Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Institut for Nanotechnology

UNI
BASEL

Molecular Electronics

from single molecules in electronic circuits to SAMs in CMOS technology

Marcel Mayor

Outline

- Electronic & Molecules ?
- History & Roots
- Single Molecule Approach
- CMOS Integration
- Nanoscale Objects
- Perspectives & Summary

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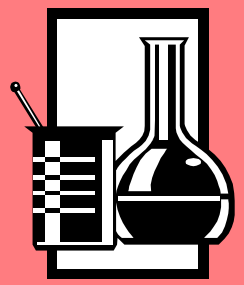


Chemistry:

Mark Elbing
Matthias Fischer
Claudia Didschies
Alfred Błaszczyc
Martin Chadim
Lijin Shu
Matthiew Koëpf
Christophe Stroh
Carsten von Hänisch

Herman von Helmholtz-Gemeinschaft

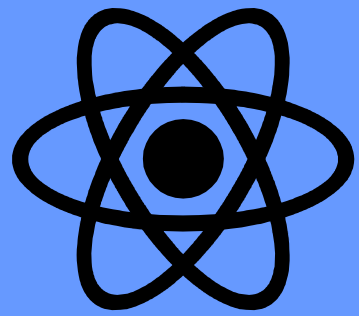
Alexander von Humboldt Foundation

Bundesministerium für Bildung und Forschung

Volkswagen Stiftung

DFG-Center for Functional Nanostructures

Infineon Technologies



Physics:

Heiko B. Weber
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Michelle Di Leo
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Rolf Ochs
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Single Molecule Transport & Electrochemistry (STM):

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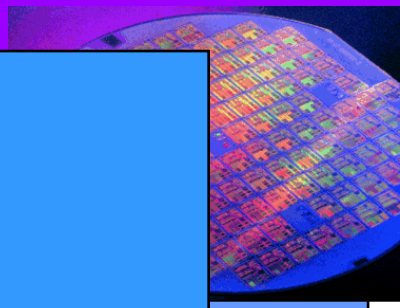
Zhihai Li
Bo Han
Gabor Meszaros
Ilya Pobelov
Gabor Nagy
Udo Linke

Claudia Didsch
Alfred Błaszczy
Martin Chadim
Lijin Shu
Matthiew Koëp
Christophe Str
Carsten von Hä

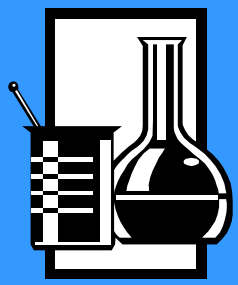
szentrum Karls
holtz-Gemeinsch
notechnology
n Helmholtz-
haft
von Humboldt
n

CMOS Integration (Infineon Technologies):

Eike Ruttkowski
Hannes Luyken
Werner Weber



Chemistry in Basel



Nicolas Weibel
Umut Soydaner
Viviana Horhoiu
Agnieszka Grochowska
Torsten Peterle
Sergio Grunder
Sandro Gabutti
Marcel Müri
David Vonlanthen

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NCCR Nanoscience

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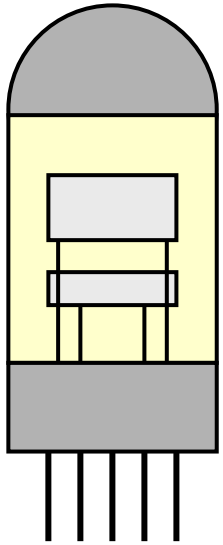
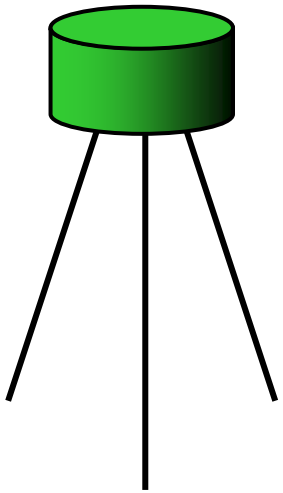
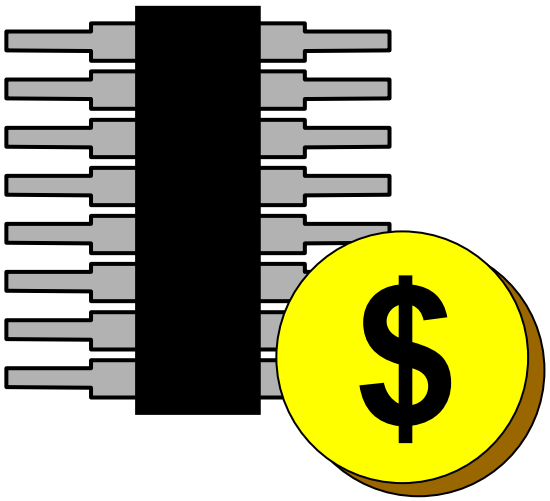
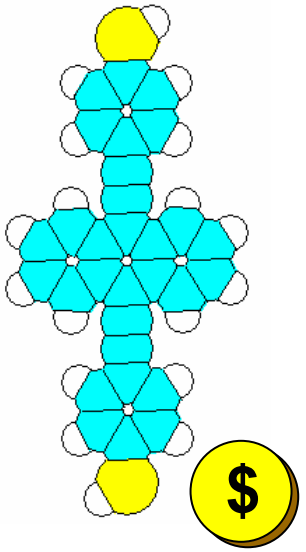
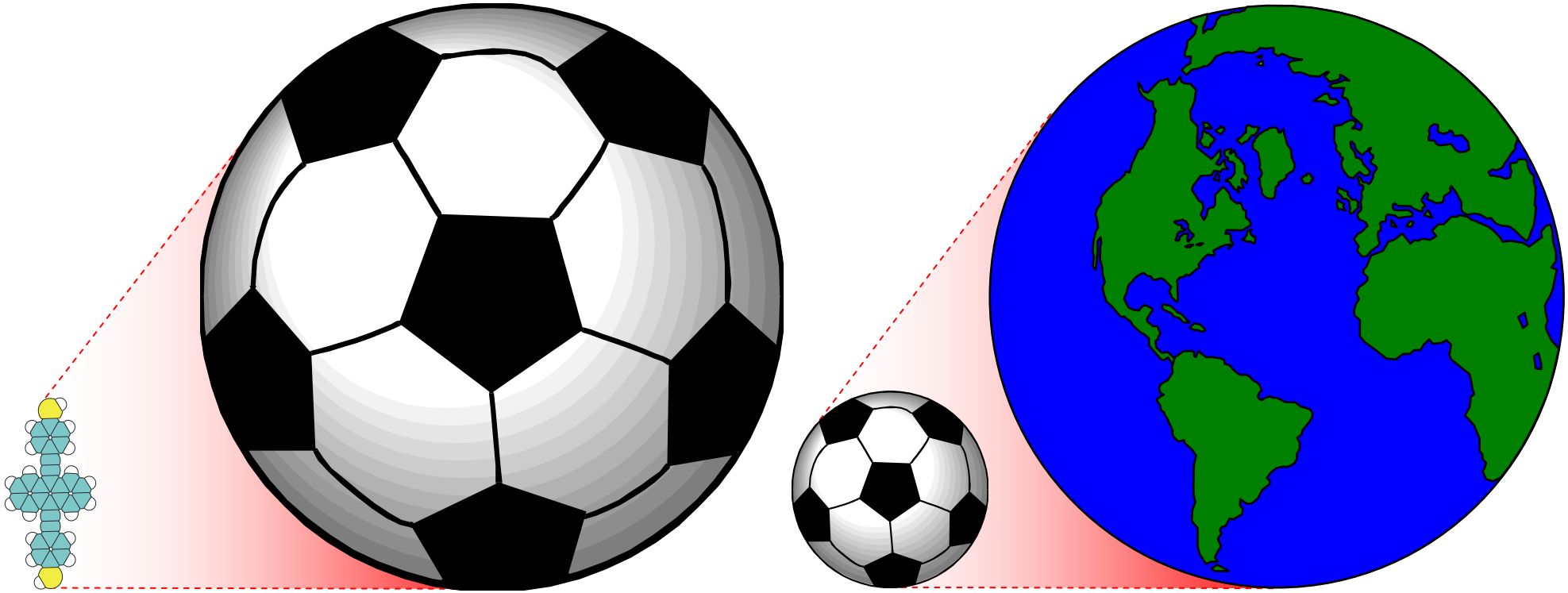
Electronics & Molecules

Tube	Transistor	Chip	Molecule ?
			
5 cm	**5 mm**	**5 μm**	**< 5 nm**
0,05 m	**0,005 m**	**0,000 005 m**	**< 0,000 000 005 m**

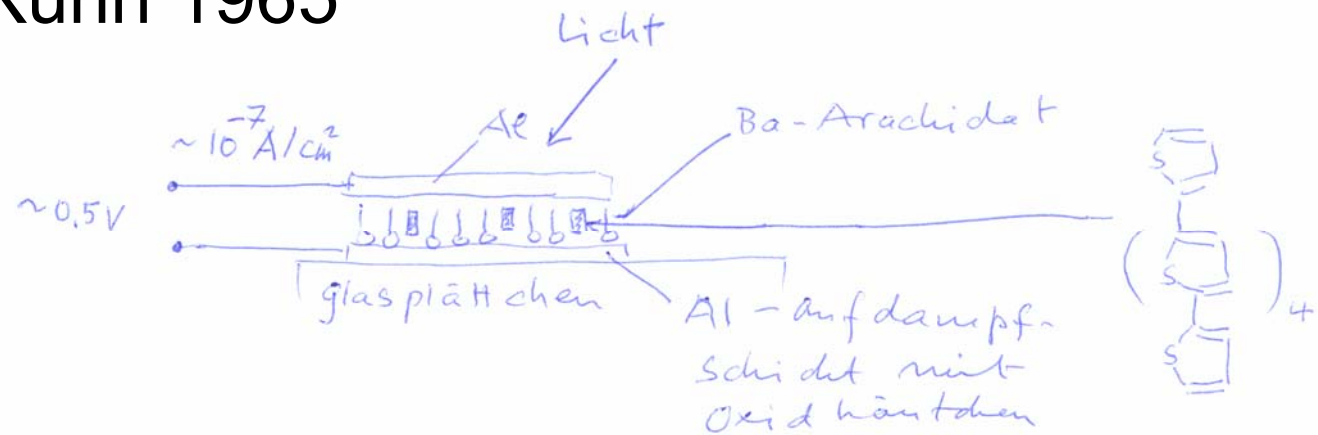
Molecules as Tiny Building Blocks ?



History:

Concept to design electronic functions by molecular organized subunits with particular physical properties:

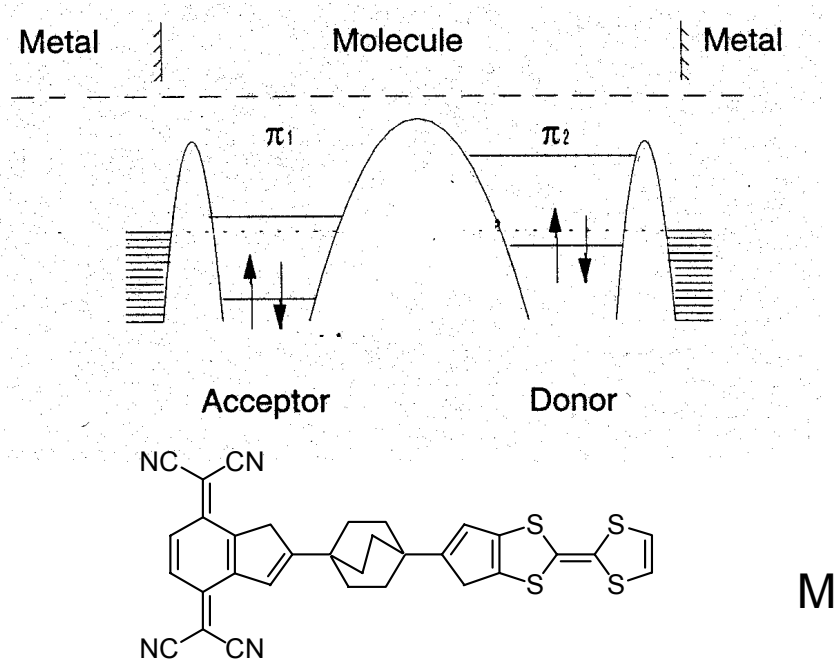
"Molecular Engineering"
described by Hans Kuhn 1965

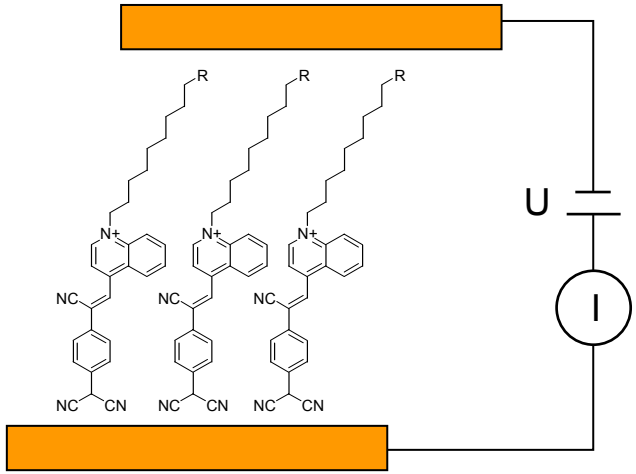


History: *Rectifier*

Theory:

A. Aviram, M. Ratner 1974

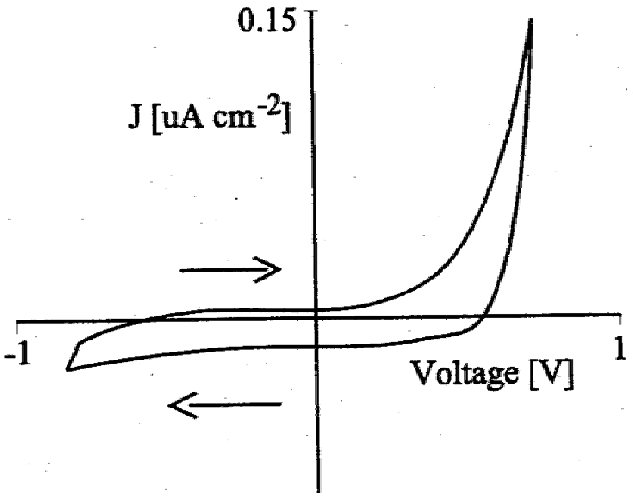




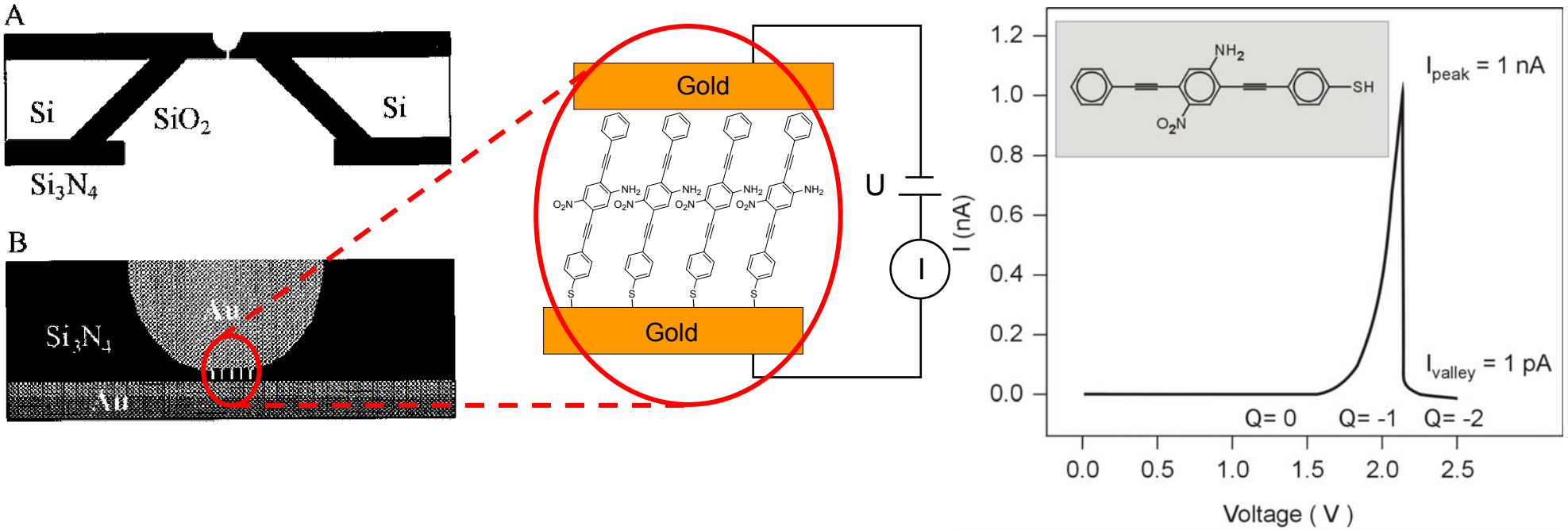
Realisation:

S. Roth et al, 1995

Metzger et al, 1997, 2001



History: *memory devices II (NDR)*

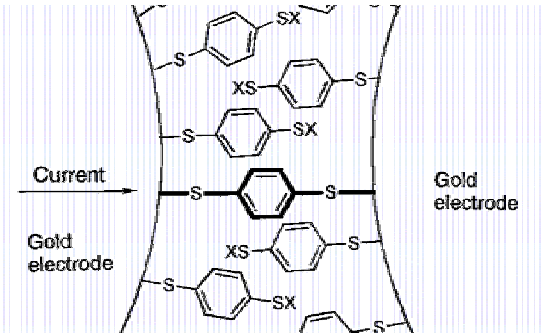


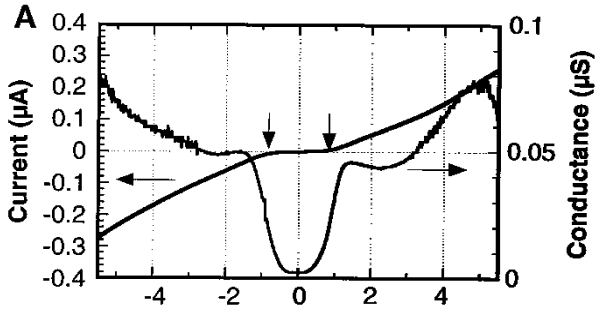
Chen, Reed, Rawlett, Tour; *Science* **286**, 1550, (1999)

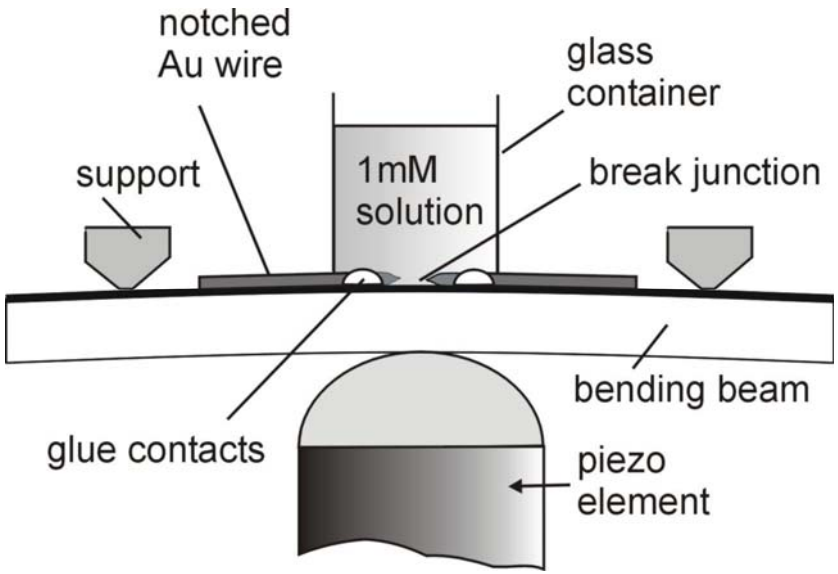
History: *single molecules*

MCB's (*Mechanically Controlled Breakjunctions*)

M. Reed et al. 1997



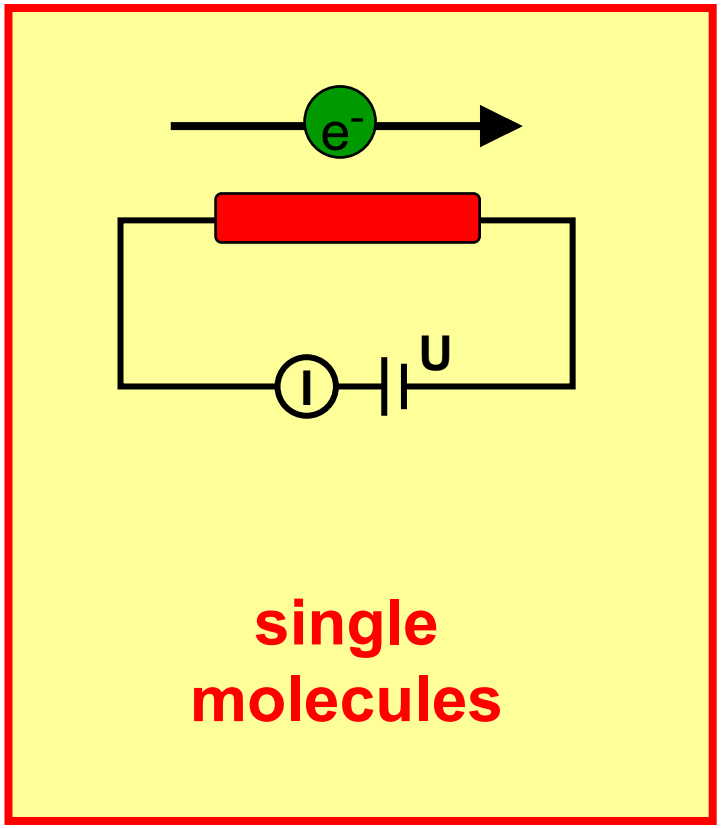




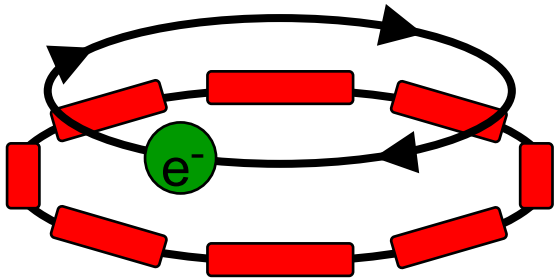
Molecular Electronics

Single Molecules as Building Blocks for Electronic Circuits ?

Concepts:



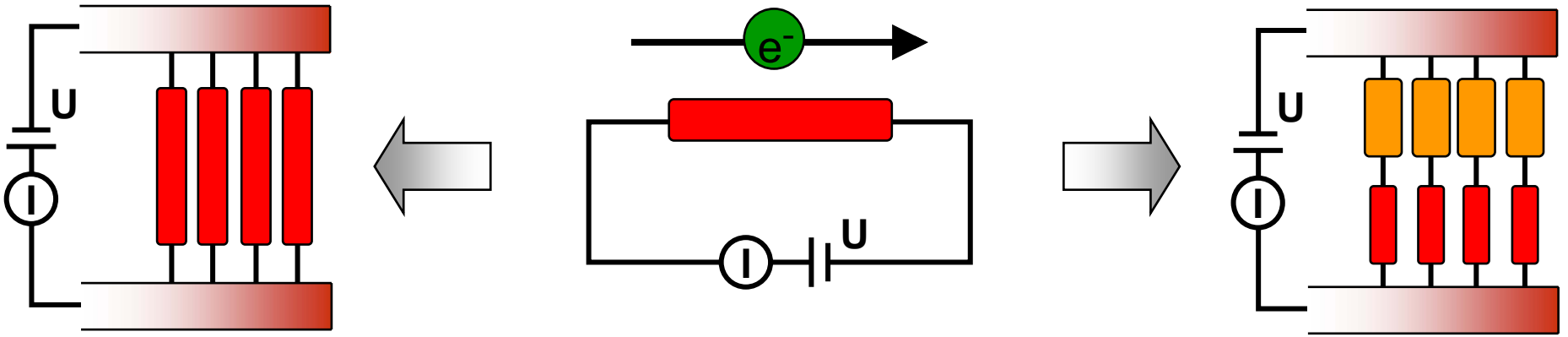
single molecules



nanoscale objects

From Single Molecules to Electronic Devices:

What do we learn from Single Molecules?

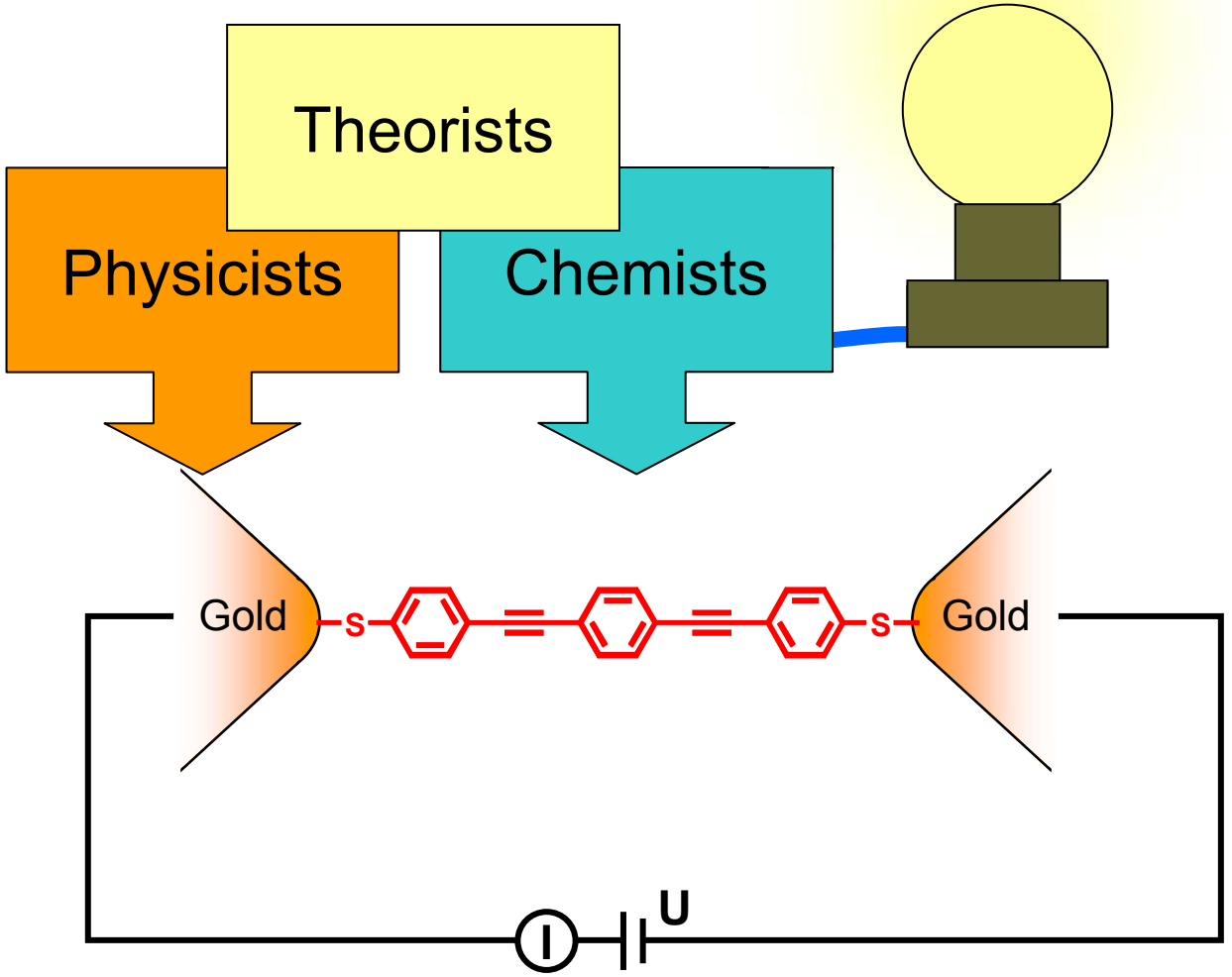


film devices

single molecules

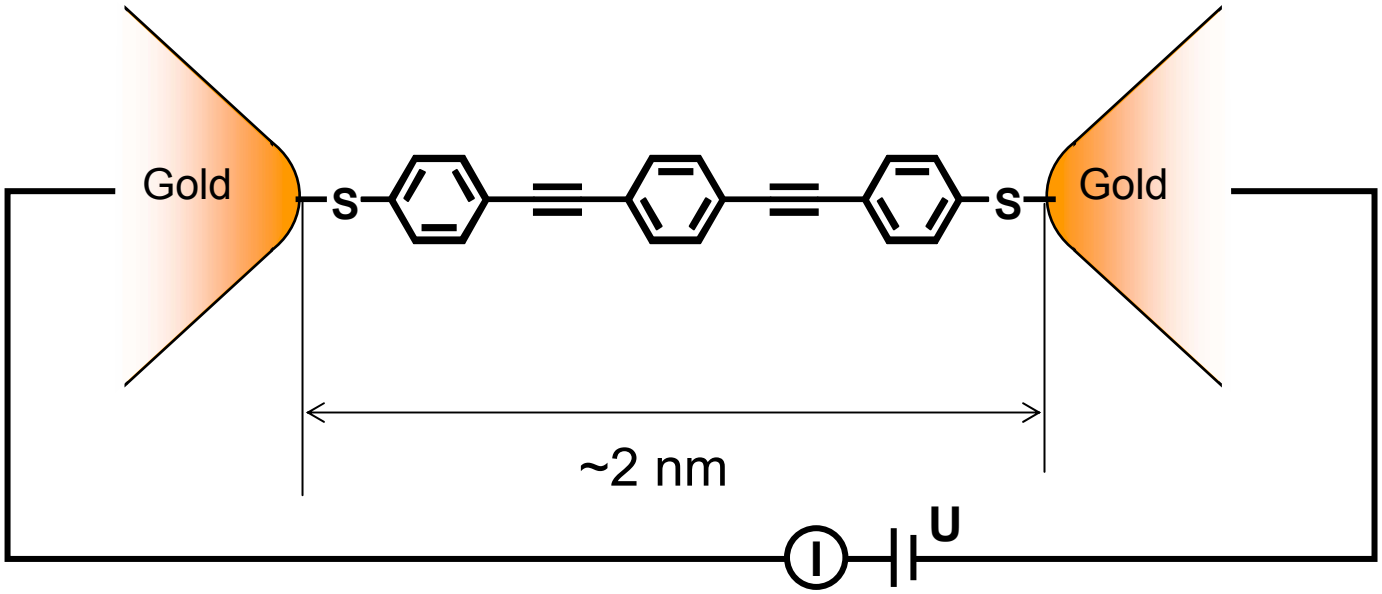
modular components ? komplex f(U) ?

Organic Molecules as Wires for e^-

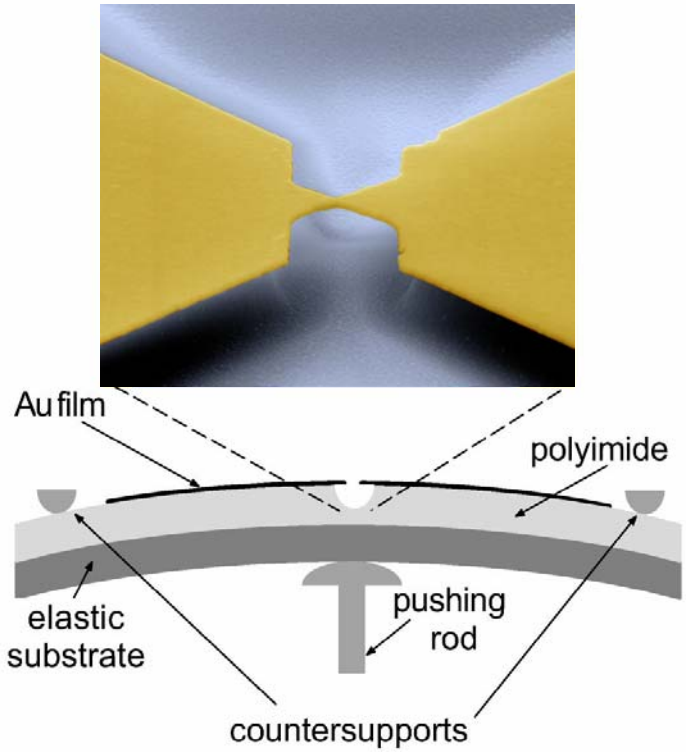


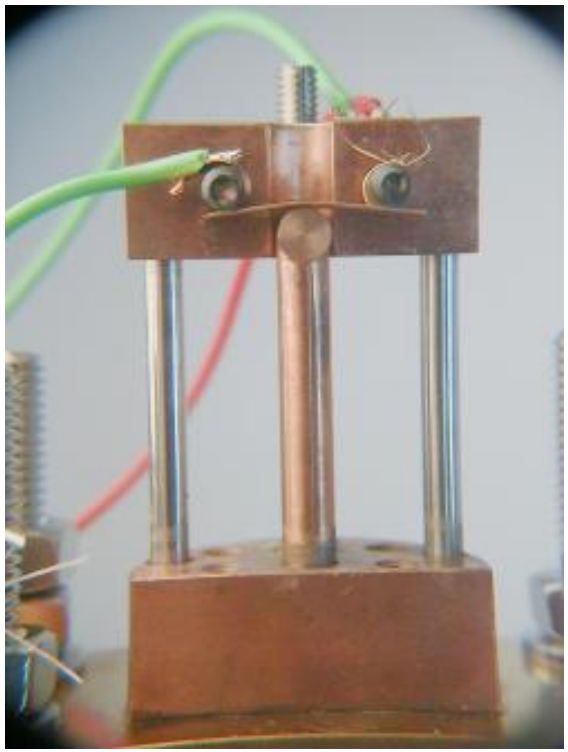
Molecules as *real* Connectors

- **Tweezers for Molecules**
- **Rigid Molecules**
- **Anchor Groups**
- **Structure *vs.* e^- Transport Correlations**



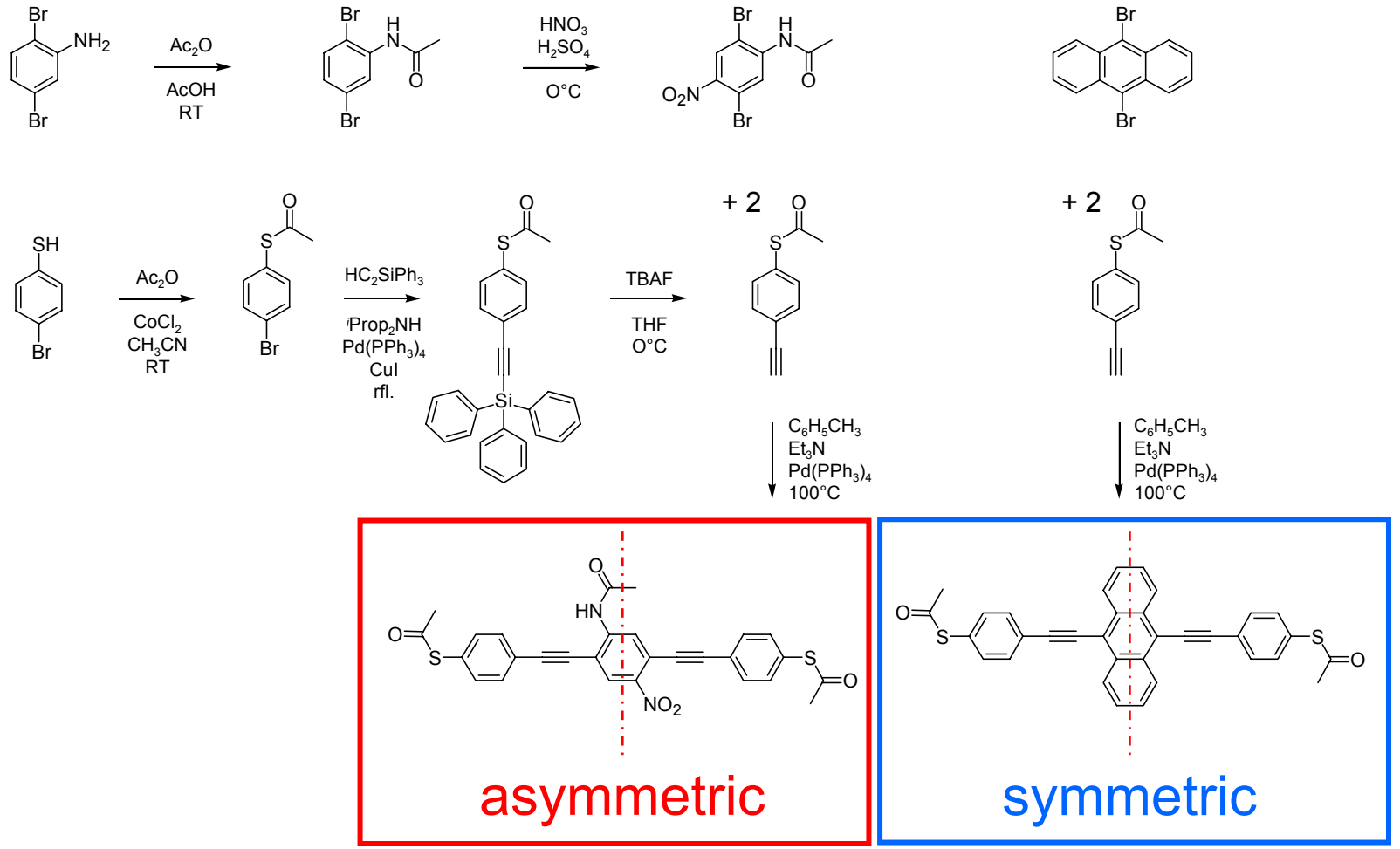
To Contact a Single Molecule:
Tweezers for Molecules





To Contact a Single Molecule:

How can we know that there is a Single Molecule ?



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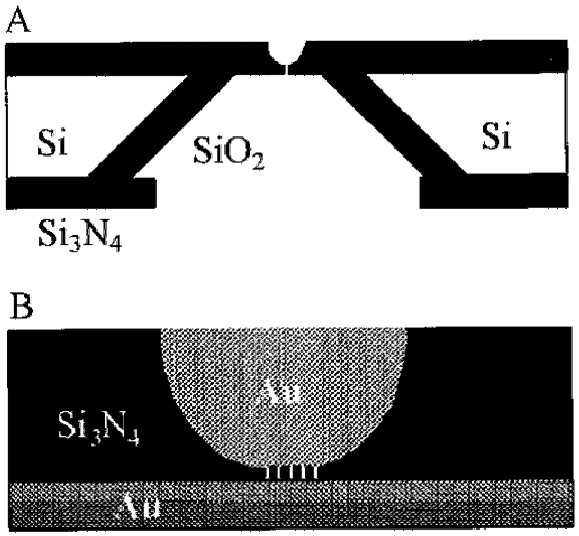
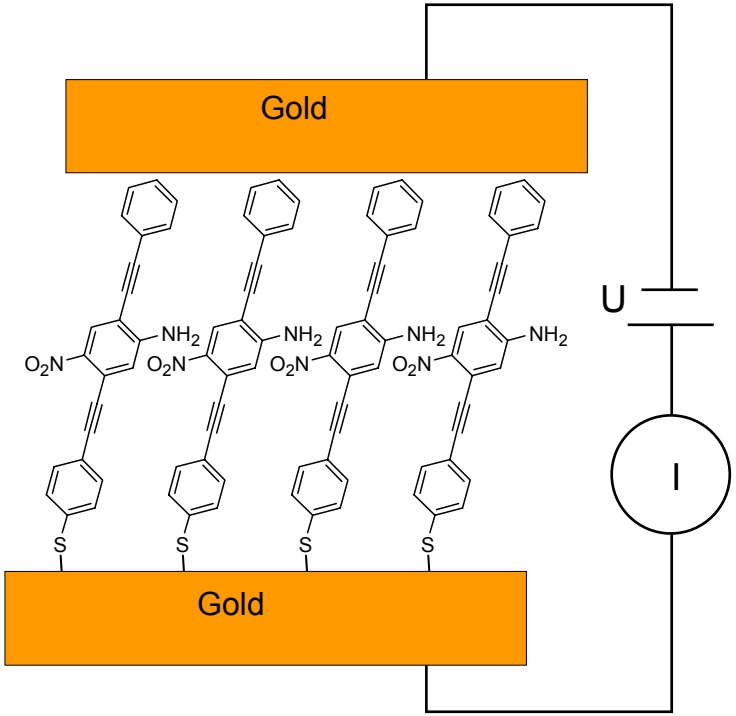
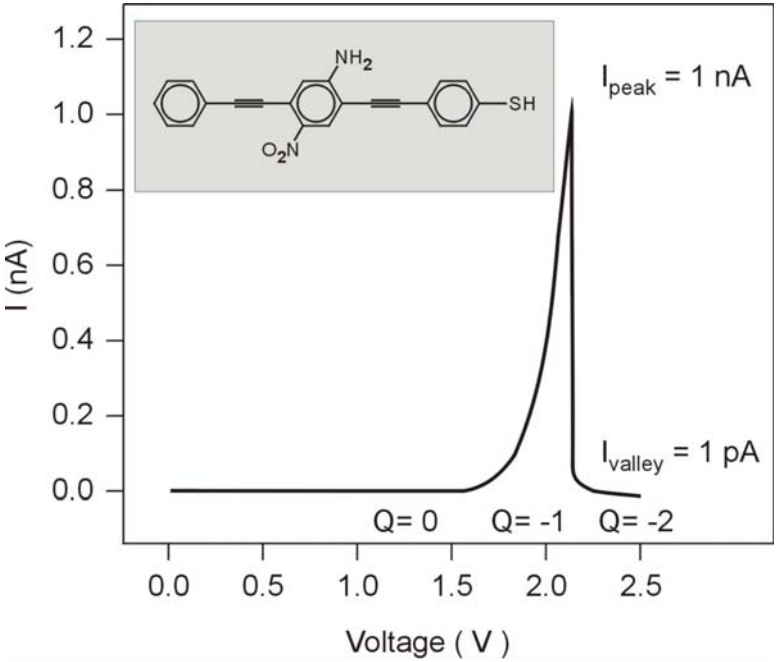
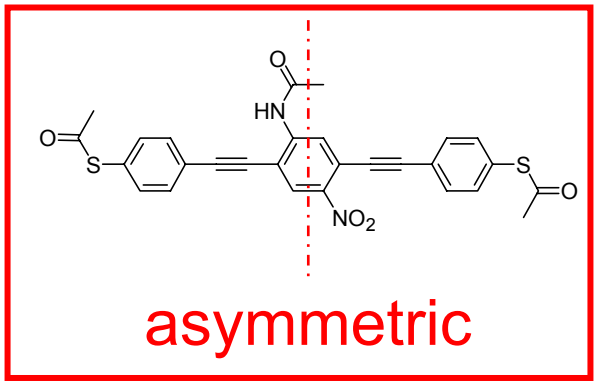
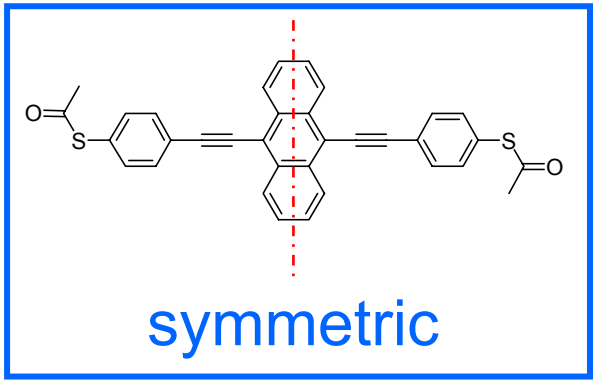
J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science*, **1999**, *286*, 1550-1552



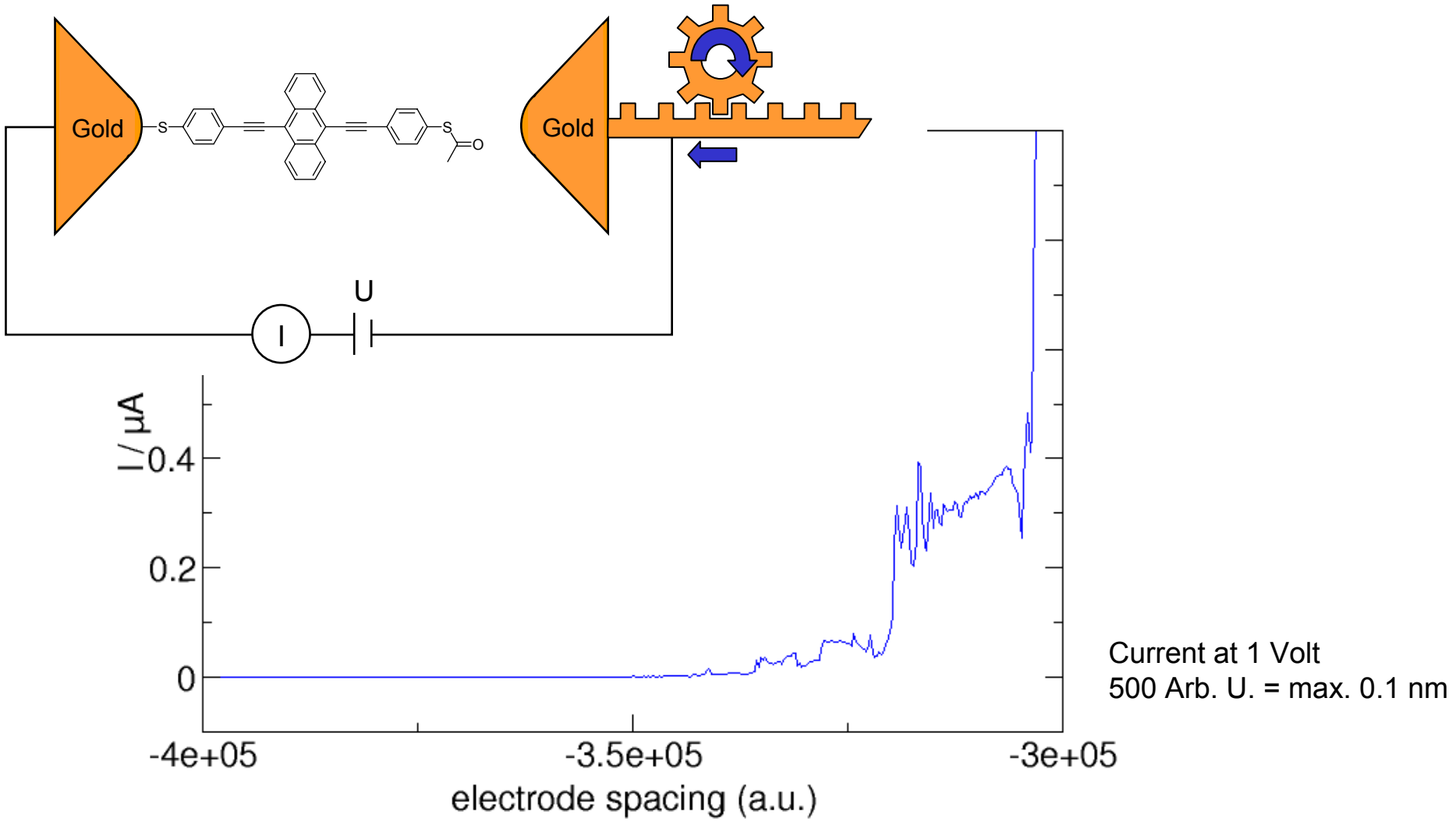






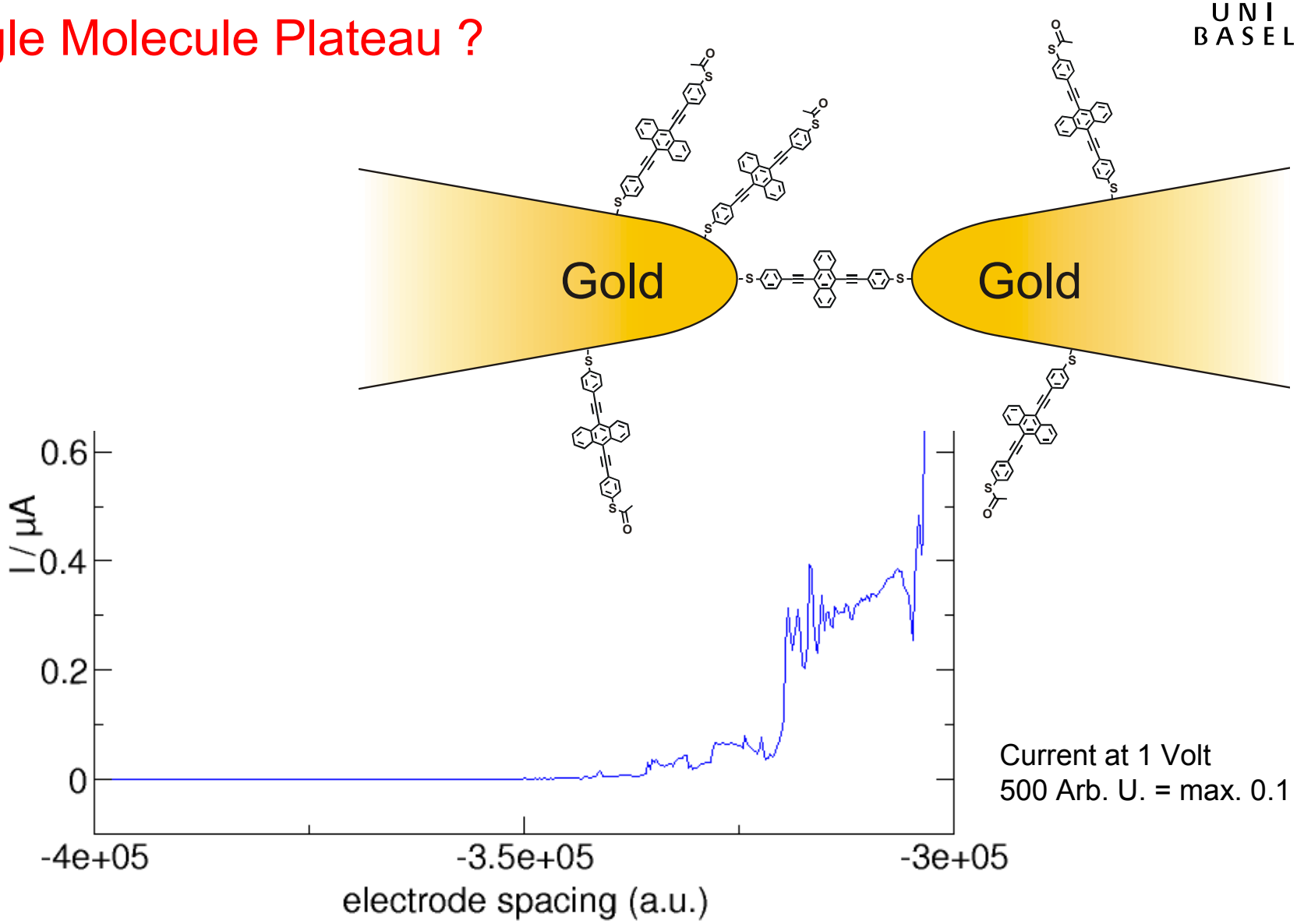


How can we know that there is a Single Molecule ?



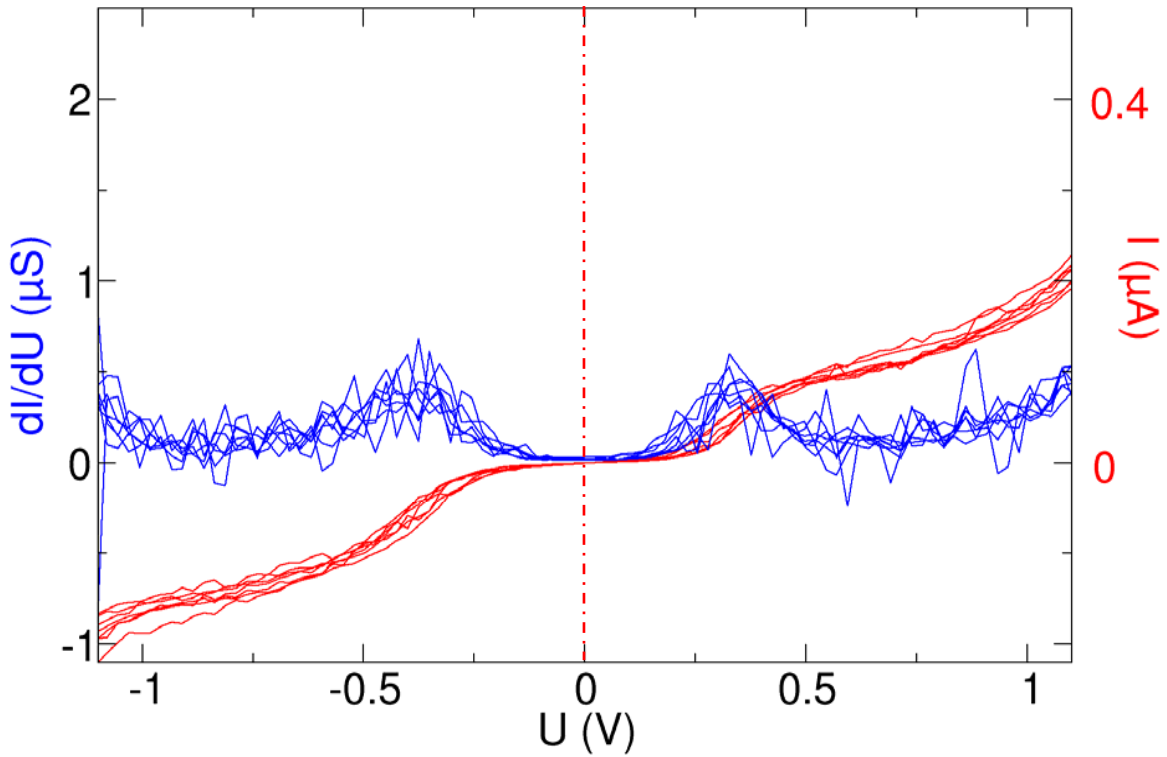
Current at 1 Volt
500 Arb. U. = max. 0.1 nm

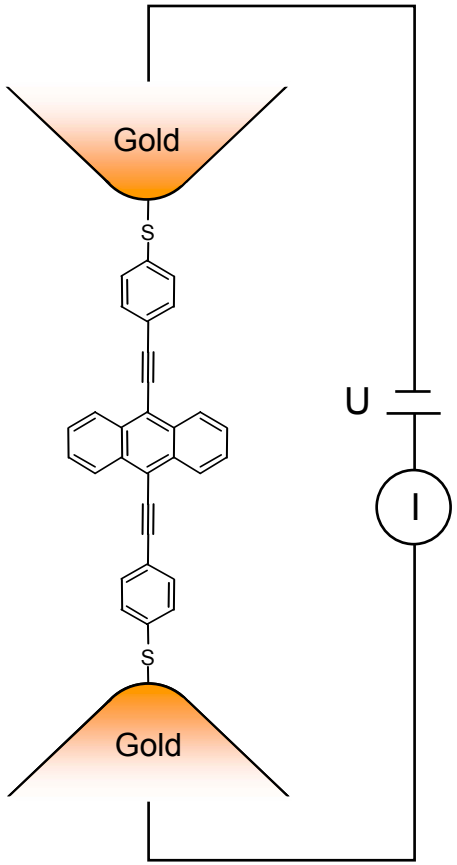
Single Molecule Plateau ?



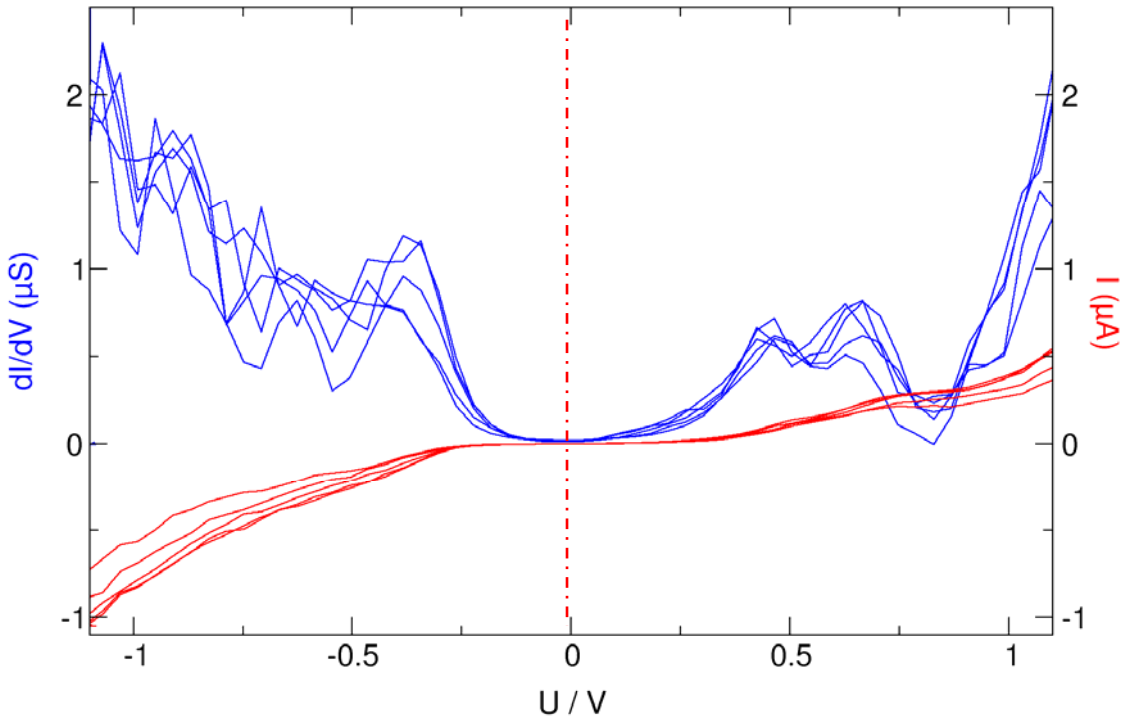
Current at 1 Volt
500 Arb. U. = max. 0.1 nm

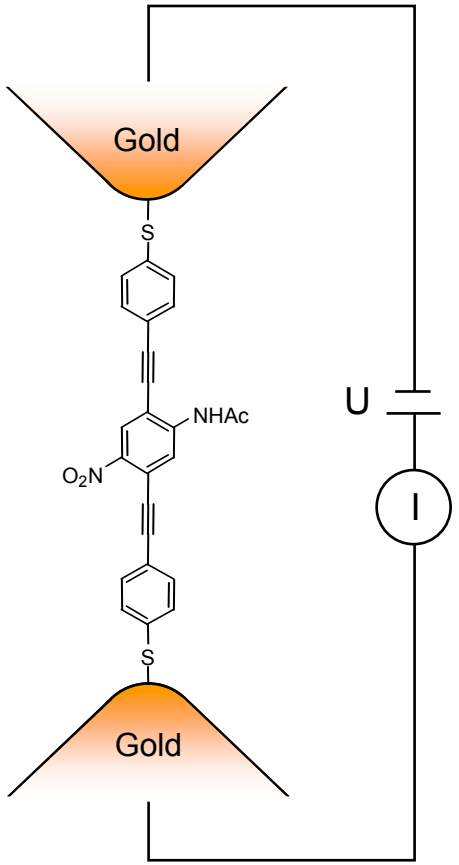
Current through Single symmetric Molecule





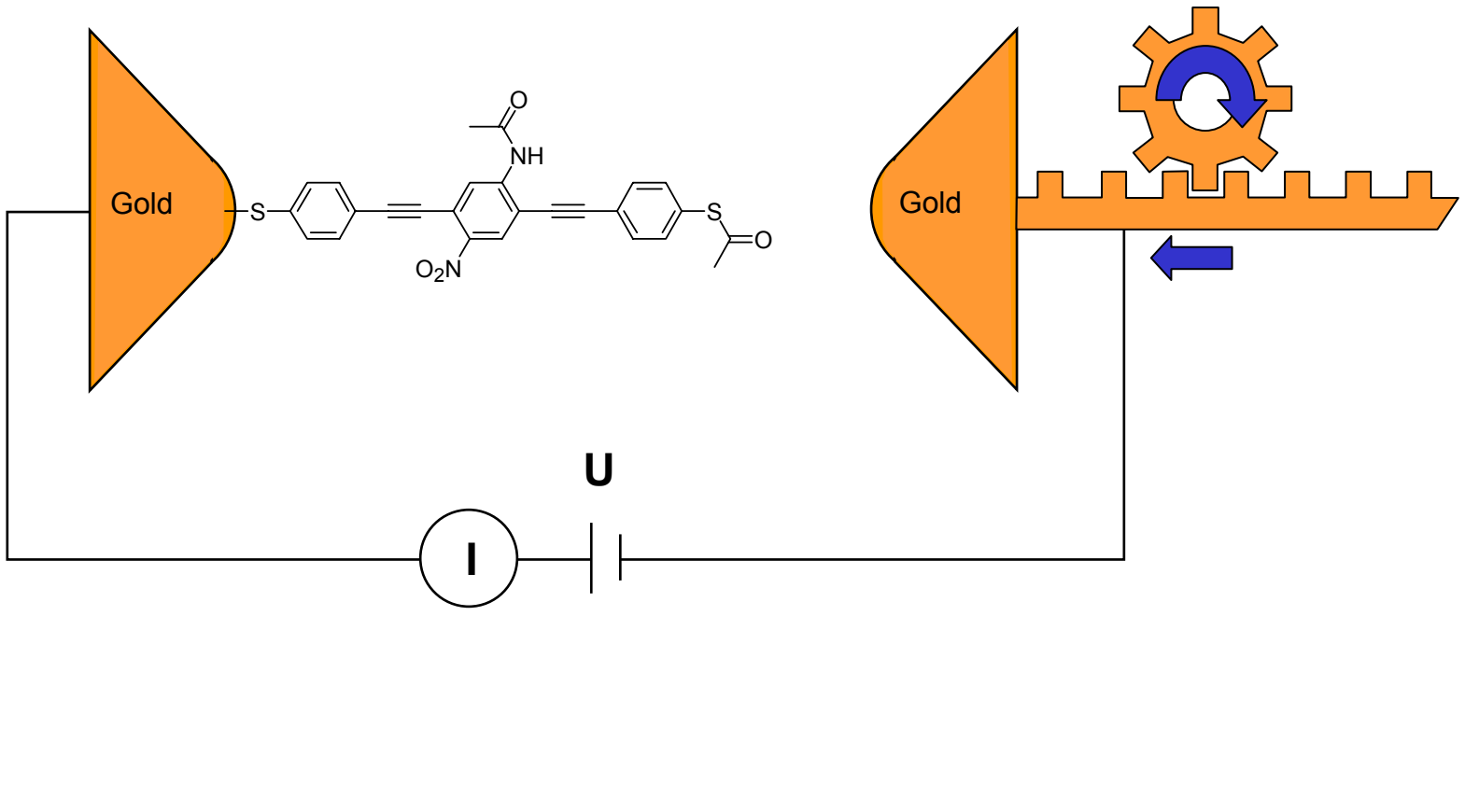
Current through Single asymmetric Molecule



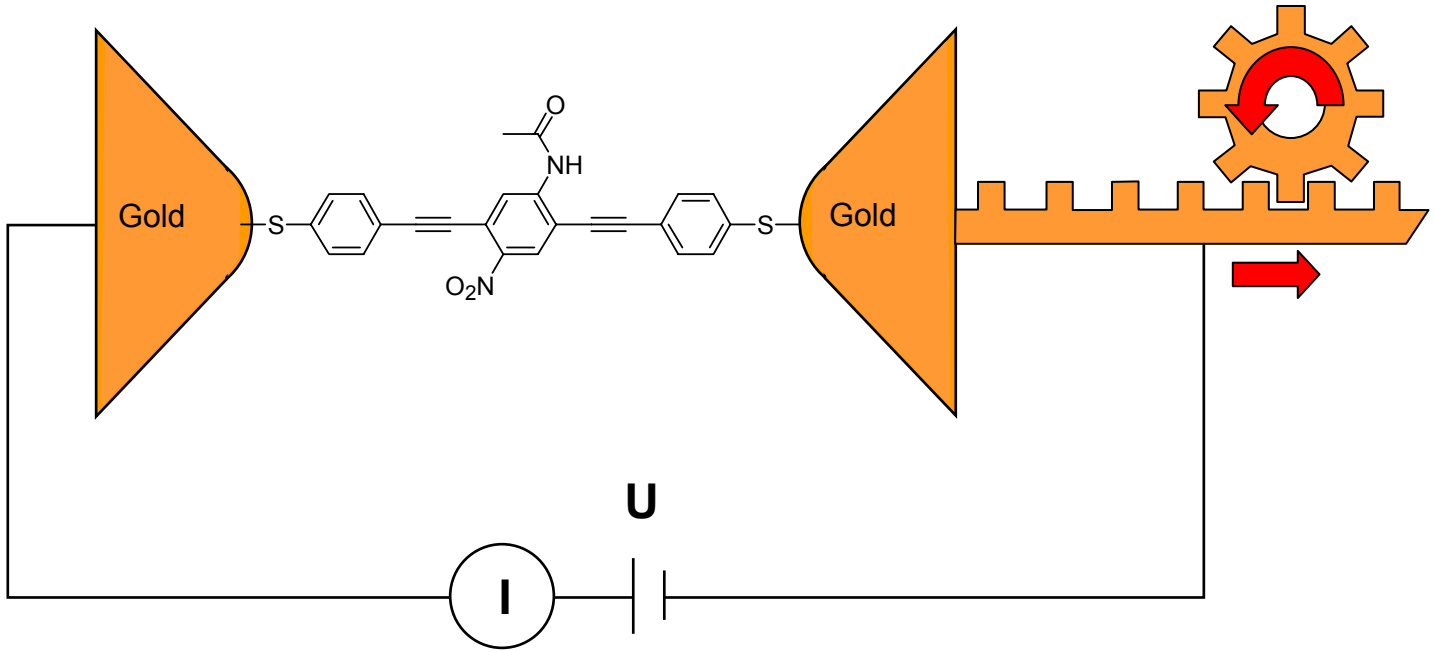


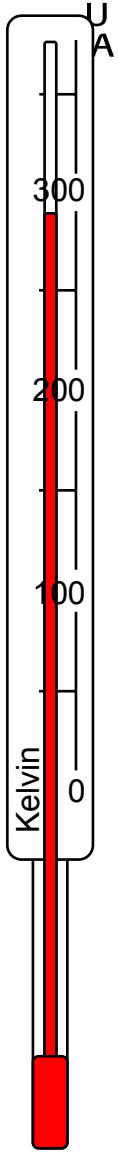
J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. v. Löhneysen; *Phys. Rev. Lett.*, **2002,** *88*, 176804.
H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs, H. v. Löhneysen; *Chem. Phys.*, **2002**, *281*, 113.

Low Temperature MCB Experiments

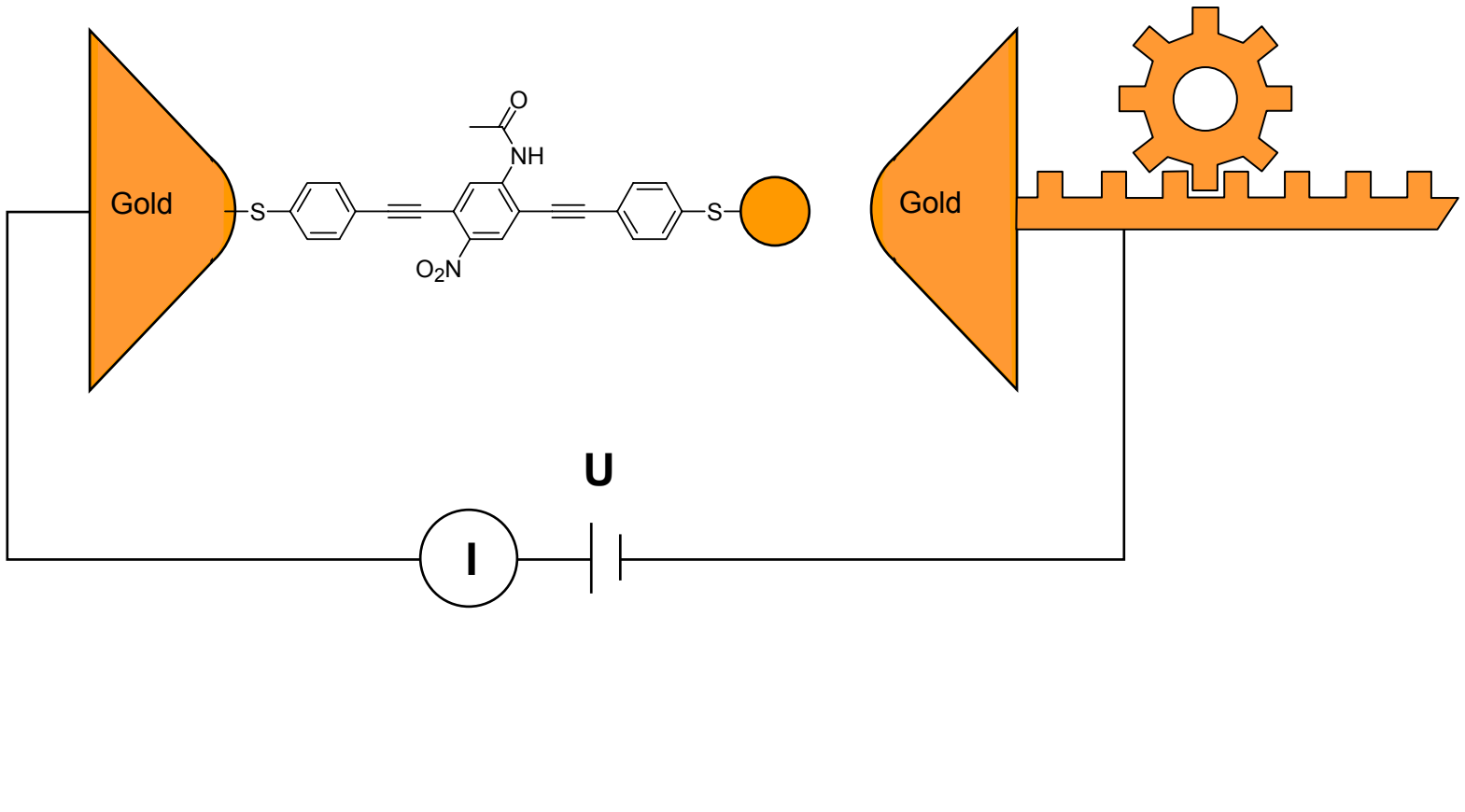


Low Temperature MCB Experiments

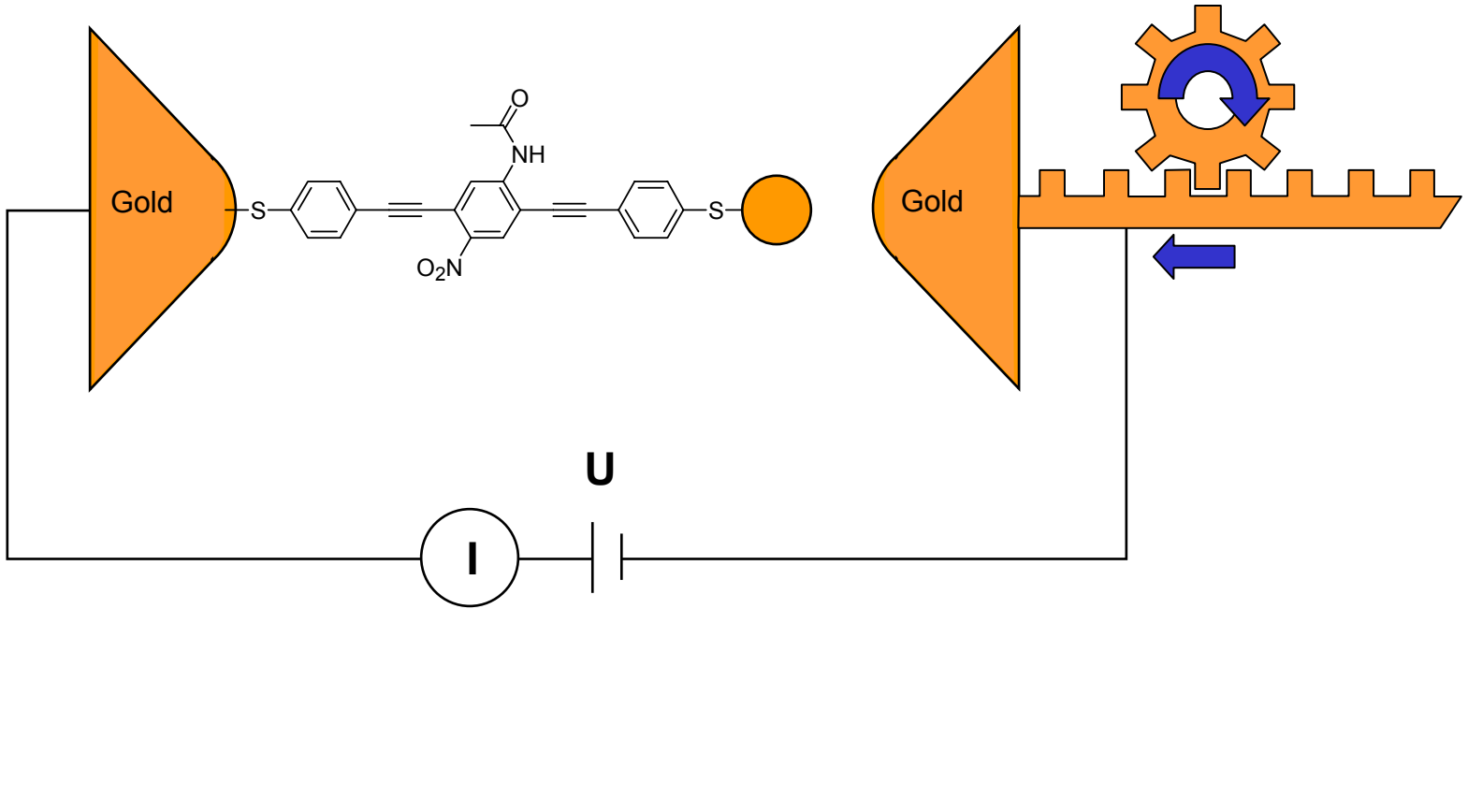




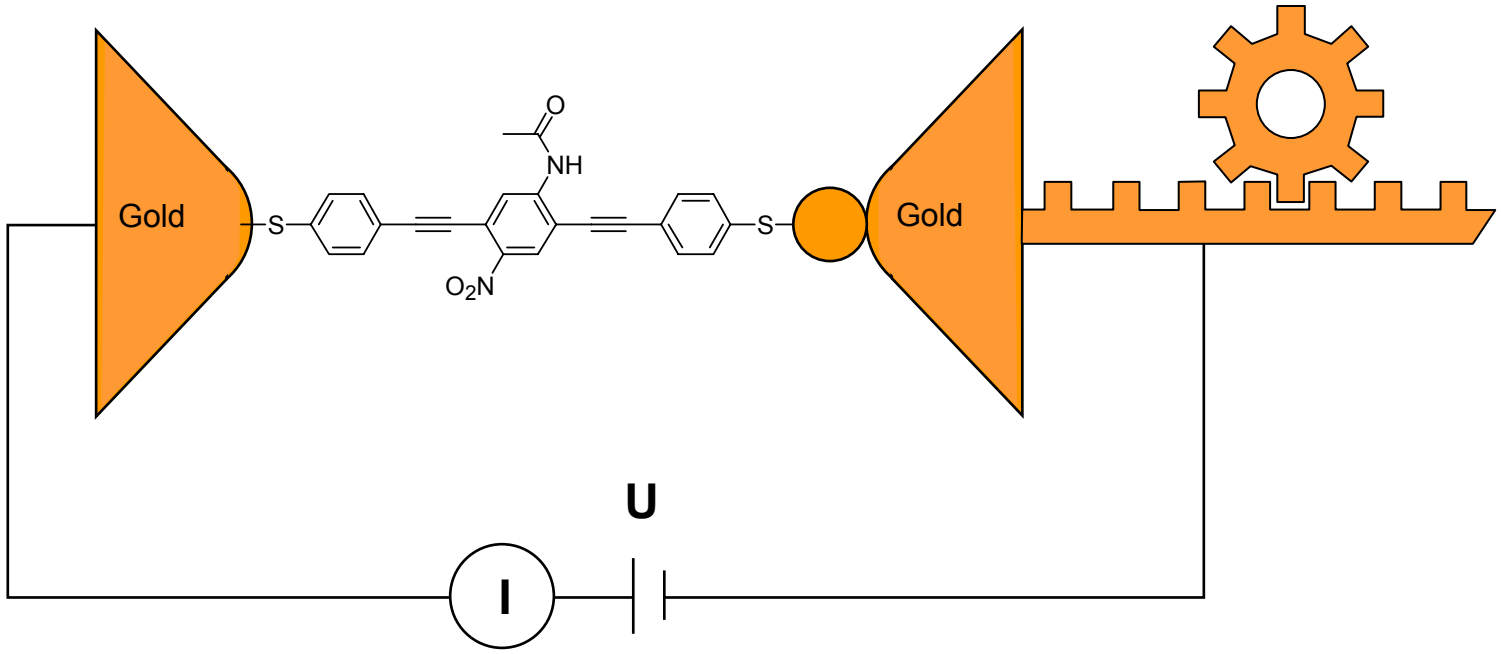
Low Temperature MCB Experiments

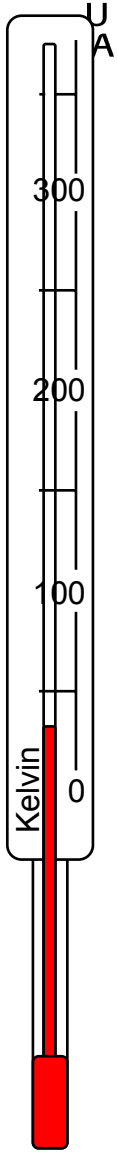


Low Temperature MCB Experiments

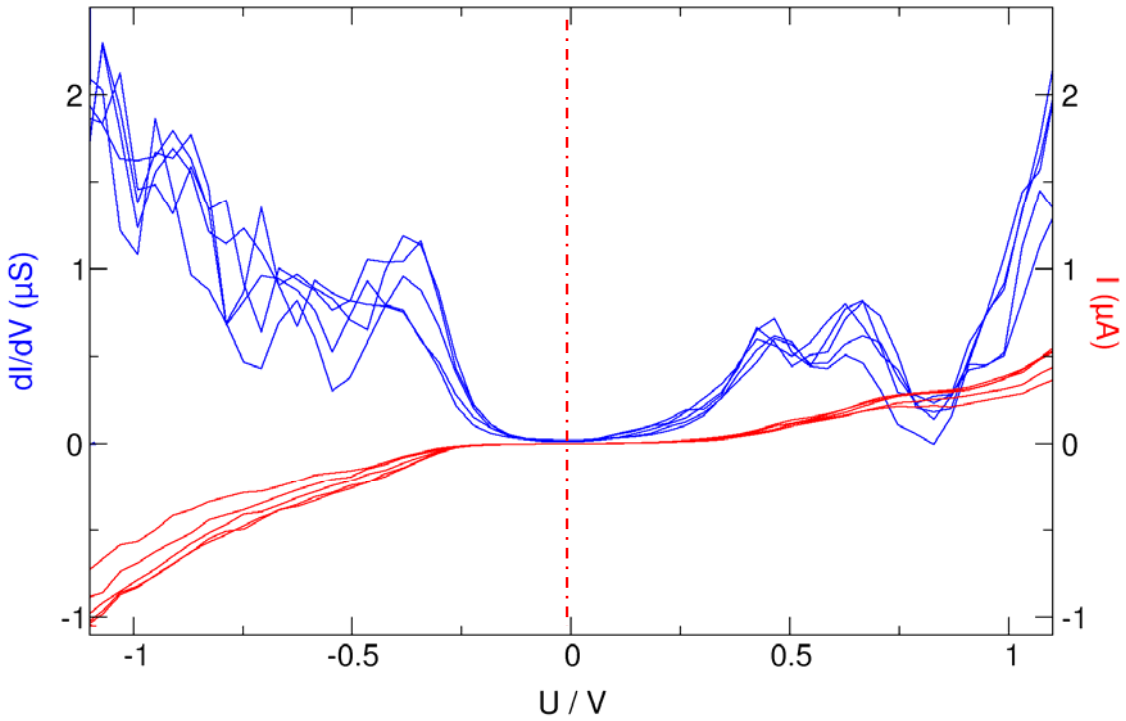


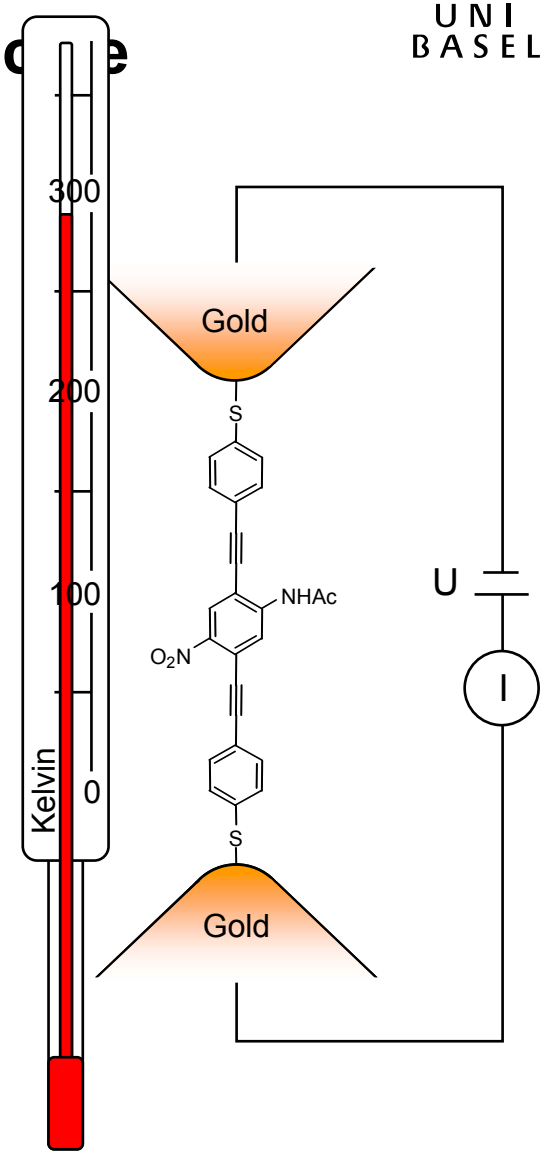
Low Temperature MCB Experiments



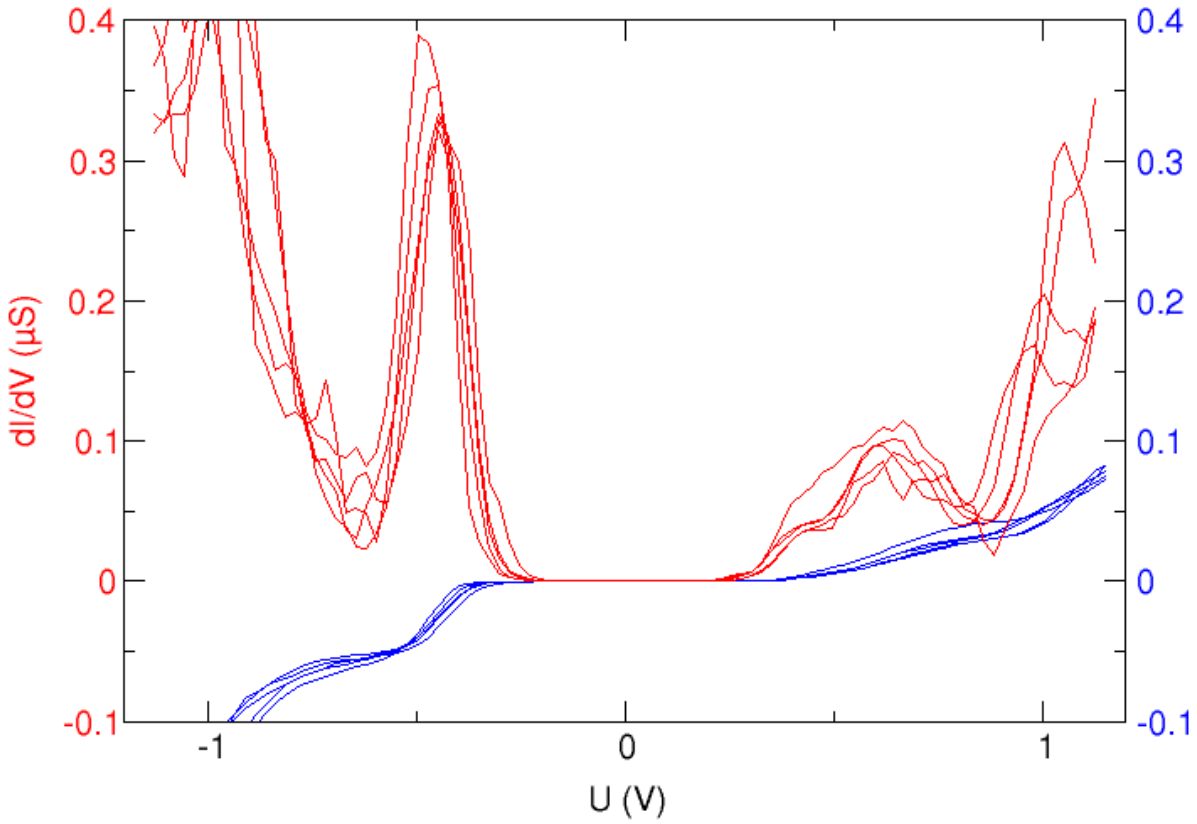


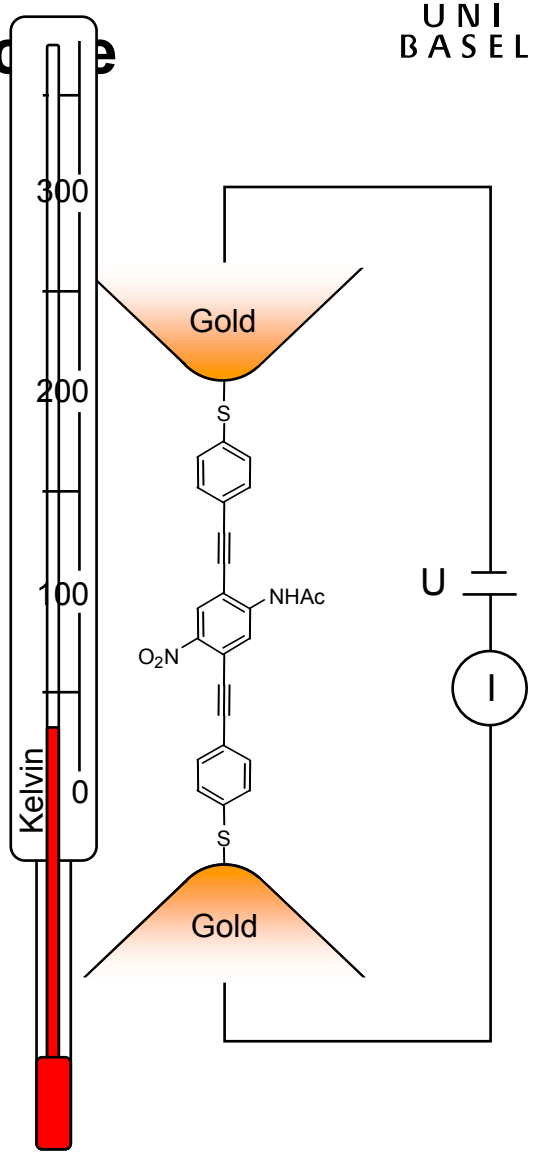
Current through Single asymmetric Molecule





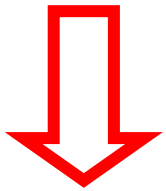
Current through Single asymmetric Molecule at low temperature





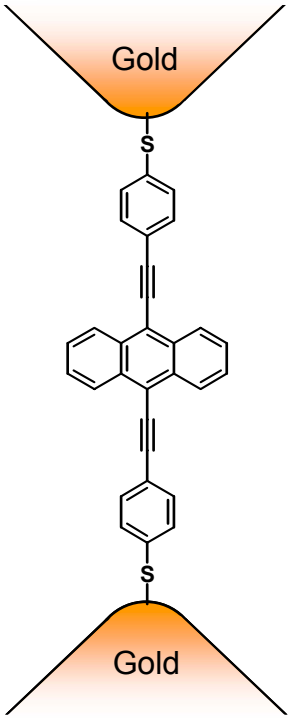
J. Reichert, H. B. Weber, M. Mayor, H. v. Löhneysen; *Appl. Phys. Lett.*, **2003,** *82*, 4137.

Current Through Single Molecule
Direct Observation of Intrinsic Molecular Features
symmetric *vs.* asymmetric
Dependence on Molecular Structure
Low Temperature Investigations

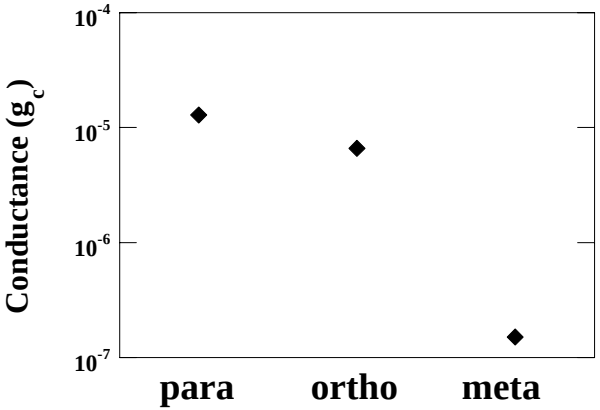


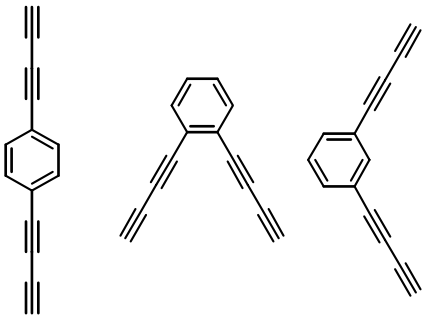
Structure *vs.* e^- Transport Correlation
Adjust the Device Resistance
Integration of Electronic Functions

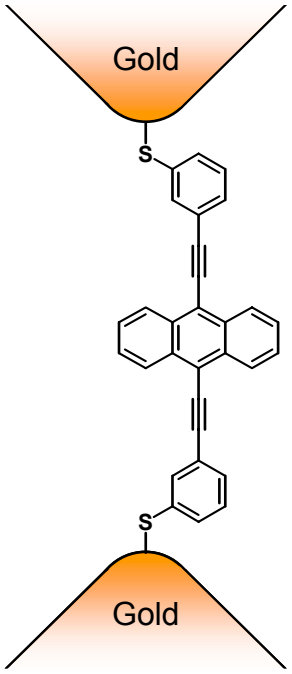
Increasing the Resistance, $R_{new} > R_{old}$
Anchor Groups in *para vs. meta*



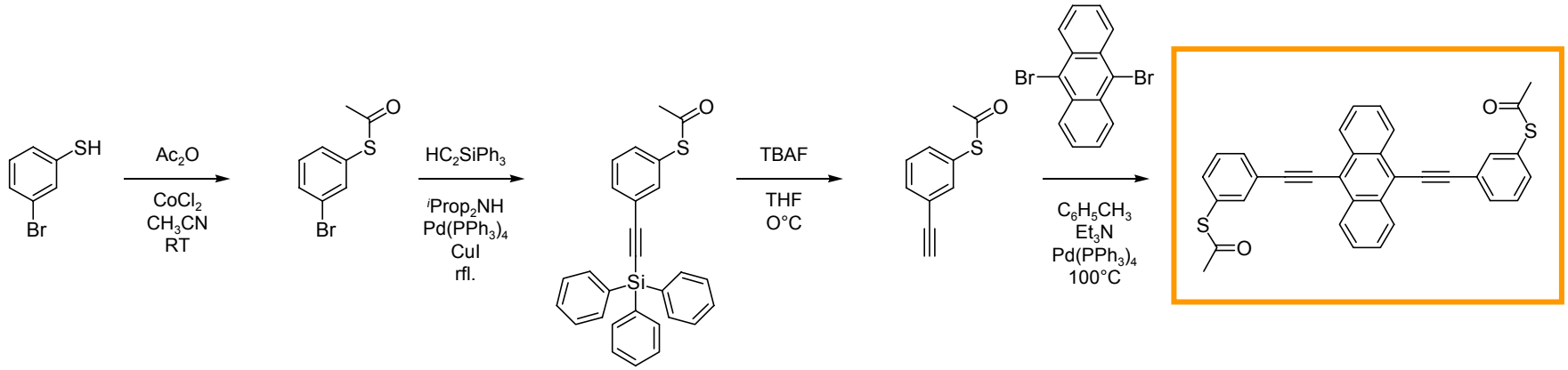
Topology effects on Conductance
by Sofia N. Yaliraki

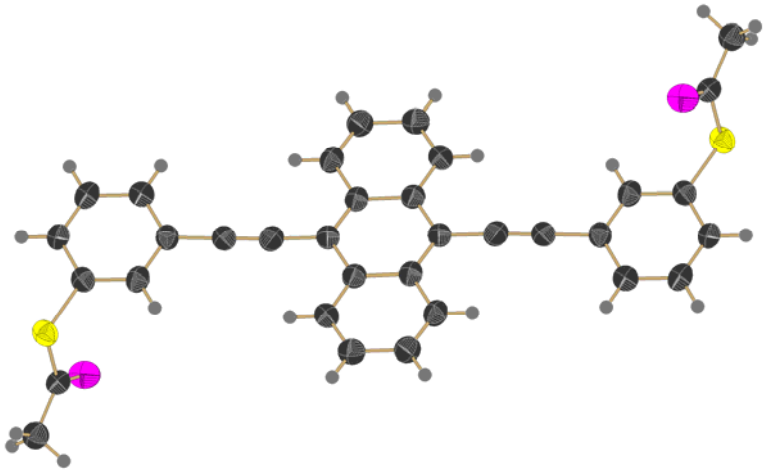




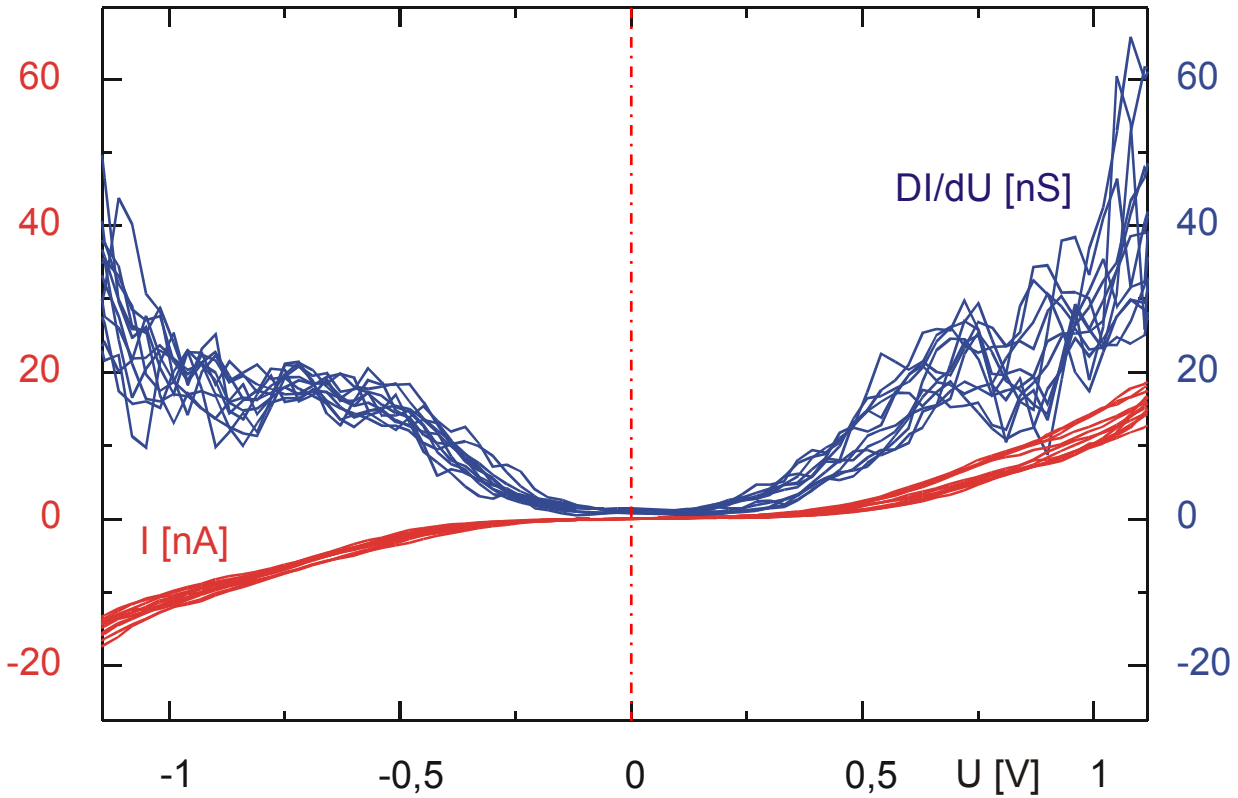


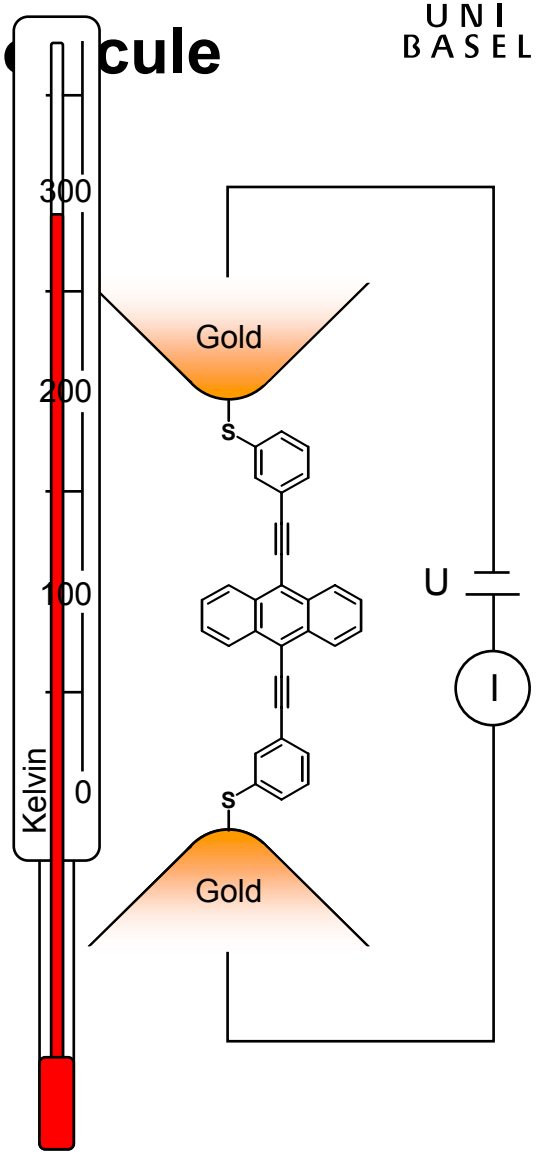
Anchor Groups in *meta* Synthesis





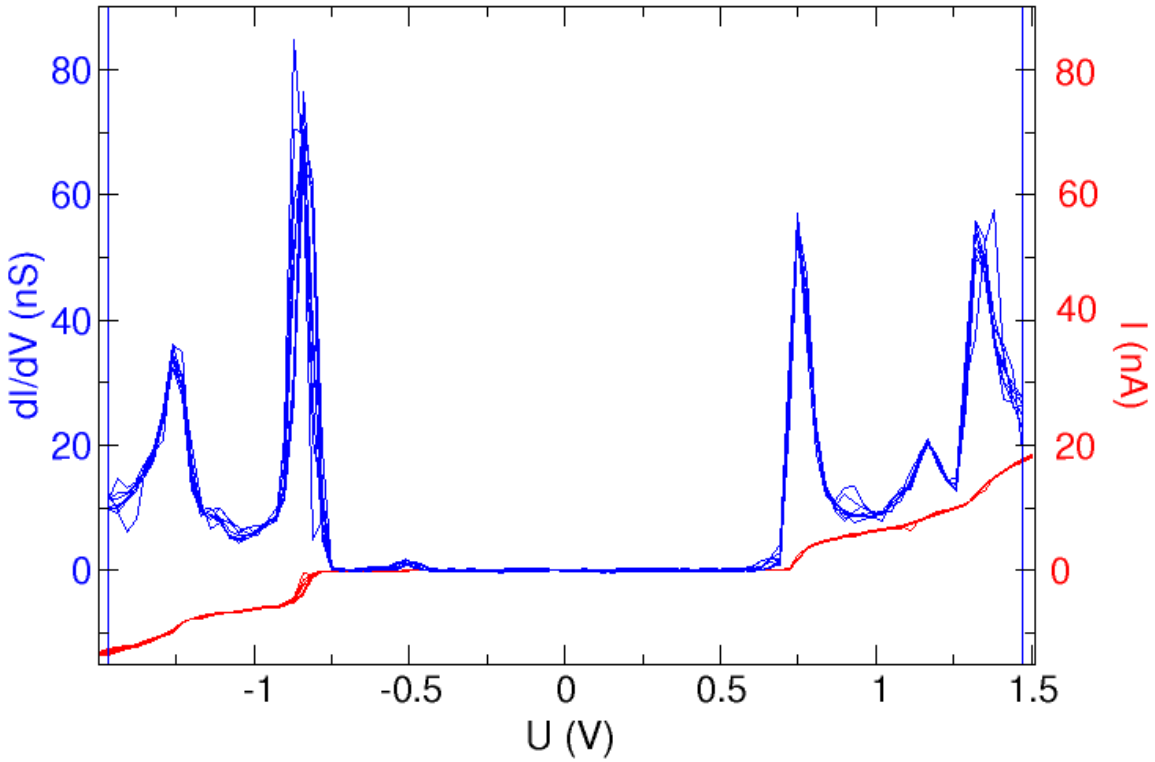
Current through Single *meta*-connected Molecule

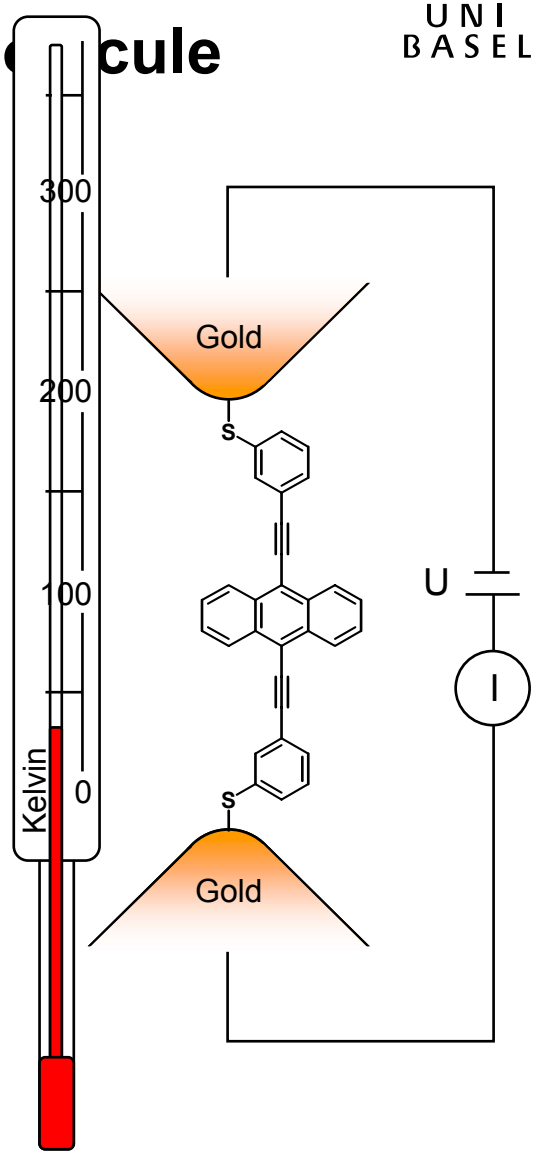




R(*meta*) ≈ 10 x R(*para*)

Current through Single *meta*-connected Molecule





U/I (*meta*) at low temp.

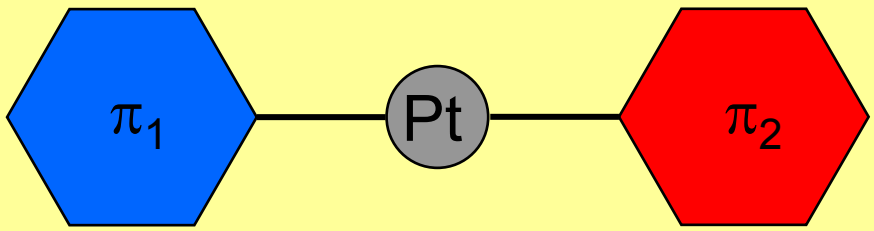
M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänisch, D. Beckmann, M. Fischer; *Angew. Chem. Int. Ed. Engl.*, **2003**, *42*, 5834

Increasing the Resistance, $R_{new} > R_{old}$

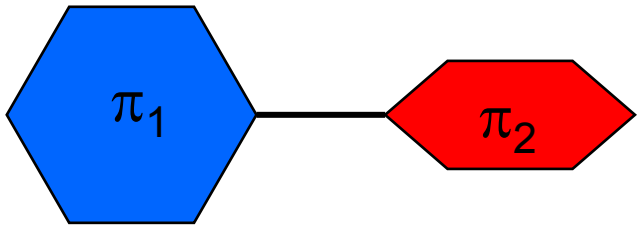
Tailor-made Bridging Structures

Interruption of the π-System

Insulating Linker between π_1 and π_2

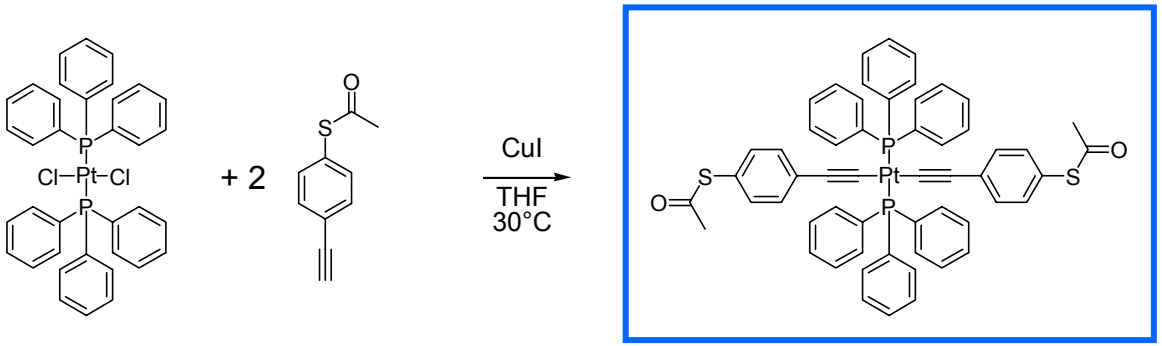


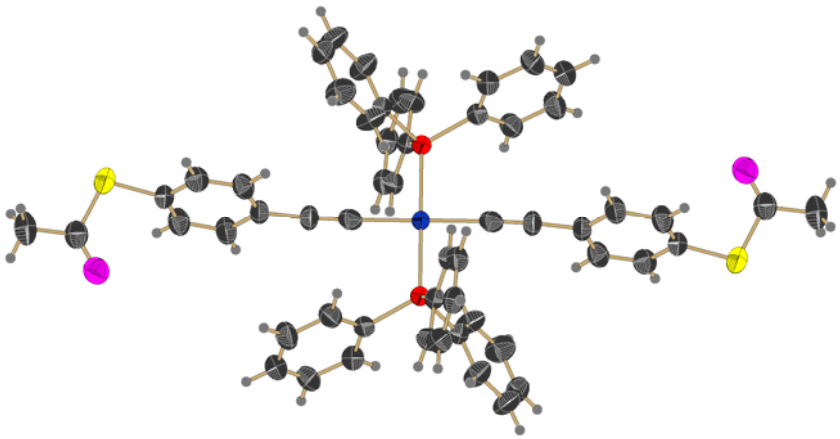
Torsion Angle between π_1 and π_2



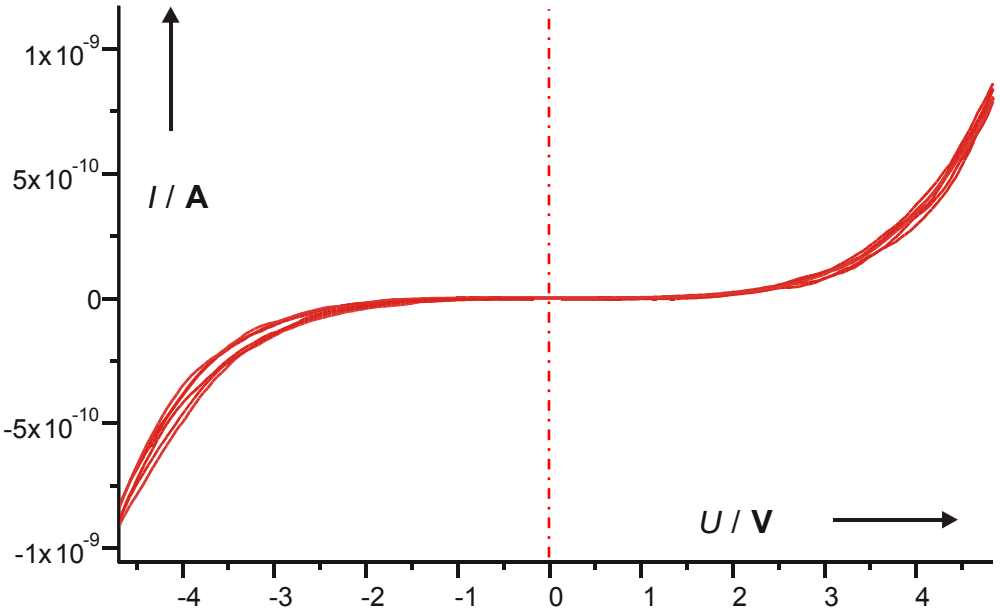
Insulating Linker between π_1 and π_2

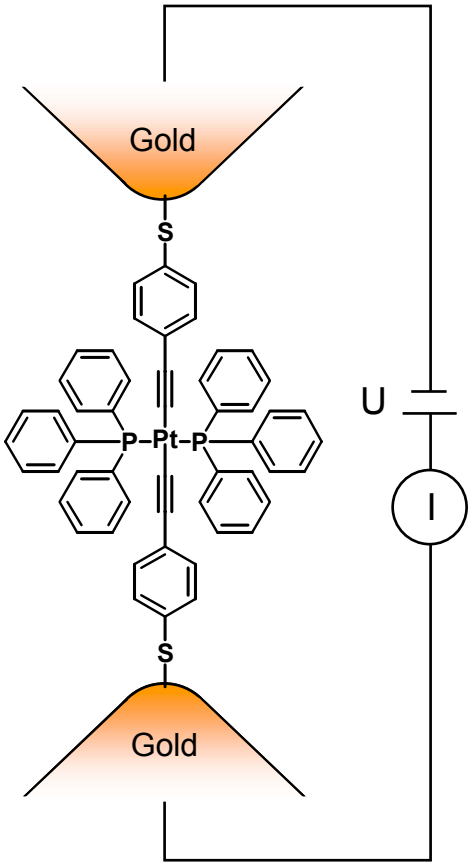
Synthesis





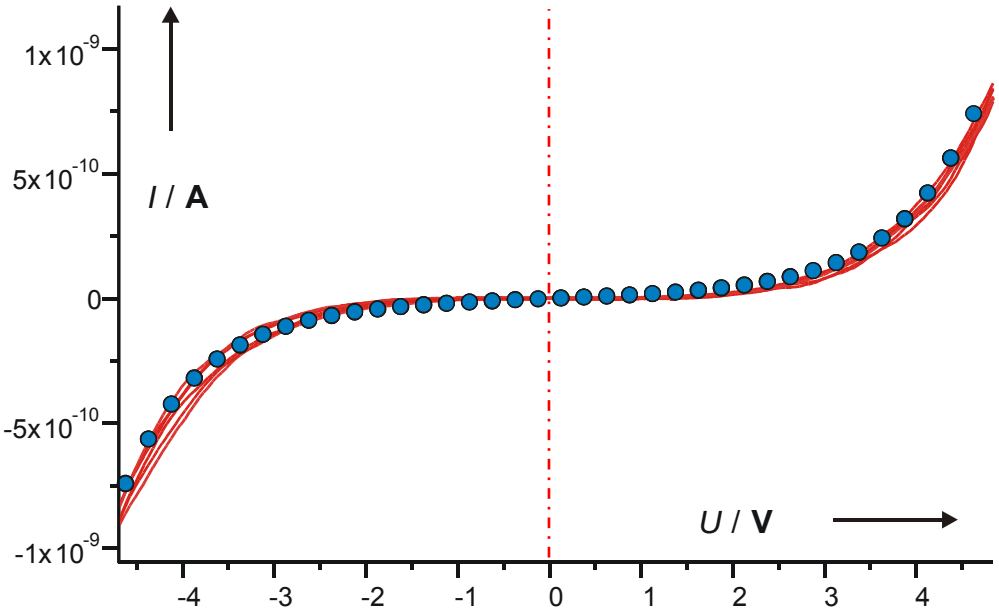
Current through Pt(II)-Complex as Insulating Linker



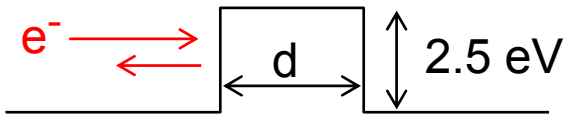


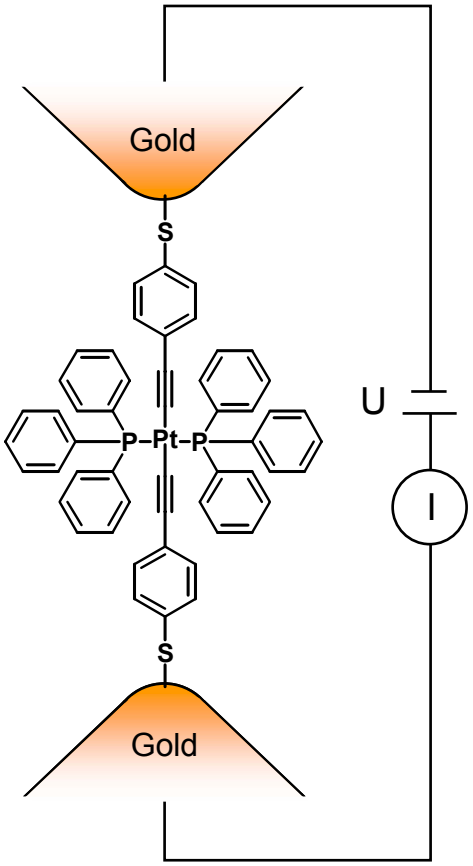
R(π-Pt-π) ≈ **1000 x R**(π-konjugated)

Current through Pt(II)-Complex as Insulating Linker



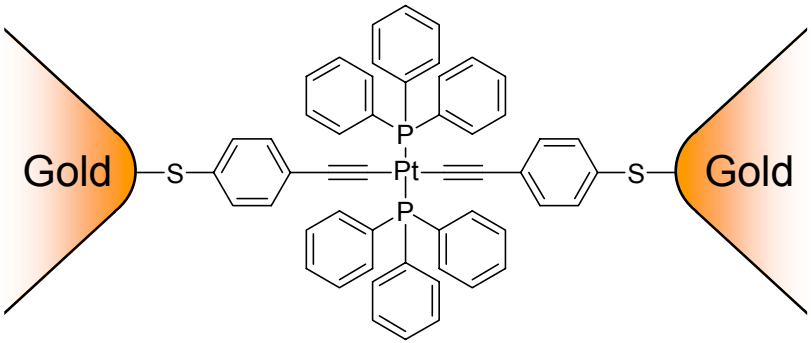
$$I = I_0(U)\cdot\exp[d\cdot\alpha\cdot(\phi_0 - eU/2)^{1/2}]$$

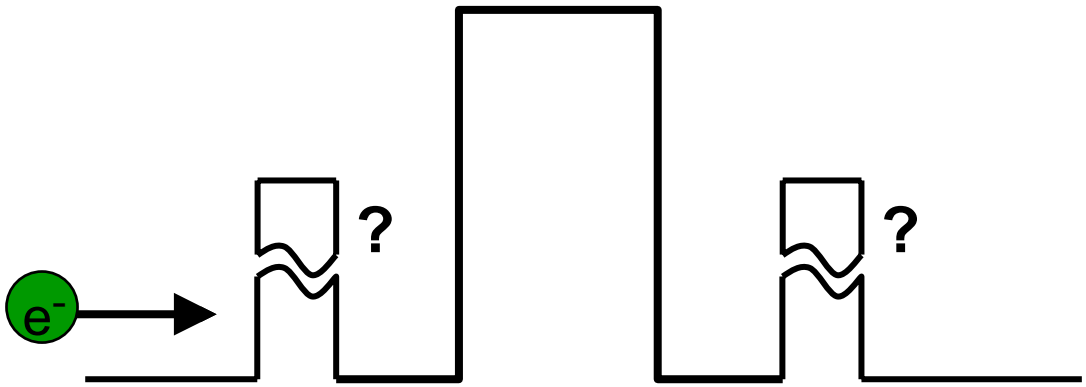




M. Mayor, C. von Hänisch, H. Weber, J. Reichert, D. Beckmann; *Angew. Chem. Int. Ed. Engl.*, **2002**, *41*, 1183.

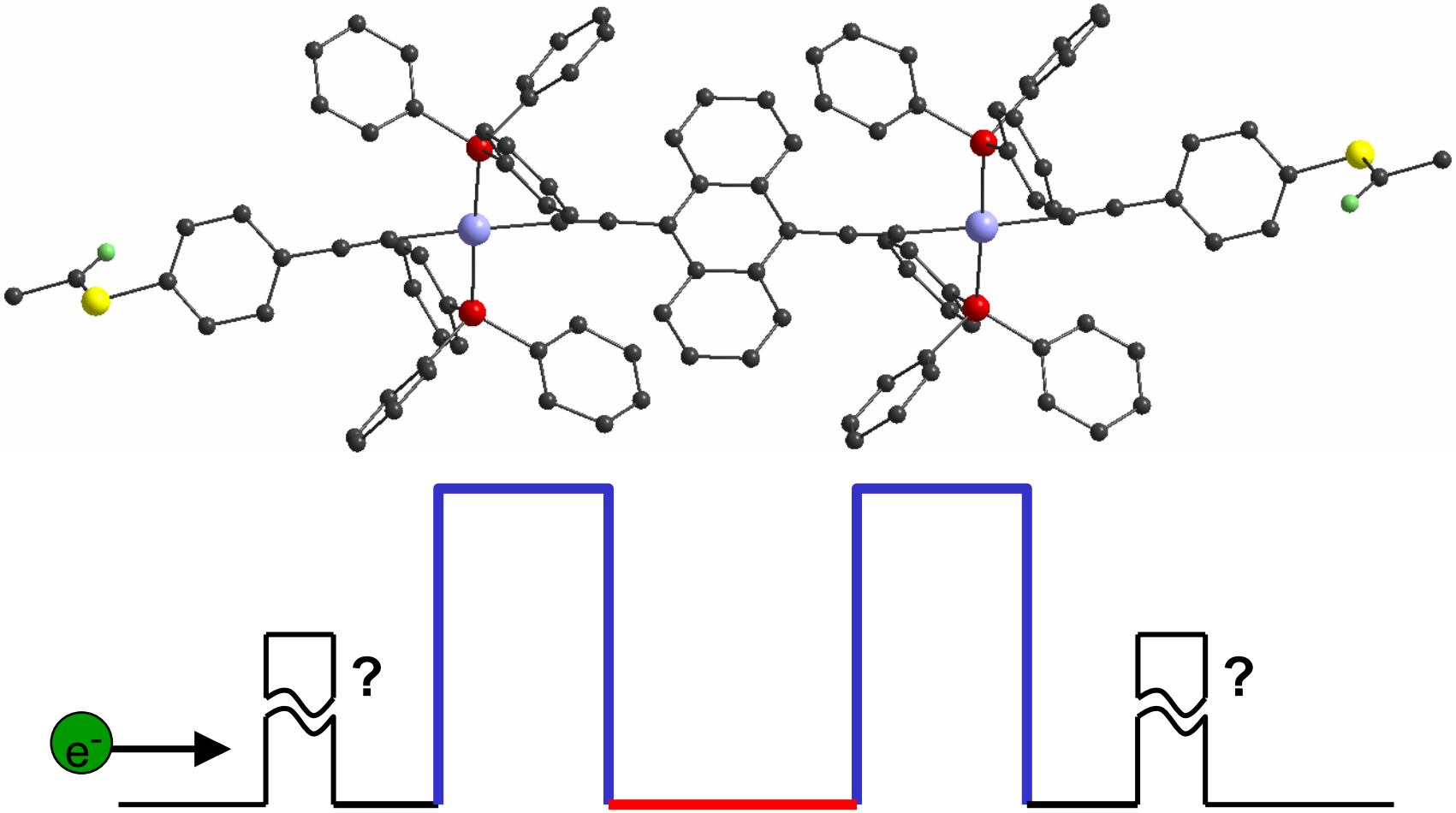
Current through Pt(II)-Complex as Insulating Linker





M. Mayor, C. von Hänisch, H. Weber, J. Reichert, D. Beckmann; *Angew. Chem. Int. Ed. Engl.*, **2002**, *41*, 1183.

Molecular Structure of Interest
between well defined tunnel barriers

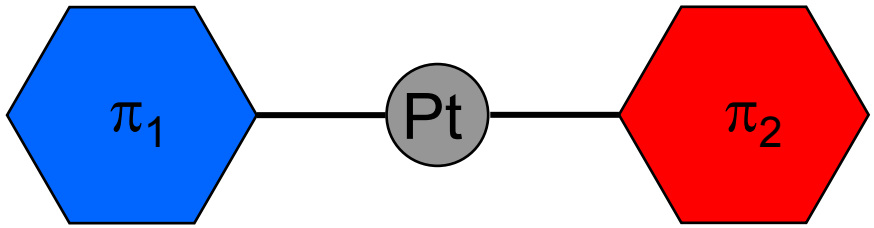


Increasing the Resistance, $R_{new} > R_{old}$

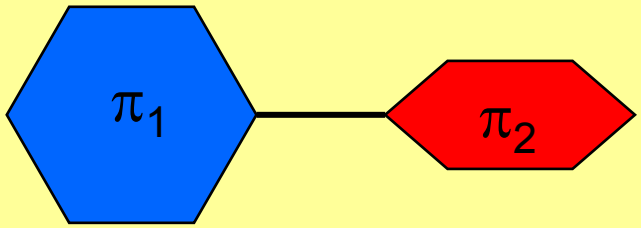
Tailor-made Bridging Structures

Interruption of the π-System

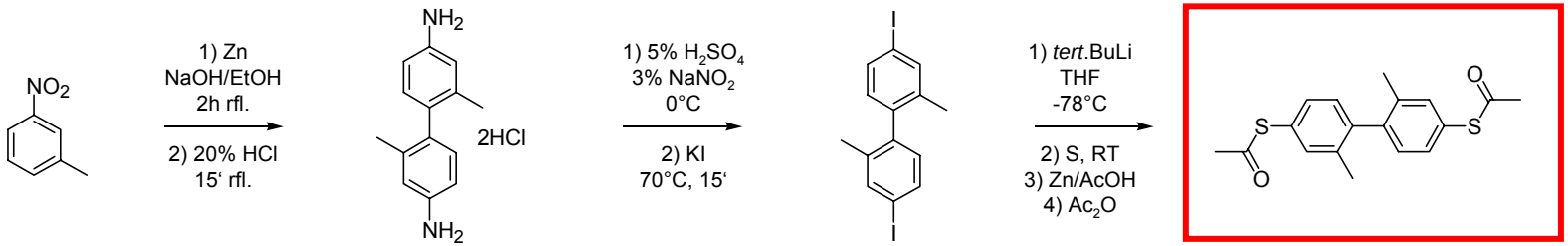
Insulating Linker
between π_1 and π_2

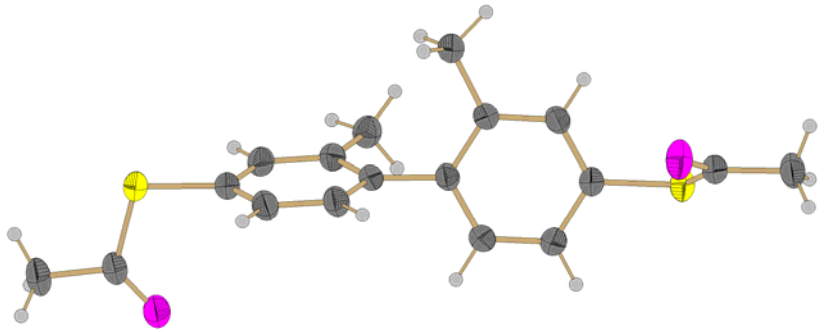


Torsion Angle between π_1 and π_2

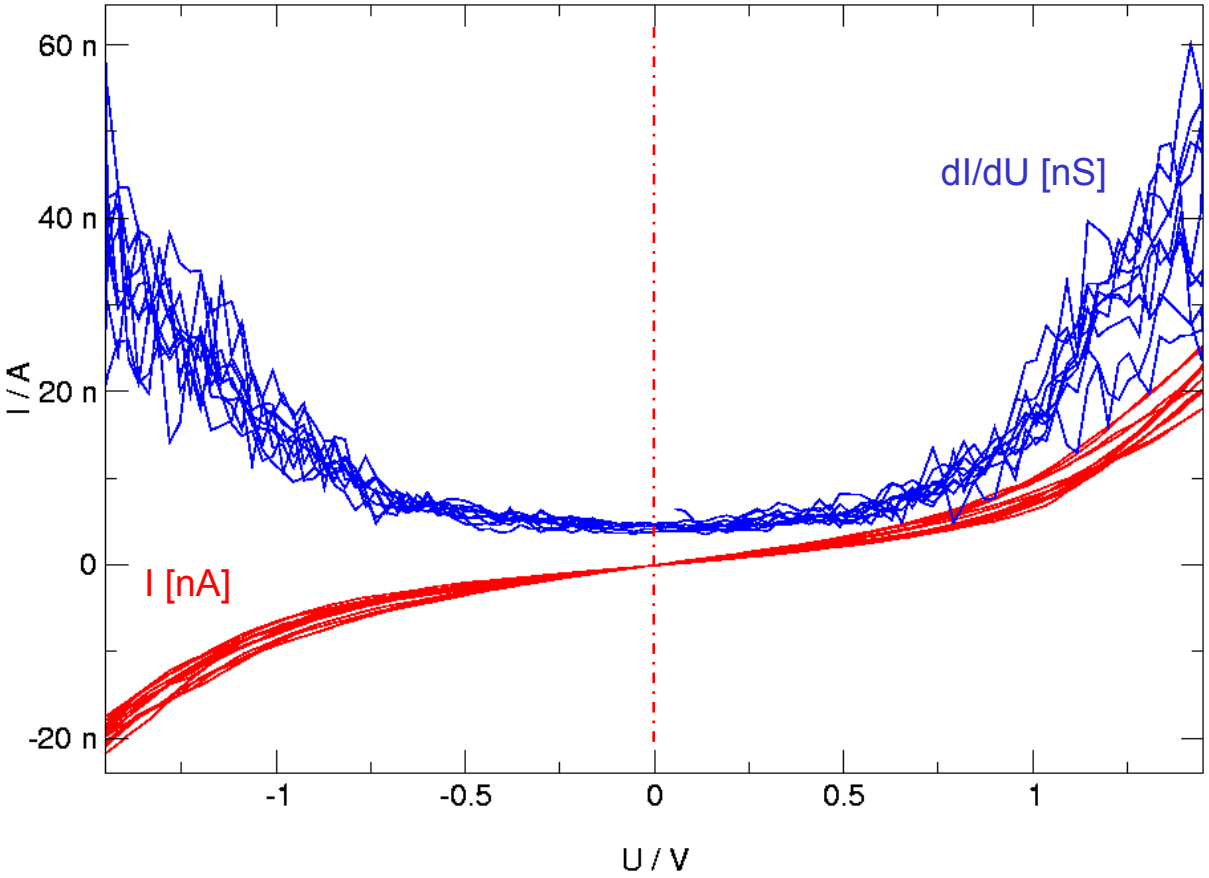


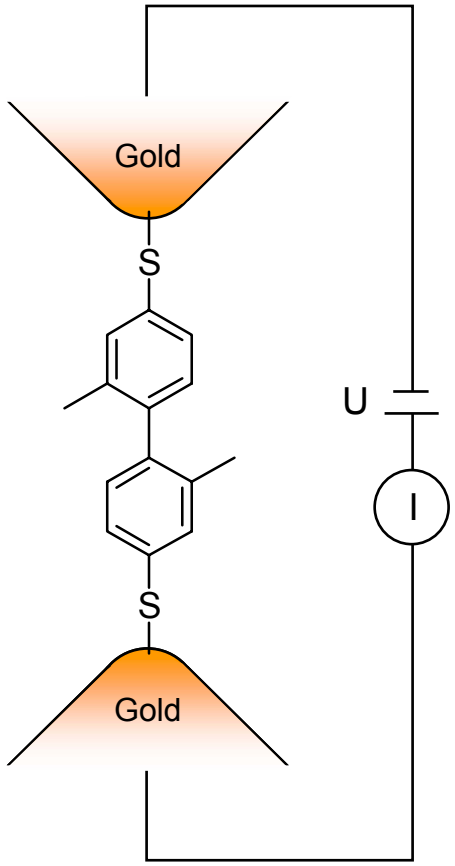
Torsion Angle between π_1 and π_2
Synthesis Biphenyl





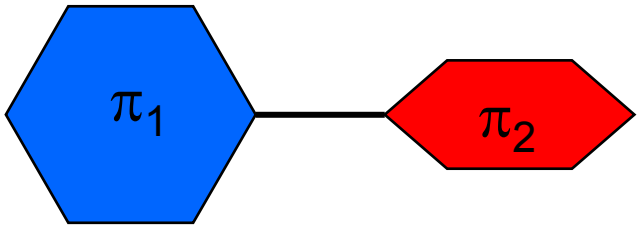
Current through Distorted Biphenyl



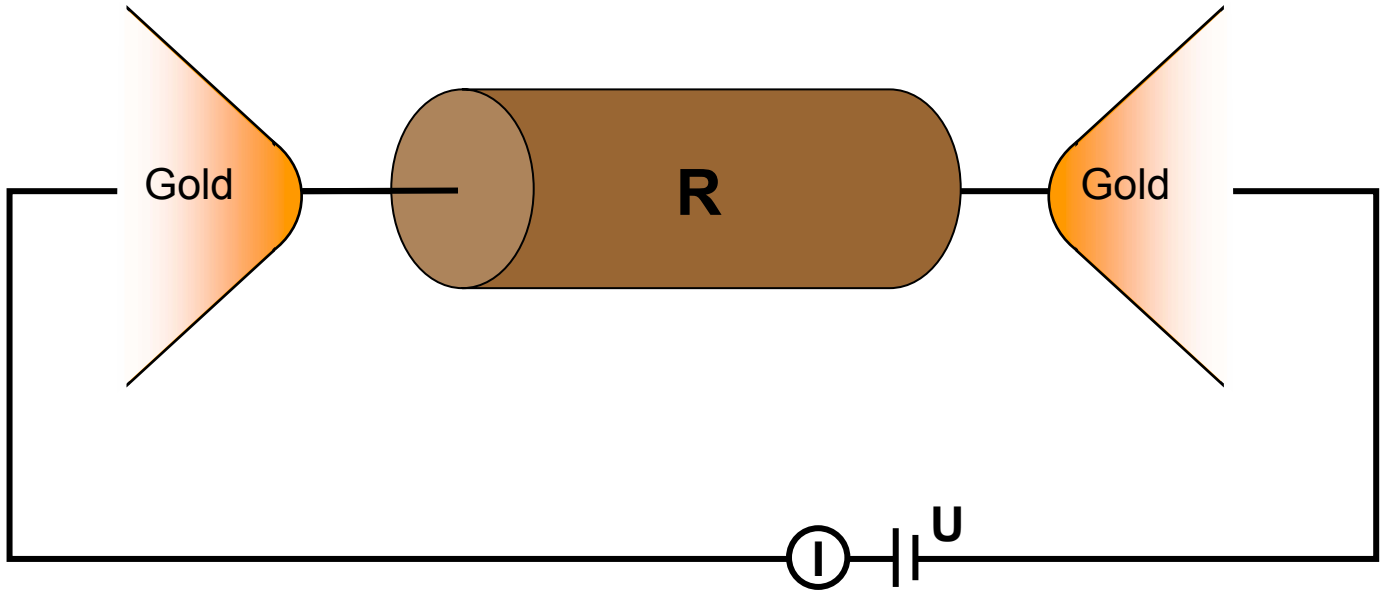


R(π-distorted) ≈ **10 x R**(π-konjugated)

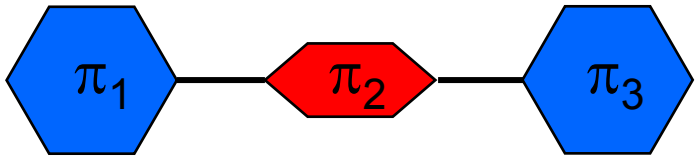
Torsion Angle between π_1 and π_2

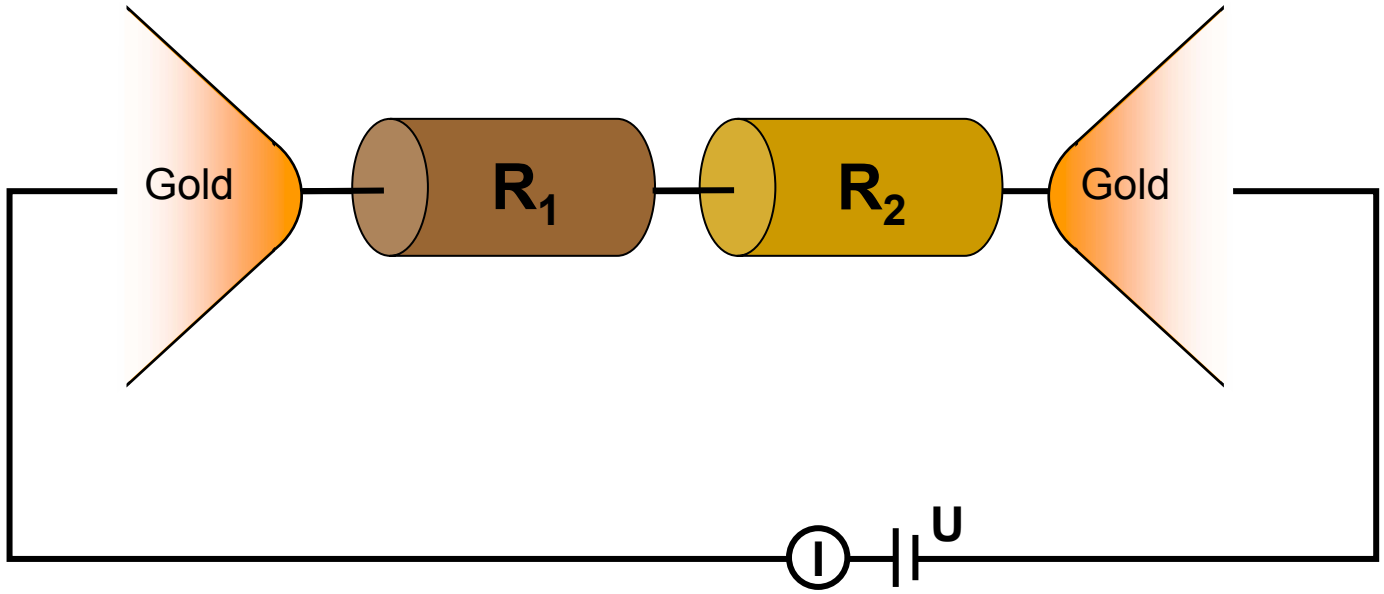


R(π-distorted) ≈ **10 x R**(π-konjugated)

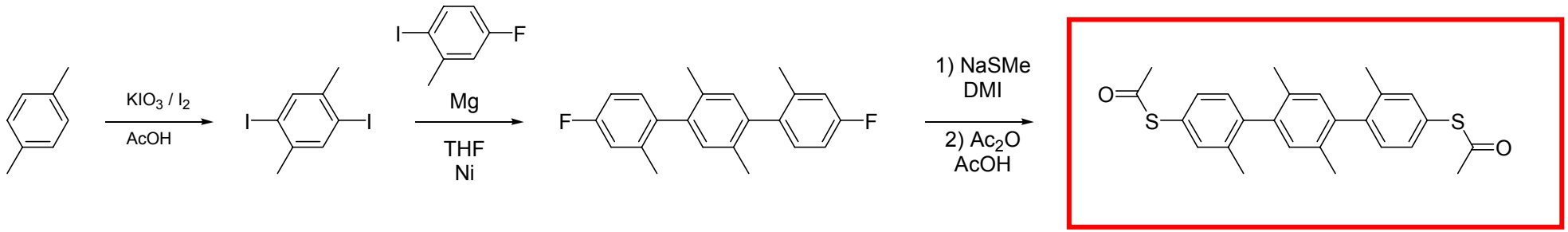


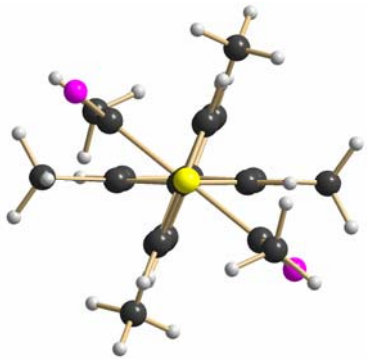
Torsion Angle between π_1, π_2 and π_3

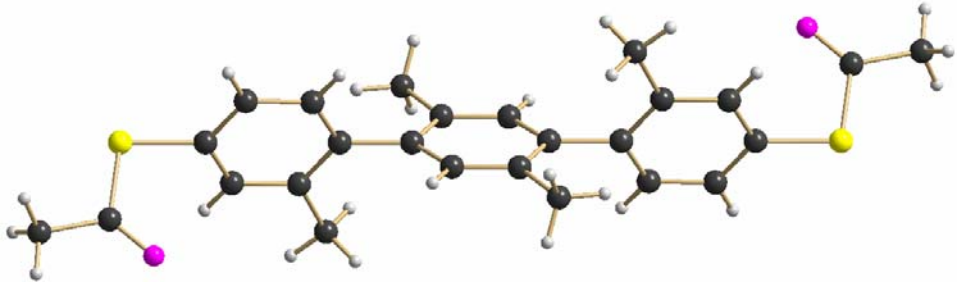




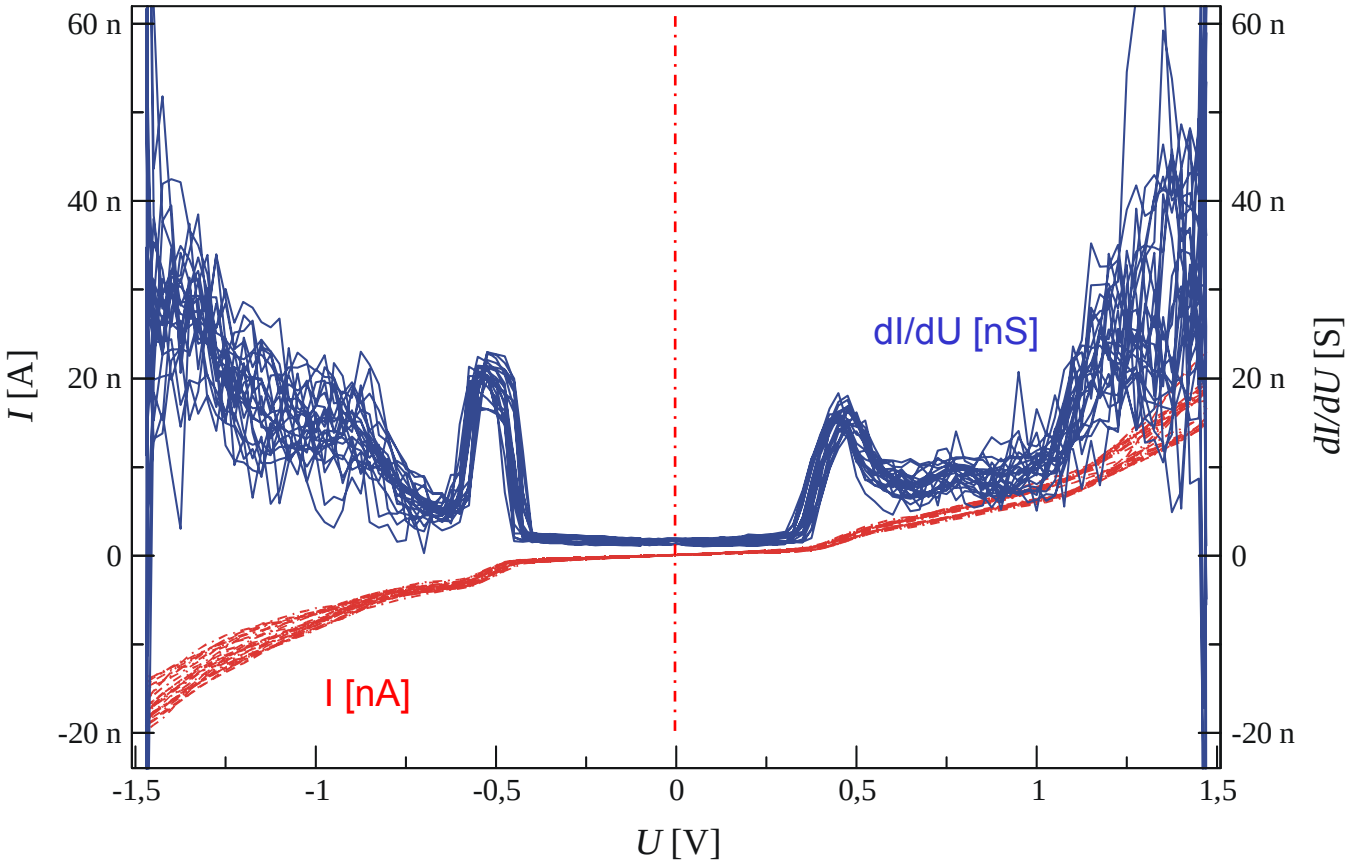
Torsion Angle between π_1, π_2 and π_3
Synthesis Terphenyl

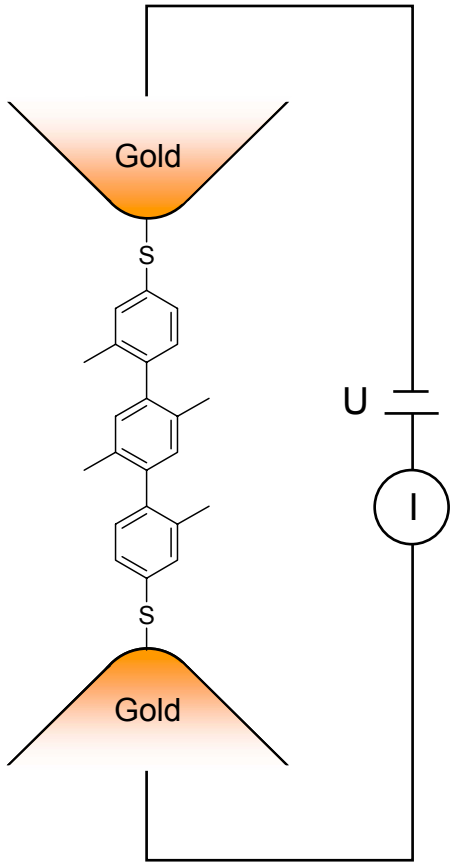






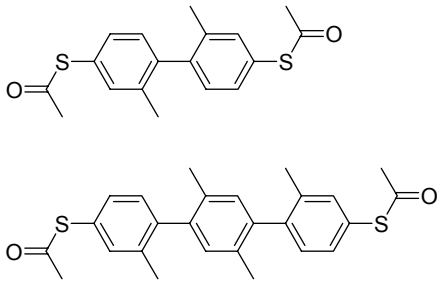
Current through Distorted Terphenyl (30K)

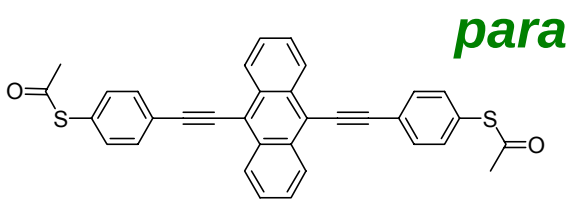




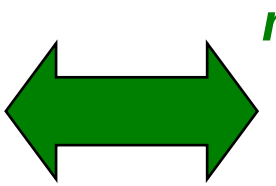
R(π-distorted) ≈ **10 x R**(π-konjugated)

Basic Aspects – First Molecules

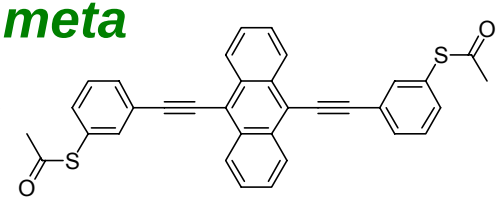




para

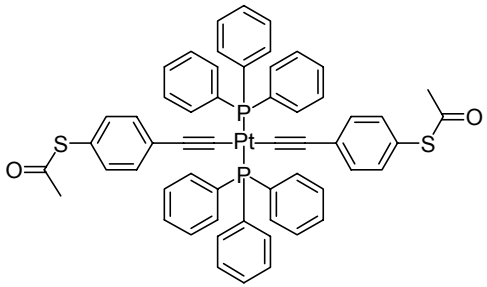


meta

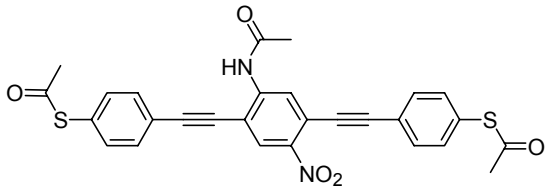


symmetric

conjugated π-system



separated π-systems

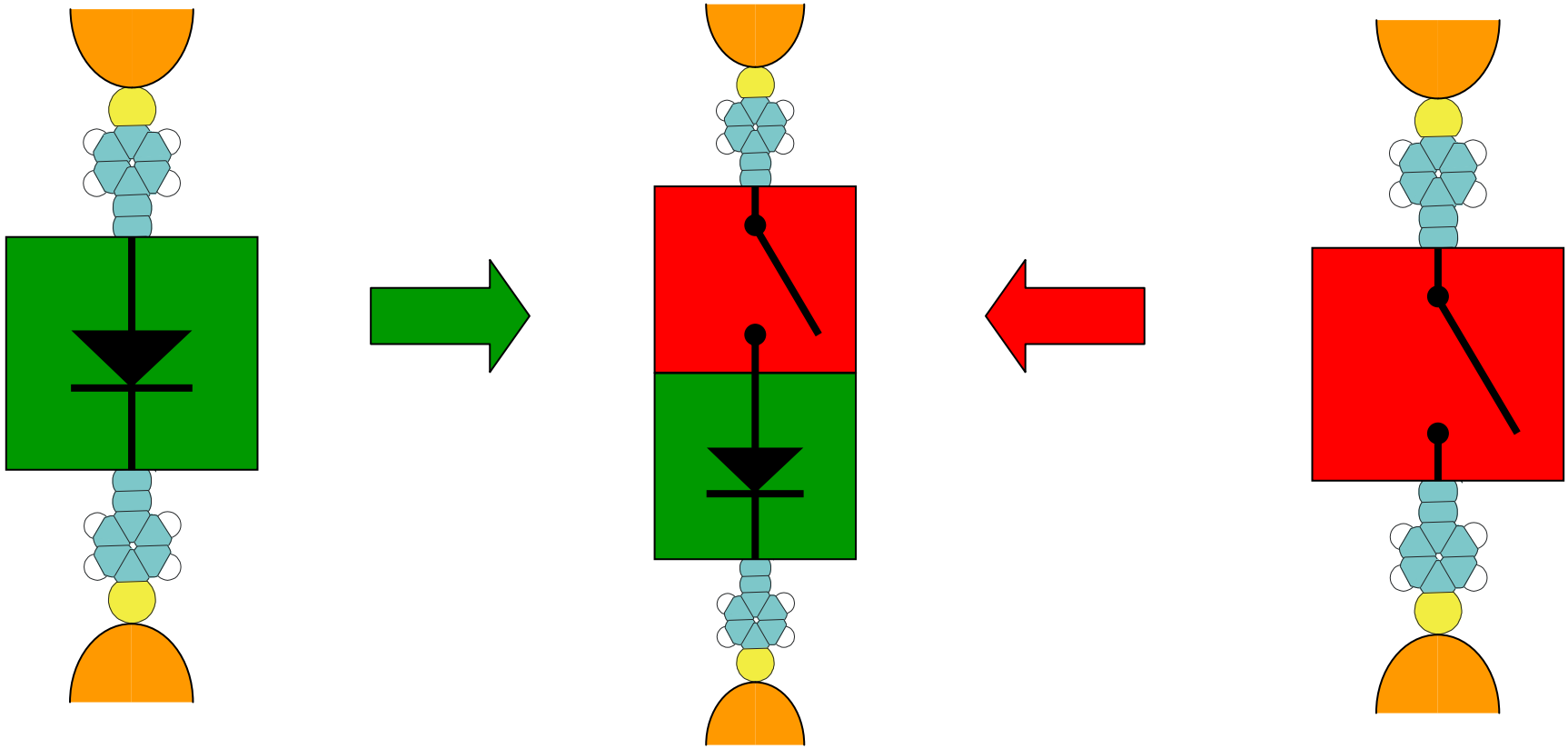


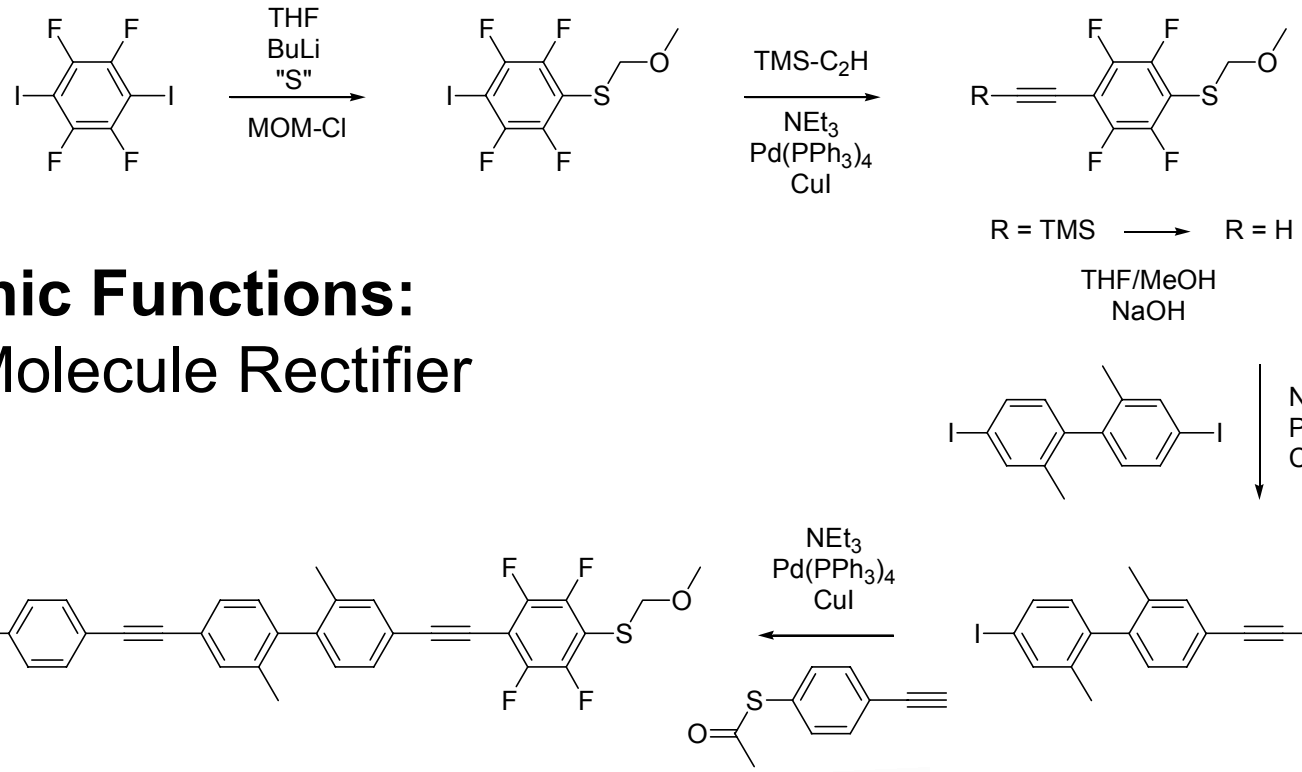
asymmetric

Perspectives

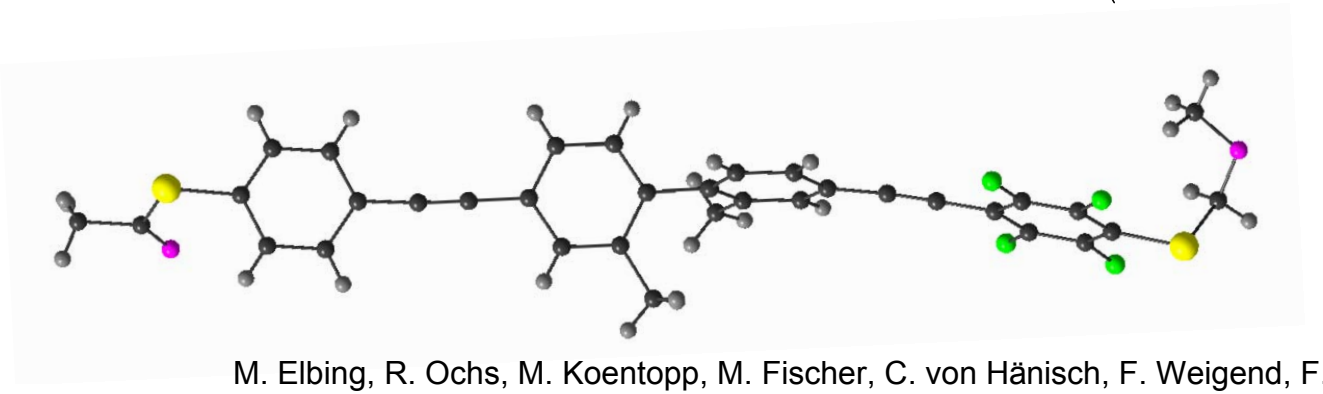
Functional Molecules

Memory Devices? NDR? Rectifiers?



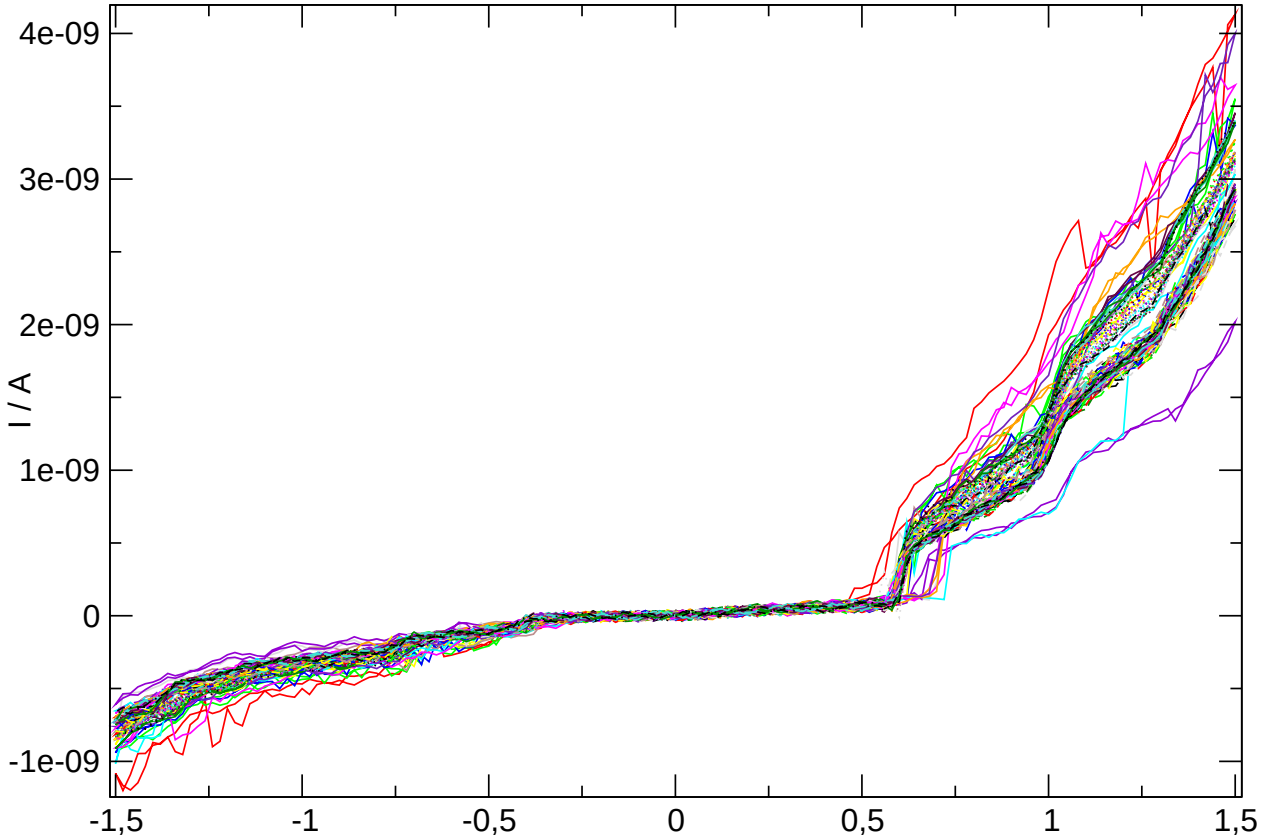


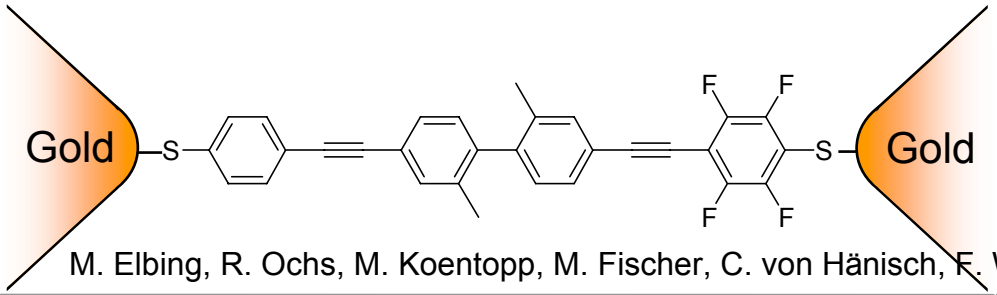
Electronic Functions:
Single-Molecule Rectifier



M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber, M. Mayor; *PNAS*, **2005**, *102*, 8815.

Electronic Functions:
Single-Molecule Rectifier





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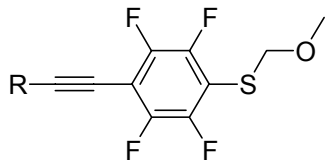
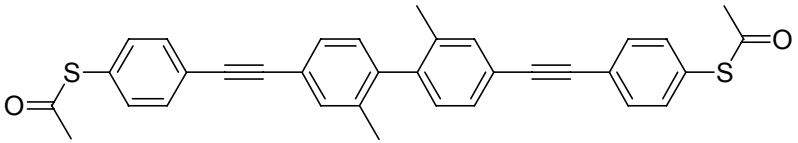
Electronic Functions:
Single-Molecule Rectifier
Control Experiments:

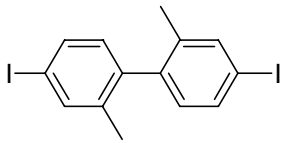


R = TMS ⟶ R = H

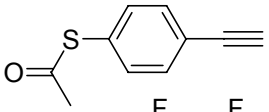
THF/MeOH
NaOH

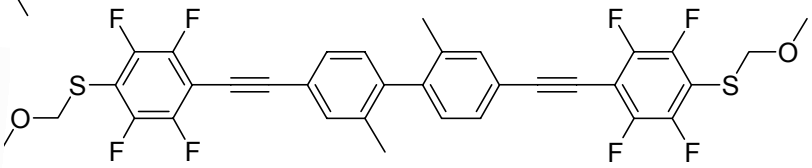


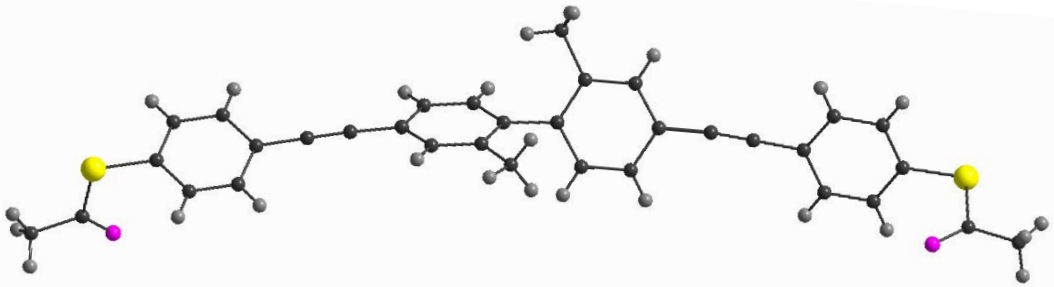
NEt_3
$Pd(PPh_3)_4$
CuI

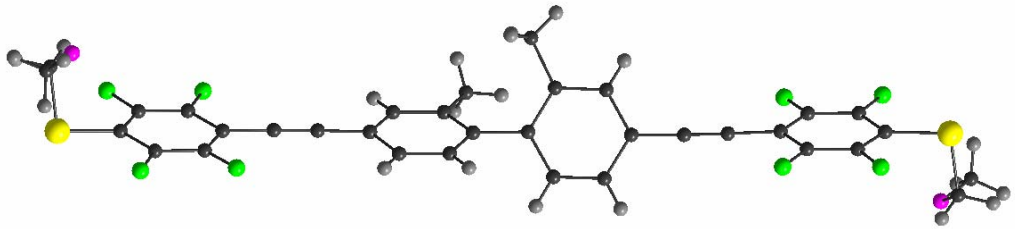


NEt_3
$Pd(PPh_3)_4$
CuI







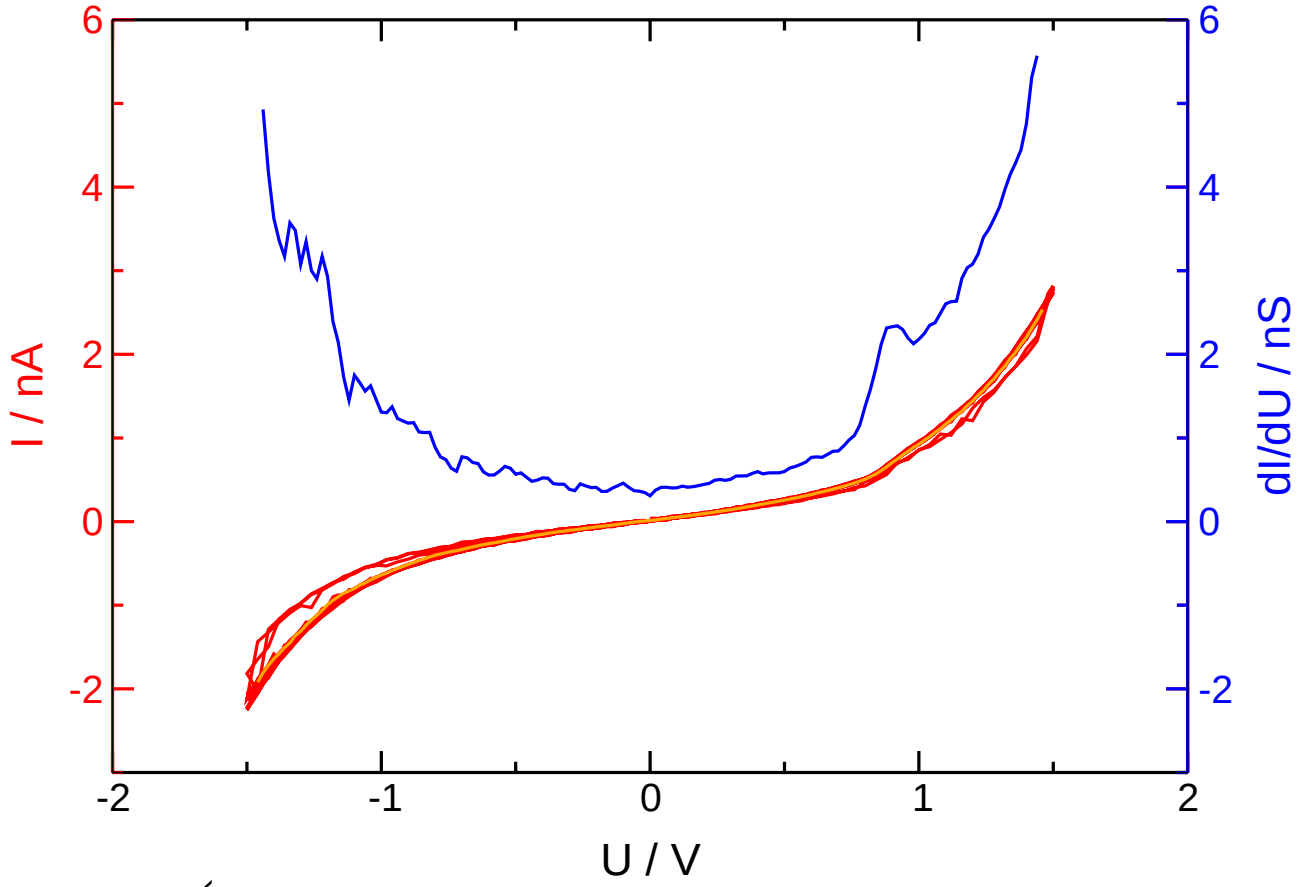


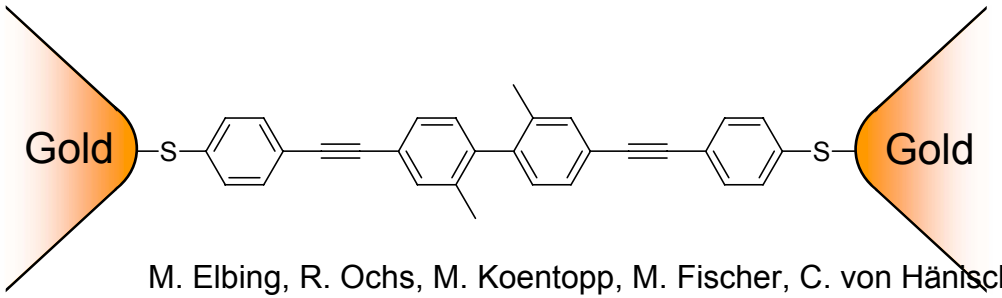
M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber, M. Mayor; *PNAS*, **2005**, *102*, 8815.

Electronic Functions:

Single-Molecule Rectifie

Control Experiments:





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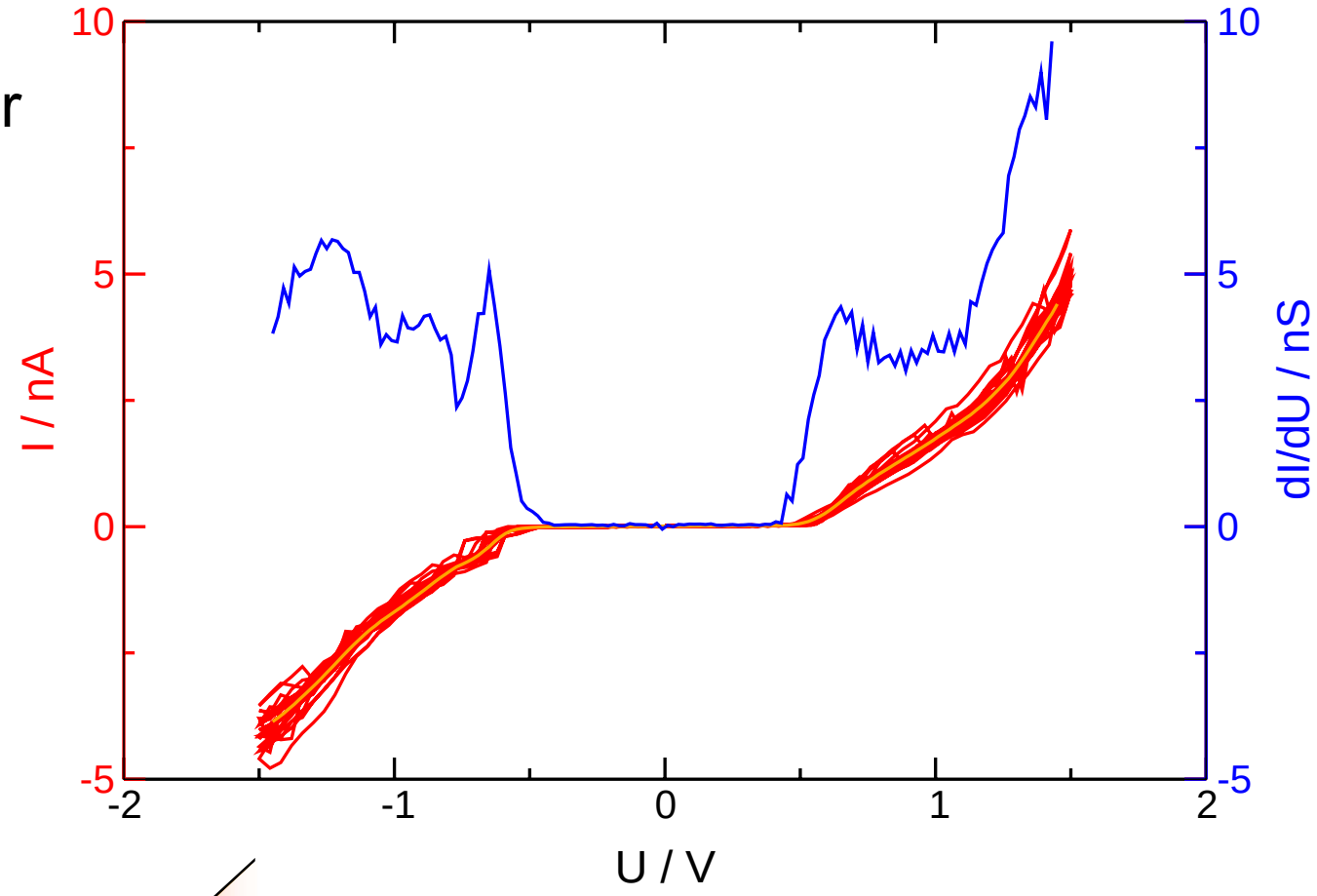
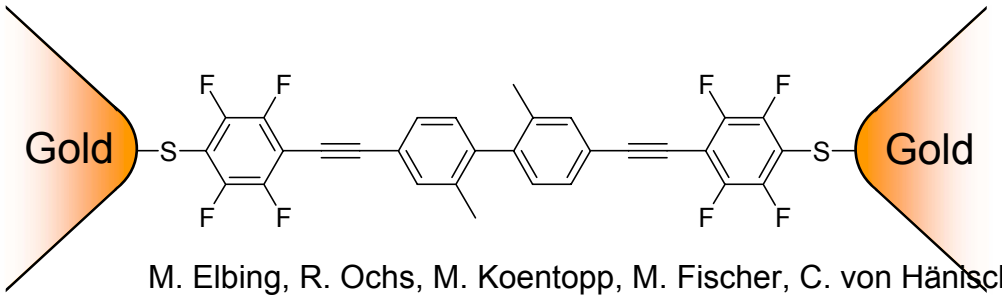
Electronic Functions:
Single-Molecule Rectifier
Control Experiments:

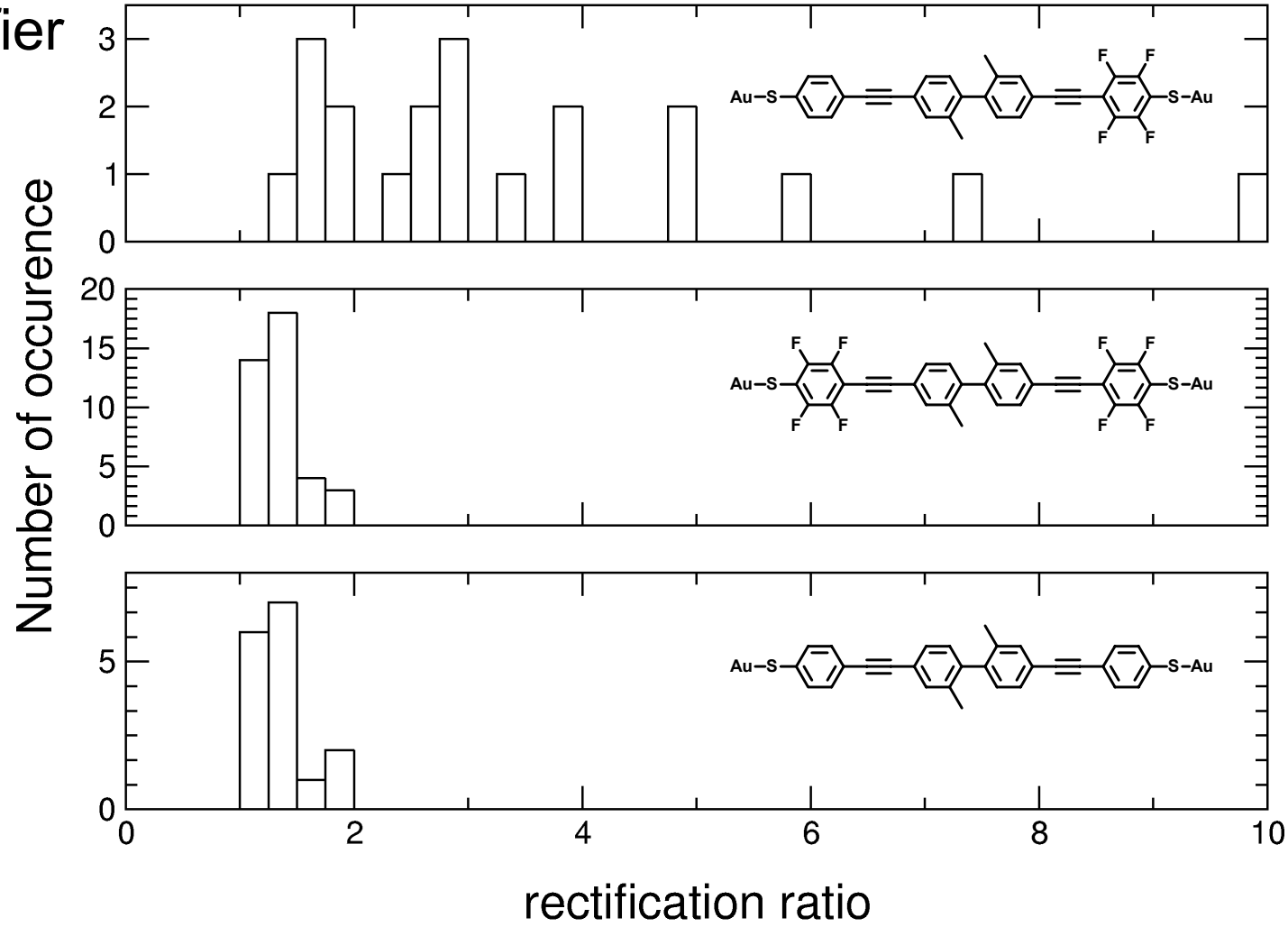




M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber, M. Mayor; *PNAS*, **2005**, *102*, 8815.

Electronic Functions:

Single-Molecule Rectifier Statistics:

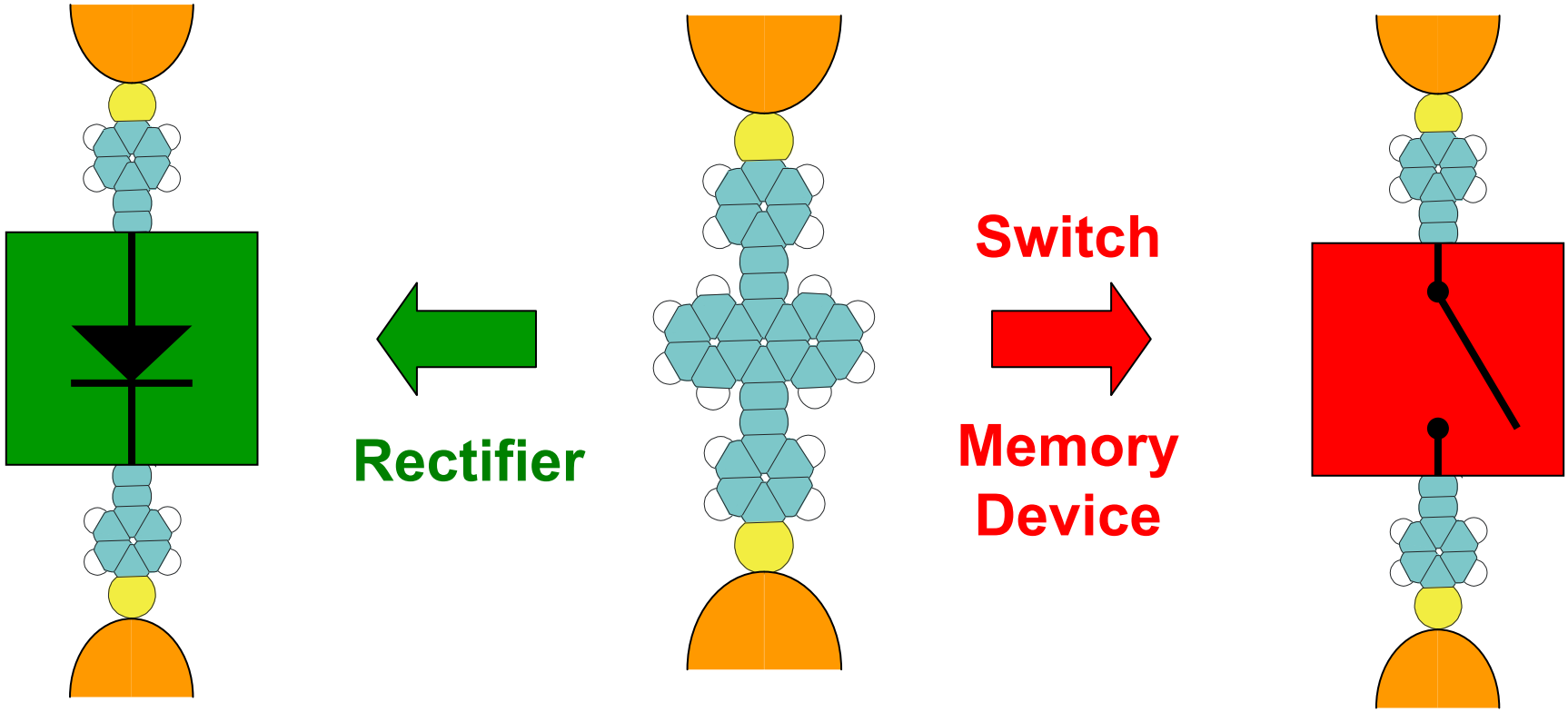


M. Elbing, R. Ochs, M. Koentopp, M. Fischer, C. von Hänisch, F. Weigend, F. Evers, H. B. Weber, M. Mayor; *PNAS*, **2005**, *102*, 8815.

Perspectives

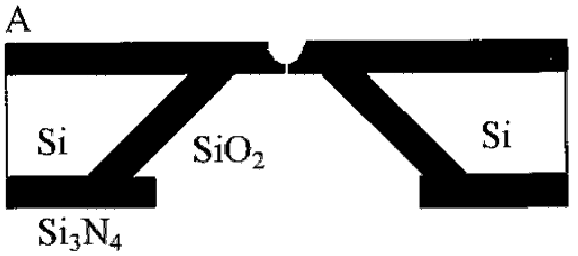
Functional Molecules

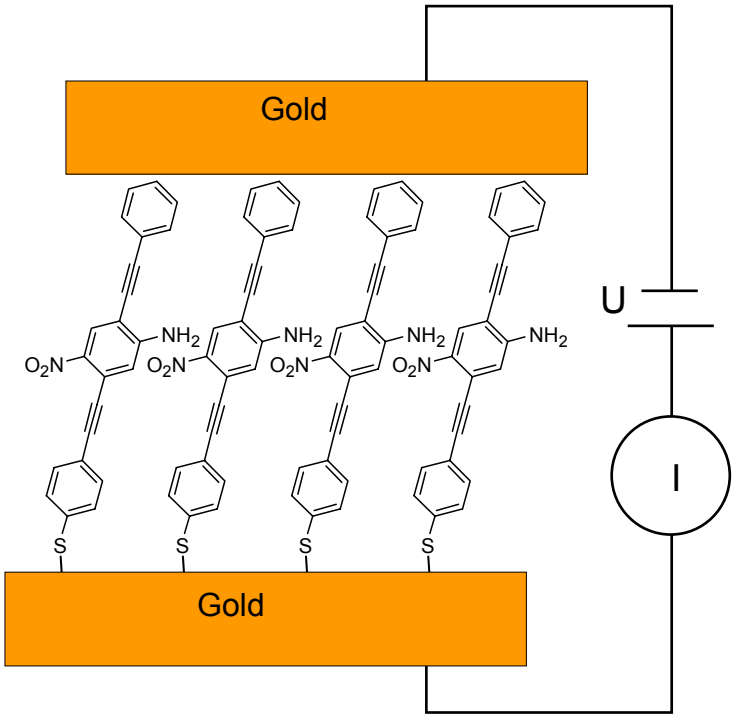
Memory Devices? NDR? Rectifiers?

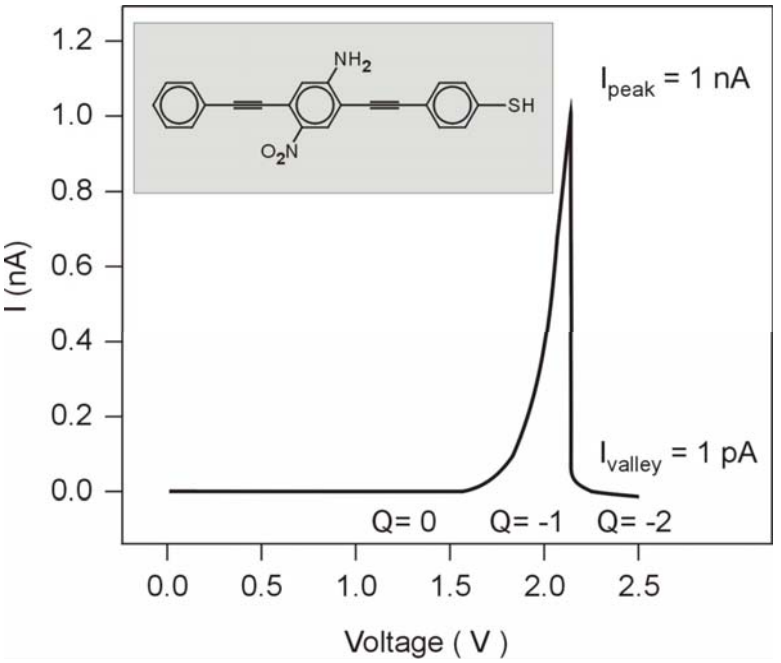


Single Molecule NDR-Device

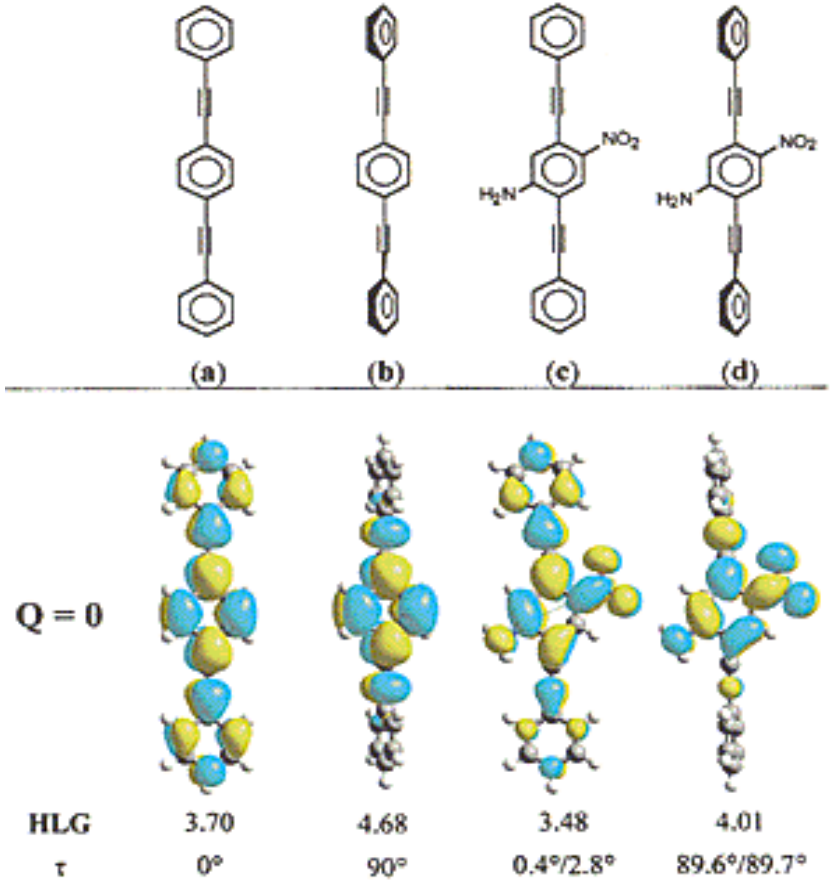
J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science*, **1999**, *286*, 1550-1552

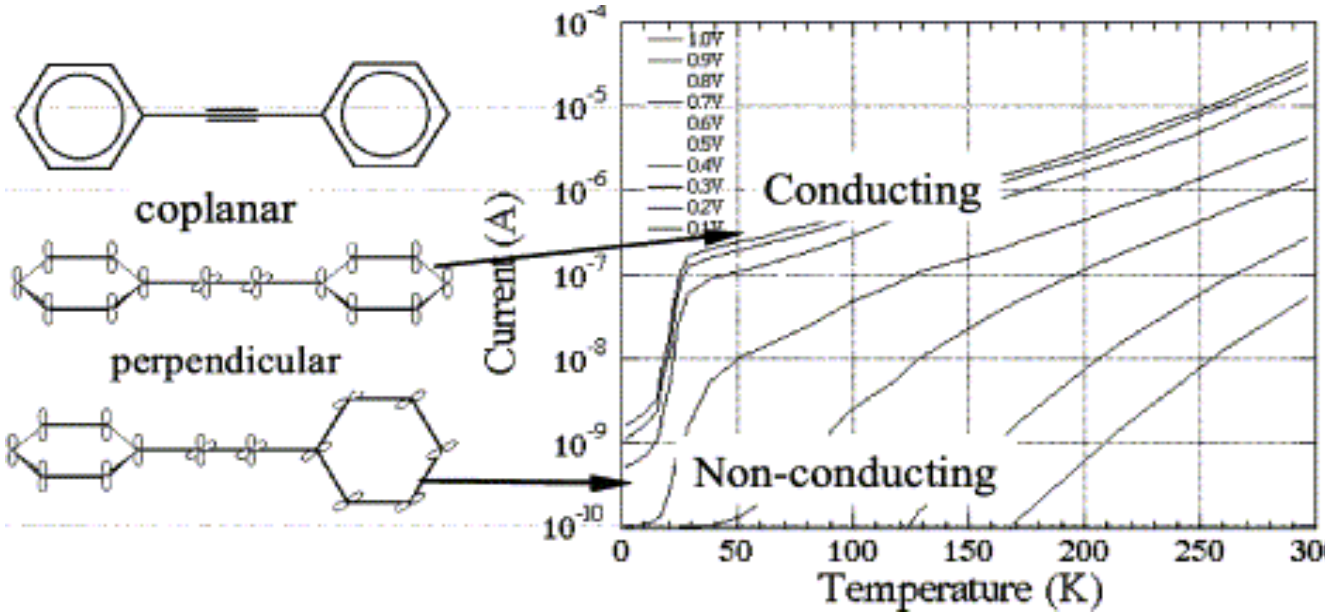






NDR-Theory Hypothesis

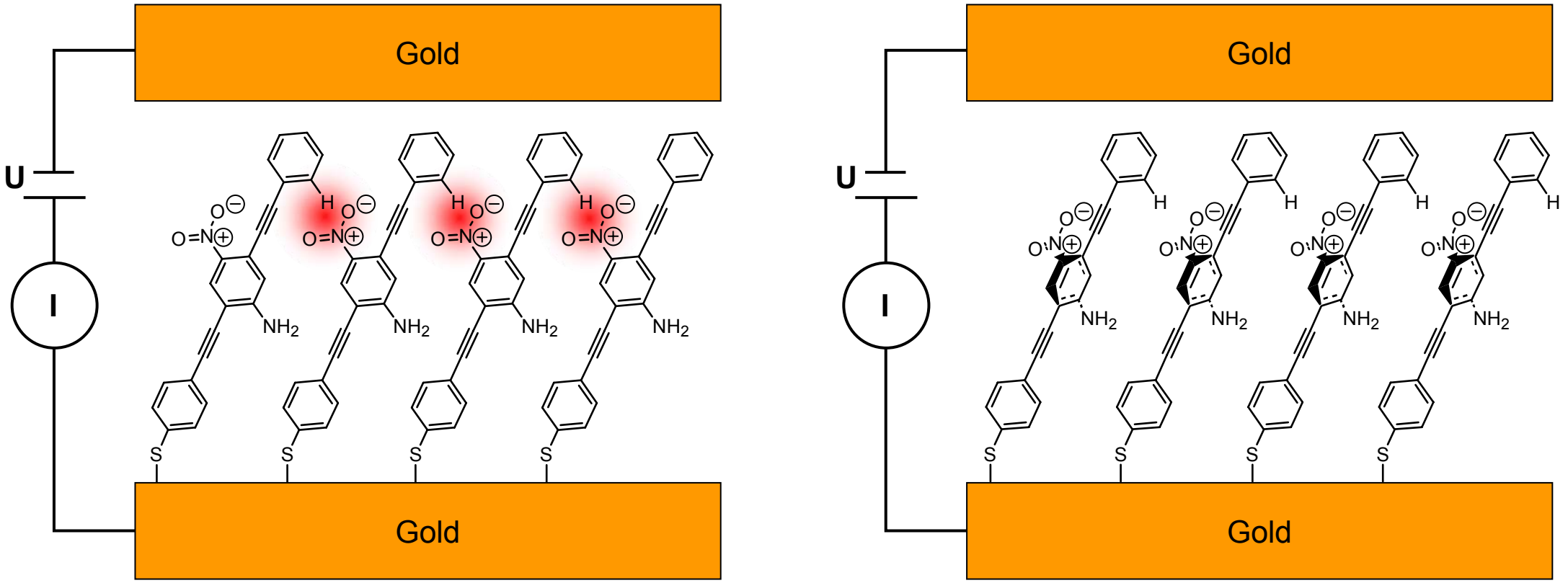




J. Chen, M. A. Reed, *Chem. Phys.*, **2002**, *281*, 127-145

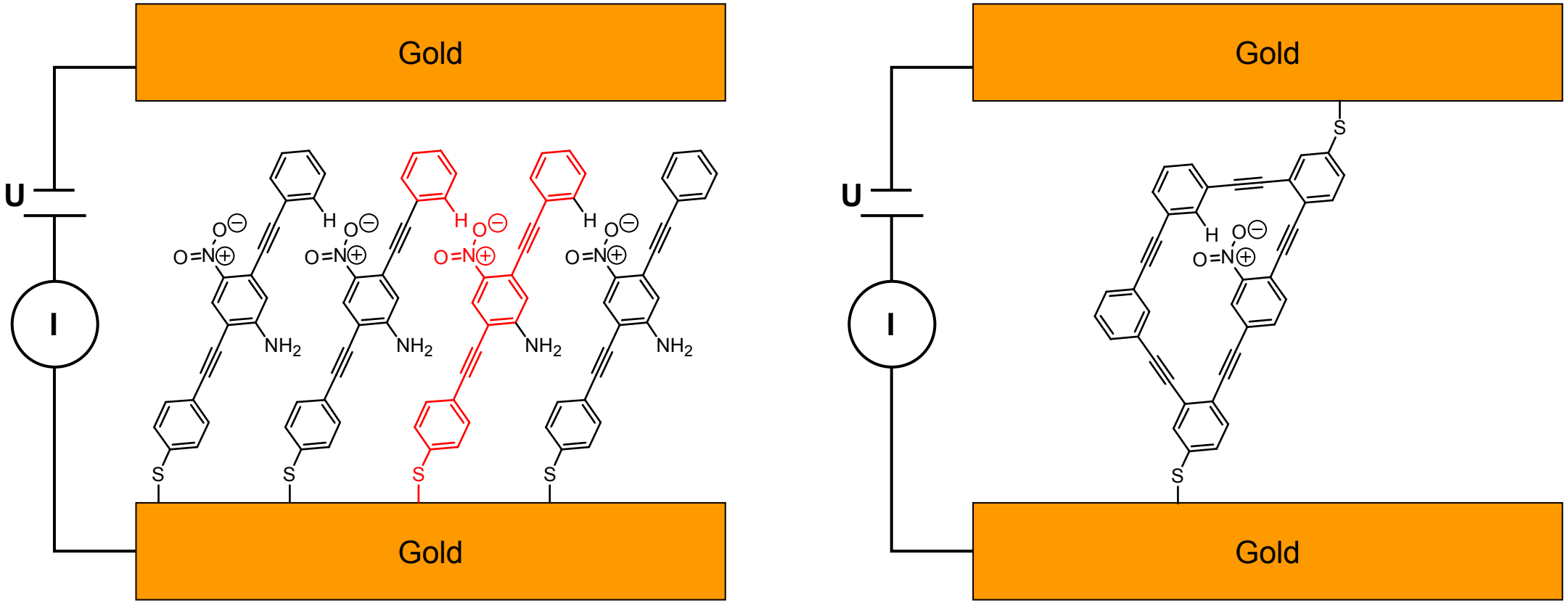
J. M. Seminario, A. G. Zacarias, J. M. Tour, *J. Am. Chem. Soc.*, **2000**, *122*, 3015-3020

Theory: Hypothesis

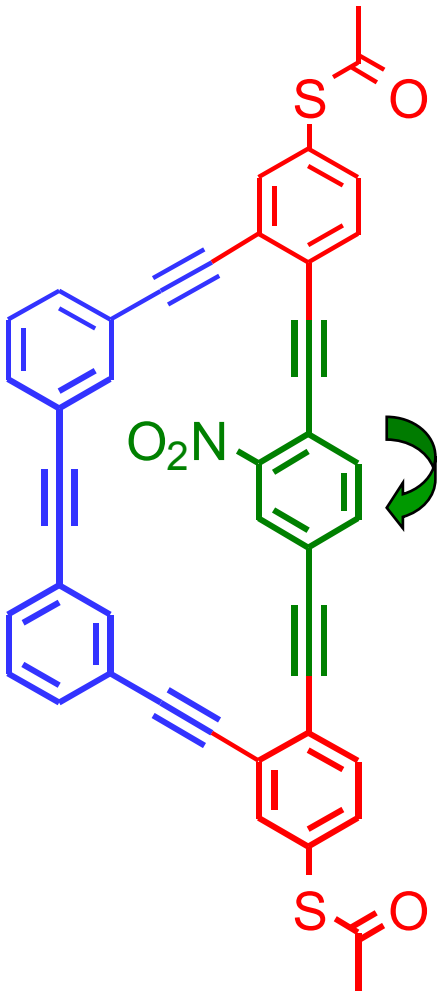


Kurt Stokbro, Jeremy Taylor, Mads Brandbyge, Pablo Ordejon, *Ann. NY acad. Sci.*, **2003**, *1006*, 212-226.
J. Taylor, M. Brandbyge, K. Stokbro, *Phys. Rev. B,* **2003**, *68*, 121101.

from assembly - to - single molecule
from intermolecular - to - intramolecular



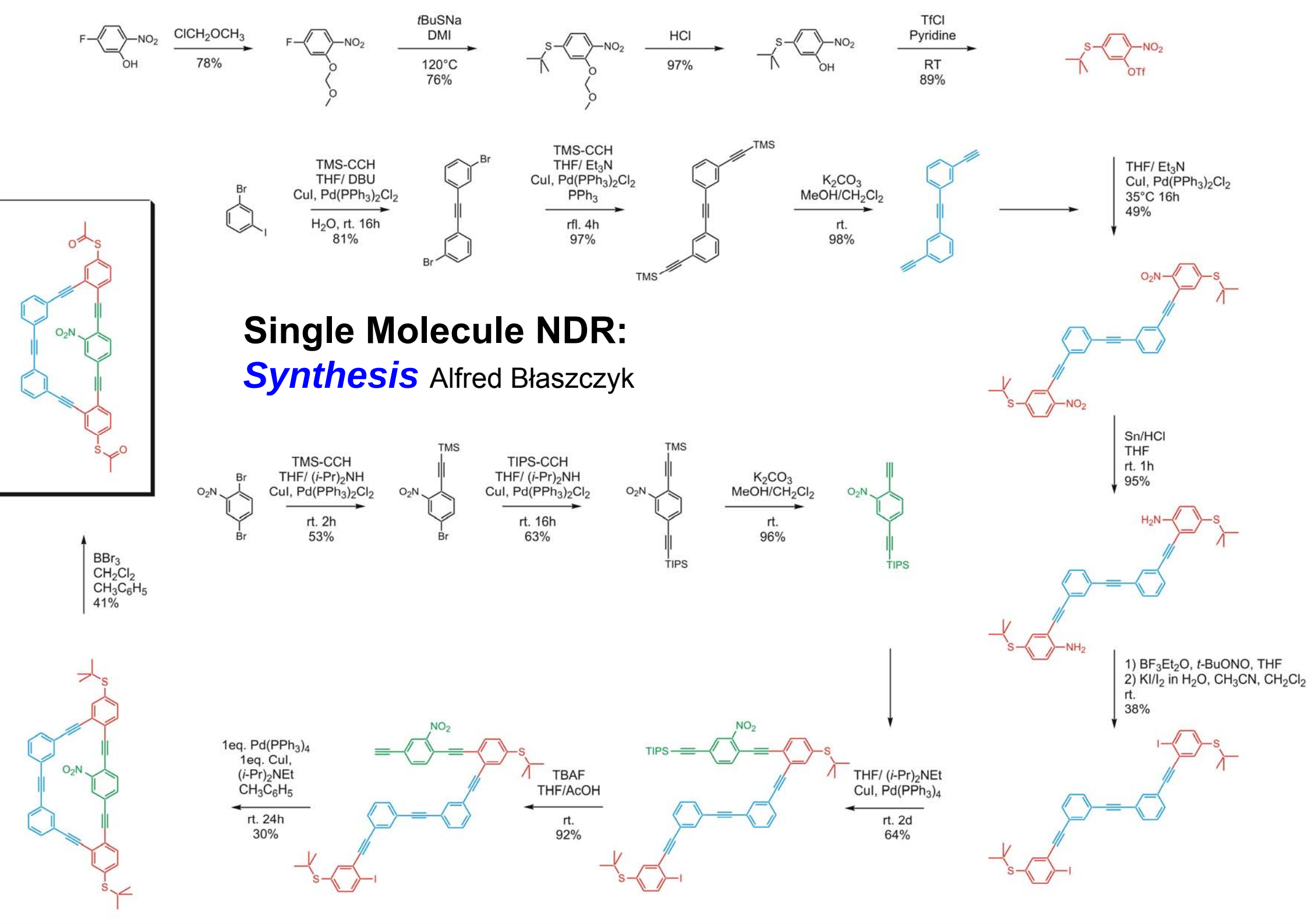
Single Molecule NDR:
modules of the targetstructure



Terminus:
anchorgroups (sulfur)
electronically active (*para*)
electronically passive (*meta*)

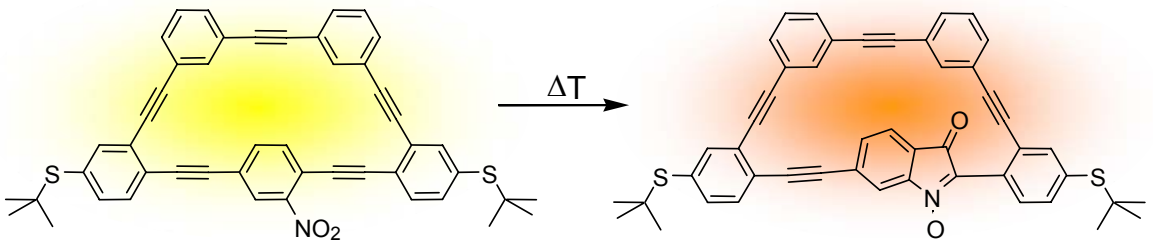
Bridge:
structure determining
planar
electronically passive (*meta*)
internal relation system

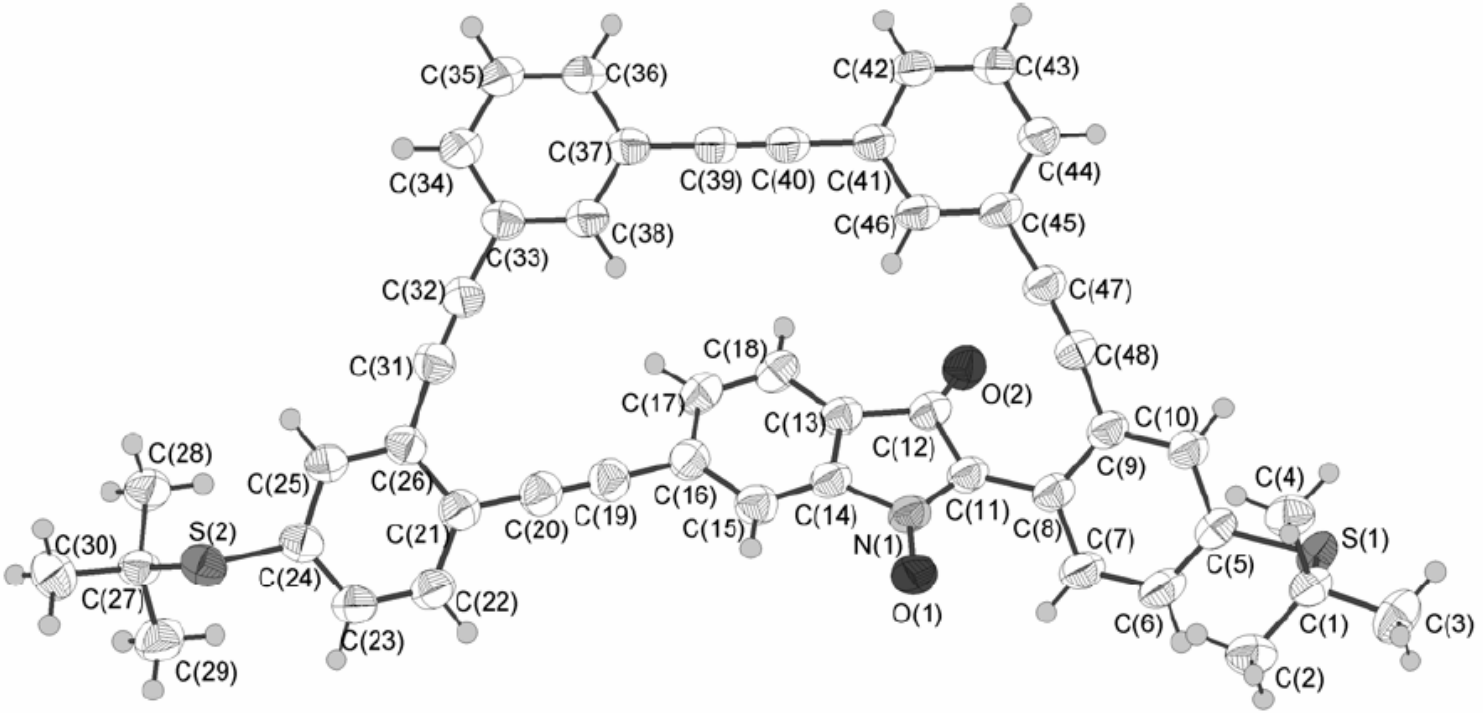
NDR-Switch:
redox aktive
bistable rotamer
electronically active (*para*)


ClCH2OCH3
78%
tBuSNa
DMI
120°C
76%
HCl
97%
TfCl
Pyridine
RT
89%
TMS-CCH
THF/ DBU
CuI, Pd(PPh3)2Cl2
H2O, rt. 16h
81%
TMS-CCH
THF/ Et3N
CuI, Pd(PPh3)2Cl2
PPh3
rfl. 4h
97%
K2CO3
MeOH/CH2Cl2
rt.
98%
THF/ Et3N
CuI, Pd(PPh3)2Cl2
35°C 16h
49%
Single Molecule NDR:
Synthesis Alfred Błaszczyk
TMS-CCH
THF/ (i-Pr)2NH
CuI, Pd(PPh3)2Cl2
rt. 2h
53%
TIPS-CCH
THF/ (i-Pr)2NH
CuI, Pd(PPh3)2Cl2
rt. 16h
63%
K2CO3
MeOH/CH2Cl2
rt.
96%
Sn/HCl
THF
rt. 1h
95%
BBr3
CH2Cl2
CH3C6H5
41%
1) BF3Et2O, t-BuONO, THF
2) KI/I2 in H2O, CH3CN, CH2Cl2
rt.
38%
THF/ (i-Pr)2NEt
CuI, Pd(PPh3)4
rt. 2d
64%
TBAF
THF/AcOH
rt.
92%
1eq. Pd(PPh3)4
1eq. CuI,
(i-Pr)2NEt
CH3C6H5
rt. 24h
30%

Single Molecule NDR:

Limited stability ?

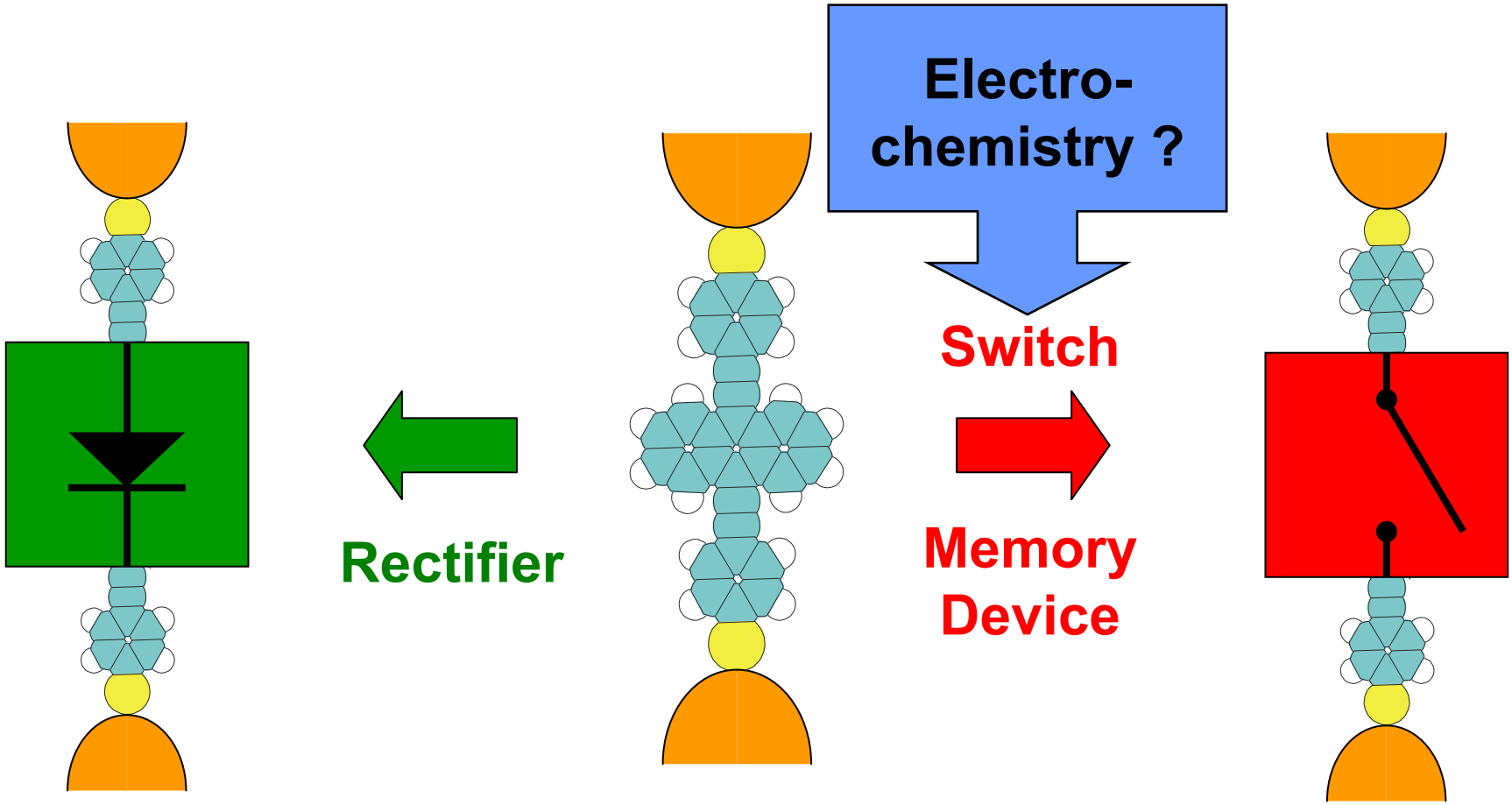




G. M. Rosen, P. Tsai, E. D. Barth, G. Dorey, P. Casara, M. Spedding, H. J. Haplern, *J. Org. Chem*. **2000**, *65*, 4460-4463

Functional Molecules:

memory devices? NDR? rectifiers?



Single Molecule Transport & Electrochemistry:

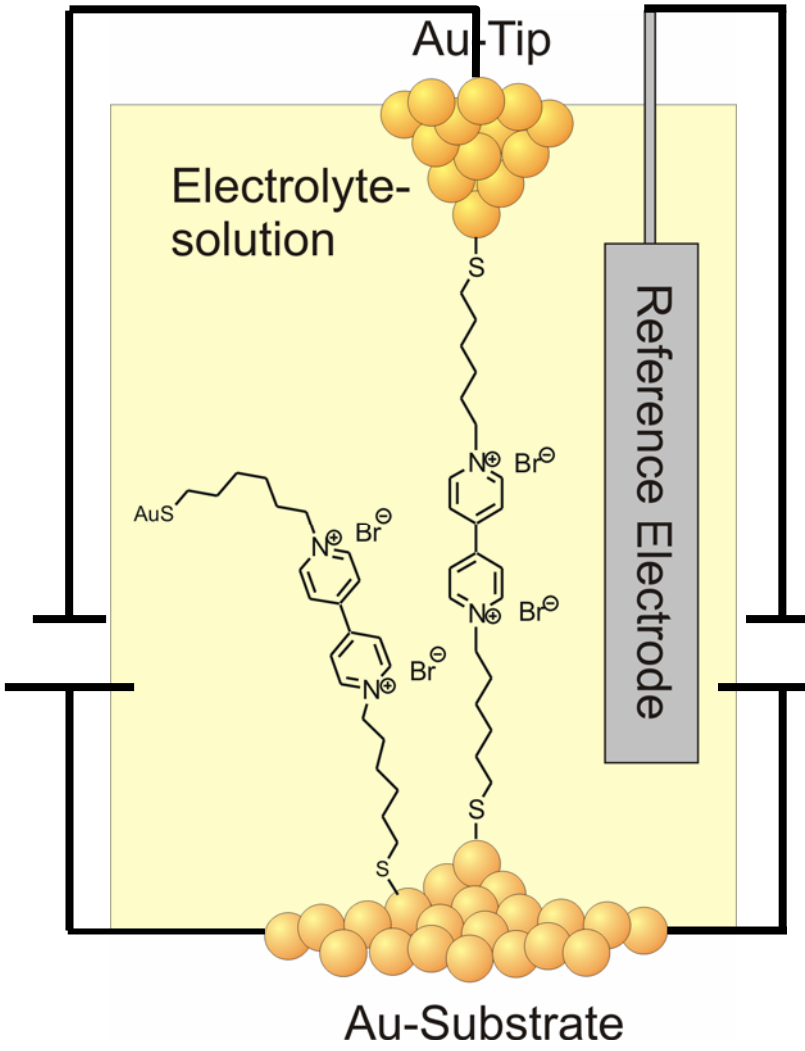
Cooperation with:

Thomas Wandlowski
Zhihai Li
Bo Han
Gabor Meszaros
Ilya Pobelov
Gabor Nagy
Udo Linke

Forschungszentrum Jülich
in der Helmholtz-Gemeinschaft

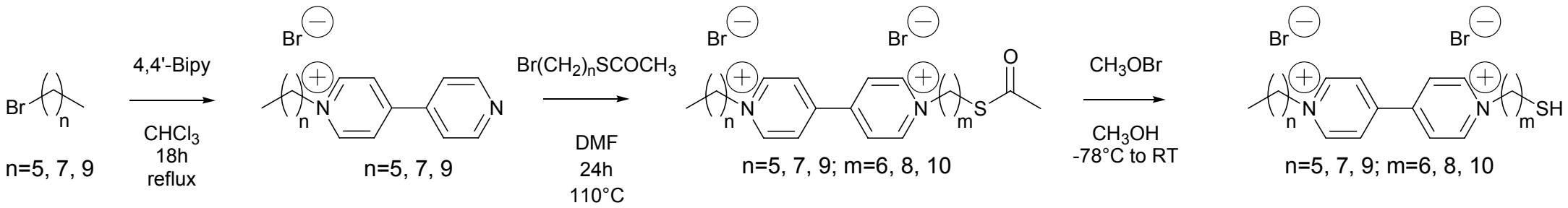
ISG3

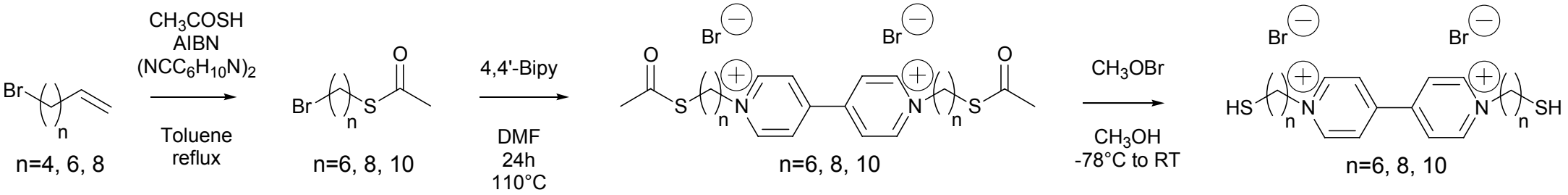
VolkswagenStiftung



Single Molecule Transport & Electrochemistry:

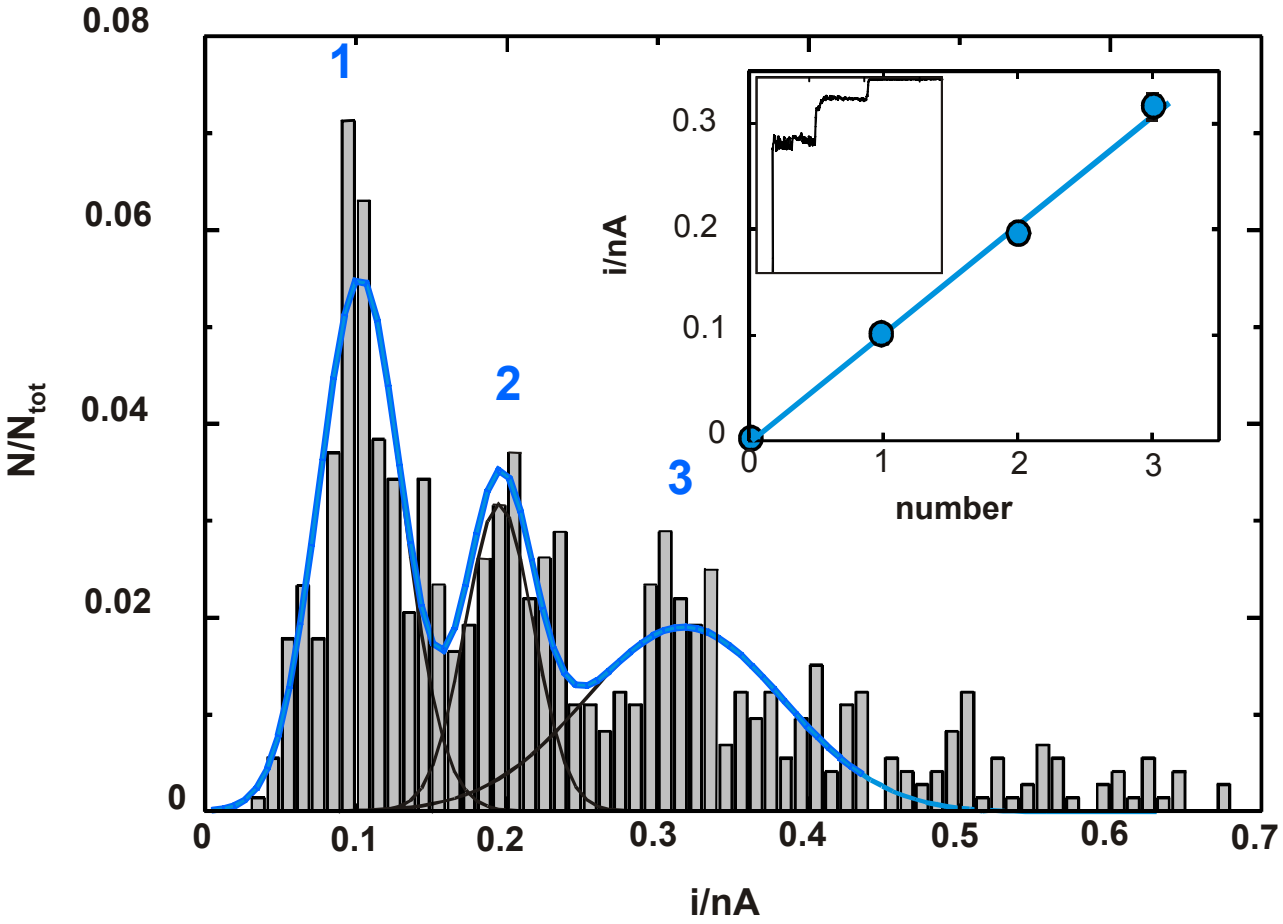
Synthesis: Alfred Błaszczyk

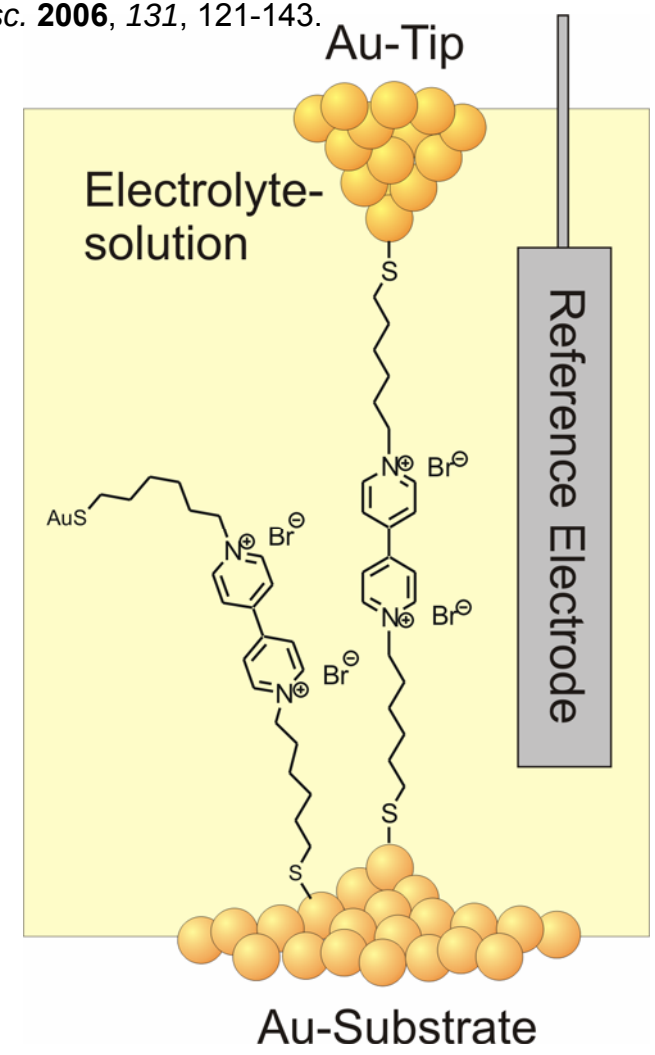




Single Molecule Transport & Electrochemistry:

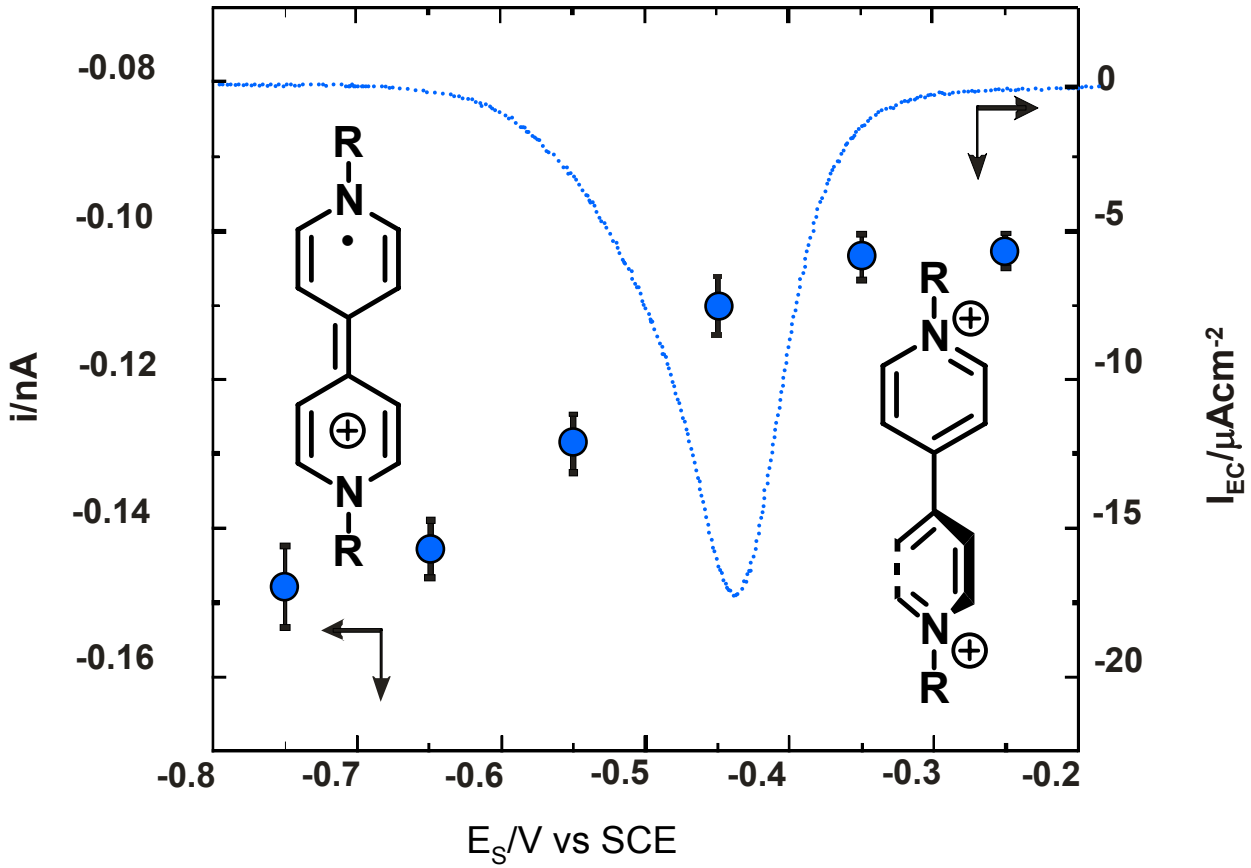
Z. Li, B. Han, G. Meszaros, I. Pobelov, Th. Wandlowski, A. Błaszczyk, M. Mayor, *Faraday Disc.* **2006**, *131*, 121-143.

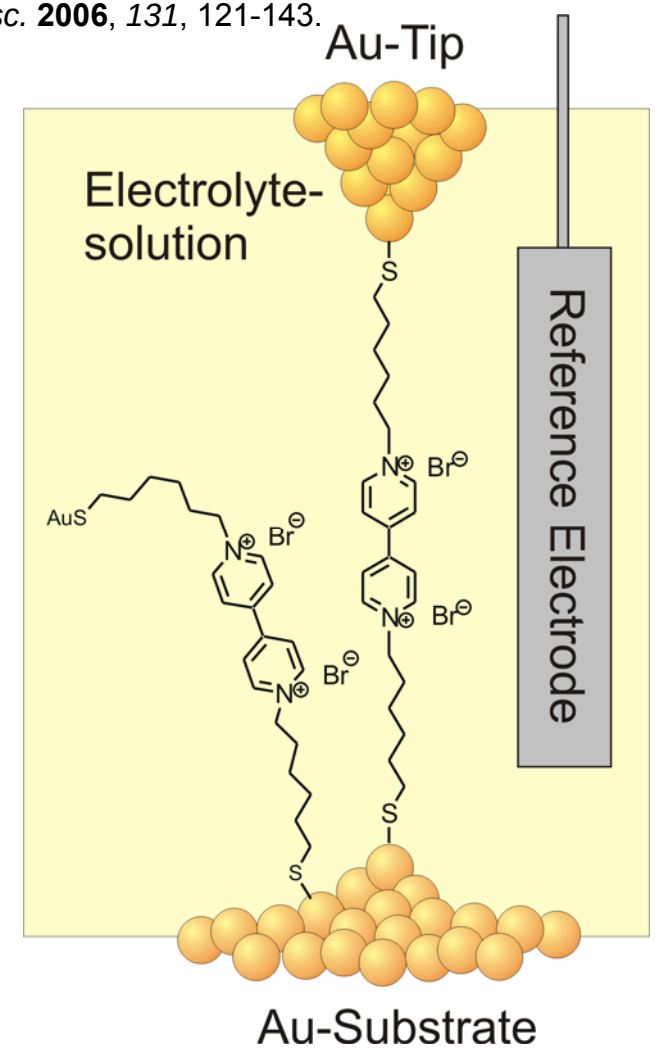




Single Molecule Transport & Electrochemistry:

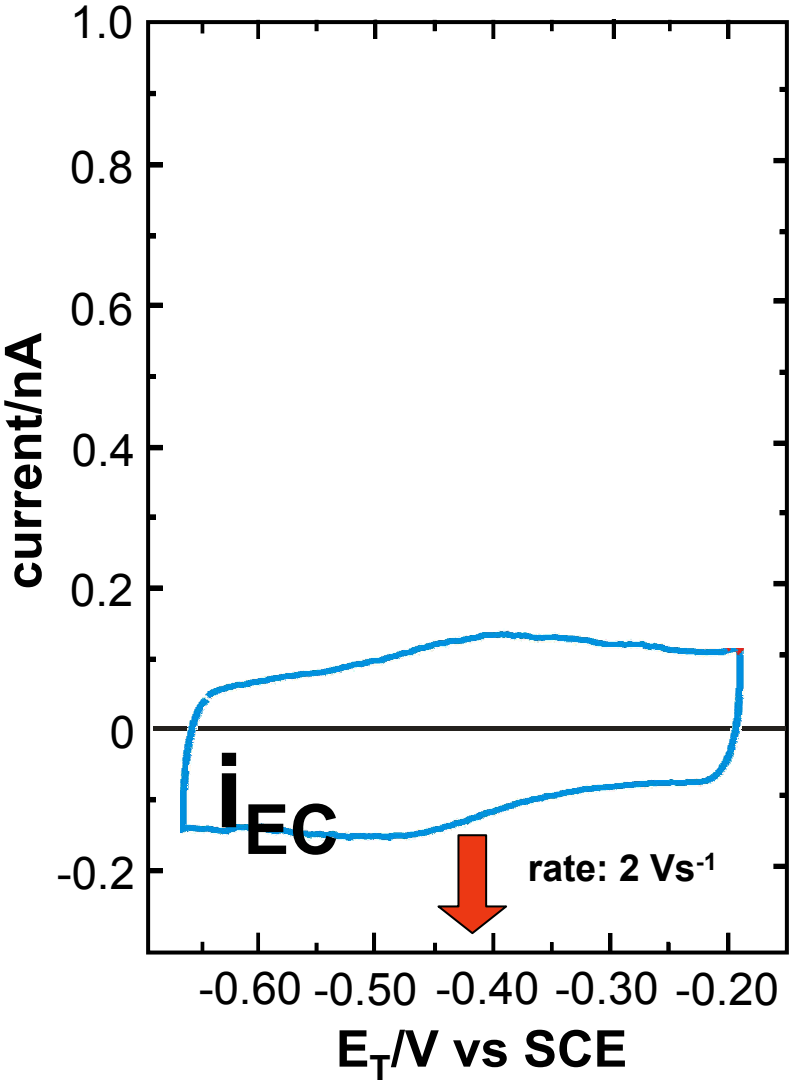
Z. Li, B. Han, G. Meszaros, I. Pobelov, Th. Wandlowski, A. Błaszczyk, M. Mayor, *Faraday Disc.* **2006**, *131*, 121-143.

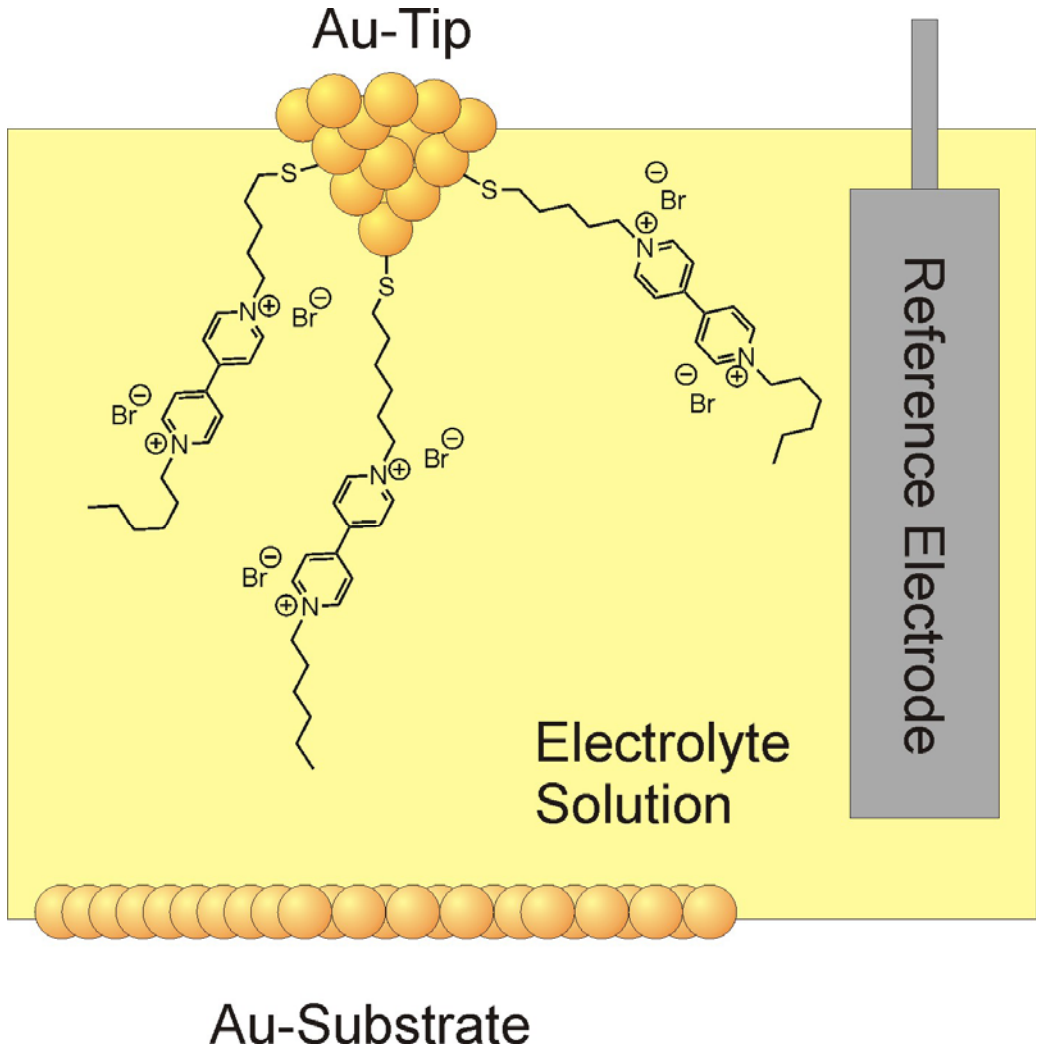




Single Molecule Tunneling:

Z. Li, B. Han, G. Meszaros, I. Pobelov, Th. Wandlowski, A. Błaszczyk, M. Mayor, *Faraday Disc.* **2005**, *131*





Tip: Au(poly)-S-6V6-H coated with PF; Substrate: Au(111)-(1x1); Electrolyte: 0.05 M KClO$_4$, pH = 7

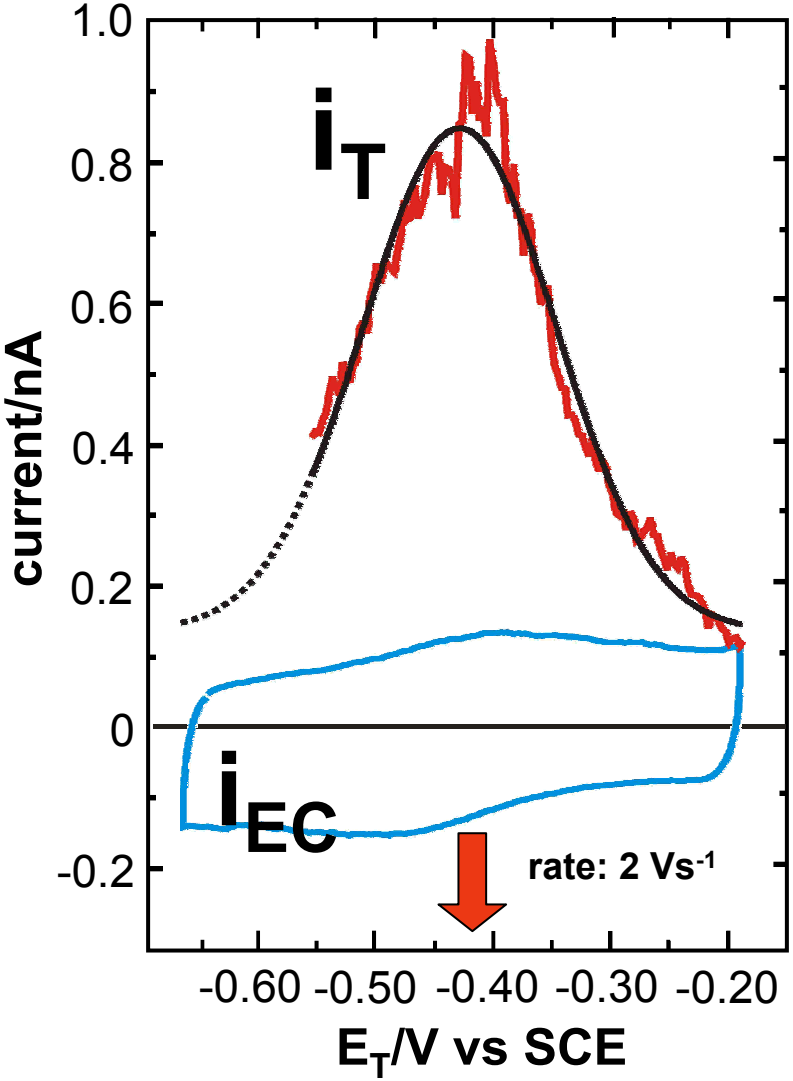
Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

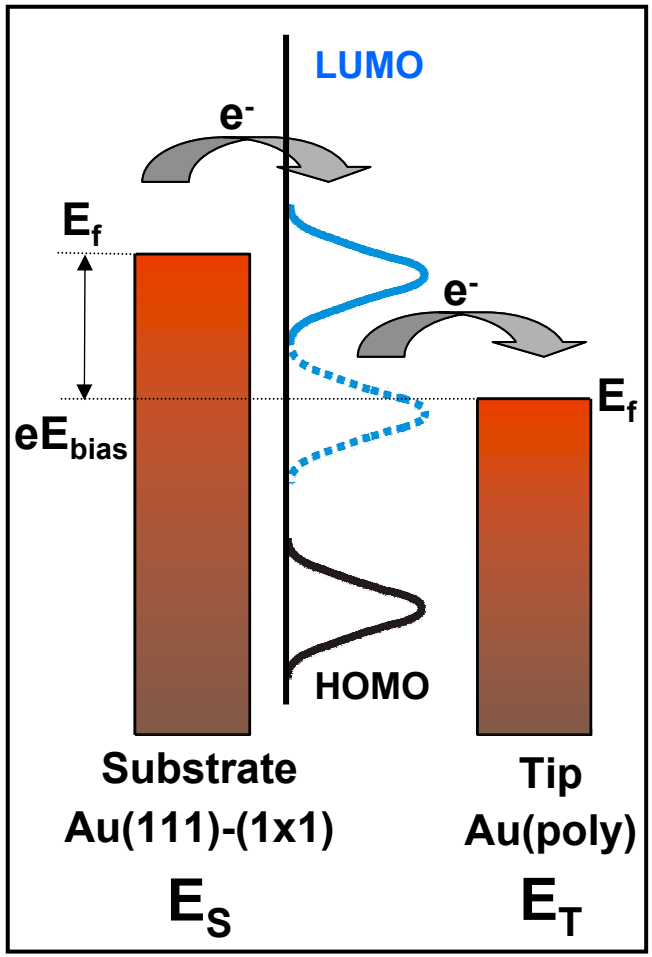
Institut for Nanotechnology

UNI BASEL

Single Molecule Tunneling:

Z. Li, B. Han, G. Meszaros, I. Pobelov, Th. Wandlowski, A. Błaszczyk, M. Mayor, *Faraday Disc.* **2005**, *131*





Two-step Sequential Electron Transfer

Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Institut for Nanotechnology

UNI BASEL

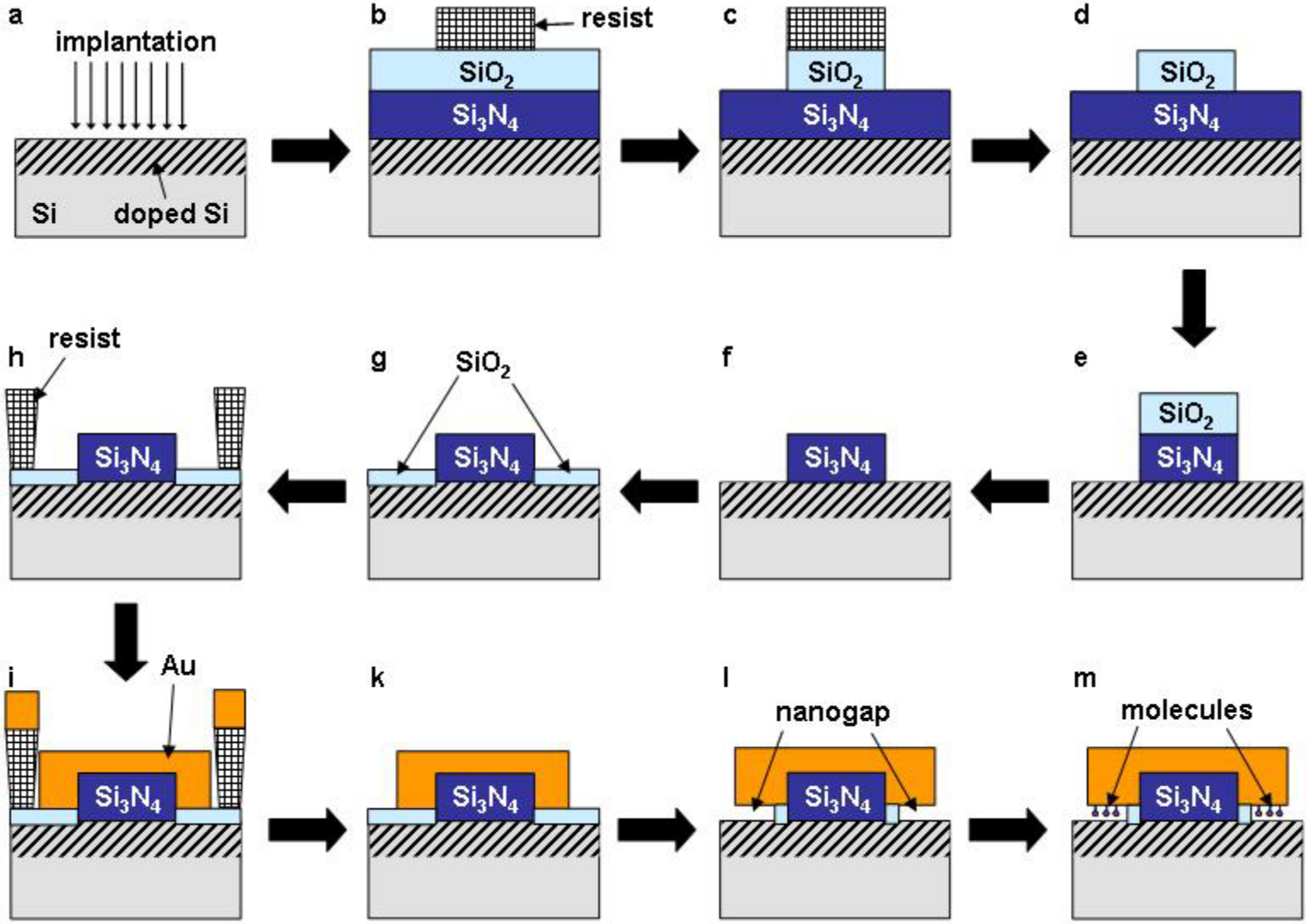
Molecular Electronics: *devices of tomorrow?*

Marcel Mayor

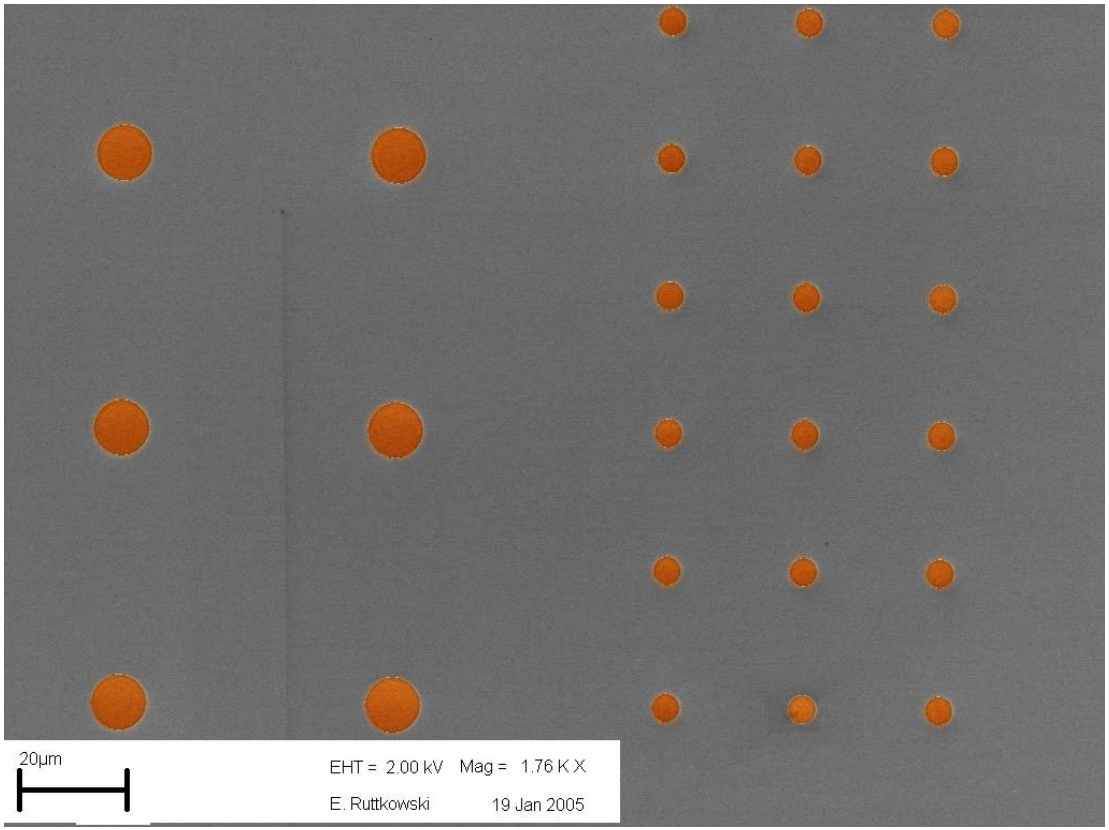
Outline

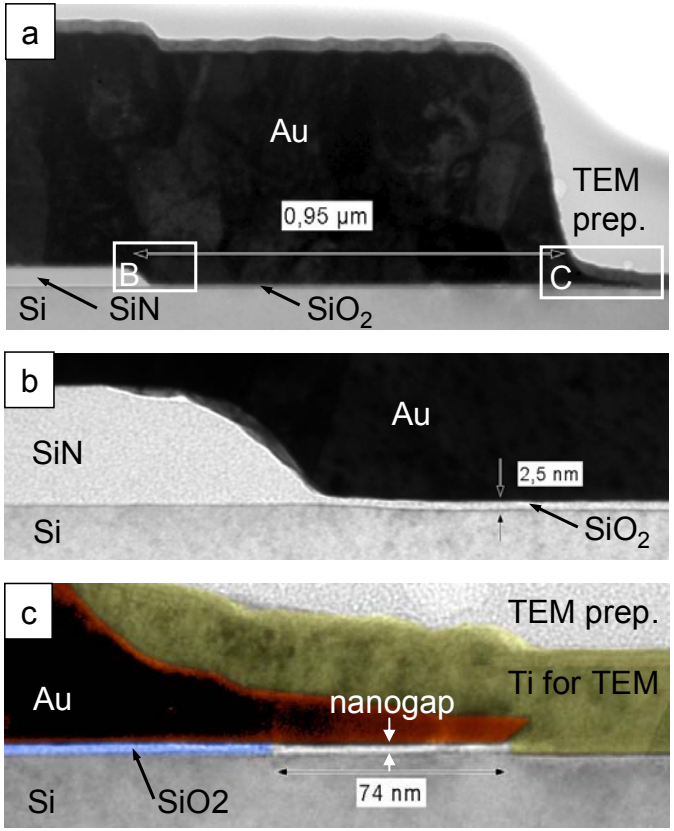
Cooperation
Infineon Technologies:
Eike Ruttkowski
Hannes Luyken
(BMBF-FZK 13 N 8360)

Golden Mushrooms:

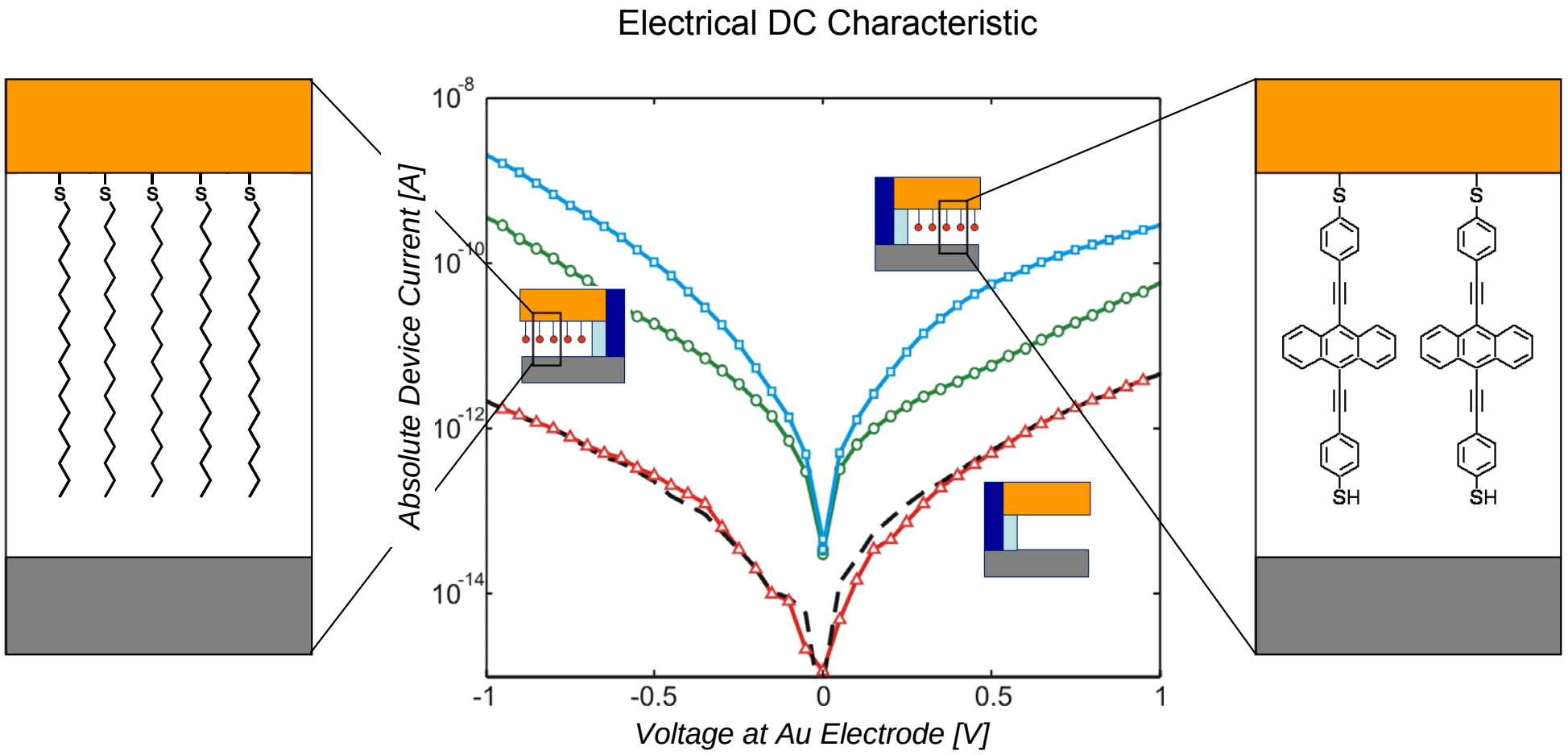


Golden Mushrooms: *TEM pictures*





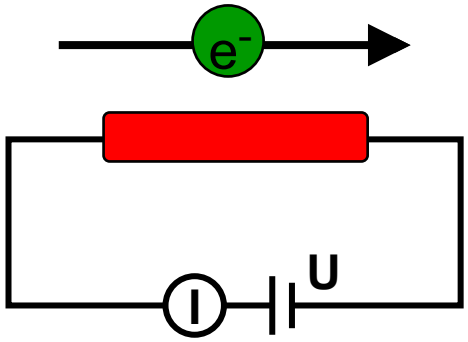
Golden Mushrooms: *measurements*



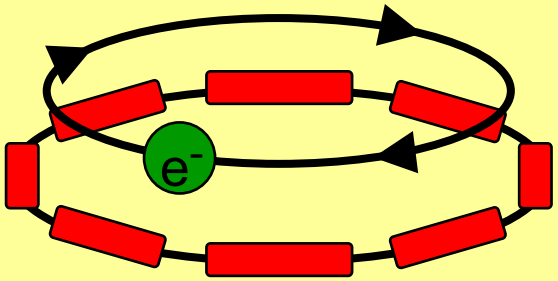
Molecular Electronics

Single Molecules as Building Blocks for Electronic Circuits ?

Concepts:

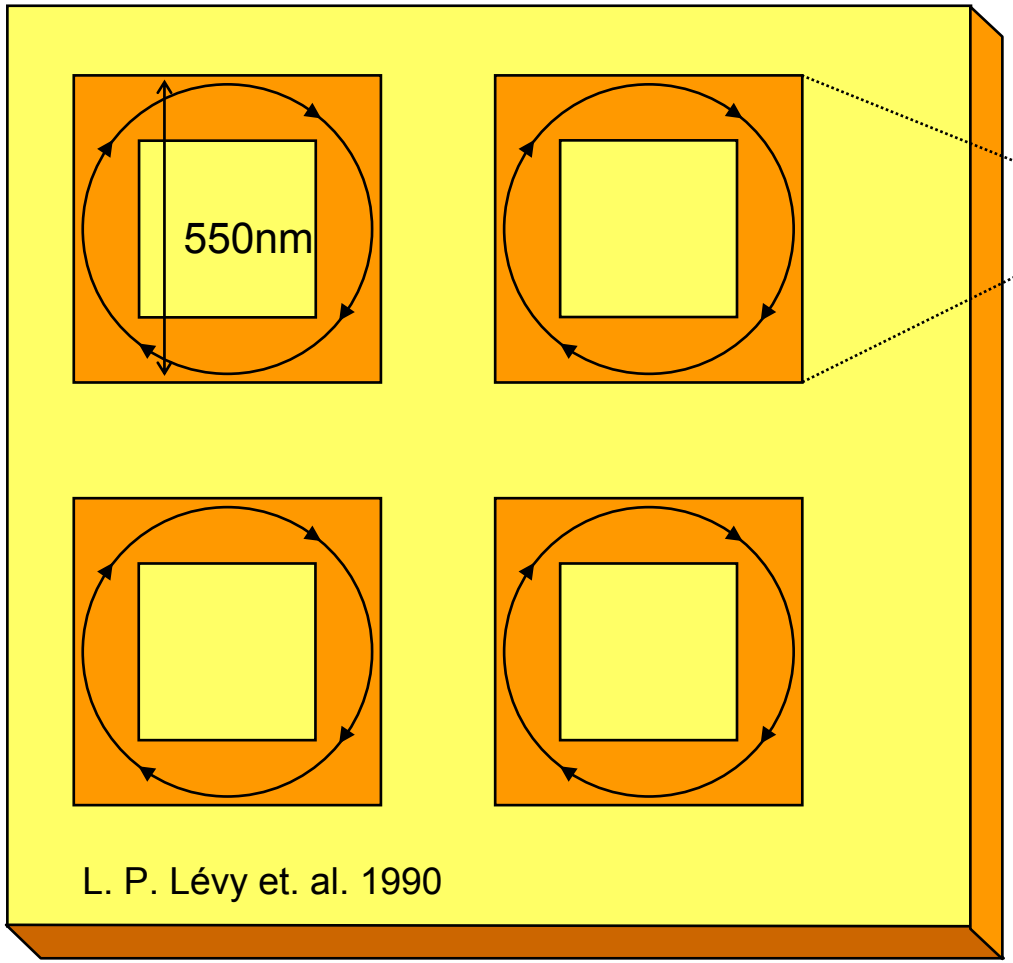


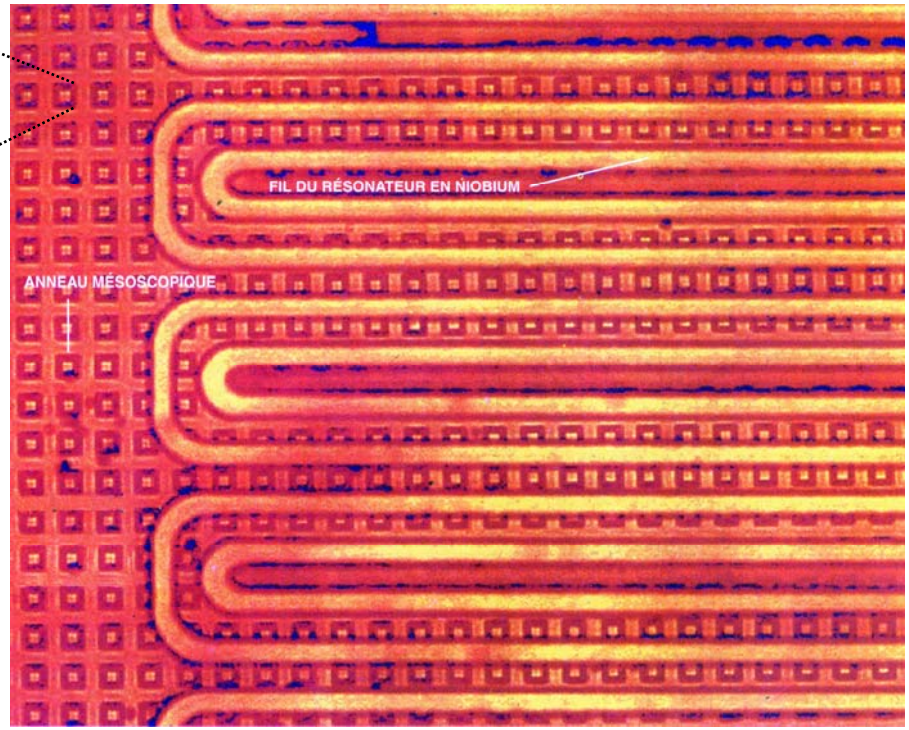
single
molecules



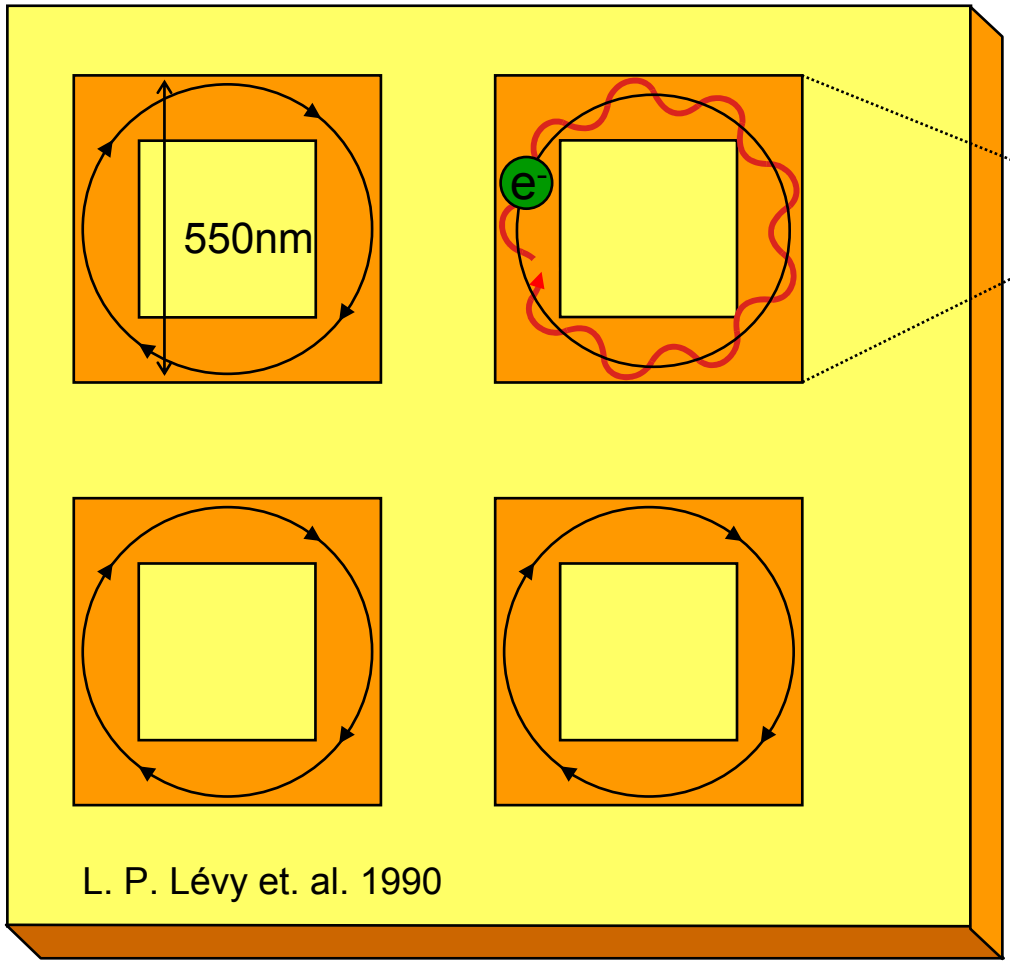
nanoscale objects

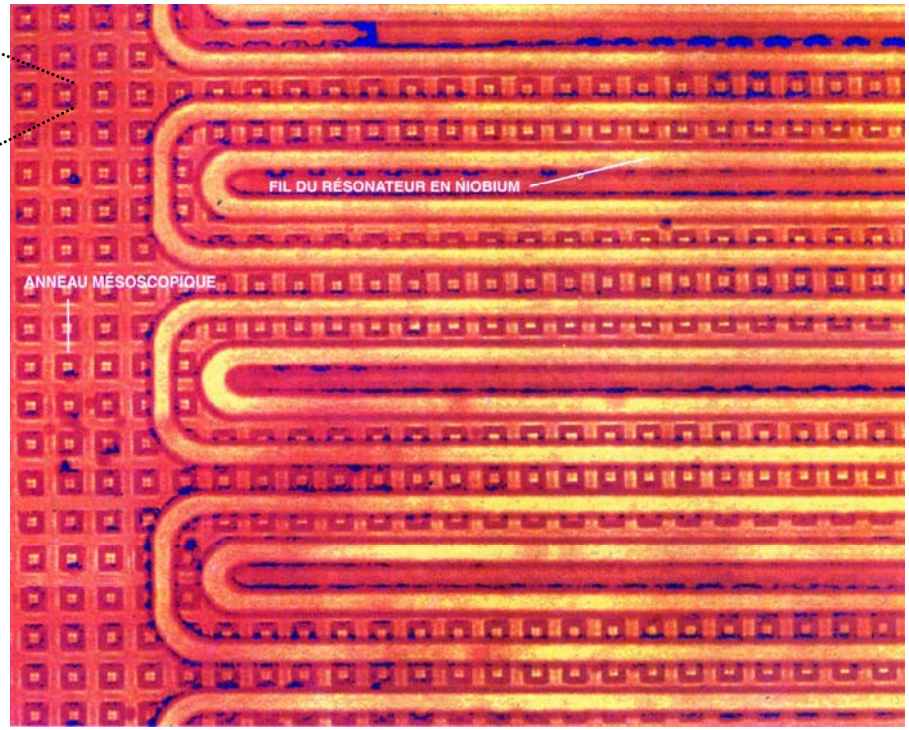
Giant Conjugated Cycles, Persistent Currents



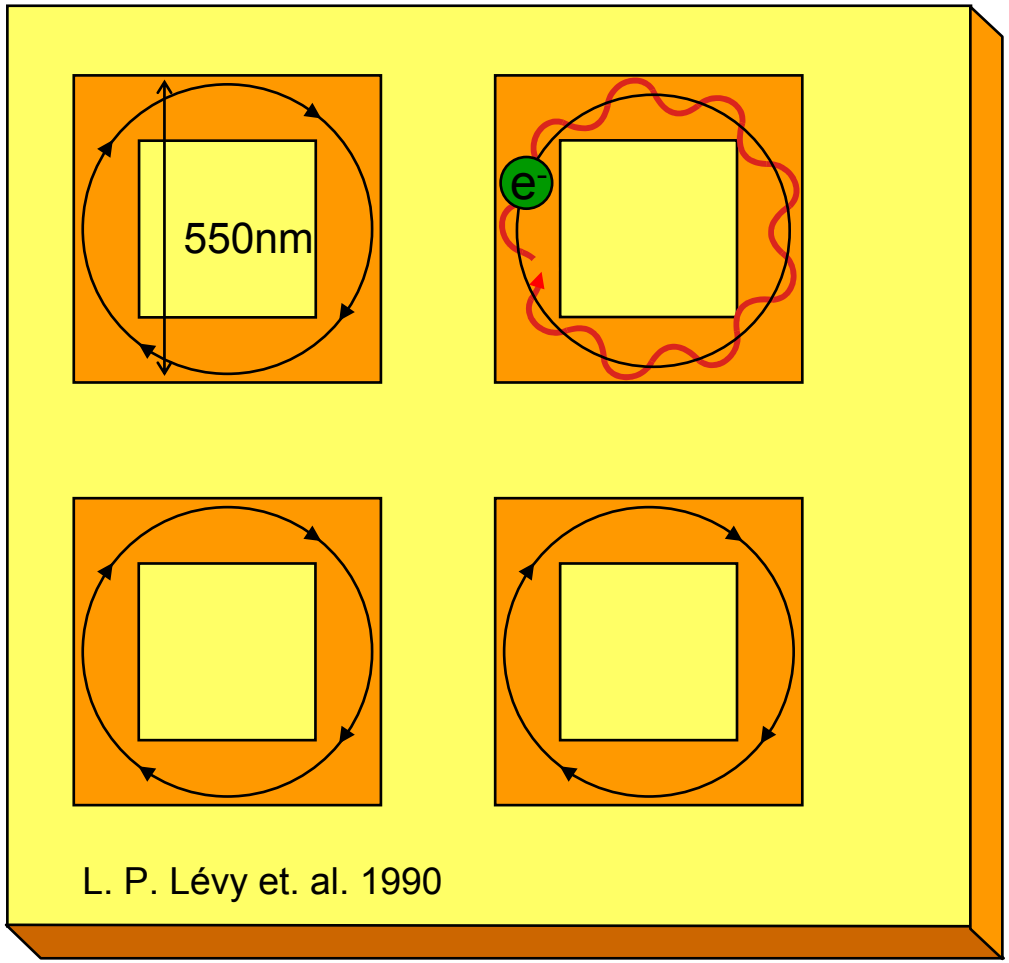


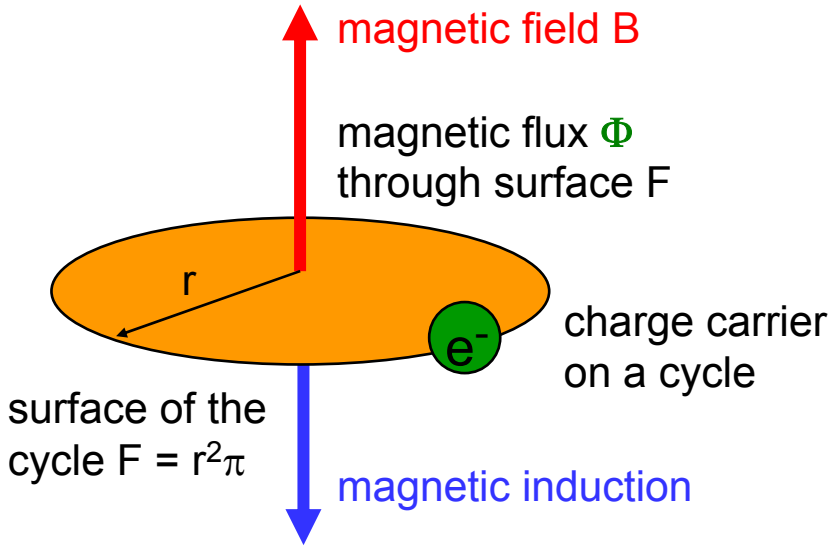
Giant Conjugated Cycles, Persistent Currents





Giant Conjugated Cycles, Persistent Currents





Giant Conjugated Cycles, Persistent Currents

$\Phi = B \times F$

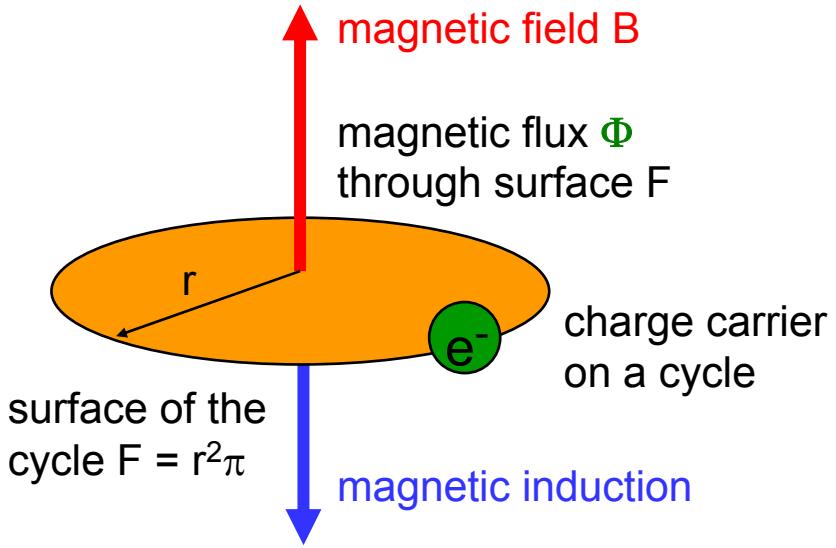
elemental flux quantum:

$\Phi_0 = h/e$

$\Phi = \Phi_0$

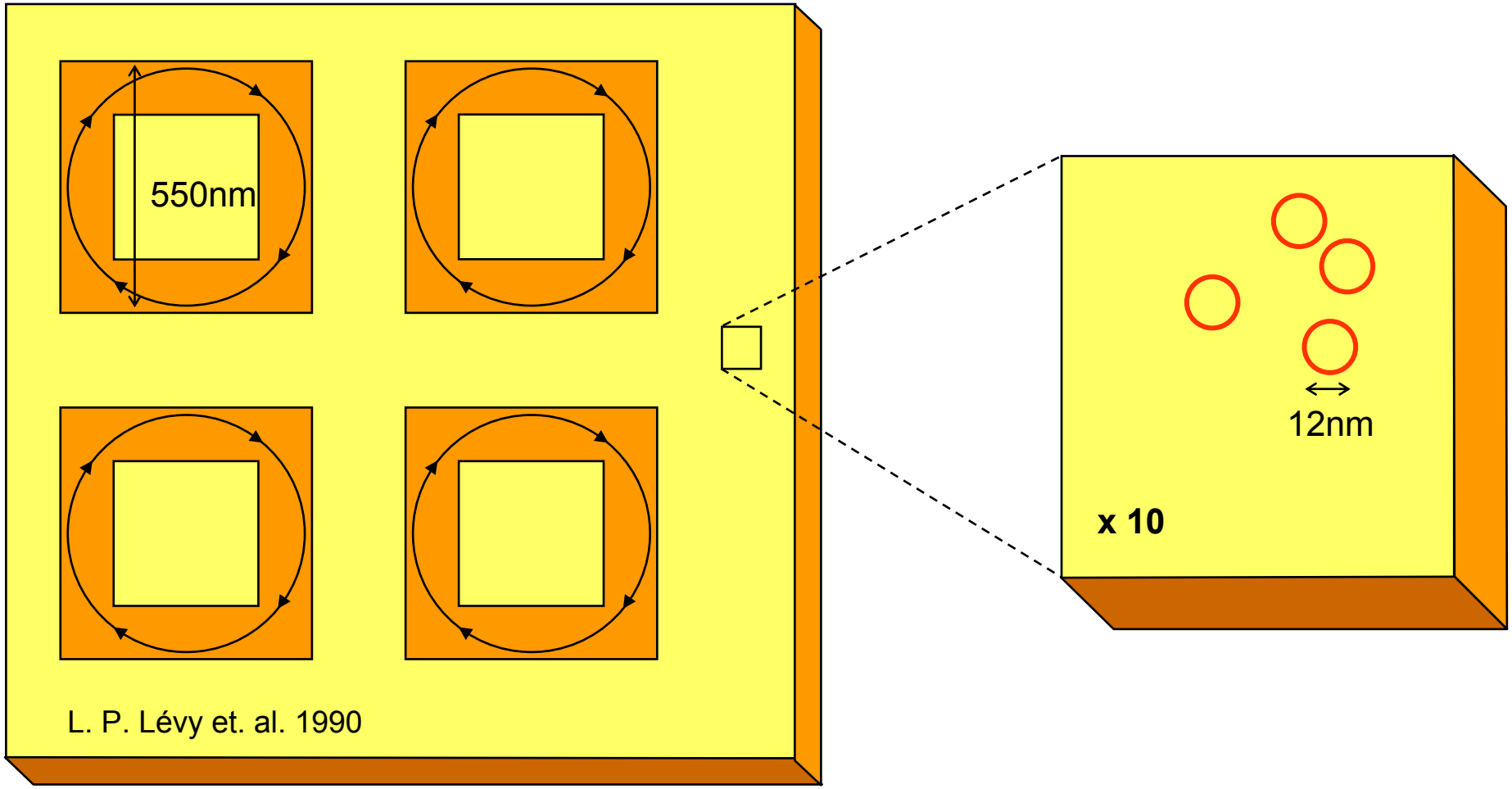
$h/e = B \cdot F = B \cdot r^2\pi$

$$r = \sqrt{\frac{h}{e \cdot B \cdot \pi}}$$

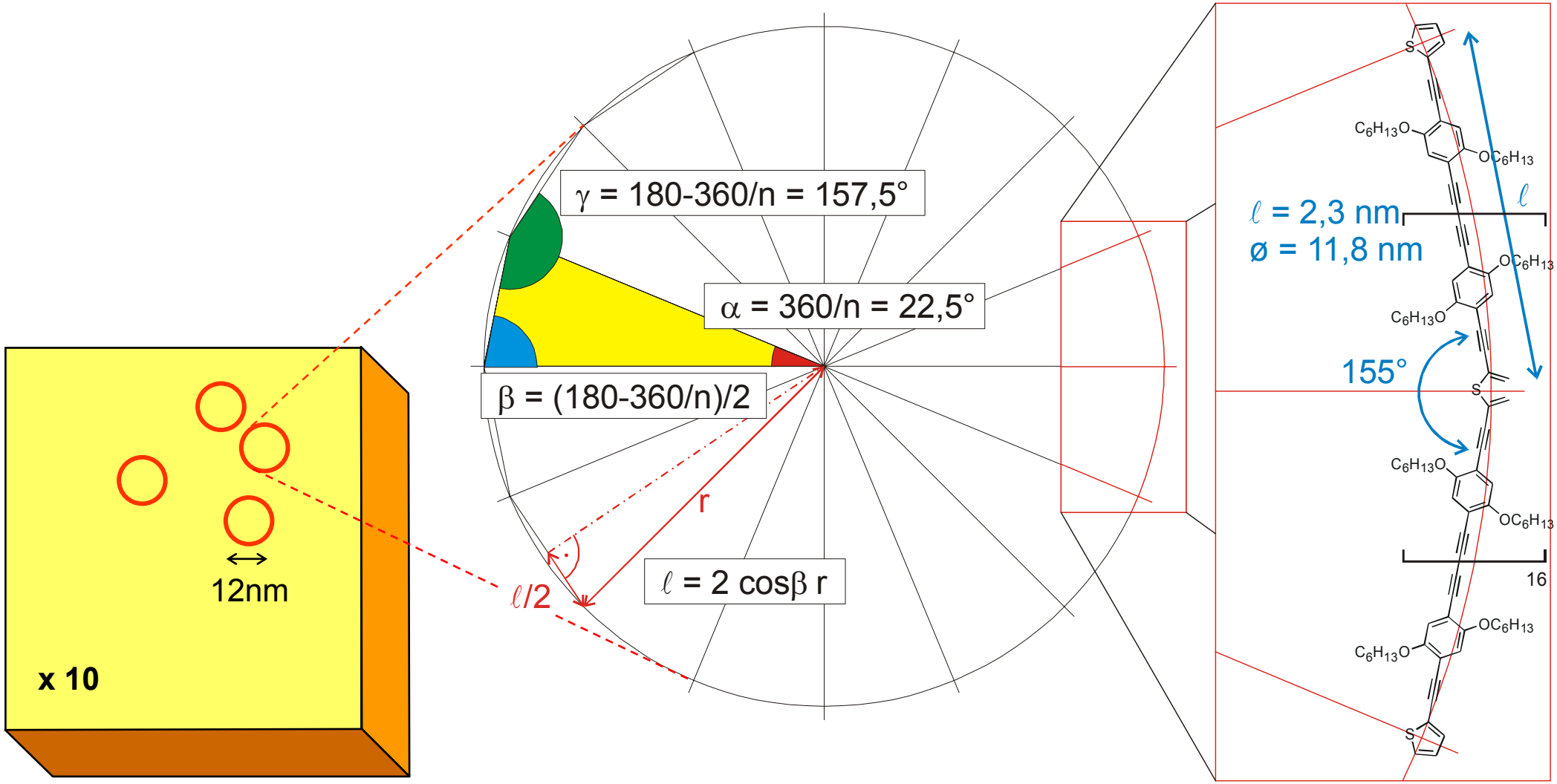


B = 30 T → r = 6.63x10^{-9}m
B = 35 T → r = 6.13x10^{-9}m
B = 40 T → r = 5.74x10^{-9}m

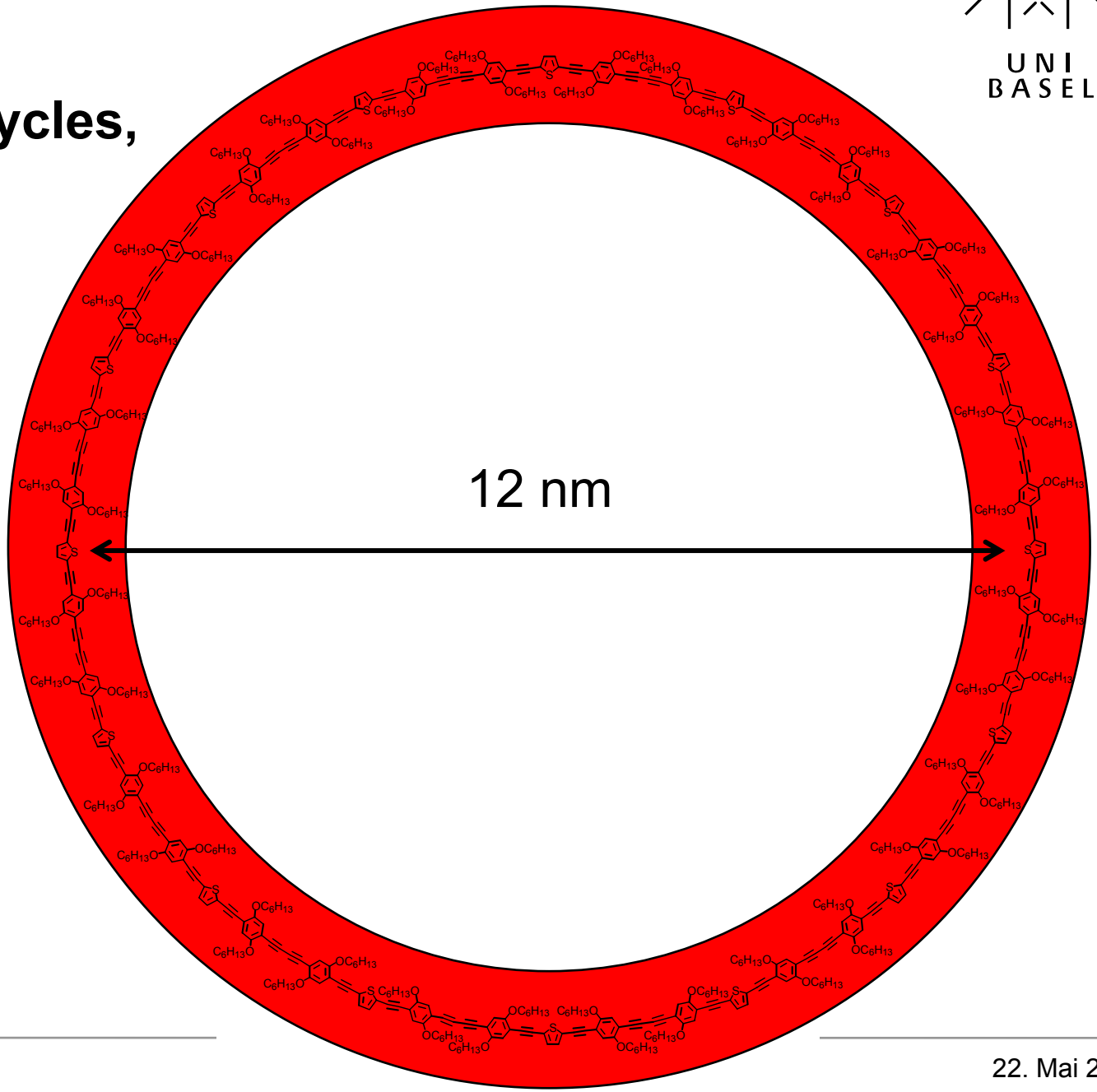
Giant Conjugated Cycles, Persistent Currents



Giant Conjugated Cycles, Persistent Currents



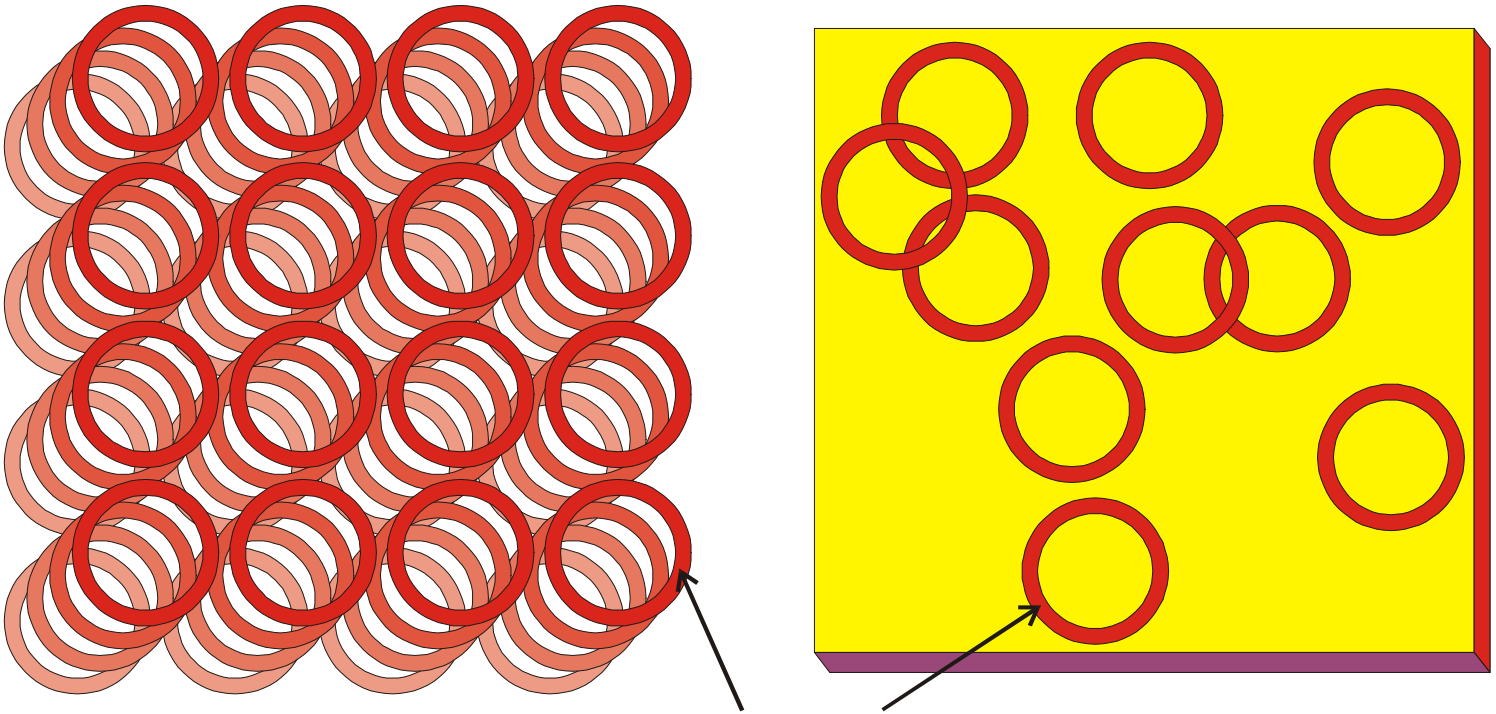
Giant Conjugated Cycles, Synthetic Target:



Persistent Current-Experiment:

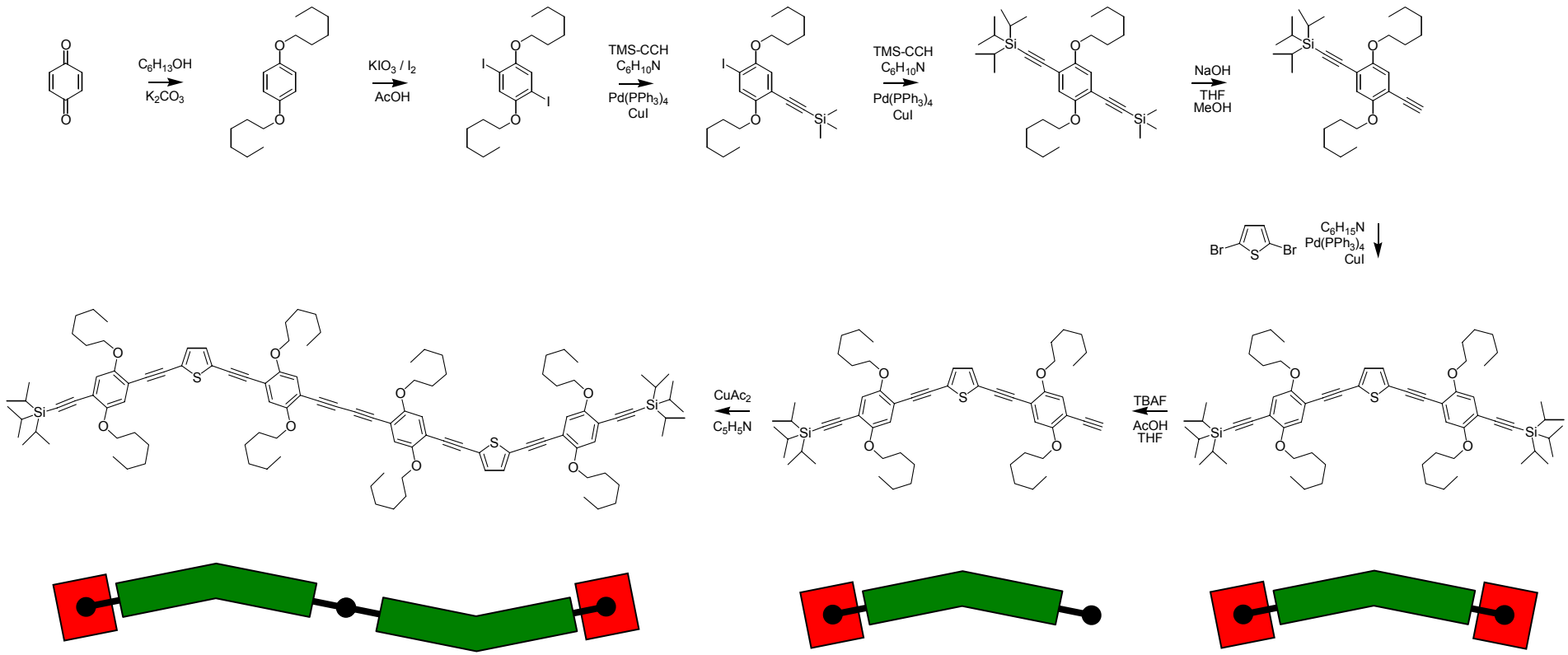
Magnetisation of a lot of ordered molecules in the crystal (3D),

Or on a lot of molecules laying on a flat surface (2D).

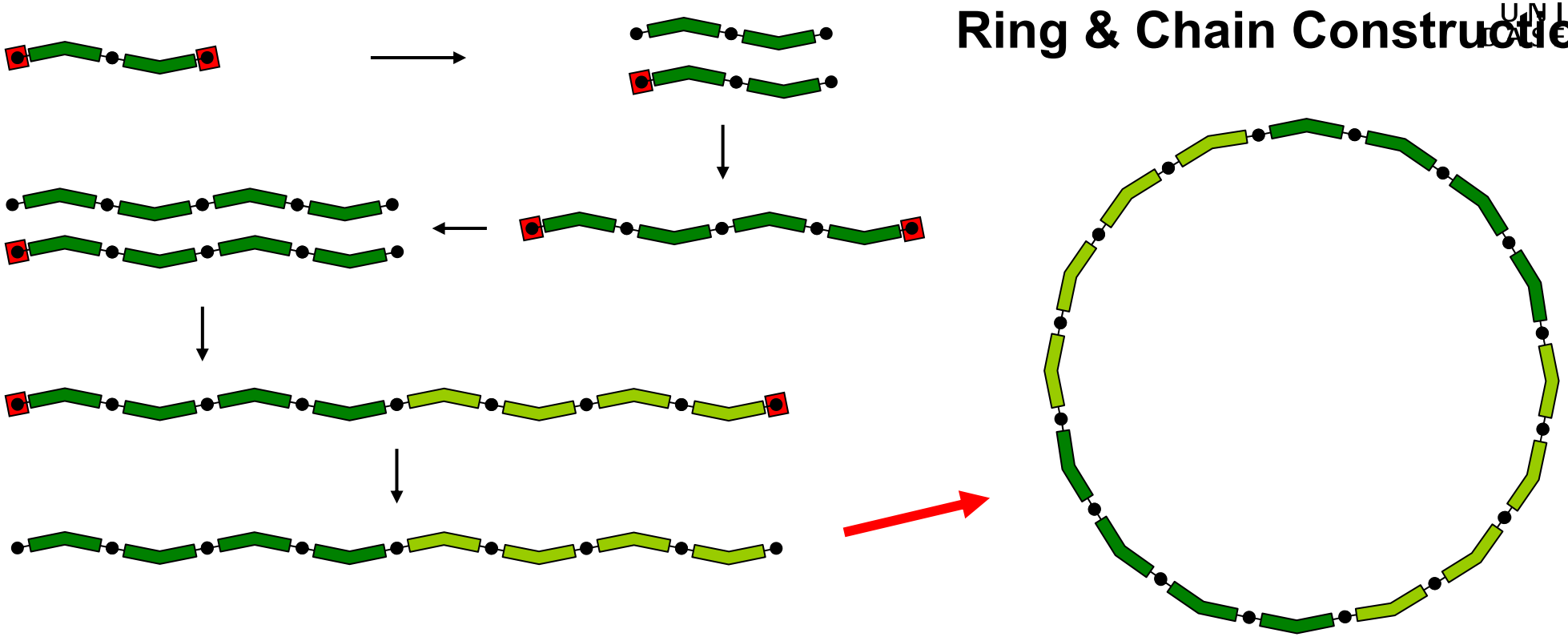


single molecule

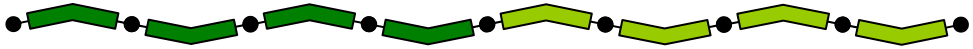
Ring Synthesis, Basic Building Block & Chain Construction



Ring & Chain Construction

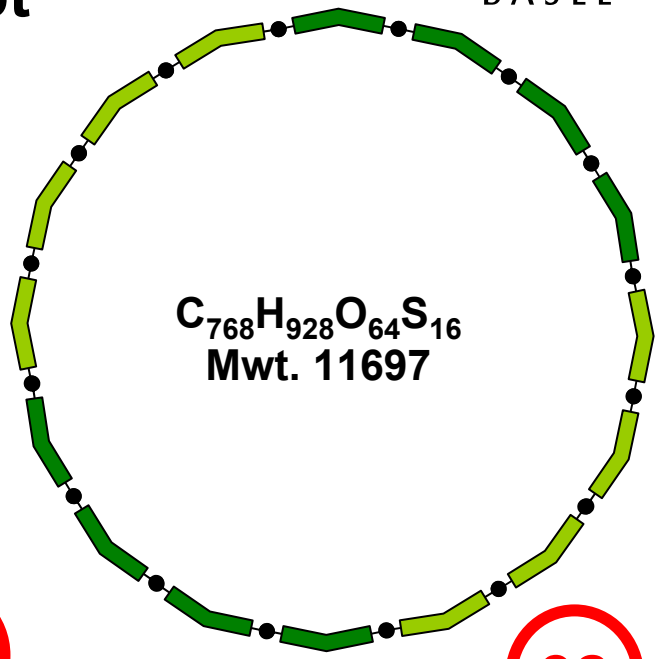


Ring Synthesis, First Attempt

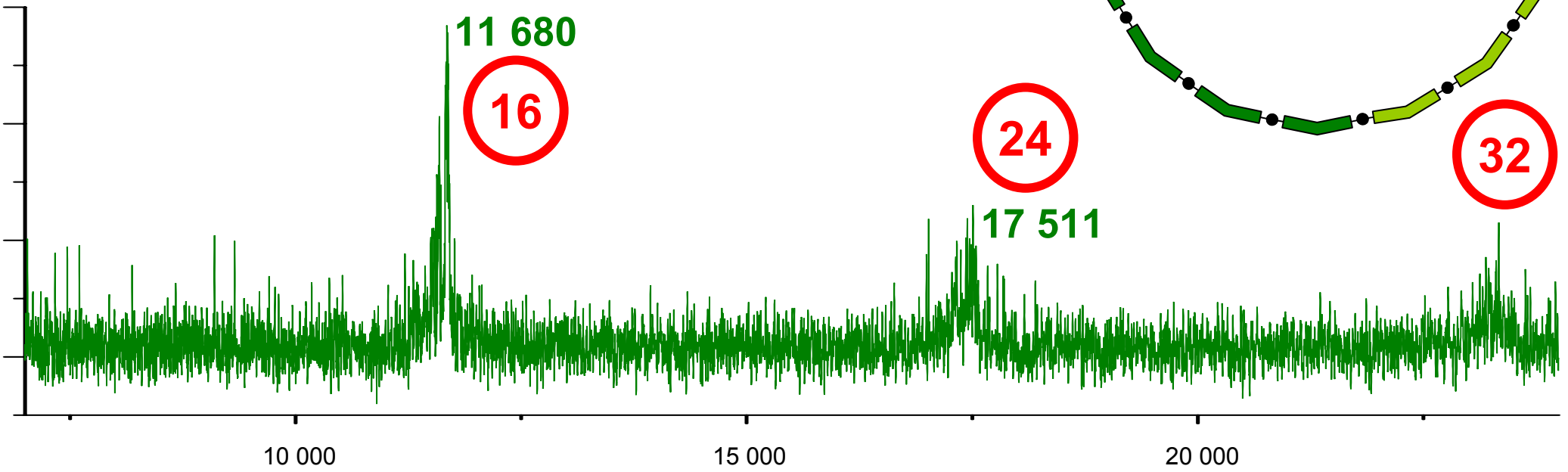


$C_{384}H_{466}O_{32}S_8$
Mwt. 5850

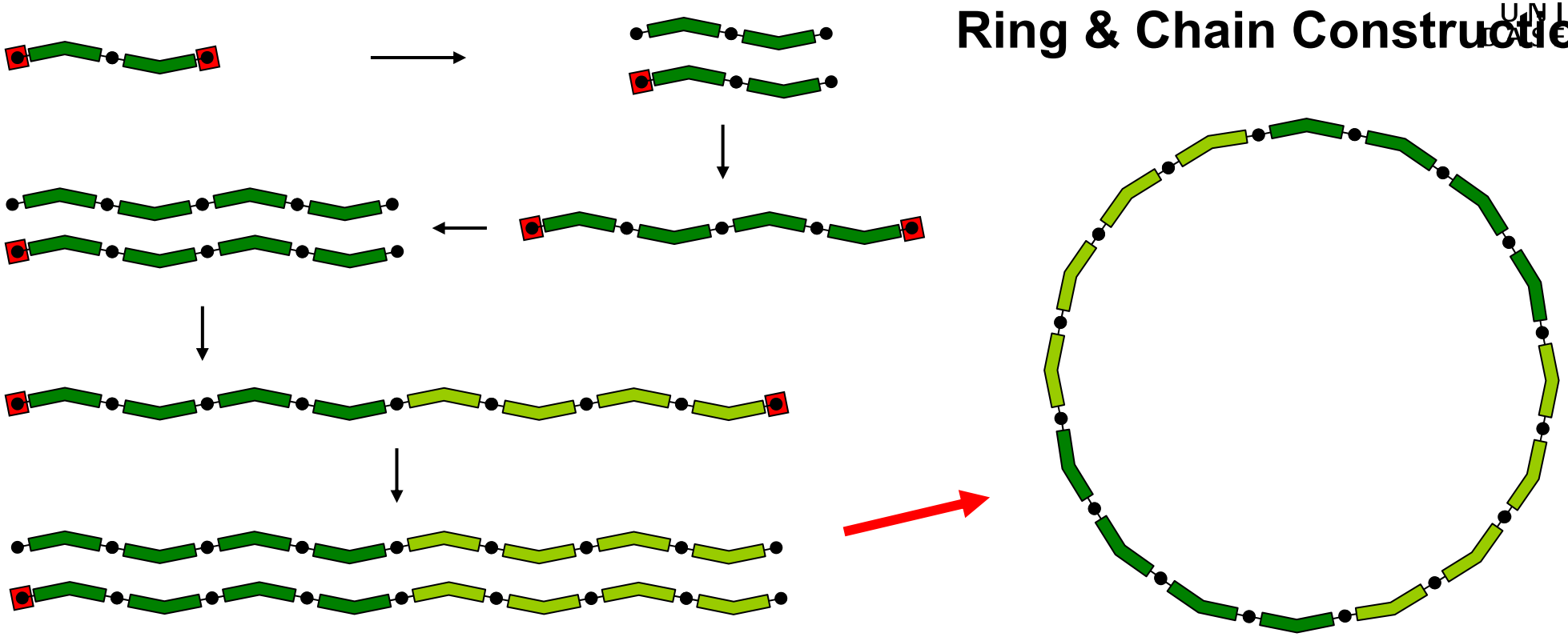
$2 \cdot 10^{-4}$M / C_5H_5N
7eq. $CuAc_2$
55°C, 14h



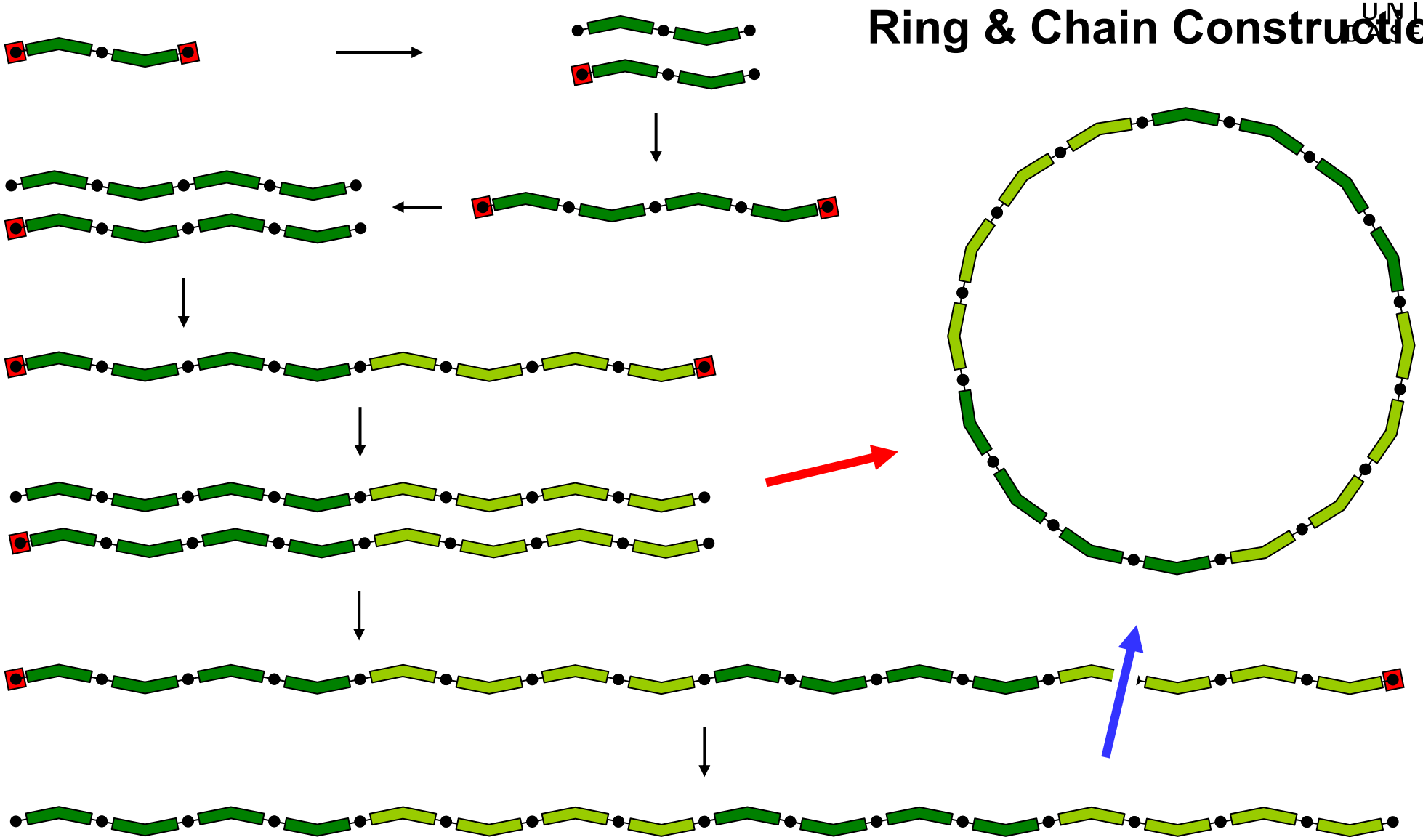
$C_{768}H_{928}O_{64}S_{16}$
Mwt. 11697



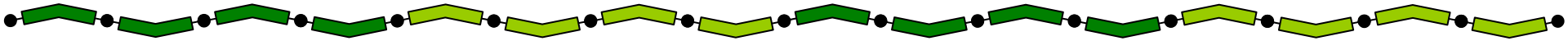
Ring & Chain Construction

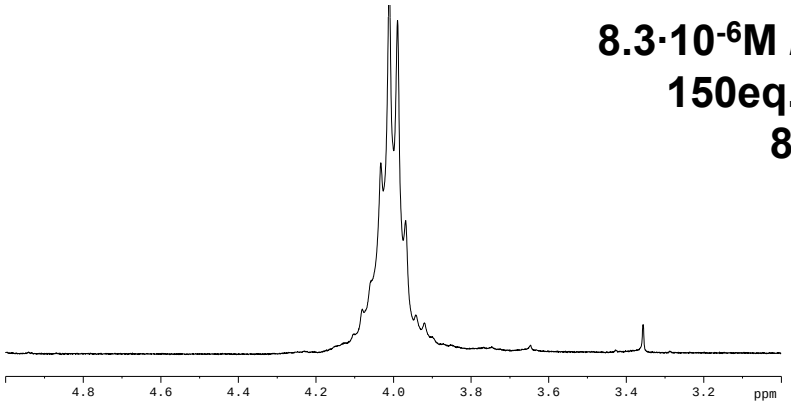


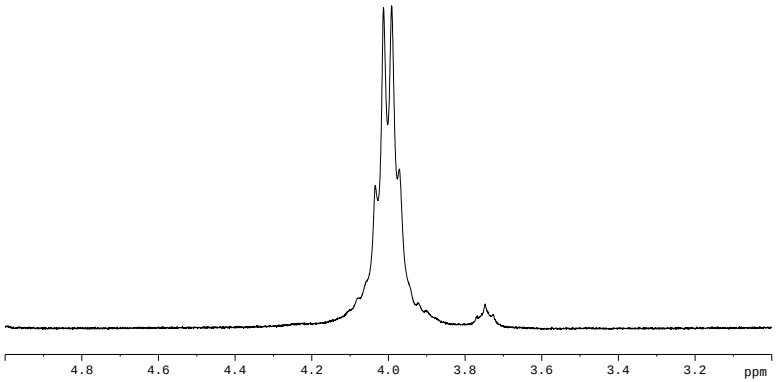
Ring & Chain Construction



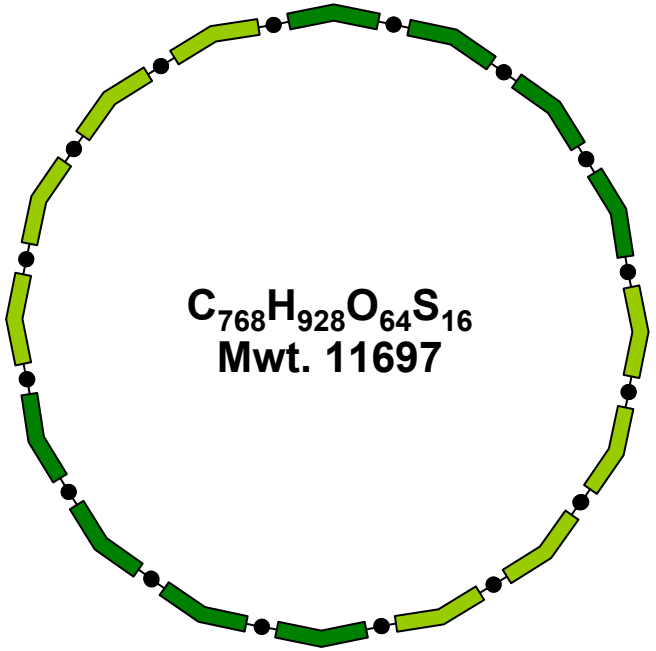
Ring Synthesis





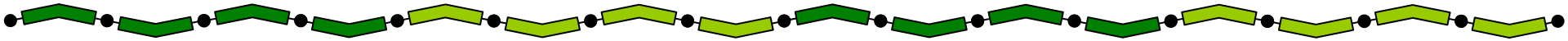


$8.3 \cdot 10^{-6}$M / C_5H_5N
150eq. $CuAc_2$
85°C, 7d



$C_{768}H_{928}O_{64}S_{16}$
Mwt. 11697

Ring Synthesis



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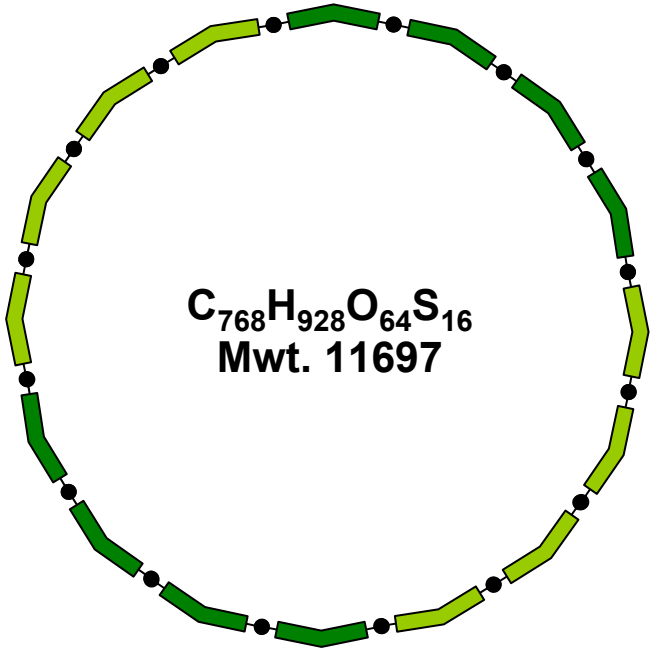
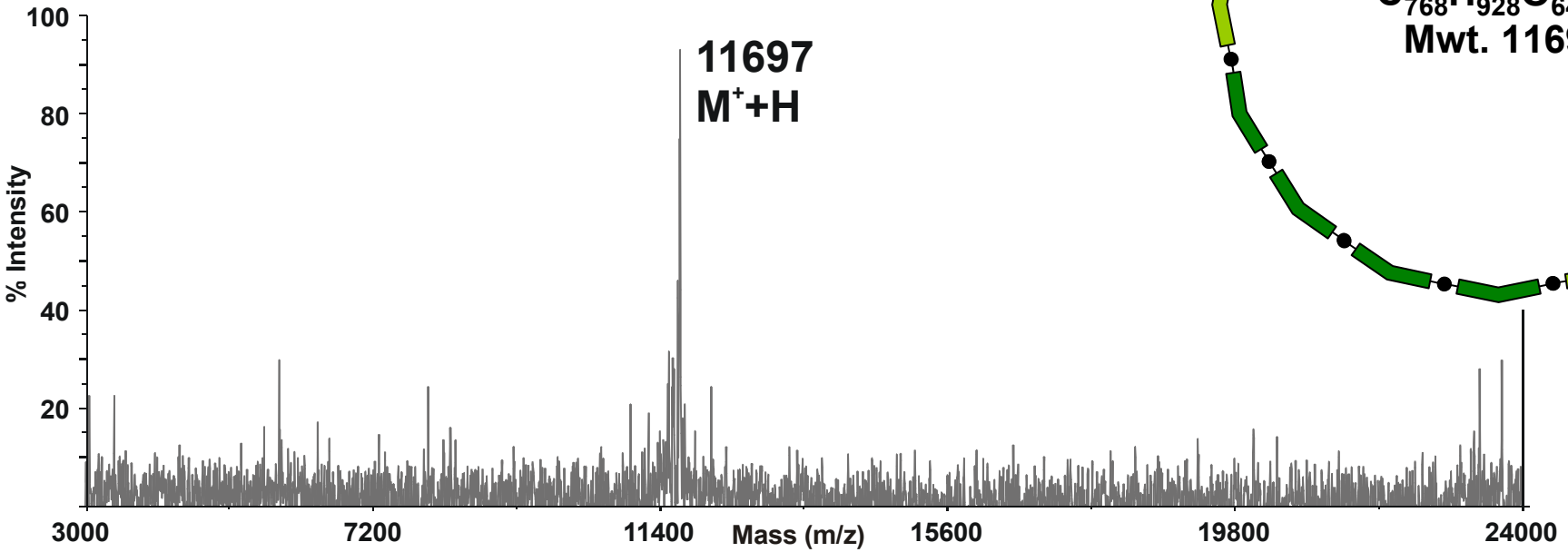
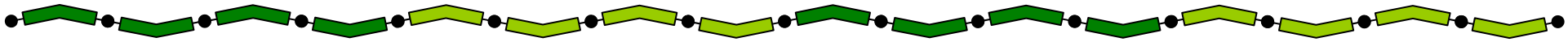
85°C, 7d

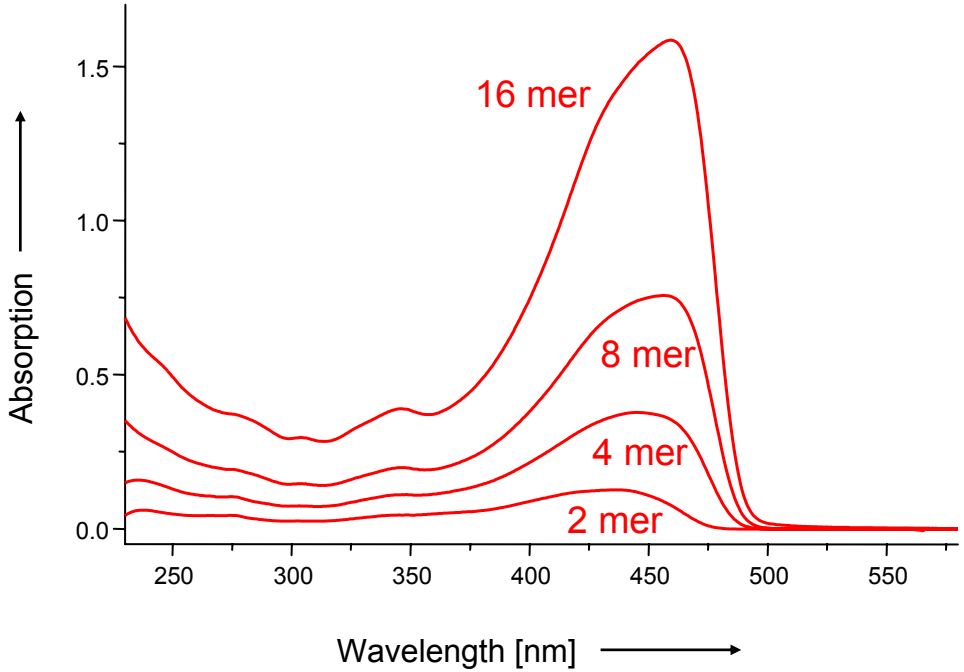


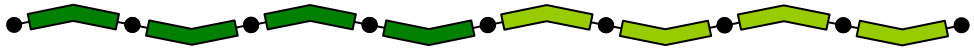


Ring, Optical Properties

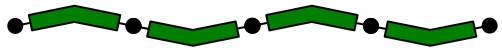


16 mer

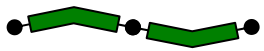




8 mer

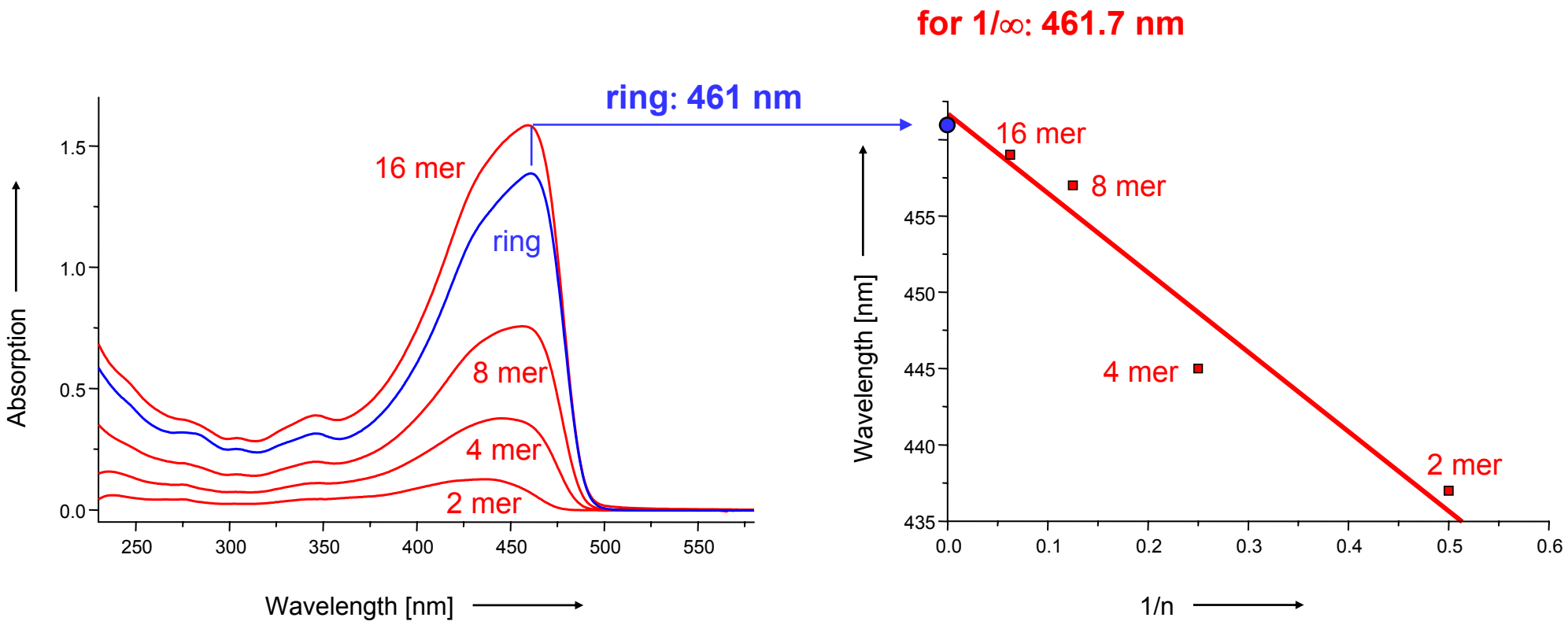


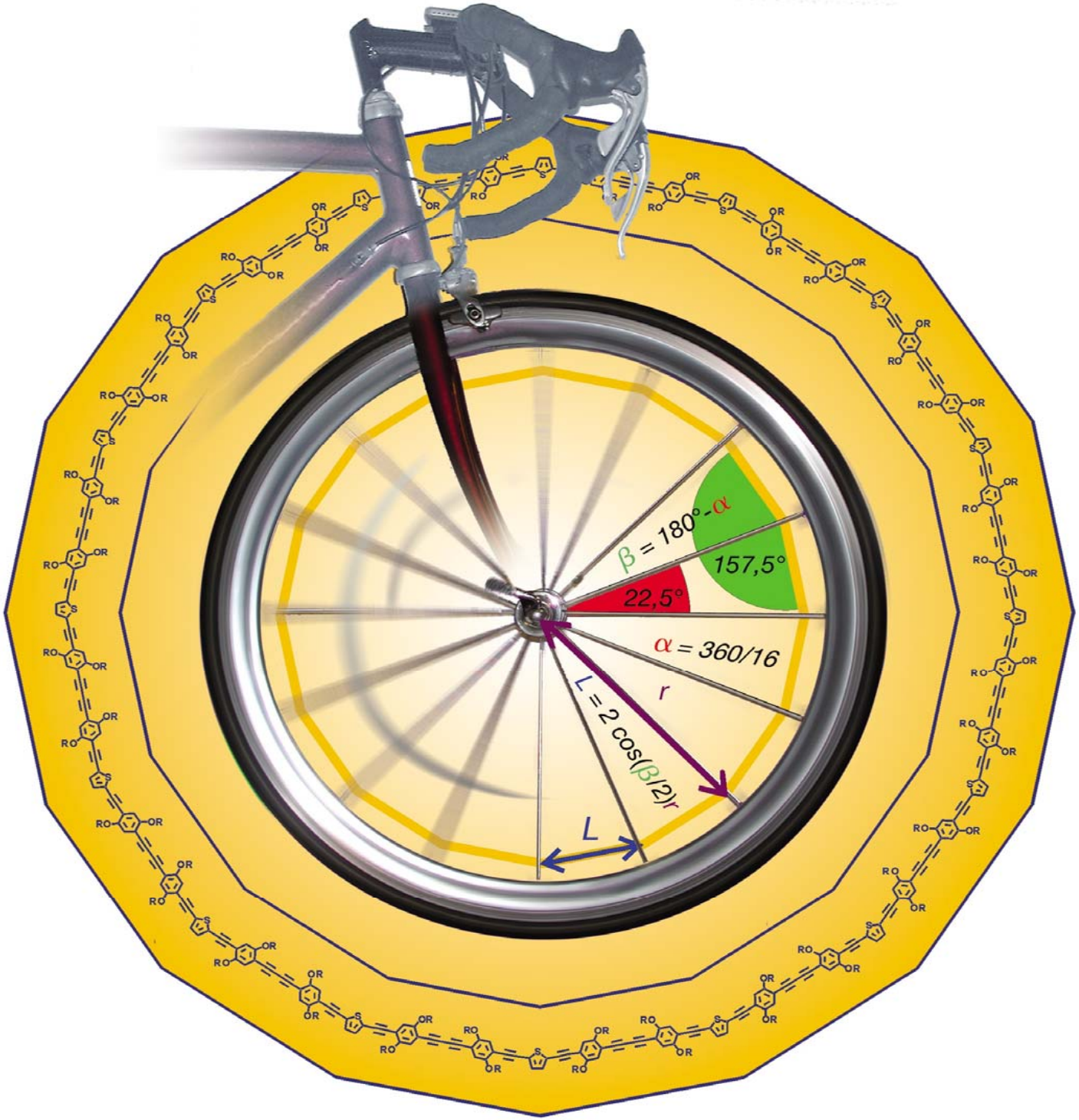
4 mer



2 mer

Ring, Optical Properties





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M. Mayor, C. Didschies; *Angew. Chem. Int. Ed. Engl.*, **2003**, *42*, 3176

Summary

roots and overview

current through single molecules

structure *vs.* e^- transport correlations

single molecules - symmetry

Tailor made resistance

designed electronic functions

single molecule electrochemistry

integration in CMOS technology

e^- mobility in nanoscale objects

giant macrocycle

Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Institut for Nanotechnology

UNI BASEL

People & Money

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Marcel Müri
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Katharina Fromm

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Rolf Ochs
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Jan Würfel
Daniel Secker

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Bo Han
Gabor Meszaros
Ilya Pobelov
Gabor Nagy
Udo Linke

CMOS integration:
(**Infineon Technologies**)
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Günter Schmid
Manuela Alba

Optical MCB:
(Würzburg)
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Sandra Dantscher

Rings on surfaces:
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Hilbert von Löhneysen
(**MPI Stuttgart**)
Klaus Kern
(**EPUL Lausanne**)
Harald Brune

2D-Arrays, electrochemical MCB & funtionlised CNTs :
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Michel Calame
Teresa Gonzalez
Jianhui Liao
Laetitia Bernard
Roman Huber
Dino Keller
Songmei Wu
Zheng-Ming Wu

STM investigations:
1) Self Assembly
(**Münster**)
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Harald Fuchs
Zhongcheng Mu

2) Surface Chemistry
Thomas Schimmel
Stefan Wallheim
Matthias Barczewski

3) Single Molecule Chemistry
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Meike Stöhr

CNT junction:
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Theory support:
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Ferdinand Evers
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Money:
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Swiss National Science Foundation
NCCR Nanoscience
DFG-Center for Functional Nanostructures CFN