Chapter 13: Transport properties of optically driven molecular switches

Elke Scheer, University of Konstanz

Exp: J. Boneberg, B. Briechle, A. Erbe, A. Karimi, Y. Kim, T, Kirchner, P. Leiderer, K. Luka-Guth, T. Pietsch, F. Strigl
Chem: A. Fedoseev, U. Groth, Th. Huhn, U. Steiner, D. Sysoiev, J. Wolf
Theo: W. Belzig, M. Bürkle, J.C. Cuevas, T. Frederiksen, A. Garcia-Lekue, T. Hellmuth, F. Pauly, L. Zotti

BADEN-WÜRTTEMBERG STIFTUNG Wir stiften Zukunft
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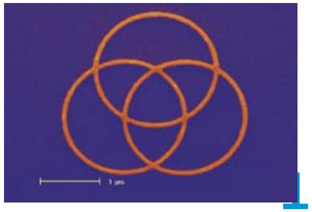


Outline

- **Foundations**

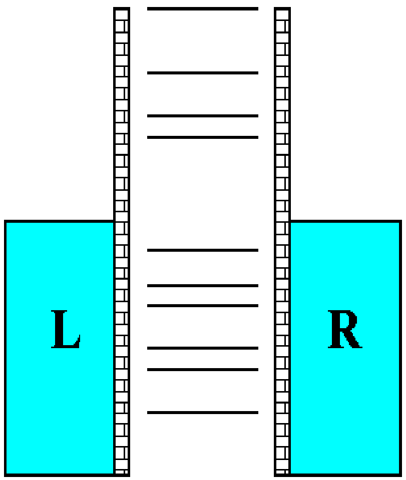
- Controllable Single-Molecule Junctions: Break Junction Technique
- Analysis of current-voltage characteristics: Resonant Level Model
- Inelastic Electron Tunneling Spectroscopy: Revealing junction configuration and some information on transmission coefficients

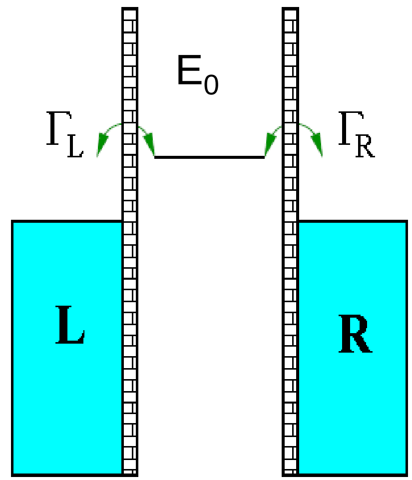
- **Optically activated molecular switches**

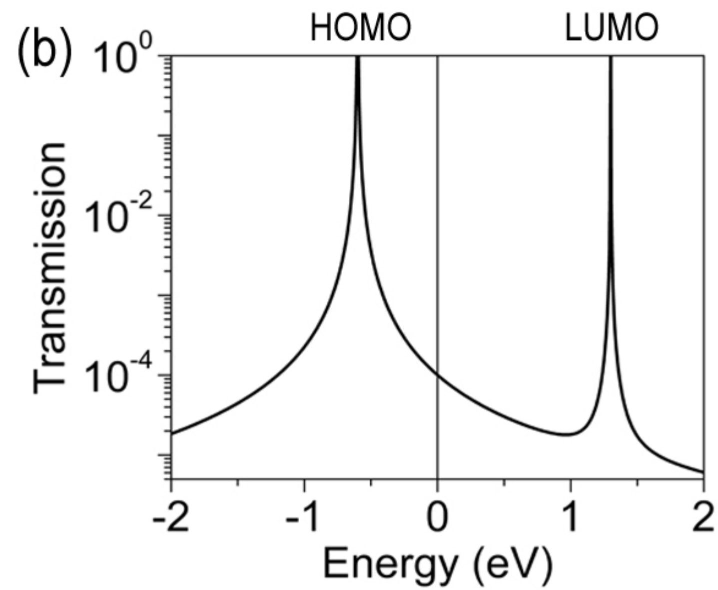
  Azobenzenes: Fano resonance

  Diarylethenes: Unconventional behavior of level alignment

Understanding IVs: Single-Level Model







$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E,V)\left[f(E - eV/2) - f(E + eV/2)\right] dE$$

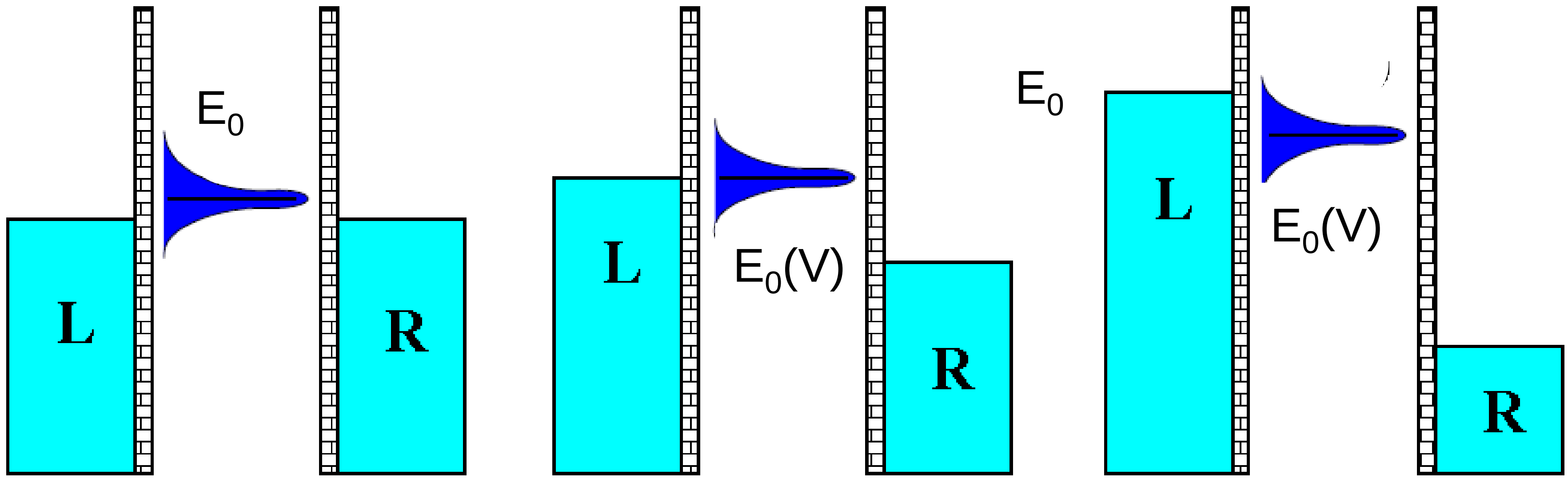
Landauer formula

$$T(E,V) = \frac{4\Gamma_L \Gamma_R}{[E - E_0(V)]^2 + [\Gamma_L + \Gamma_R]^2}$$

L. Zotti, Th. Kirchner, J. C. Cuevas, F. Pauly, Th. Huhn, J. Wolf, E. Scheer, A. Erbe, SMALL **6**, 1529 (2010)

See also: Huisman et al., Nano Lett. **9**, 3909 (2009)

Understanding IVs: Single-Level Model



$$I(V)=\frac{2e}{h}\int_{-\infty}^{\infty}T(E,V)\left[f(E-eV/2)-f(E+eV/2)\right]dE$$

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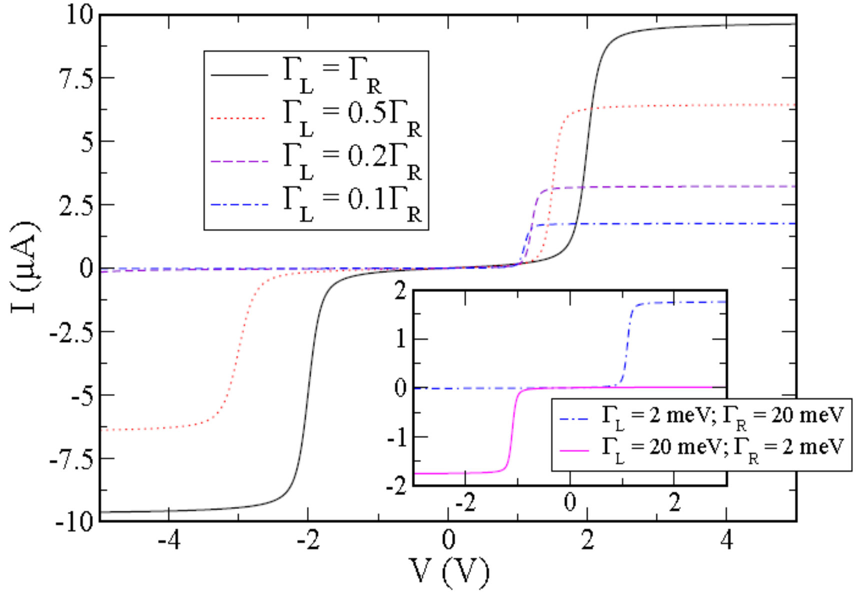
L. Zotti, Th. Kirchner, J. C. Cuevas, F. Pauly,
Th. Huhn, J. Wolf, E. Scheer, A. Erbe,
SMALL **6**, 1529 (2010)
See also: Huisman et al., Nano Lett. **9**, 3909 (2009)

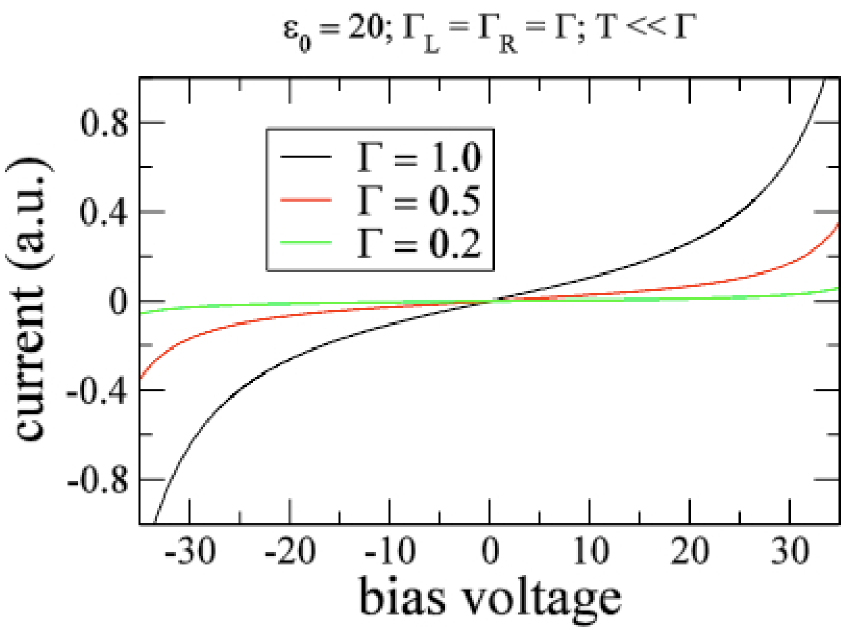
(Off-)resonant tunneling

Asymmetric coupling :
Asymmetric I-Vs

$$if \;\; \alpha = \Gamma_R / \Gamma_L$$

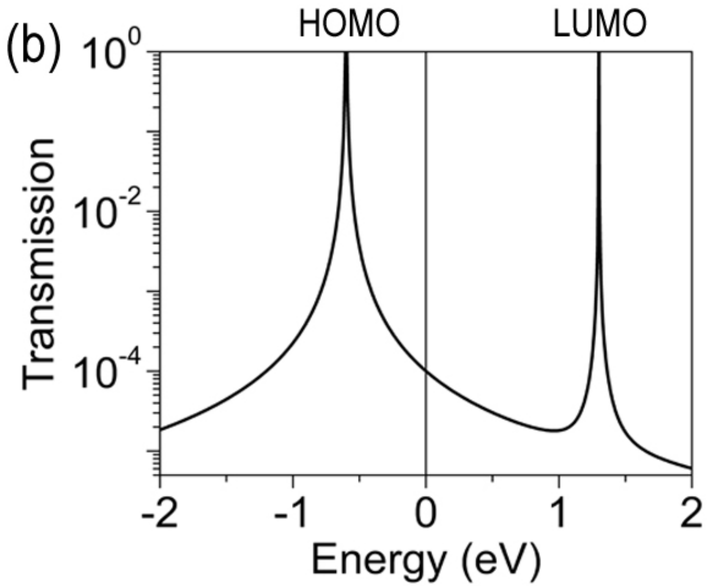


Off resonant case:
molecules as tunneling junctions



L. Zotti et al, Small 6 1529 (2010)

Resonant level model



Assumption: HOMO and LUMO well-separated $E_{LUMO}-E_{HOMO} >> \Gamma$

$$I(V) = \frac{2e}{h}\int_{-\infty}^{\infty} T(E,V)\left[f(E-eV/2) - f(E+eV/2)\right]dE$$

Landauer formula

$$T(E,V) = \frac{4\Gamma_{HOMO}{}^2}{[E-E_{HOMO}]^2 + 4\Gamma_{HOMO}{}^2} + \frac{4\Gamma_{LUMO}{}^2}{[E-E_{LUMO}]^2 + 4\Gamma_{LUMO}{}^2}$$

L. Zotti et al., Small **6**, 1529 (2010), E. Huisman et al., Nano Lett. **9**, 3909 (2009), W. Hong et al. Beilstein J. Nanotechology (2012), ...

Current-voltage characteristics and the single-level model: The role of the end-group / metal combination

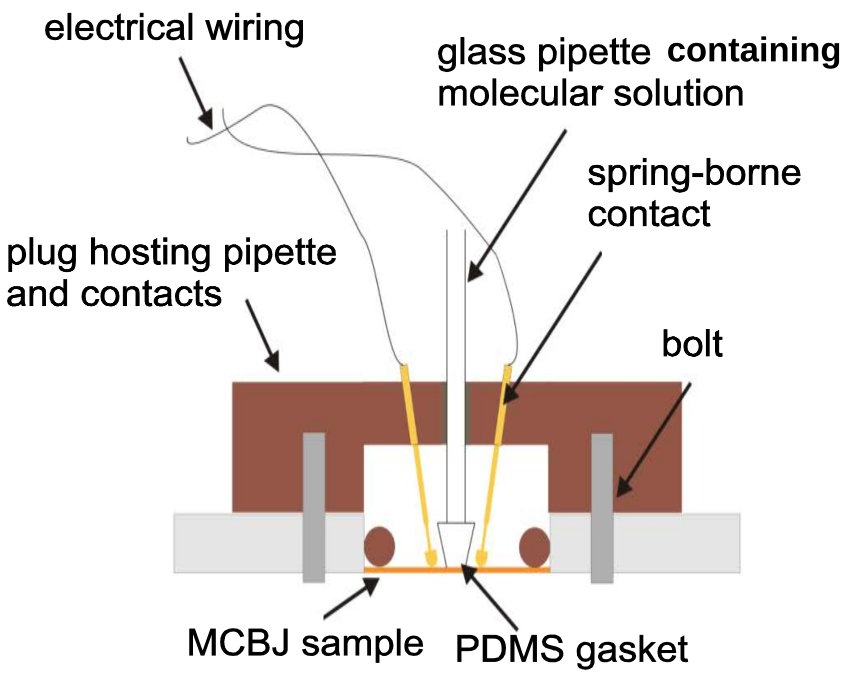
L. Zotti, Th. Kirchner, J. C. Cuevas, F. Pauly, Th. Huhn, J. Wolf, A. Erbe, Small 6, 1529 (2010)

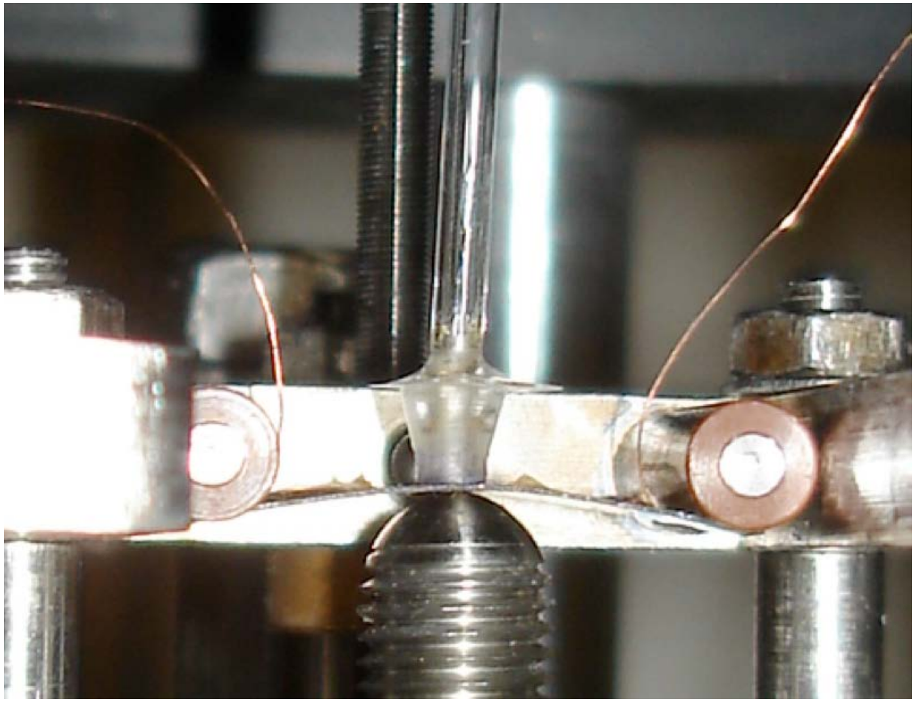
Y. Kim, H. Song, F. Strigl, H.-F. Pernau, T. Lee, E. Scheer, Phys. Rev. Lett. **106**, 196804 (2011).

Y. Kim, Th. Hellmuth, M. Bürkle, F. Pauly, E. Scheer, ACS Nano **5**, 4104 (2011).

Liquid MCBJ

Characterization of molecules in liquid environment

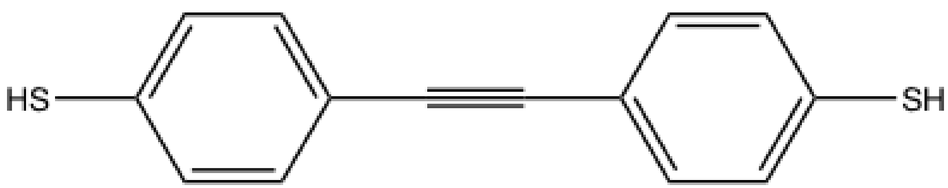




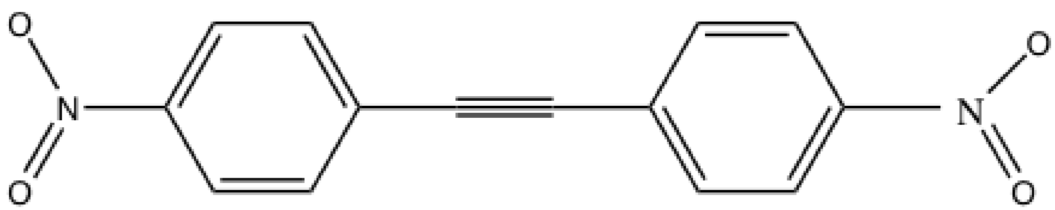
See also: L. Grüter et al., Small **1**, 1067 (2005)

Role of linker groups: simple molecules

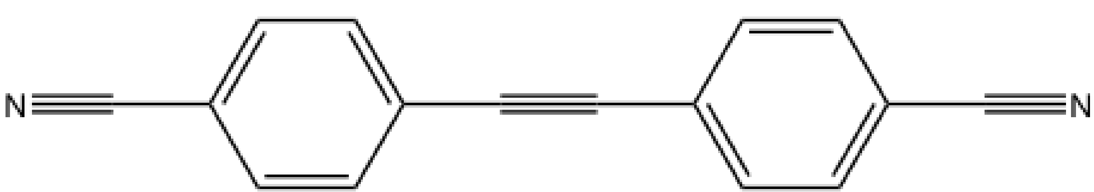
- Basic molecule: Bis-tolane
- Conjugated => conductive
- Change of linker groups



BTT: Bis-thiotolane



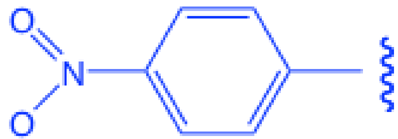
BNT: Bis-nitrotolane



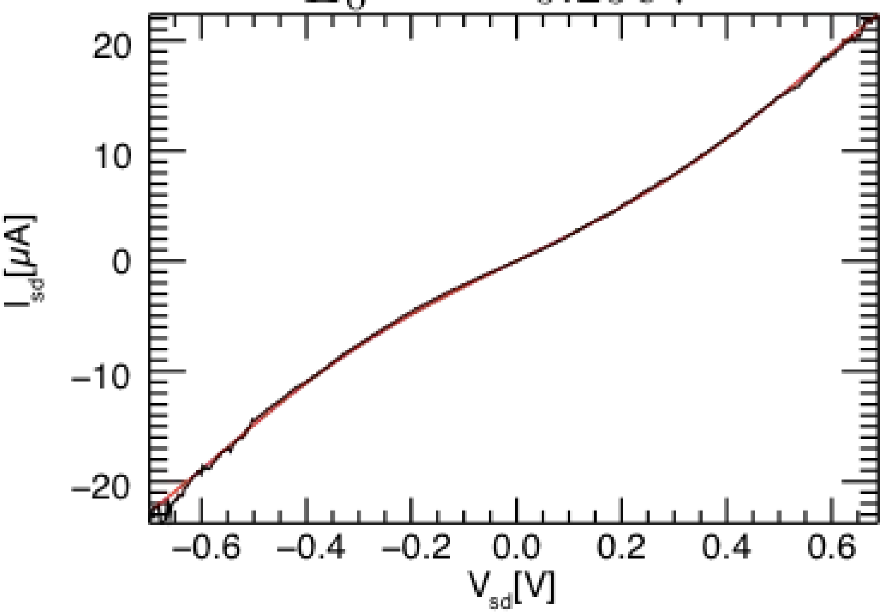
BCT: Bis-cyanotolane

IV curves with various linkers

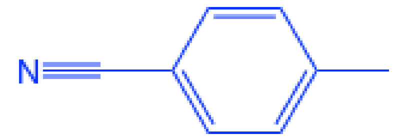
Nitro



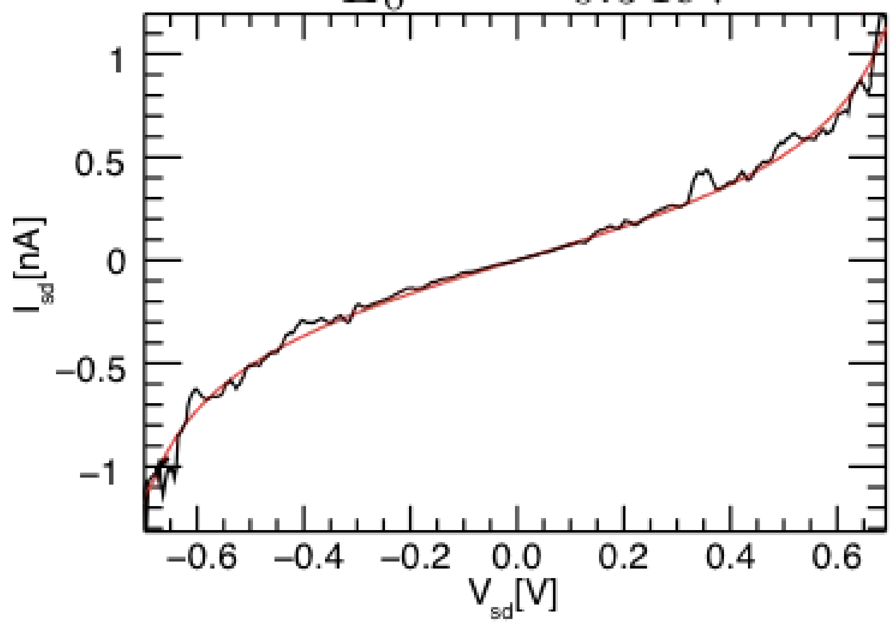
$$\Gamma_L = \Gamma_R = 0.094\text{eV}$$
$$E_0 = 0.29\text{eV}$$



Cyano



$$\Gamma_L = \Gamma_R = 0.85\text{meV}$$
$$E_0 = 0.54\text{eV}$$



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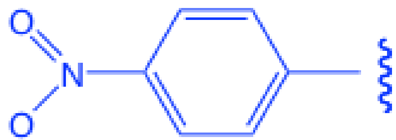
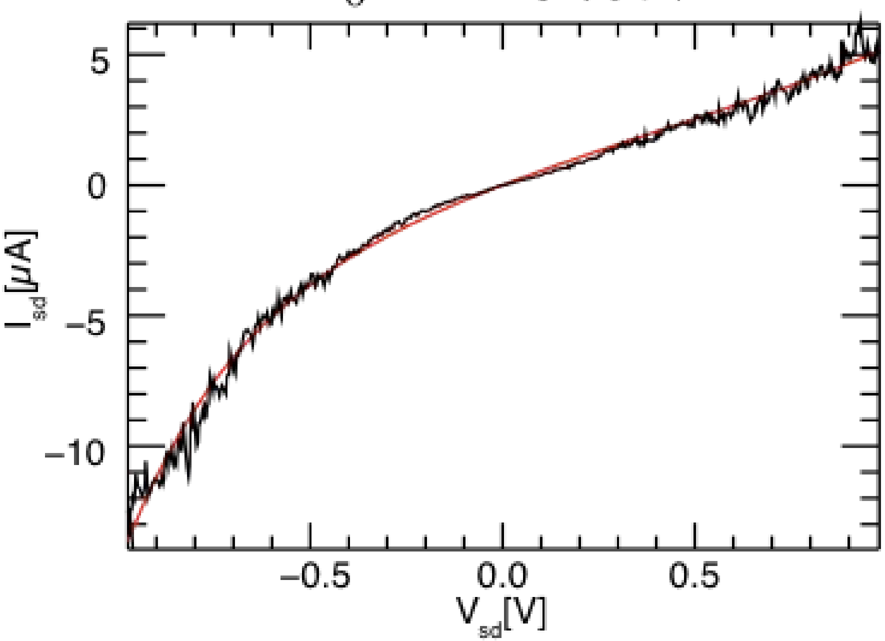
Asymmetric coupling

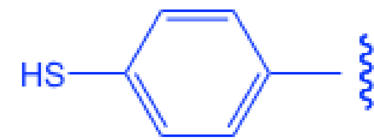
Nitro



$$\Gamma_L = 0.13\text{eV}$$
$$\Gamma_R = 0.09\text{eV}$$
$$E_0 = 0.79\text{eV}$$

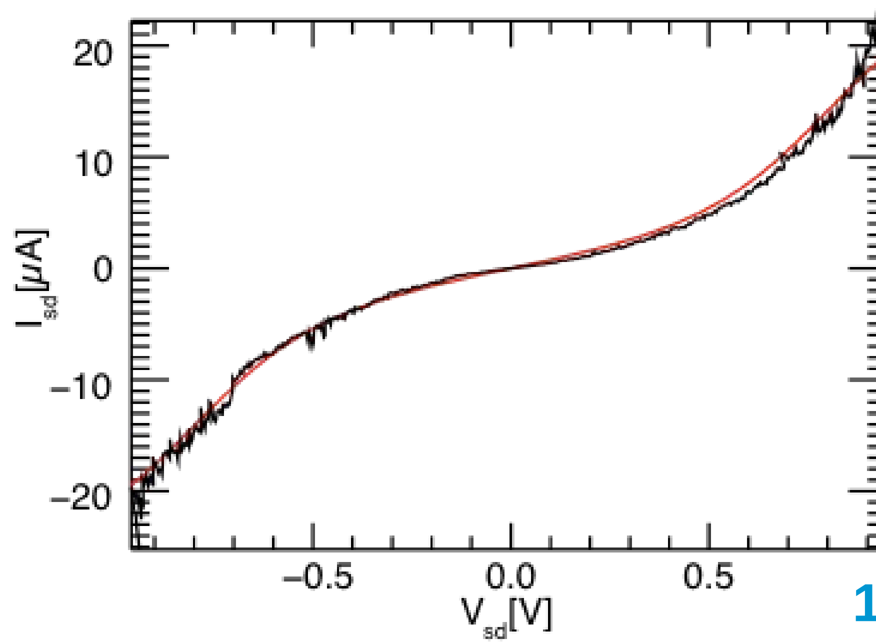


Comparison to thiol



✓ symmetric curves

$$\Gamma_L = \Gamma_R = 0.065\text{eV}$$
$$E_0 = 0.4\text{eV}$$



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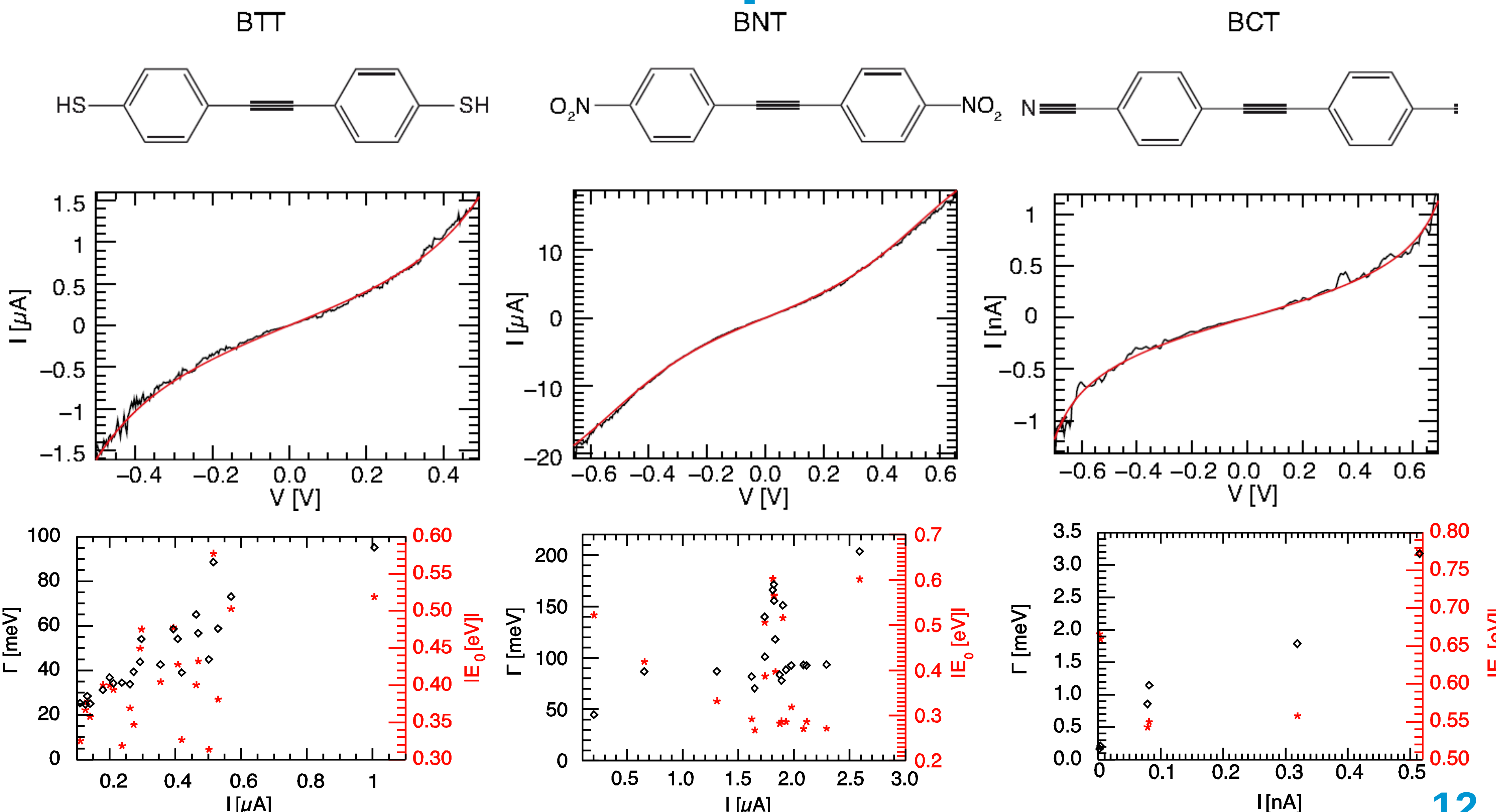
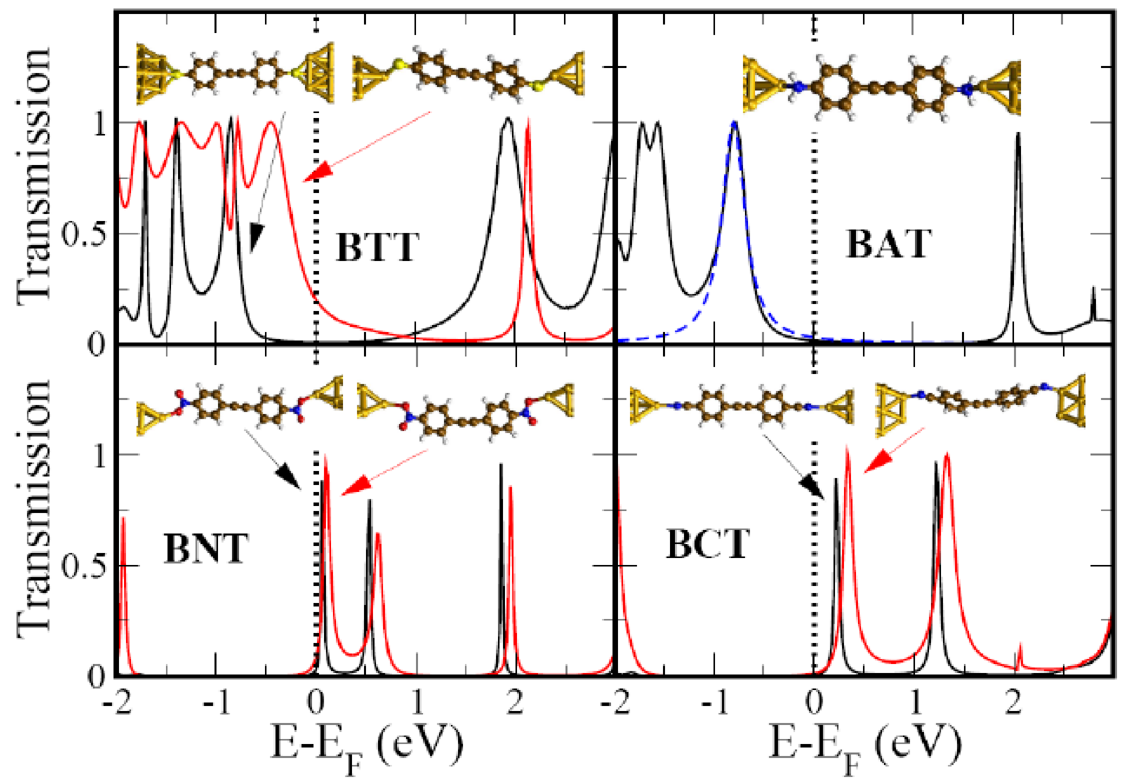
Statistical comparison of linkers



L. Zotti, Th. Kirchner, J. C. Cuevas, F. Pauly, Th. Huhn, J. Wolf, E. Scheer, A. Erbe, SMALL **6**, 1529 (2010)

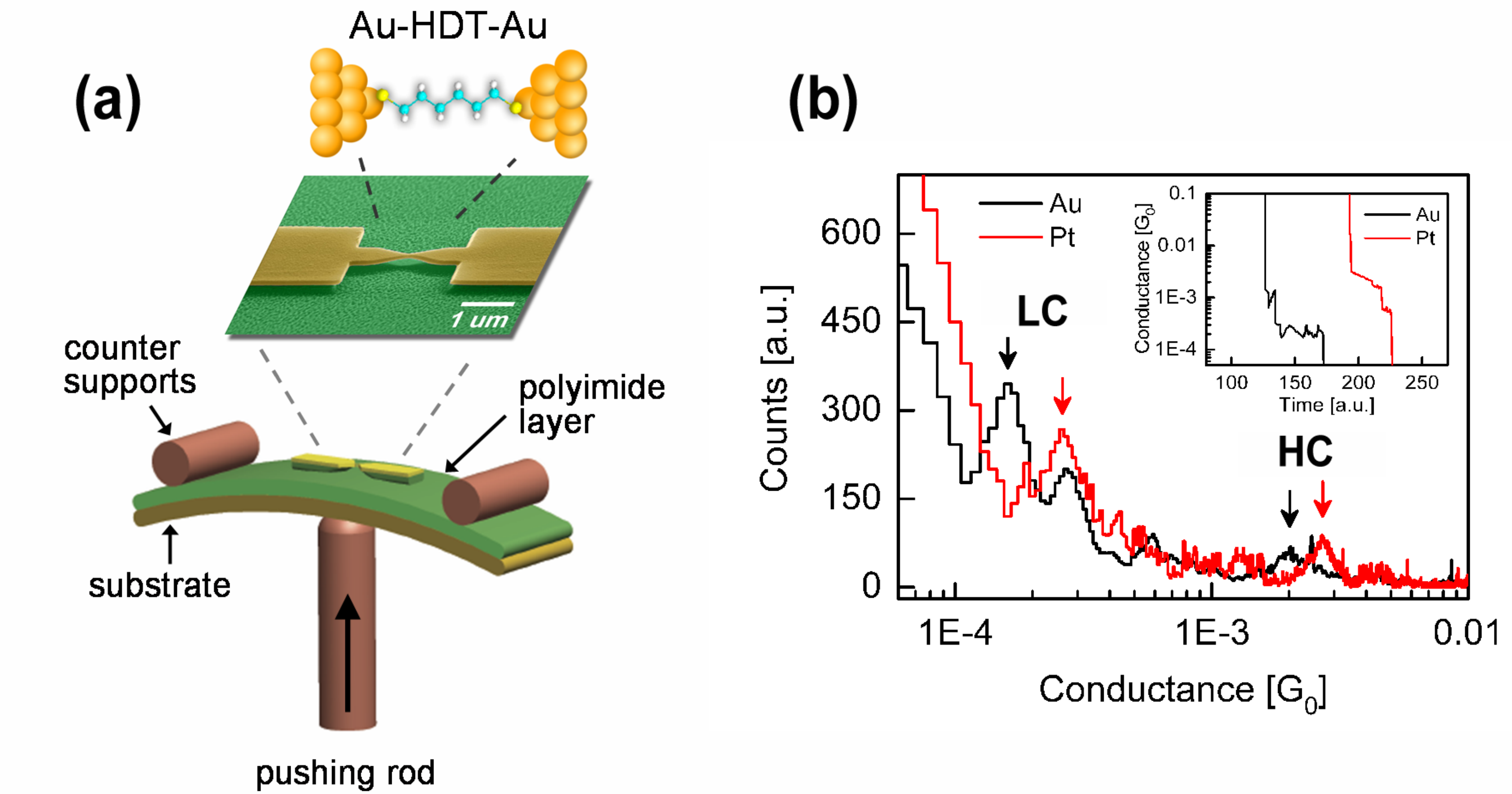
Transmission function of molecular junctions

- Quantum chemistry & DFT
- Approximation to single Lorentzian valid
- Linkers determine nature of transport
- BTT & BAT: HOMO
- BNT & BCT: LUMO



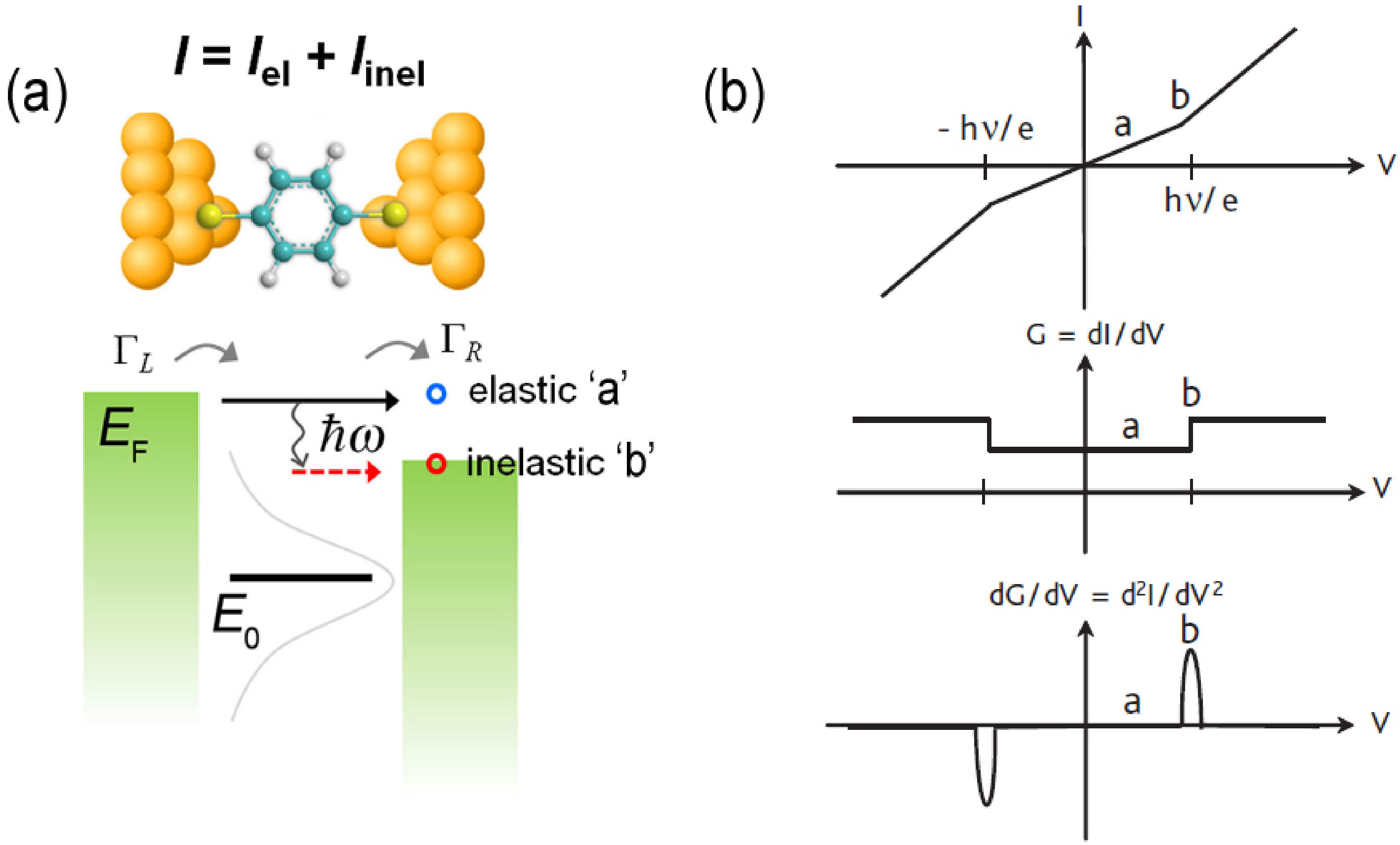
L. Zotti, Th. Kirchner, J. C. Cuevas, F. Pauly, Th. Huhn, J. Wolf, E. Scheer, A. Erbe, SMALL **6**, 1529 (2010)

MCBJ at low temperature: Opening Traces and Conductance Histograms



Y. Kim, F. Strigl, H.-F. Pernau, H. Song, T. Lee, E. Scheer, Phys. Rev. Lett. **106**, 196804 (2011)

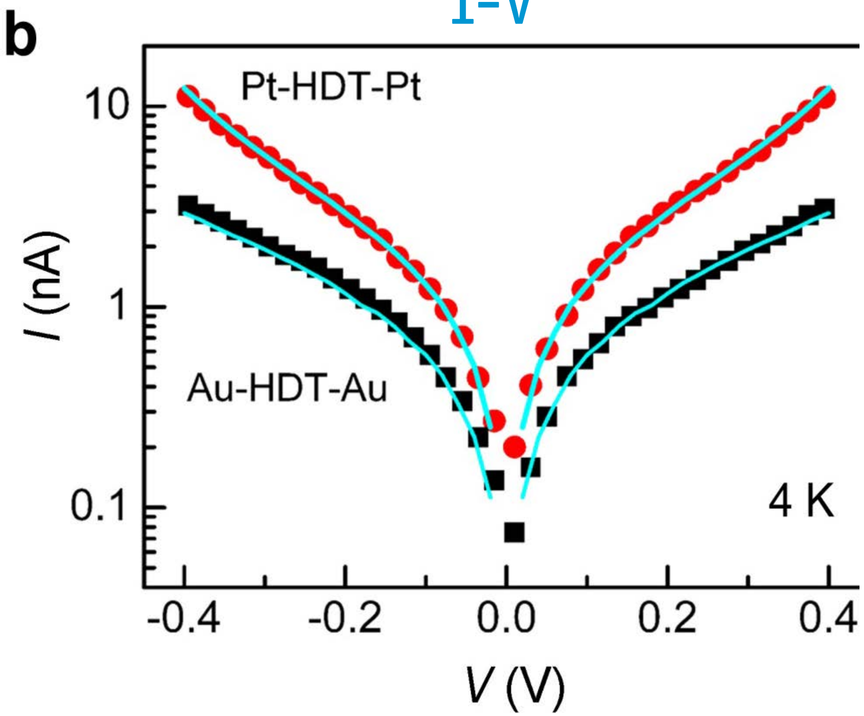
Inelastic Electron Tunneling Spectroscopy (IETS)



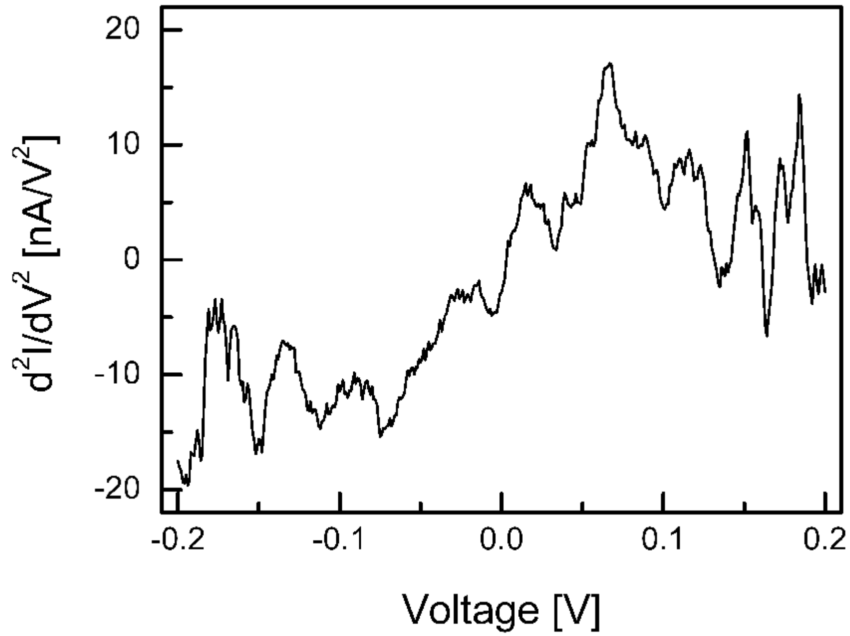
M. A. Reed, Mat. Today (2008), Troisi & Ratner, Small (2008), Arroyo et al., Nano Lett. (2010)

Examples: I-Vs and IETS @ 4.2 K

I-V



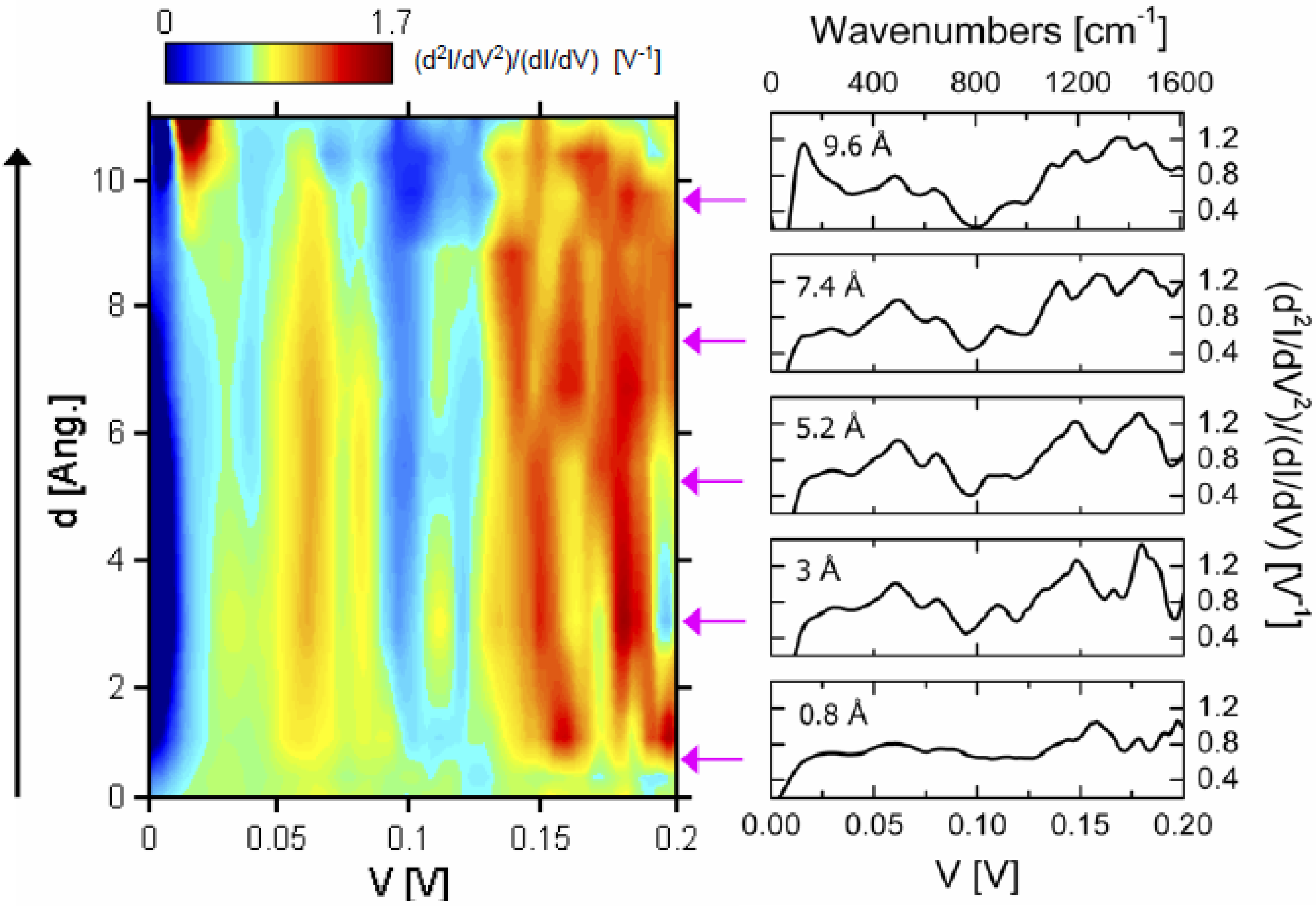
d²I/dV²



Au-HDT-Au: $\Gamma_{L,R} = 120$ meV, $E_0 = 2.35$ eV

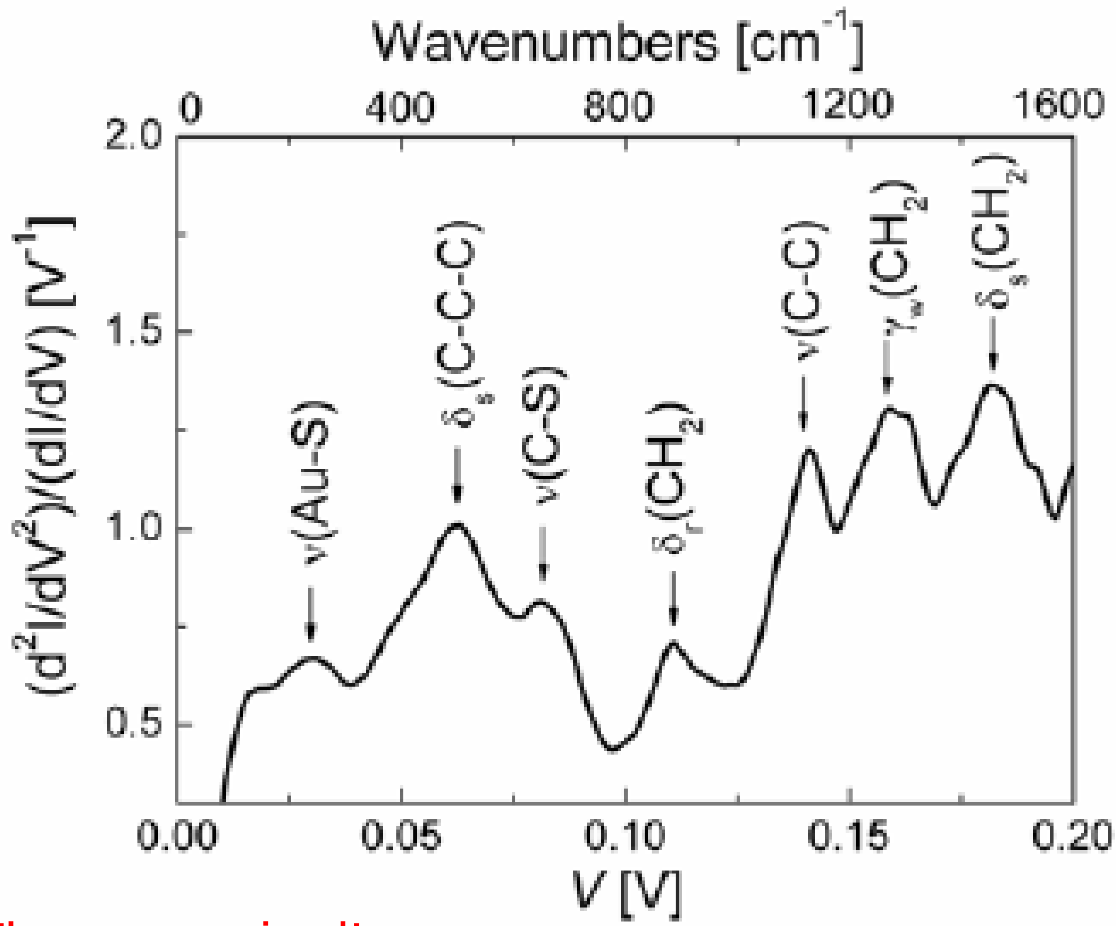
Pt-HDT-Pt: $\Gamma_{L,R} = 110$ meV, $E_0 = 1.93$ eV

Au-HDT-Au under stretching



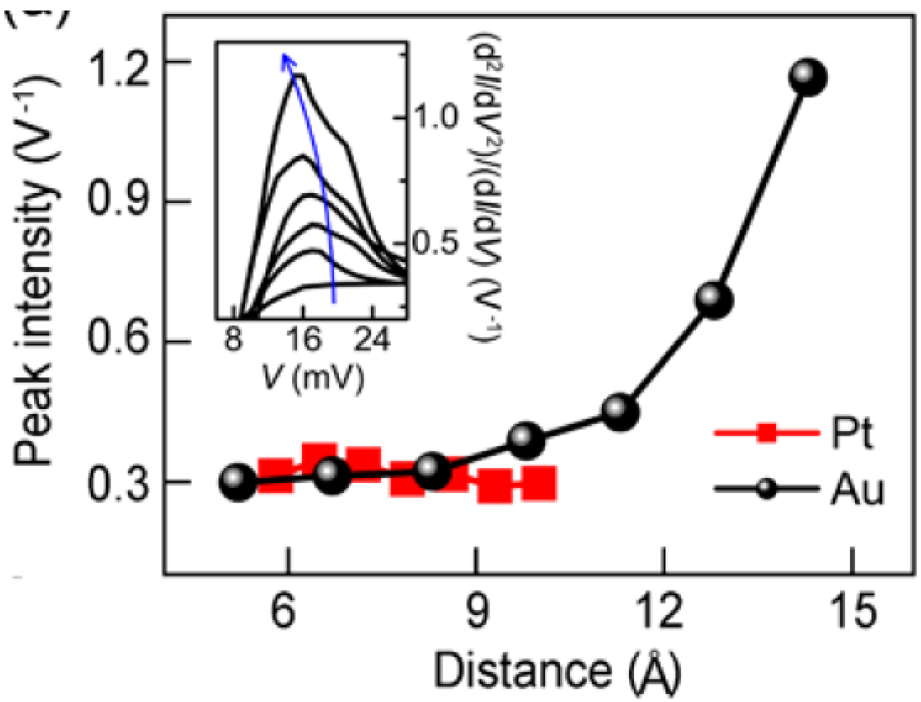
-> Not all modes observable in any configuration

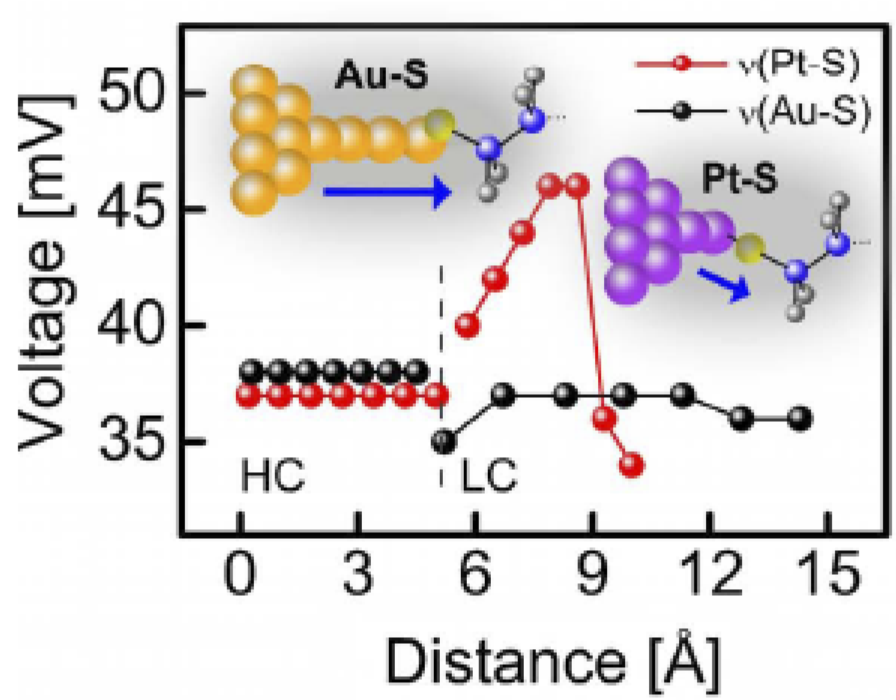
Assignment of modes



-> Theory required!

Role of contact metal: Pt-HDT-Pt vs. Au-HDT-Au



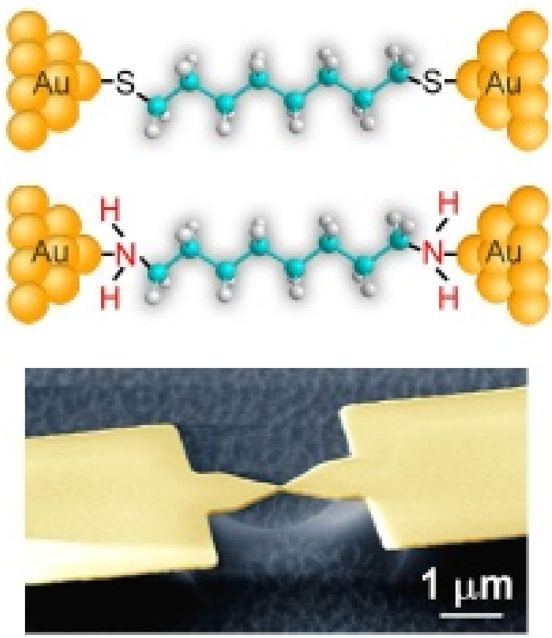


Amplitude of Au phonon mode increases, Pt mode remains constant

Energy of Au-S mode constant, Pt-S: „guitar string“ -> chain formation for Au, no chains for Pt

Y. Kim, F. Strigl, H.-F. Pernau, H. Song, T. Lee, E. Scheer, Phys. Rev. Lett. **106**, 196804 (2011)

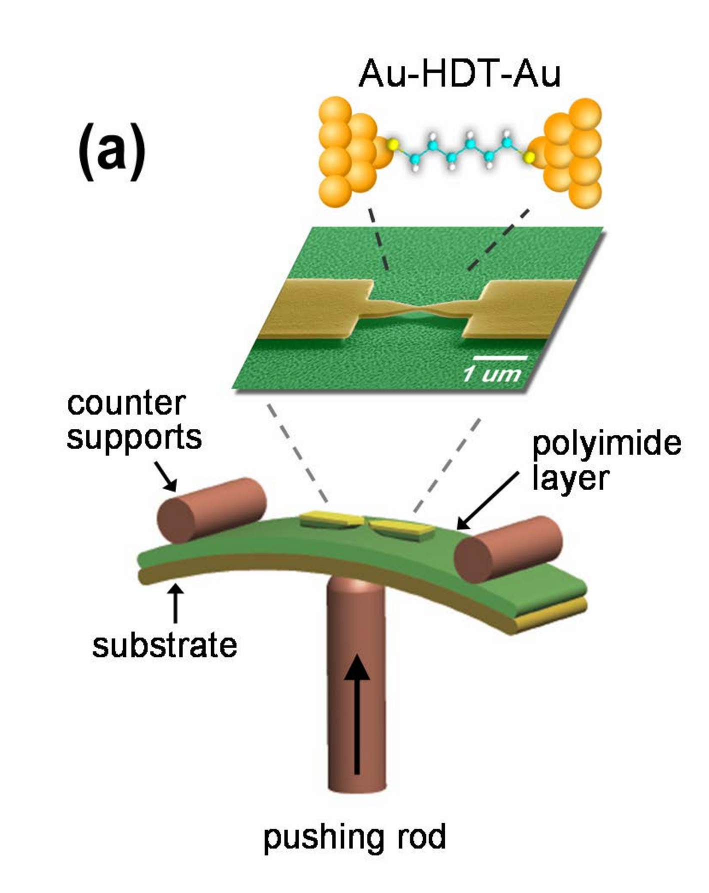
I-Vs and IETS of model molecules under stretching

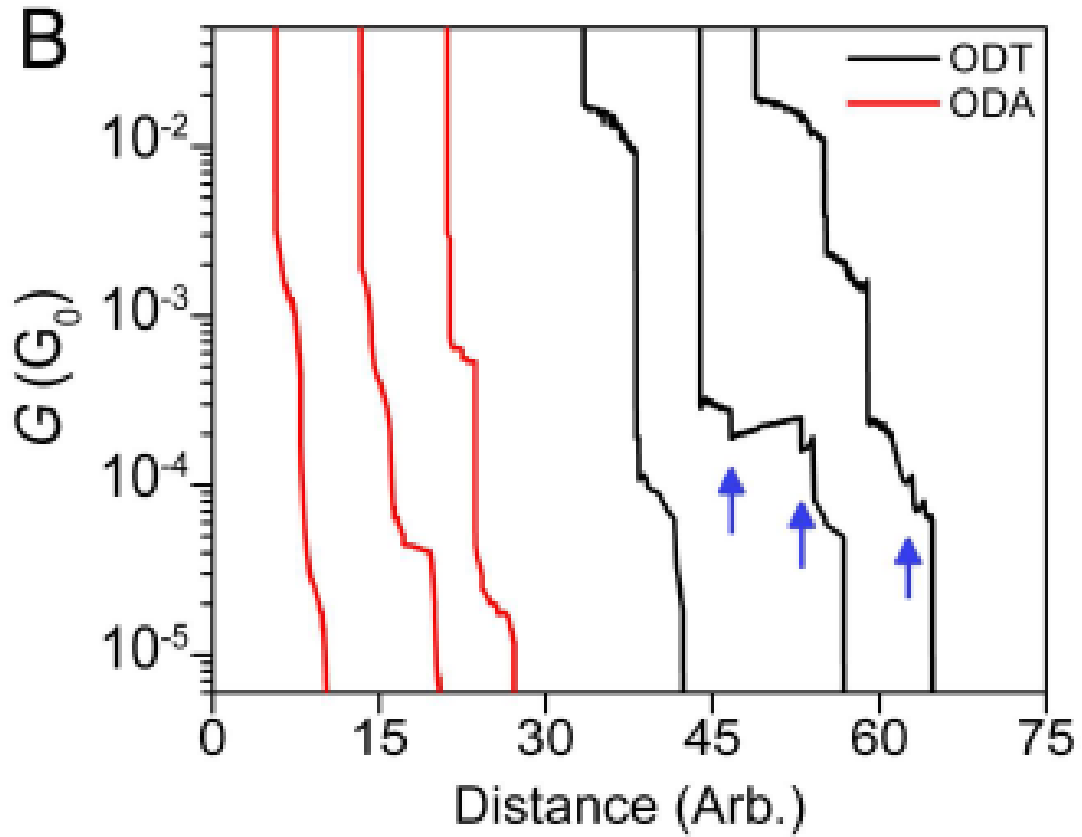


Y. Kim, Th. Hellmuth, M. Bürkle, F. Pauly, E. Scheer, ACS Nano **5**, 4104 (2011).

Au chain formation with ODT

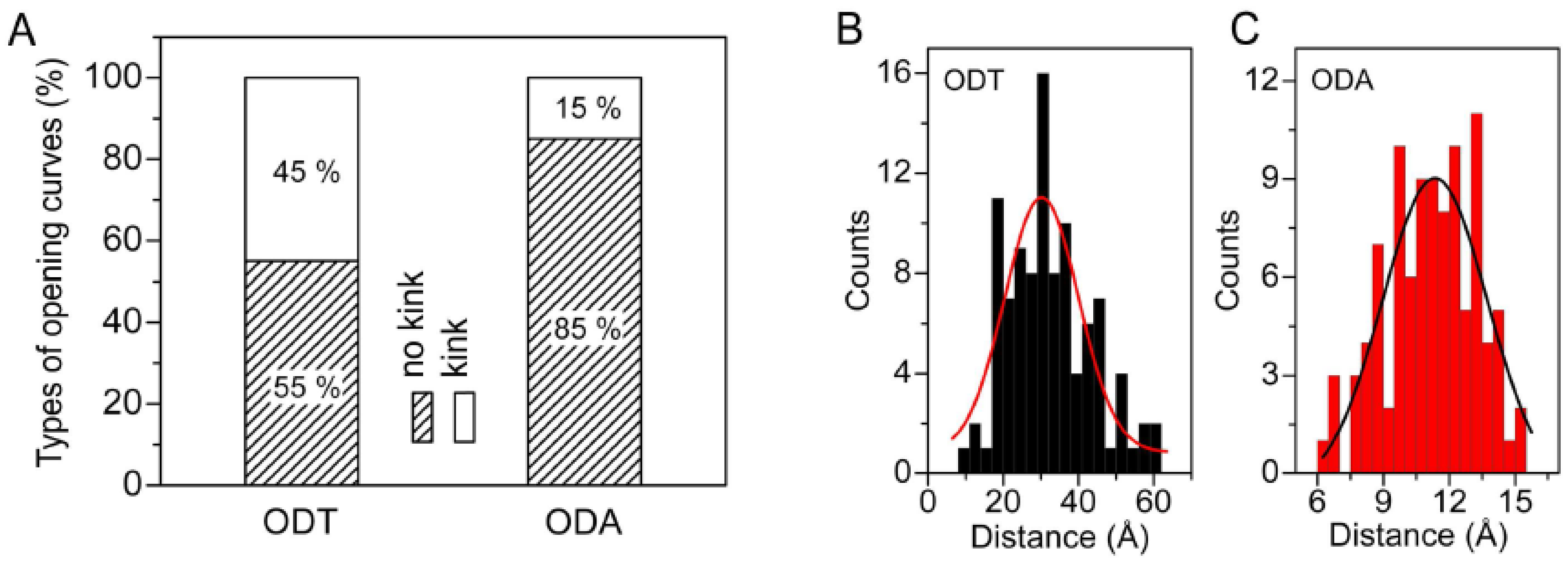
Role of the binding group: ODA and ODT on Au electrodes





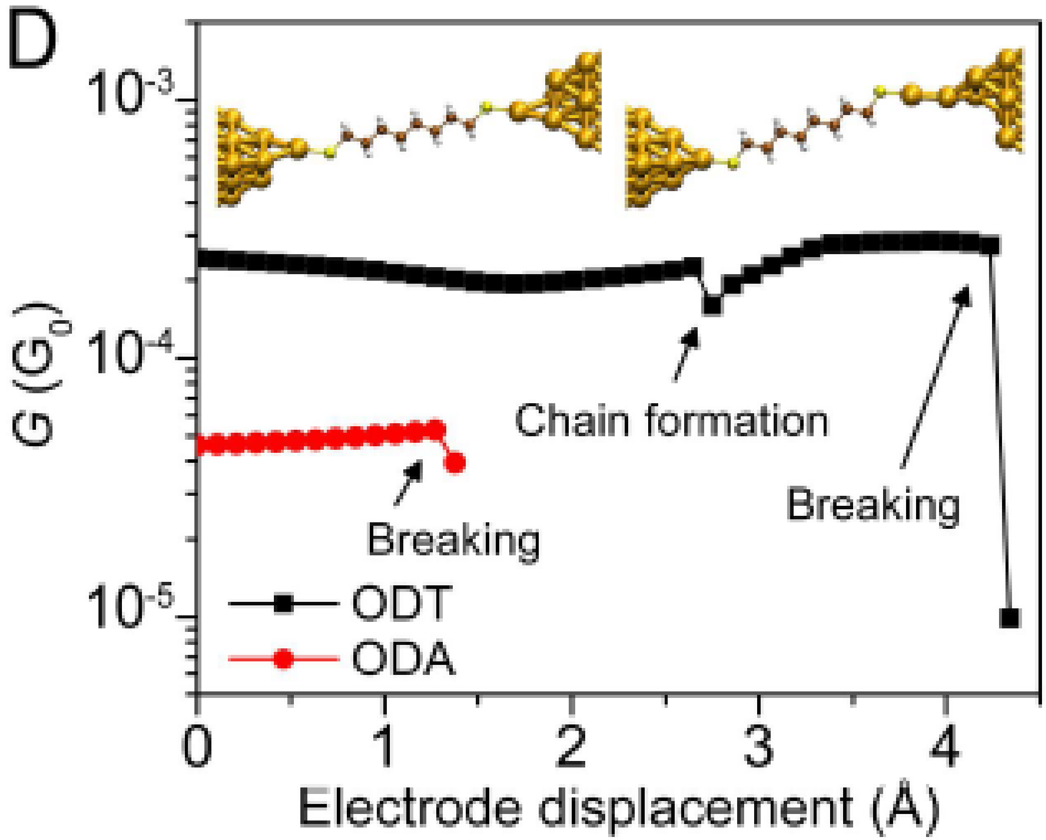
Y. Kim, Th. Hellmuth, M. Bürkle, F. Pauly, E. Scheer, ACS Nano **5**, 4104 (2011).

Role of the binding group: ODA and ODT on Au electrodes



Y. Kim, Th. Hellmuth, M. Bürkle, F. Pauly, E. Scheer, ACS Nano **5**, 4104 (2011).

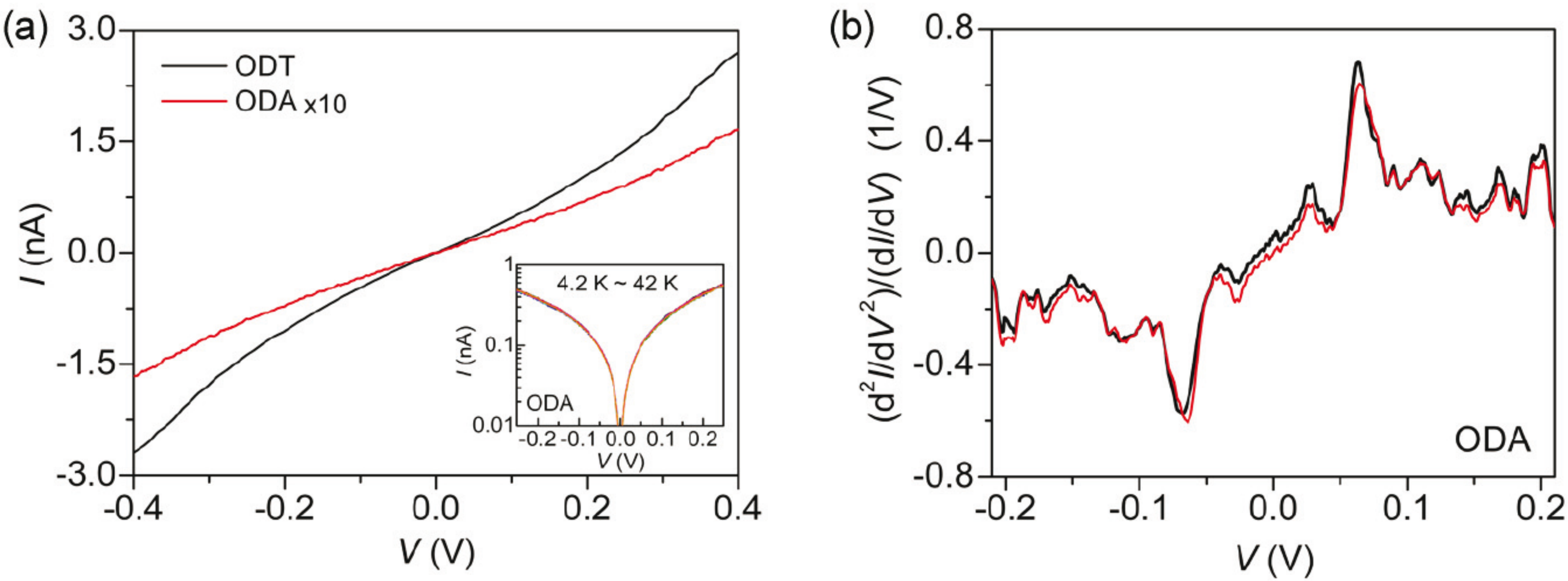
Role of the binding group:
ODA and ODT on Au electrodes



structure +DFT+ NEGF calculation

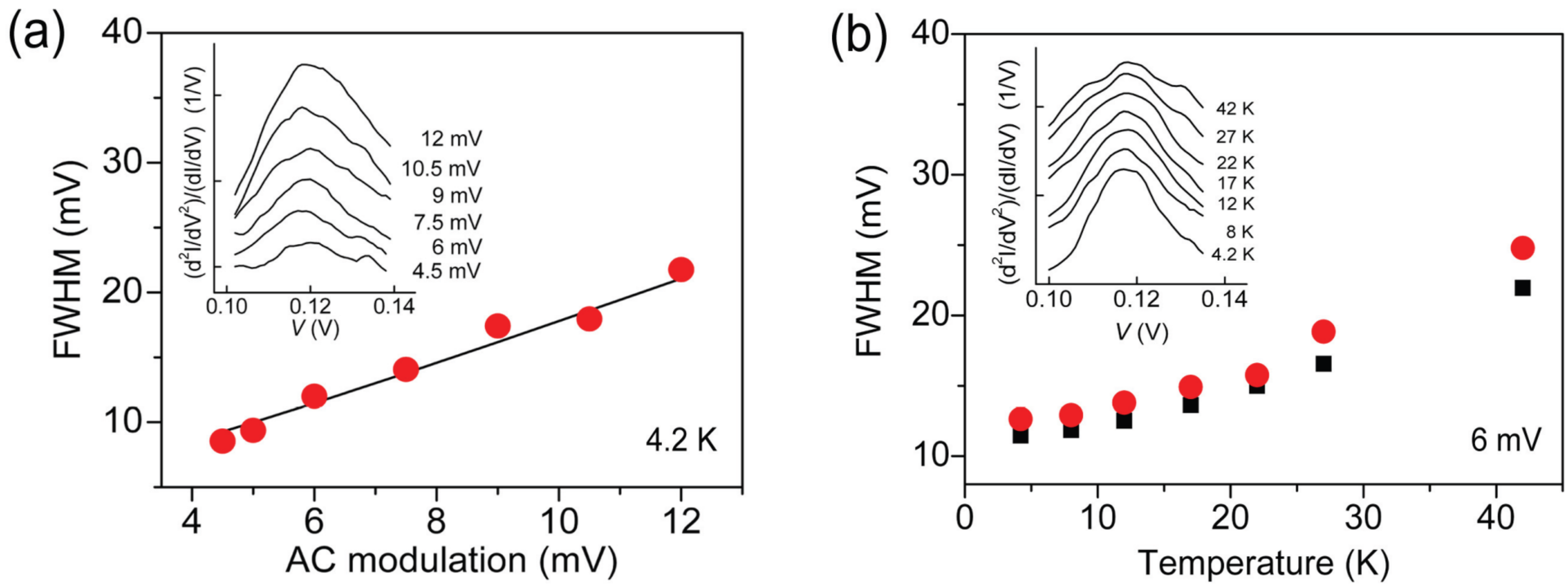
Y. Kim, Th. Hellmuth, M. Bürkle, F. Pauly, E. Scheer, ACS Nano **5**, 4104 (2011).

Example IETS of ODA @ 4.2 K



Y. Kim, Th. Hellmuth, M. Bürkle, F. Pauly, E. Scheer, ACS Nano **5**, 4104 (2011).

Linewidth broadening of IETS of ODA



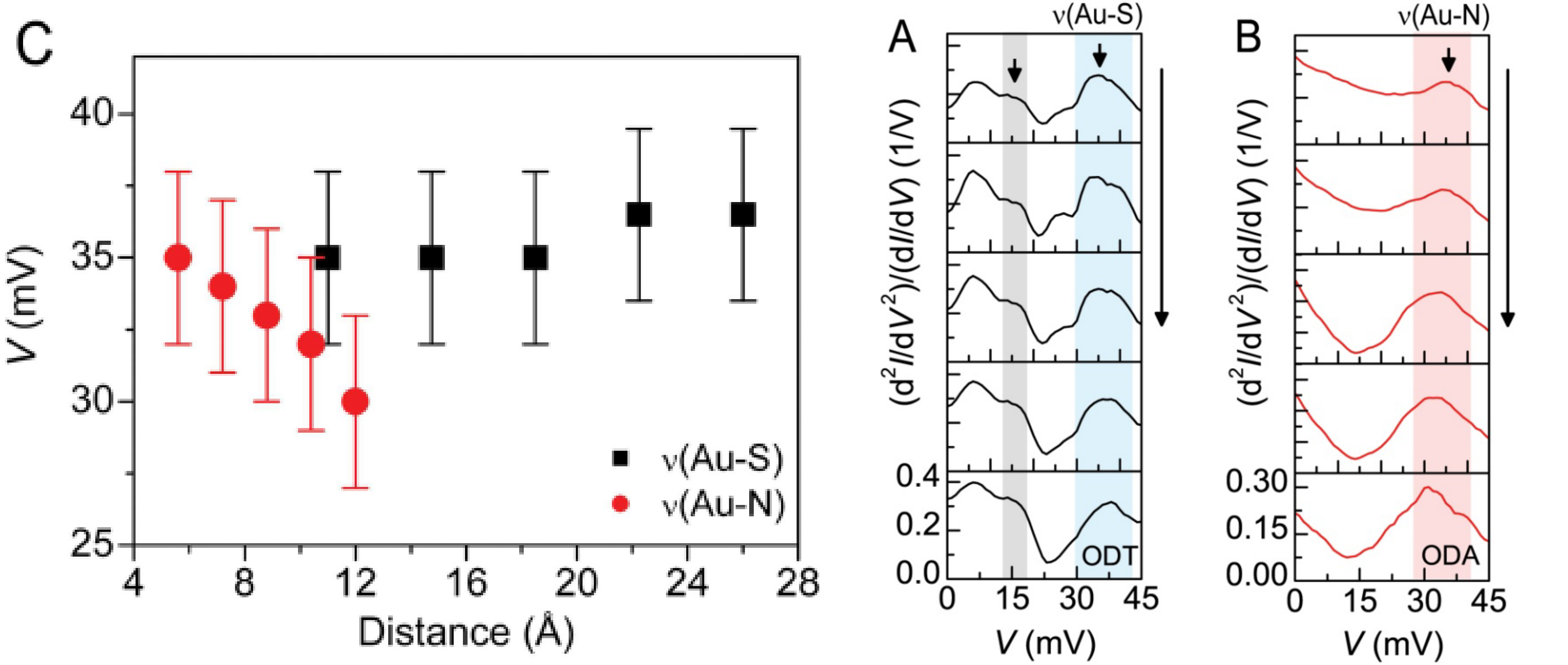
Experimental linewidth W_{exp} given by intrinsic linewidth W_I, thermal broadening k_BT and modulation voltage V_{ac} :

$$W_{exp} = [(5.4k_BT)^2 + (1.7V_{ac})^2 + (W_I)^2]^{1/2}$$

a) V dependence at fixed T: black line: linear fit -> $W_I = 4.9 \pm 0.8$ meV
b) T dependence at fixed V_{ac}: black squares: theoretical expectation, red dots: experimental findings

T = 4K: $5.4k_BT = 1.8$meV

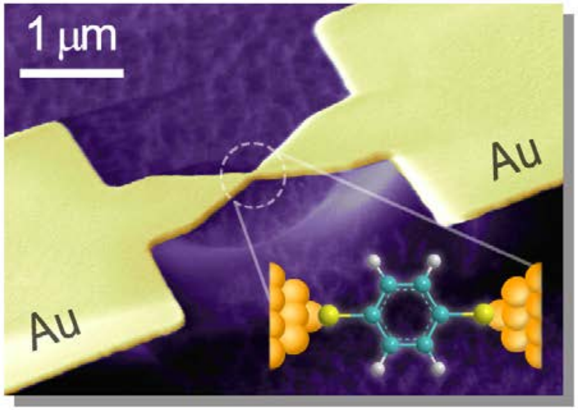
Stretching dependence of IETS

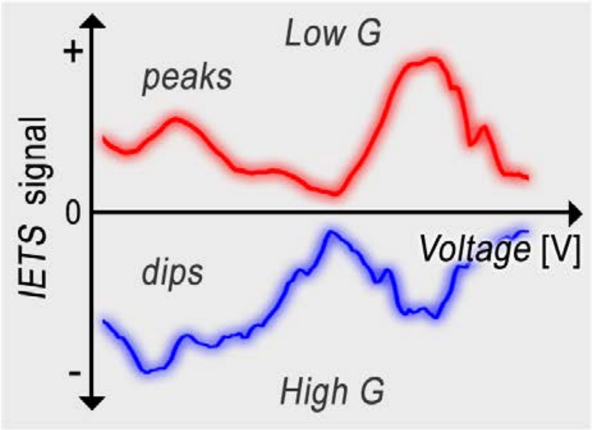


Au-Amine bond weakens upon stretching, short stretching length
Au-Thiol bond robust -> formation of a gold chain

Y. Kim, Th. Hellmuth, M. Bürkle, F. Pauly, E. Scheer, ACS Nano **5**, 4104 (2011).

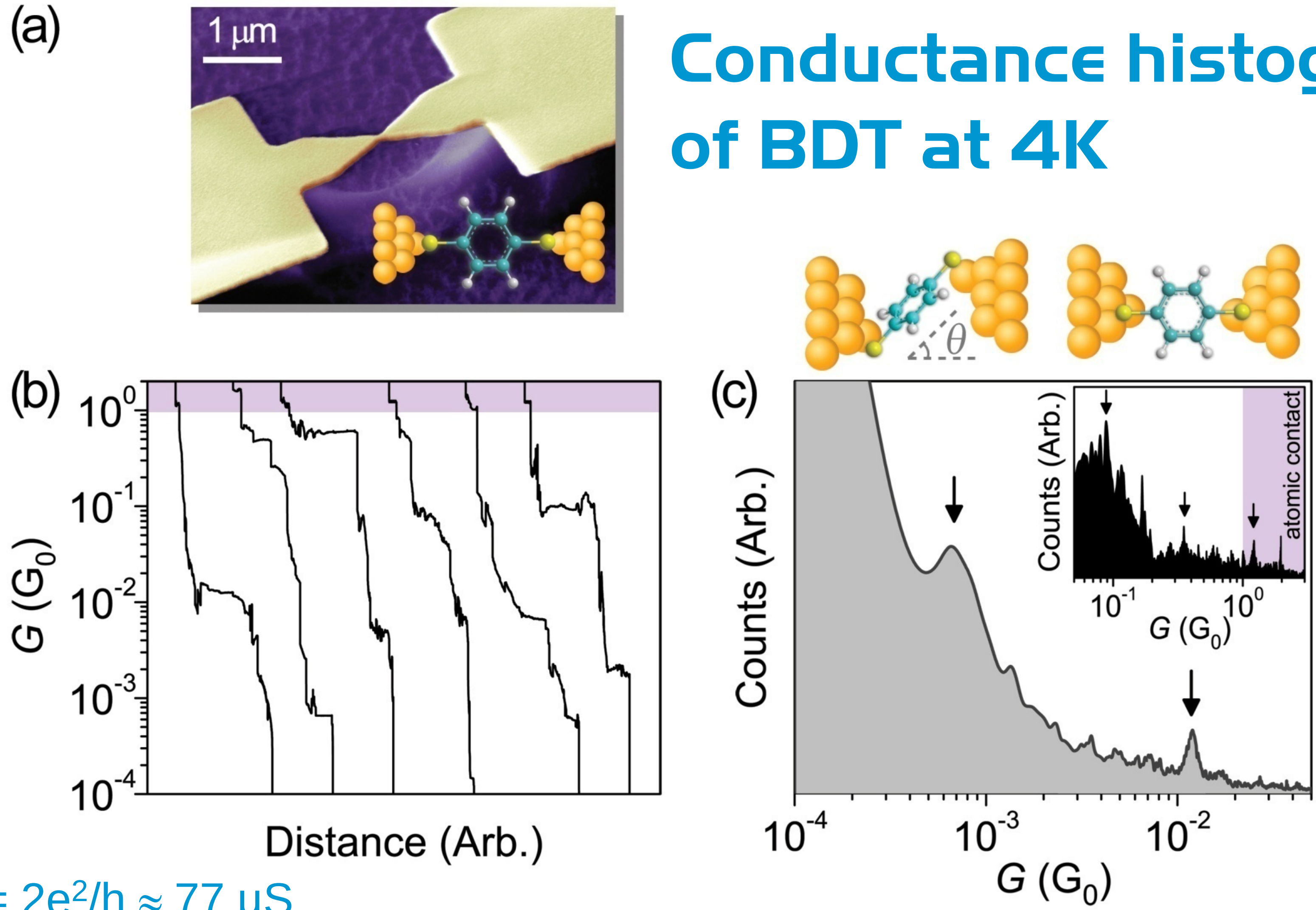
BDT: Analysis of I-Vs and IETS for revealing electronic structure





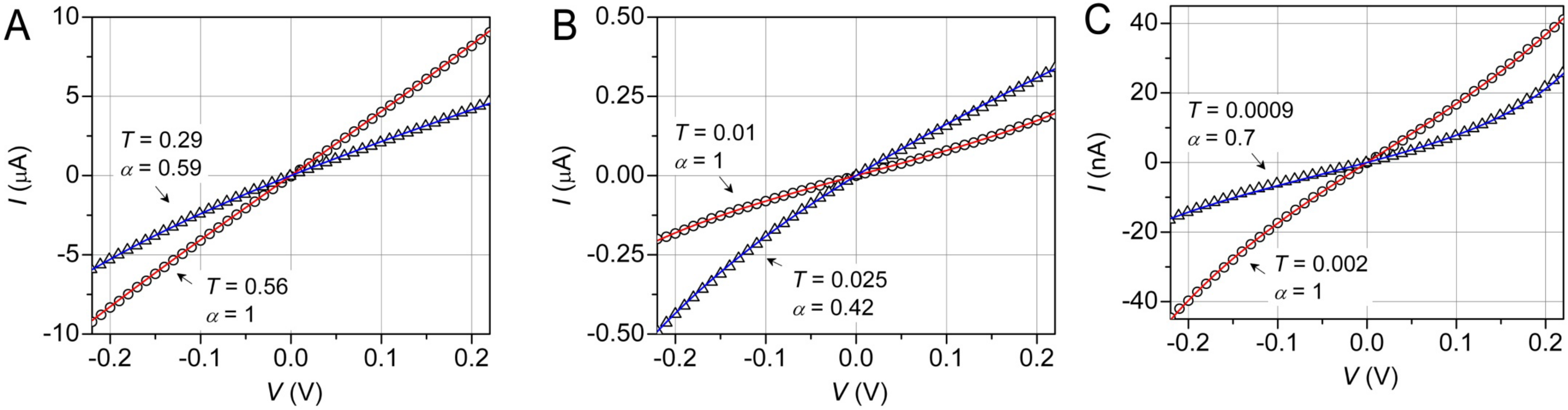
Y. Kim, T. Pietsch, A. Erbe, W. Belzig, E. Scheer, Nano Lett. **11**, 3734 (2011)

Conductance histogram of BDT at 4K



$G_0 = 2e^2/h \approx 77\ \mu S$

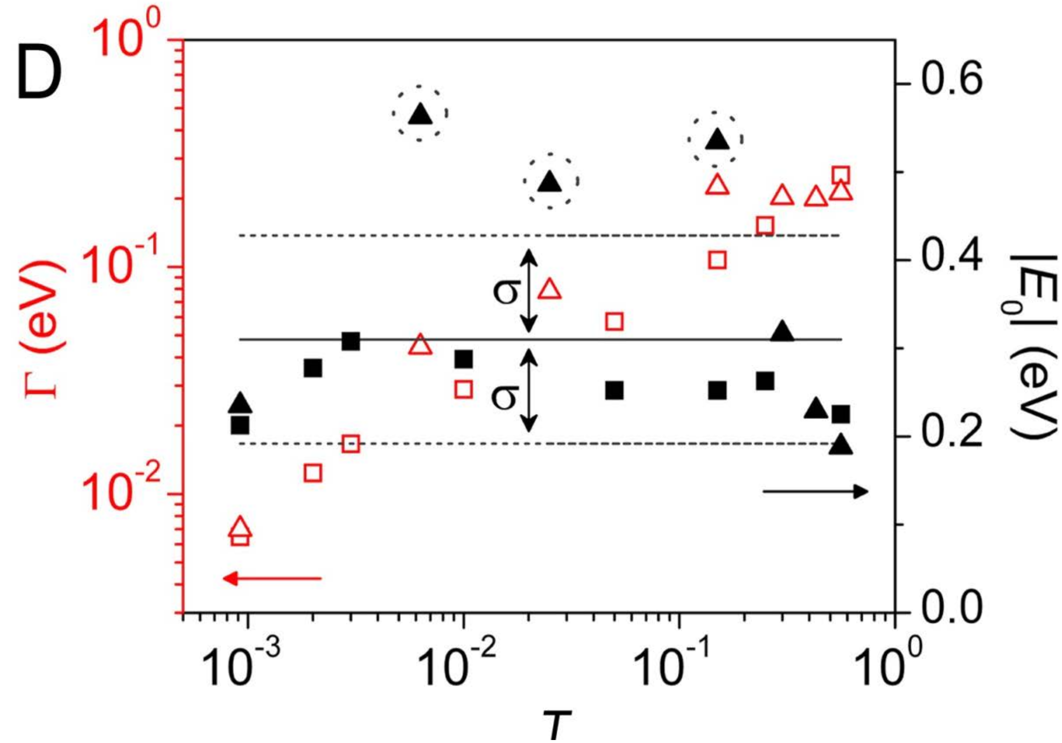
Au-BDT-Au: highly conductive and non-symmetric coupling possible



$$E_0(V) = E_0 + \left(\frac{\Gamma_L - \Gamma_R}{\Gamma_L + \Gamma_R}\right)\frac{eV}{2}$$

$$\alpha = \Gamma_R / \Gamma_L$$

I-Vs of Au-BDT-Au: wide conductance range



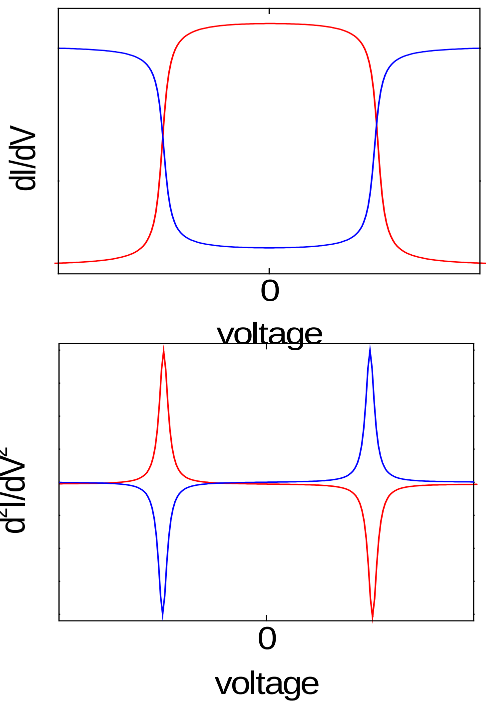
Quantitative agreement with GW calculations: $E_0 = 0.3$ eV
Strange et al., Phys. Rev.B **83**, 115108 (2011)

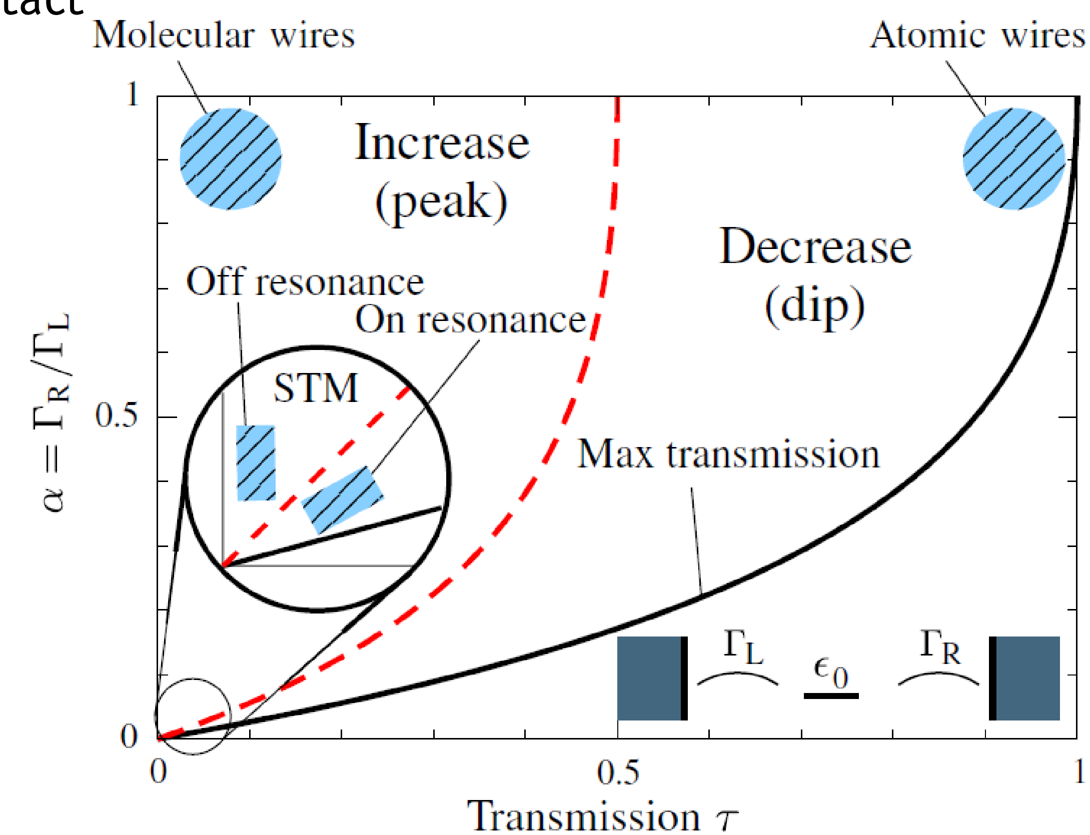
PCS vs. IETS: Sign change of d^2I/dV^2

Prediction for a single-channel contact

$\tau > 0.5\ \tau_{max}$: dip in d^2I/dV^2

$\tau < 0.5\ \tau_{max}$: peak in d^2I/dV^2





Paulsson *et al.* PRL **100** 226604 (2008)

Theory see also: L. de la Vega *et al.* PRB **73**, 075428 (2006)

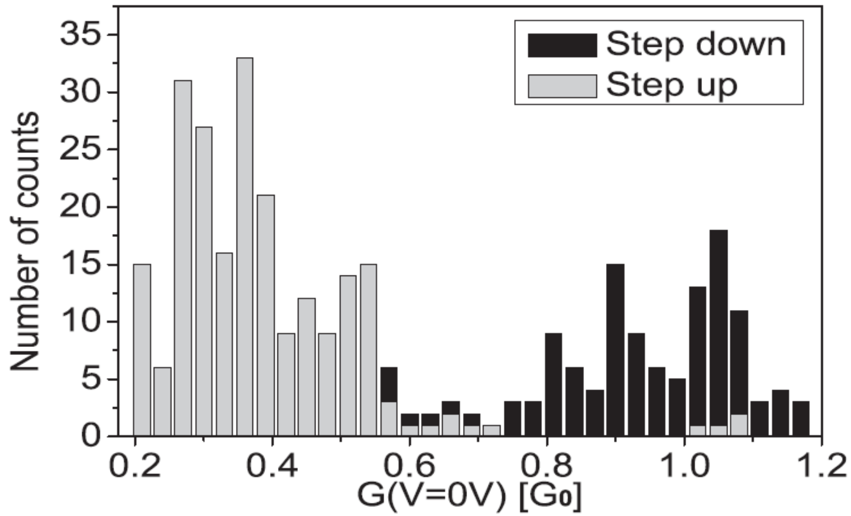
Experiments: Tal *et al.* PRL **100** 196804 (2009)

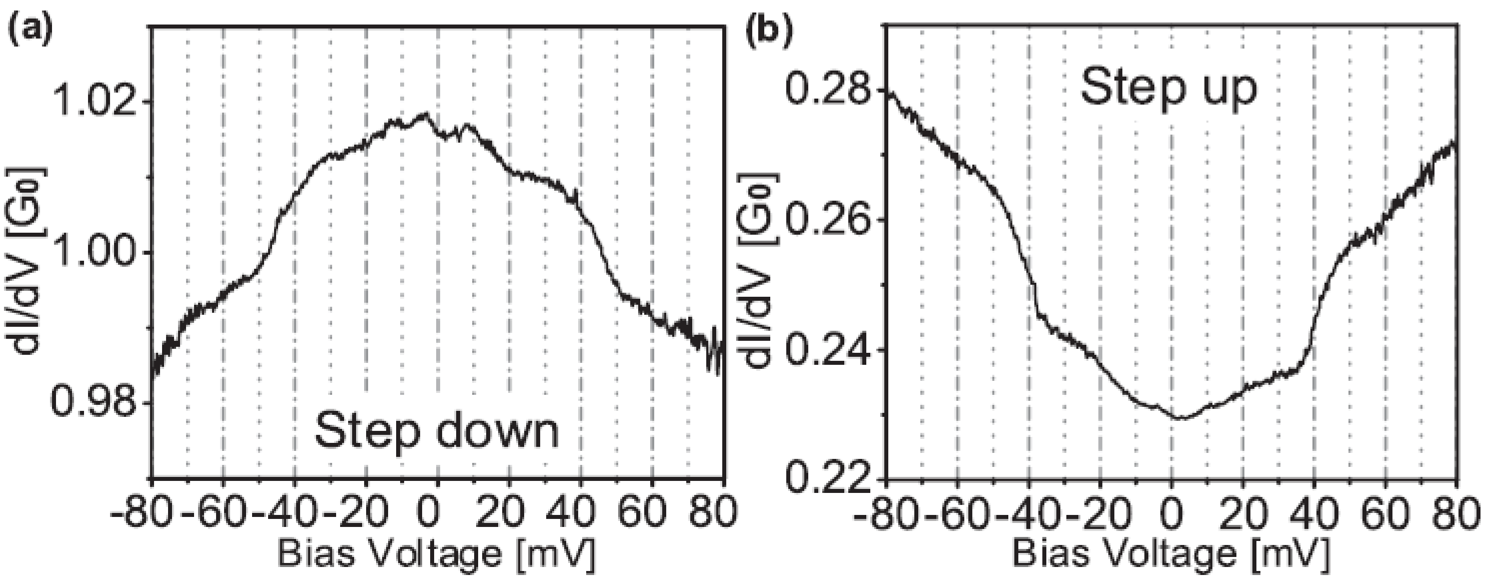
Pt/H_2O

- $0.2 < G/G_0 < 1.2$
- Sign change observed ~0.6 G_0

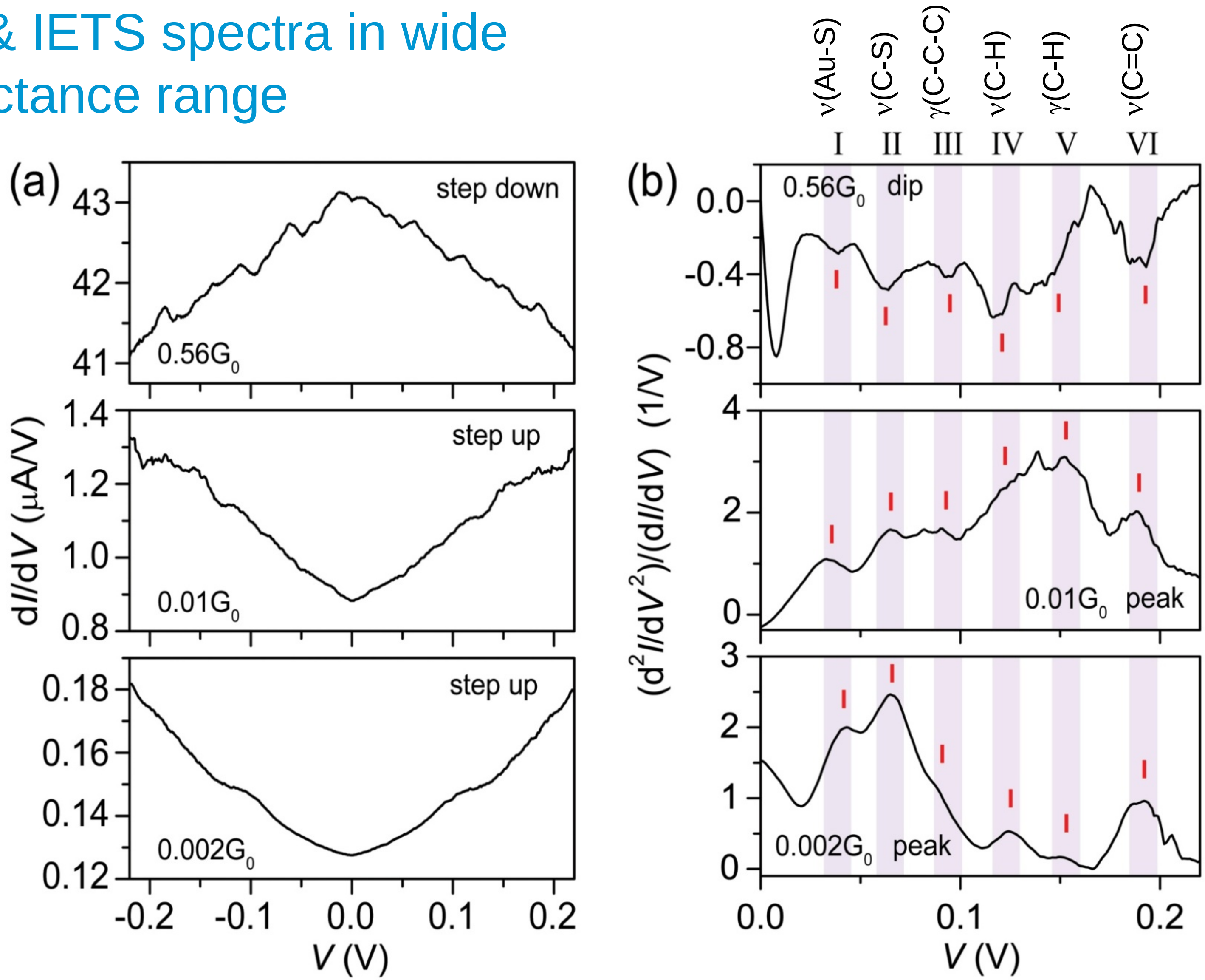
-> 2-channel contacts

Tal *et al.* PRL **100** 196804 (2009)

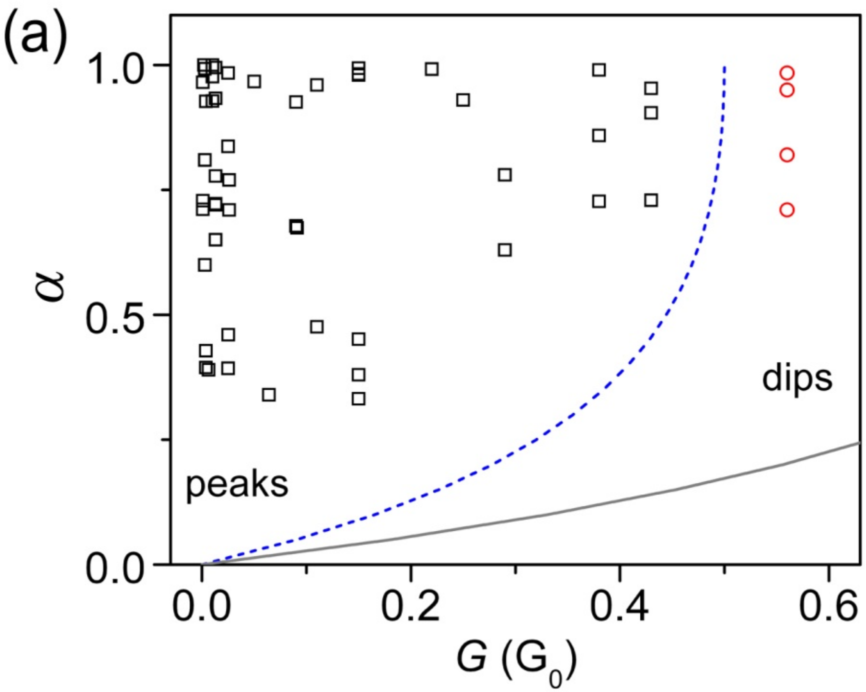


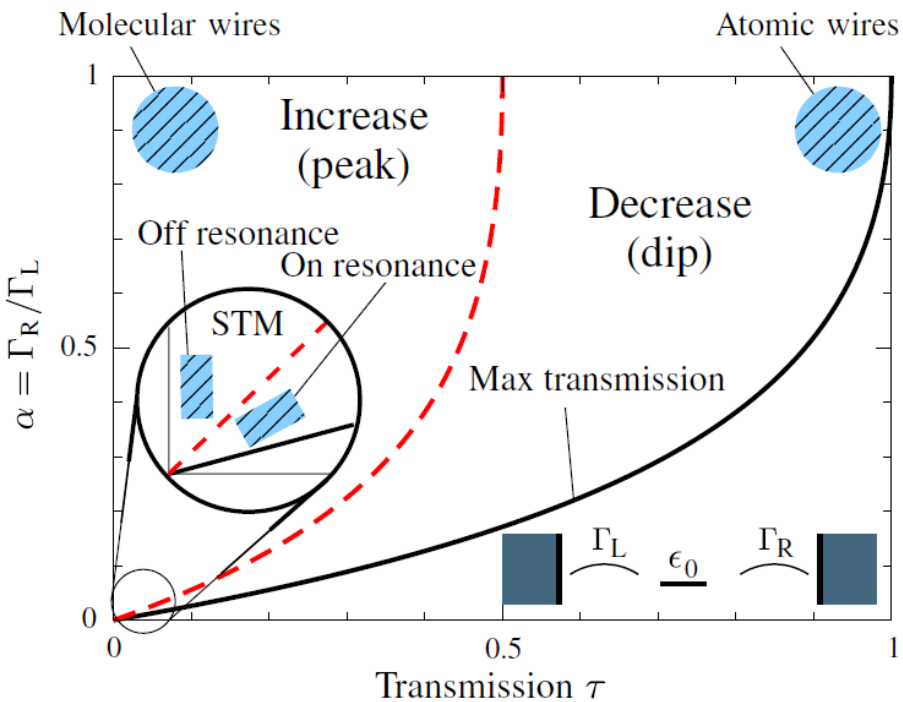


d*I*/d*V* & IETS spectra in wide conductance range



Transition from PCS to IETS in Au-BDT-Au





$$T_{crossover} = 2\alpha / (1+\alpha)^2\, T_{max}$$

T_{max} = 0.83 (Strange et al, PRB 2011)

IETS amplitude $\propto$ 1-2T

Summary I

- Single-level model successfully describes the I-Vs of single-molecule junctions of "simple molecules" in a wide conductance range.
- Microscopic parameters E_0 and Γ can be deduced and compared with ab initio results.
- Variable electrodes & IETS enable to reveal junction configuration and influence of anchor group and electrode material)

Towards optically driven molecular switches

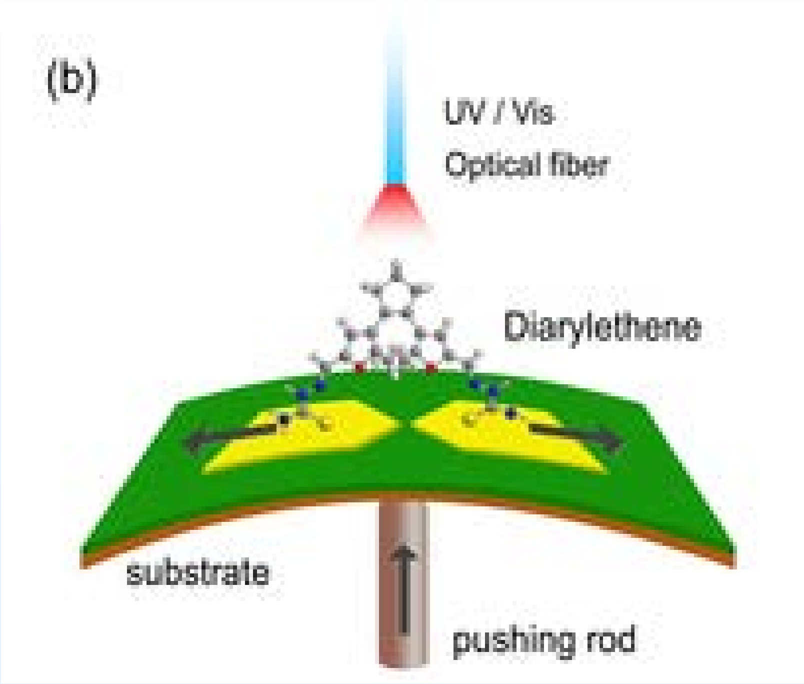
<u>Goal:</u> Reversible conductance switching of a single-molecule junction by light

<u>Issues:</u>

- Conductance, junctions, suitable molecules
- Role of electrodes: Optical antennae?

  D. Guhr et al., PRL 99, (2007)

  D. Benner et al., NJP, 2013



D. Sysoiev et al., Chem. Eur. J. **17,** 6663 (2011)

Y. Kim et al., Nano Letters **12**, 3736 (2012)

B.M. Briechle et al., Beilstein J. Nanotech. **3**, 703 (2012)

D. Sysoiev et al., Chem. Commun. **48**, 11355 (2012)

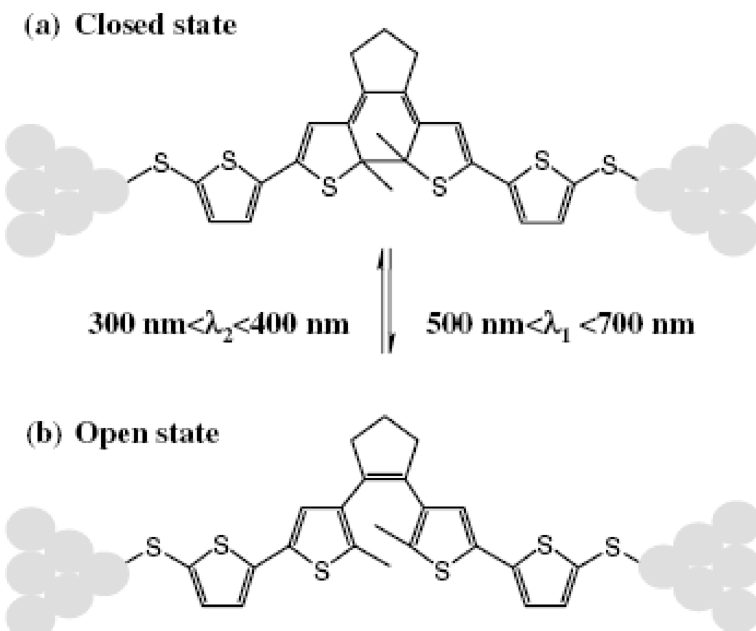
Y. Kim et al., Phys. Rev. Lett. **109**, 226801 (2012)

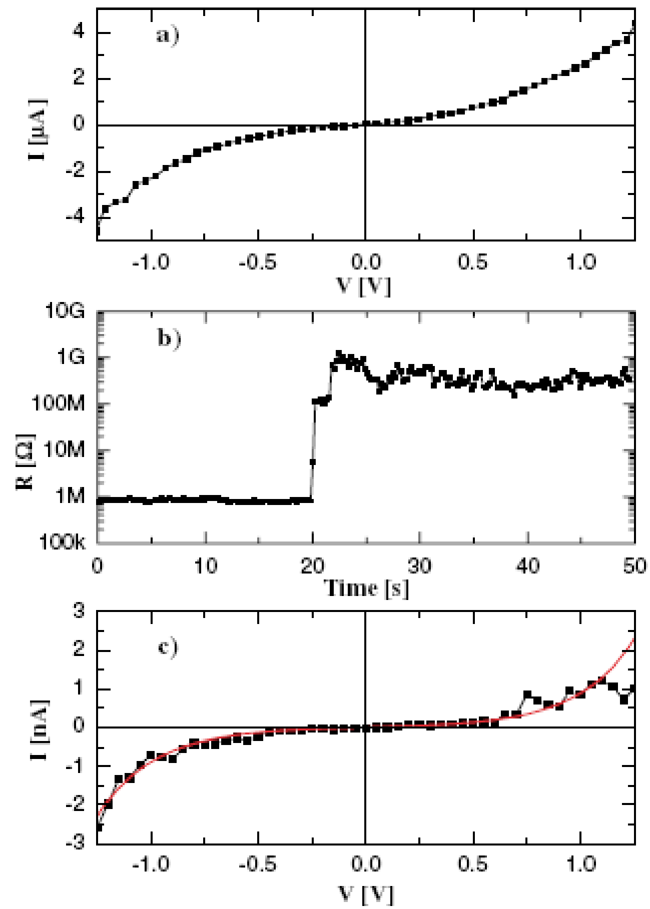
Towards optically driven molecular switches

Requirements:

- Bind reliably & specifically
- Switches reliably between two states
- No or small length change upon switching
- Sufficient flexibility to adopt to electrode gap
- High quantum yield for switching
- Two states clearly distinguishable
- Reasonable current level in both states

Light-induced conductance switching of Diarylethenes

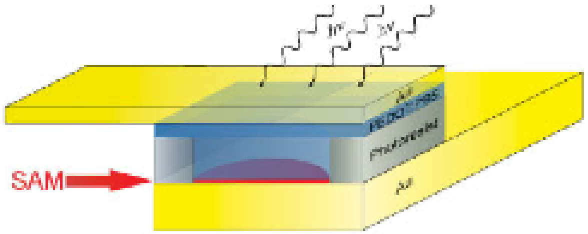


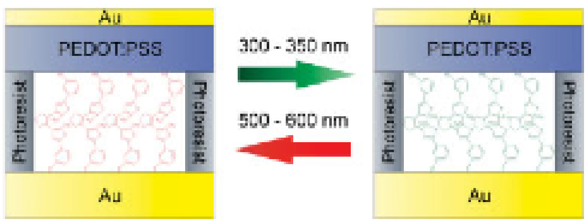


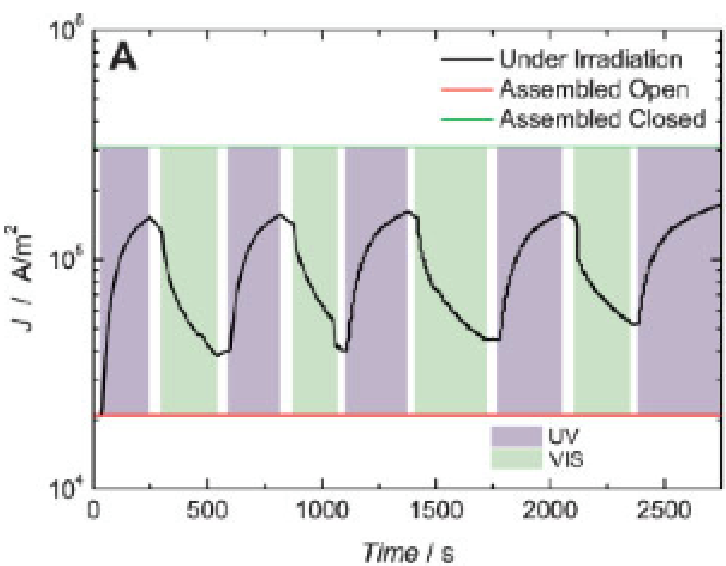
Irreversible off-switching

D. Dulic et al., Phys. Rev. Lett. **91**, 207402 (2003)

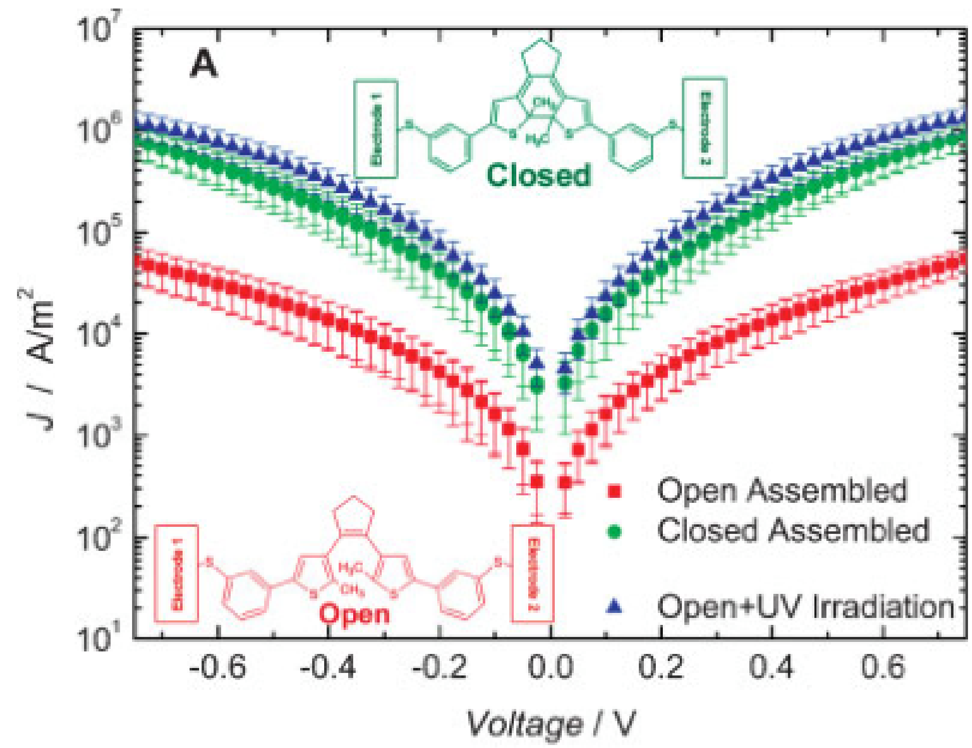
Measurements on ensembles of molecules





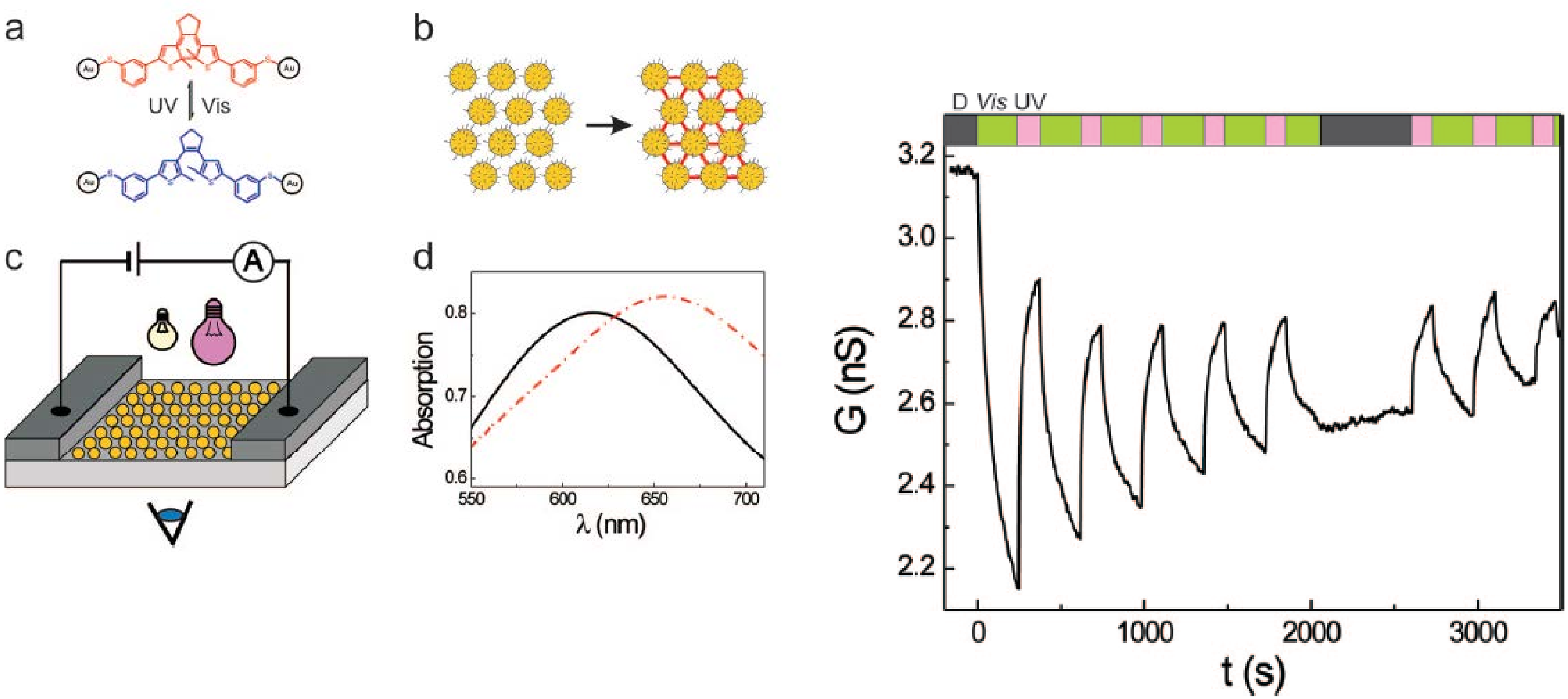


Reversible optically-driven switching observed on ensembles



Kronemeijer *et al.* Adv. Mater. (2008)

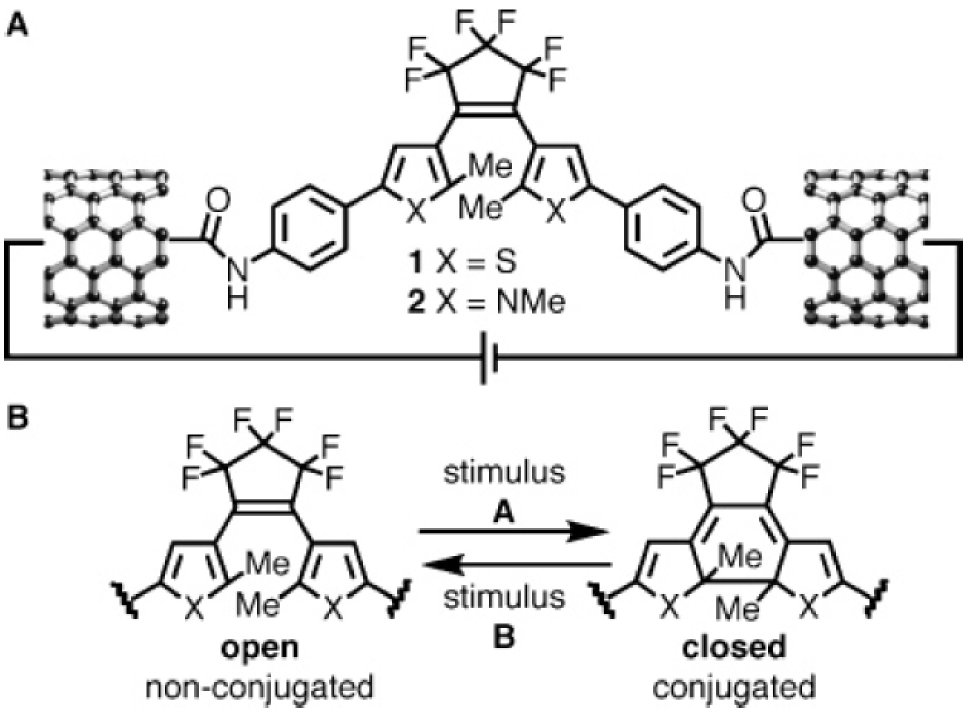
Light-induced Conductance Switching of Molecules



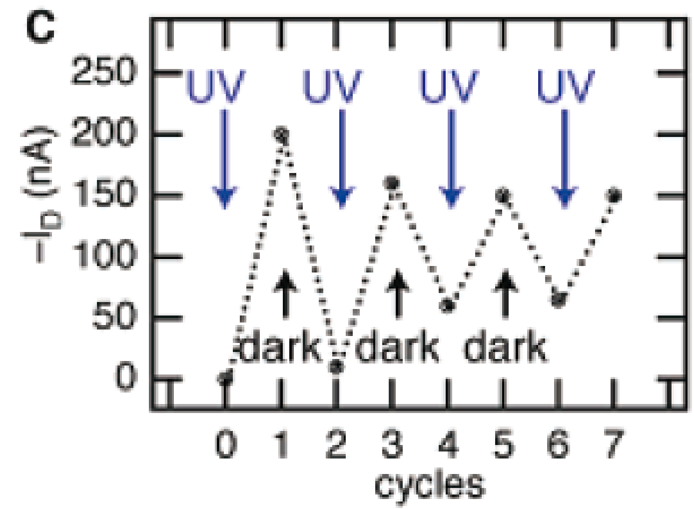
Ar atmosphere, RT

S.J. van der Molen, Nano Lett. 9, 76 (2009)

Single-Molecule Light-induced Conductance Switching : CNT electrodes



Optical closing &
Thermal opening reaction



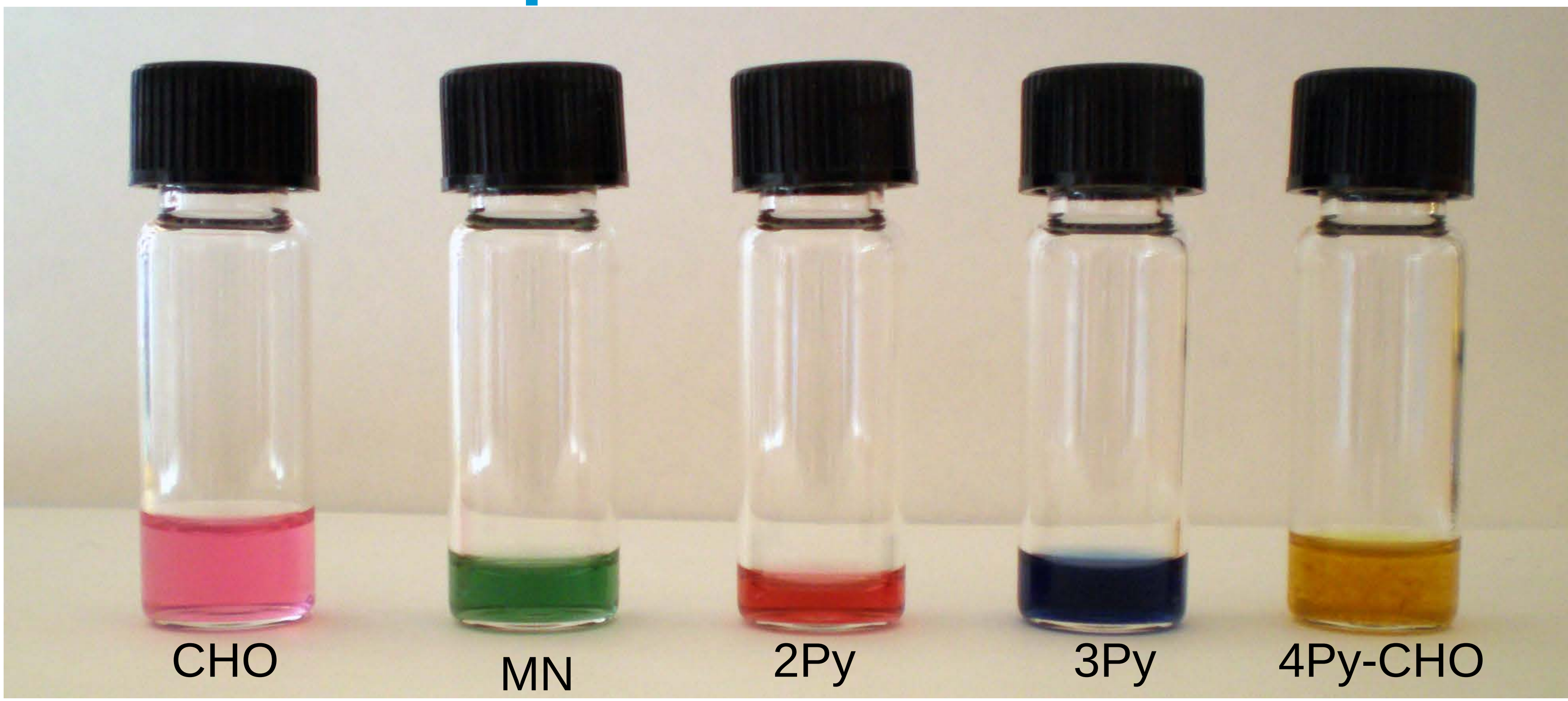
Species 2

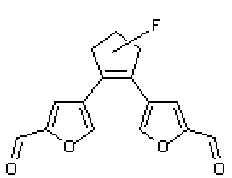
Extension of π system reduces quantum yield
Irreversible switching for thiophene switch (species 1)

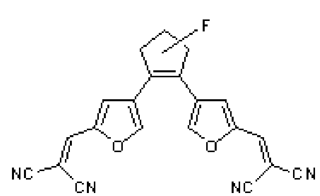
A.C. Whalley et al, JACS 129, 12590 (2007)

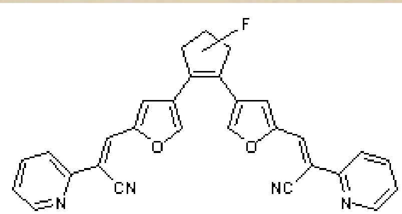
Universität
Konstanz

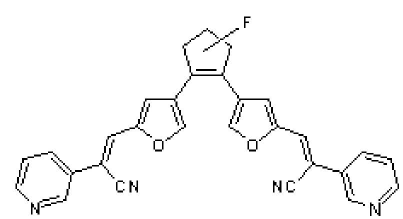
Sulfur-free photochromic molecules

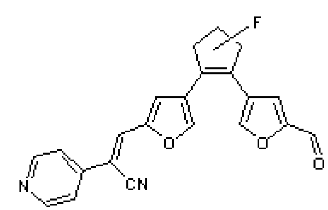



C5F-CHO


C5F-MN

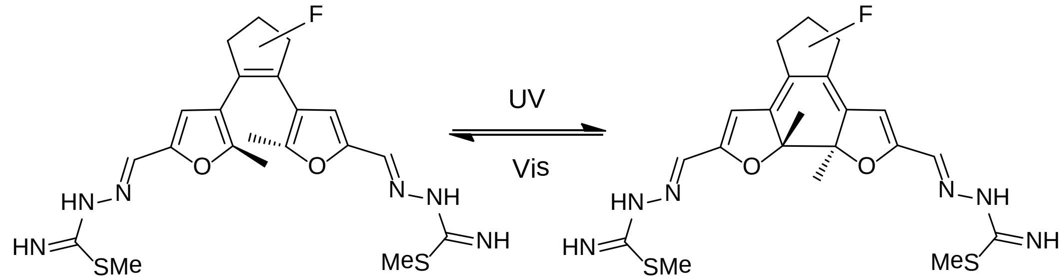

C5F-2Py

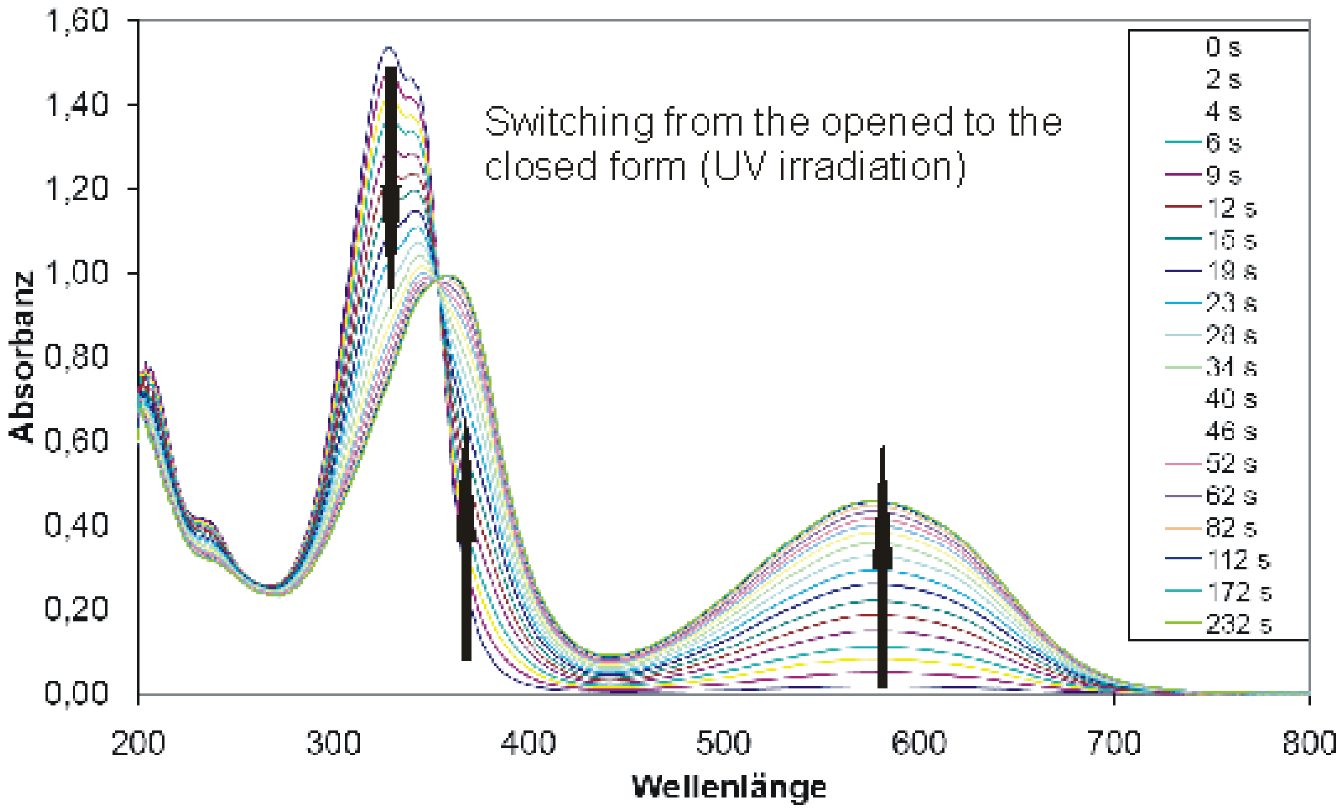

C5F-3Py


C5F-4Py-CHO

UV-Vis spectra

Thiol-terminated molecule





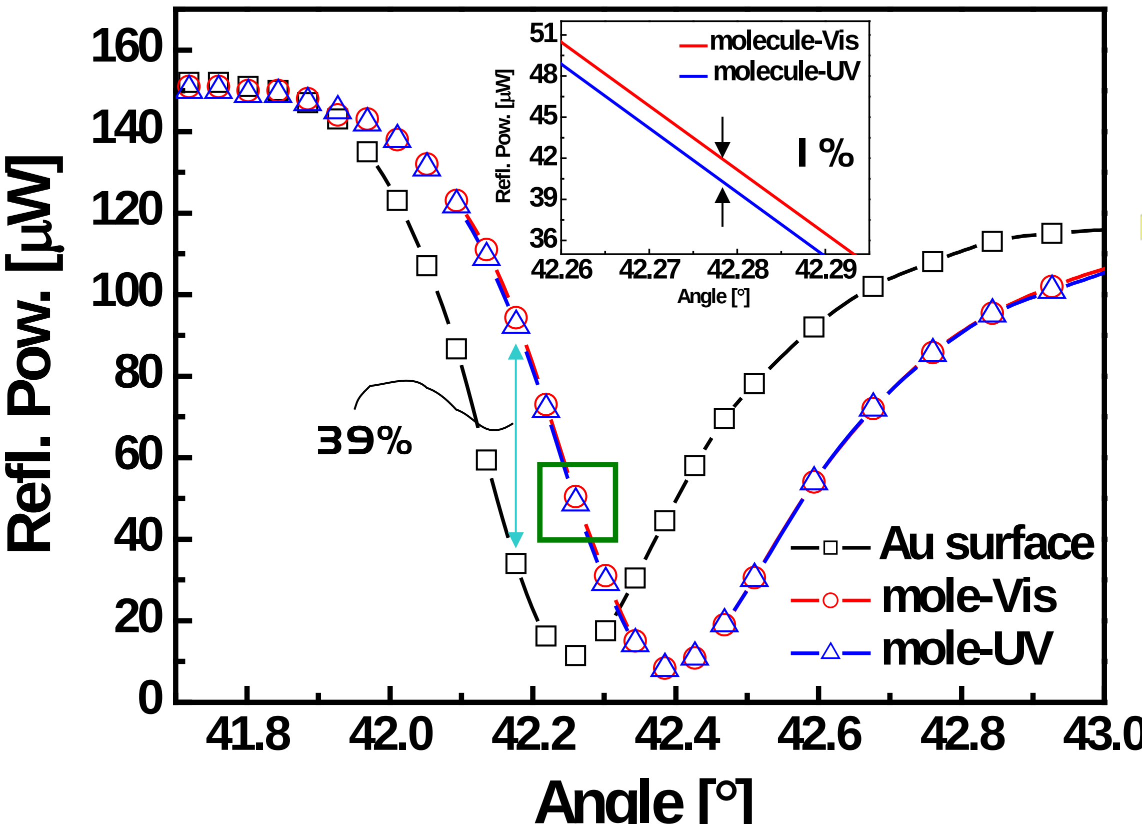
MTSC

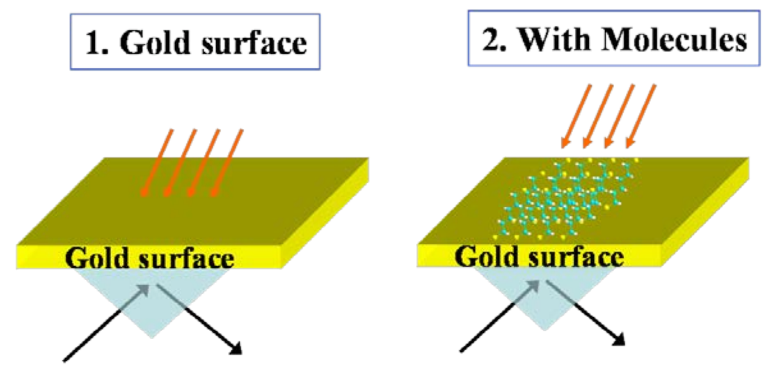
Surface-plasmon resonance

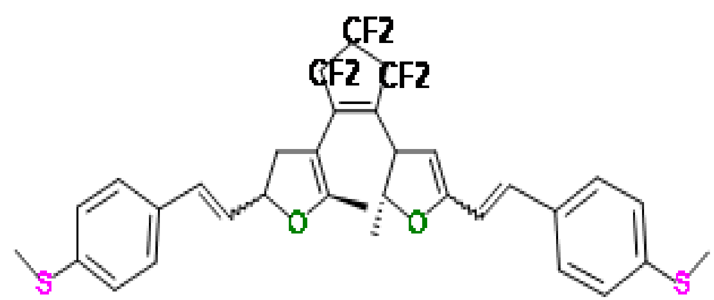
Thiol-terminated dry molecule/Au

λ = 980 nm

d = 47 nm

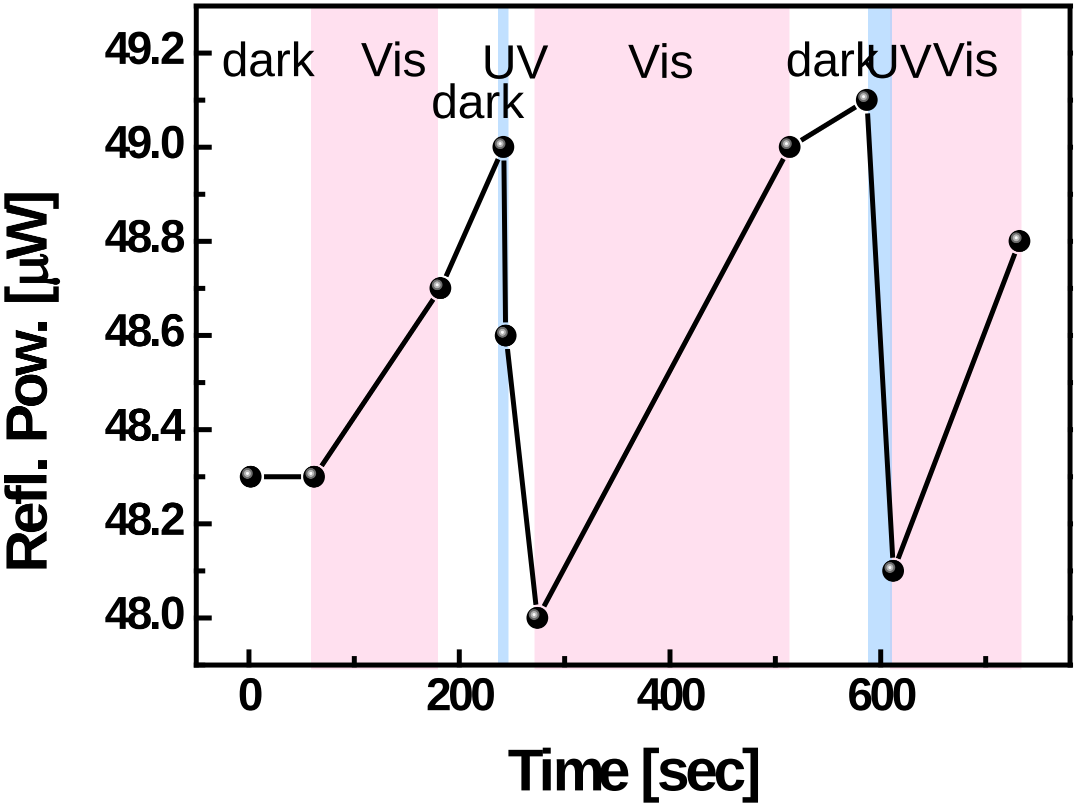


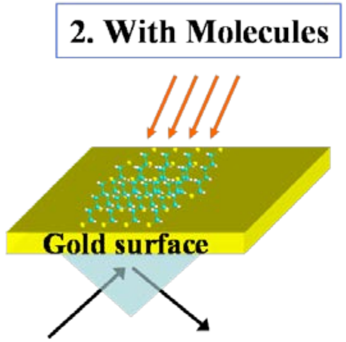




pSME

Thiol-terminated dry molecule/Au



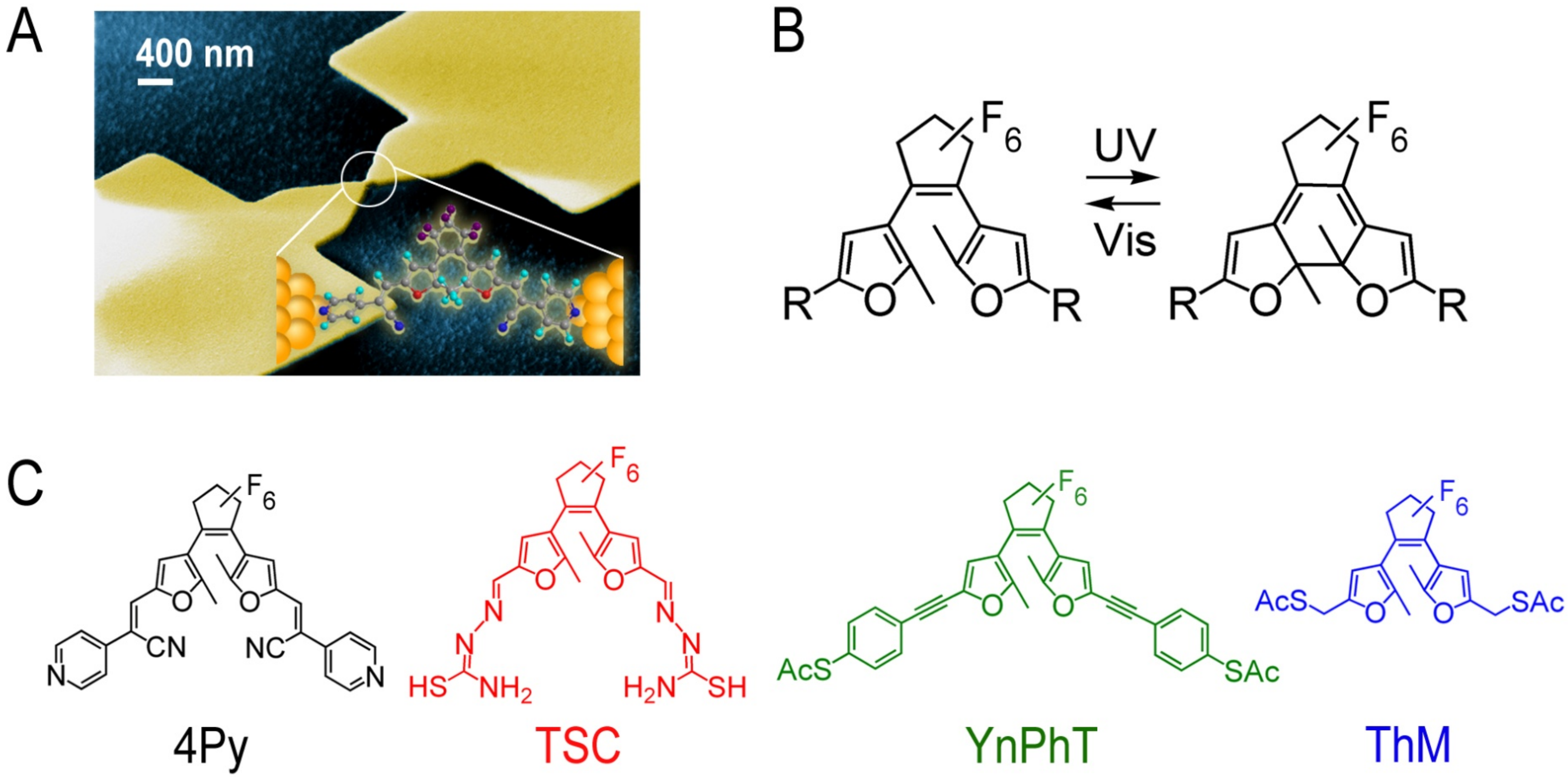


Reversible switching of molecule in contact with Au

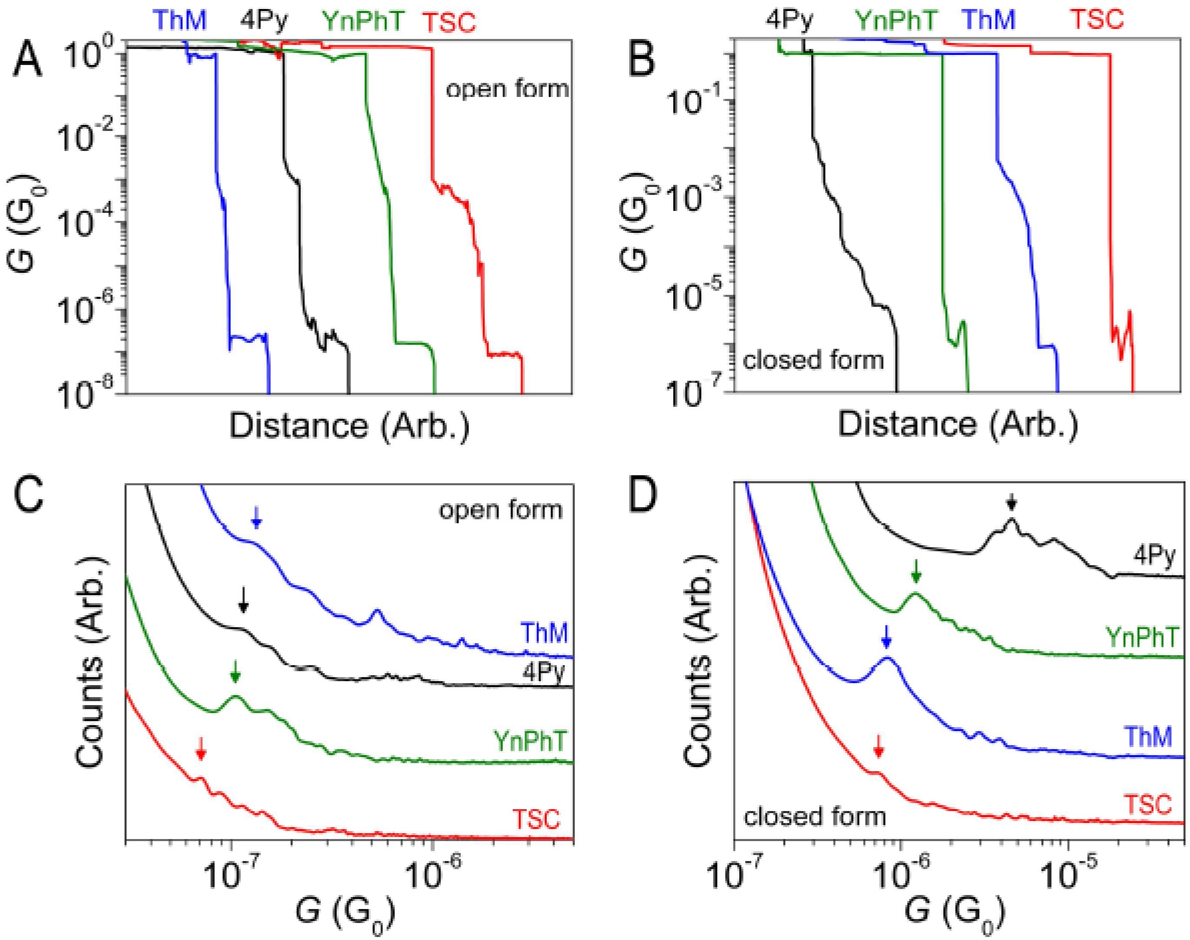
pSME

Equivalent findings for TSC, 4Py, MN, RN, MTSC, CHO, THM, YNPh

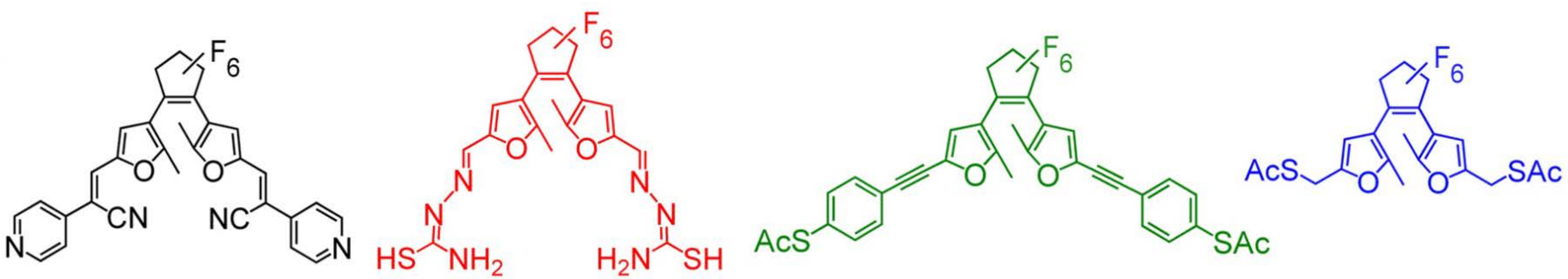
Single-molecule transport at 4 K



Experiment: Conductance at 4K



Single-molecule transport at 4 K



4Py TSC YnPhT ThM

Closed conductance (10^{-7} G_0):

50 > 8 ~ 13 > 8

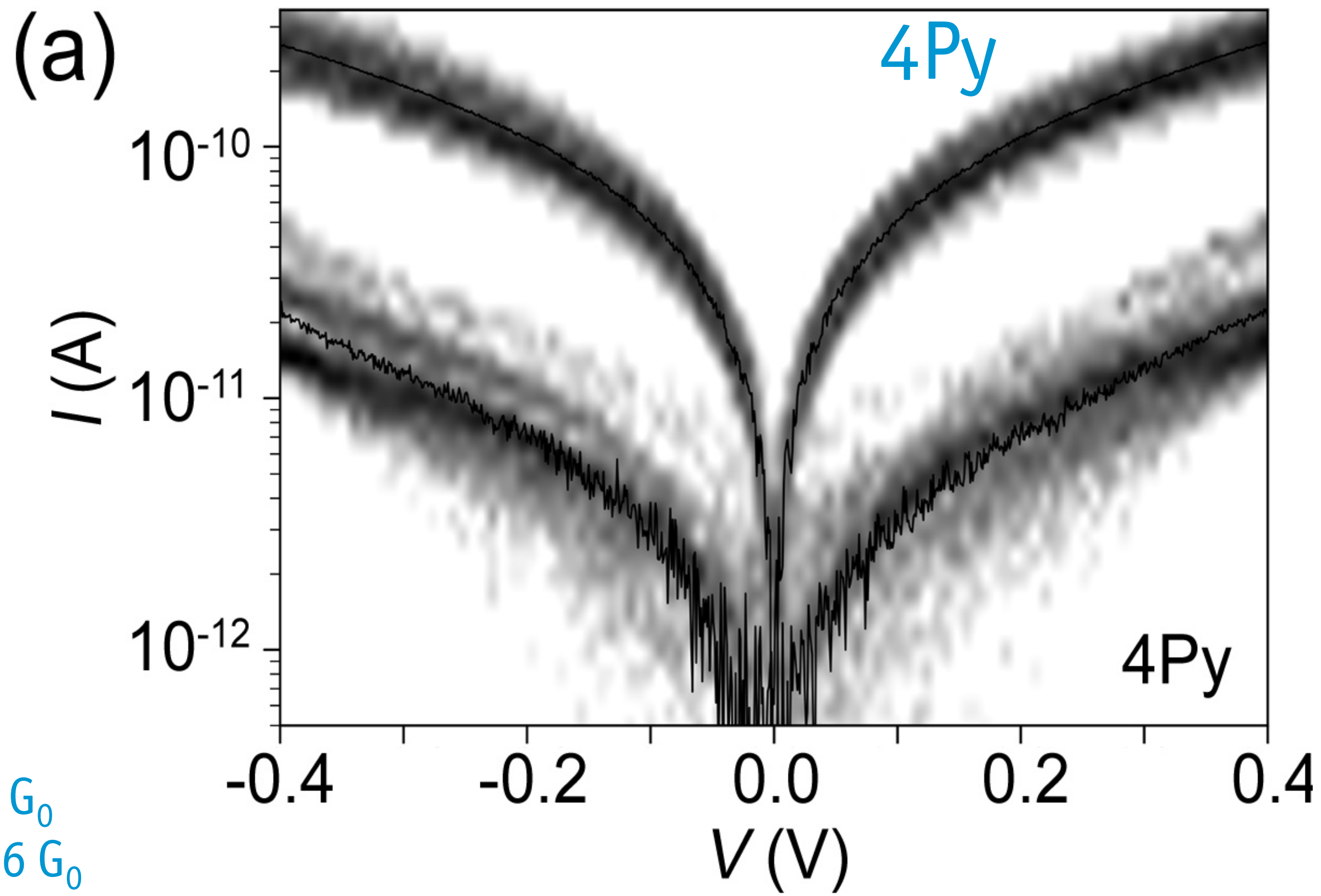
Switching ratio:

38 > 10 ~ 12 > 6

Experiment: I-Vs at 4K

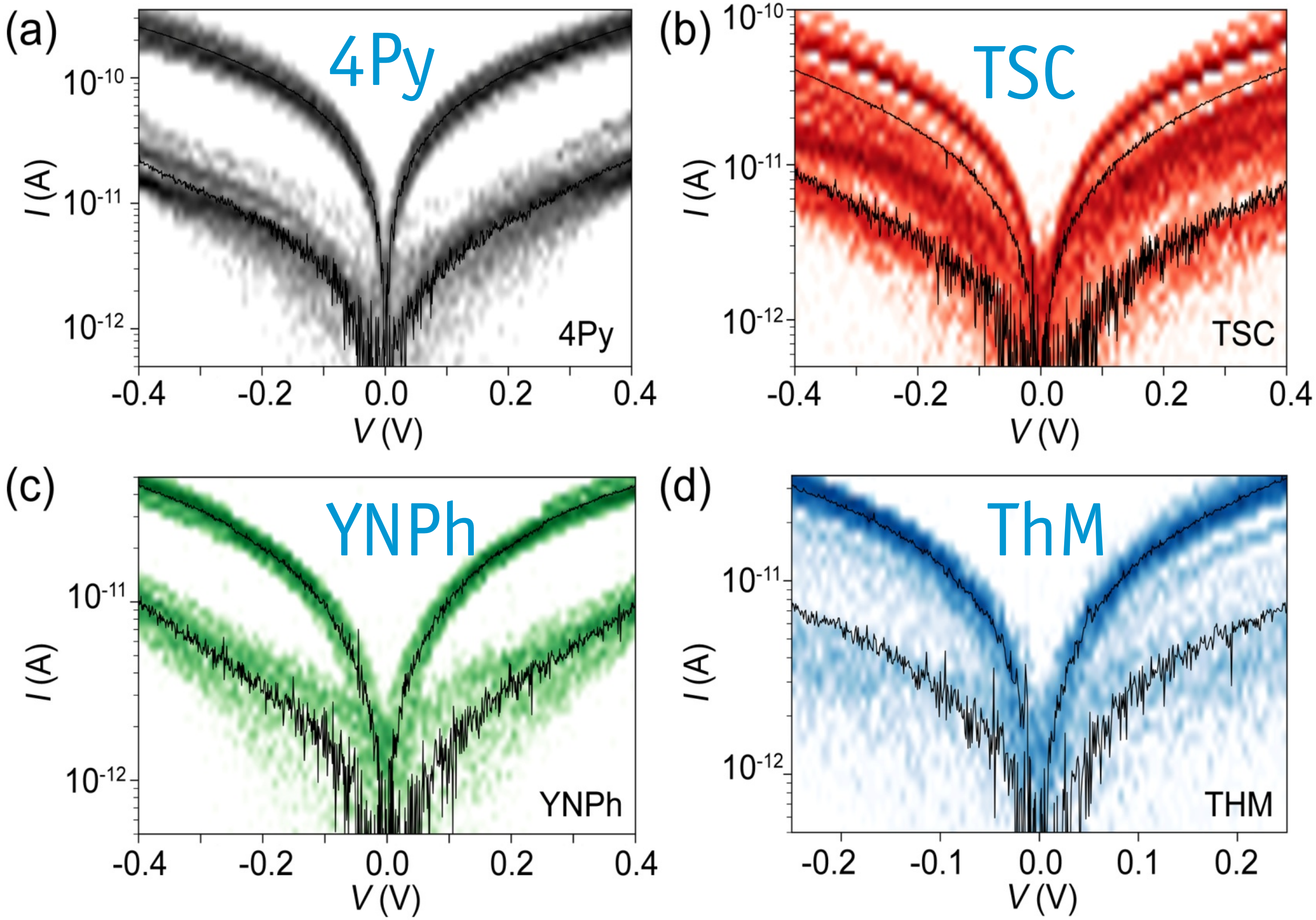
Closed
Γ= 1.3 meV
E_0 = 500 meV

Open
Γ= 0.24 meV
E_0 = 350 meV

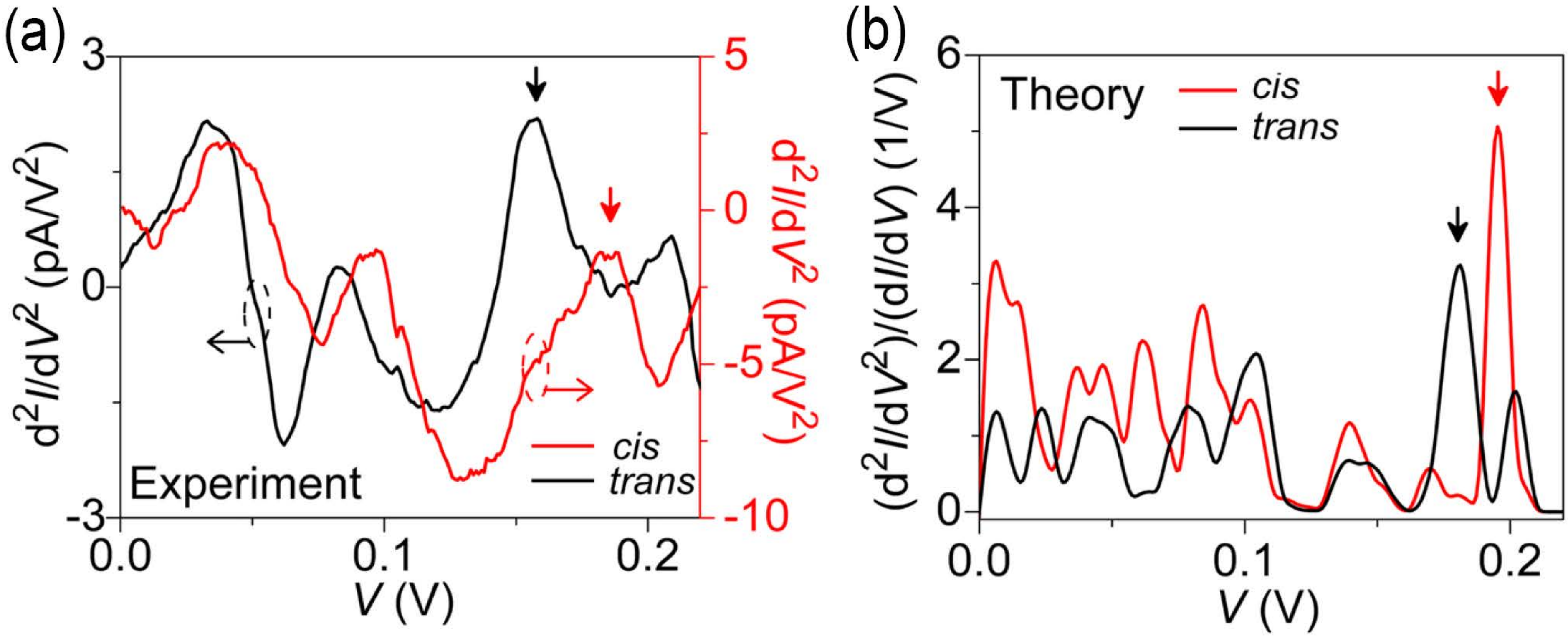


Open ring ~ 1.2E-7 G_0
Closed ring ~ 4.6E-6 G_0

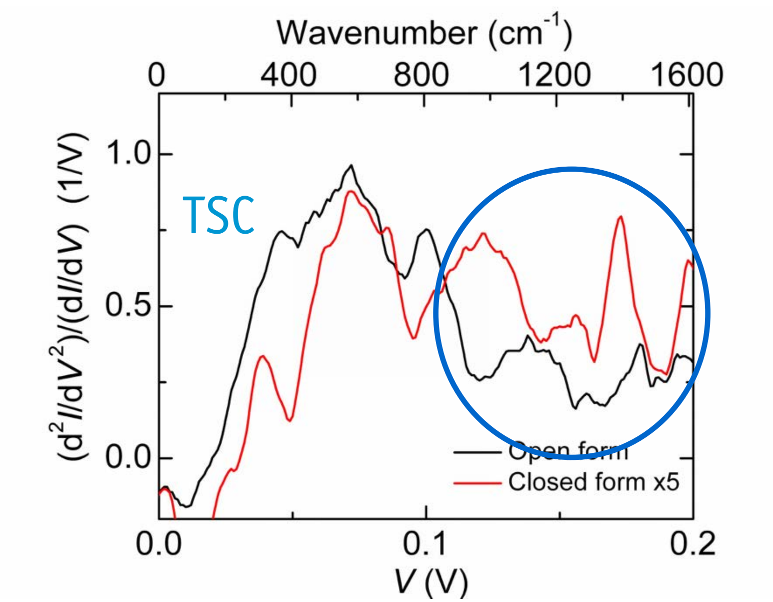
Experiment: I-Vs at 4K

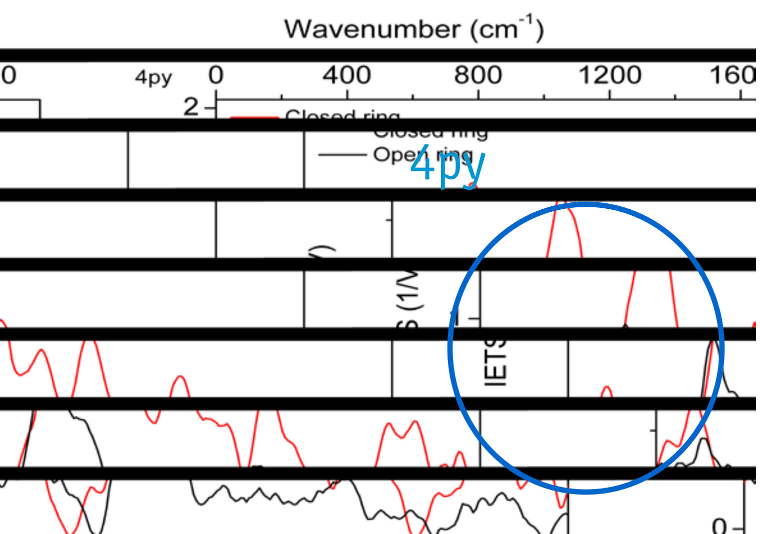


IETS: Shift of N-N stretching mode



IETS in open & closed forms





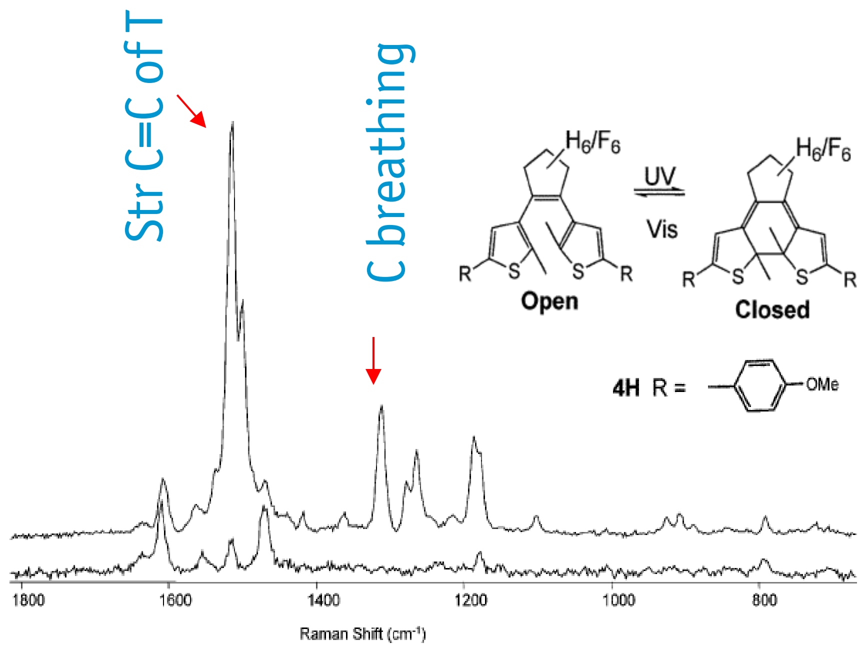


Fig. 12 Raman spectra of **4Ho** (lower spectrum) to **4Hc** (upper spectrum)—irradiation at 313 nm, spectra recorded at $\lambda_{exc} = 785$ nm, 6×20 s accumulations.

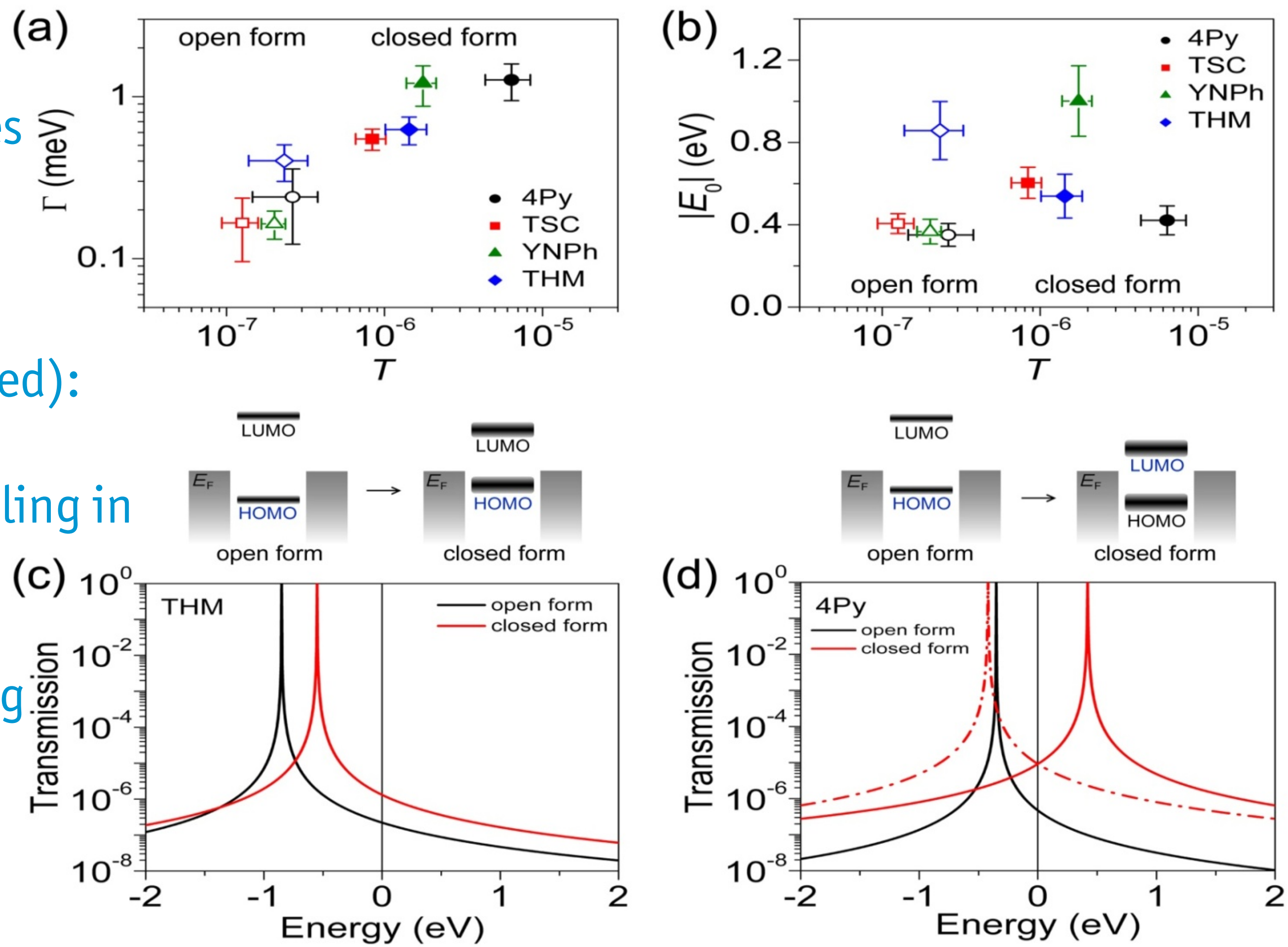
Org. Biomol. Chem. 4, 2387 (2006)

C: cyclopenten
T: thiophenen

Level alignment: HOMO/LUMO switching?

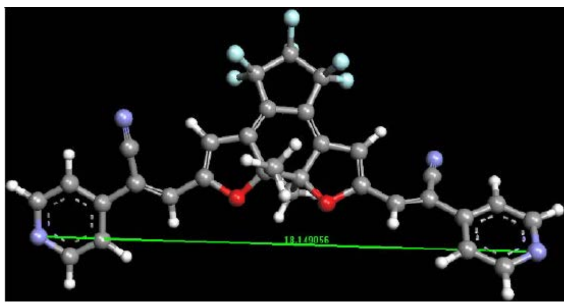
THM (non-conjugated):
- Level alignment behaves as expected.

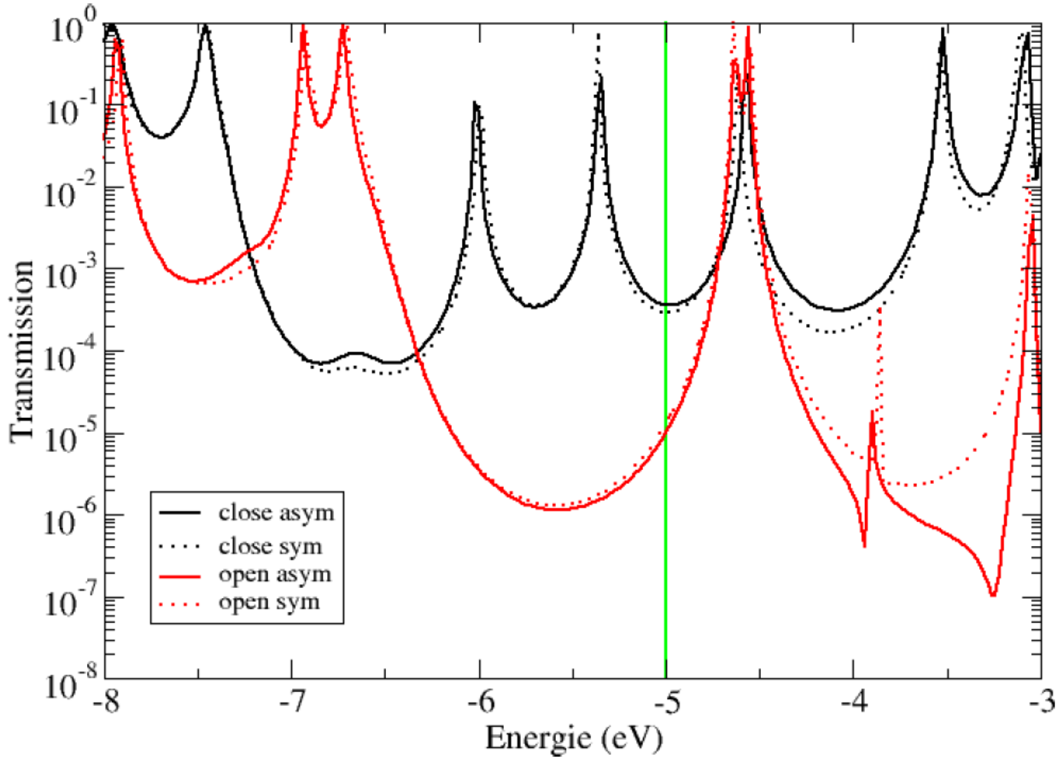
4Py, TSC, YnPh (conjugated):
- Bad level alignment in closed form, good coupling in closed form
- Good level alignment in open form, bad coupling in open form



Theory: Transmission function

4Py





Open ring ~ 8E-6 G_0
Closed ring ~ 3E-4 G_0

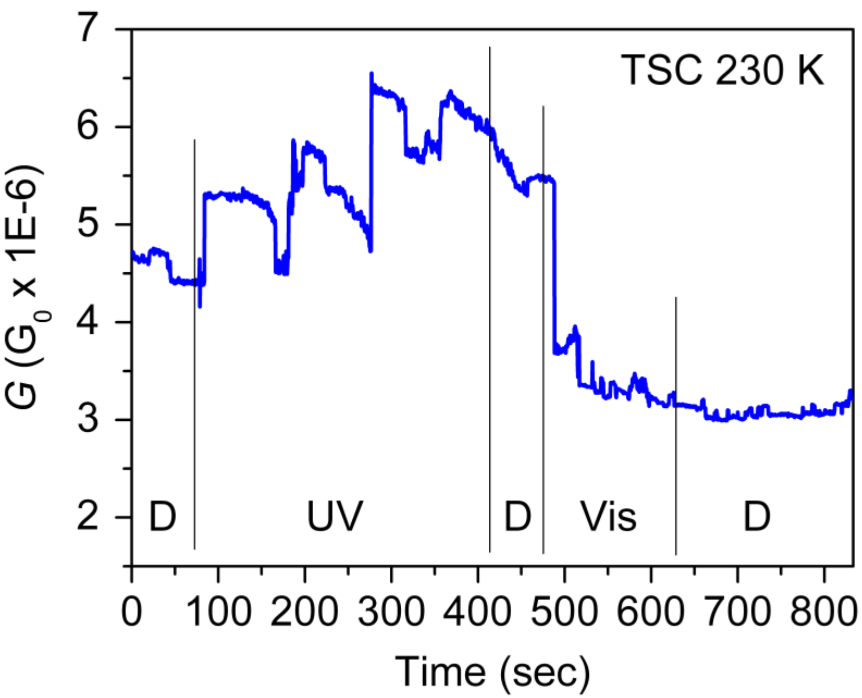
G_{close}/G_{open} ~ 40

Courtesy: F. Pauly, Th. Hellmuth

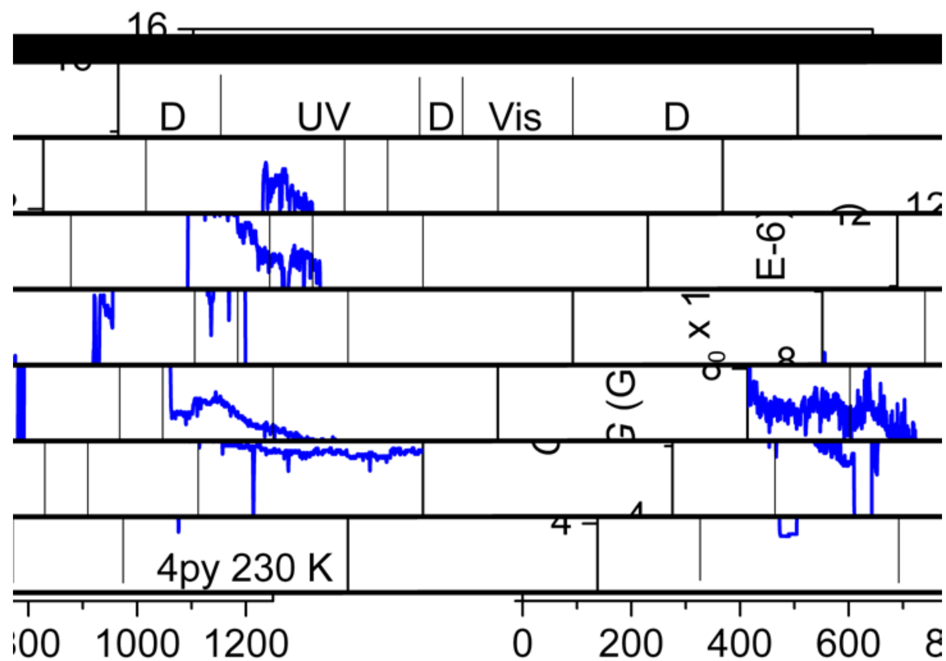
Conductance Switching at 230 K

0.05 mW/cm^2

TSC

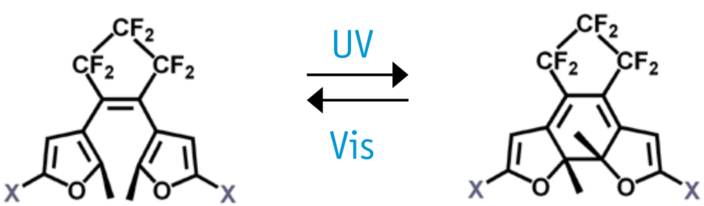


4Py

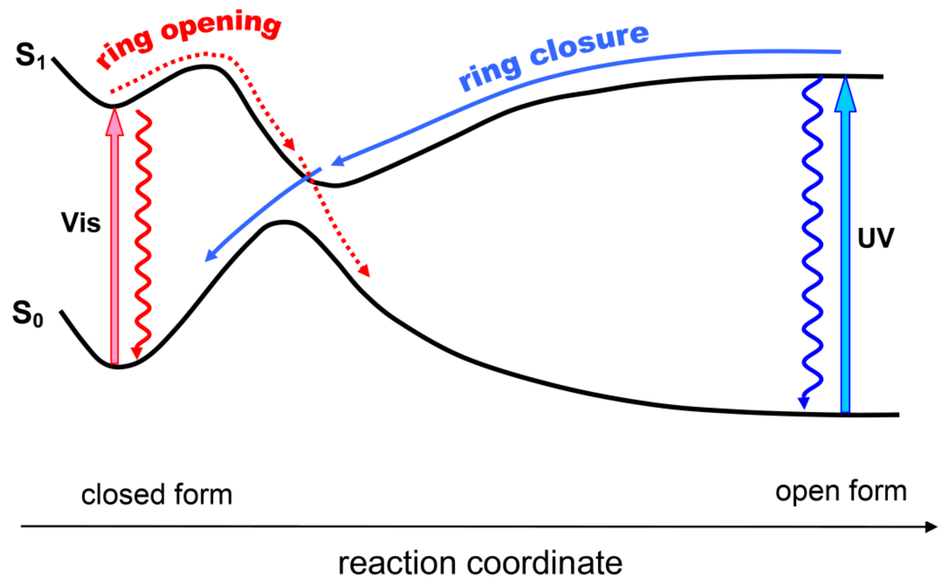


Single-molecule switching

Diarylethene



open *closed*

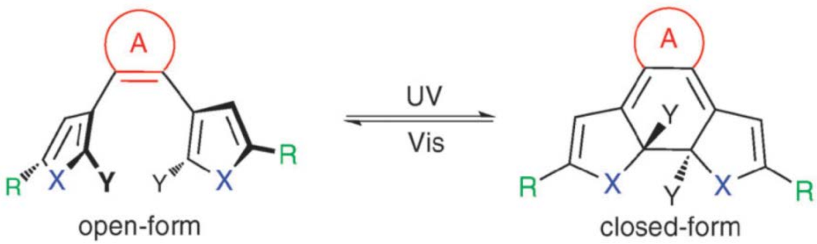


M. Irie, *Photoreactive materials for ultrahigh-density optical memory*, Elsevier: Amsterdam, 1994

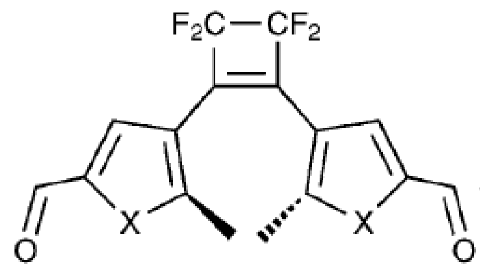
B. Feringa, *Molecular Switches*, 2^{nd} edition, VCH-Verlag, 2011

Further optimization of switching properties

The diarylethene family:

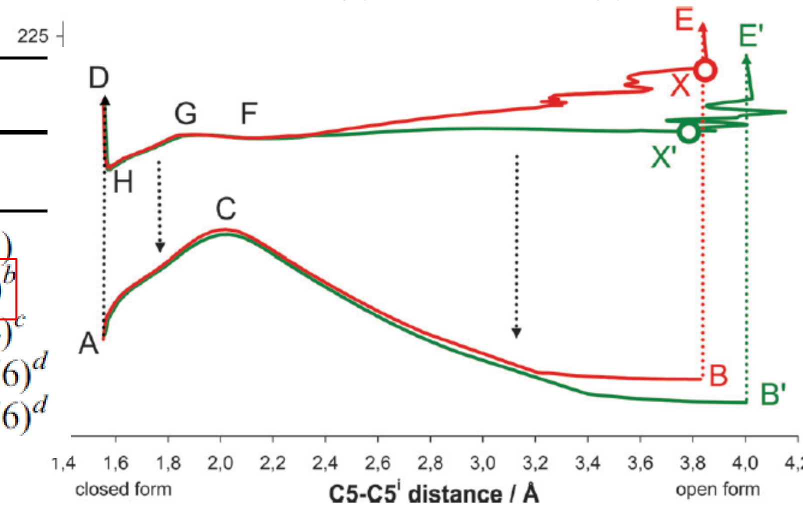


Tuning the quantum yield: A-ring



X = O: C4F-CHO (**2**)   X = S: C4F-T-CHO (**5**)

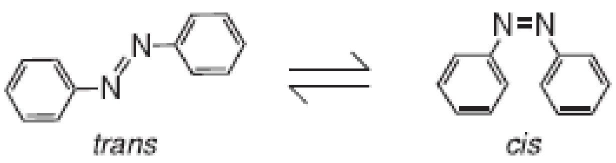
	$\phi_{o\rightarrow c}$ (313 nm)		$\phi_{c\rightarrow o}$ (λ_2 [nm])	
π-Substituent	C4F-	C5F-	C4F-	C5F-
NPA	14	20	8.6 (438)	9.0 (438)
CHO	1.0[b]	34[b]	46 (576)[b]	14 (576)[b]
T-CHO	2.6[b]	86 (351)[c]	8.8 (576)[b]	3.6 (514)[c]
TSC	0.024	28[d]	2.4 (576)	0.49 (576)[d]
MTSC	0.039	38[d]	1.0 (576)	0.32 (576)[d]

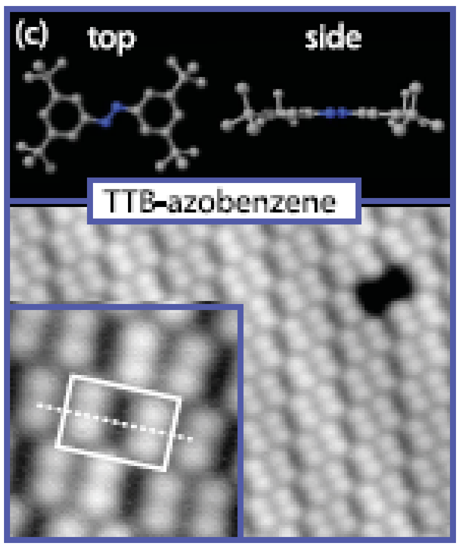


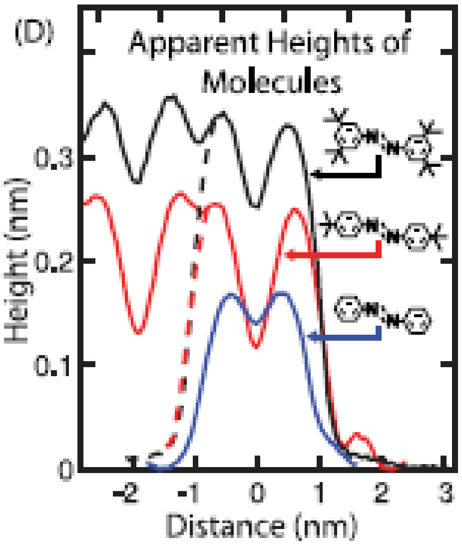
CASSCF & DFT calculation

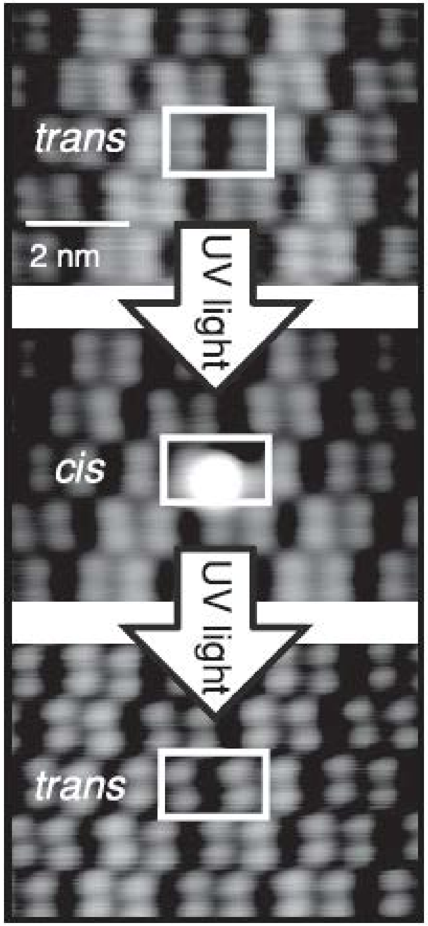
D. Sysoiev et al., Chem. Commun. **48**, 11355 (2012)

Azobenzene switches

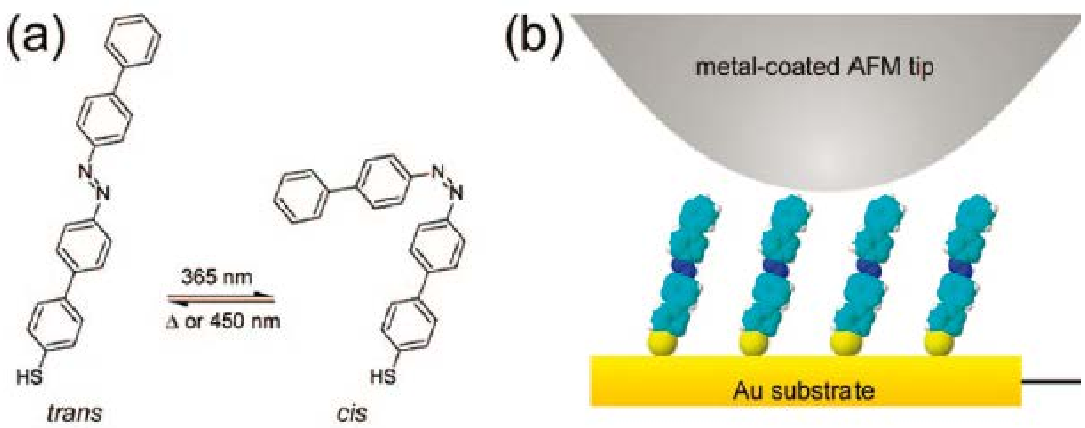


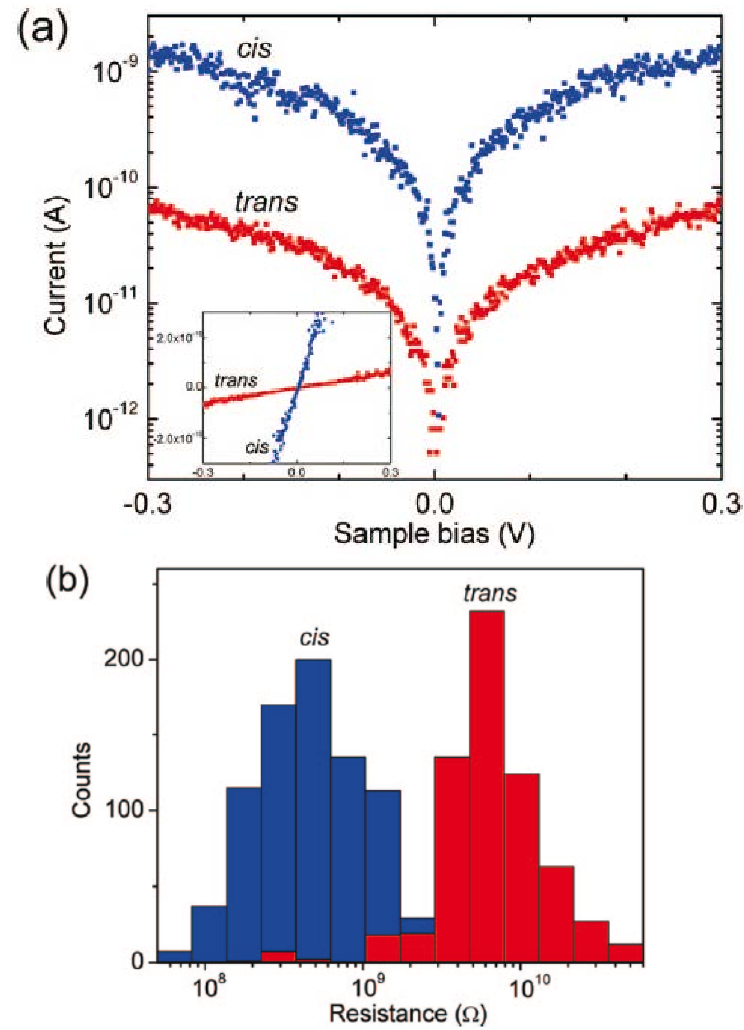






Azobenzene switches





Theory: CNT-Azo-CNT

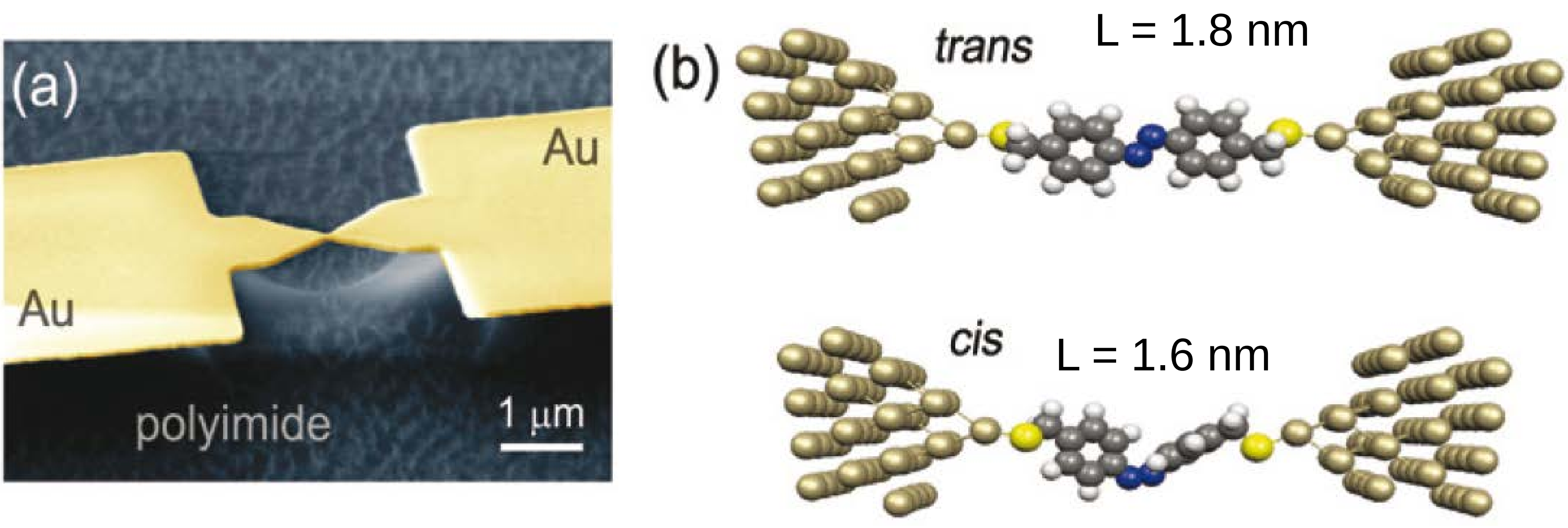
Del Valle et al, Nature Nano 2, 176 (2007)

$G_{trans} > G_{cis}$

M. Mativetsky et al, JACS 130, 9210 (2008)

Azobenzene-based switches

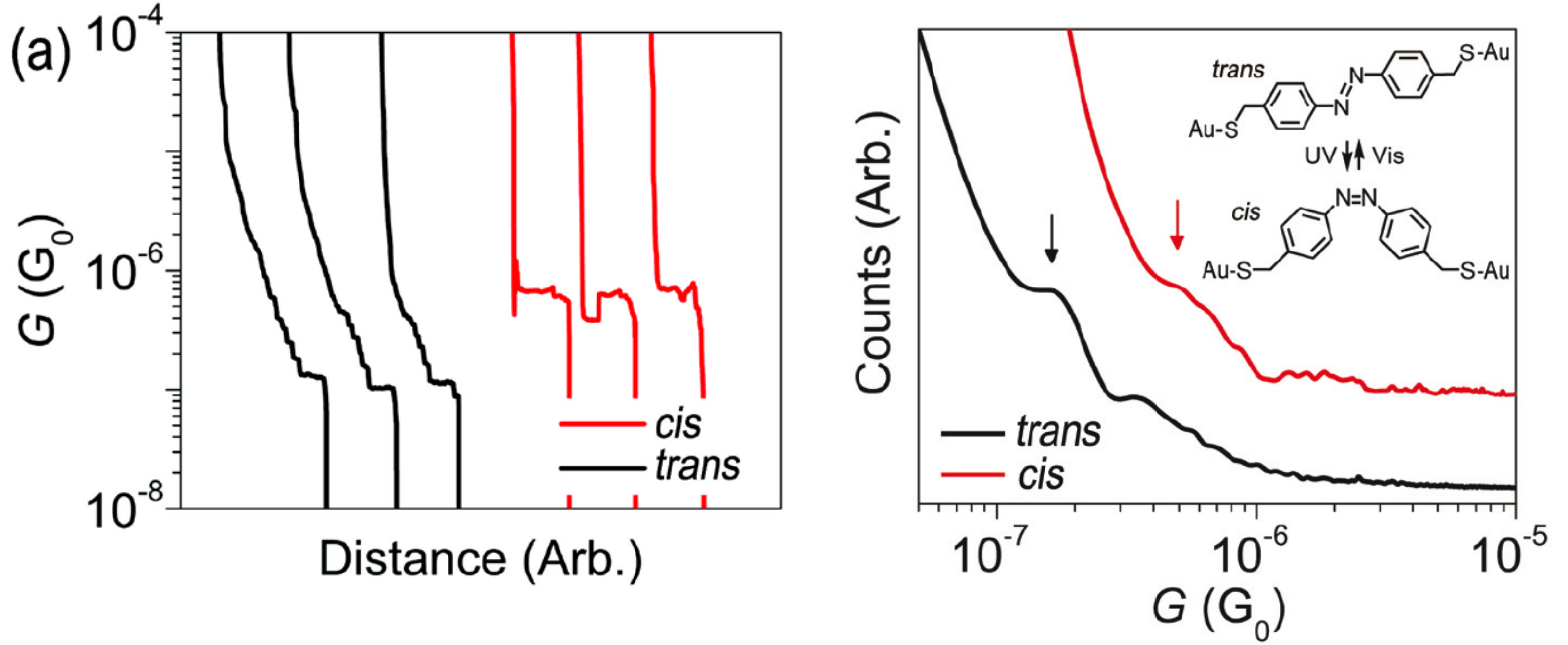
Decoupling of switching core by CH2 group



Y. Kim, A. Garcia-Lekue, D. Sysoiev, T. Frederiksen, U. Groth, E. Scheer, PRL 109, 226801 (2012)

Universität Konstanz

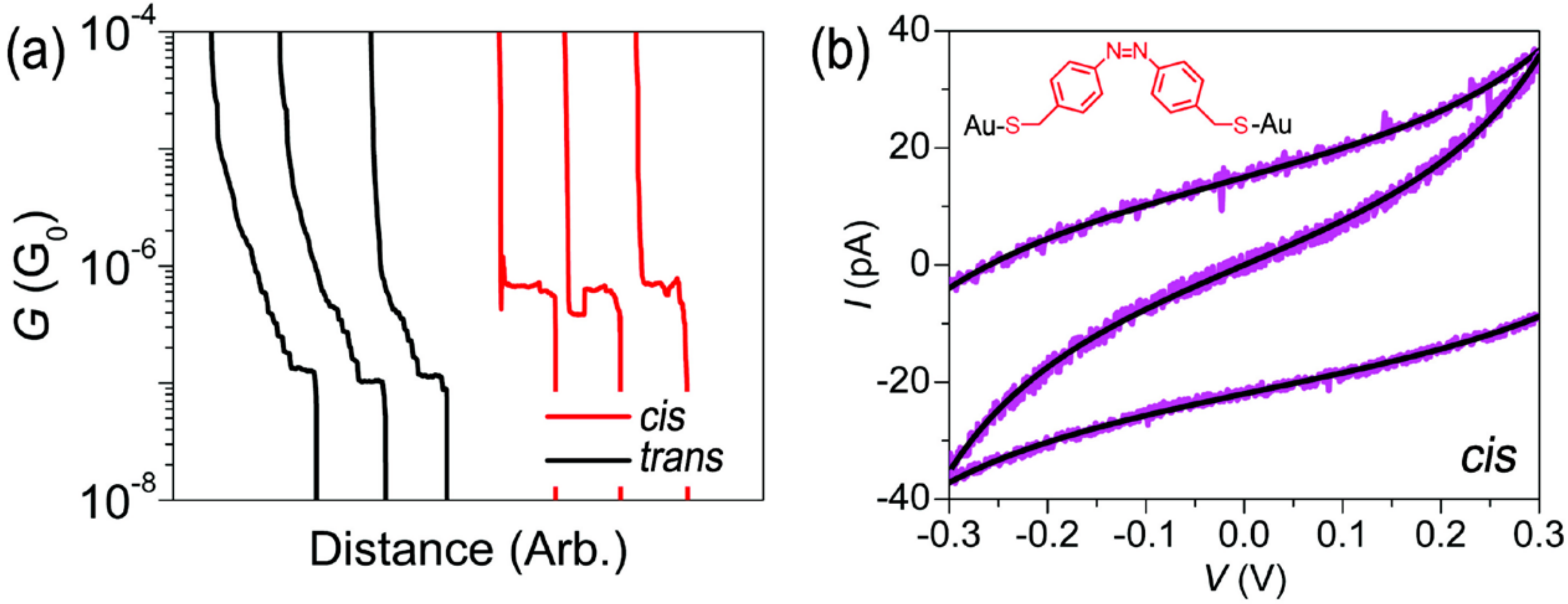
Single-molecule transport at 4 K



cis **has higher conductance than *trans*:** $G_{cis}/G_{trans} \sim 3$

Y. Kim, A. Garcia-Lekue, D. Sysoiev, T. Frederiksen, U. Groth, E. Scheer, PRL 109, 226801 (2012)

Single-molecule transport at 4 K



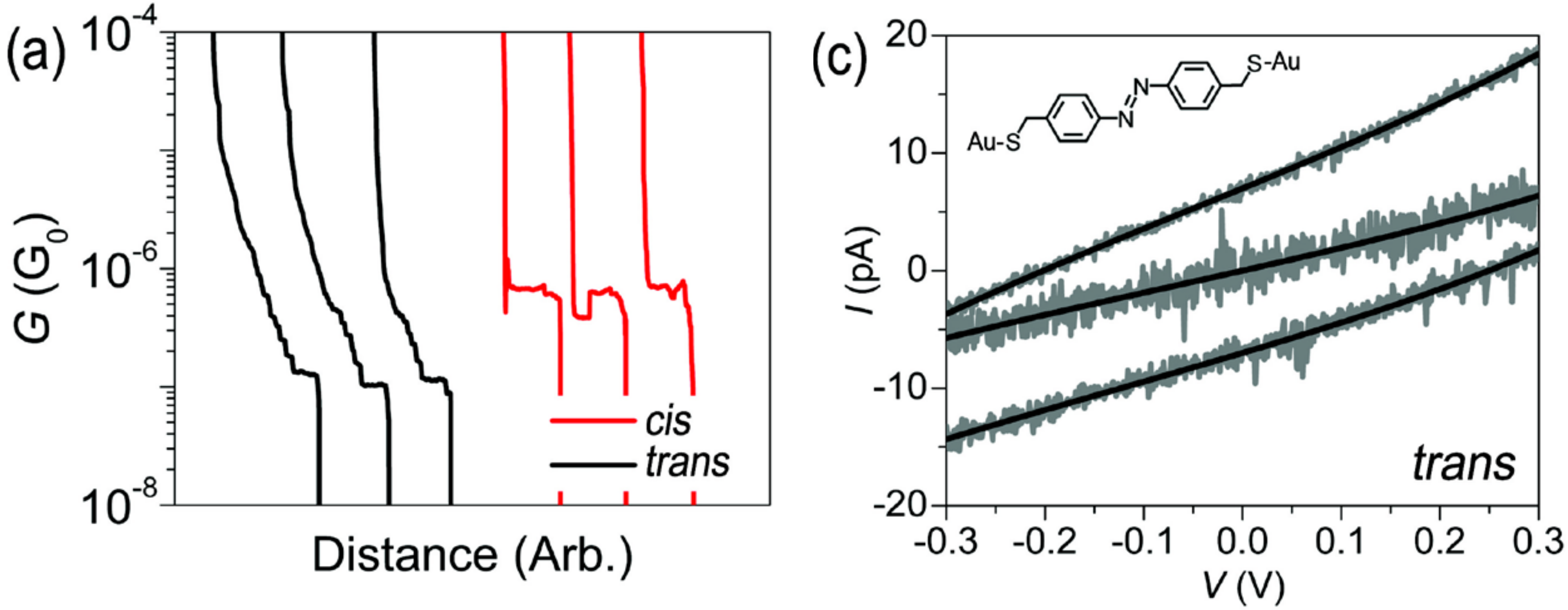
Fitting with single-level model :

cis: $E_0 = 0.36$ +/- 0.05 eV, $\Gamma = 0.28$ +/- 0.1 meV

trans: $E_0 = 0.52$ +/- 0.06 eV, $\Gamma = 0.26$ +/- 0.06 meV

Y. Kim, A. Garcia-Lekue, D. Sysoiev, T. Frederiksen, U. Groth, E. Scheer, PRL 109, 226801 (2012)

Single-molecule transport at 4 K



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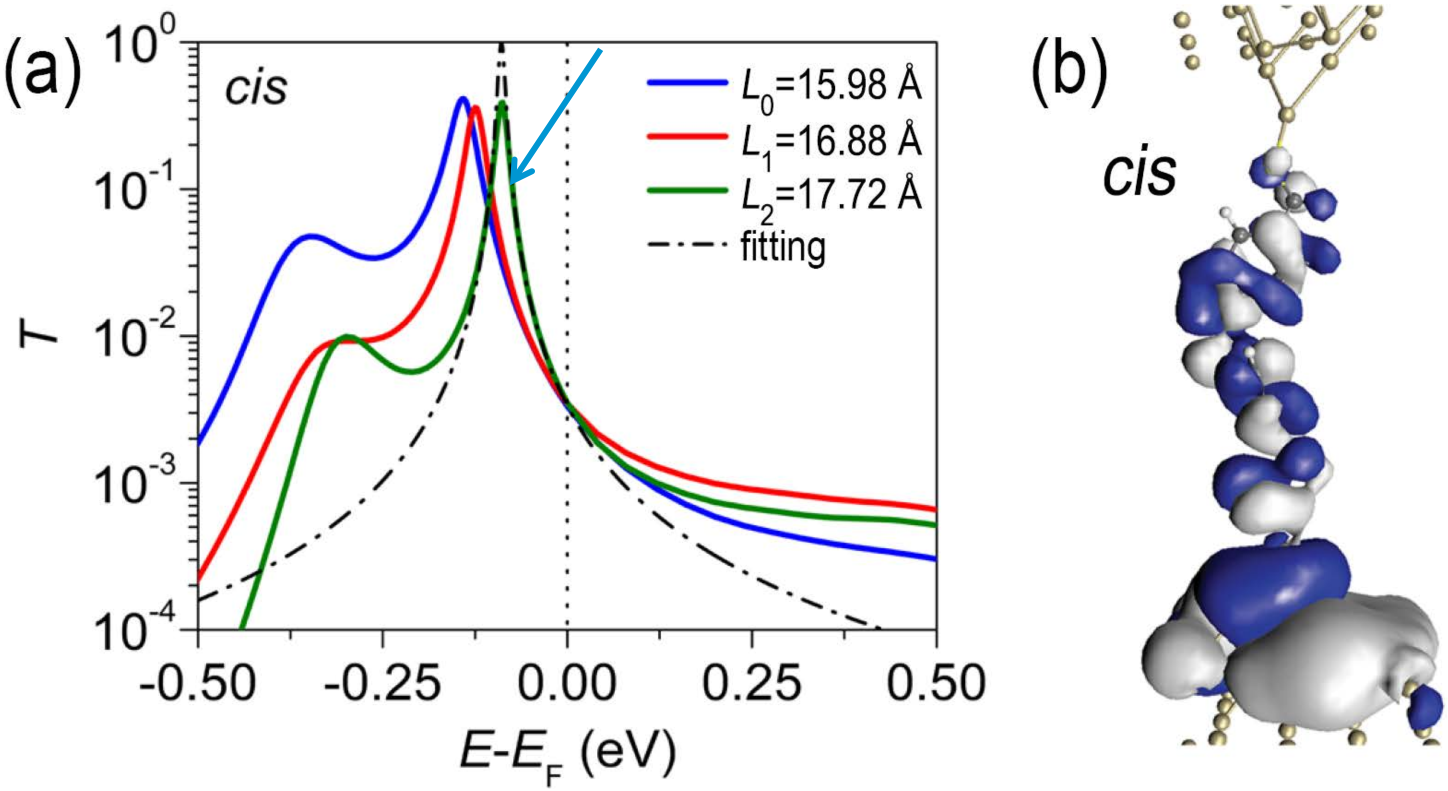
Y. Kim, A. Garcia-Lekue, D. Sysoiev, T. Frederiksen, U. Groth, E. Scheer, PRL 109, 226801 (2012)

Transmission function

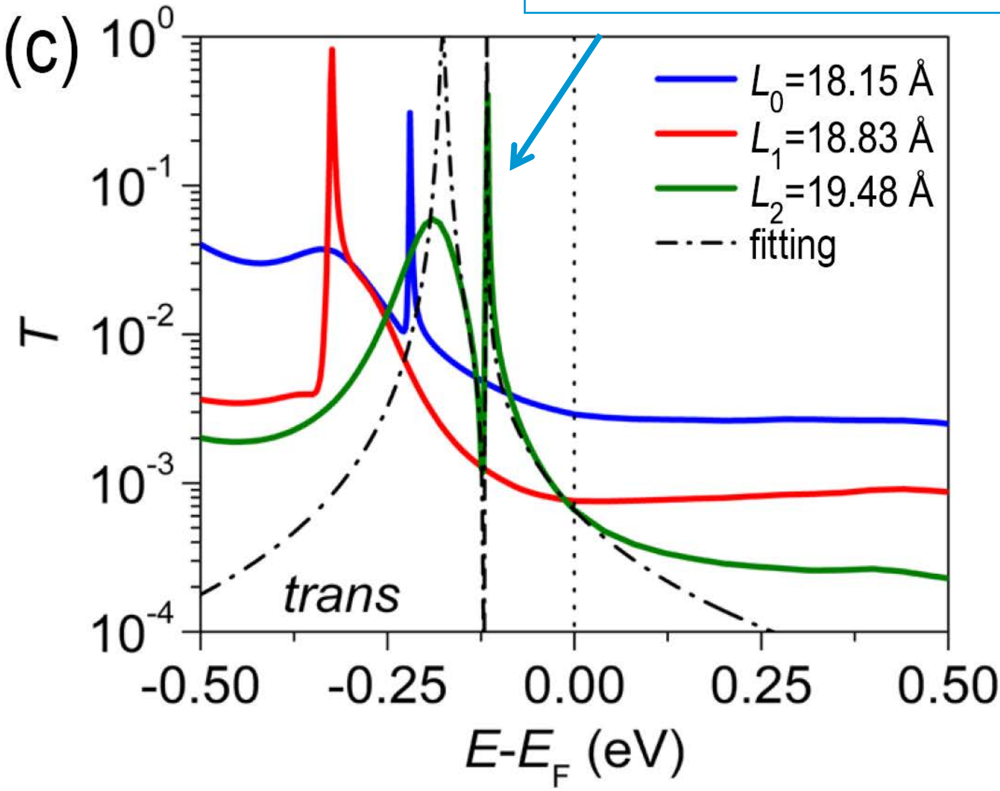


cis conformation

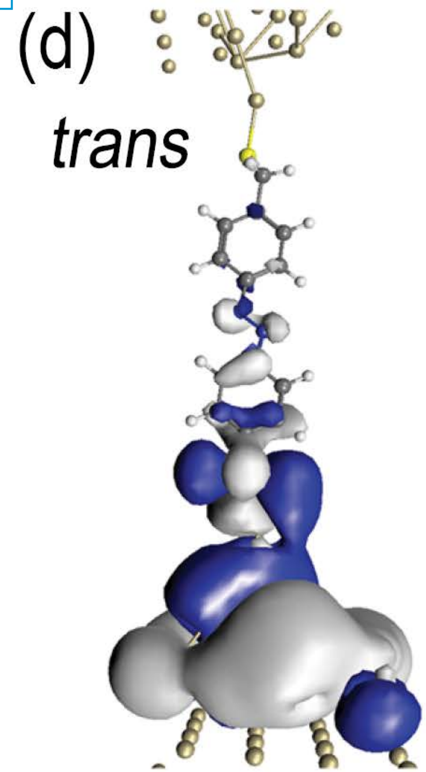
HOMO

Transmission function

HOMO localized at N-N

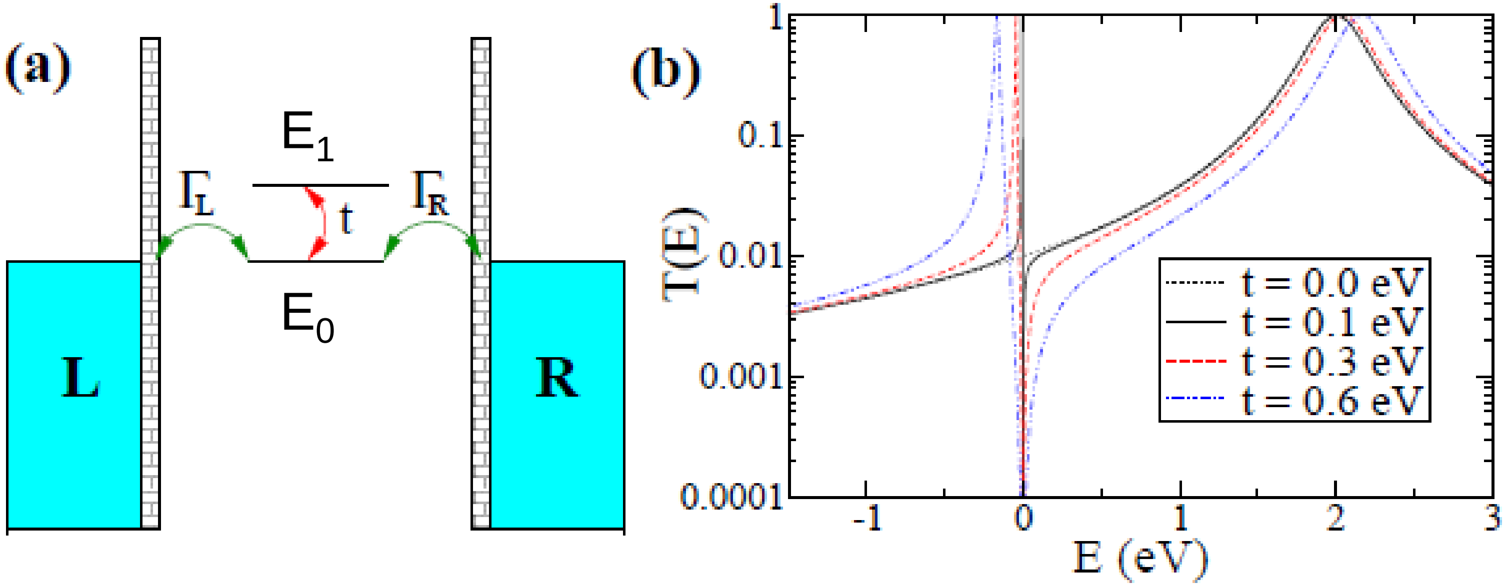


trans conformation



HOMO-1

Fano Resonance



$$T(E) = \frac{\Gamma^2}{\left[E - E_0 - t^2/(E - E_1)\right]^2 + \Gamma^2}$$

Summary

- Lower conductance of *trans*–AzoTM caused by Fano resonance
- Unexpected electronic structure of conjugated diarylethene switches: Indication for switching from HOMO transport in open form to LUMO transport in closed form

Open Questions & Outlook

- Enhancing quantum yield and conductance!
- Making on/off switching ratio more symmetric
- Reversible optical switching of current in a single-molecule device at low temperature possible?
- Switching mechanism: direct photoexcitation or metal-mediated?
- Plasmon enhancement by antenna action of electrodes?