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LETTERS

Measurement of the conductance of single conjugated molecules

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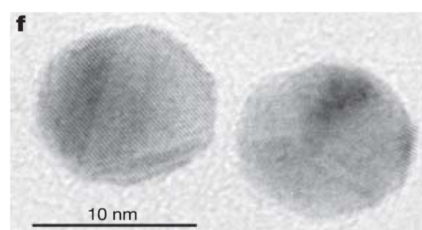
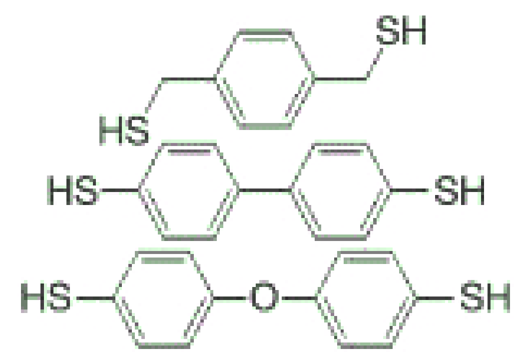
Electrical conduction through molecules depends critically on the delocalization of the molecular electronic orbitals and their connection to the metallic contacts. Thiolated (−SH) conjugated organic molecules are therefore considered good candidates for molecular conductors[1,2]: in such molecules, the orbitals are delocalized throughout the molecular backbone, with substantial weight on the sulphur–metal bonds[1–4]. However, their relatively small size, typically ~1 nm, calls for innovative approaches to realize a functioning single-molecule device[5–11]. Here we report an approach for contacting a single molecule, and use it to study the effect of localizing groups within a conjugated molecule on the electrical conduction. Our method is based on synthesizing a dimer structure, consisting of two colloidal gold particles connected by a dithiolated short organic molecule[12,13], and electrostatically trapping it between two metal electrodes. We study the electrical conduction through three short organic molecules: 4,4′-biphenyldithiol (BPD), a fully conjugated molecule; bis-(4-mercaptophenyl)-ether (BPE)[14], in which the conjugation is broken at the centre by an oxygen atom; and 1,4-benzenedimethanethiol (BDMT), in which the conjugation is broken near the contacts by a methylene group. We find that the oxygen in BPE and the methylene groups in BDMT both suppress the electrical conduction relative to that in BPD.



BDMT

BPD

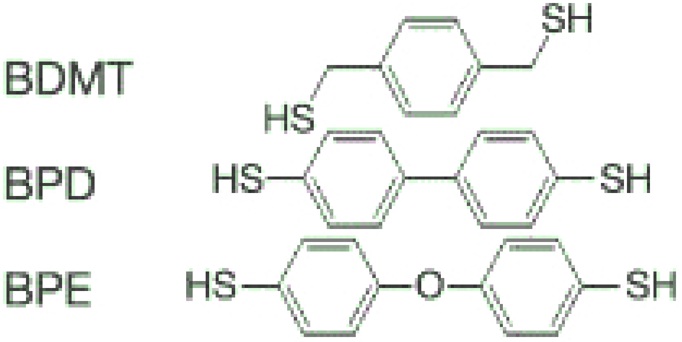
BPE



Measurement of the conductance of single conjugated molecules

Summary

- **Technique**: New approach to contact single molecules
- **Subject:** Study the effect of localizing groups on the electrical conduction of three related molecules



Outline

- Contact single molecules
- Dimer Based contacting scheme
- Studied molecules
- Measurements and discussion

Contact single molecules

Need for nm-sized gaps, various methods:

- Electron beam lithography
- Mechanical break junctions
- Electromigration

HERE: DIMER-BASED CONTACTING

IDEA: dimer of gold colloids bridged by a single molecule

ADVANTAGES:

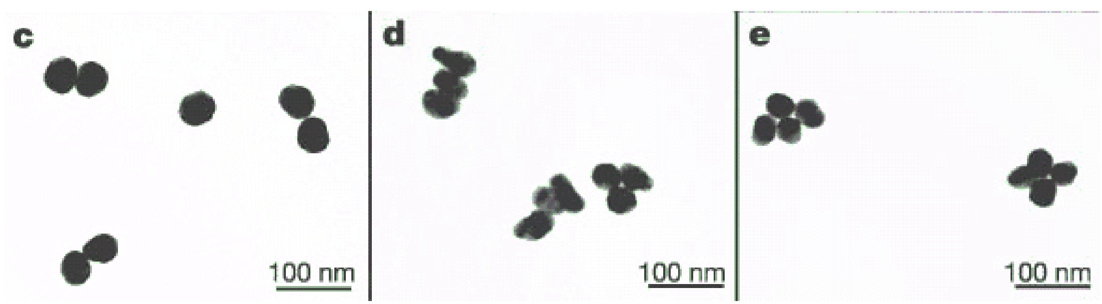
- ✓ Fabricate gaps sized ~ 50 nm instead of few nm
- ✓ Single-molecule devices can be fabricated with high certainty
- ✓ Contacts are well defined and can be characterized separately
- ✓ Allows the measurement of T-dependence and over long periods of time

Dimer based contacting (I)

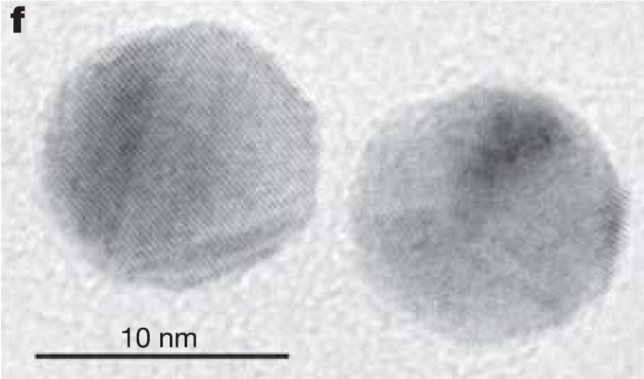
- **Start:** Mix a solution of dithiolated molecules with citrate protected gold colloid ($C_{molecule}/C_{colloid} \approx 1/10$)

- Thiolated molecules substitute the citrate anions forming stable Au-S bonds

- Gold particles are clustered to molecule-bridges oligomers



TEM images

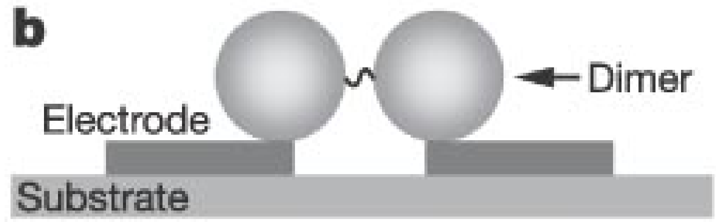


- Separation of the oligomers by centrifugation

- **Result: molecule-bridged dimers** verified by gap size and Raman spectroscopy

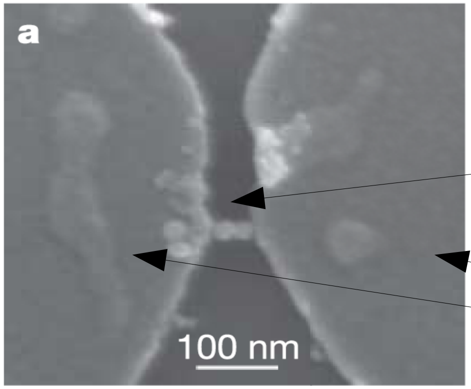
Dimer based contacting (II)

- **Next step:** Attach the dimer to electrodes by electrostatic trapping



- Gold electrodes defined on a silicon substrate using e-beam lithography
- Electrode spacing ~50 nm to attach dimers of ~60 nm (30 nm colloidal particles)
- Success rate: 45% dimer / 55% single gold particle (easy to distinguish)
35% low conductance / **10% high conductivity dimers**

SEM image of a trapped dimer:



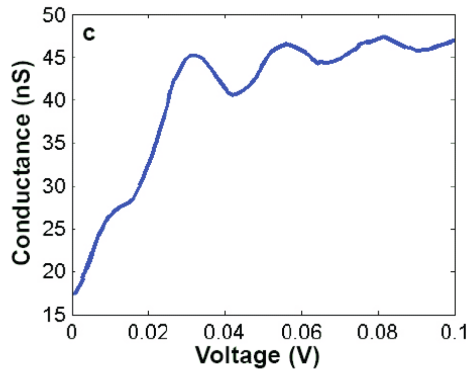
molecule-bridged dimer

electrodes

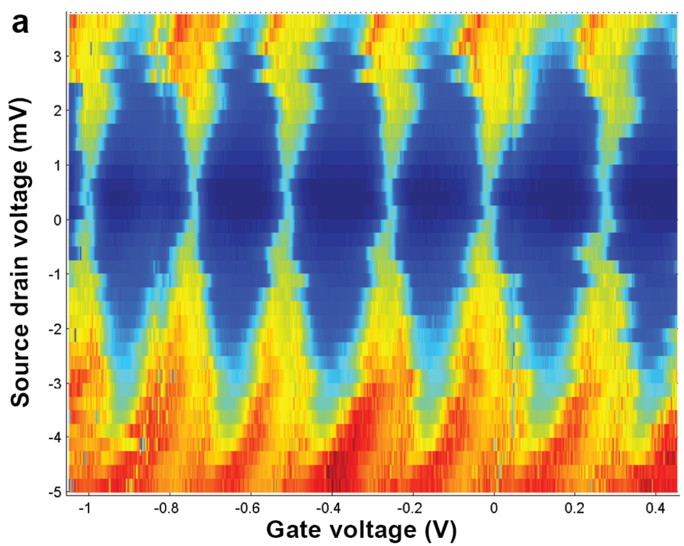
Single Colloid

Attach single gold particle: I-V characteristics of the contacts

- Coulomb blockade staircase of ~ 20-30 meV
- Gate voltage applied: diamond structure
- Characteristics of a single-electron transistor



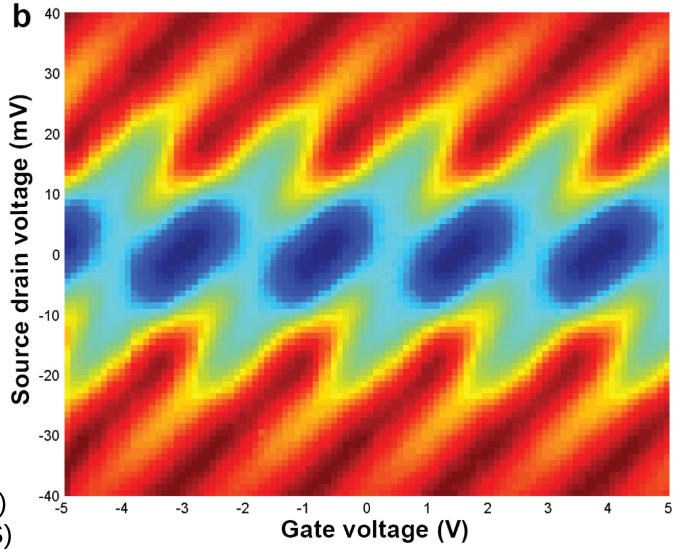
- tunnel barrier between gold particles and electrodes(~ 10 MΩ, due to ligands)



40 nm colloid

(nearly identical input and output barriers)

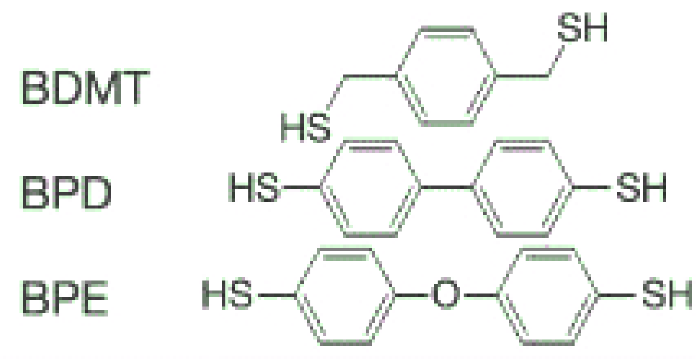
blue: low conductance(0 nS)
red: high conductance (3 nS)



30 nm colloid

(different input and output barriers)

Studied molecules



BDMT: 1,4-benzenedimethanethiol

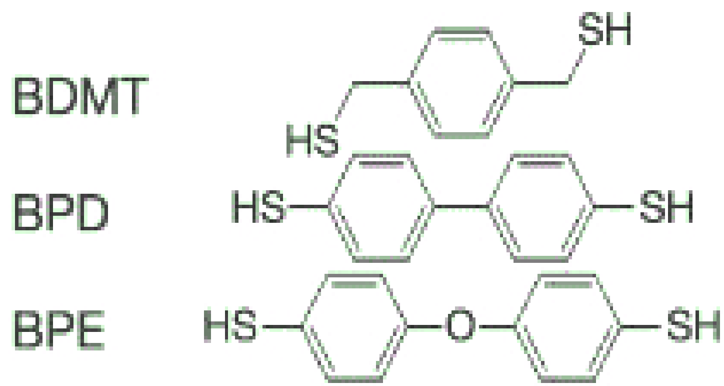
BPD: 4,4'-biphenyldithiol

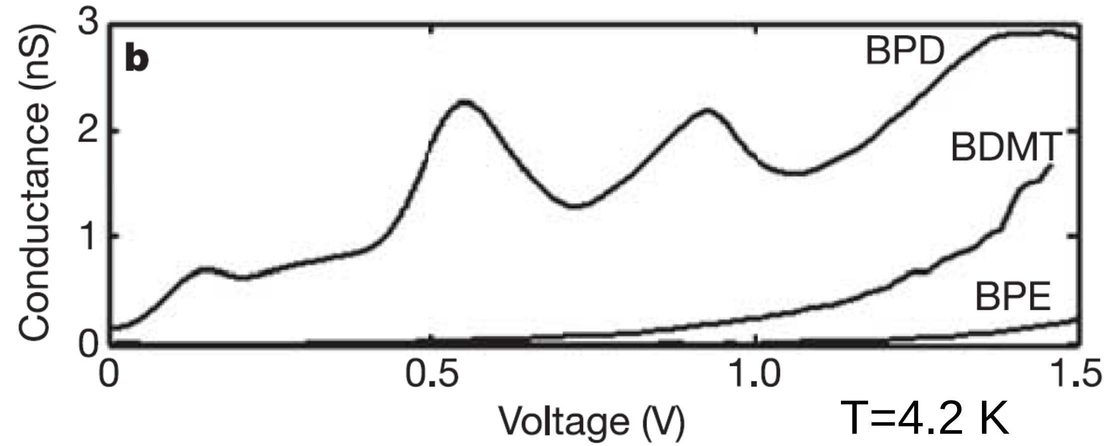
BPE: bis-(2-mercaptophenyl)-ether

- Size(BDMT) ~ 0.9 nm
- BPD: Fully conjugated molecule
- BPE: Conjugation broken at the center by an oxygen atom
- BDMT: Conjugation broken near the contacts by a methylene (CH_2) group

⇒ **different conductance behavior expected**

Conductance through single molecules



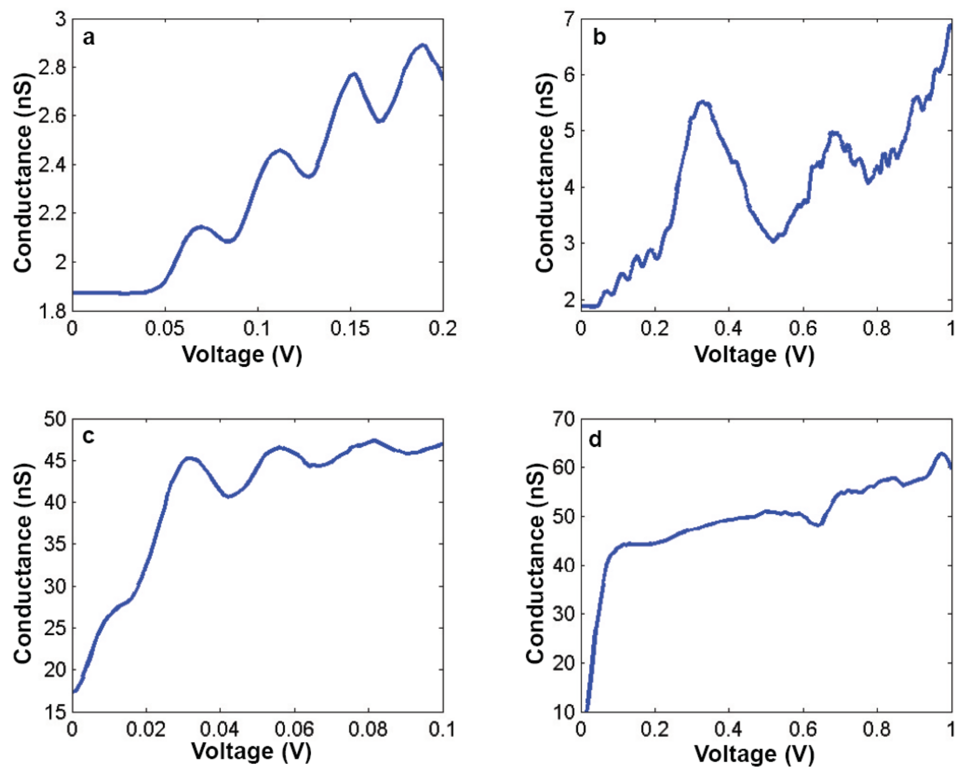


measured differential conductance is of molecular origin:

- Apparent gap (between BPD and BDMT/BPE)
- Exponential turn on of conductance in case of BDMT/BPE
- **BPD**: series of conductance peaks not connected with charging of gold particles (~300 meV vs.~20 meV)
- **BDMT/ BPE**: conduction turns on at much higher voltages (>0.5 V), no secondary peak structure observed

⇒ **Localizing groups interfere with conjugation and suppresses conductance**

Comparison single colloid / dimer



a,b: BPD-bridged dimer

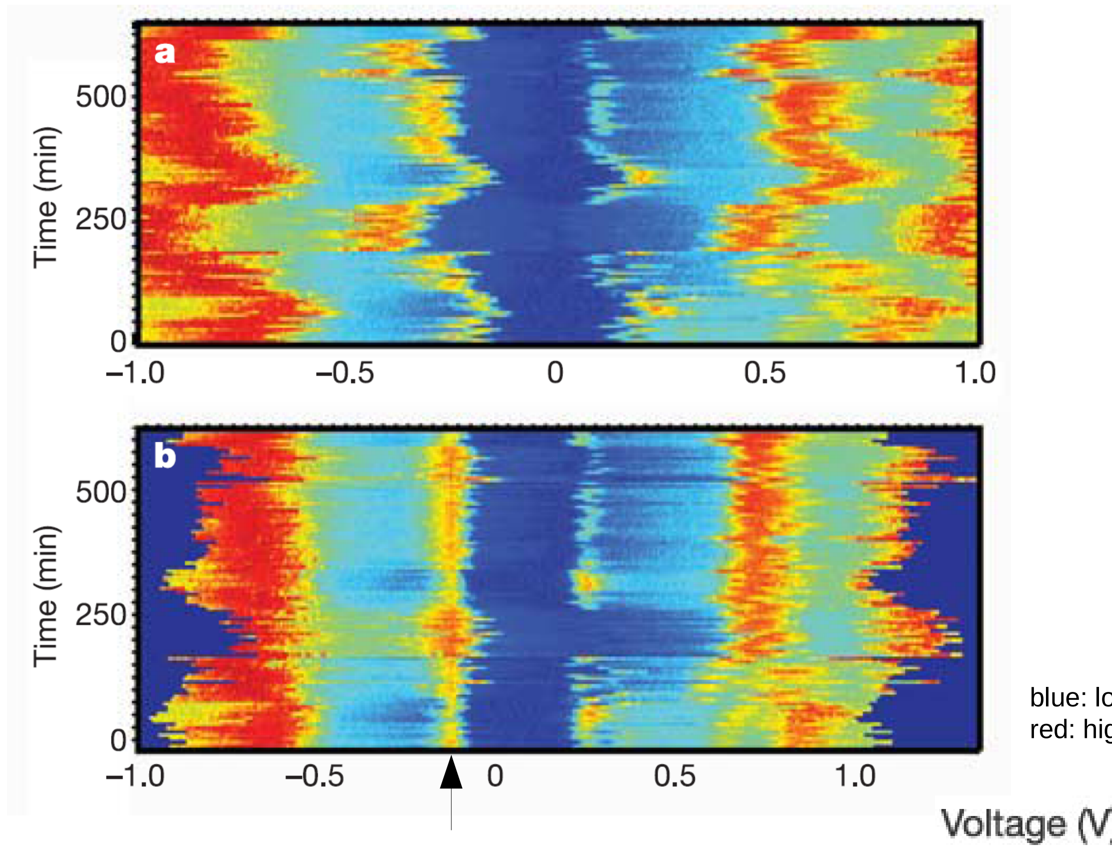
c.d: single colloids

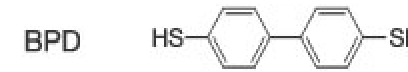
- **Coulomb blockade oscillations:**
  ~35meV dimer (a) and ~25 meV single colloid(c) **originate from single colloids**

- **Single colloid**: conductance up to 60 nS (at 1 V)

- **Dimer**: significantly lower conductance, pronounced secondary peak structure
  hundreds of meV apart, superimposed single colloid oscillations

Temporal fluctuations (BPD)



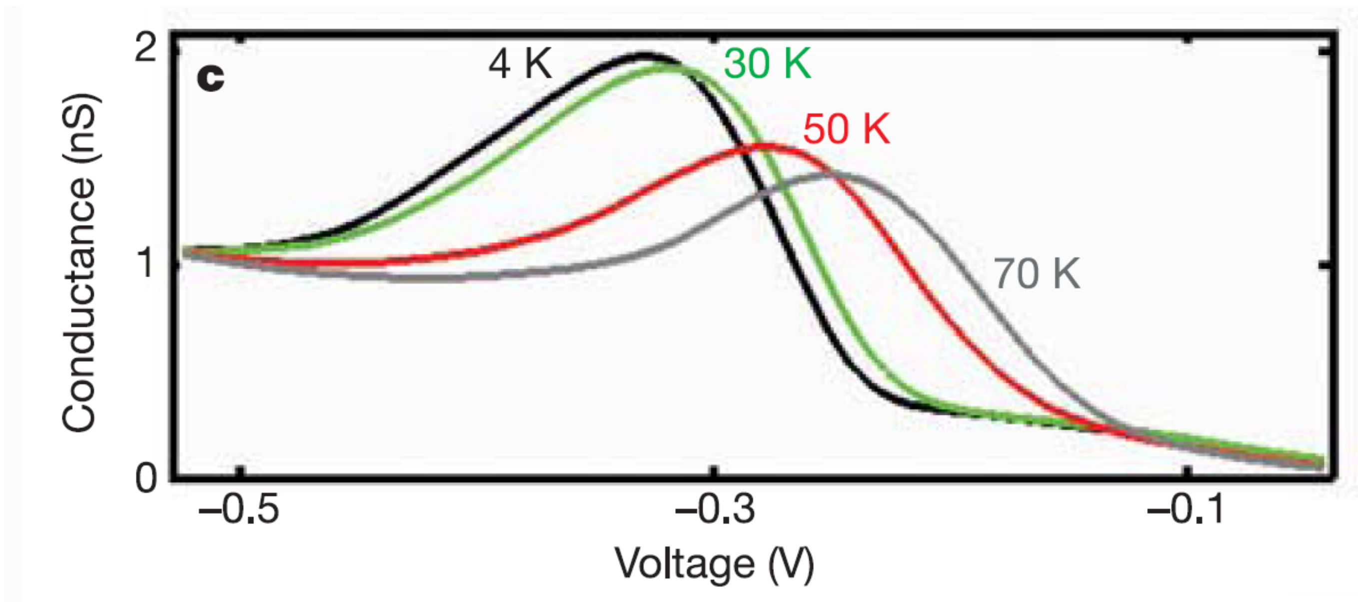


blue: low conductance(0 nS)
red: high conductance (3 nS)

Conductance measurements of **one** dimer as a function of time:

- Strong temporal fluctuations (hundreds of mV) in peak position (see a)
- Rigid shift (see b: one peak aligned)
- Typical of electrostatically gated Coulomb blockade systems with different input and output capacitances

Temperature dependence (BPD)

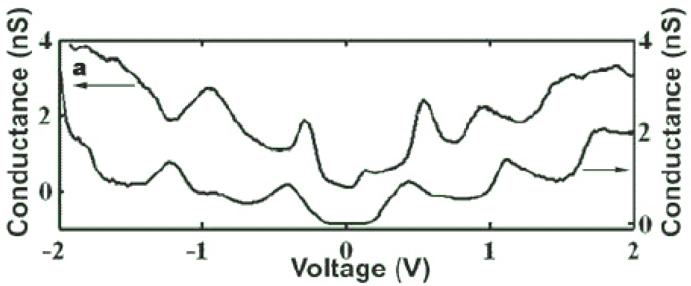


Conductance measurement of **one** dimer as a function of temperature:

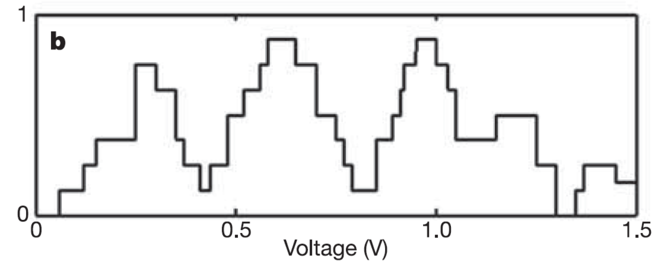
- Shift of peak due to gating
- Peak broadens, decreases height, area approximately constant
- Broadening: change in thermal distribution of electrons in the leads (~ $2k_BT$)

Sample fluctuations (BPD)

Conductance measurement for two independent samples of BPD:



Histogram of peak positions collected from 9 devices:



- Variations between samples: no rigid shift (see a)
- Differences in the values of conductance (up to factor 10)
- Histogram of peak positions (b):
  peak structure survives averaging over many samples: variability of peak positions smaller than peak spacing

averaged spectrum (b) agrees with results obtained from self assembled monolayers of BPD but not with theoretical calculations.

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Conclusion

- Present a method to contact and measure single molecules
- Investigate the vital role of conjugation on the conductance through molecules: localizing groups suppress the electrical conductance
- Temperature dependence of conductance
- Temporal and Sample fluctuations