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Nanotechnology. Science or fiction?

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The paper can be treated as a short introduction to nanotechnology and nanoscience bearing in mind evolution of these terms over years. We will introduce basic ideas of nanotechnology like bottom-up versus top-down philosophy, assemblers and nanomachines. Finally, critics of nanotechnology from physical and chemical points of view will be presented leading to hardcore and pragmatic definitions of nanotechnology and nanoscience. The second part of the paper stands on the pragmatic definition of nanotechnology. The basic obstacles to a further miniaturization of conventional semiconductor devices and application of 0D, 1D and 2D semiconductor quantum devices in electronics will be addressed. Basic principles of operation of molecular electronic devices based on self-assembled molecules will be addressed. The author's scanning tunnelling microscopy and spectroscopy results on self-assembled molecules and derivative adducts to C_{60} molecules will be presented and discussed.

Key words: *nanotechnology, nanoscience, molecular electronics*

1. Brief introduction to nanotechnology

The term "nanotechnology" was for the first time used in 1974 by Prof. Norio Taniguchi in his paper: *On the Basic Concept of Nanotechnology* [1]. Nanotechnology was defined as follows: "Nanotechnology mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or one molecule" [1].

However, it is commonly recognized that the origins of nanotechnology date from 1959 when at an American Physical Society meeting Prof. Richard Feynman gave his special lecture entitled: *There is plenty of room at the bottom* [2]. In this lecture, he noted that the fundamental principles of physics do not speak against possibility of building things "from the bottom up" using atoms as the building blocks. This revolutionary idea (bottom-up) was treated by majority of physicists as a "next Feynman's joke" and it has been forgotten until eighties last century when Dr. Eric Drexler wrote his book *Engines of Creation – The Coming Era of Nanotechnology* [3]. In this, and

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especially in his next book [4] he described his own understanding of nanotechnology that is the way of building small and large structures atom by atom or molecule by molecule using nanorobots (nanobot's), particularly assemblers and replicators.

The Drexler's way building of things was (and still is) in contradiction to the traditional building paradigm in which we take away material until what is left is the product. In the new bottom-up philosophy (Feynman, Taniguchi, Drexler – FTD) we add atoms or molecules until the product is created. This philosophy seems very simple and obvious, however it could not appear before quantum mechanics had been developed and understood. It is worth to note that the bottom-up philosophy has been discovered by Nature millions and millions years ago, and is commonly utilized in biological systems.

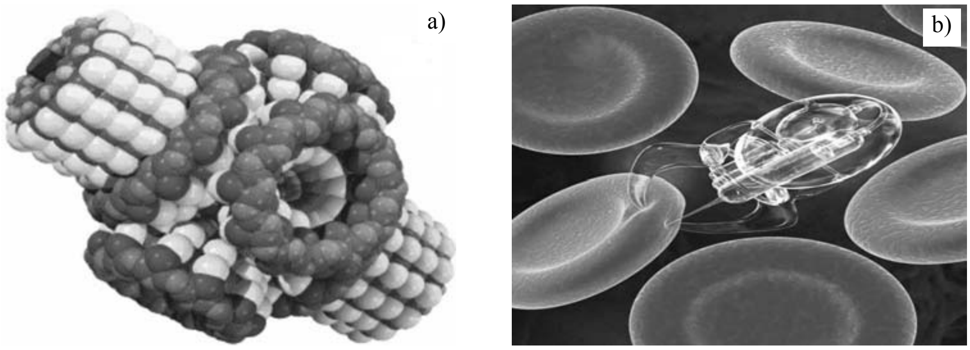

Fig. 1. Visions for the future: a) molecular gear [5], b) microscopic machine travelling through the bloodstream, injecting or taking samples for tests [6]

The essential part of the Drexler idea was to build molecular counterparts of a classical devices like gears, pumps, pipes, gear-wheels, bearings, clamps and so on (see Fig.1a, for example [5]). Using these molecular components creation of nanomachines like: nano-spy, nano-doctor (see Fig. 1b [6]) or, for instance, mechanical nanocomputers would be possible. What is more, these nanometer scale technologies can probably enable mechanical, electronic, chemical and quantum mechanical integration between silicon and carbon systems leading to creation of cybernetics organisms (Cyborgs) [7]. It is commonly believed that the appearance of the nanotechnology/nanotechnologies ideas can directly lead to the next revolution in our human life, just after information technology (IT) and biotechnology (Biotech) revolutions [8]:

1800–1900: First industrial revolution (automation age);
1900–1950: Quantum revolution (atomic age);
1950–2000: IT revolution (electronic age);
2000–2050: Biotech revolution (genomic age);
2050–2100: Second industrial revolution (nano age).

Since the beginning, Drexler's idea has attracted much criticism coming mainly from physicist and chemist communities [9]. It has been argued that Drexler's molecular counterparts of classical devices are unstable form the chemical point of view or should be even explosive. Furthermore, organic and quantum chemists claimed that chemical synthesis of such huge and big molecules is not possible at all. Physicists pointed out the problems with communication and energy supply to nanomachines. The problems with molecular fluctuations and scalability were also considered. Of particular importance is the latter problem because physical properties of condensed matter dramatically change below 100 nm. It was also proved that the tip of scanning tunnelling microscope (STM) could not be easily used as a manufacturing device due to extremely small speed and low reliability [7]. In particular, it is difficult to imagine that STM can be applied to build three-dimensional structures from isolated atoms [7, 10].

These obstacles and problems related to nanotechnology led to much more pragmatic definition of nanotechnology which can be acceptable for physicists and chemists:

The hardcore definition: Atom or molecular scale assembling or self-organization.

The Pragmatic definition: Novel effects due to controlled structuring in the size range from 1 nm to few 100 nm.

The appearance of the pragmatic definition of nanotechnology stimulated lots of theoretical and experimental studies related to phenomena and processes, which take place in nanoscale. A new scientific discipline called nanoscience has been established. However it should be remembered that the all current technologies containing magic term ‘nano’ are little related to ambitious nanotechnology program/philosophy predicted by FTD. What is more, the term “nano” opens lots of “doors” and is commonly abused by scientists who are not interesting in ambitious nanotechnology goals – it seems that they are interested in funding only [7].

In conclusion, it seems that nanotechnology considered in terms of their hardcore definition should be still treated as a fiction rather than science. However, it is worth to remember that the fundamental principles of physics do not speak against the bottom-up philosophy as Feynman said about 45 years ago.

2. The pragmatic definition of nanotechnology. The case of molecular electronic devices

2.1. Introduction

As we noted, the pragmatic definition of nanotechnology stimulated lots of theoretical and experimental studies related to phenomena and processes which take place in nanoscale. These studies were mainly focused on designing and building new molecule-based electronic devices called molecular electronic devices (MEDs), applications of carbon nanotubes (CNs) and nanowires in electronics, stamping techniques for micro- and nanofabrication, microfluids and nanoelectromechanical systems [11].

Particularly, studies in MED/CN areas were stimulated by the fact that in IT we still need smaller transistors, because smaller transistors switch faster and allow a greater number of processors to be built within the same space. However, there were some obstacles to further miniaturization of the conventional metal-oxide-semiconductor-field-effect-transistors (MOSFETs) like: appearance of high electric fields, problems with heat dissipation, shrinkage of the oxide layers caused by heat and electric fields, and vanishing of bulk properties ([12] and references therein). In order to overcome these problems, physicists focused on low-dimensional systems of electrons namely: two-dimensional systems of electrons (2D) called quantum wells (QWs), one-dimensional systems of electrons (1D) called quantum wires (QWRs) and zero-dimensional systems of electrons (0D) called quantum dots (QDs) [12–15]. Particularly, in the case of 0D system, the electron density of state function (DOS) consists of several peaks and this system can be directly used to build a quantum dot transistor (QDT) as presented in Fig. 2.

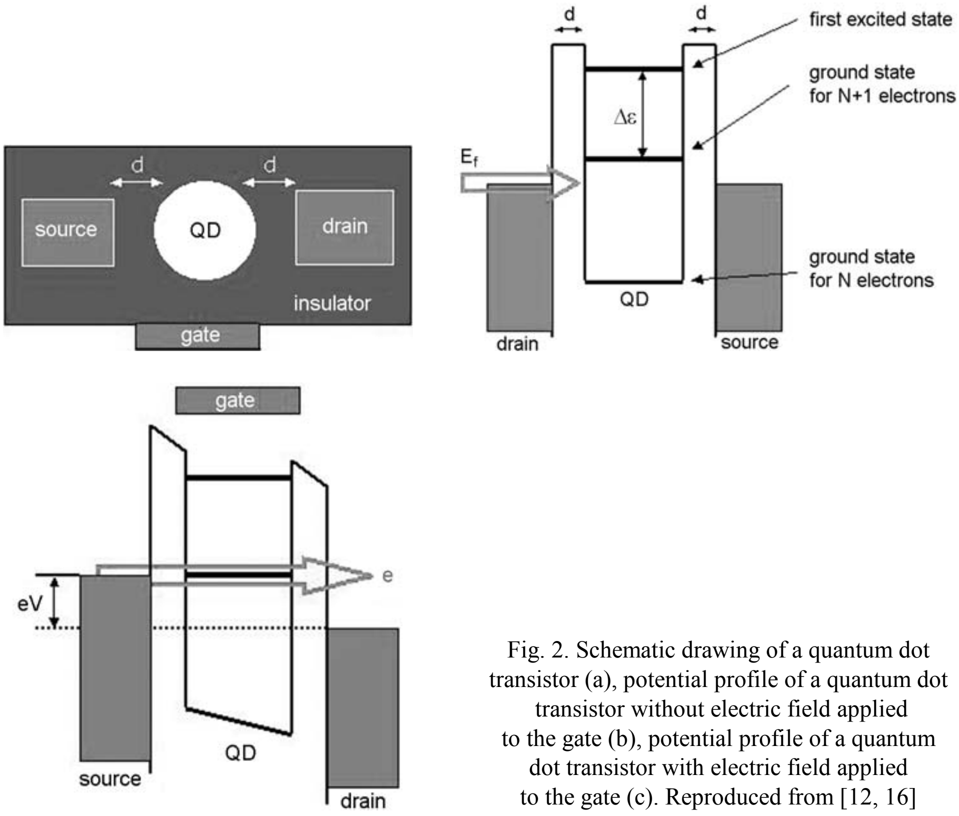

Fig. 2. Schematic drawing of a quantum dot transistor (a), potential profile of a quantum dot transistor without electric field applied to the gate (b), potential profile of a quantum dot transistor with electric field applied to the gate (c). Reproduced from [12, 16]

The central part of the QDT is QD containing discrete energy levels, and two electrodes called source (S) and drain (D). The principle of operation of the QDT is based on the fact that flow of electrons from the source to the quantum dot and after that from the quantum dot to the drain is completely controlled by the bias voltage applied to the gate – the resonant tunnelling. However, there were also some obstacles to manufacture quantum devices based on low-dimensional systems of electrons, namely: cryogenic operation, extreme sensitivity of the tunnelling current to width of the potential barriers, and extreme difficulty of making islands and tunnelling barriers precisely and uniformly [12].

As a result at the beginning of nineties of the last century, the attention has been turned towards marriage of electronics with chemistry – a new paradigm called molecular electronic devices (MEDs) has been established [11, 12]. This new paradigm was based on the fact that there exist a variety of molecules conducting electric current via resonant tunnelling process or the Coulomb blockade effect occurring in structures with small molecular feature sizes. Briefly, the goal of molecular electronics is to find individual molecules (or carbon nanotubes) to perform functions in electronic circuits commonly performed by semiconductor devices [11].

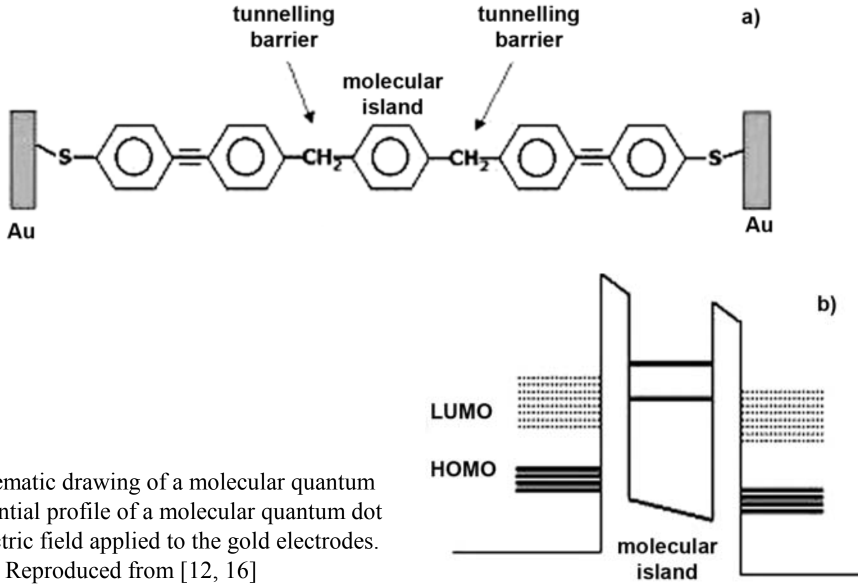

Fig. 3. Schematic drawing of a molecular quantum dot (a), potential profile of a molecular quantum dot without electric field applied to the gold electrodes. Reproduced from [12, 16]

The simplest possible molecular QD is presented in Fig. 3a ([12] and references therein). In this system two –CH_2– groups play a role of tunnelling barriers, while the isolated phenyl group is treated as a molecular quantum dot with discrete energy levels (molecular island). The whole molecular QD structure is connected to the gold electrodes by polyphenylene chains and sulphur atoms. The presented potential profile (Fig. 3b) of molecular QD system shows that we could expect appearance of resonant tunnelling process when we apply bias voltage between gold electrodes. As a result, it is possible to build a molecular resonant tunnelling diode and then molecular resonant tunnelling transistor ([12] and references therein).

There are two types of molecules that have been proposed as the potential basis for molecular electronic devices: polyphenylene based chains and carbon nanotubes [11, 12, 16]. However, the question was open whether a molecule taken individually had appreciable conductance, and whether a molecule taken individually could act as an electrical switch. Most of the experiments related to measurements of electrical conductance of a molecules and carbon nanotubes have been done using scanning tunnelling microscopy and spectroscopy (STM/STS) techniques [13, 16, 17]. This is because STM/STS configuration can be treated as a natural double barrier system with a molecule located between the surface and the tunnelling tip.

The next part of this paper is devoted to presentation of some results related to studies of electrical conductance of a molecules using STM/STS techniques.

2.2. Resonant tunnelling effects on molecules

Recently, we studied processes leading to formation of one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) molecular crystals on surfaces by STM technique [18,19]. Furthermore, we were interested in a detailed understanding of the tunnelling spectra recorded by STS, which can be used to determine whether the resonant tunnelling effect via molecular energy levels takes place. In this case, the adsorbed molecule is treated as a quantum well with electronic states between tunnelling barriers. The first barrier is formed between the tunnelling tip and molecule, the second one is formed between a molecule and surface. The surface modulates the molecule states into resonances, which spread throughout the molecule gap. When the voltage bias is sufficient to adjust the quantum state inside the well to be within the range of energies for the tip conduction band, the well is in resonance and the current can flow onto the molecule and out to the substrate. Otherwise, the current is blocked indicating that the system is out of resonance. As a result, current–voltage characteristic with nearly flat regions (NFR) or negative differential resistance regions (NDR) can be observed. The operation effectiveness of molecular devices strongly depends on the peak to valley ratio on tunnelling current characteristic. To enhance this ratio, low temperature or eventually very small quantum well (molecule) are required.

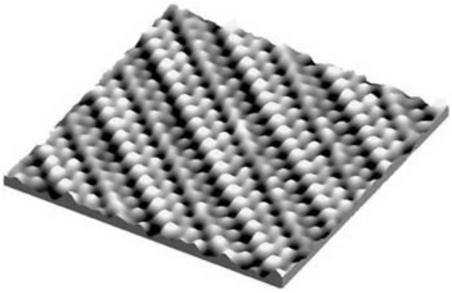

Fig. 4. The STM images of the 8OCB liquid crystal molecules deposited on graphite. Field of view: 23 nm×23 nm

In Figure 4, we present self-assembled monolayer (SAM) of *n*-octylyoxy -4-cyanobiphenyl (8OCB liquid crystal) molecules deposited on the (0001) basal plane of highly oriented pyrolitic graphite (HOPG).

The tunnelling *I–V* curve recorded over pure graphite is presented in Fig. 5a and is typical of this material [18–20]. The *I–V* curve recorded over 8OCB SAM structure retains an asymmetric shape typical of pure graphite, however additional effects are also visible, including nearly flat regions of the tunnelling current (Fig. 5b) and negative differential resistance on the *I–V* characteristics (Fig. 6).

In our interpretation, at low bias voltages electrons are transported via non-resonant tunnelling through the tails of the molecular levels (mainly HOMO and LUMO) which are Lorentzian enlarged by the molecule-surface interactions. These tails give rise to the LDOS near the Fermi level and lead to non-zero tunnelling current for bias voltages within the HOMO-LUMO energy gap. More precisely, the non-resonant tunnelling regime results in linear *I–V* characteristic at low voltages.

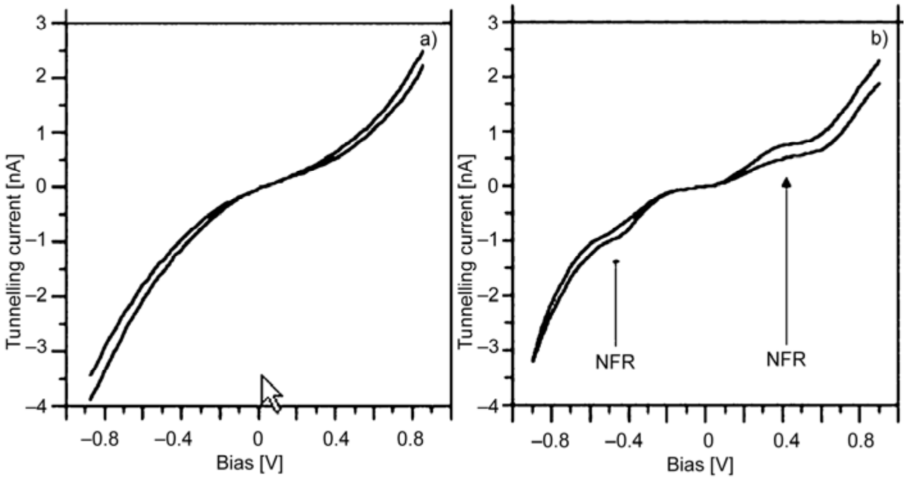

Fig. 5. Typical current–voltage curve recorded over the pure graphite (a), current–voltage curves recorded over the 8OCB SAM structure (b). Reproduced from [18, 19]

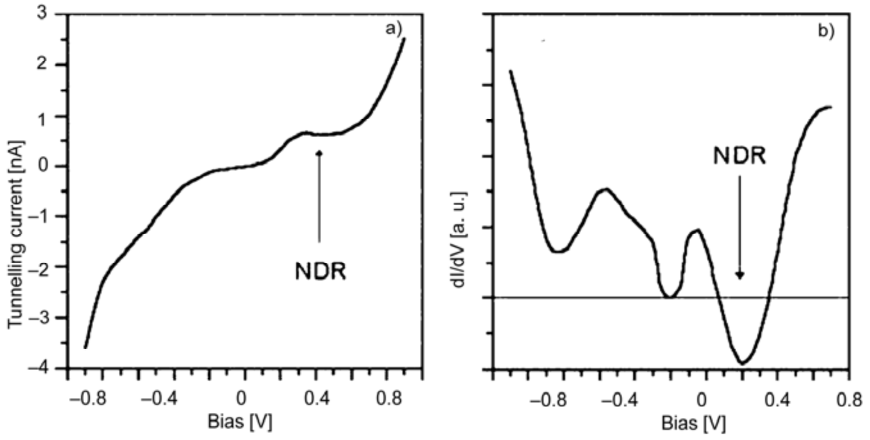

Fig. 6. Current–voltage curves where a distinct negative differential resistance occurs (a), and the normalized first derivative of the *I–V* curve presented in Fig. 6a (b). The NDR dip intersecting the zero level of the normalized conductance. The NDR is marked by an arrow. Reproduced from [18, 19]

This is presented in Figs. 5b and 6a, especially for the occupied electronic states. However, when the voltage bias is sufficient to adjust the discrete energy levels inside the well (8OCB molecule) to be within the range of energies for the tip conduction band, as explained before, the well is in resonance and the current can flow onto the molecule and out to the substrate. Otherwise, the current is blocked, i.e. the system is out of resonance. As a result, *I–V* characteristic with NFR or NDR regions can be observed (Figs. 5b and 6a). On the *dI*/*dV* and (*dI*/*dV*)/(*I–V*) curves the resonant states appear as a pronounced peak. When the system is out of resonance the pronounced dips on the *dI*/*dV* and (*dI*/*dV*)/(*I–V*) characteristics are observed (Fig. 6b).

The *I–V* curves presented in Figs. 5b and 6 clearly show that we deal with resonant tunnelling which takes place on molecules.

2.3. Charging effects on molecules

One of the fundamental problems was the question whether a molecule can be treated as a Coulomb blockade structure or not. In order to answer this question, the STM configuration was used. In the STM configuration, the tunnelling tip is placed above a molecule deposited on an insulating layer. The latter is grown on a conductive material. The vacuum gap between a tip and a molecule and an insulating layer form a well-defined double junction system. Furthermore, a configuration without any insulating layer is also considered as a Coulomb blockade structure. In this system, one barrier is formed between an STM tip and a molecule and the other one is a space interval at a molecule/substrate interface. A double junction system can be described by the orthodox theory which considers the electron transport as a sequence of instantaneous tunnelling events and results in the suppression of the tunnelling current near zero bias voltage – the Coulomb gap ([21, 22] and references therein). The gap has the voltage width $\Delta E = e/2C_\Sigma$, where $C_\Sigma = C_1 + C_2$ is the total capacitance of the junction, C_1 is the capacitance of the tip/ molecule junction and C_2 is the capacitance of the molecule/substrate interface. In addition to the Coulomb gap, a strongly asymmetric junction system ($R_1 >> R_2$, $C_1 >> C_2$, $R_\Sigma \approx R_1$, $C_\Sigma \approx C_1$, where $R_\Sigma = R_1 + R_2$ denotes the total junction resistance, R_1 is the resistance of the tip/molecule junction and R_2 is the resistance of the molecule/substrate interface) exhibits a series of steps on the current–voltage characteristic – the Coulomb staircase. The steps have the voltage width $\Delta V = e/C_\Sigma$ and the current rise $\Delta I = e/R_\Sigma C_\Sigma$. The only exception is the first current step, where $\Delta I = e/2R_\Sigma C_\Sigma$. The steps are observed for the temperatures $kT < e^2/2C_\Sigma$.

In our experiments, we investigated the sodium dioctyldithiophosphate (NaDDP) molecules deposited from solution on the (0001) graphite substrate as presented in Fig. 7 [21, 22]. However, it is difficult to suggest a model which arranges molecules on the graphite substrate since the obtained topographical results are strongly affected by the electronic states of the molecule/graphite system.

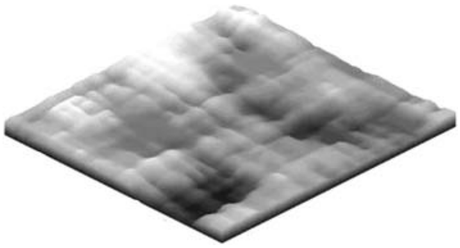

Fig. 7. The 28.8 nm×28.8 nm STM image of the NaDDP molecules deposited onto graphite substrate. Reproduced from [21, 22]

In Figure 8a the *I–V* curves recorded at the same tunnelling conditions over various points on the topography presented in Fig. 7 are shown. In Figure 8b, the theoretical *I–V* curve calculated using the orthodox SET model with the fitting parameters $C_1 = 1.6\times10^{-19}$ F, $C_2 = 5\times10^{-20}$ F, $R_1 = 1.6\times10^{9}\,\Omega$, $R_2 = 1\times10^{5}\,\Omega$, $T = 300$ K is shown [22]. We found that a reasonable fit can be made at low bias voltages but at higher bias the tunnelling current is larger than the orthodox theory predicts. This is caused by non-linear conductance of the tunnel junction, i.e. suppression of the tunnel barrier at high bias voltages.

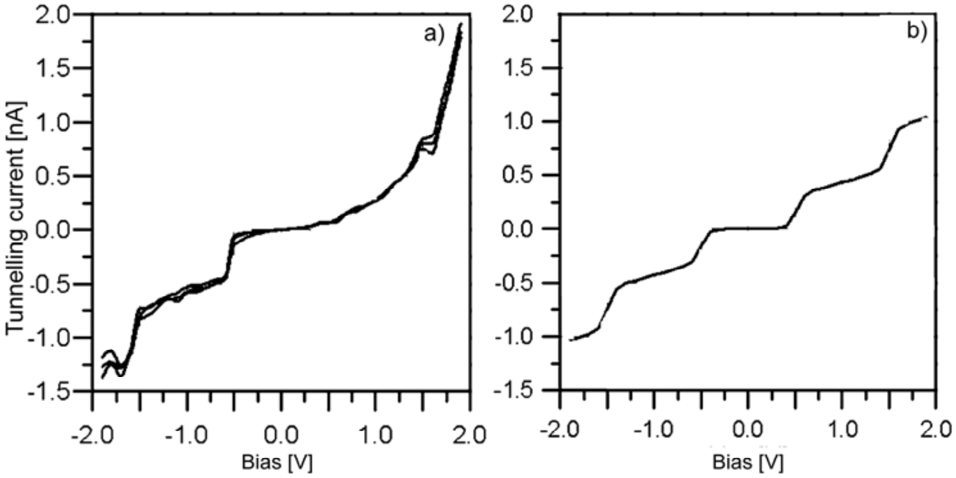

Fig. 8. The *I–V* curves recorded at three different points over NaDDP molecules presented in Fig. 7 (a) and the theoretical *I–V* curve calculated using the orthodox SET model. Reproduced from [21, 22]

Another discrepancy to be observed easily is the asymmetry of current flow for negative and positive voltage bias. The gap and the steps are pronounced at the negative part of the spectra, i.e. for occupied states. The presence of the asymmetry of tunnelling current can be explained considering the effects of the discreteness of the energy spectrum in a molecule. The *I–V* curves presented in Fig. 8a clearly shows that we deal with the Coulomb blockade which takes place on molecules.

2.4. Changes of conformation of a molecule caused by the tunnelling tip

Nano-fabrications of materials realized by scanning tunnelling microscopy tip seems to bee very important in creation of electronic devices in a nanometre scale. Particularly, external electric field generated by the tunnelling tip can be used to change molecule conformation, i.e., it is possible to rotate an active part of the molecule (Fig. 9a) [23, 24]. The STM experiments presented here were performed on the C_{60}ONCFn complexes consisting of the ferrocene (Fn, $C_5H_5FeC_5H_5$) bound to C_{60} at the 6–6 bond by a heterocyclic ring [23, 24]. The cyclopentadienyl ring (cp, C_5H_5) and heterocyclic ring may be either parallel or perpendicular to each other.

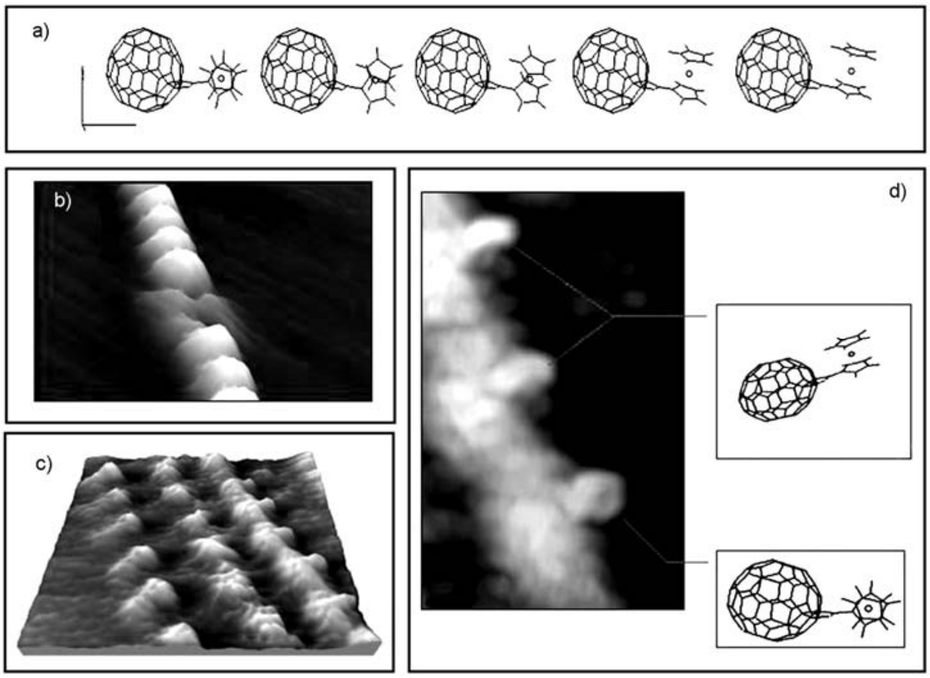

Fig. 9. The snapshot of the C_{60}ONCFn molecule during rotation caused by electric field generated by the tunnelling tip (a), the example showing that the tunnelling tip can be used to change position of the C_{60} molecule in the C_{60} molecular chain (b), 23 nm×23 nm STM image showing well separated four chains built of the C_{60}ONCFn complexes (c), STM topography showing changes of conformations of the C_{60}ONCFn molecules caused by electric field of the tunnelling tip (d)

In our experiments, it was possible to show that the C_{60}ONCFn complexes form a well ordered, self-assembled monolayer (SAM) on the HOPG(0001) surface as presented in Fig. 9c. Because this molecular matrix was formed spontaneously on the graphite substrate we did not need to use the STM tip in order to form such a structure though the STM tip can be easily used as a nanofabrication device (Fig. 9b). Furthermore, we believe that it was possible to change conformation of molecules caused by the electric field of the tip as shown in Fig. 9d.

3. Conclusions

A brief introduction to nanotechnology/nanoscience and molecular electronic devices is presented. Our STM/STS experiments performed on molecules showed both occurrence of the resonant tunnelling and the Coulomb blockade effects. The results presented lead to the conclusion that the external electrode can control flow of the electric current across the molecule. The observed phenomena can be directly applied in construction of molecular transistors.

Studies performed on fullerene adducts were intended to find molecules whose structure may be changed by external electric field leading to storing information in molecular structure. These experiments can lead to future design and construction of molecular memory.

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