Lecture 9: STM study of single-molecule electronics

Background and significance of molecular electronics: *why critical to study at single-molecule level?*

<u>Part 1</u>: Single-molecule conductivity estimated by current/voltage (I/V) measurement:

1. Monolayer systems,
2. Nano-electrode systems,
3. AFM/nanoparticle approach,
4. STM break-junction approach.

<u>Part 2</u>: Single-molecule FET :

1. Comparison between bulk phase FET and molecular FET,
2. Mechanism of molecular FET: Hopping vs. Tunneling,
3. Fabrication and characerization of single-molecule FET devices: Nanogap electrode system vs. STM break-junction technique.
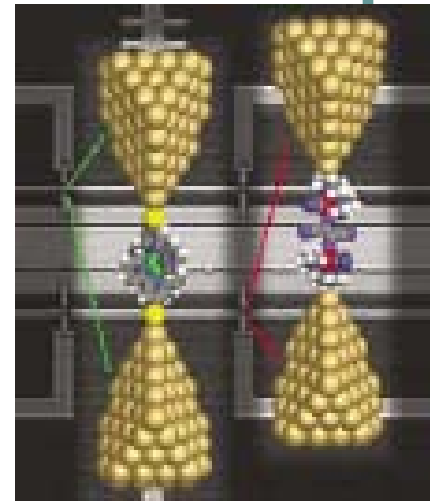
Where the idea of molecular electronics came from ...

Prof. Mark Ratner, Department of Chemistry, Northwestern University

Why Molecular Electronics?

- <u>Possibility</u> proved by both theoretical and experimental work.

  1). In 1974, Aviram and Ratner proposed the idea of molecular diode for rectifying, followed by many other theoretical researches.

   A. Aviram, & M.A. Ratner Chem. Phys. Lett. **29**, *277 (1974).*
   "Molecular Rectifiers"

  2). In 1990's, molecular electronic devices have been fabricated based on nano-electrode systems.

- <u>Demanded</u> by the miniaturization of electronic devices.

  1). Faster computers are required --- *Tera* Hz processor with molecular transistors.

  2). Limit of photo-lithographic methods (a few hundreds nm).

  3). High density memory chips.

  4). Sensors, switches, LEDs, photovoltaics, etc.

Highly Conductive Molecular Wires

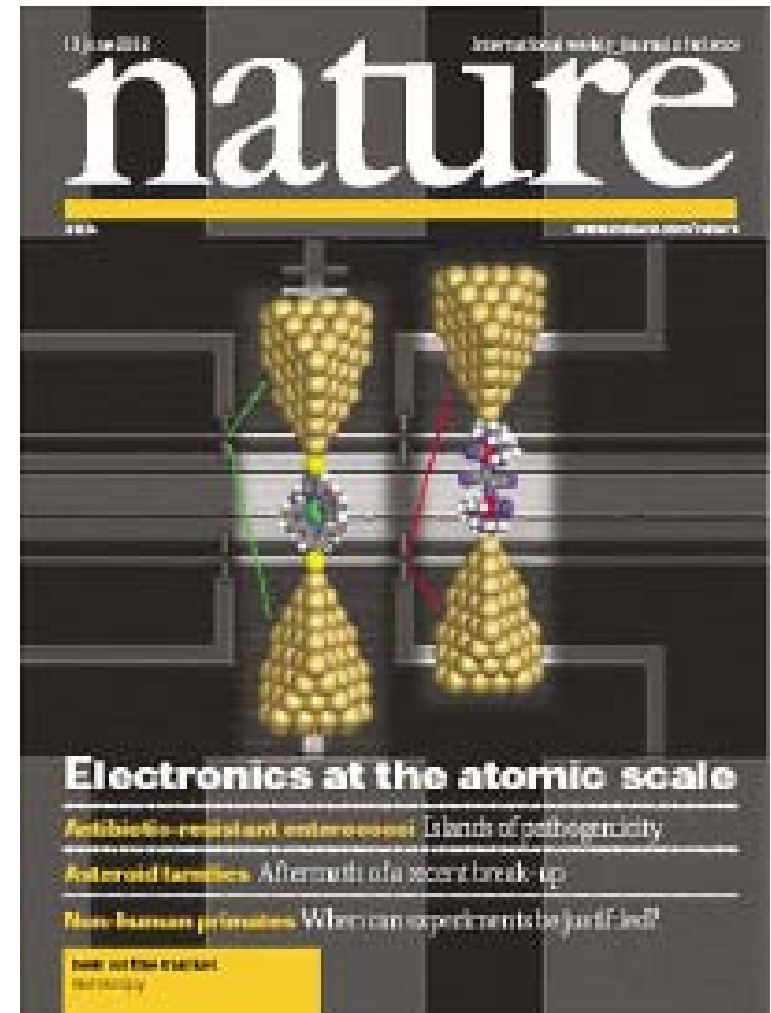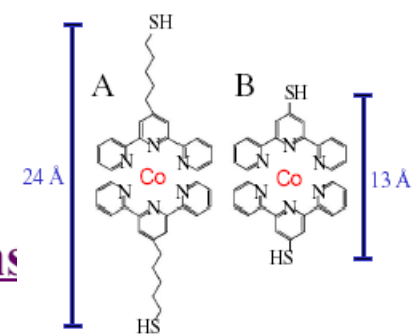|	Cross-section size (nm^2)	Current Density (electrons/nm^2 sec)
1 mm copper wire	~ 3×10^{12}	~ 2×10^{6}
	~ 0.05	~ 4×10^{12}
Carbon nanotube	~ 3	~ 2×10^{11}

Why at Single-molecule level?

1. Bulk systems contain large number of molecules that are not necessarily present exactly the same, i.e., the orientation and configuration of molecules, as well as local environment, may be different among the molecules.

2. Traditional bulk measurements are based on average of all the individual molecules, and an assumption that all the component molecules (though the same in chemical composition) are the same in terms of the physical and chemical properties (like the electrical conductivity as concerned in this lecture).

3. Single-molecule measurement removes the average, by measuring only one molecule at a time, enabling to reveal the difference between the individual molecules that may be caused by the different orientations or configurations of molecules, or their local environments like polarity.
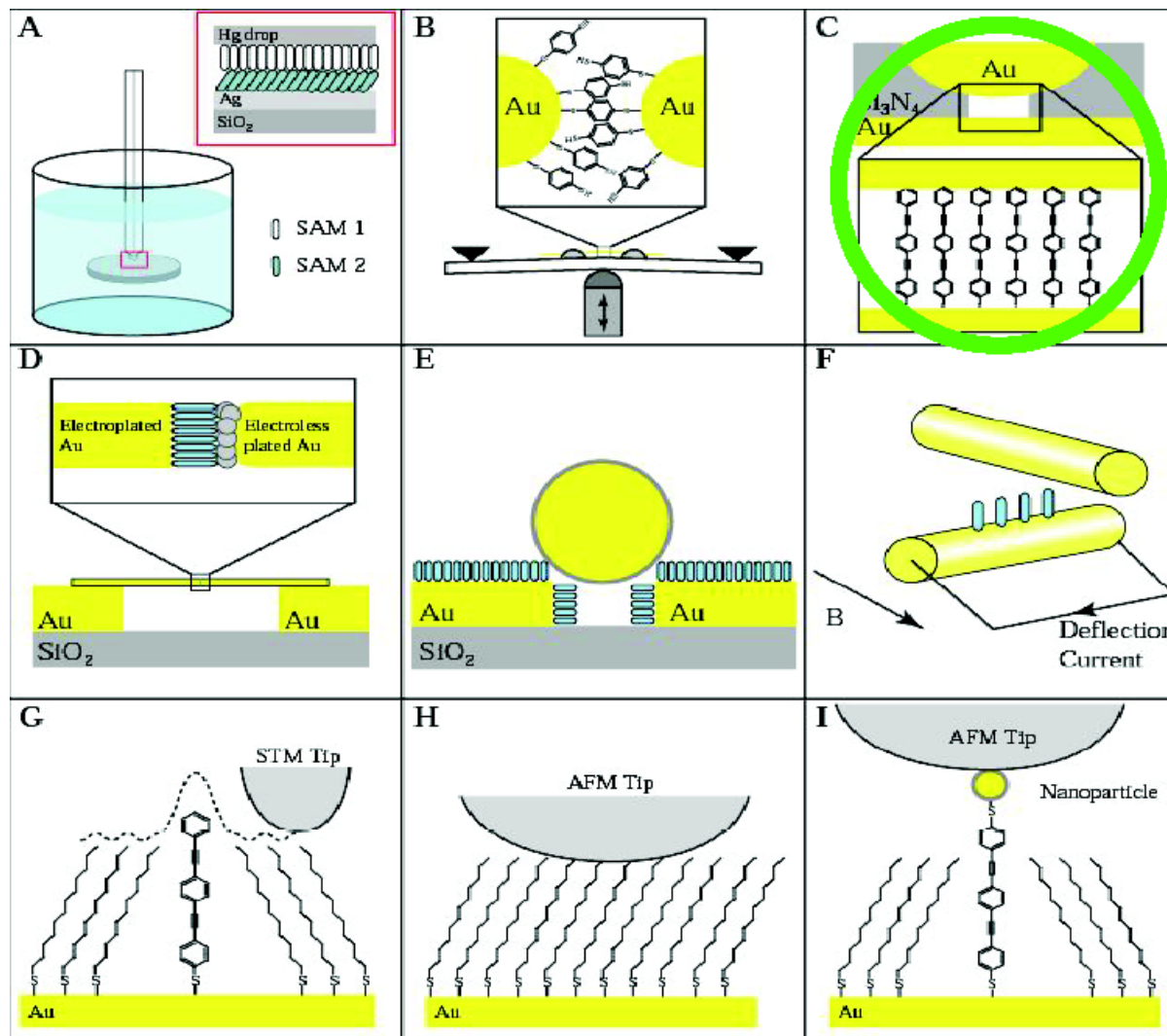
Breakthrough of the year 2001:
Molecules get wired.

GATED
Single wire junctions

A   B

24 Å   13 Å

Science
21 December 2001
Vol. 294   No. 5551
Pages 2417-2616   59

Breakthrough
of the Year

Nanocircuits

AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

nature
13 june 2002   International weekly journal of science

Electronics at the atomic scale

Antibiotic-resistant enterococci Islands of pathogenicity
Asteroid families Aftermath of a recent break-up
Non-human primates When can experiments be justified?

Different Experimental Systems for Calibration of Molecule Conductivity

The Reality of Molecular Electronics

Ultimate goal --- Interconnecting and integrating million or billions of
molecular units into a functional *chip*.

Challenge --- An Intel P4 chip has ~ <u>50 M</u> transistors; if replaced with
molecular units, it will have more than <u>billions</u> of molecules.

**Long Term Approach** --- large scale assembly and organization of molecules.

Short Term Promise --- *Single-Molecule Devices (switch & sensor).*
Understanding of the fundamental processes of charge
transfer through molecules and interfaces.
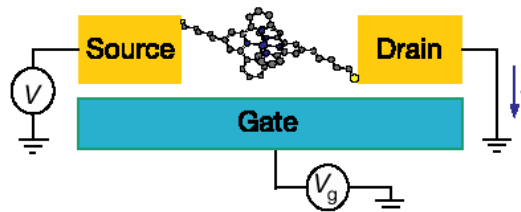
# Challenges of *Current/Voltage* (I/V) Measurement

- Contact Problem --- *molecules really bonded to the electrode?*

- Single-Molecule? *--- not sure.*

- Measurement *--- ensemble and average.*

- Electrode Fabrication *--- low production yield for small gap.*
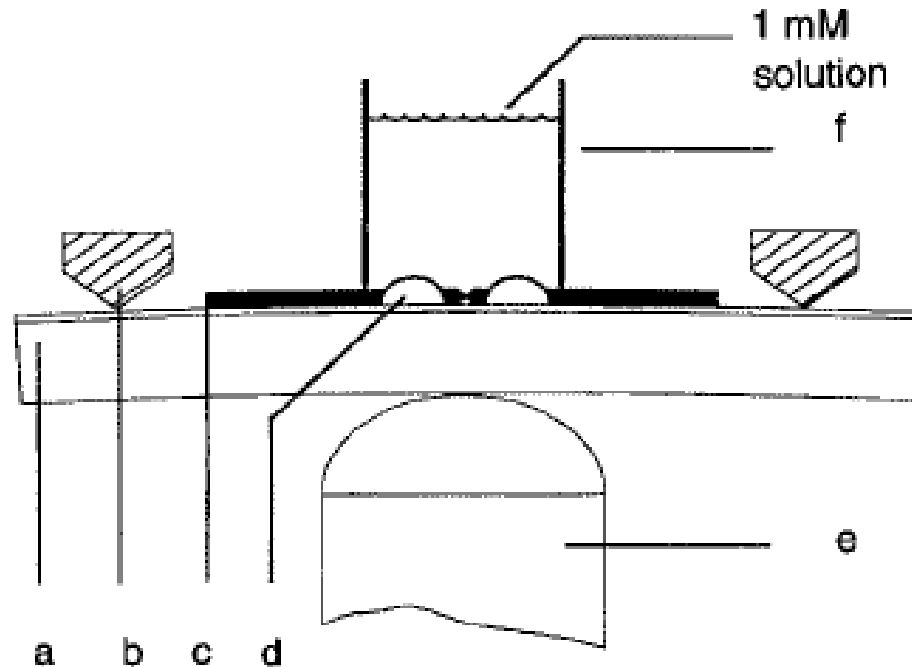

Molecular FET Device

A few molecules   Contact problem
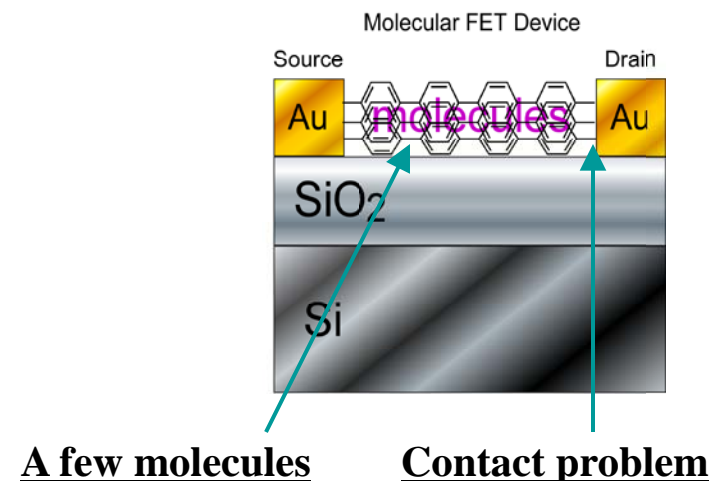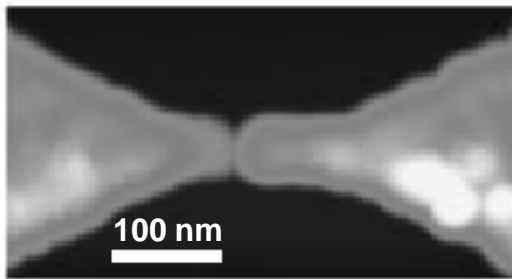
Fabrication and Evaluation of Molecular Devices:
1) Current/Voltage Measurement

- Surface deposited electrode

  systems: *distance fixed.*

- Piezo controlled electrode

  system: *distance adjustable.*

- AFM/STM based

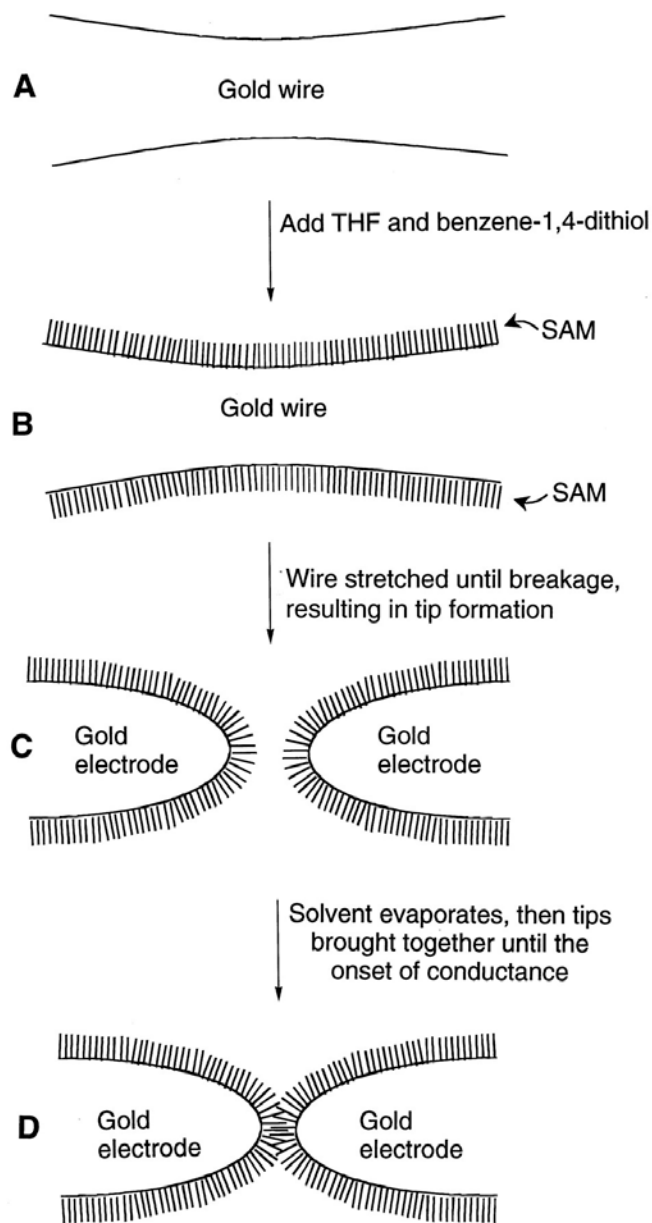 measurement: *flexible for*

  various kinds of samples.
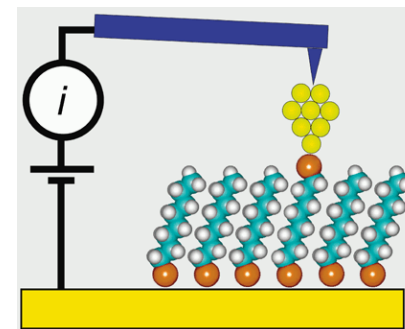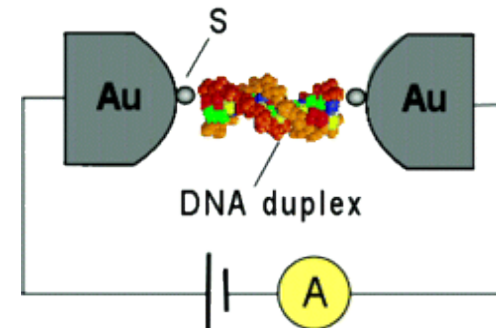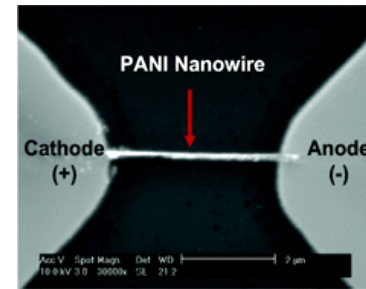
The first break-junction by Reed

Fig. 1. A schematic of the MCB junction with (a) the bending beam, (b) the counter supports, (c) the notched gold wire, (d) the glue contacts, (e) the pizeo element, and (f) the glass tube containing the solution.

The first break-junction by Reed

(**A**) The gold wire of the break junction before breaking and tip formation.

(**B**) After addition of benzene-1,4-dithiol, SAMs form on the gold wire surfaces.

(**C**) Mechanical breakage of the wire in solution produces two opposing gold contacts that are SAM-covered.

(**D**) After the solvent is evaporated, the gold contacts are slowly moved together until the onset of conductance is achieved.

Reed and Tour, SCIENCE, VOL. 278, 1997, p252
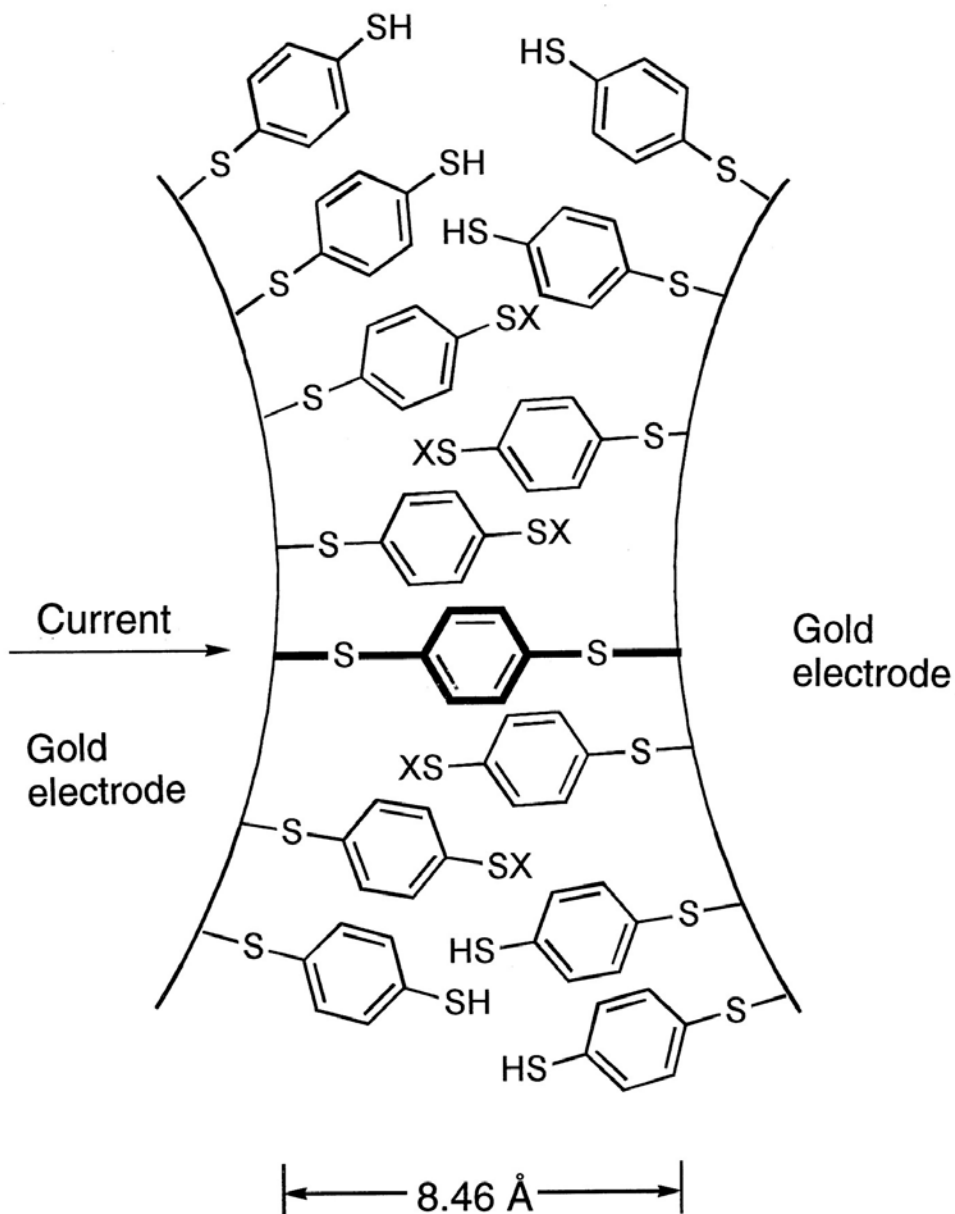
A schematic of a benzene-1,4-dithiolate SAM between proximal gold electrodes formed in an MCB.

The thiolate is normally H-terminated after deposition; end groups denoted as X can be either H or Au, with the Au potentially arising from a previous contact/retraction event. These molecules remain nearly perpendicular to the Au surface, making other molecular orientations unlikely

Reed and Tour, SCIENCE, VOL. 278, 1997, p252

Example #1: Reproducible Measurement of Single-Molecule Conductivity

X. D. Cui,[1] A. Primak,[2, 3] X. Zarate,[2] J. Tomfohr,[1] O. F. Sankey,[1] A. L. Moore,[2] T. A. Moore,[2] D. Gust,[2] G. Harris,[3] S. M. Lindsay[1]

[1] Department of Physics and Astronomy,
[2] Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA.
[3] Motorola, 2100 East Elliot Road, AZ34/EL 704, Tempe, AZ

85284, USA.
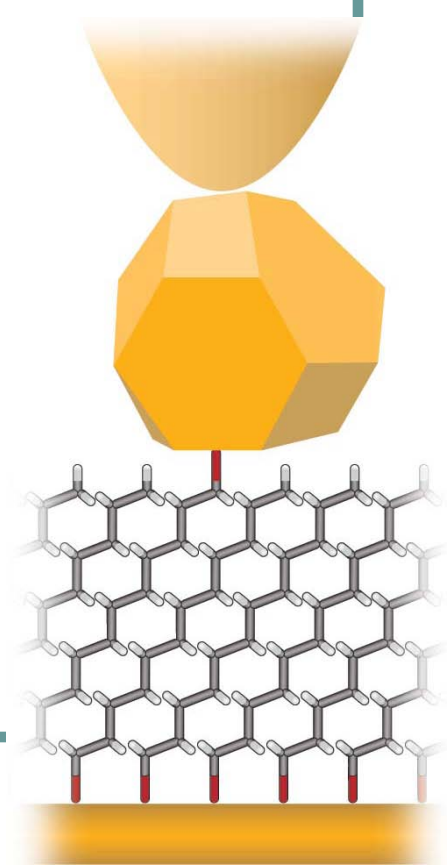
Significance

- Wiring a single molecule into an electrical circuit by chemically bonding each end to a metal conductor is a key requirement for molecule-based electronics.

- Although conceptually simple, this goal has proven elusive.

- A wide variety of methods have been developed and used for contacting molecules.

- However, unambiguous contact to a **single molecule** is difficult to achieve, as shown by large disparities in conductivities reported for identical or similar molecules.

- Calculated conductivity can disagree with experimental results by <u>several orders</u> of magnitude.

- In many cases, electrical connections to the molecules have been made via **nonbonded** mechanical contacts rather than chemical bonds, and it is likely that this may account for some of the discrepancies.
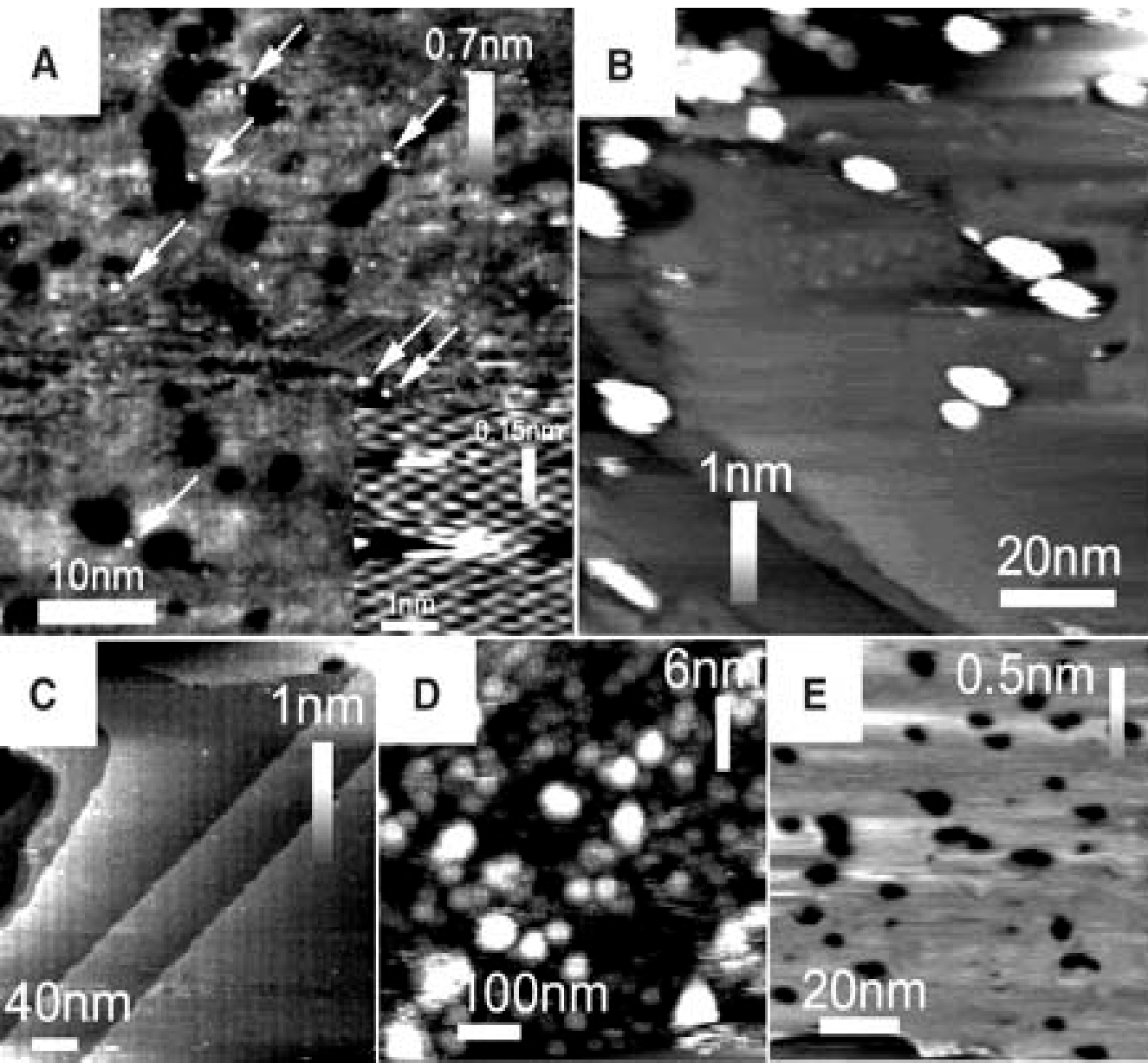
A) 1,8-octanedithiol molecules inserted into an octanethiol monolayer. Arrows point to the protruding thiols (shown at molecular resolution in the inset). The bright spots increase in density, but not in apparent size, with increasing dithiol exposure. (**B**) A mixed monolayer similar to that shown in (A) after incubation with gold nanoparticles that attached to the protruding thiols. The density of attached gold particles is of the same order of magnitude as the density of protruding thiols measured in A). (**C**) Pure 1,8-octanedithiol monolayer.
(**D**) The same monolayer after incubation with the gold nanoparticle suspension and rinsing, showing that the whole surface is covered with large gold aggregates.
(**E**) A pure octanethiol monolayer subjected to the same treatment, showing that no gold particles are bound.

STM images

(**A**) Schematic representation of the experiment. The sulfur atoms (red dots) of octanethiols bind to a sheet of gold atoms (yellow dots), and the octyl chains (black dots) form a monolayer. The second sulfur atom of a 1,8-octanedithiol molecule inserted into the monolayer binds to a gold nanoparticle, which in turn is contacted by the gold tip of the conducting AFM.

(**B**) $I(V)$ curves measured with the apparatus diagrammed in (A). The five curves shown are representative of distinct families, $NI(V)$, that are integer multiples of a fundamental curve, $I(V)$ ($N = 1, 2, 3, 4,$ and 5).

(**C**) Curves from (B) divided by 1, 2, 3, 4, and 5.

(**D**) Histogram of values of a divisor, X (a continuous parameter), chosen to minimize the variance between any one curve and the fundamental curve, $I(V)$. It is sharply peaked at integer values 1.00 ± 0.07 (1256 curves), 2.00 ± 0.14 (932 curves), 3.00 ± 0.10 (1002 curves), 4.00 ± 0.10 (396 curves) and 5.00 ± 0.13 (993 curves). (Spreads are ±1 SD.) Of 4579 randomly chosen curves, over 25% correspond to the $X = 1$ (single-molecule) peak.

Setup: conducting AFM.
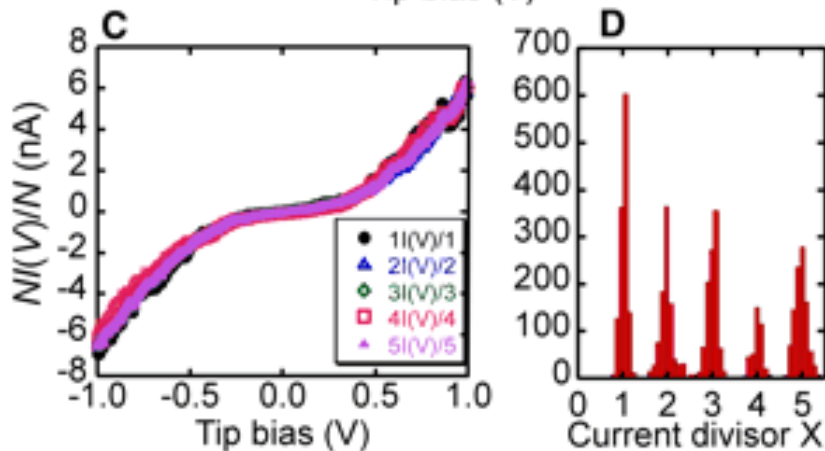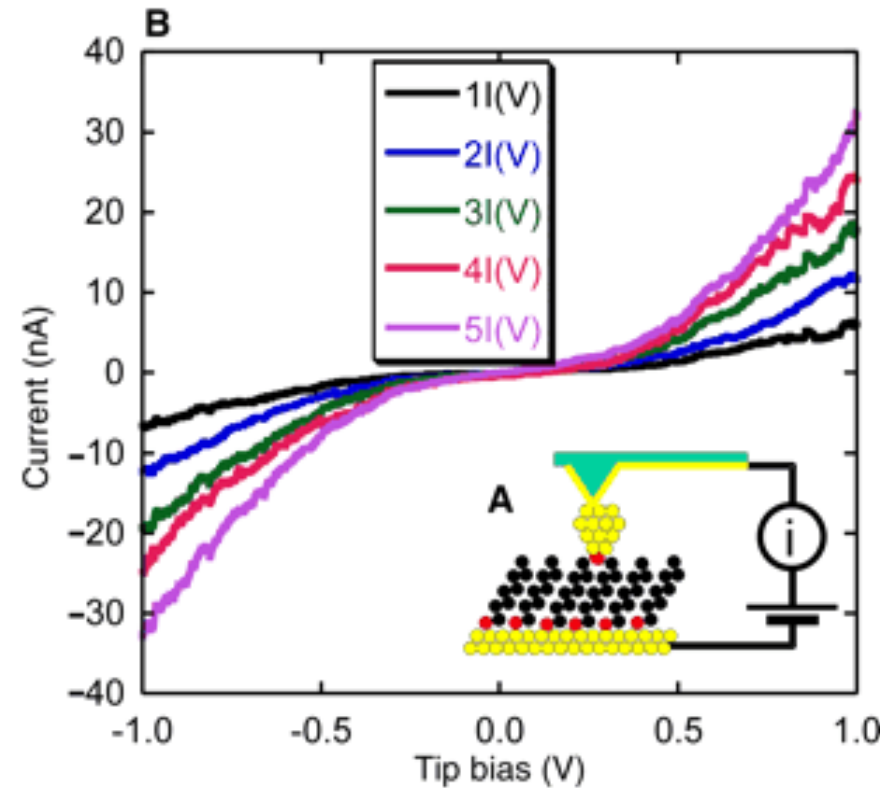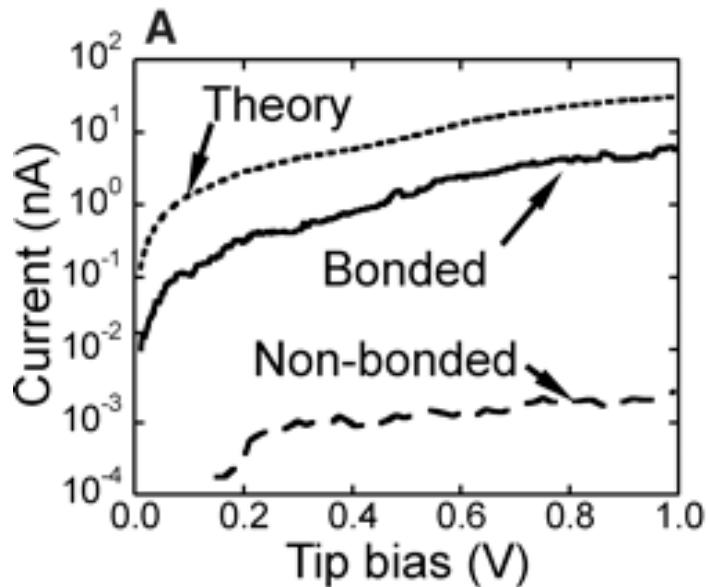
(**A**) Current (on a log scale) as a function of voltage as calculated from first principles with no adjustable parameters (dashed line), as measured for a bonded single molecule (solid line), and for a nonbonded contact (contact force = 6 nN) to the surrounding octanethiol matrix (broken line) (noise-dominated data at low bias are suppressed).
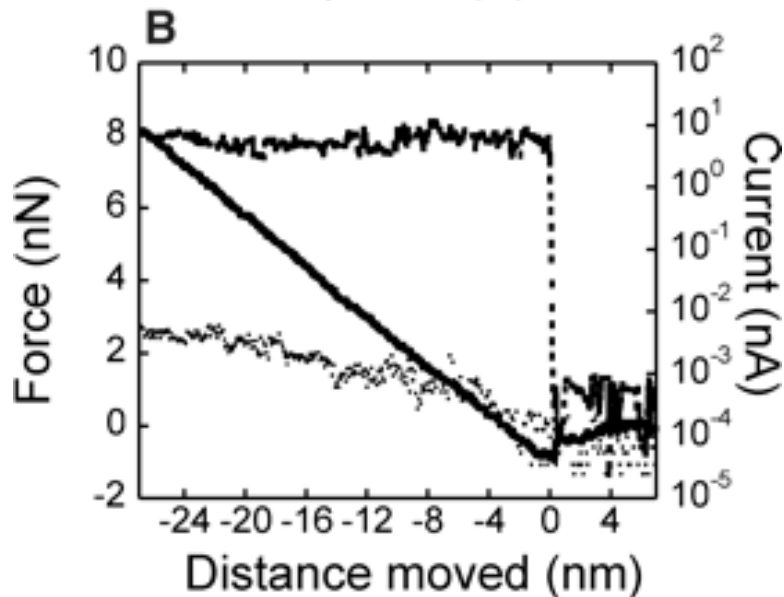
(**B**) Current and force measured as a conducting AFM cantilever (biased at +1 V) is moved toward the sample surface. Nominal contact is achieved at 0 distance, and negative values imply continued motion toward the Au(111) interface. When the probe approaches a gold nanoparticle, the current (dashed line) through the nanoparticle jumps to its final value on contact. When the surrounding octanethiol matrix is contacted, current (dots) is much smaller and depends on force (heavy solid line).

Nongjian J. Tao

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A general method for calibrating the conductivity of any molecules that are ended with thiol (-SH) or amine ($-NH_2$) that can strongly bind to gold.


(A)

(B)

(C) single molecular bridge

(D)
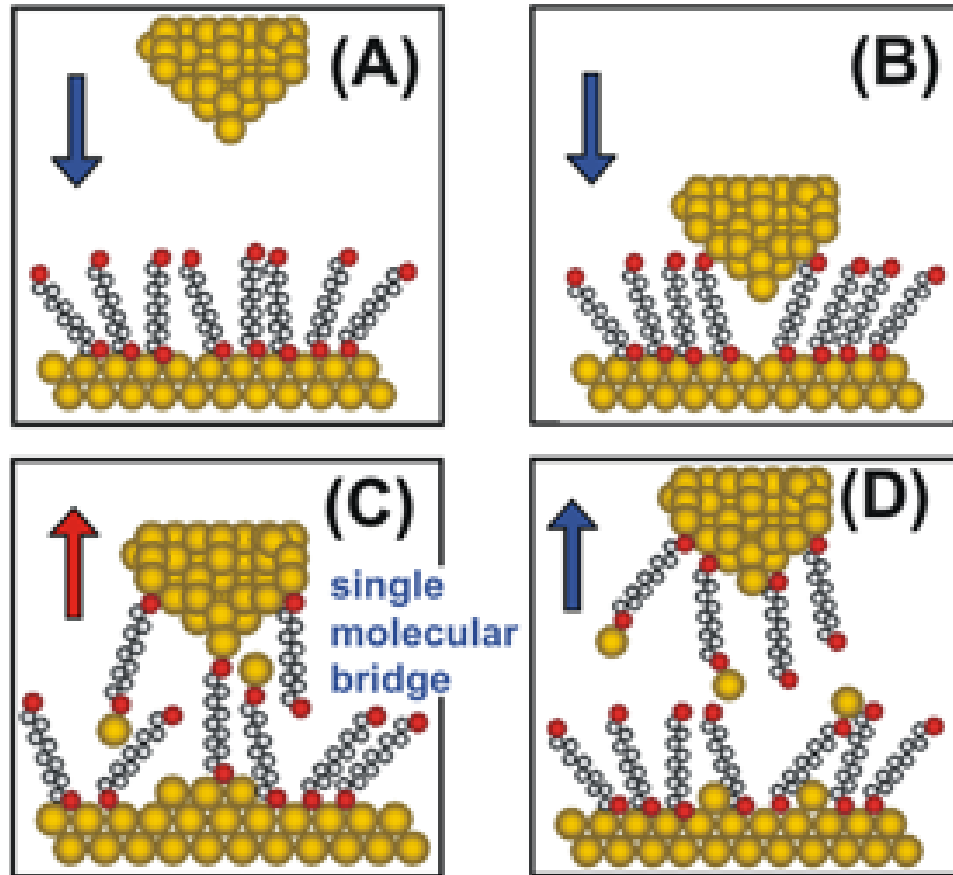
Significance

- The basic question that remains a subject of debate --- *what is the resistance of a simple molecule*, such as an alkane chain, covalently attached to two electrodes?

- Large disparities have been found between different experiments, which reflects the difficulty of forming identical molecular junctions.

- Even if the resistance of a molecular junction is reproducibly measured, *ensuring that the resistance is really due to a single molecule is another substantial challenge*. Cui work is still based on averaged analysis, not direct addressing a single-molecule.

- In Cui *et al.* work, the molecular junction was measured hundreds of times so that statistical analysis could be performed.

- However, the procedure involves several **elaborate** assembly steps, and the measured resistance is complicated by a **Coulomb blockade** effect due to finite contact resistance between the AFM probe and the gold nanoparticle.
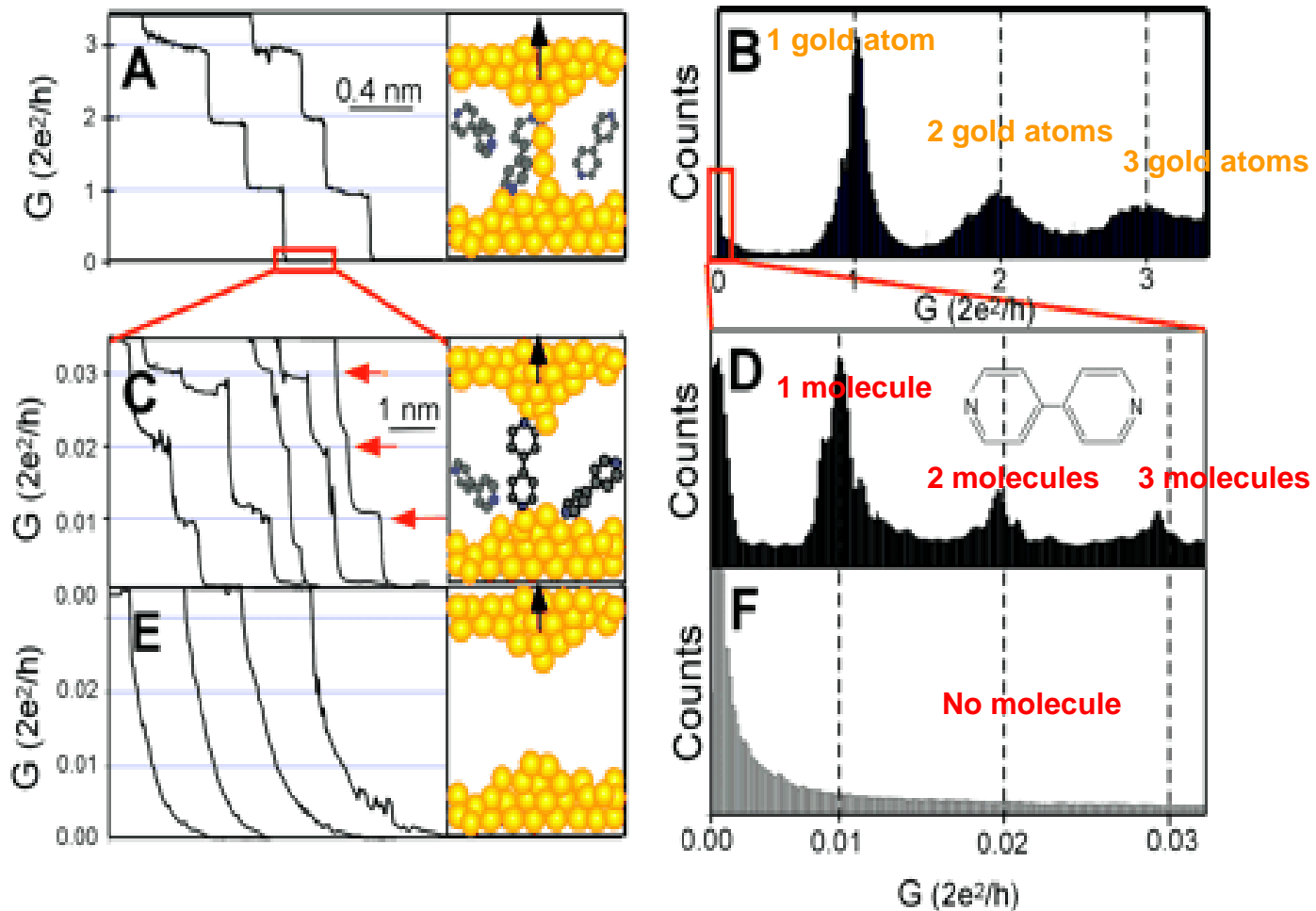
(**A**) Conductance of a gold contact formed between a gold STM tip and a gold substrate decreases in quantum steps near multiples of G_0 (= $2e^2/h$) as the tip is pulled away from the substrate. (**B**) A corresponding conductance histogram constructed from 1000 conductance curves as shown in (A) shows well-defined peaks near 1 G_0, 2 G_0, and 3 G_0 due to conductance quantization. (**C**) When the contact shown in (A) is completely broken, corresponding to the collapse of the last quantum step, a new series of conductance steps appears if molecules such as 4,4' bipyridine are present in the solution. These steps are due to the formation of the stable molecular junction between the tip and the substrate electrodes. (**D**) A conductance histogram obtained from 1000 measurements as shown in (C) shows peaks near 1 x, 2 x, and 3 x 0.01 G_0 that are ascribed to one, two, and three molecules, respectively. (**E** and **F**) In the absence of molecules, no such steps or peaks are observed within the same conductance range.

All STM techniques!
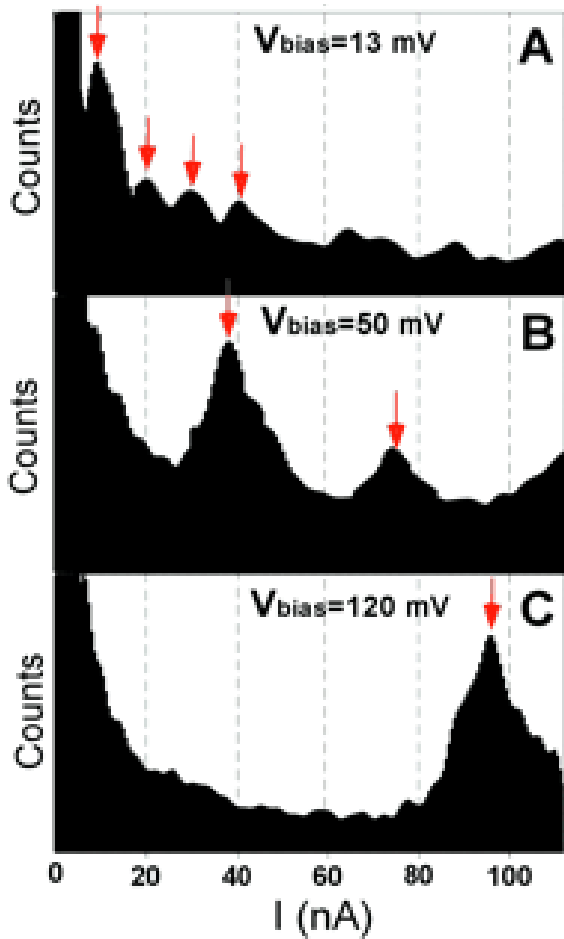
(**A** to **C**) Current histograms of 4,4' bipyridine constructed from 1000 measurements at different bias voltages (V_{bias}). Peak currents increase with the bias voltage and are used to obtain characteristic *I-V* curves.

(**D**) *I-V* curves from the first three peaks.

(**E**) When the second peak is divided by 2 and the third peak by 3, all the three curves collapse into a single curve. The dashed line shows the differential conductance (dI/dV).
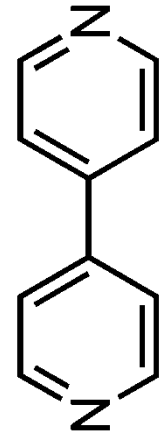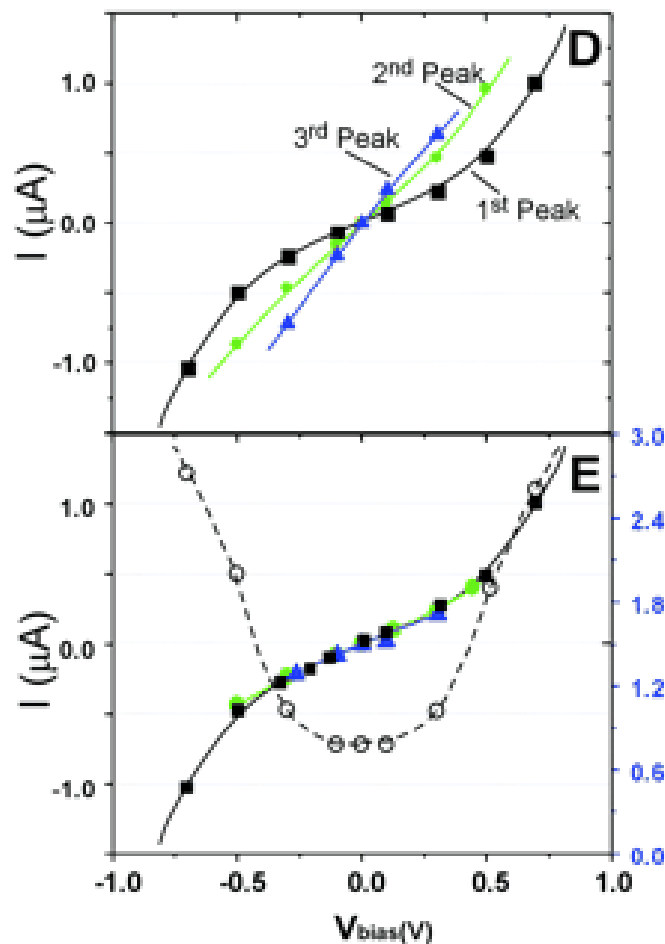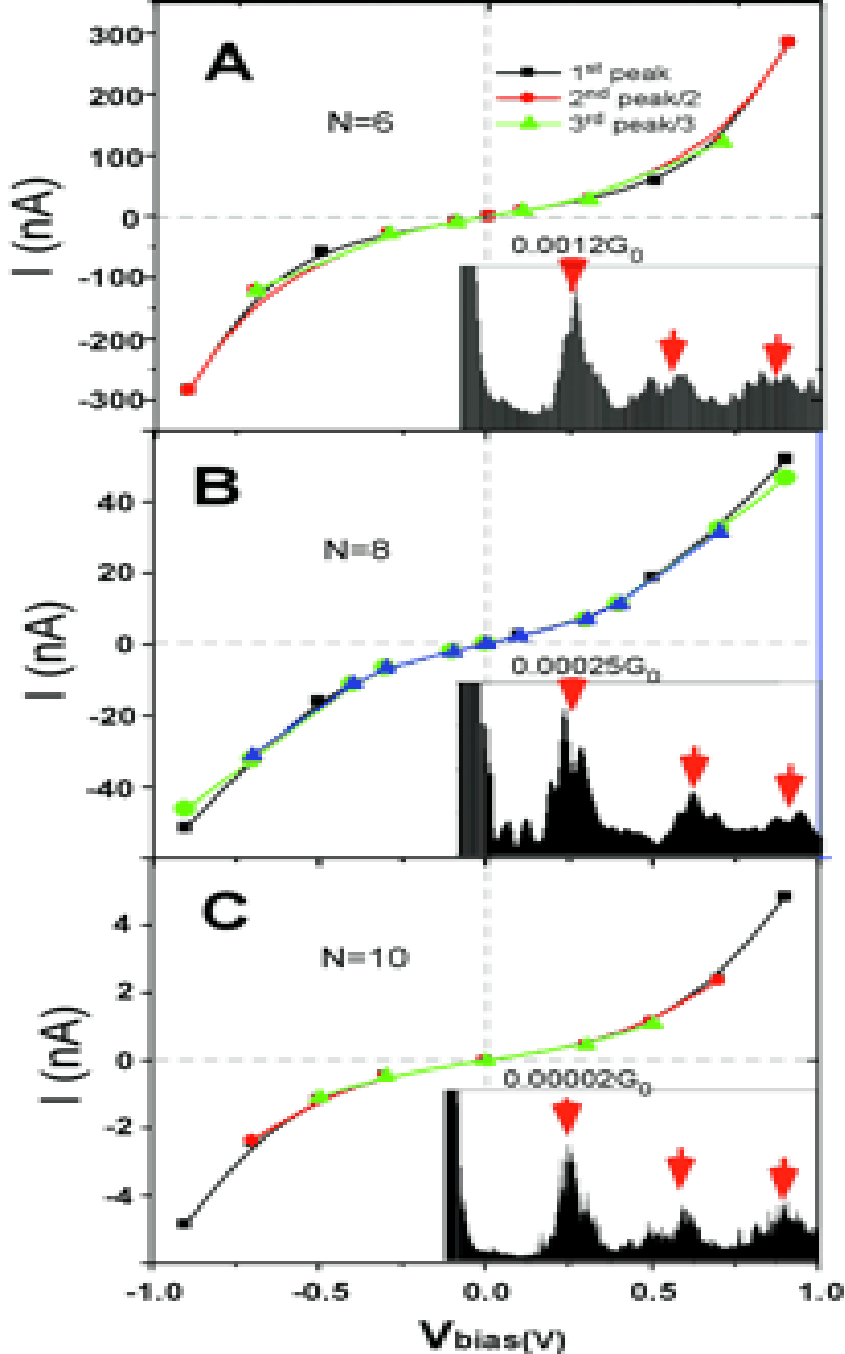
I-V curves.

(**A**), hexanedithiol, HS-(C$_6$H$_{12}$)-SH

(**B**), octanedithiol, HS-(C$_8$H$_{16}$)-SH

(**C**), decanedithiol, HS-(C$_{10}$H$_{20}$)-SH

In each case, the *I-V* curves from the second and third current peaks are also plotted together with that of the first peak after dividing them by 2 and 3. The inset in the lower right corner of each panel is a conductance histogram for each molecule.

Marcus Theory: *Electron Transfer*

$$k_{et} = Ae^{\beta d}$$

k_{et} is the electron transfer rate, referred to the current here,

A is the constant depending on molecular structure, temperature, media.

β is the attenuation of the electronic coupling.

d is the distance for electron transfer.

For conjugate molecules (conducting), electron transfer is weakly dependent on distance, thus β is small; for non-conducting molecules, electron transfer is strongly dependent on distance, thus β is large.

Rudolph A. Marcus:
Professor of Chemistry at CalTech,
Nobel Laureate 1992.
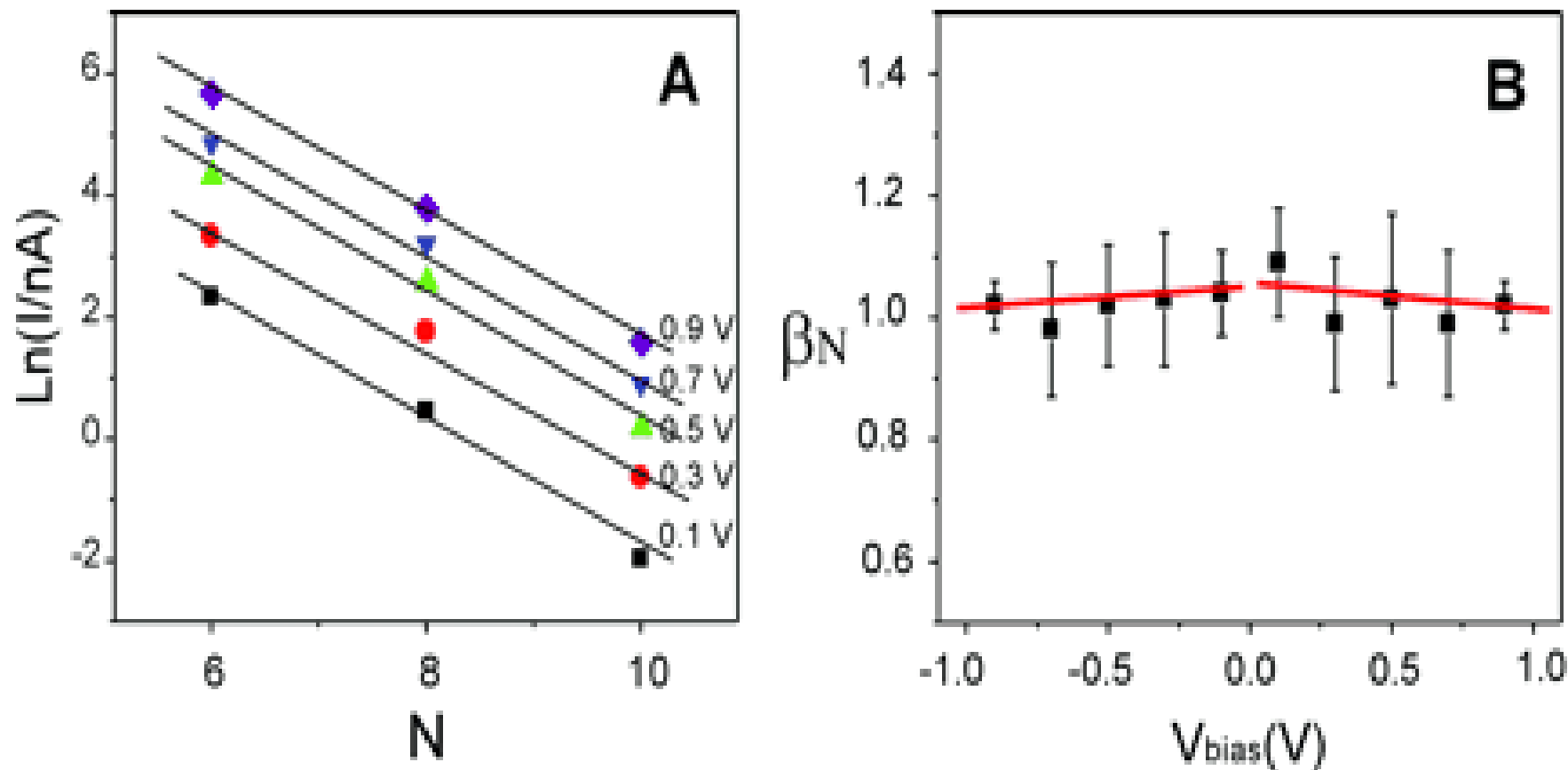
Fig. 4. (A) Natural logarithm of current versus N (the number of carbon atoms in the N-alkanedithiols) at various bias voltages. The solid lines are linear fits that yield β_N. (B) β_N versus V. The solid line is a fit to the simple square barrier model $\beta_N(V) = \beta_N(0)\sqrt{1 - \alpha V/\Delta E}$, where ΔE is the energy difference between the Fermi level and the closest molecular orbital, and $\alpha = 0.5$ reflects a uniform electric field. The fitting parameters are $\beta_N(0) = 1.04 \pm 0.05$ and $\Delta E = 5 \pm 2$ eV.

Transient conductance traces and the corresponding conductance histograms.

(a, b) gold point quantum contact

(c, d) BDT junctions

(e, f) BDMT junctions

One more σ-bond decreases the conductivity by 2 orders of magnitude!
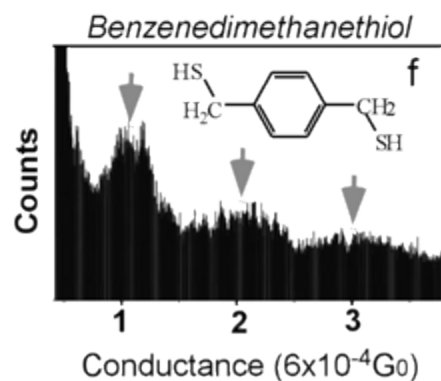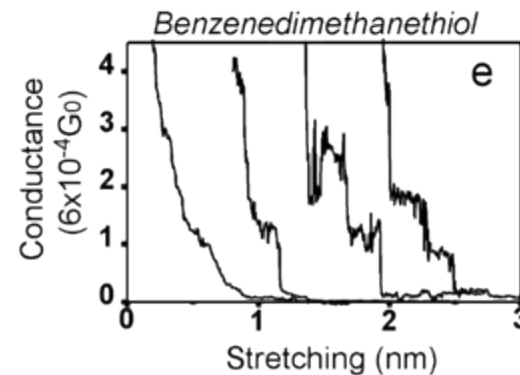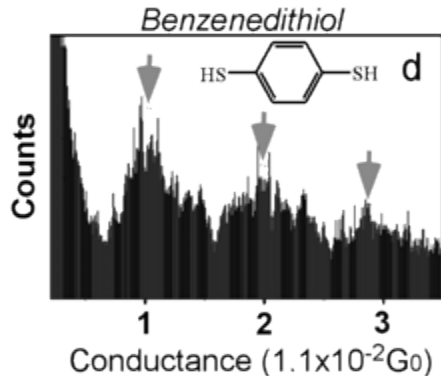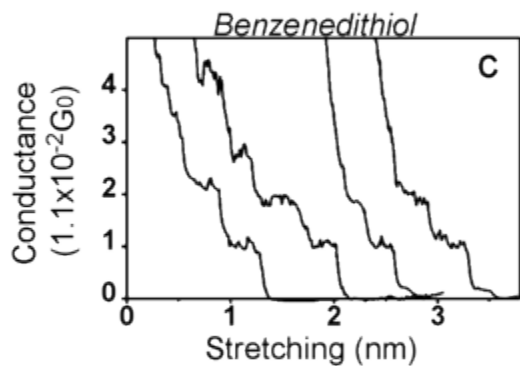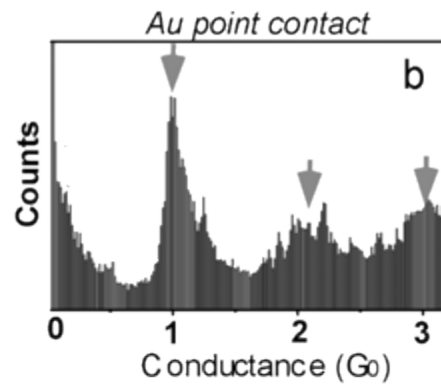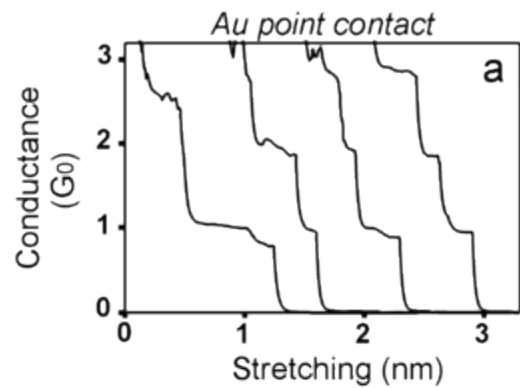
Example #3: calibration of molecular conductivity

Figure labels: *Au point contact* (a), *Au point contact* (b), *Benzenedithiol* (c), *Benzenedithiol* (d), *Benzenedimethanethiol* (e), *Benzenedimethanethiol* (f)

Axes: Conductance (G0), Stretching (nm), Counts, Conductance (G0), Conductance (1.1×10⁻²G0), Conductance (6×10⁻⁴G0)
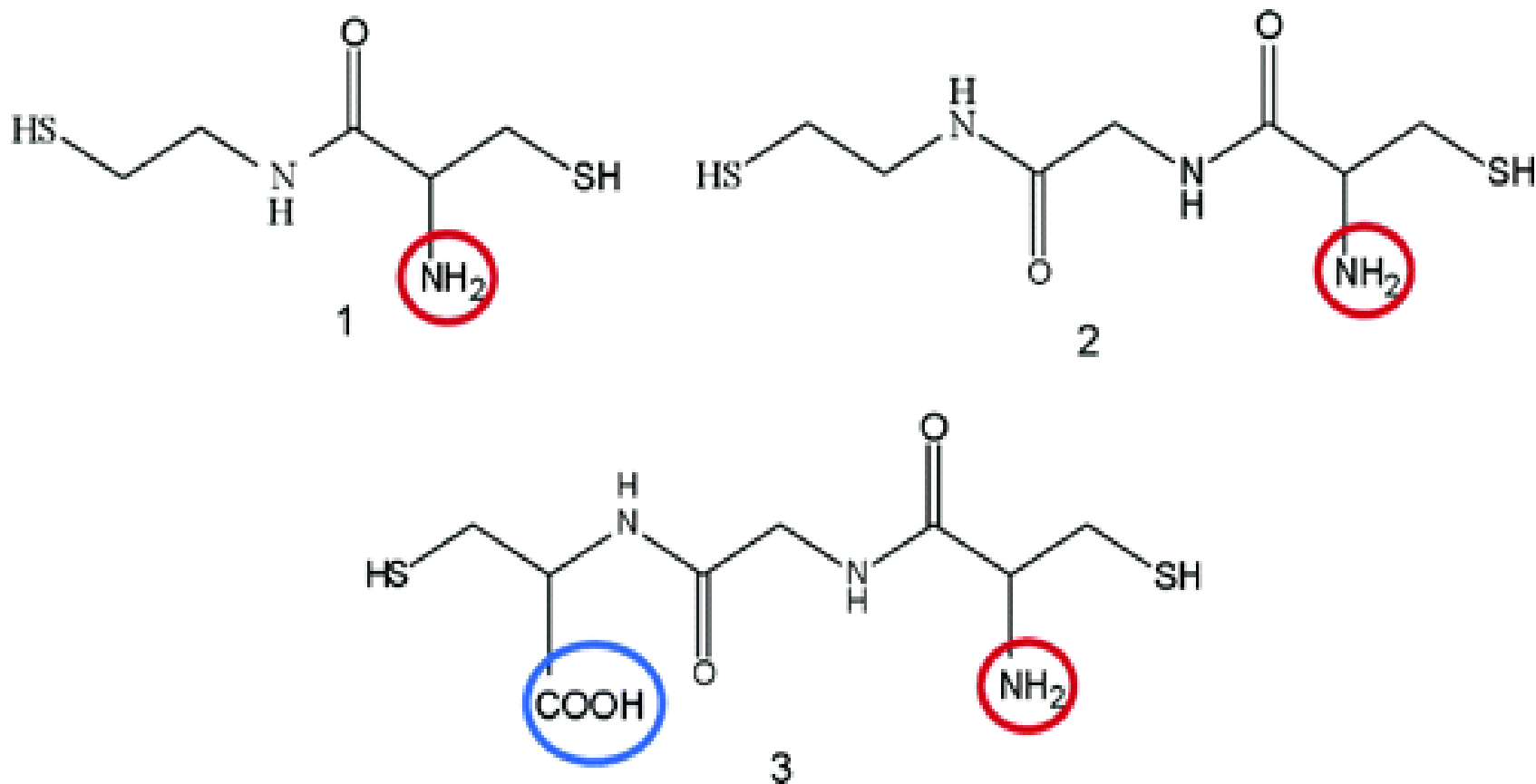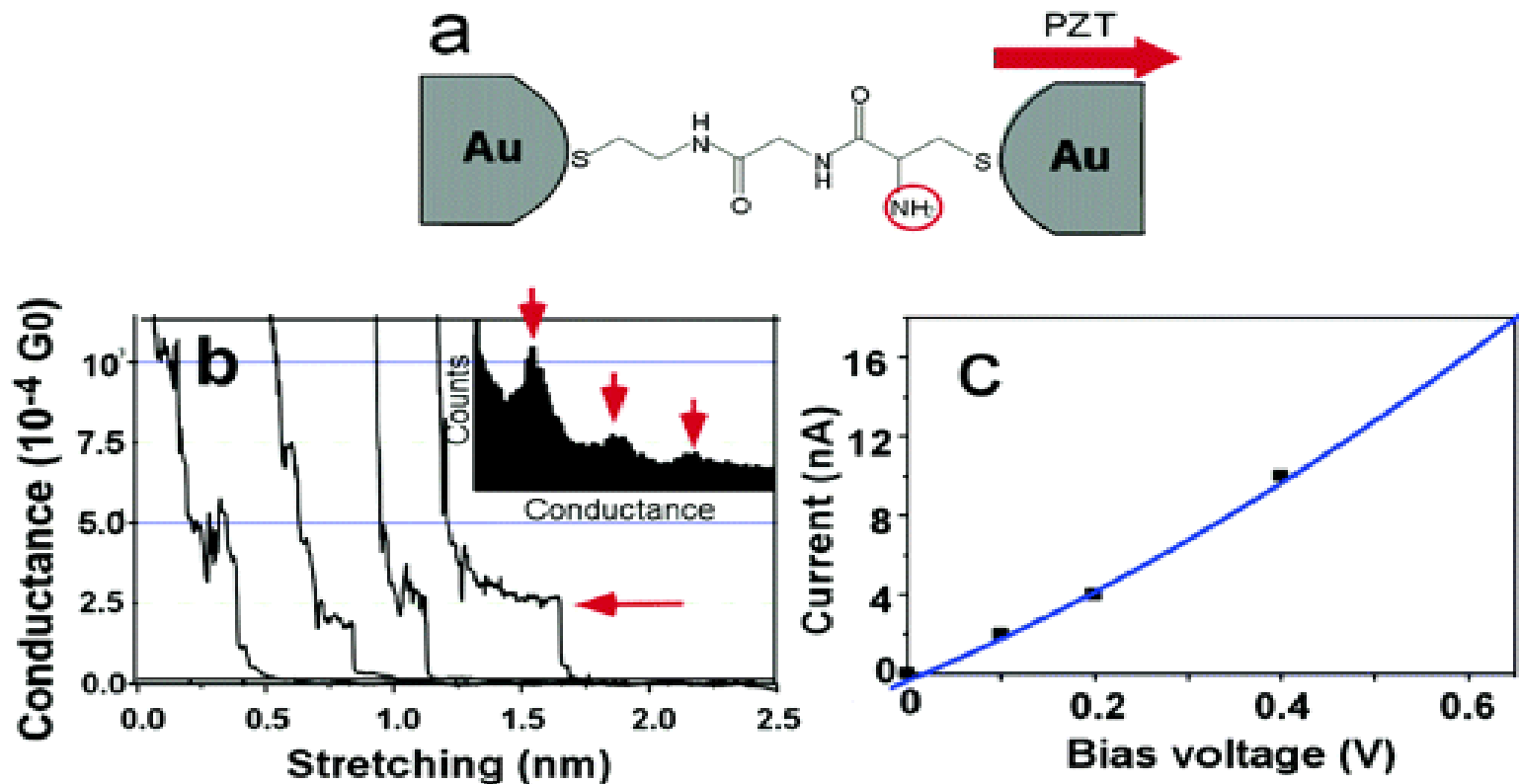
(a). Schematic illustration of a molecular junction formed by separating two electrodes.

(b). Several typical conductance curves of Peptide 1 during the formation of molecular junctions. The discrete changes in the conductance are due to the breakdown of individual molecules. The inset in (b) is a conductance histogram constructed from over 500 individual conductance curves, showing peaks near integer multiples of $2.5 \times 10^{-4}\ G_0$.

(c) *I-V* characteristic of Peptide 1 determined from conductance histograms at different bias voltages.
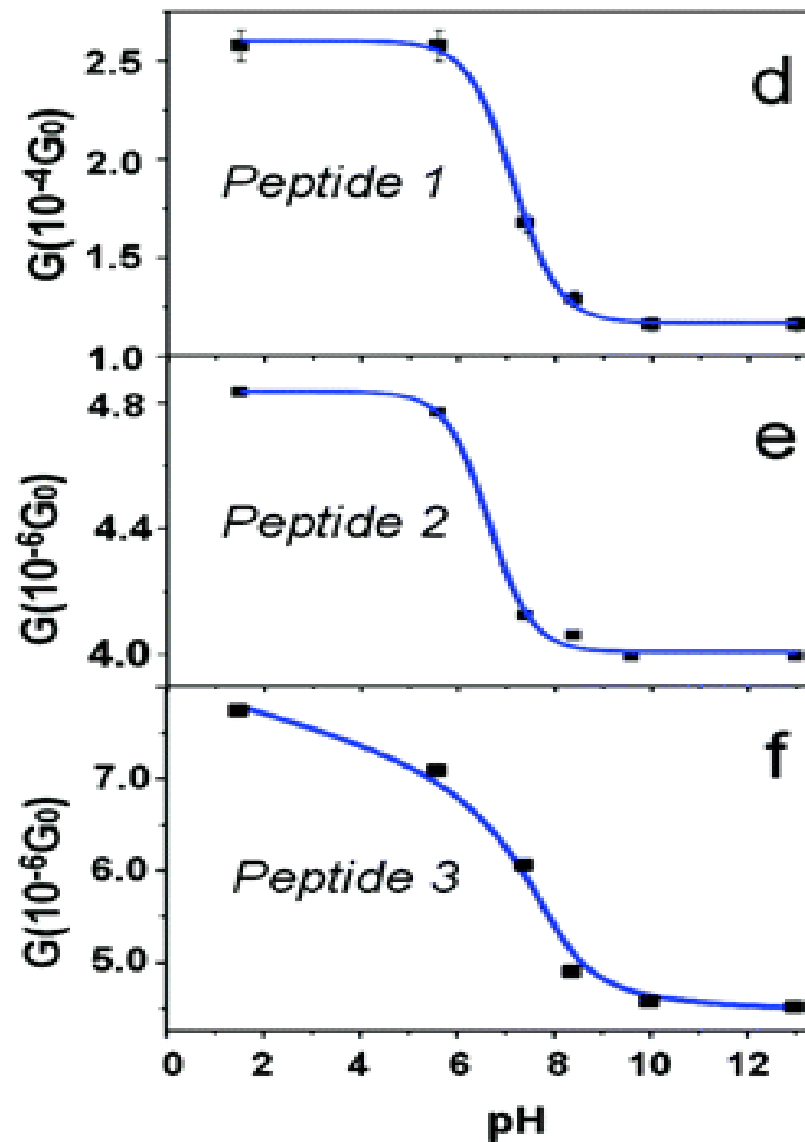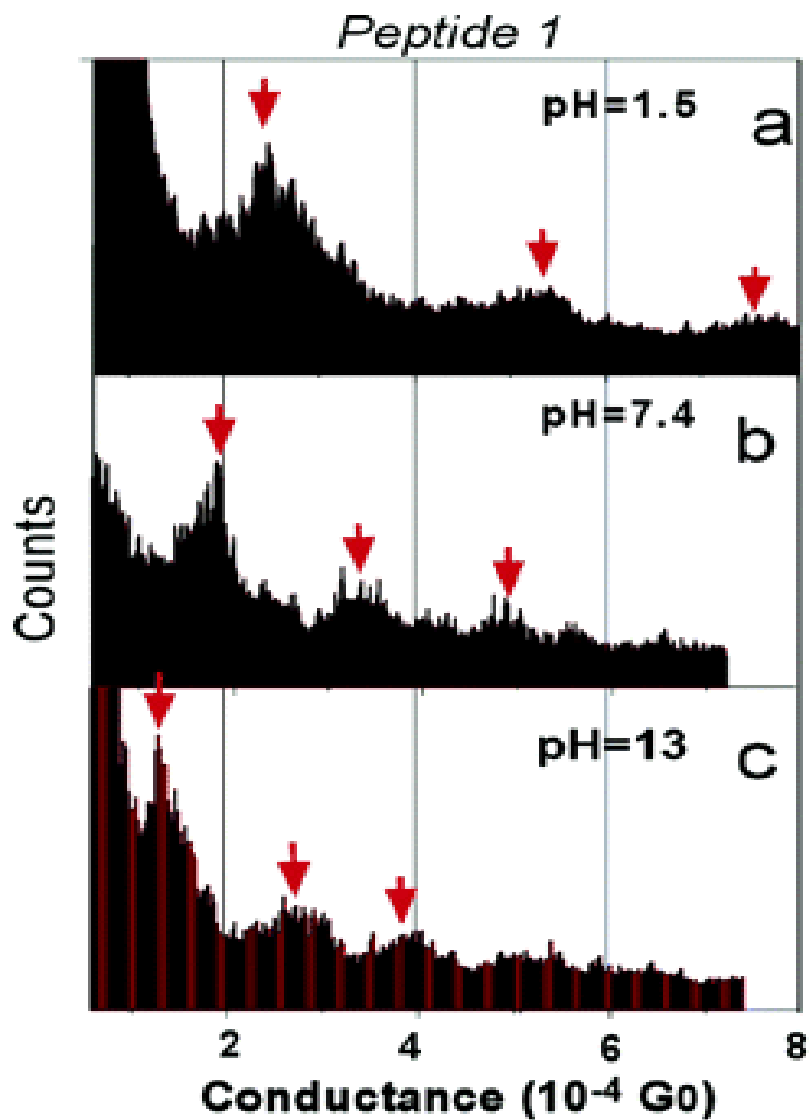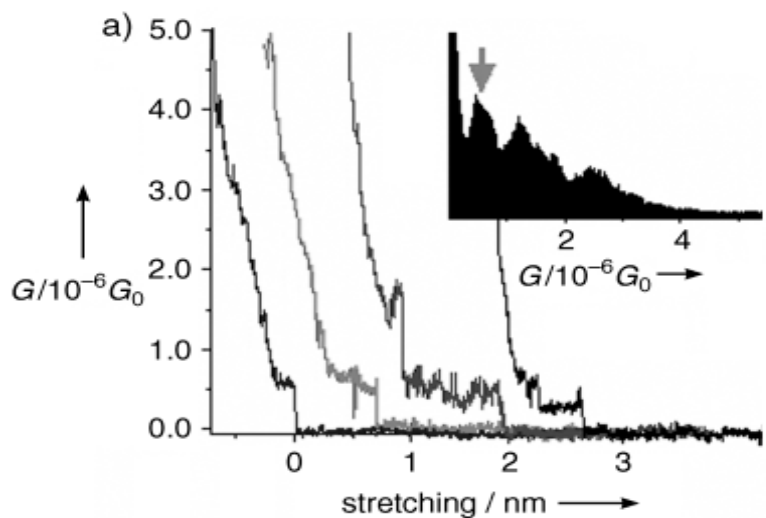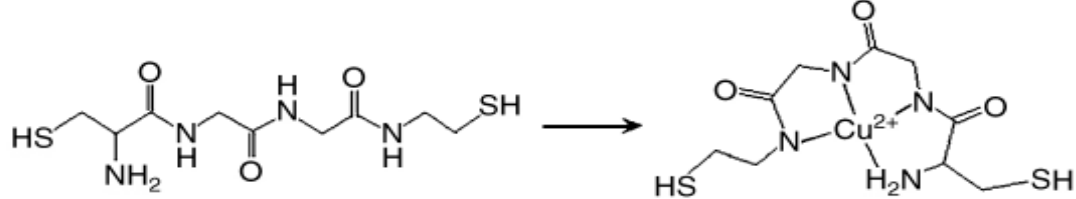
(a-c) Conductance histograms of Peptide 1 obtained at various solution pH. Conductance vs pH for Peptides 1 (d), 2 (e), and 3 (f). The solid lines are guide for the eye.

Example #5: a Single-molecule sensor for metal ions
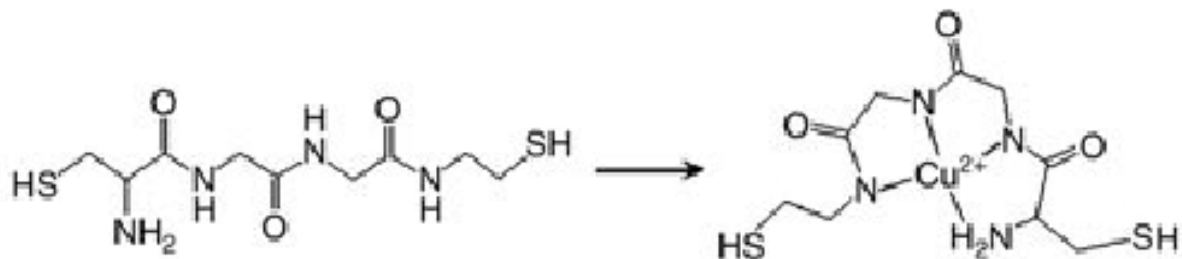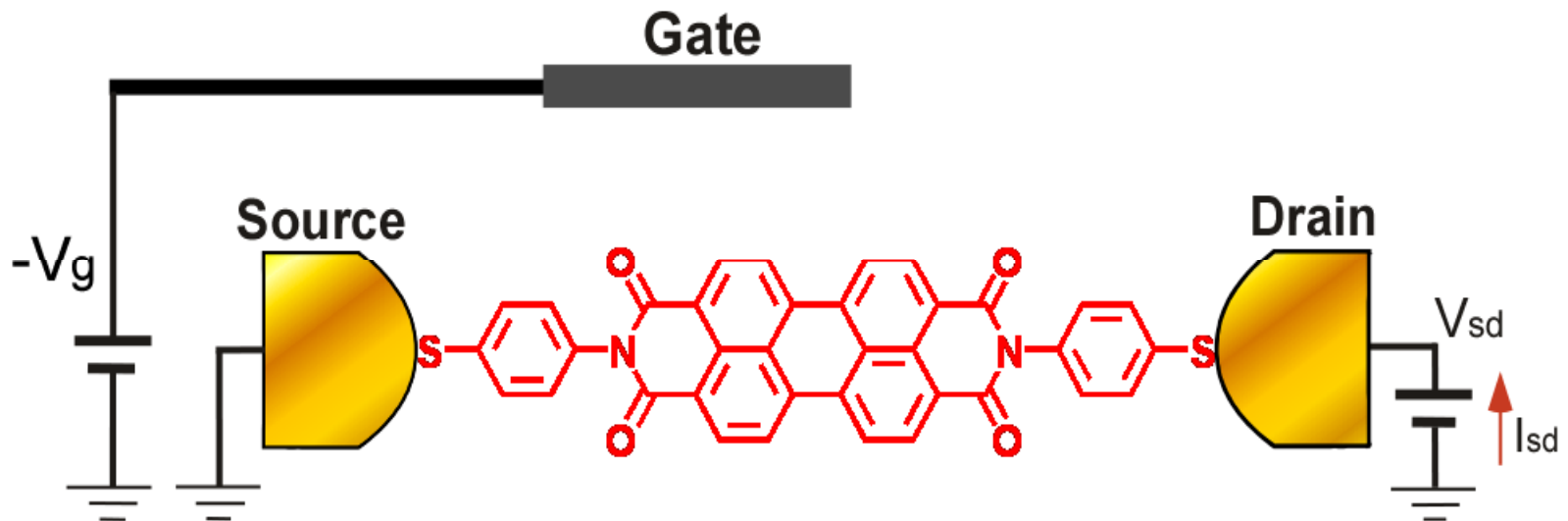

Conductivity increased upon metal binding!
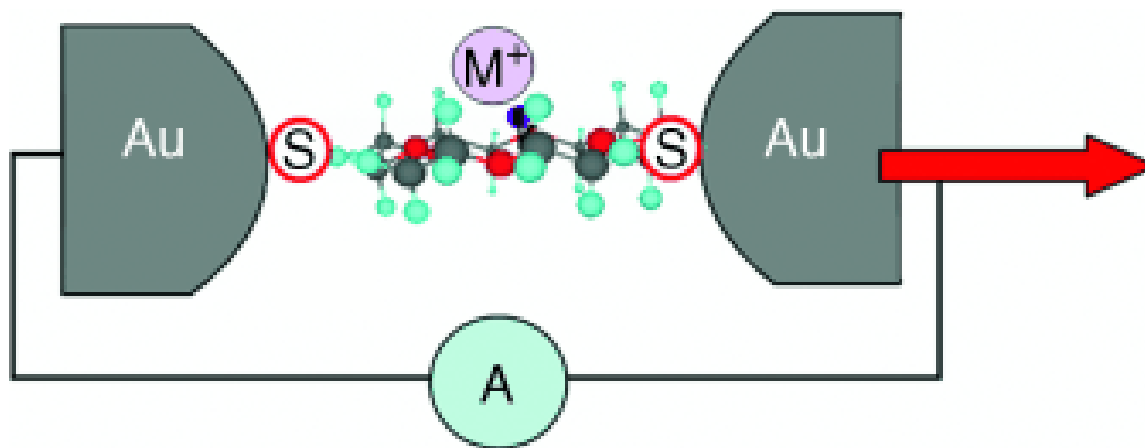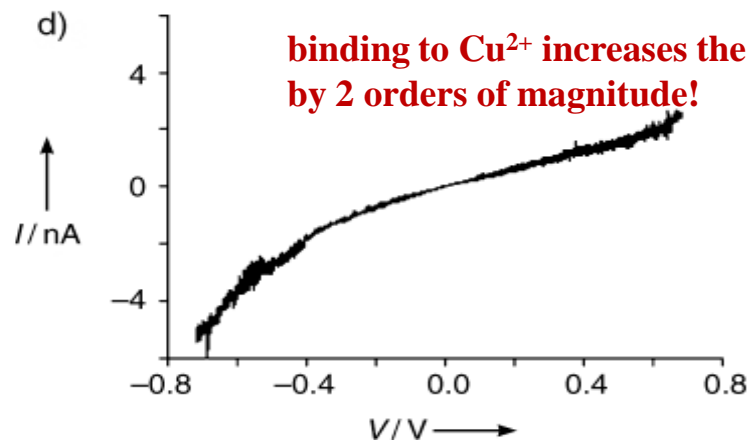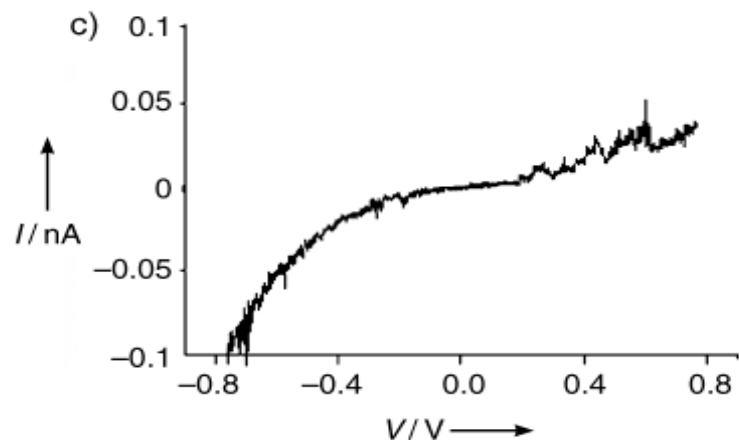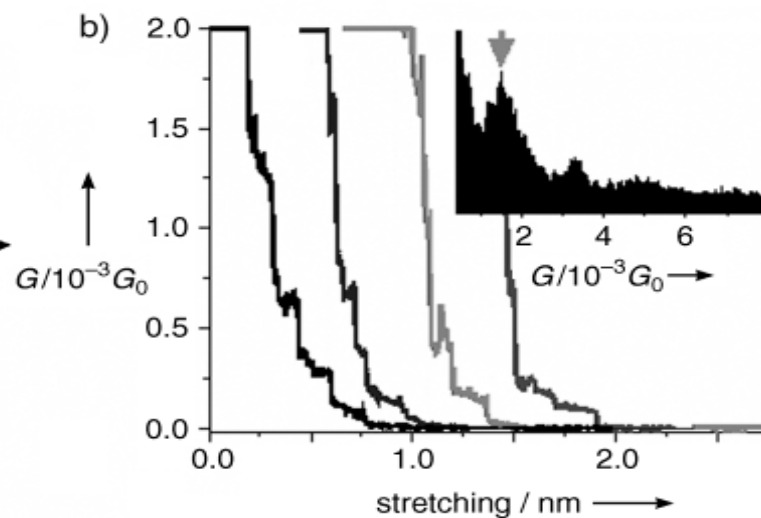
Individual conductance curves of cysteamine-Gly-Gly-Cys: a) before and b) after binding to Cu^{2+}
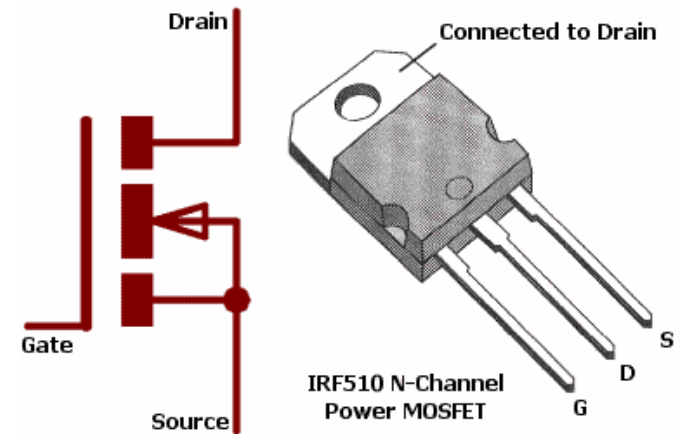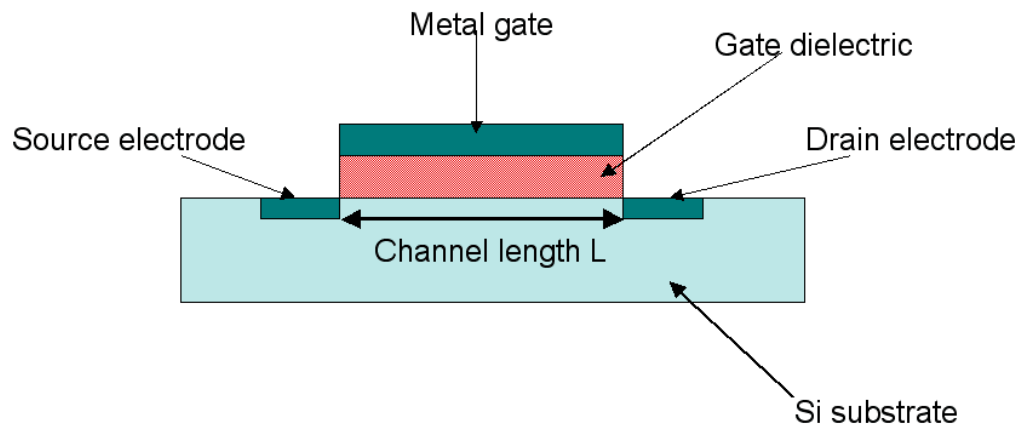
Angewchem, 2004,43,6148

Building upon the reliable measurement of single-molecule conductivity, people moved on to study the field-effect transistor (FET) behavior, simply by applying a third bias (electrode)

Single-molecule FET

Structure of a FET

Metal gate

Gate dielectric

Source electrode

Drain electrode

Channel length L

Si substrate

Drain

Connected to Drain

Gate

Source

IRF510 N-Channel
Power MOSFET

S

D

G

Most common FET is the so-called MOSFET: metal oxide semiconductor field-effect transistor, which has used the most in computer chips.

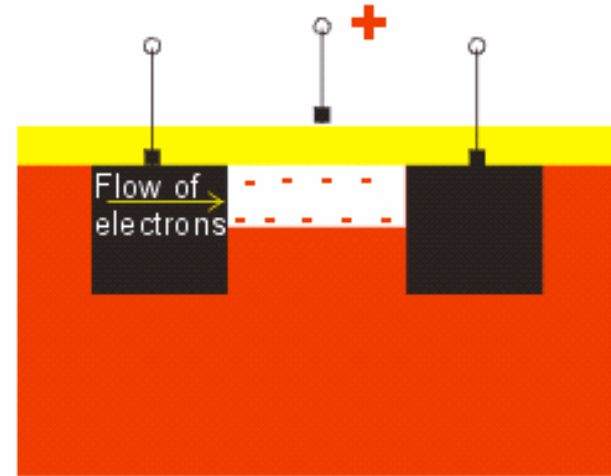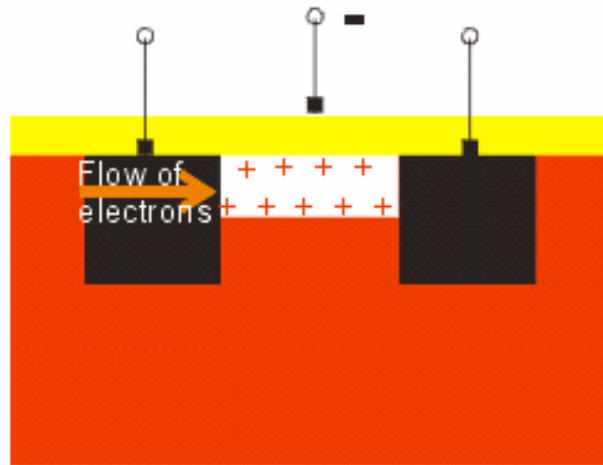# Function of FET

- The building blocks of silicon-based microelectronics are field effect transistors (FET).

- The basic function of an FET is to switch electrical current between two electrodes on and off with a gate electrode.

Working mechanism for a *N-channel* FET

- *When a negative charge is applied above the layer of oxide, the **n-channel** attracts most available positive charges (holes) towards itself (since opposite charges attract). Thus the flow of electric current, which is actually the flow of negatively charged **electrons** is reduced due to the presence of the opposite positive charge.*
- *This is called as **Depletion** of current.*

- When a positive charge is applied above the layer of oxide, the **n-channel** attracts more electrons towards itself. Thus the flow of current, which is nothing but the flow of electrons, is **enhanced** by these surplus electrons.

Driving Moore's law forward: creating nanometer size gate
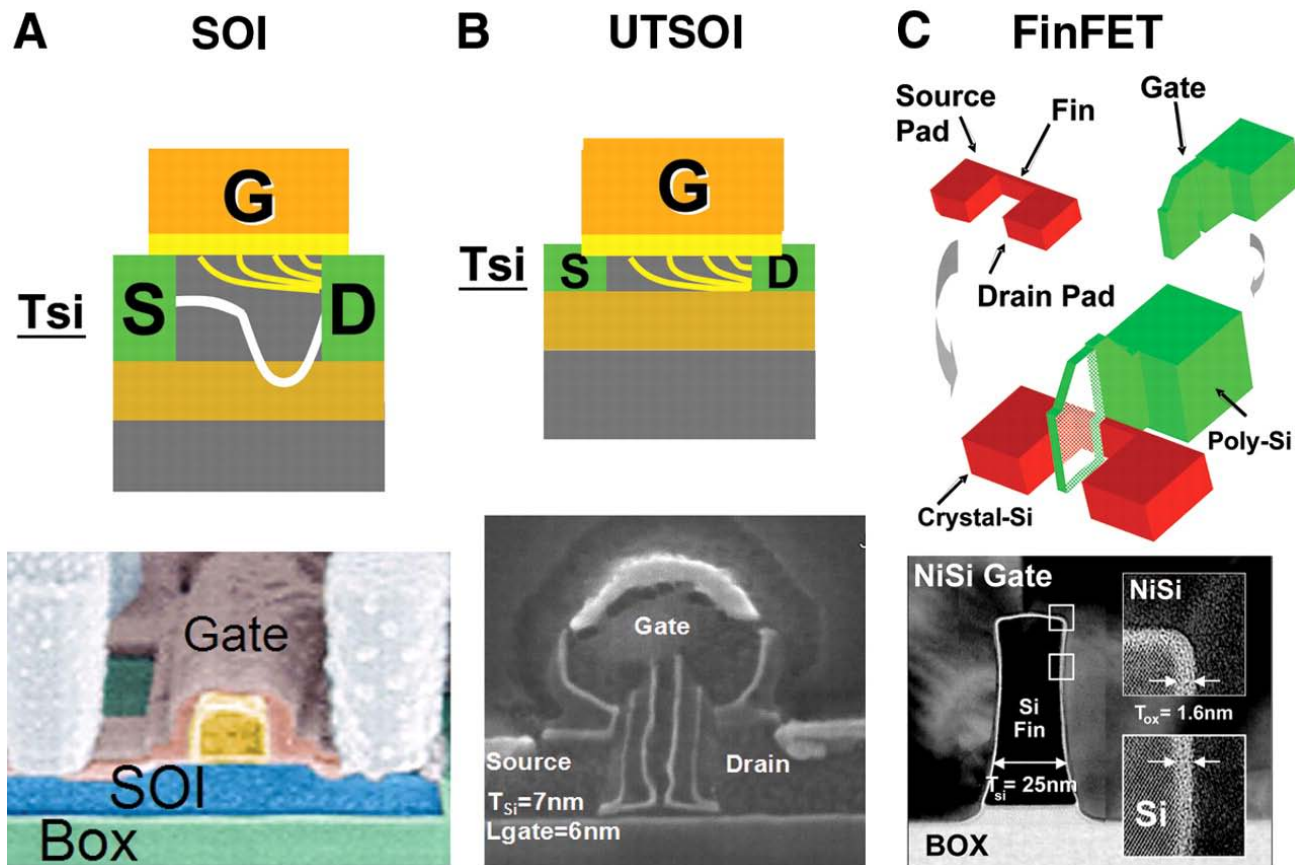
Device schematics and cross sections for (**A**) SOI MOSFET, (**B**) UTSOI MOSFET, and (**C**) FinFET double-gate MOSFET. SOI: silicon on insulator; UTSOI: ultrathin silicon on insulator

Challenges in Miniaturization of Silicon Devices

- When silicon devices are down to nanometers, significant leaking of electrons (information) would be a severe problem, which cannot be overcome by current lithography technology.
- When gate size is smaller than 10 nm, direct tunneling between source and drain would become dominant, i.e. the current is no longer controlled by the depletion layer, which is in turn determined by the gate voltage.
- Such a problem can be overcome by using different dielectric materials for the gate, and/or using different channel materials which have appropriate depletion properties.

- However, using a molecule as the channel provides a totally different approach.

In molecules, electron move locally between quantized energy levels within the molecular chains.

Building a single molecule FET is naturally considered to be a critical step towards the ultimate goal of molecular electronics.

Charge transport through molecules

- Hopping mechanism --- the classic understanding based on redox reactions.

   one electron transferred from the source electrode to the redox center of the molecule, then transferred to the drain electrode. The driving force for each step of the transfer is due to the bias applied between the source and drain. (draw the scheme on board)

- Tunneling mechanism --- the quantum mechanical understanding.

   when the LUMO level of the molecule is aligned (*via the gate voltage*) to be the same as the Fermi level of the electrode (source for n-type or drain for p-type), an efficient electron transfer occurs, due to the resonant tunneling between the two energy levels. (draw the scheme on board)

- This was predicted for the first time by *Di Ventra* in 2000, using DFT calculations.

Theoretical Prediction of Single-Molecule Transistor

Di Ventra, et al. *Appl. Phys. Lett.* **76**, 3448-3450 (2000).
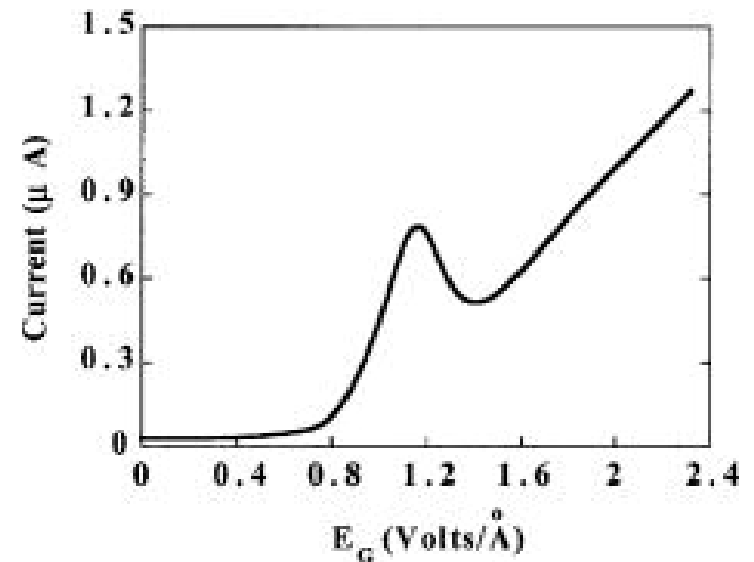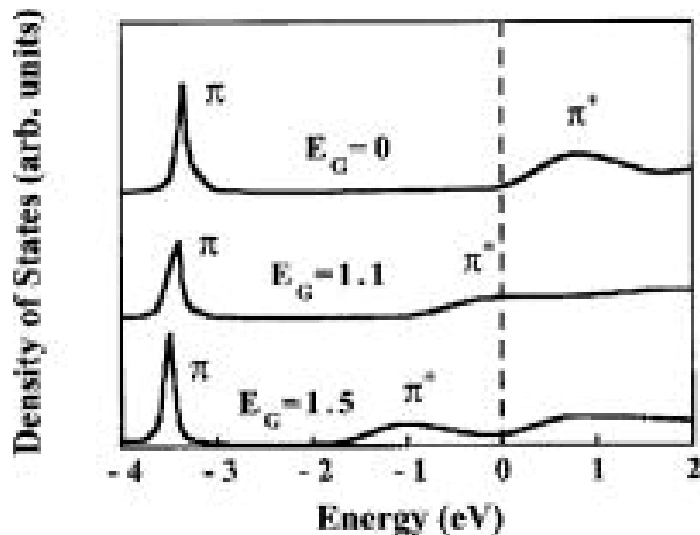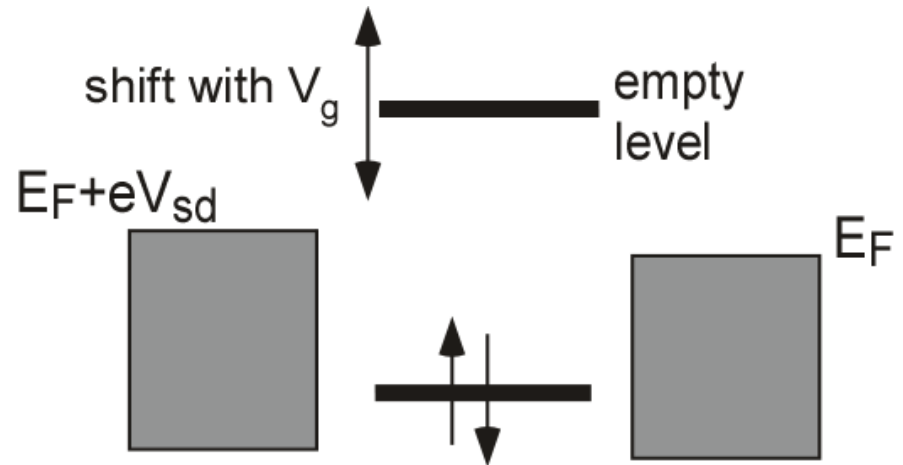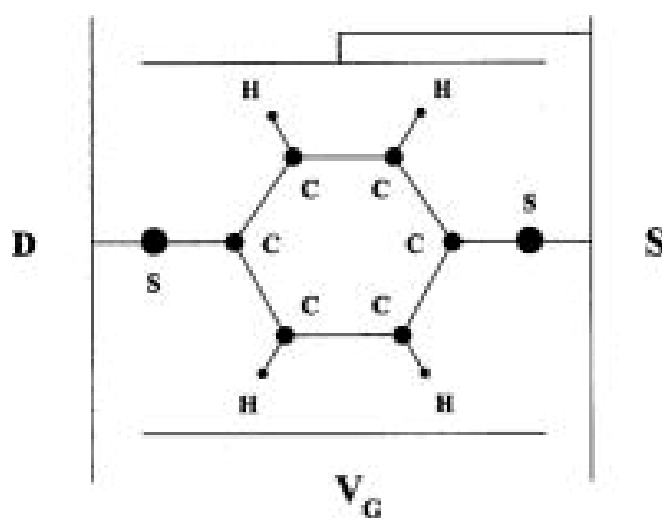
# Technical challenges in fabrication and characterization of single-molecule FET

- Theoretical models have predicted that the conductance of a single molecule can be modulated with a gate electrode in a fashion of conventional FET.

- Experimental demonstration of this FET behavior in single molecules has, however, been a difficult challenge because it requires one to:

    1) find a reliable method to wire a single molecule to the source and drain electrodes;
    2) place the gate electrode a few Å away from the molecule to achieve the required gate field.

- FET-like behavior has been successfully demonstrated in carbon nanotubes and nanowires (1998 to 2003, the contact problem has got overcome).

- From later 1990's, people have been trying to address the molecular FET behavior using the nano-gap electrode systems, which works well for nanotubes and nanowires.

Room-temperature transistor based on a single carbon nanotube

SANDER J. TANS[1], ALWIN R. M. VERSCHUEREN[1] & CEES DEKKER[1]
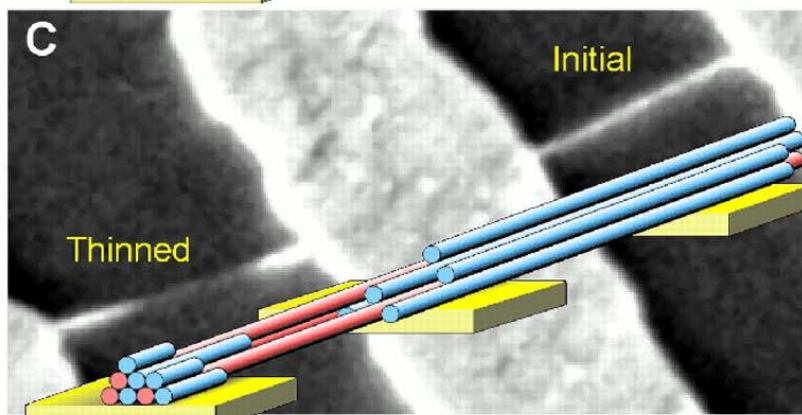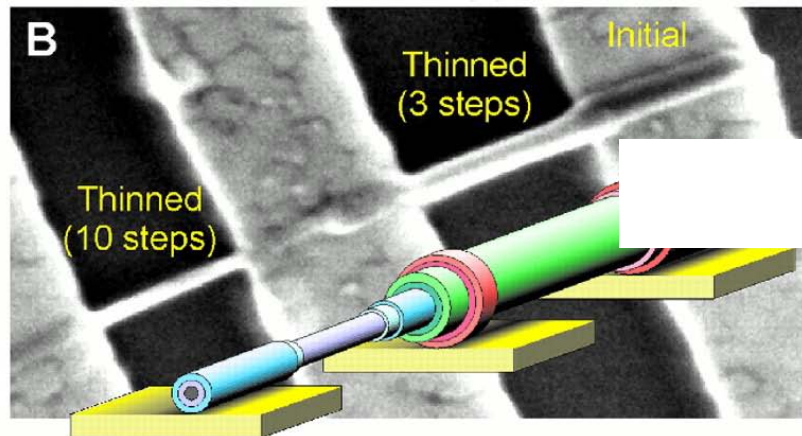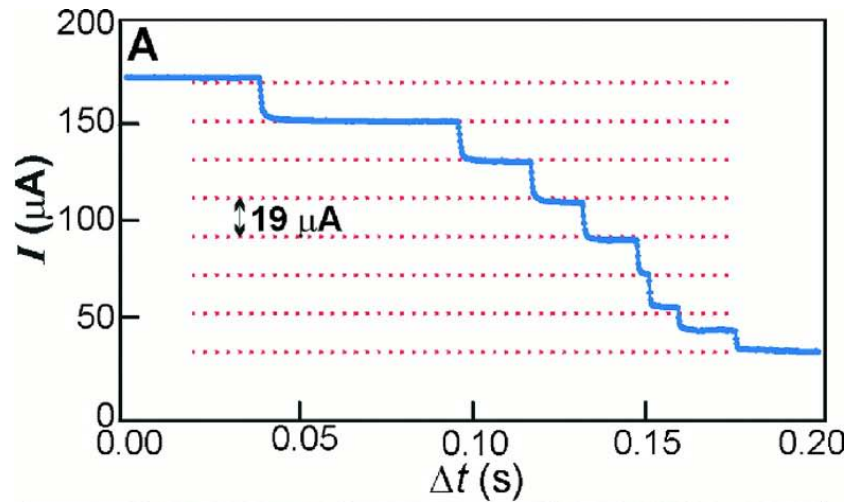
Department of Applied Physics and DIMES, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands
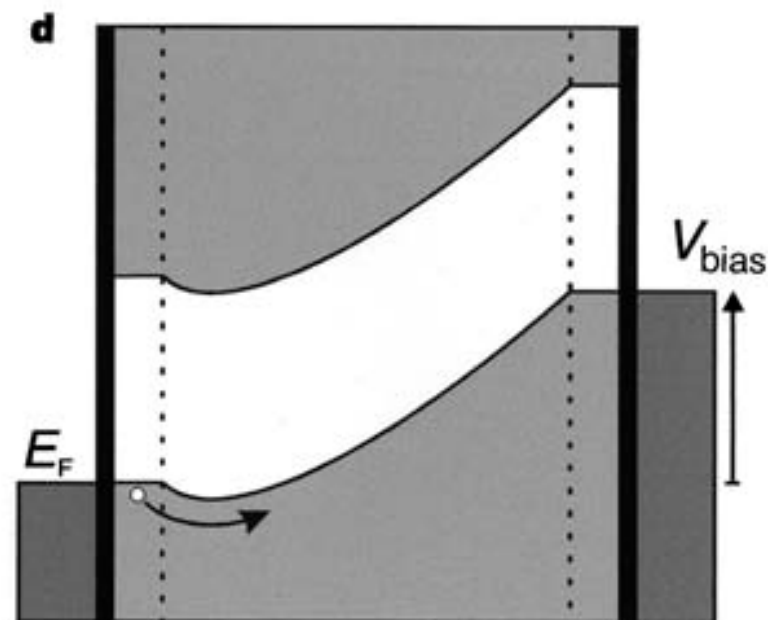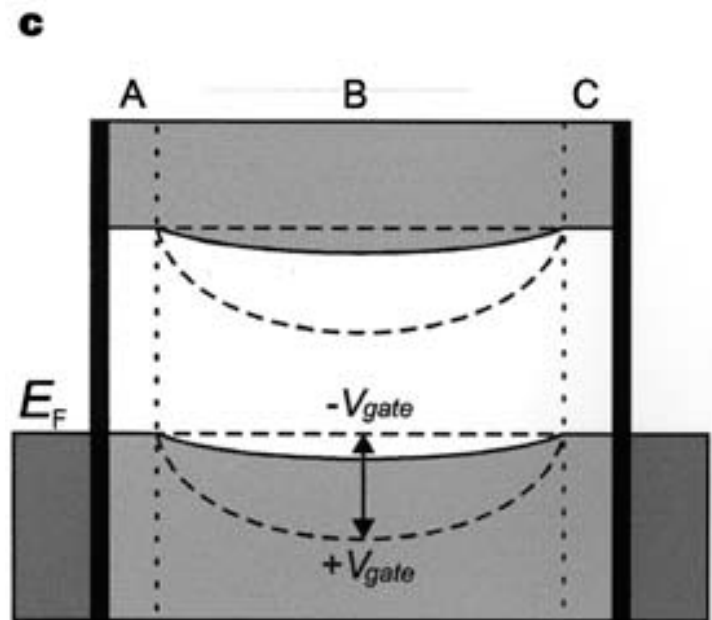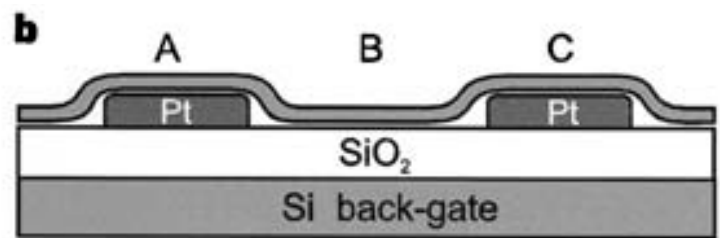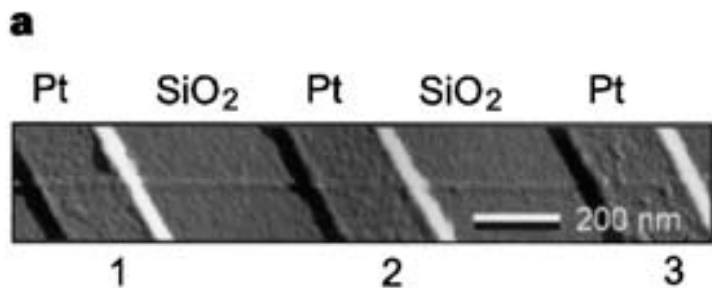
Engineering Carbon Nanotubes and Nanotube Circuits Using Electrical Breakdown

Philip G. Collins, Michael S. Arnold, Phaedon Avouris*

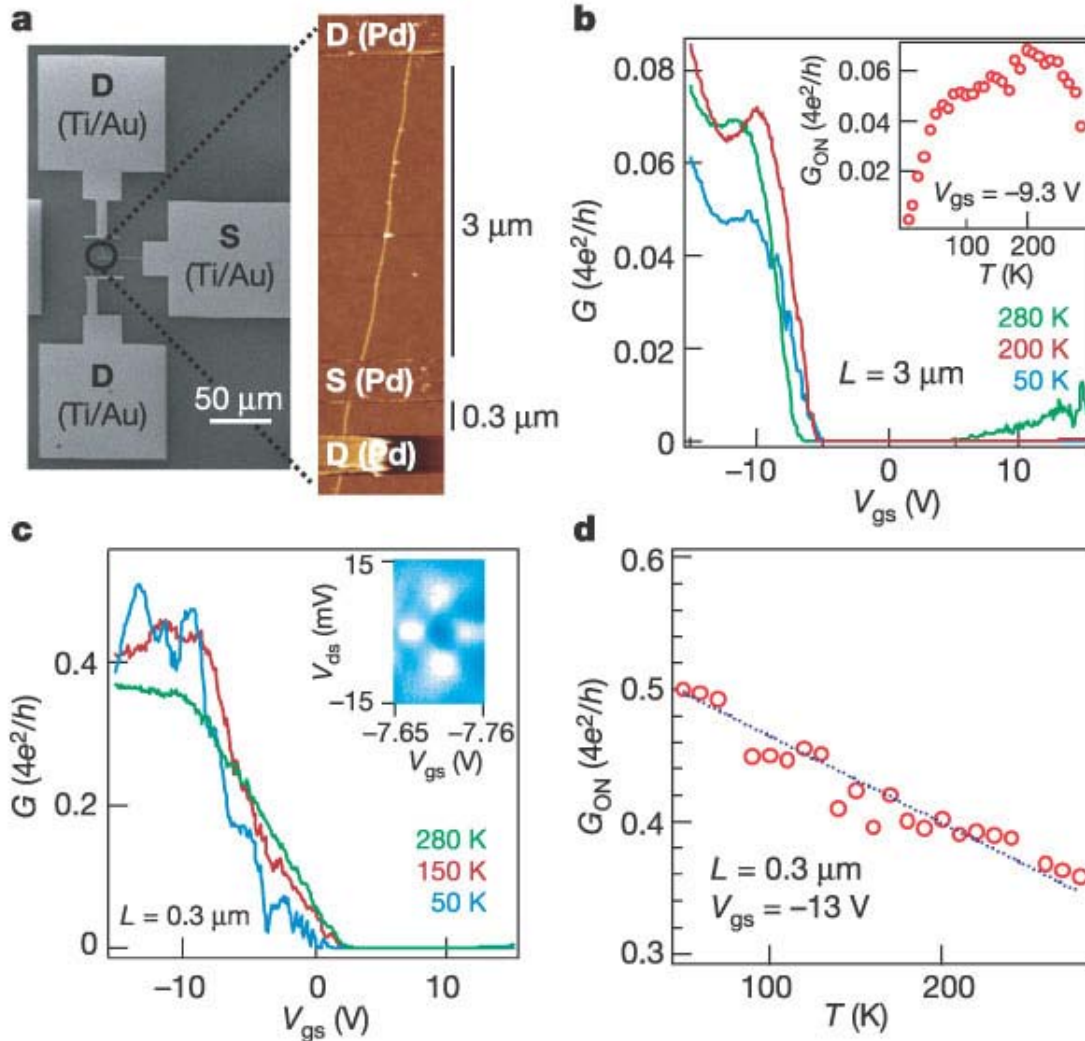*IBM T. J. Watson Research Center, Yorktown Heights, NY 10598, USA.*

Ballistic carbon nanotube field-effect transistors

ALI JAVEY[1], JING GUO[2], QIAN WANG[1], MARK LUNDSTROM[2] & HONGJIE DAI[1]

[1] Department of Chemistry, Stanford University, California 94305, USA
[2] School of Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47907, USA
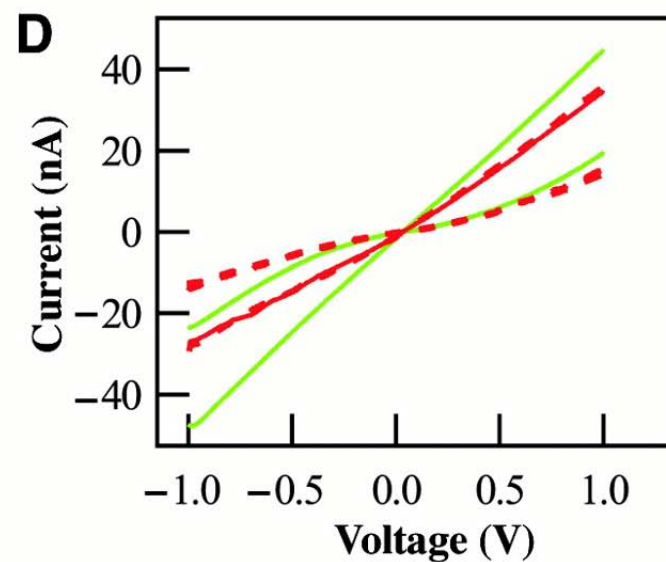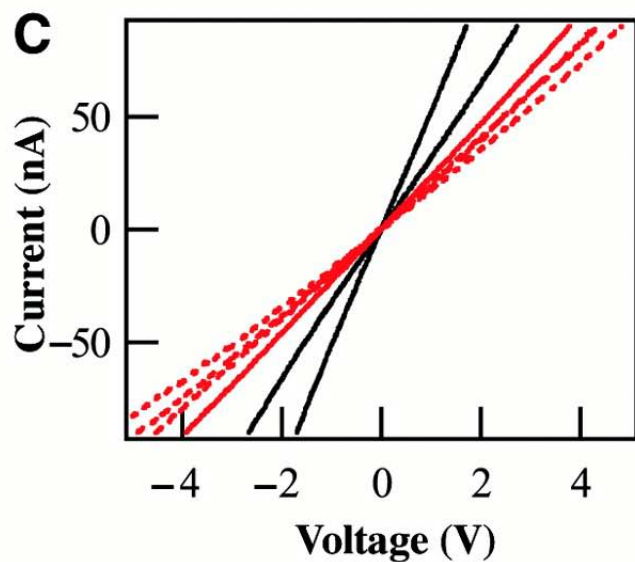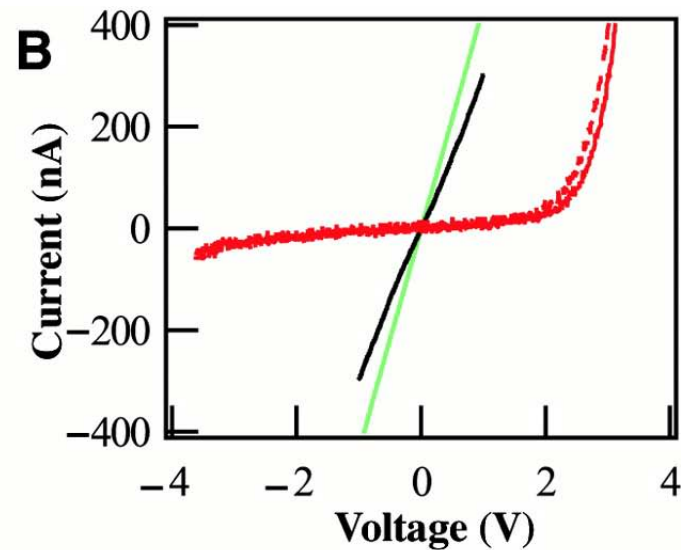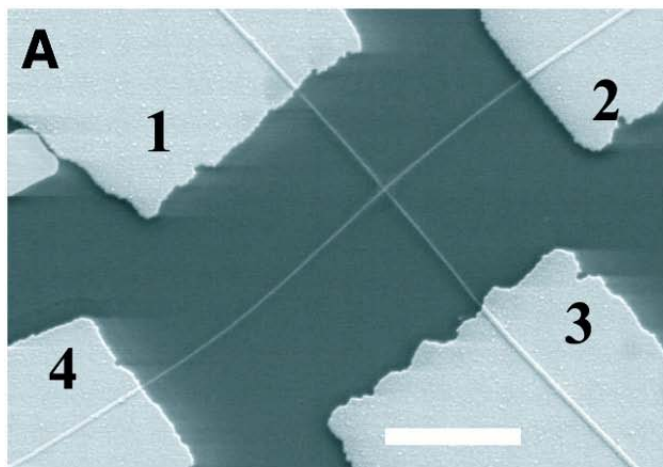
Functional Nanoscale Electronic Devices Assembled Using Silicon Nanowire Building Blocks

Yi Cui, Charles M. Lieber*

1 Department of Chemistry and Chemical Biology and
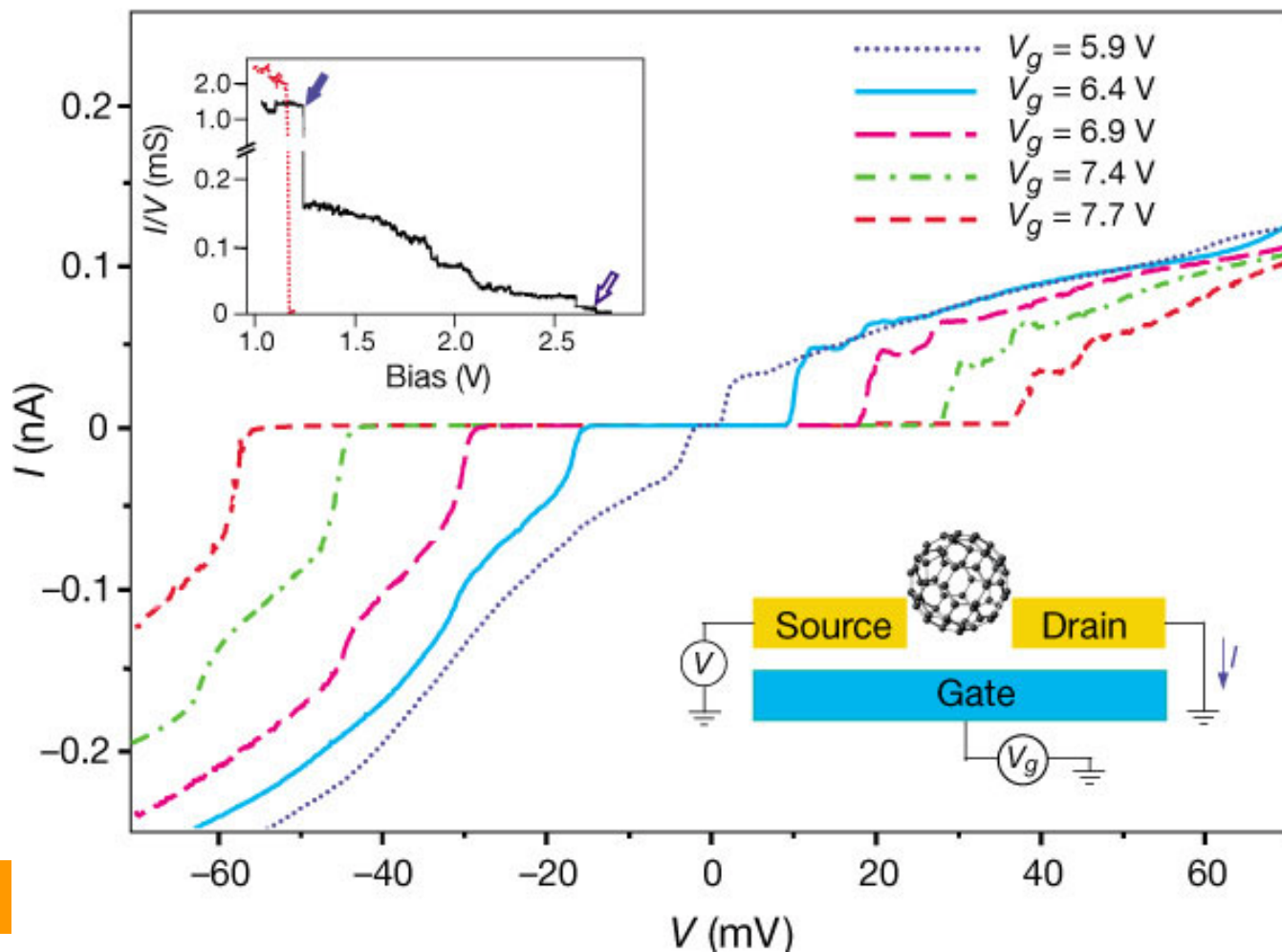2 Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.

Nanomechanical oscillations in a single-C60 transistor

HONGKUN PARK*‡§, JIWOONG PARK†, ANDREW K. L. LIM*,
ERIK H. ANDERSON‡, A. PAUL ALIVISATOS*‡ & PAUL L. MCEUEN†‡

T: 1.5 K

Coulomb blockade and the Kondo effect in single-atom transistors
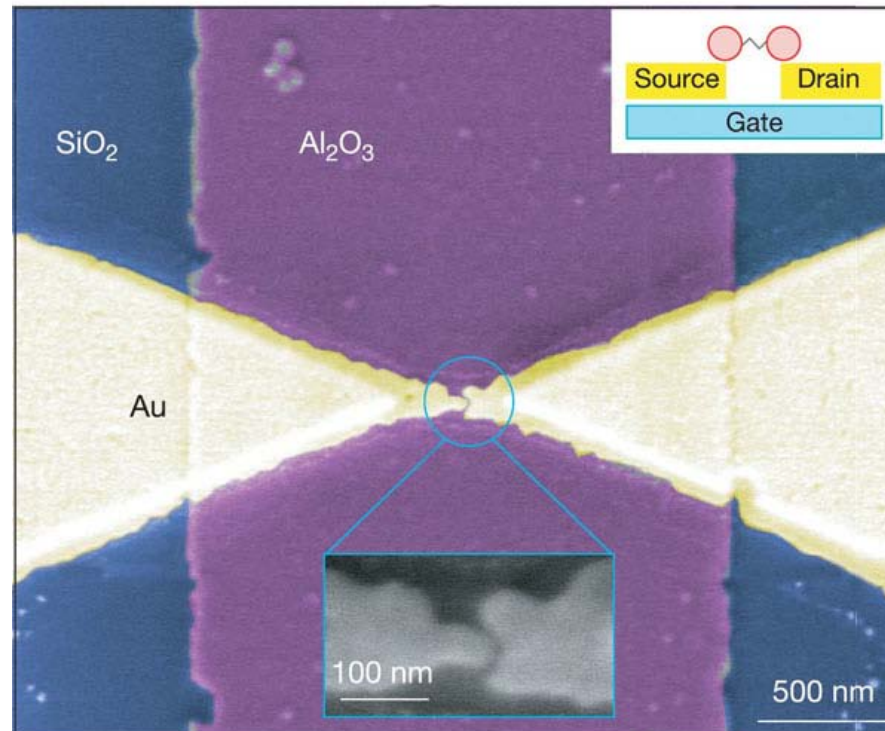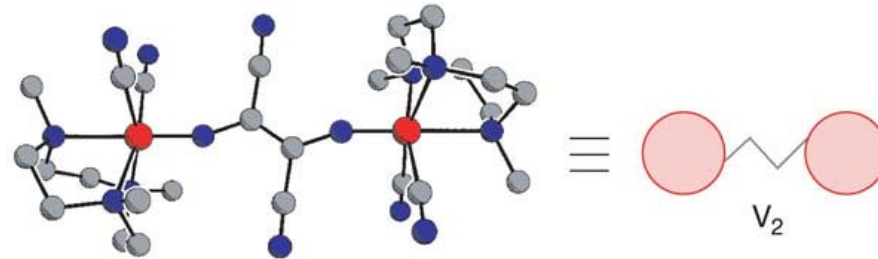
JIWOONG PARK*†‡, ABHAY N. PASUPATHY*‡, JONAS I. GOLDSMITH§, CONNIE CHANG*,
YUVAL YAISH*, JASON R. PETTA*, MARIE RINKOSKI*, JAMES P. SETHNA*,
HÉCTOR D. ABRUÑA§, PAUL L. MCEUEN* & DANIEL C. RALPH*
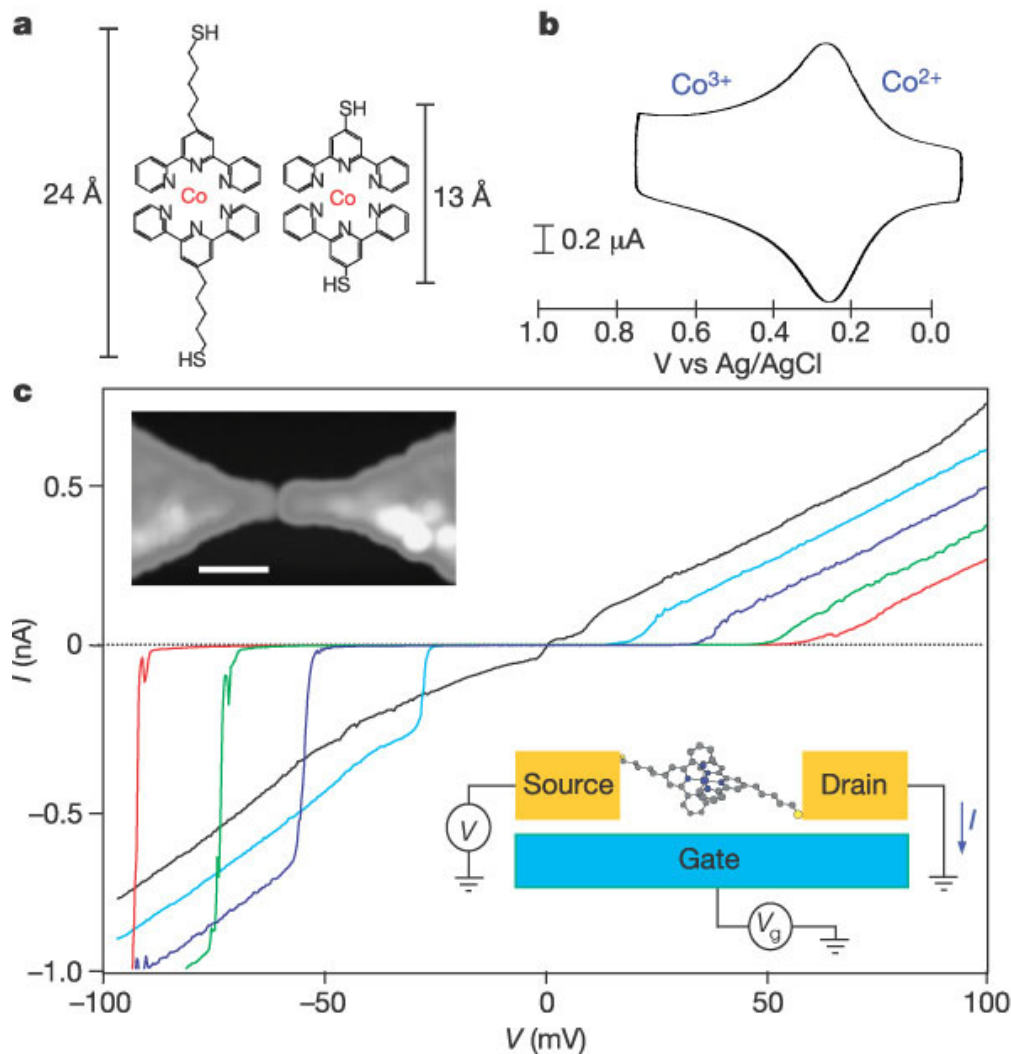
T: 1.5 - 25 K

Kondo resonance in a single-molecule transistor
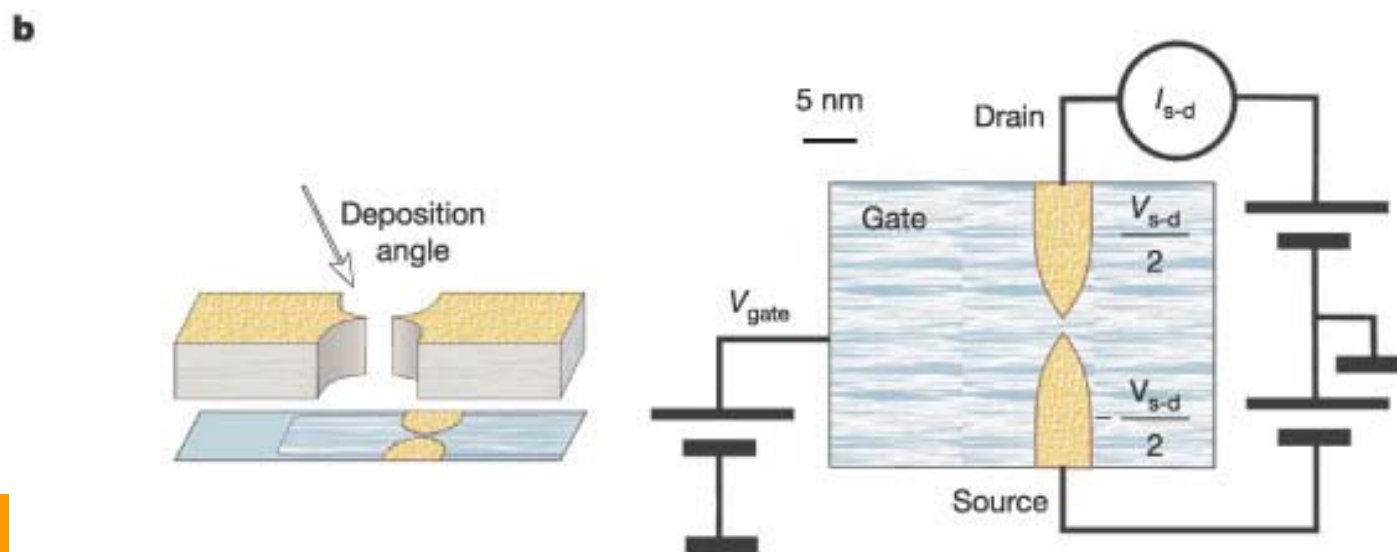
WENJIE LIANG*, MATTHEW P. SHORES†, MARC BOCKRATH*, JEFFREY R. LONG† & HONGKUN PARK*

T: 0.3 - 20 K

Single-electron transistor of a single organic molecule with access to several redox states

SERGEY KUBATKIN1, ANDREY DANILOV1, MATTIAS HJORT2, JÉRÔME CORNIL2,3, JEAN-LUC BRÉDAS2,3,*, NICOLAI STUHR-HANSEN4, PER HEDEGÅRD4 & THOMAS BJØRNHOLM4


T: 4 K

Disadvantages and problems with nano-electrode measurement

- A single-molecule measurement can hardly assured --- actually an ensemble measurement on a few or a small group of molecules.

- Contact problem --- can hardly assure each of the molecules in good contact with electrodes.

- Gate effect may be not optimized due to the long distance from the channel molecules (> 1 nm).

- All measurements were carried out at low temperatures, like 4K (liquid helium).

- FET behavior of molecules at room temperature must be different from that at low temperatures. Thermal agitation may bring difficulty to the molecular alignment (contact) and the electronic leaking in the nano-electrode systems (due to tunneling).

- Room temperature measurement should provide more reliable information concerned the FET process and the future application in chip devices.

Example #1:
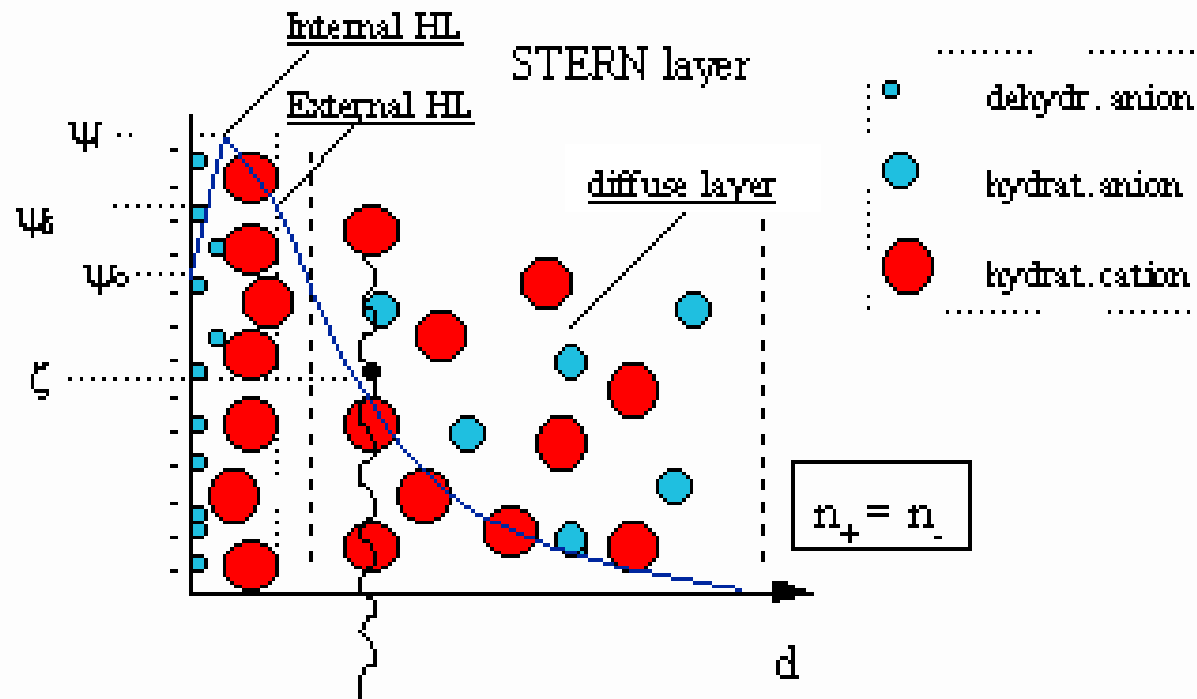# STM based electrochemical approach to Single-Molecule FET
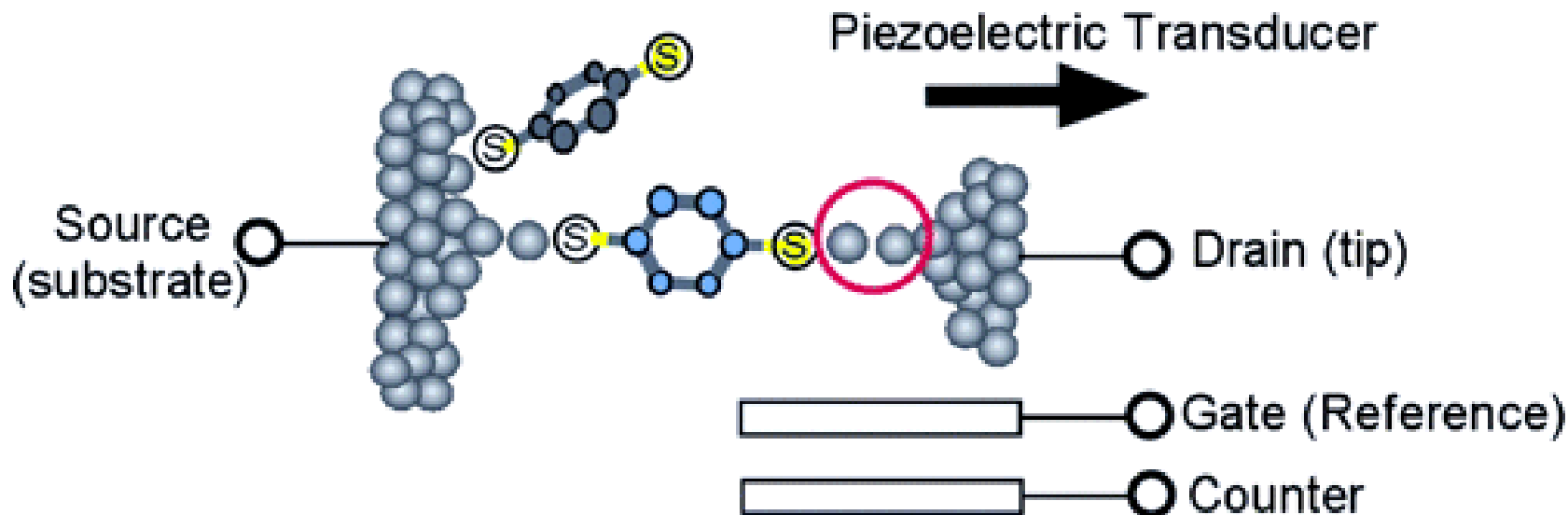
- gate voltage falls across the double layers at the electrode-electrolyte interfaces;

- the effective gate-molecule distance is only a few Å, the double layer thickness.

Tao et al. Nano Letters, *4* (2), 267 -271, 2004.
Zang and Tao et al. **J. Am. Chem. Soc. 127** (2005) 2386-2387 .

Large gate effect through double layer

- Local potential (ζ potential) can be adjusted by the bias between the electrode and a reference electrode;
- Thickness of a double layer, a few ions, < 1 nm;
- A local potential gradient as large as 1 V/Å can be obtained --- large gate field.

Example #1:
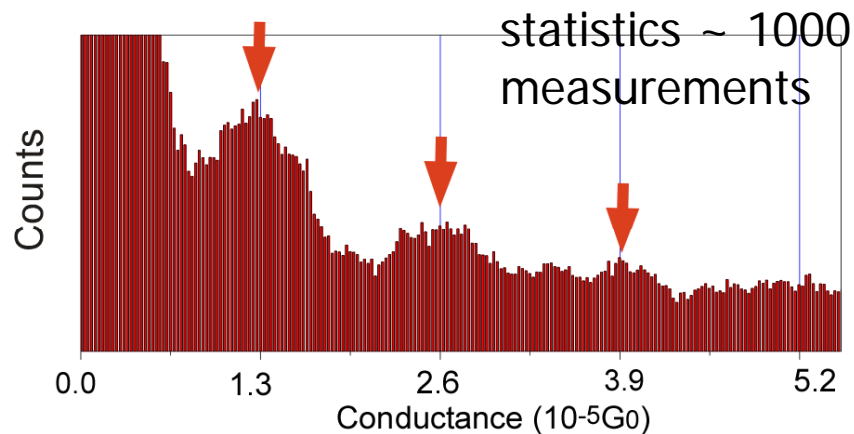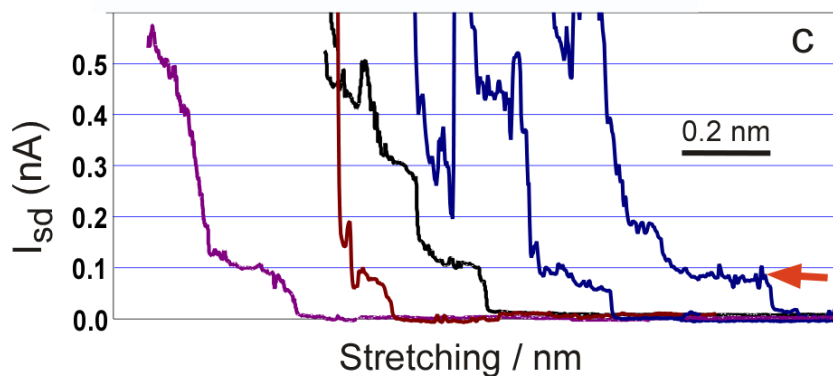# STM based electrochemical approach to Single-Molecule FET

- Here we demonstrate a single molecule *n-type* transistor in which the current through the molecule can be reversibly controlled with a gate electrode over nearly *three orders of magnitude* at room temperature.
- The molecule is wired to two gold electrodes (source and drain) via gold-thiol bonds, and the number of wired molecules is determined by statistical analysis of a large number of molecular junctions.
- A large gate field is achieved using an electrochemical gate in which the gate voltage is applied between the source and a gate in the electrolyte.
- Since the gate voltage falls across the double layers at the electrode-electrolyte interfaces, which are only a few ions thick, a field close to ~ 1V/Å can be reached.

A Single-Molecule Room-Temperature Transistor
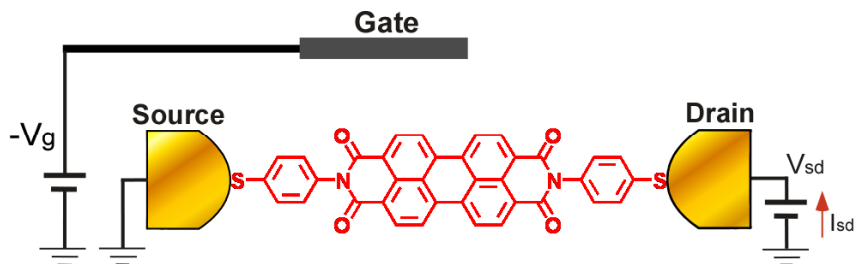
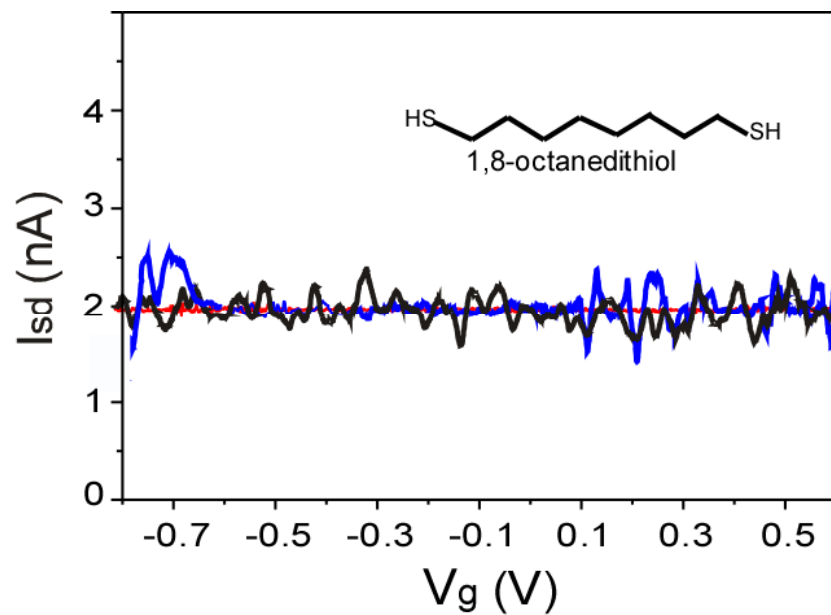## Why PTCDI molecules?

- N-type characteristic;
- High photo and thermal stability

  --- *crucial for room temperature*

  and single-molecule level.

statistics ~ 1000 measurements

Zang and Tao et al. **J. Am. Chem. Soc. 127** *(2005) 2386-2387 .*

Gate Modulation

shift with V_g — empty level

E_F+eV_{sd} E_F

*Zang and Tao et al. **J. Am. Chem. Soc. 127** (2005) 2386-2387 .*
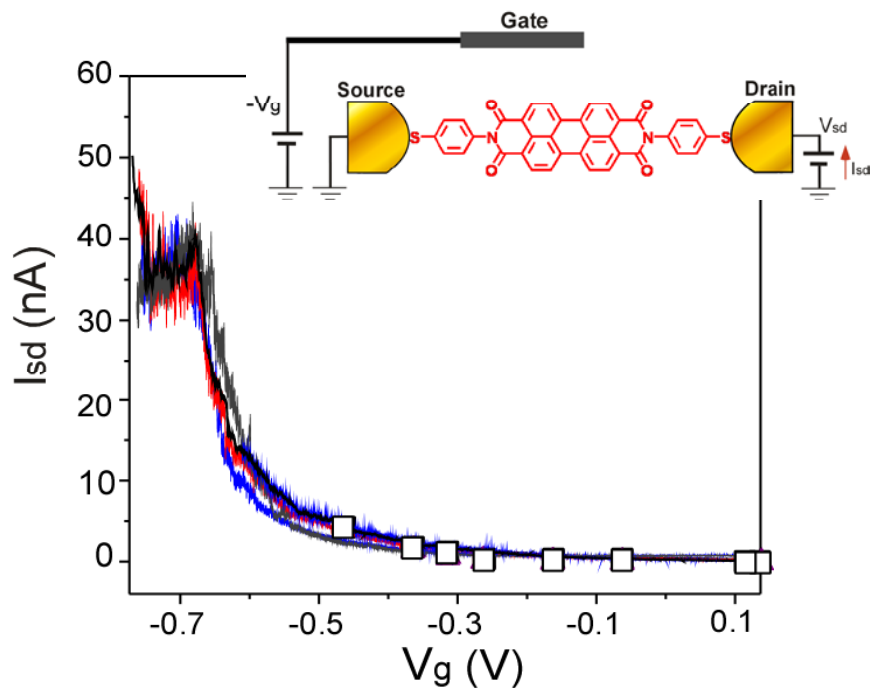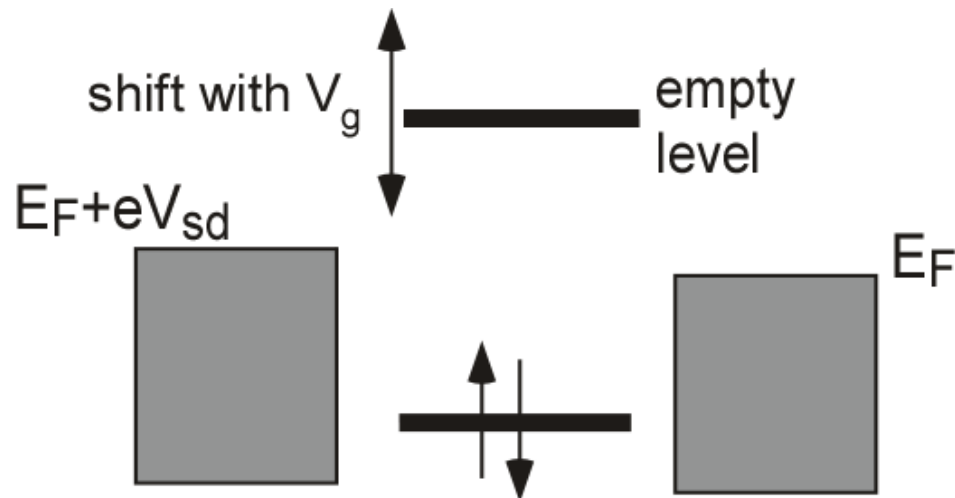
Gate Modulation of I/V Curves

Linear I/V behavior at low gate voltage
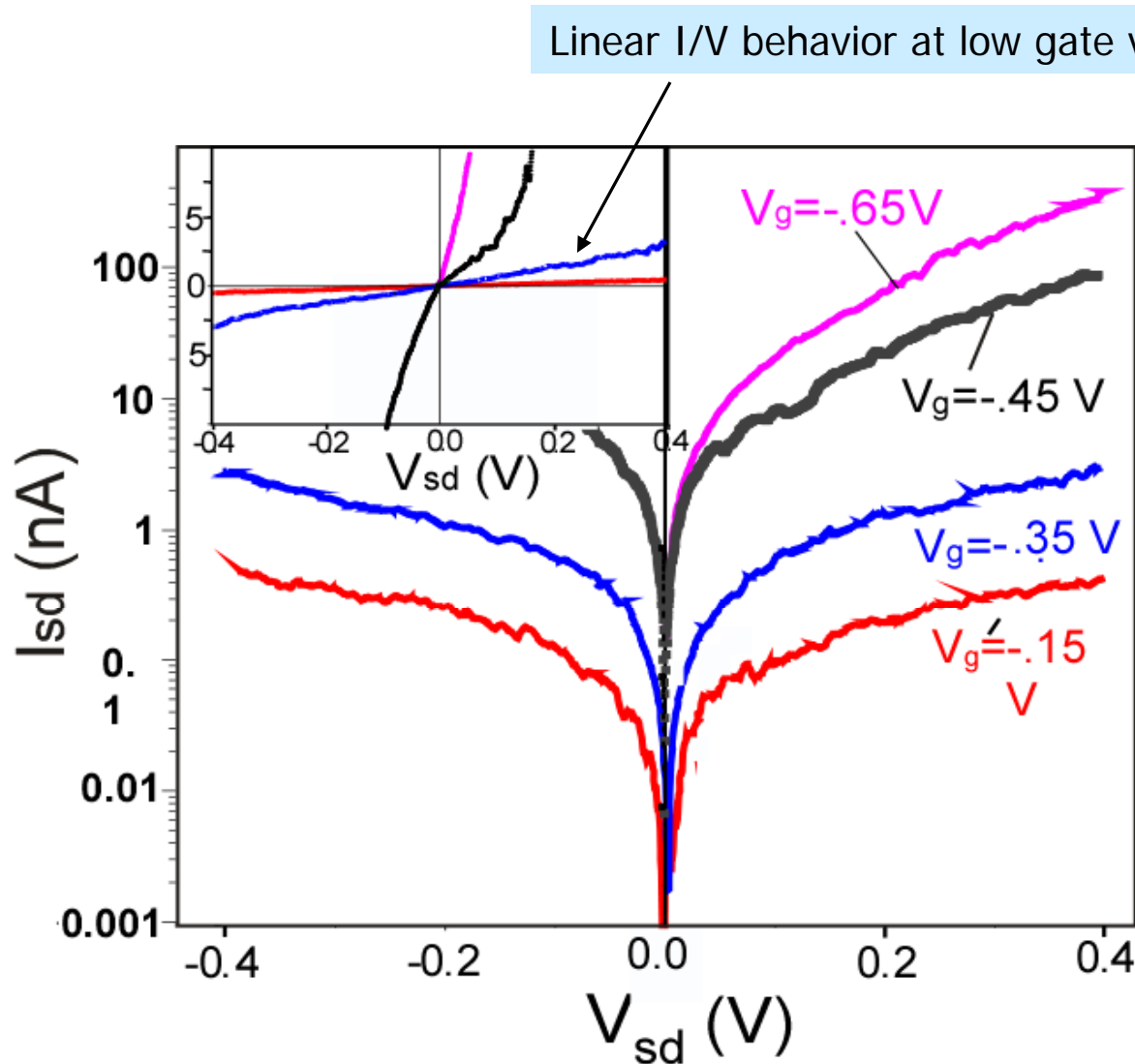
On/off ratio ~ **1000**; Large Gate Effect.

*Zang and Tao et al. **J. Am. Chem. Soc. 127** (2005) 2386-2387 .*

Energy Levels of MOs of T-PTCDI: *bond vs. unbound*
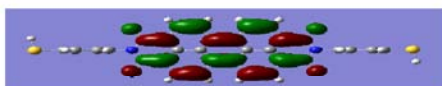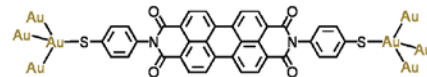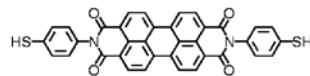
PTCDI LUMO ——————— -3.81 V	-3.70 V ——————— S-phenyl MO	
	-4.11 V ——————— PTCDI LUMO	
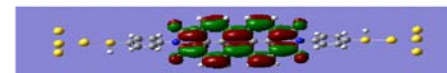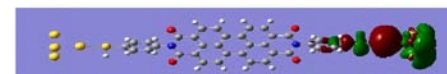
- E_F of SHE -4.40 V -

- E_F of gold -5.30 V -
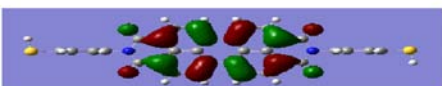
PTCDI HOMO ——⇅—— -6.31 V	-6.64 V ——⇅—— PTCDI HOMO	
S MO ——⇅—— -6.94 V	-6.86 V ——⇅—— S MO	
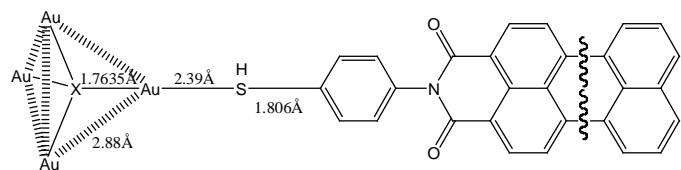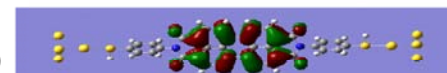
MO (B3LYP/6-311g**//B3LYP/6-31g*) (Au:LAND2DZ ECP)

Energy Levels of MOs of 1,4-benzenedithiol: **p-type**

A small conjugate system
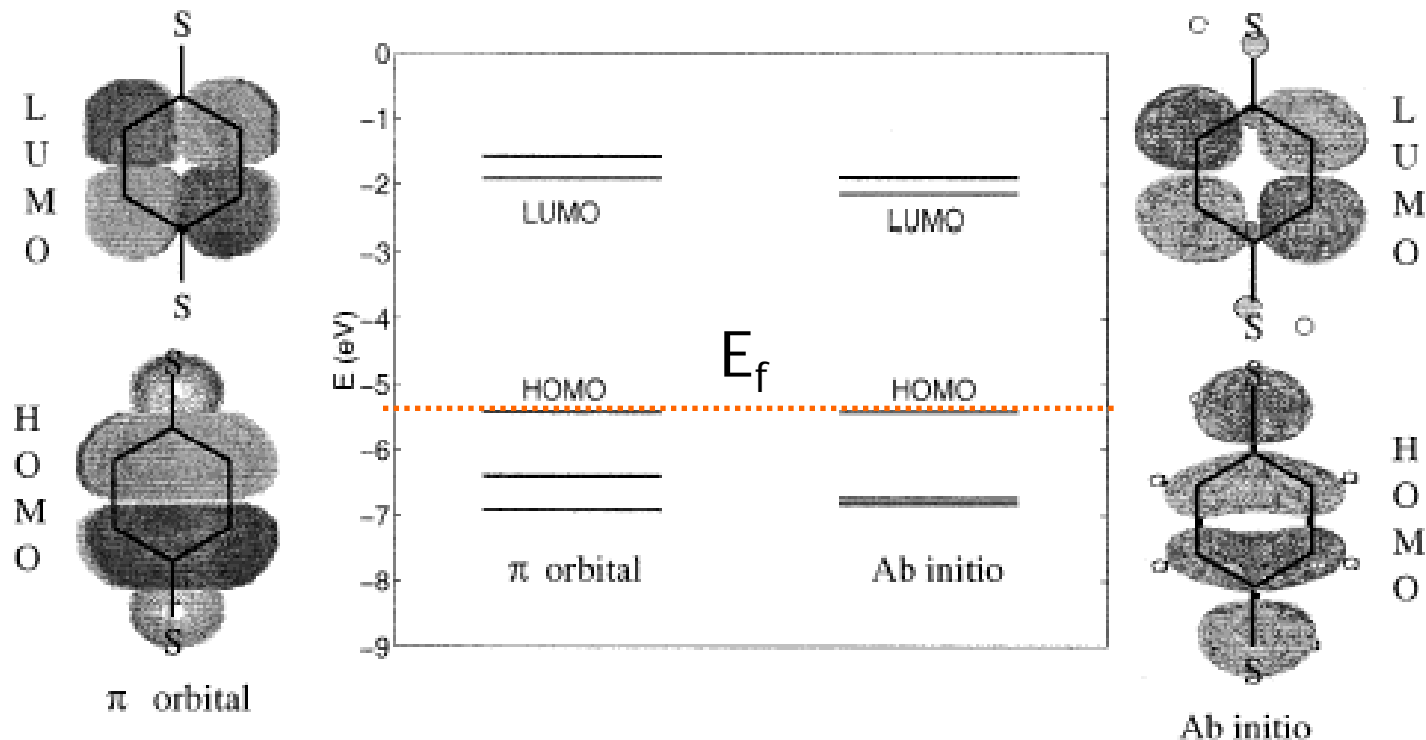
- LUMO is far away from the Fermi level of electrode (gold), implying a p-type characteristic of the molecule.
- Highly conducting at zero gate voltage due to the lining up between the LUMO and Fermi levels --- no gate effect.
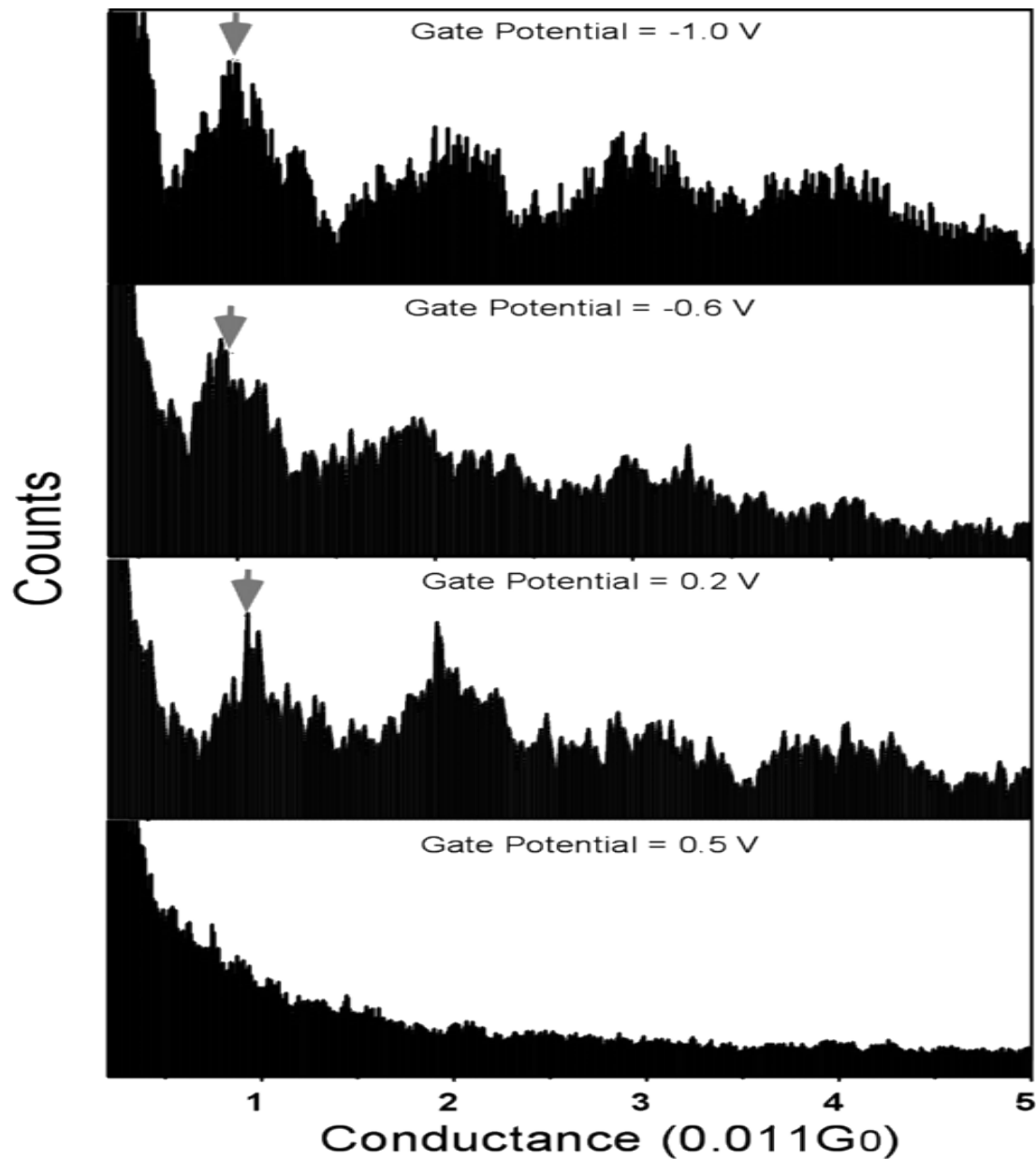
Conductance of 1,4-benzenedithiol junctions at different electrochemical gate voltages.

Measured at a fixed bias voltage (100 mV).

No gate effect!

Tao et al. Nano letters,2004,4,267-271
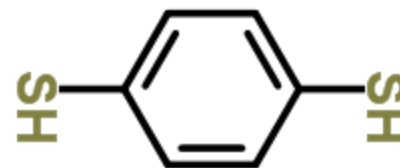
What is unique for PTCDI molecules?

- **Alkyl-dithiols**: insulator --- *no gate modulation*;
- **(Oligo-)Benzene-dithiols**: highly conjugated (conducting?) --- *hardly see gate modulation*;
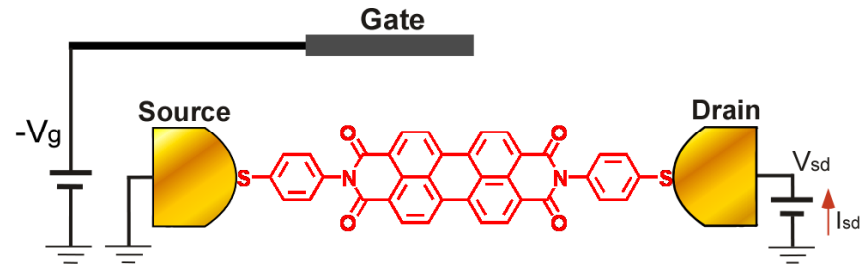
- **PTCDI-dithiols**: large gate modulation
  - a). Two node positions at the nitrogen;
  - b). How does the electron-transport happen?
  - c). Vibrational coupling between the S-phenyl and perylene orbitals?
  - d). Is the coupling dependent on local electrostatic field (as implied by the observation of the PTCDI dimers)?
  - e). Both S- and phenyl orbitals are strongly conjugated with the gold, and the orbital levels gets re-positioned.
  - f). A descent model (for gate effect) is needed to explain the role of the "node", and to correlate this to the gate modulation.
  - g). Tunneling (role of perylene unit?) or hoping (donor - acceptor (donor) – acceptor mechanism?) what is exactly the accepting state?

Example # 2:

bottom-up approach towards graphene transistors

On/Off ratio ~ 10^2

Zang, Tao et al. Nature Commun. **1**, 1-5 (2010).
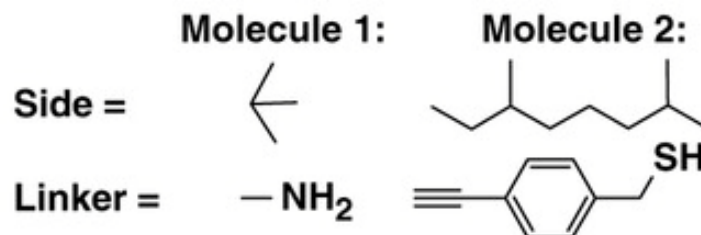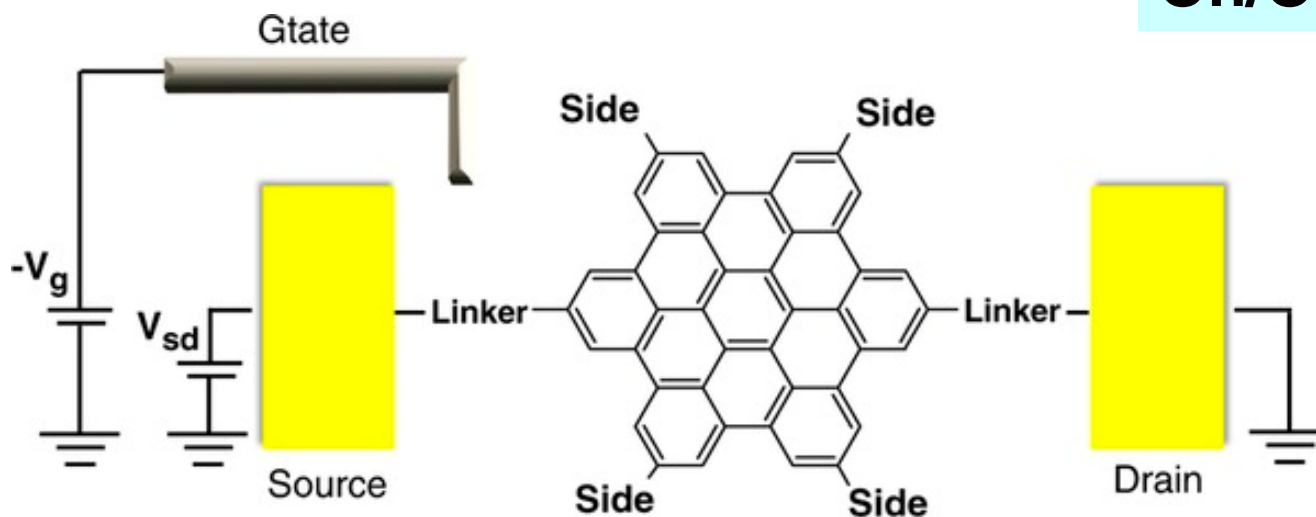
Example # 2:

Background and significance of **graphene** transistors

- Graphene, made of carbon atoms connected in a honeycomb structure, possesses huge electrical mobility, which is a critical parameter determining the speed of components like transistors.

- However, the band-gap of large area graphene is zero, producing On/Off ratio close to 1 (basically no switching) when employed in transistors.

- To enlarge the band-gap, graphene must be tailored into smaller ones. This brings numerous uncertainties (or non-uniformness) including the dimensions (tailored along which direction?), sizes, chemical composition at edges (oxidized vs. un-oxidized carbons), etc.

- Alternatively, bottom-up approach by chemical synthesis would be ideal to make uniform, chemically controlled graphenes.

- Examples #2 represents such an approach.
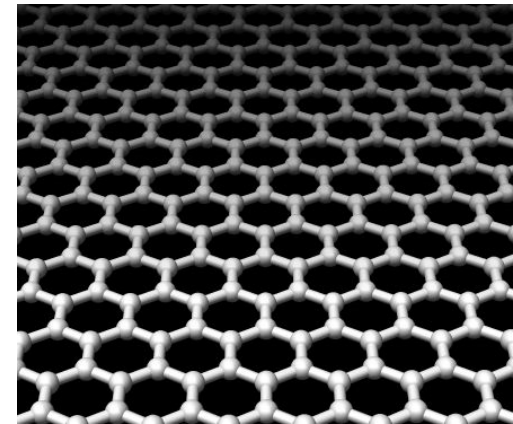
Example # 3:

Field regulation of single-molecule conductivity by a charged surface atom

Paul G. Piva[1,2], Gino A. DiLabio[2], Jason L. Pitters[2], Janik Zikovsky[1], Moh'd Rezeq[1,2], Stanislav Dogel[1], Werner A. Hofer[3] & Robert A. Wolkow[1,2]

Chemistry Highlights 2005

Key advances have been made this year in organic and inorganic chemistry, biochemistry, nanotechnology and other areas
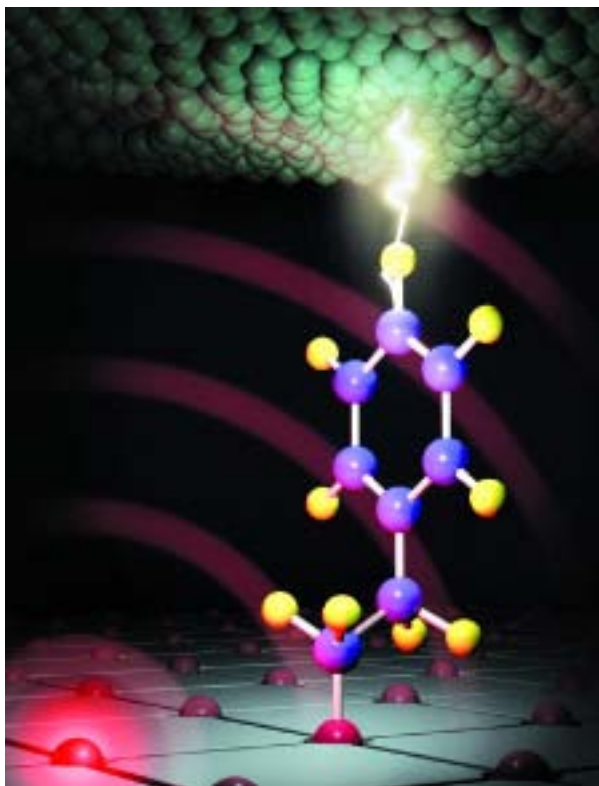
Taking Charge Wolkow and coworkers found that the electric field from a surface ion (glowing red) can be used to regulate electrical conductivity between a nearby molecule and a scanning tunneling microscope tip (green).
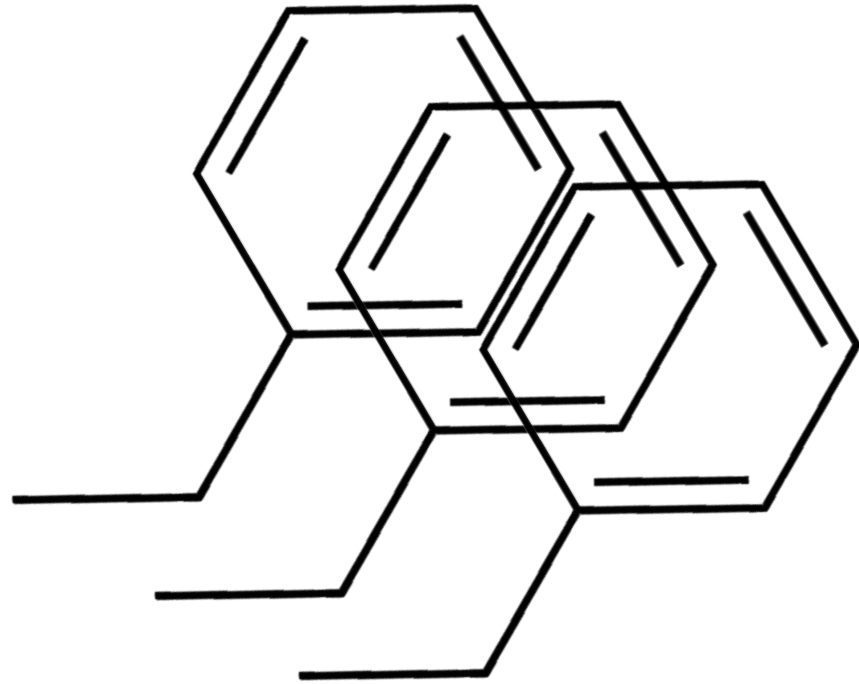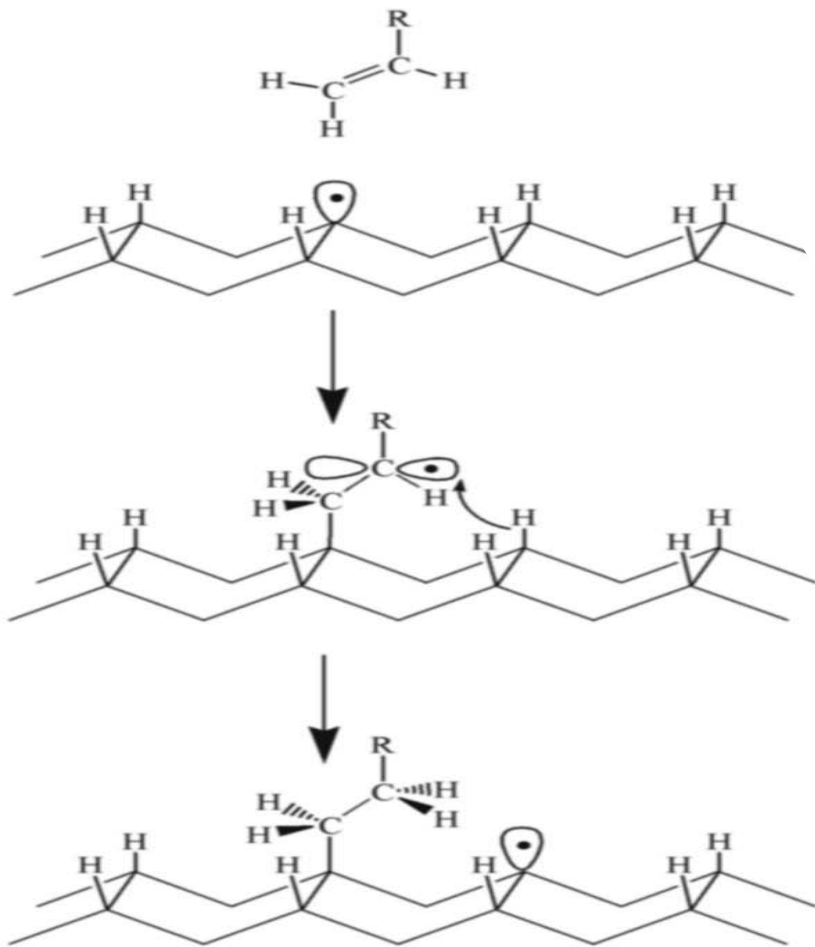
Proposed chain reaction mechanism for self-directed growth of molecular nanostructures on silicon.
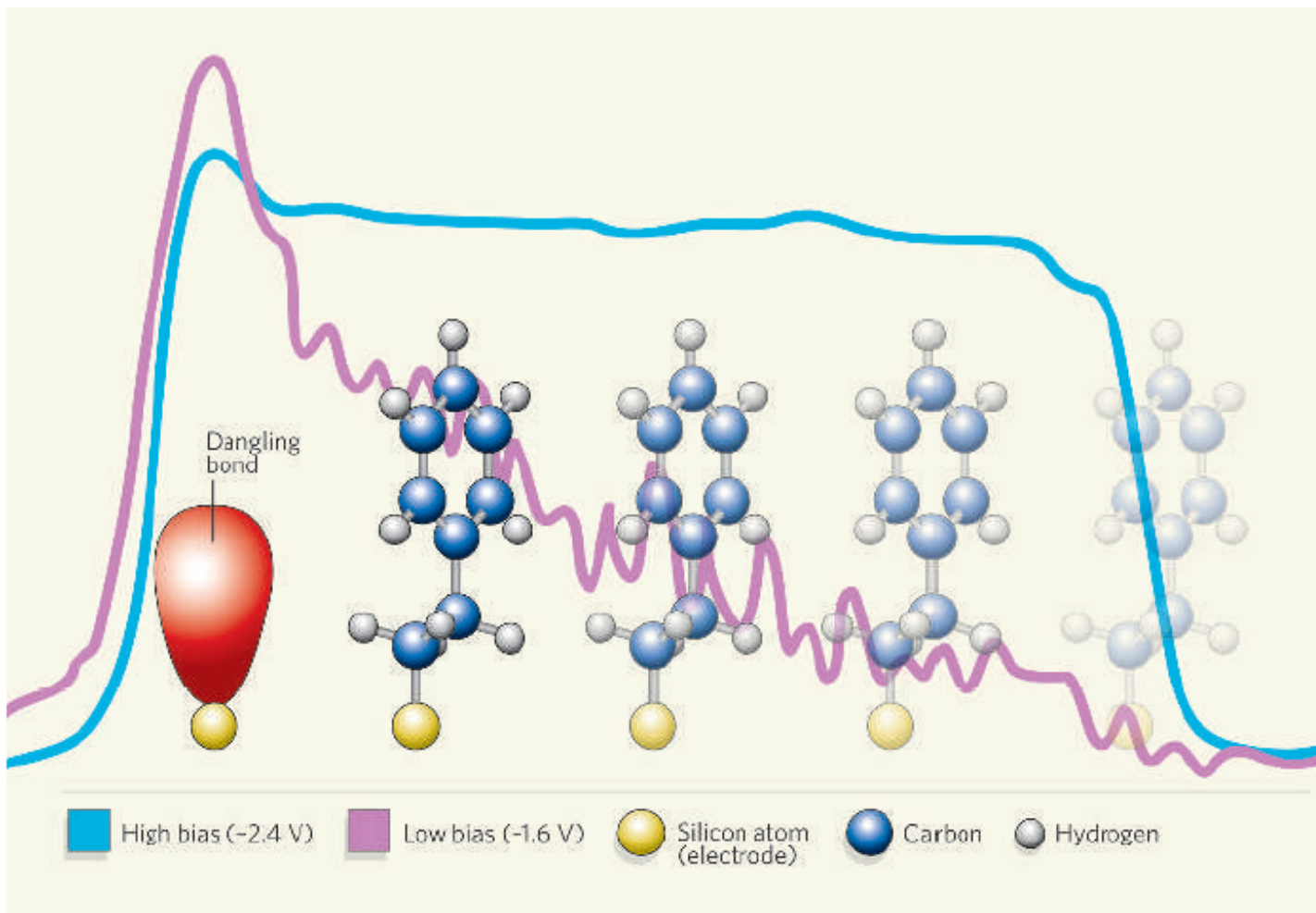
Figure 1 | Dangling potential. The polymerization of a molecule (here an organic styrene-derived molecule, not to scale) on a silicon substrate stops abruptly at a dangling-bond site. The blue and purple lines indicate the height of the molecules, as seen by a scanning tunnelling microscope (STM) — a measure of the charge transport across the molecules. At higher bias (blue line), all molecules are 'turned on', and appear bright in the STM picture. At lower bias (purple line), all molecules should appear dark. Wolkow *et al.*[1], however, discover that the electrostatic potential of the negatively charged dangling bond causes the nearest molecules to remain bright. This suggests that such structures could be used to manipulate charge transport through molecular junctions. (Figure adapted from Fig. 1 of ref. 1.)

Structure of styrene lines
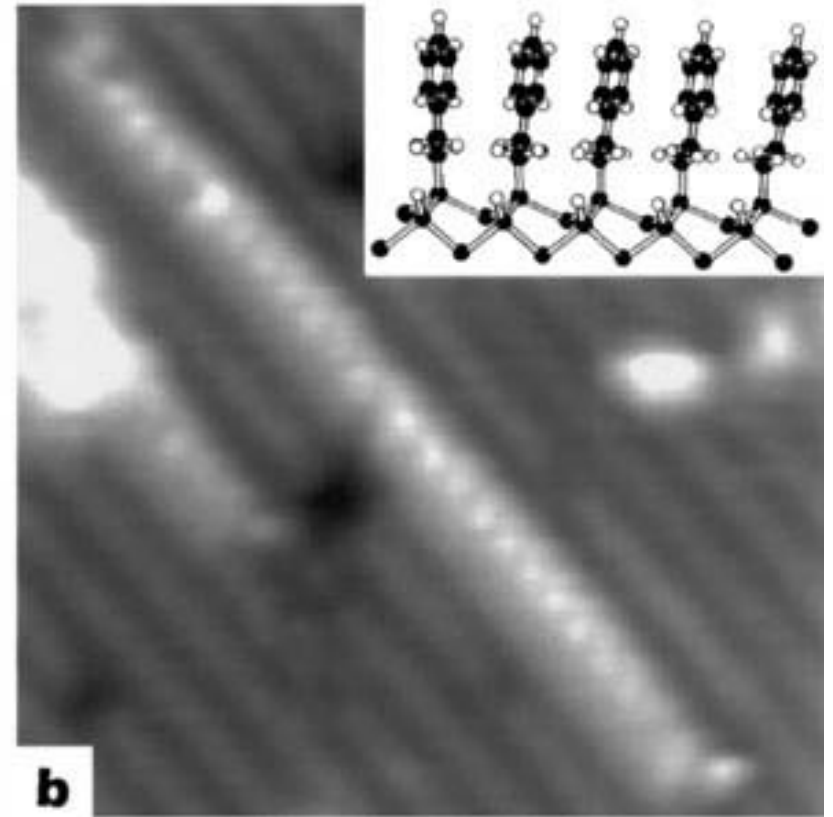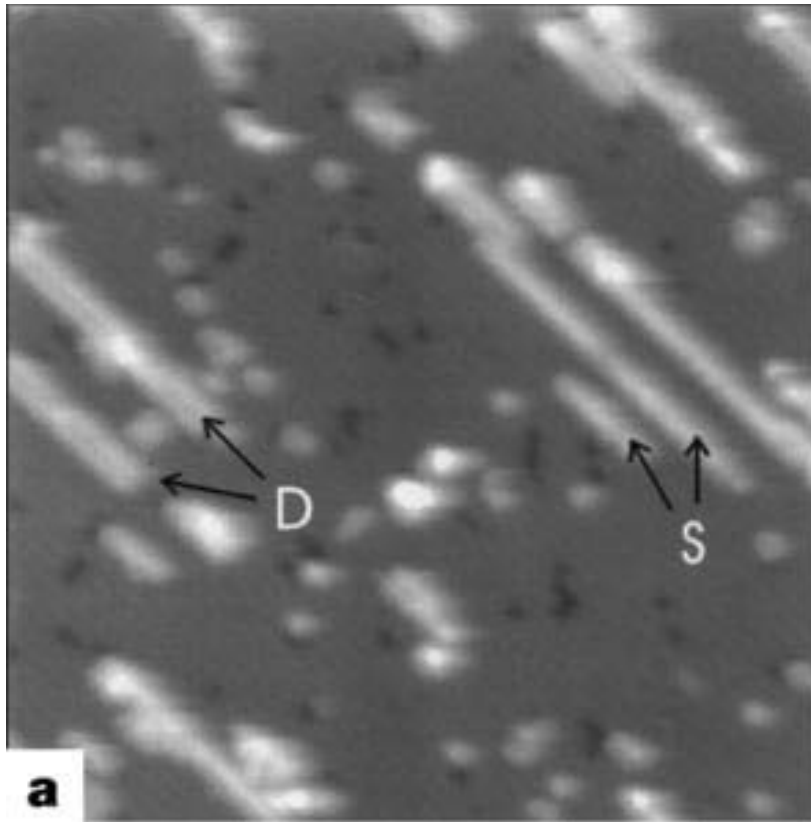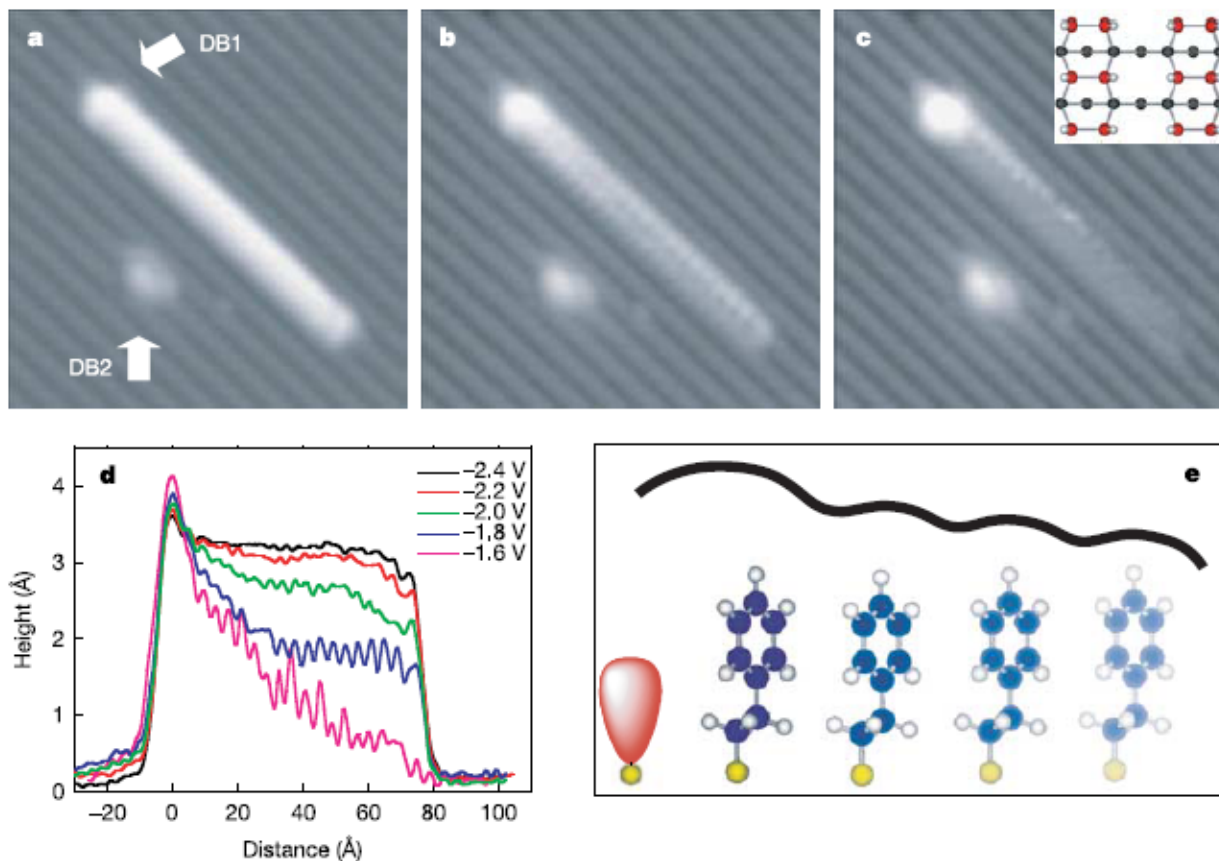
Figure 1 | Visualization of the electrostatic potential emanating from a point source. a, STM image of highly n-type doped H-Si(100), with negatively charged dangling bonds labelled DB1 and DB2. The prominent white bar is a line of surface-bound molecules. At increased sample bias of -2.4 V, molecular π-states are 'turned on', causing molecules to appear bright (topographically elevated) and of nearly constant height across the line. **b**, At an intermediate bias of -1.8 V, molecules appear darker, increasingly so at greater distances from DB1. **c**, In the absence of a negative dangling bond all molecules would appear dark at -1.6 V, but the molecules nearest to the dangling bond remain prominent. Molecules near the dangling bond experience a greater effective tip–sample bias due to the negatively charged dangling bond's electrostatic potential. Inset, a schematic of the silicon surface studied. **d**, Cross-sectional occupied-state height profiles taken along the molecular line for given sample bias voltages. The effect of DB2 is particularly evident as a broad maximum in the -2.0-V cross-section. **e**, Schematic showing the spatial relationship between the dangling bond (red paraboloid), styrene-derived molecules, and silicon substrate. Yellow, blue, and white spheres represent silicon, carbon and hydrogen atoms, respectively. The fading represents the diminishing appearance of the molecules due to reduced conduction, as seen in the experimental images. The black line is a representation of the height profile of the image. The dark line shows the sloping topographic envelope observed under low-bias conditions resulting from the negatively charged dangling bond. Images and linescan data were acquired at a constant tunnel current of 40 pA. Image areas are 10 nm $\times$ 10 nm.

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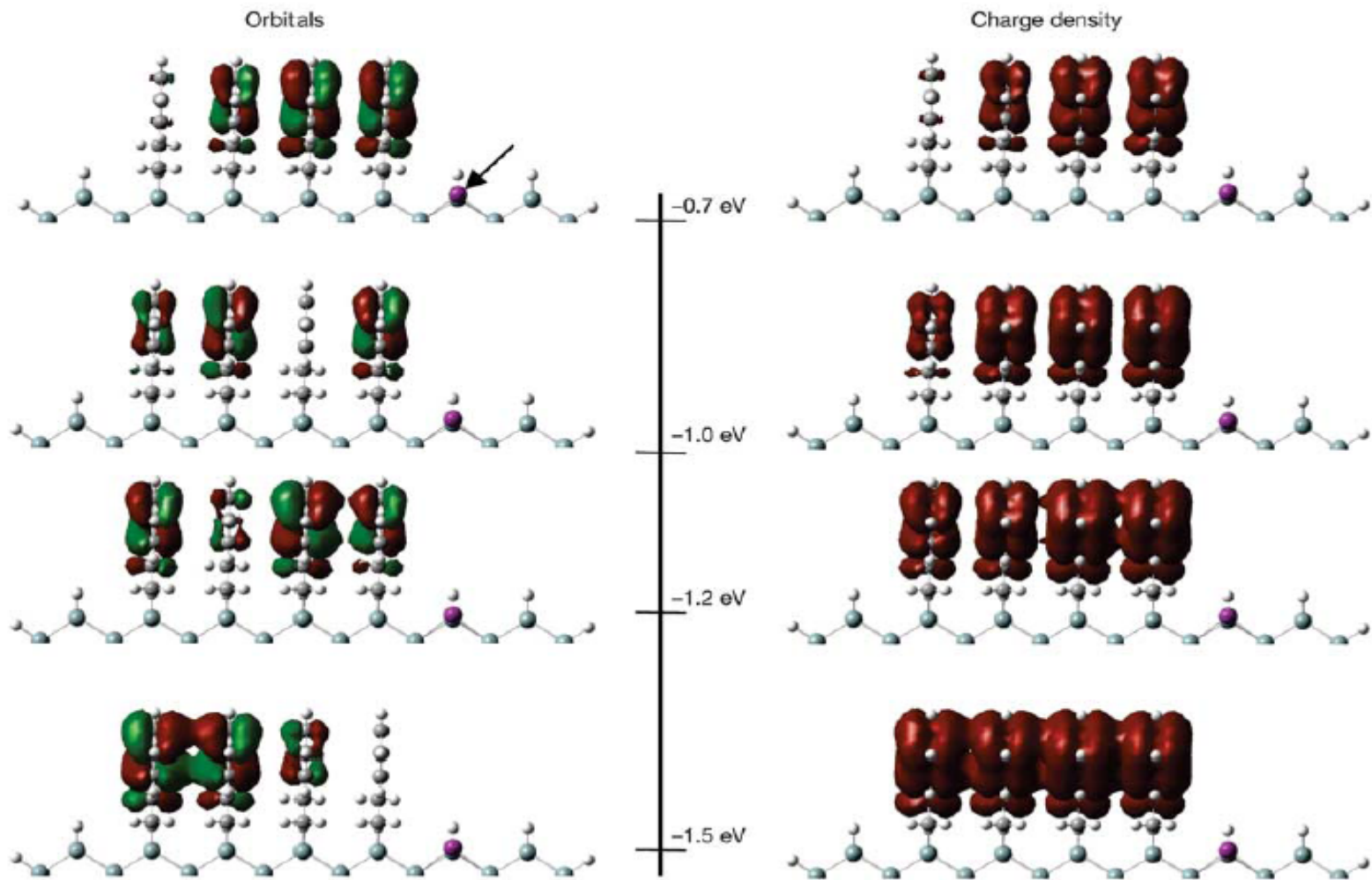
Figure 4 | Orbitals and charge densities near a dangling bond. Left, representative orbitals showing that the highest-energy molecular state is localized near the negative dangling bond (indicated by the purple sphere and arrow), while molecular states deeper in the occupied manifold are localized farther from the negative dangling bond (top to bottom). Right, charge-density surfaces of molecular states as a function of energy. Top is the charge density of the highest molecular state. Each subsequent surface represents the sums of charge densities of molecular states from the top of the valence band to the indicated energy. These surfaces demonstrate that the slope effect appears at smaller-magnitude scan biases and disappears (images become flat) at higher-magnitude scan biases in agreement with the STM measurements. For clarity, a row of silicon dimers has been removed from the model.

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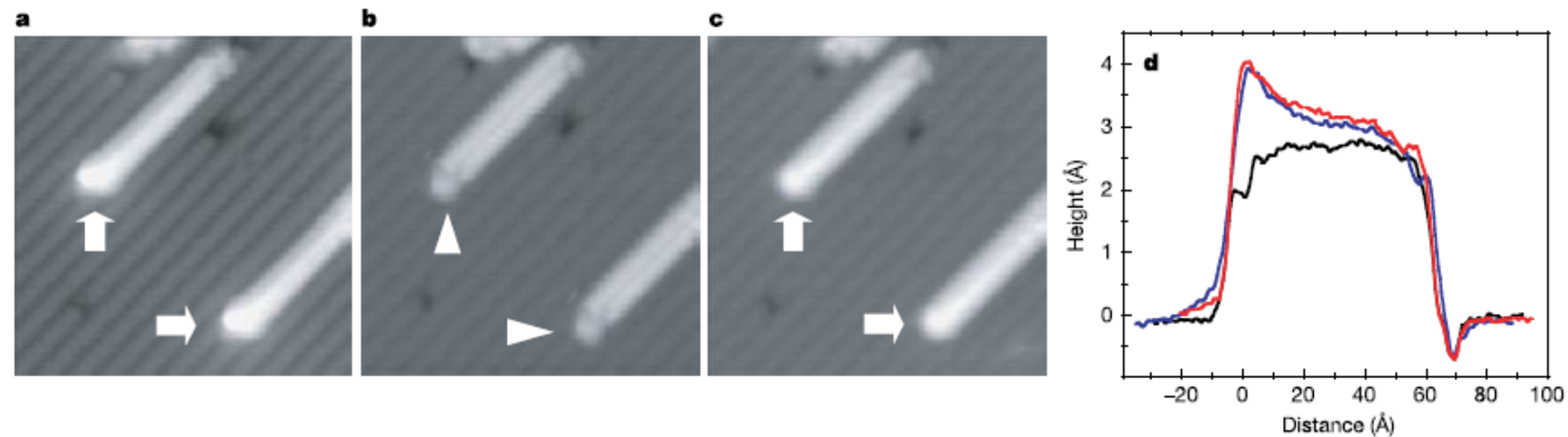
Figure 3 | Reversible modification of dangling bonds. The 'capping' and 'uncapping' of dangling bonds correlates with the disappearance and reappearance of the slope effect, as illustrated in the 10 nm × 10 nm STM images acquired at −1.9 V and 50 pA. **a**, Sloping styrene lines with a dangling bond at the end of each line, indicated by arrows. **b**, One TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) molecule reacted at each dangling bond as indicated with wedges. Charge, and therefore slope, are absent. **c**, TEMPO molecules are removed by scanning at −3 V. The charged dangling bonds, indicated by arrows, are regenerated and the slope reappears. **d**, Profiles of styrene lines from the upper left corners of panels **a**, **b** and **c** are shown in blue, black and red, respectively.

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Example # 4:

STM Approach to a Single-Molecule Chemical-Field-Effect Transistor
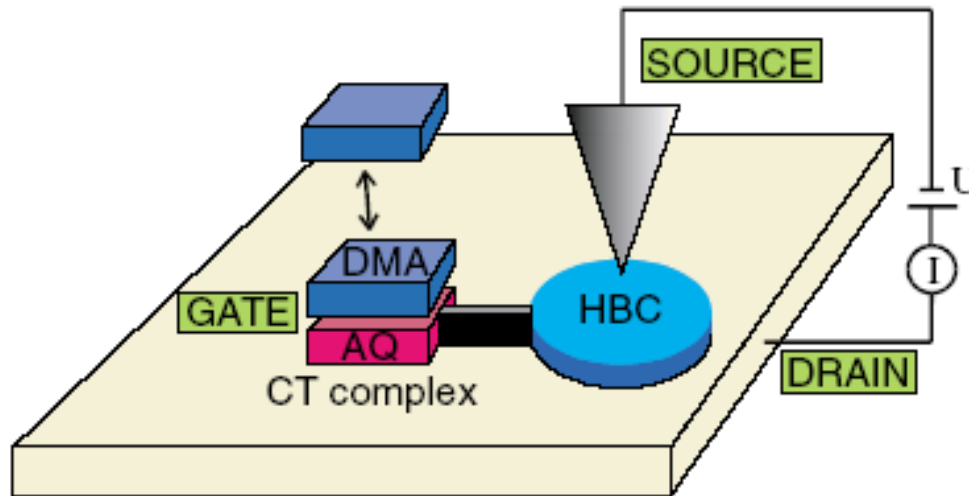
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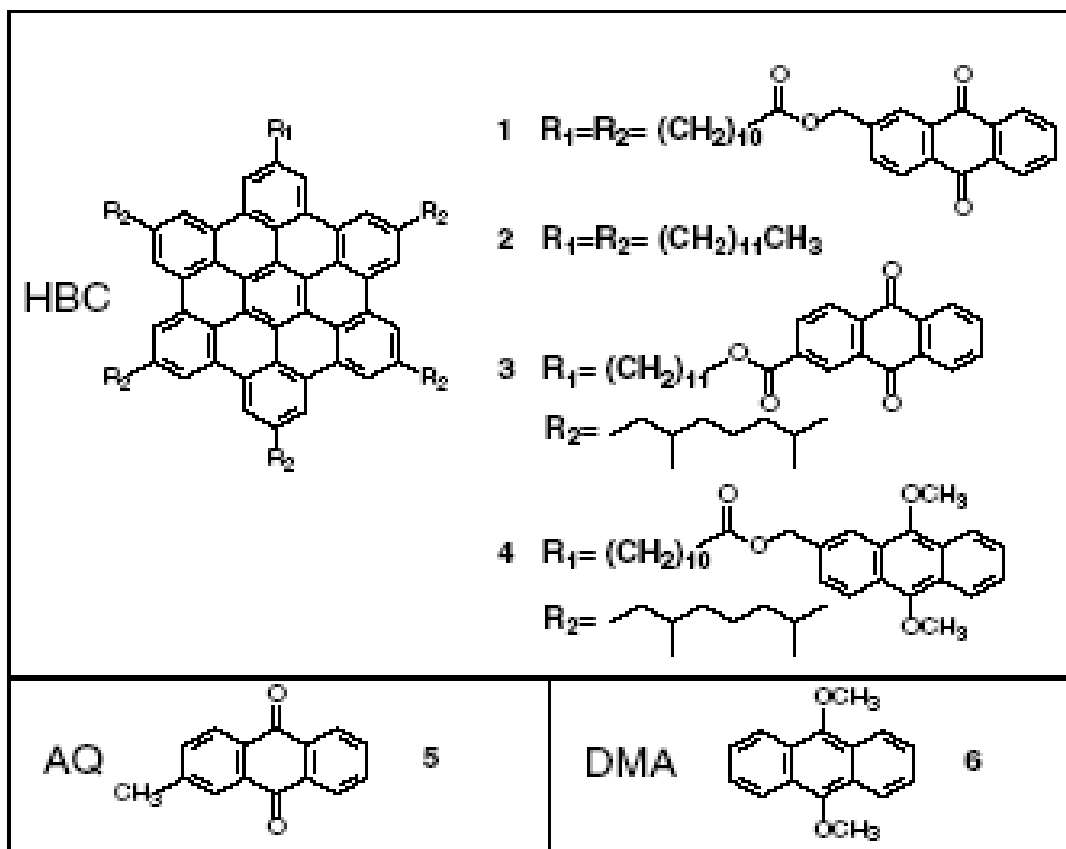
Chemical formulas of the employed materials:
hexa*peri*hexabenzocoronene (HBC) decorated with six anthraquinone
(AQ) functions (**1**), hexaalkyl-HBC (**2**), HBC bearing either one AQ (**3**) or one 9,10-
dimethoxyanthracene (DMA) function (**4**), methyl-AQ (**5**), and DMA (**6**).

# Why chemical-field gate?

- Field effect transistors have been fabricated with carbon nanotubes and single molecules. The electrodes, however, were macro- or mesoscopic and not readily scalable to nanoscale dimensions.
- Under ultrahigh vacuum (UHV) conditions, STM can detects the coupling of adsorbed atoms to electronic surface states .
- Here an example of a prototypical three-terminal device at the solid-liquid interface, in which the current through a hybrid-molecular diode is modified by nanometer-sized *charge transfer complexes* ("nanogates") covalently linked to the molecule in the STM junction.
- The gate effect is attributed to an interface dipole which shifts the substrate work function by 120 meV. It is induced by the complexes from electron acceptors covalently bound to the molecule in the gap and electron donors coming from the ambient fluid.
- This proof of principle is regarded as a major step towards monomolecular electronic devices.
- The key molecule for the present study is an hexa*peri*hexabenzocoronene (HBC) derivative with six strong electron acceptor substituents [anthraquinone (AQ)], which can form *charge transfer complexes* with an electron donor such as [9,10-dimethoxyanthracene (DMA)].
- Spectroscopic data were accepted only if imaging was stable with a typical contrast before and after measuring current-voltage (*I-V*) characteristics and if there was no lateral shift between images of forward and backward scan direction.
- Tunneling spectra of a number of molecules were averaged, provided they met the setting of the feedback loop with acceptable accuracy (~ 10%).
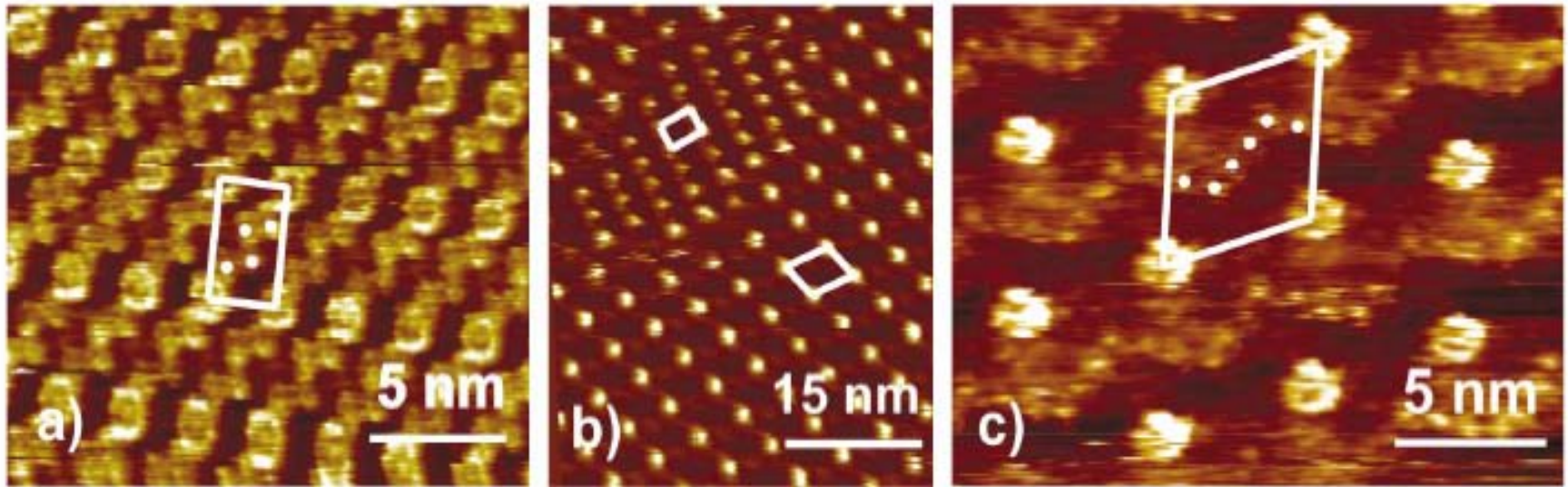
STM current images of highly ordered monolayers on highly oriented pyrolytic graphite of (a) 1 ($Us = 1.4$ V, $It = 300$ pA), (b) 1+6 ($Us = -1.4$ V, $It = 108$ pA), (c) 1+6 ($Us = -1.2$ V, $It = 270$ pA).

Unit cells, AQs in (a) and charge transfer complexes in (c) are indicated.
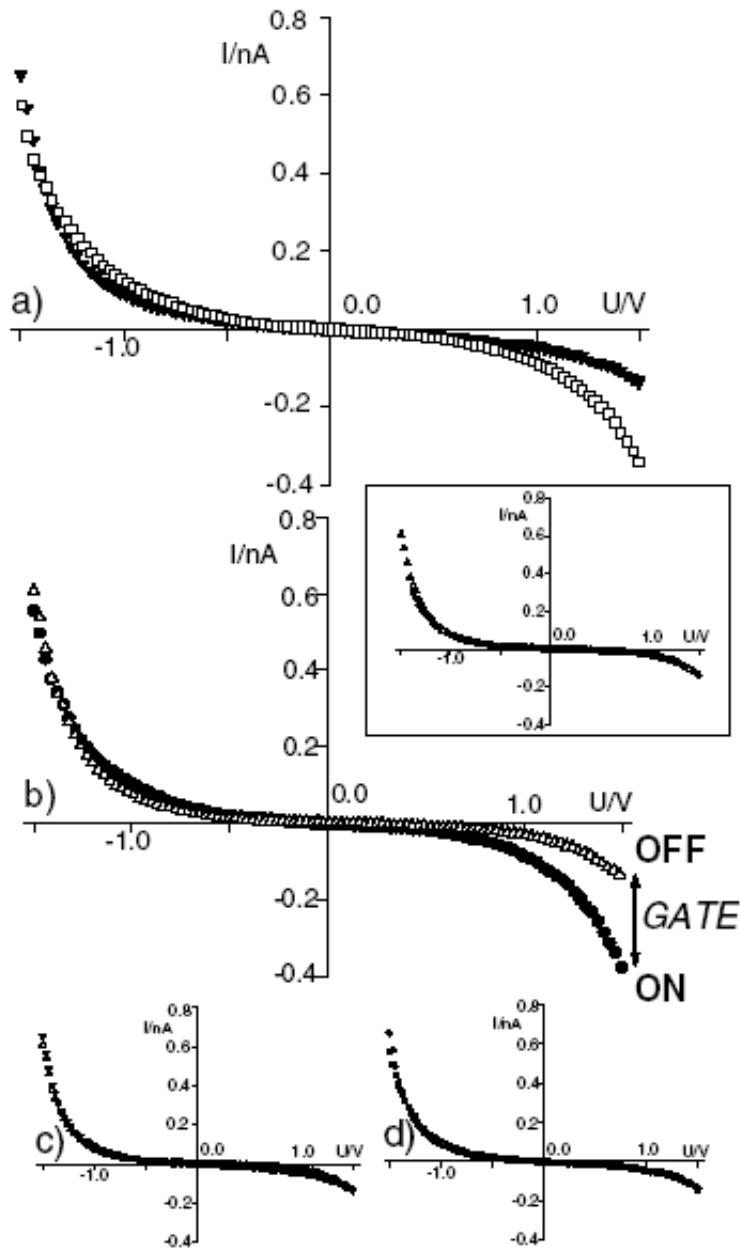
I-V's (raw data) through

(a) HBC cores (solid triangles) and alkyl chains (open squares) in monolayers of **1**.

(b) HBC cores in domains of **1+6** where CT complexes are adsorbed (solid circles) or not adsorbed (open triangles). Inset: shifted and normalized data.

(c) HBC cores in monolayers of **1+6** where no CT complexes are present (open triangles) and in monolayers of **1** (solid triangles).

(d) HBC cores in monolayers of **2+6** (solid squares) and **2** (open circles). The size of the symbols reflects the experimental error.