

Molecular rectifiers and transistors based on π -conjugated materials

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Abstract

Concepts and experimental results related to molecular rectifiers and transistors are reviewed. ‘Devices’ based on donor- σ bridge-acceptor molecules, conjugated zwitterionic molecules, macrocyclic molecules, metal clusters, fullerenes and carbon nanotubes are discussed. Current-voltage characteristics showing rectifier properties are presented, as well as experiments in which the current-voltage characteristics are modulated by a gate voltage (transistor effect). © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the last two decades ‘molecular electronics’ has been the topic of many conferences, workshops and publications, and the quest for molecular rectifiers and molecular transistors has inspired many investigations in physics, chemistry and materials science. Often the mere possibility of ‘molecular rectification’ and ‘molecular switching’ has been questioned and, on the other hand, the demonstration of the sheer existence of such effects has led to unrealistic expectations for short-term applications. As a matter of fact, rectification and switching are not at all unusual. The relevant questions are whether devices based on molecular materials are better than existing devices or whether we can expect that they will become better one day.

Fig. 1 shows a diode and a transistor symbolically, where we simply define a diode as a two-terminal device and a transistor as a three-terminal device. The contacts are already named ‘source’, ‘drain’ and ‘gate’, in analogy to semiconductor technology. A typical experiment consists of filling the black box with a molecular material and measuring current-voltage characteristics between source and drain, as shown in Fig. 2, where benzene has been chosen as a fairly simple example of a π -conjugated molecule. If no precautions are taken, the characteristics are neither linear nor symmetric, and some sort of *rectification* is the rule rather than the excep-

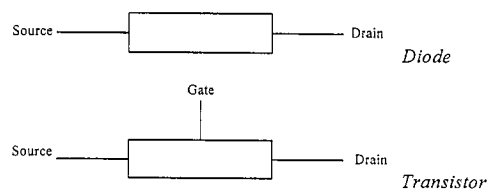


Fig. 1. Symbolic representation of diodes and transistors. With precautions, most two-terminal devices are rectifying to some extent and most three-terminal devices behave like (low quality) transistors.

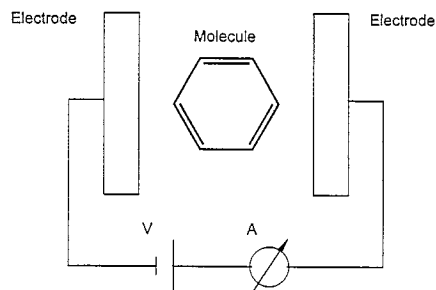


Fig. 2. Schematic set-up of an experiment in molecular electronics.

tion. Similarly, in most cases the current-voltage characteristics can be modulated by changing the potential at the gate and the device acts as a *transistor*. The actual problem is to assign the rectification and transistor effects in an unambiguous way to the molecular properties of the material in the box. Can the experimental results be reproduced? Can they be understood? Can they be controlled?

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2. Rectifiers — concepts

It has been known for a long time that many organic solids are semiconductors. Just think of phthalocyanines, the photoconductive properties of which are the basis for our copy machines and laser printers. A large impact on the field of molecular electronics emerged from organic charge transfer salts like TTF–TCNQ [1]. The compound TTF (tetrathiafulvalene) is an organic donor and TCNQ (tetracyanoquinodimethane) an acceptor. Crystals of TTF–TCNQ are composed of alternating stacks of TTF and TCNQ, and electrons are transferred from the donor to the acceptor moiety. Because of this charge transfer there are partially filled bands for both of the stacks and the material behaves as an organic metal. Fig. 3 presents a didactic route from TTF–TCNQ crystals to rectifying molecules: the mixed crystal with sequence DADADADA is metallic. If we could arrange all donors on one side and all acceptors on the other side, with sequence DDDAAA, we would have the analog to a semiconductor pn junction. Of course, for a rectifying device we do not need the bulk crystal, a bilayer DA will do, and if we link donor and acceptor by a covalent bridge we have a ‘rectifying molecule’. Along these lines a molecular rectifier was proposed by Aviram and Ratner in 1974 [2].

The basic idea of the Aviram–Ratner rectifier is that charge transport through the molecule will be by tunneling and that the molecular levels of the π -conjugated donor and acceptor moieties will participate in the tunneling process. Some of these molecular levels are energetically close to the Fermi level of the electrode metals between which the molecule is placed and by applying a bias voltage to the electrodes the Fermi level is brought into resonance with the molecular levels. Due to the asymmetry of the molecule, resonance is more easily obtained for one bias polarity than for the other. The level scheme of the Aviram–Ratner rectifier is illustrated in Fig. 4.

In Aviram and Ratner’s original proposal both the orbitals of the donor and the acceptor moiety are used for resonant tunneling. It turns out that rectification can be obtained with one π orbital alone, if the molecule is placed in an off-center position between the two electrodes. This situation is indicated in Fig. 5.

As for today, in the literature, experimental results on three types of rectifying molecules have been reported:

(i) D- σ -A molecules: these are molecules with a ‘sigma’ bridge between donor and acceptor, as in the Aviram–Ratner proposal. A σ bridge is a bridge with saturated bonds. Such molecules have two separated π systems: one at the donor, the other at the acceptor moiety (Fig. 6).

(ii) D- π -A molecules: here the bridge is also a π conjugated system (unsaturated bonds, regular alternation of single and double bonds) and the donor and acceptor π systems are strongly coupled. There is electron transfer from donor to acceptor, both moieties are ionized, the molecule is called ‘zwitterionic’ (Fig. 7).

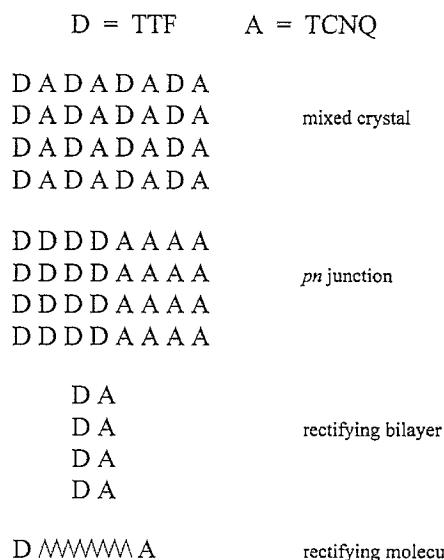


Fig. 3. Didactic route from bulk TTF–TCNQ crystal to rectifying molecule.

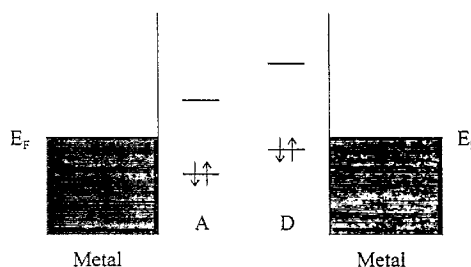


Fig. 4. Level scheme of Aviram–Ratner rectifier. Due to the asymmetry of the molecule the voltage for resonant tunneling depends on bias polarity.

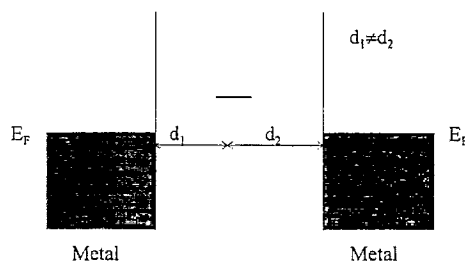


Fig. 5. Molecular rectifier with one single π -conjugated system only, but in an asymmetric position.

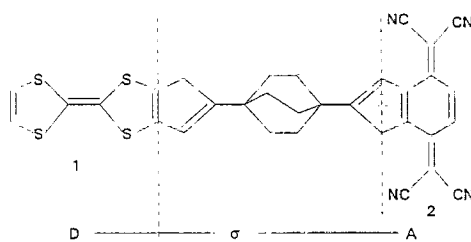


Fig. 6. Rectifying molecule of D- σ -A type, as proposed by Aviram and Ratner [2].

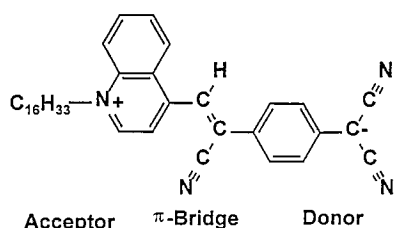


Fig. 7. Rectifying molecule of D- π -A type. Rectification of this 'zwitterionic' molecule has been demonstrated by Martin et al. [3].

(iii) Molecules with only one π system, which must be asymmetrically placed between the two external electrodes (Fig. 8).

The energy level scheme and the expected current–voltage characteristics for a diode consisting of one single π -conjugated molecule between external electrodes is shown in Fig. 9. At this point it is perhaps important to note that the 'molecular device' is never the molecule alone. It is always the system of molecule plus electrodes. In Fig. 9 the asymmetric current–voltage characteristic comes about from the fact that the bias voltage does not only shift the Fermi level of the

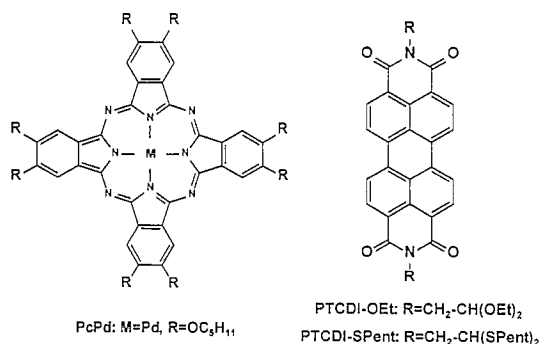


Fig. 8. Examples of molecules with only one π -conjugated system, which can be used in molecular rectifiers (phthalocyanine and perylene derivatives) [4].

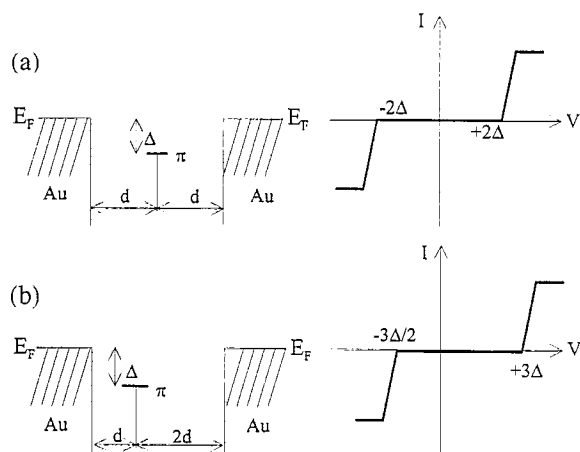


Fig. 9. 'Molecular rectifier' consisting of one π -conjugated molecule between metal electrodes. Level scheme and expected current–voltage characteristics. Δ is the energy difference from the π -orbital of the molecule to the Fermi level of the electrode. (a) Symmetric case with equal distance d to the electrodes. (b) Asymmetric case with distance d to one electrode, $2d$ to the other.

electrodes but also the potential at the position of the molecule. This shift is larger if the molecule is closer to the electrode [5]. Consequently, resonance occurs at a lower voltage if the electrons tunnel from the far-away electrode through the molecule.

Often the question is asked as to how much current can pass through a molecule without destroying it by Joule heating. Especially with respect to this question the *system aspect* is important: molecule *plus* electrodes. As long as tunneling is elastic (no internal modes in the molecule are taken into account) energy is dissipated at the electrodes, not in the molecule.

3. Rectifiers — experiments

In the schematic set-up of Fig. 2 a molecule is placed between two metal electrodes. In practice, very often one of the electrodes is a conducting substrate, the molecule (or many molecules) is incorporated in an ordered film (e.g. a Langmuir–Blodgett film), and the other electrode is either a vacuum-deposited thin metal layer or the tip of a STM (scanning tunneling microscope).

Fig. 10 shows an early rectifying experiment by Aviram and Joachim [6]. D- σ -A molecules are placed between a STM tip and a conducting substrate. The dashed line represents the oscilloscope trace of the bias voltage (-0.5 to $+0.5$ V) and the solid line the current response (several nanoamperes). As is clearly seen, the response is larger for negative bias. Admittedly there were problems with the reproducibility of the data, but the value of this early experiment is to demonstrate that molecular rectification is within the sensitivity of our instruments.

Figs. 11–14 show further current–voltage characteristics of molecular rectifiers published in the literature: Fig. 11 from Martin et al. [7], a film of zwitterionic molecules between flat contacts; Fig. 12 from Bykov [8], C-60 fullerene between STM tip and graphite; Fig. 13 from Stabel et al. [9], coronene between STM and graphite; and Fig. 14 from Metzger et al. [10], zwitterionic molecule between STM and graphite. It should be noted that: coronene in Fig. 13 is a molecule with only one π -conjugated system; the authors used an alkylated derivative of the molecule; and the symmetric trace (a) cor-

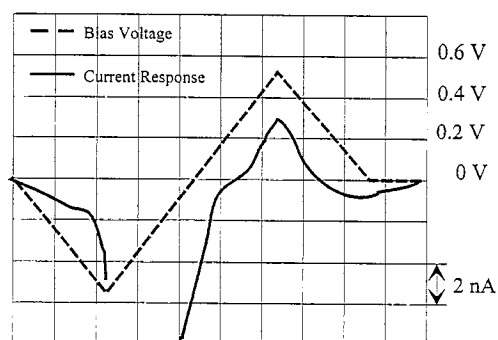


Fig. 10. Molecular rectification experiment by Aviram et al. [6].

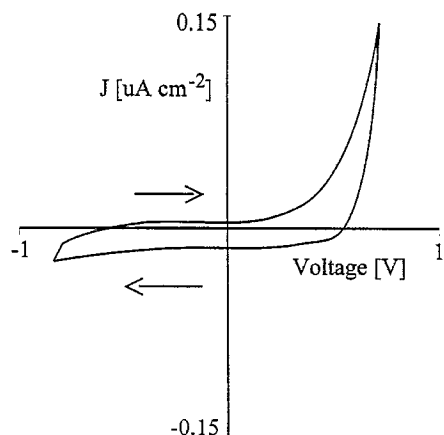


Fig. 11. Rectification by layers of zwitterionic molecules between flat electrodes (after Martin et al. [7]).

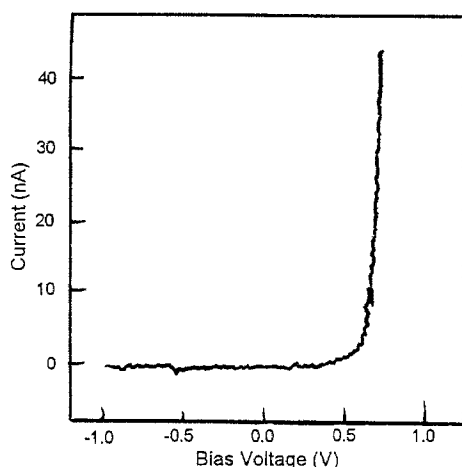


Fig. 12. Rectifying tunnel characteristics of C-60 fullerene between STM tip and graphite (after Bykov [8]).

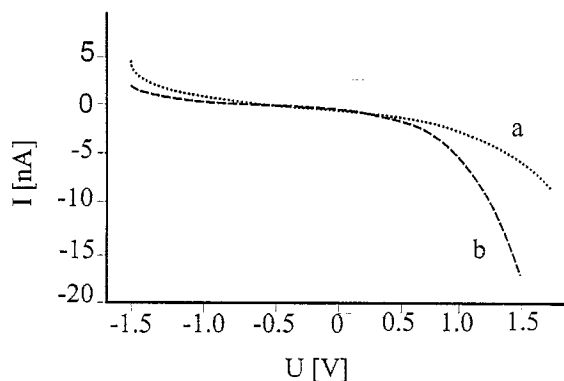


Fig. 13. Rectifying coronene between STM tip and graphite. Trace (a): 'blind experiment' with tip over inert alkyl chains. Trace (b): asymmetric characteristics if tip is over the π -conjugated part of the molecule (after Stabel et al. [9]).

responds to a blind experiment where the STM tip is over an alkyl chain, whereas for recording the rectifying trace (b) the tip was over the π -conjugated part.

Tunneling experiments through carbon nanotubes on graphite are similar. Fig. 15 compares tunnel characteristics

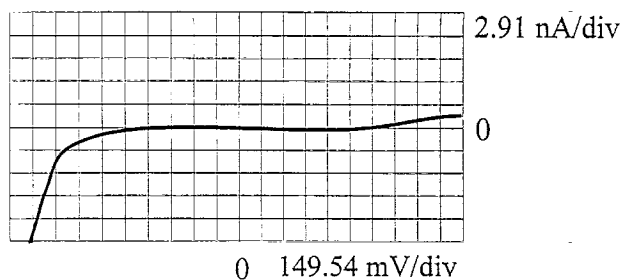


Fig. 14. Rectification with zwitterionic molecules between STM tip and graphite (after Metzger et al. [10]).

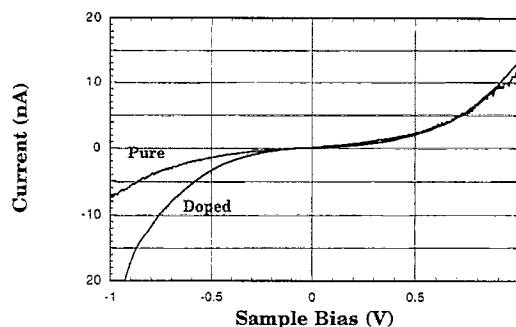


Fig. 15. Current-voltage characteristics in STM experiment on carbon nanotube on graphite substrate (after Carroll et al. [11]).

of pure and boron-doped nanotubes [11]. In this case not only the current-voltage characteristics were recorded but also attempts were made to extract the density of states from the derivatives of the curves. The density of states reveals a gap for the pure tube and a peak somewhat below the Fermi level for the boronated tube. (Perhaps it should be noted here that there is a conceptual difference between the analysis of the rectifying properties along the lines of Fig. 9 and density of states evaluation from tunnel spectroscopy: Fig. 9 assumes that the potential of the molecule 'floats', so that it shifts if the potential is changed at either of the electrodes. The density of states experiment assumes perfect electric coupling to the substrate and negligible influence of the STM tip.)

So far all experiments reported here have been carried out at room temperature. Fig. 16 shows a tunneling experiment at liquid helium temperature: Langmuir-Blodgett films of phthalocyanine and of perylene derivatives between gold electrodes [12]. At low temperatures much more structure is seen in the current-voltage curves. As discussed in Fig. 9, the pronounced thresholds at -0.5 and $+1.0$ V are interpreted as tunneling into the π -orbitals of phthalocyanine. These molecules are closer to one of the electrodes, the perylene layers act mainly as a spacer to keep the distance to the other electrode. The characteristics are very asymmetric and the device evidently is a rectifier. In addition to the thresholds, there are steps in the curve, and from the derivative in the inset of the figure we see that these steps are fairly well described as equidistant. Thus, they resemble Coulomb staircases known from single electron charging effects in inorganic quantum dots [13]. Coulomb staircases from single molecules are not possible, since degenerate states are needed

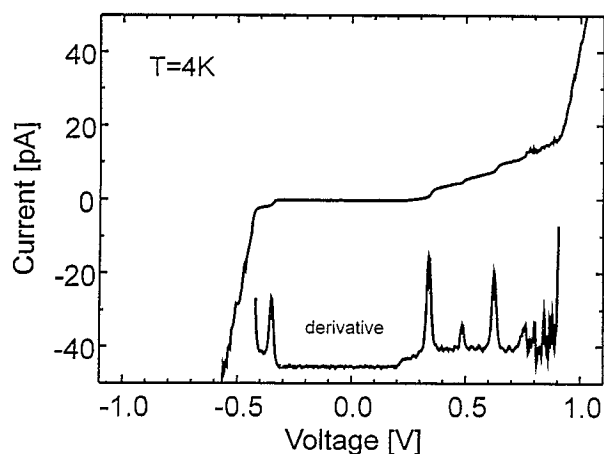


Fig. 16. Rectifying device consisting of phthalocyanine and perylene Langmuir–Blodgett films between flat gold electrodes (after Fischer et al. [12]).

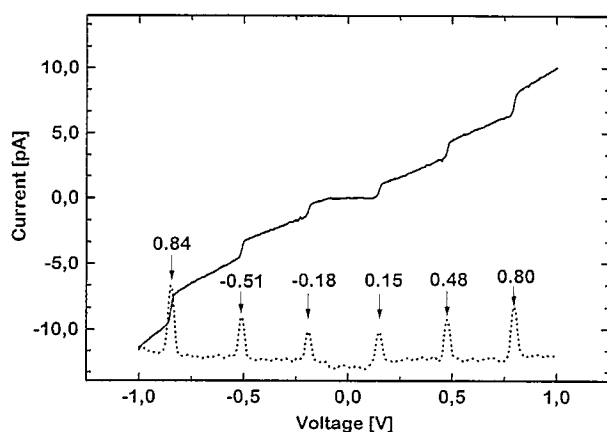


Fig. 17. Coulomb staircase in current–voltage characteristics of gold cluster incorporated in inert Langmuir–Blodgett film (after Philipp et al. [14]).

to accommodate more than one electron. We could think of charging a stack of molecules. Alternatively gold clusters might have migrated from the gold electrodes into the film and thus opened an additional tunneling channel.

A Coulomb staircase from gold clusters in Langmuir–Blodgett films is shown in Fig. 17 [14]. In this case the organic layer did not contain any π -orbitals. But thiol groups were introduced with the hope that the sulfur would covalently attach to the gold electrodes and stabilize the organic/inorganic interface. Apparently, the sulfur did attach to the gold but it did not stabilize the interface. Instead, gold clusters were drawn out and incorporated in the film. A special sample preparation technique allows us to visualize these clusters in a high resolution electron microscope — and the clusters lead to beautiful Coulomb staircases in the current–voltage characteristics!

4. Transistors

We have already mentioned that the current–voltage characteristics can be modulated by bringing a gate electrode close

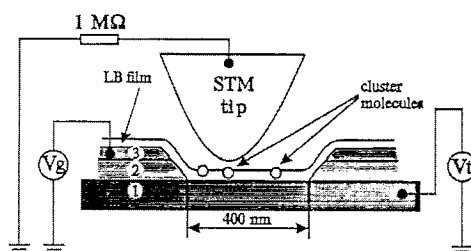


Fig. 18. 'Molecular transistor' based on the cluster molecule carborane. The STM tip acts as source, the graphite substrate (1) as drain, and the gold layer (3) as gate. Layer (2) is an insulating SiO₂ film (after Soldatov et al. [15]).

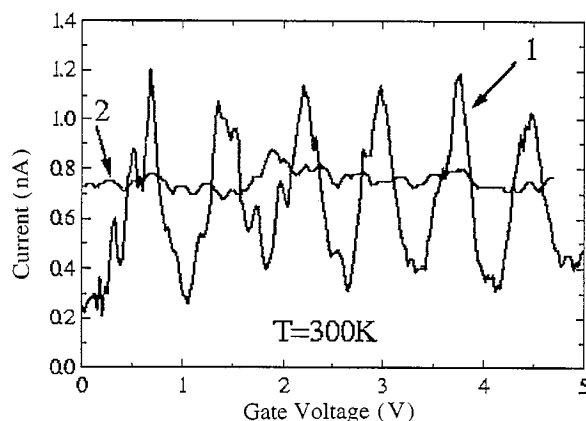


Fig. 19. Modulation of tunnel current through carborane molecule by change of gate voltage. Trace (1): strong modulation if tip is over a carborane molecule. Trace (2): background noise if tip is far from carborane molecule (after Soldatov et al. [15]).

to the 'active' molecule and changing the potential there. Fig. 18 shows such a set-up by Soldatov et al. [15]: carborane is incorporated as 'cluster molecules' into a Langmuir–Blodgett film. Electrons tunnel from the STM tip through the molecular orbitals of carborane into the graphite substrate. A gold layer near the tip acts as gate electrode. The oscillations in trace (1) of Fig. 19 demonstrate how the tunneling current is modulated by changing the gate potential. Trace (2) corresponds to a blind experiment when the STM tip is over an inert part of the film and when only noise is observed.

Another 'molecular transistor' has been investigated by Tans et al. [16]. Carbon nanotubes were deposited over a Si/SiO₂ substrate with a lithographic array of Pt electrodes on a sub-micrometer scale. One of the nanotubes came to lie over two platinum electrodes so that tunneling experiments Pt–nanotube–Pt could be carried out. Coulomb steps similar to those of Fig. 17 were observed, a very exciting observation by itself! But luckily there was even a third electrode nearby, which could be used as a gate. Fig. 20 shows the Coulomb steps in the current versus bias voltage characteristics. The traces (A), (B) and (C) correspond to different gate voltages.

5. Conclusions

Perhaps it is justified to compare the present state-of-the-art of molecular electronics with that of semiconductor tech-

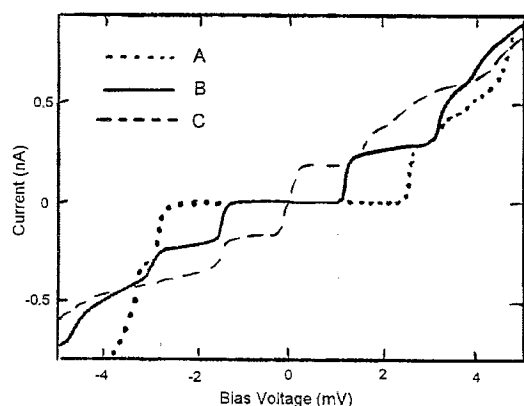


Fig. 20. Carbon nanotube as field-effect transistor. The current-voltage characteristics of a nanotube lying over two platinum electrodes (source and drain) show steps typical for a Coulomb staircase. Changing the potential at a third electrode nearby (gate) leads to large modifications of the characteristics. Traces (A), (B), and (C) correspond to different gate voltages (after Tans et al. [16]).

nology of the late 1930s: we understand the basic principles, but there is a long way to go until we can control the material properties with the same perfection as we can do for silicon. In addition, we have to consider the big lead in man-years which silicon has compared to any other material, so that a new technology will have a hard time to catch up. It would be helpful if there were technical applications at an intermediate level of material perfection. Fortunately, this is the case with organic light-emitting diodes [17], and we can hope that this field and molecular electronics will stimulate each other.

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