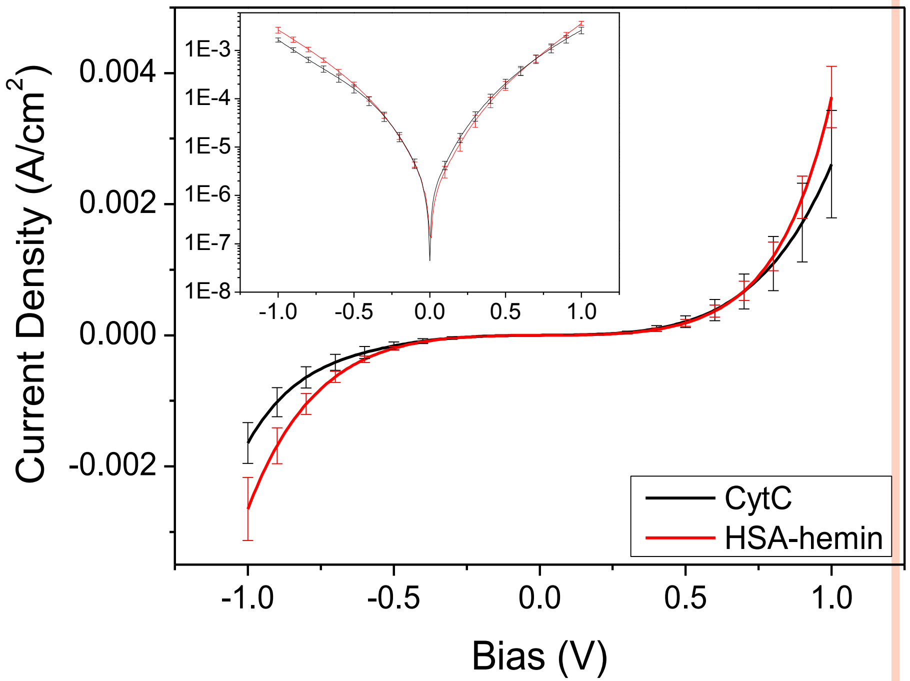






‘DOPING’ SERUM ALBUMIN WITH HEMIN





 Amdursky et al., PCCP 2013

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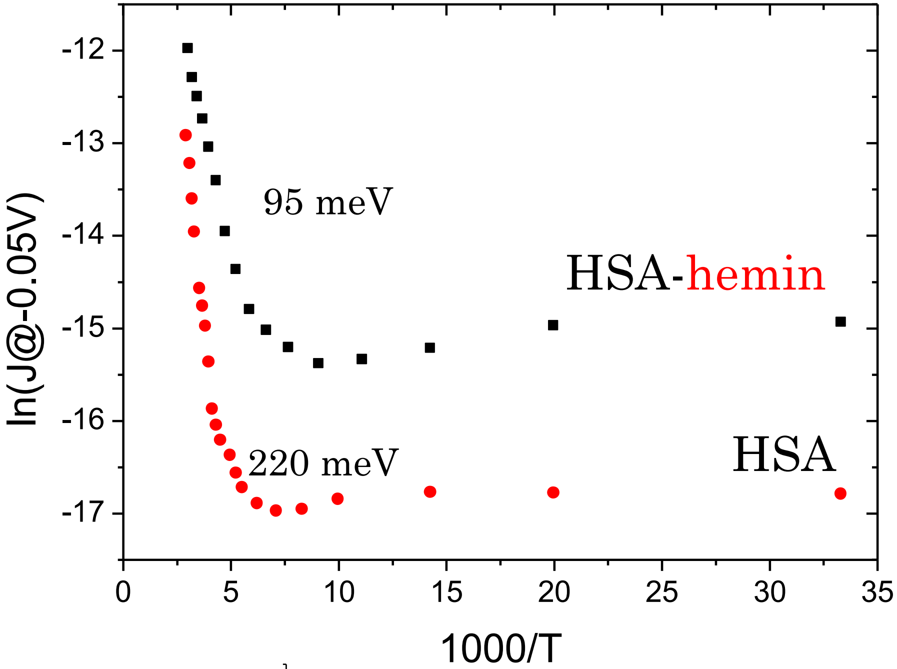
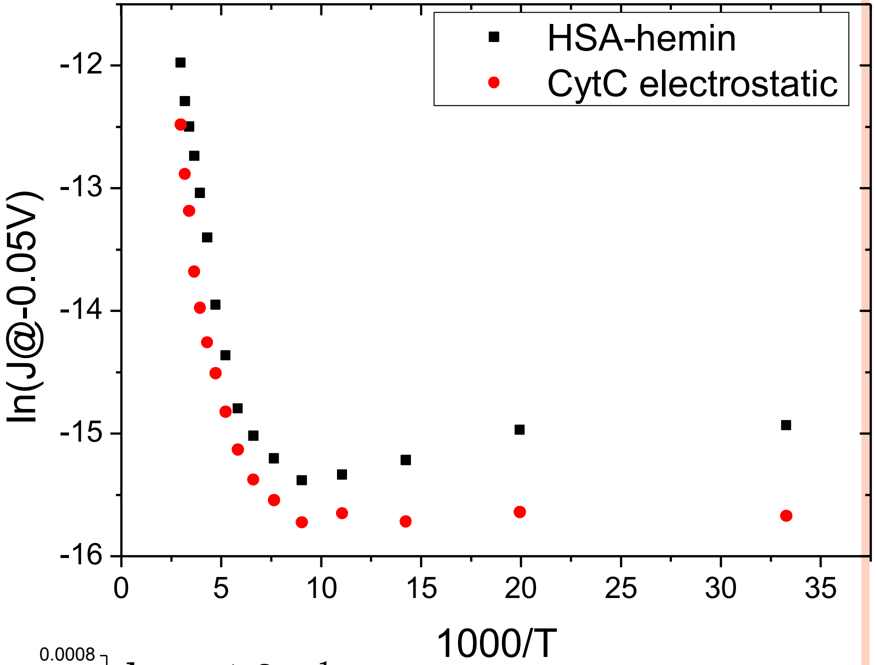
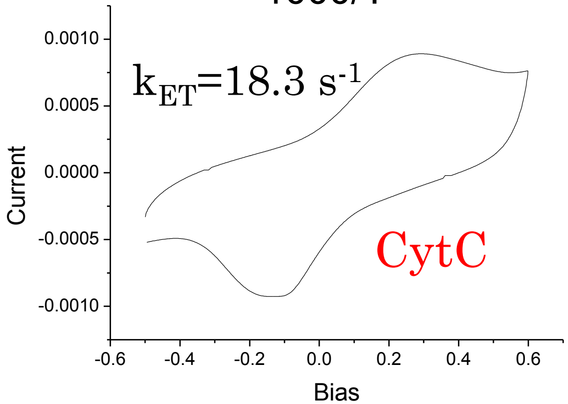
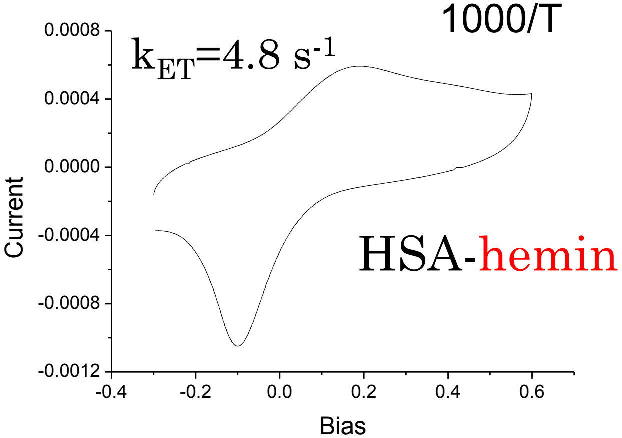
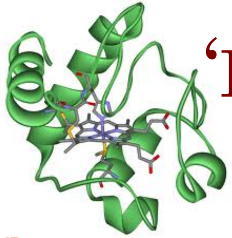




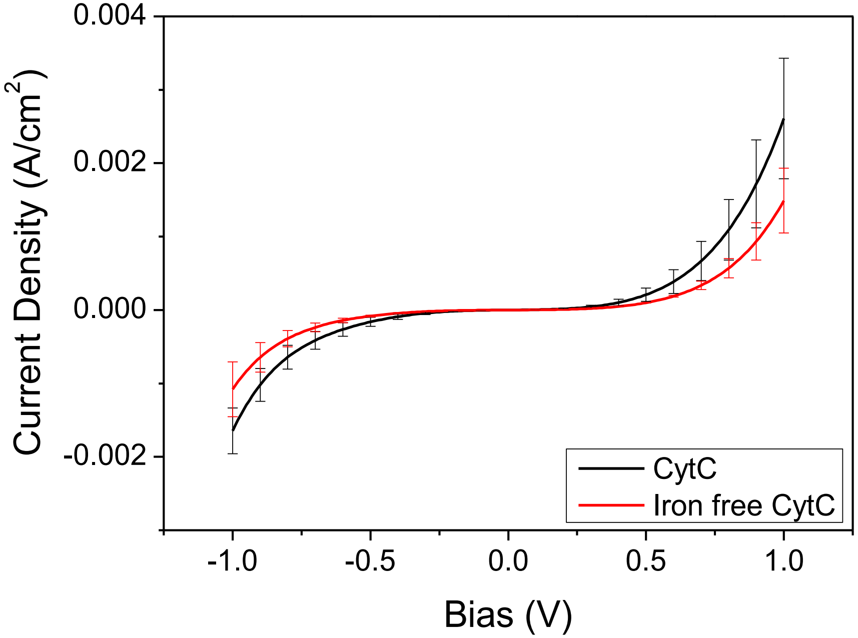


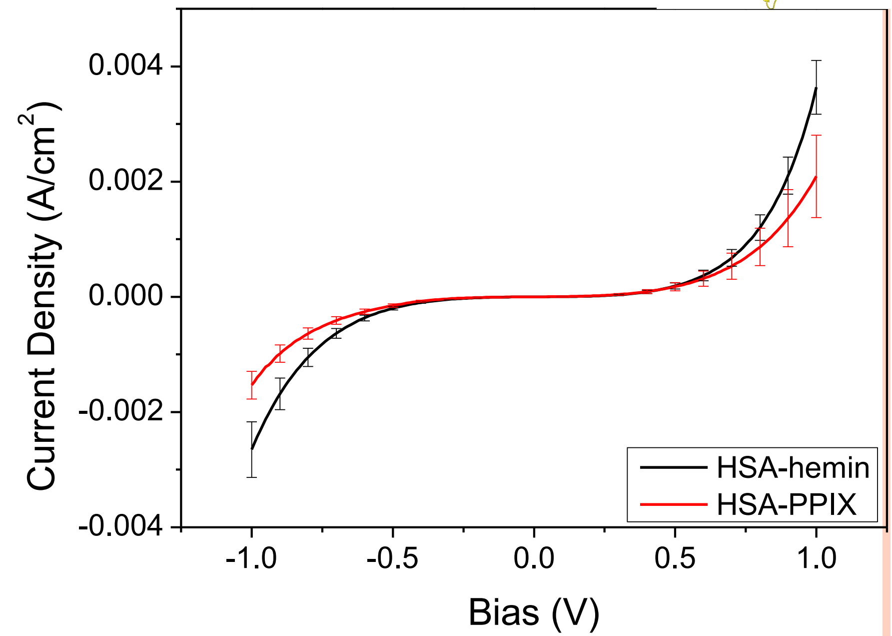


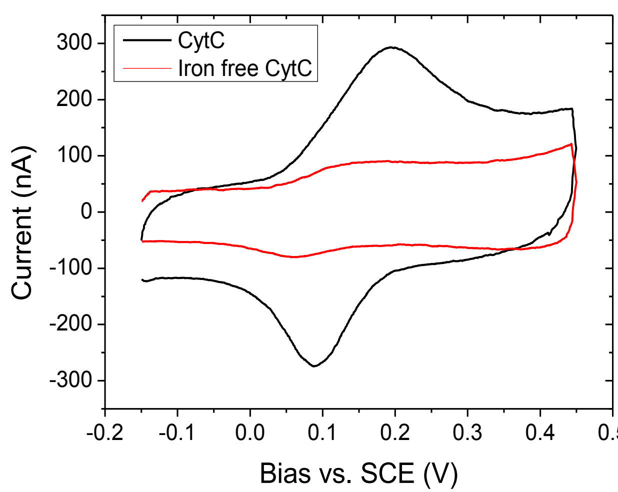
Amdursky et al., PCCP 2013

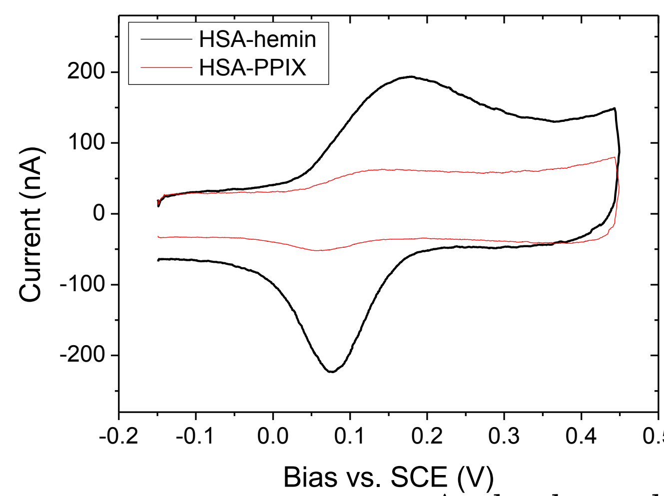


'DOPING' SERUM ALBUMIN WITH HEMIN
WHAT IS THE ETP MEDIATOR?









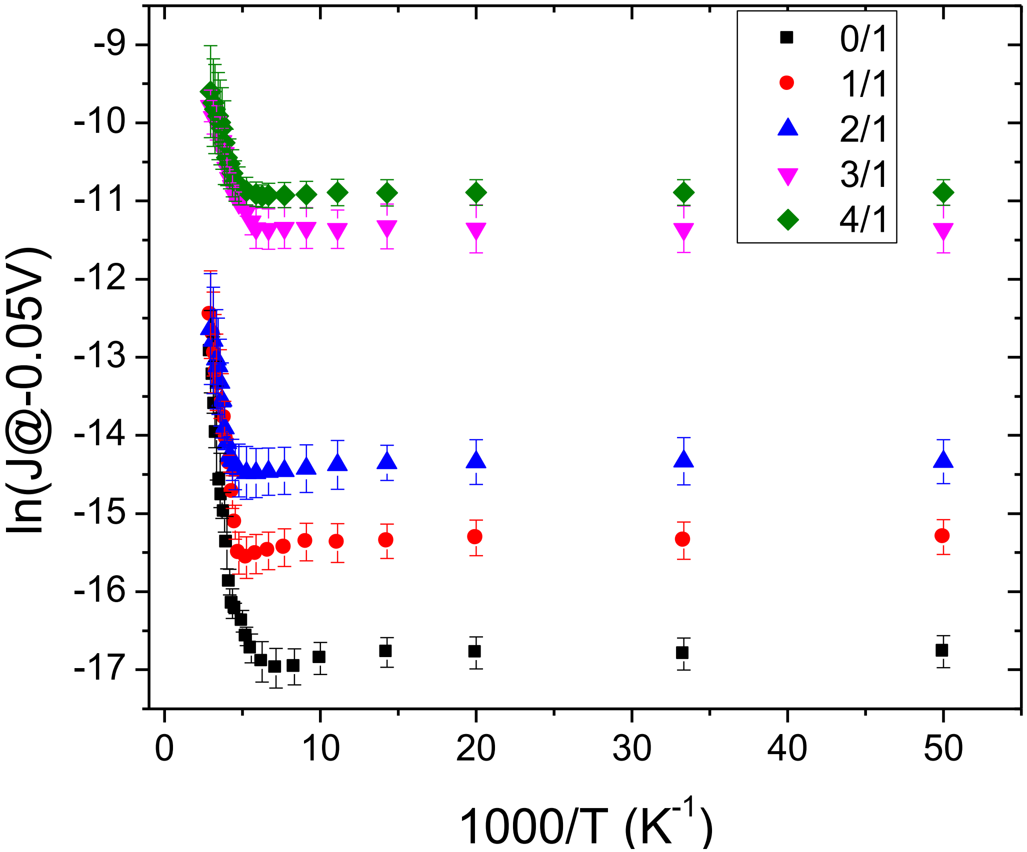
 Amdursky et al., PCCP 2013

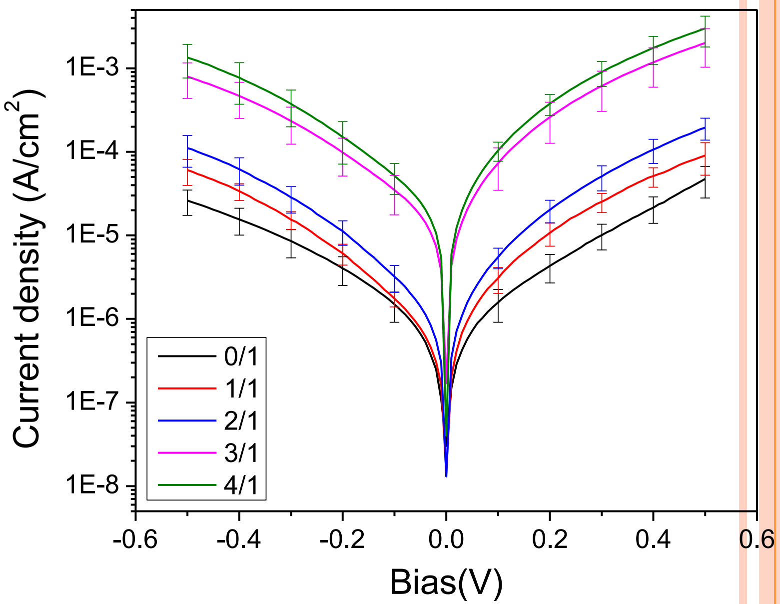
‘DOPING’ SERUM ALBUMIN WITH HEMIN
WHAT IS THE ETP MEDIATOR?

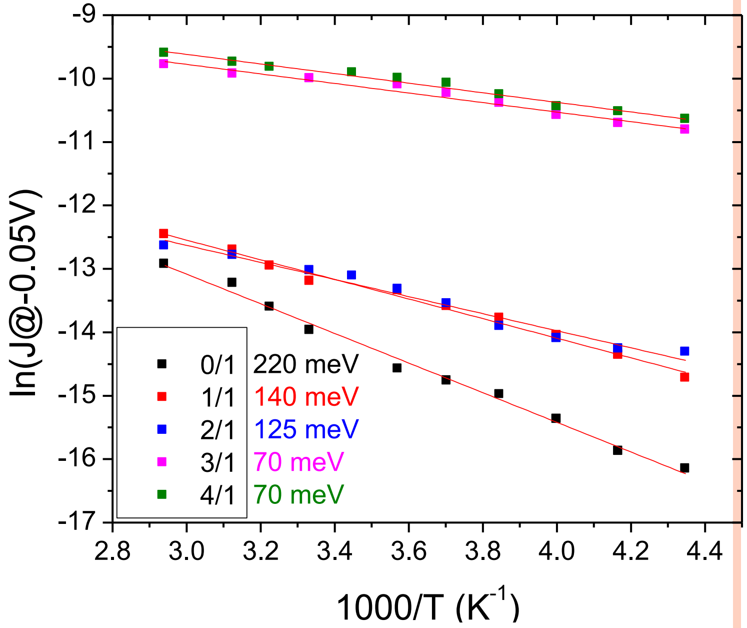
In **ETp** the **conjugated porphyrin** ring, rather than the Fe ion **is the main mediator,** while **ET** is controlled by the **$Fe^{2+/3+}$ redox** process!

 Amdursky et al., PCCP 2013

'DOPING' SERUM ALBUMIN WITH **RETINOATE**

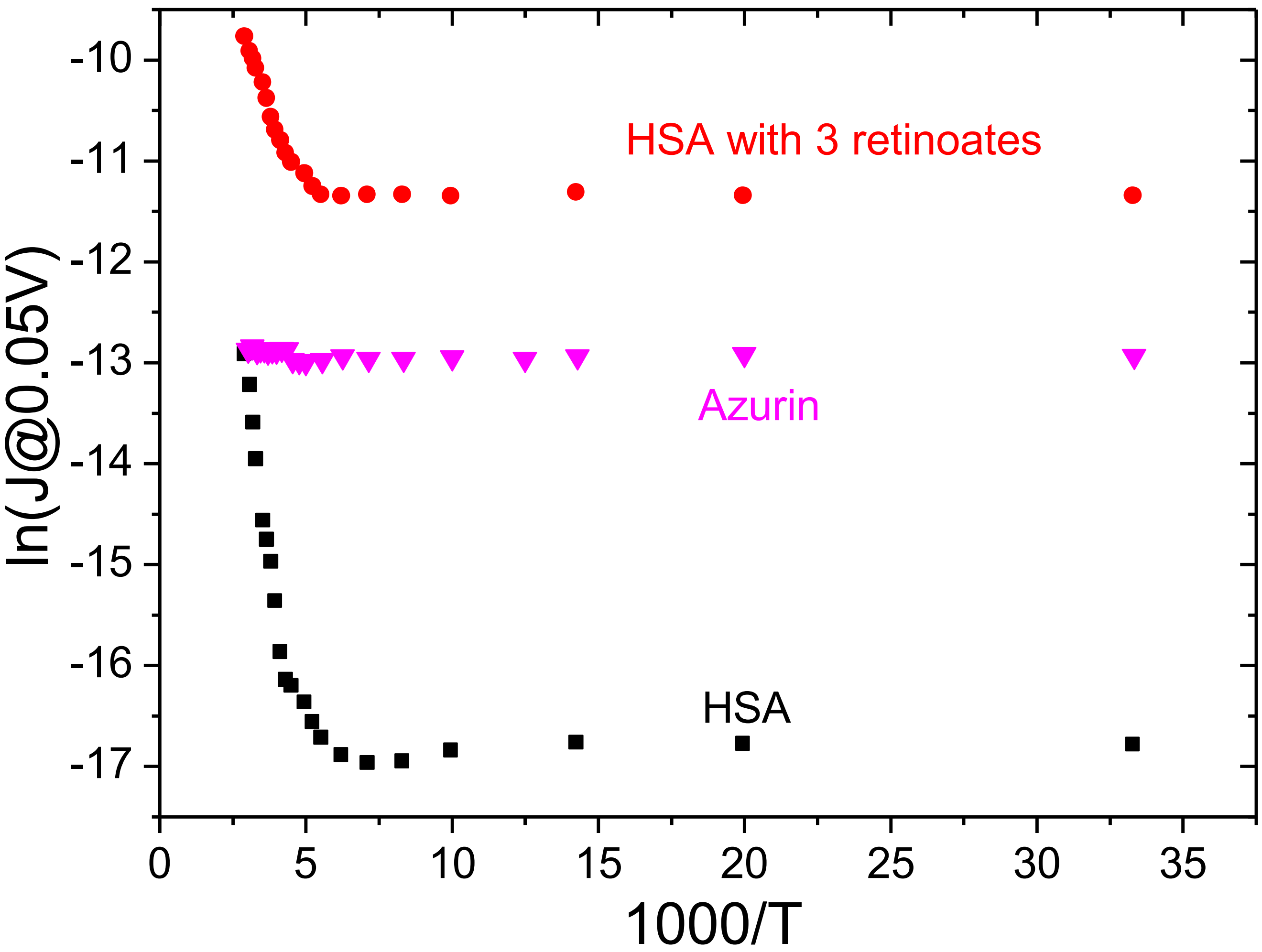






Amdursky et al., JACS 2012

The power of protein 'doping'



CONCLUSIONS

- Proteins can serve as solid-state Electron transport media, from macro to nano scales
- Mechanisms of electron transport are similar to hopping and tunneling, as seen from
  - Temperature- dependent conduction
- Proteins can be viewed as electronic conducting material with the possibility of doping, as seen from
  - Comparing conduction through modified proteins
- Both the type of protein-electrode contact, and its orientation relative to the electrodes, are important
- ETp can teach about ET and *vice versa,*

  but … *only ETp is relevant for solid-state bioelectronics*

Conclusions

Molecule	Room Temp. R (Ω*nm^2) for ~4 nm length
Conjugated	$\sim 10^{7}$ - 10^{9}
DNA	$\sim 10^{7}$ - 10^{10}
Proteins	$\sim 10^{9}$ - 10^{11}
Saturated	$\sim 10^{18}$ - 10^{22} (extrapolated!)

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