

# Nano-scale protonic rectifier

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## Abstract

The work describes a new approach to the molecular electronics: nano-scale protonic rectifier. The concept and experimental results are presented and discussed. We have developed a method to fabricate nano-scale protonic devices. Self-assembled monomolecular layer of 3-mercaptopropionic acid (MPA) has been spread onto a gold covered glass plate, then the second layer was formed with 3-aminopropyltriethoxysilane (APTES) and stabilised by condensation triethoxysilil ends. The structure and electrical properties of the complex layer were examined with scanning tunnelling microscope (STM). We found a strong asymmetry of the  $I-V$  characteristic owing to rectifying behaviour of the layer. This is the first protonic rectifier of a nanometer thickness. © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Molecular nanometer-scale devices have for decades been in the centre of interest for many physicists and chemists [1–8]. Recently, single electron tunnelling effects and quantum size effects in isolated nanoparticles (“quantum dots”, QD) attract considerable attention, e.g., isolated  $C_{60}$  molecules have been used as ideal QDs [6]. Also molecular rectifiers and transistors are still in the centre of interest [9]. In 1984 we have reported intramolecular rectifying properties of a polarised N–O bond which is in fact one of the first subnanometer rectifiers. However, this is a totally intramolecular process observed only due to NMR experiments [3]. Our new and more practical approach to this problem combines molecular self-assembly and a rectifying behaviour based on the proton transport [10,11]. Self-assembly processes and supramolecular structures are the most promising for today’s materials science leading to nano-structured materials and nano-technology. A very interesting finding of great potential impact in this field has recently been published by Stupp et al. [12].

Protons are well known to be highly mobile in coupled hydrogen bonding systems, e.g., water. Water behaves as an intrinsic protonic semiconductor which can be doped to form protonic analogues of p-type and n-type semiconduct-

ing materials. Previously, a macroscopic rectifier diode based on protonic p–n junction has been constructed in our laboratory [10,11]. Now, we have developed a method to fabricate nano-scale protonic devices. Self-assembled monomolecular layer of 3-mercaptopropionic acid (MPA) has been spread onto a gold covered glass plate. Then, the second layer was formed with 3-aminopropyltriethoxysilane (APTES) owing to reaction between amino and carboxylic groups and stabilised by condensation triethoxysilil ends (Fig. 1).

## 2. Experimental

The gold film freshly evaporated onto a glass substrate 3 mm × 3 mm cleaned carefully before use, or after annealing, was covered with MPA as a monomolecular layer formed during 15 h in a self-assembly process. MPA solution in ethanol (0.2 cm<sup>3</sup> MPA and 6 cm<sup>3</sup> of ethanol) was used at room temperature. The layer was washed with ethanol and dried in an inert atmosphere (argon). Then, MPA layer has been derivatised with APTES solution (0.2 cm<sup>3</sup> APTES and 10 cm<sup>3</sup> of ethanol, in 30–45 min at room temperature) giving a complex molecular system with a hydrophilic layer inside (MPA-APS). The resulting layer was washed, dried and left in a clean box for at least 12 h to stabilise it due to condensation of triethoxysilil groups.

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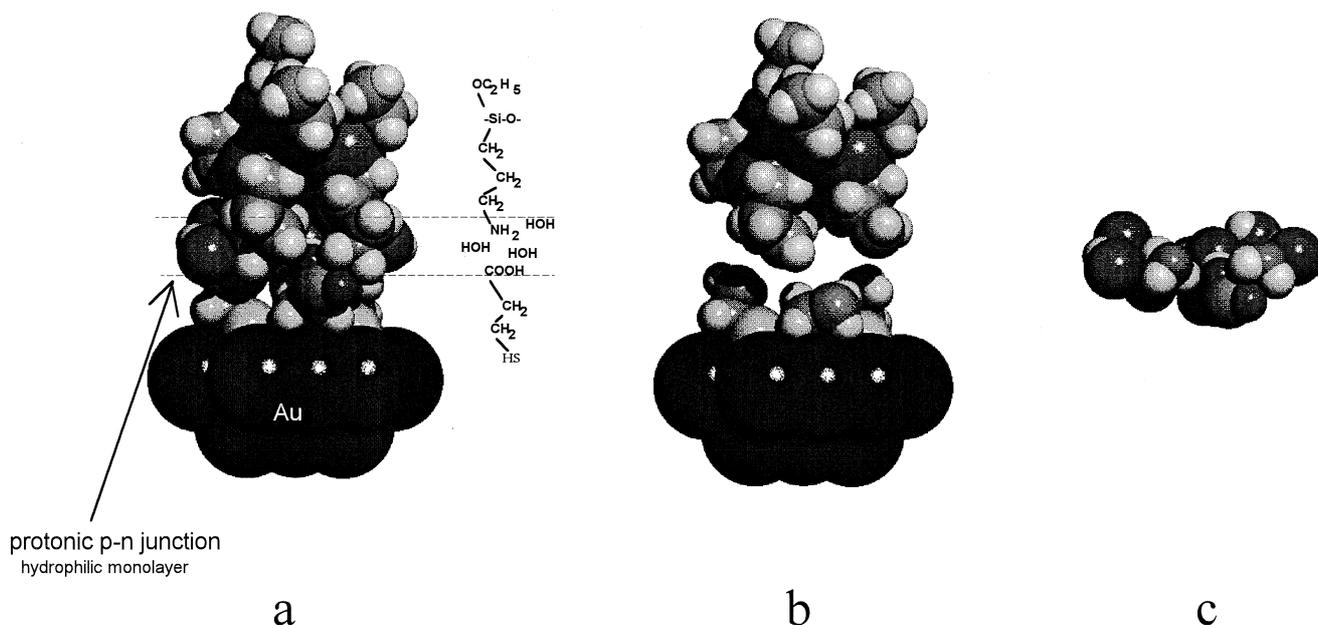


Fig. 1. The structure of the molecular complex layer MPA-APS (a computer model) with a protonic p-n junction formed in the internal hydrophilic layer: the whole structure of optimised geometry (a), the same model after extraction of a hydrophilic layer (b) and the hydrophilic layer (c).

The self-assembly process has been monitored with the aid of a scanning tunnelling microscope [13] and on a more traditional way by measurements of contact angles (a classical method was applied, but the modern experimental set-up with testing laser beam has also been used due to courtesy of The Institute of Molecular Physics of the Polish Academy of Sciences in Poznań). The contact angle for water at pH 7 is  $32^\circ$  for Au substrate and  $39^\circ$  for acid-functionalised MPA self-assembled layer. After treatment the MPA layer with ammonium hydroxide the contact angle takes a value of  $14^\circ$  (water, pH 7) which is unstable and slowly increases with time. The contact angle for a glass substrate modified with APTES only is  $43^\circ$  at pH 7 and about  $20^\circ$  at pH 1 (HCl) due to protonation of  $\text{NH}_2$  groups. The value observed for the unmodified glass substrate is about  $30^\circ$ , and the contact angle for a fully hydrophobic glass substrate modified with *n*-octyltriethoxysilane reaches a value of  $99^\circ$ . In the case of the complex layer MPA-APS the contact angle lays in the range  $25^\circ$ – $57^\circ$  with a random distribution from sample to sample.

Transmission electron microscope (TEM) JEOL JEM 1200 EX II was operated at the voltage of 80 kV. A small piece of gold film was removed from glass substrate and placed on a microscope grid. The monomolecular layer was observed at the edge of the gold film modified with MPA. The thickness of the layer measured directly on micrographs is about 1.5 nm.

The infrared spectra were measured with the aid of FT-IR Bruker spectrophotometer model IFS 113v (KRS-5, ATR technique). Fluorolub was used to make a better optical contact with the layer examined. Scanning tunnelling microscope (STM) was available due to courtesy of

The Institute of Physics, Technical University in Poznań, a Pt/Ir tip was used.

### 3. Results and discussion

We found the surface of a gold film to be modified as the contact angle for water at pH 7 has changed from  $32^\circ$  for Au substrate into  $39^\circ$  for acid-functionalised MPA self-assembled layer. The surface appears to be a bit more hydrophobic after modification with MPA. Treatment the MPA layer with ammonium hydroxide before measurements gives rise to a decrease in the contact angle up to  $14^\circ$  (water, pH 7) which is characteristic for a more hydrophilic surface formed by ionised COOH groups. Thus, we have an evidence that the carboxylic groups are reactive in the formed layer and will also be able to react with  $\text{NH}_2$  groups of APTES. To obtain the reference data for  $\text{NH}_2$ -functionalised layer we have also measured the contact angle for a glass substrate modified with APTES only getting the value of  $43^\circ$  at pH 7 and about  $20^\circ$  at pH 1 (HCl) due to protonation of  $\text{NH}_2$  groups. Again, modification with APTES makes the surface more hydrophobic. It becomes hydrophilic after treatment with an acid. That means, that APTES molecules are linked to the glass surface through Si–O bounds leaving free  $\text{NH}_2$  ends. We note that the contact angle for a fully hydrophobic layer prepared on a glass substrate with *n*-octyltriethoxysilane reaches a value of  $99^\circ$  and the value observed for an unmodified glass substrate is about  $30^\circ$ . In the case of the complex layer MPA-APS we found the contact angle of  $57^\circ$  maximum with a random distribution from sample to

sample over a relatively wide range ( $25^{\circ}$ – $57^{\circ}$ ). This is because of perturbations in the structure of the layer. Even in the best case we have observed domains of different electrical properties, clearly seen in the STM images [13].

The infrared spectra measured with the aid of a FT-IR spectrophotometer (KRS-5, ATR technique) show typical absorption at  $3480\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$  ( $\nu_{\text{N-H}}$ ,  $\text{NH}_2$ ) for the APTES monolayer, and about  $1700\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ,

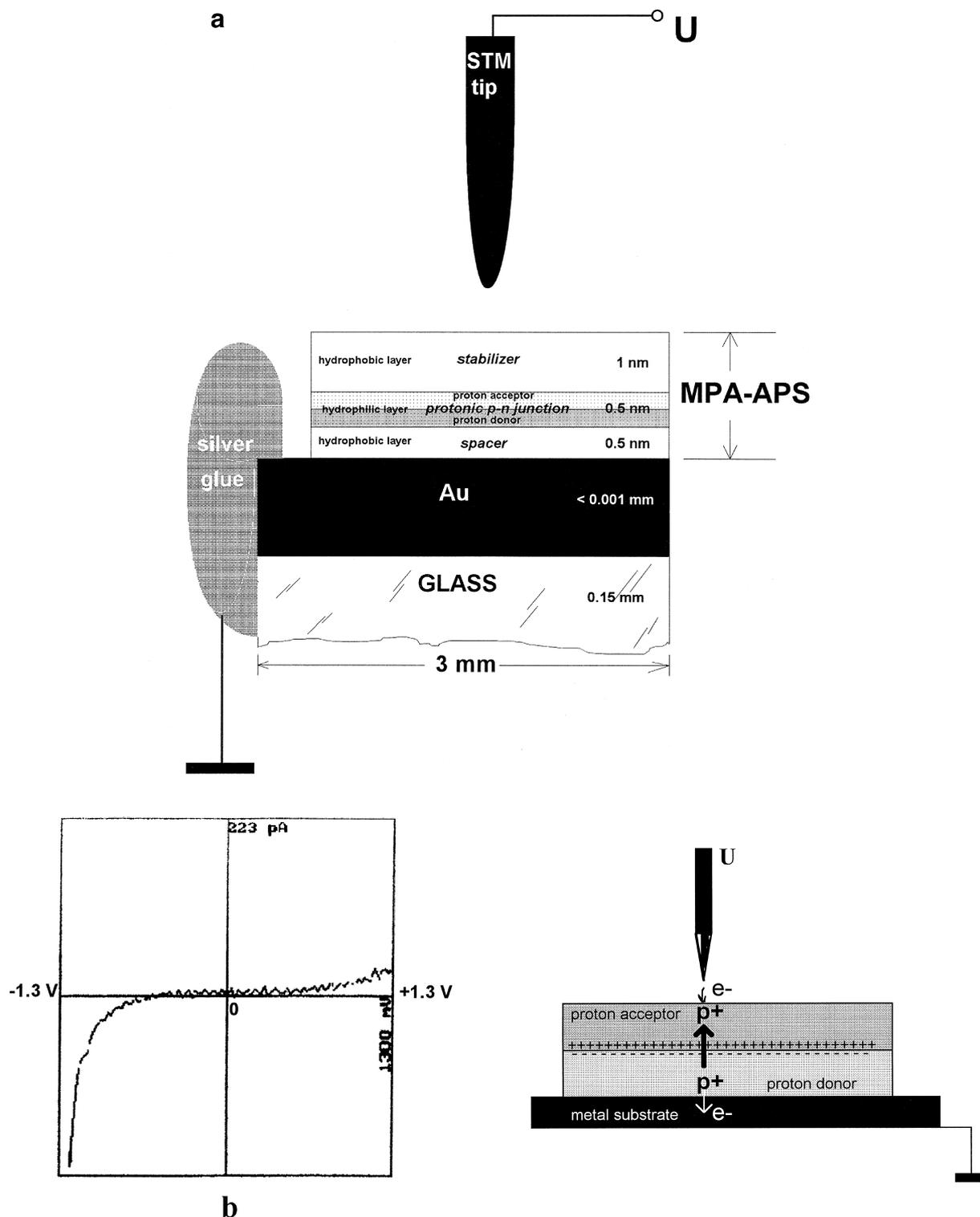


Fig. 2. (a) A scheme of the protonic nano-rectifier and the experimental set-up for measurements of current–voltage ( $I$ – $V$ ) characteristics with STM. (b) An asymmetric  $I$ – $V$  diagram found for a MPA-APS layer. Forward direction is typical for a protonic p–n junction [10,11].

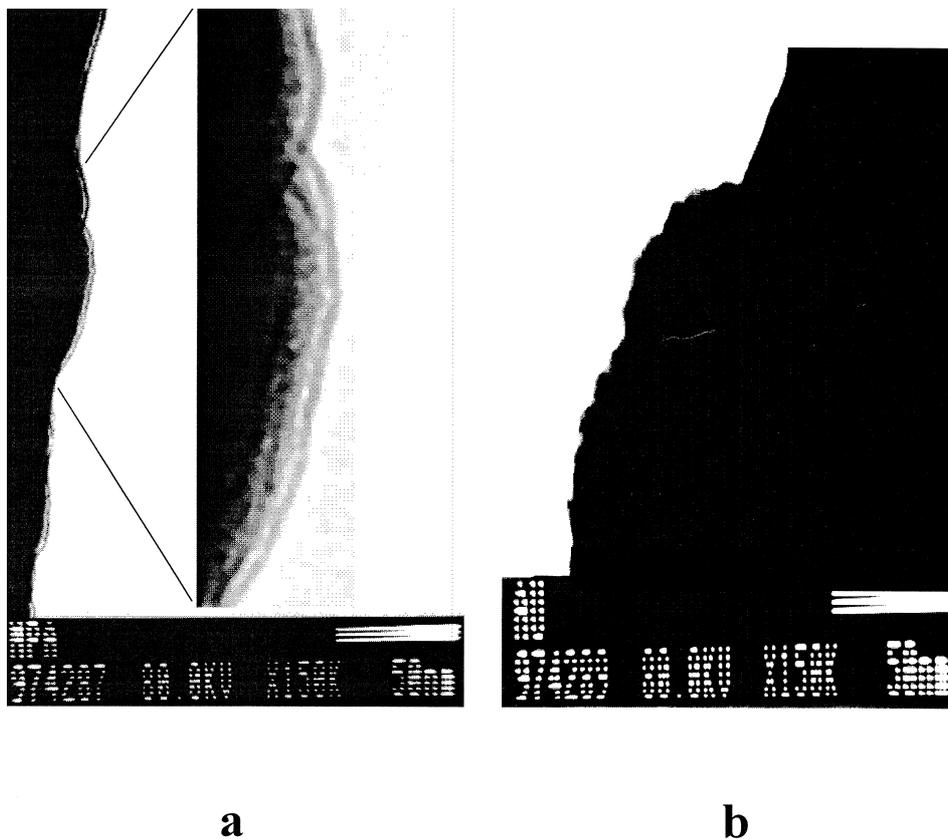


Fig. 3. TEM micrographs of a gold film modified with MPA (a) and unmodified (b).

COOH) for the monolayer formed by MPA molecules. Similar absorption is observed in the case of MPA-APS but the peaks are broad and shifted towards the lower frequency. The most characteristic feature is a very low intensity of the absorption measured for all the monolayers examined (typical spectra were presented elsewhere [14]). Despite this, FT-IR ATR enables us to detect  $\text{NH}_2$  and COOH groups, if present, and to conclude the interactions between them and the environment. The broadening of the absorption peaks is attributed to hydrogen bonding and a shift results from ionisation owing to acid-base reaction

between  $-\text{COOH}$  and  $\text{NH}_2$  groups, particularly in the presence of water molecules, leading to formation of  $\text{COO}^-$  and  $\text{NH}_3^+$ , respectively.

Taking into account these results and the observation that the external surface of the complex layer MPA-APS is hydrophobic (contact angle  $57^\circ$ ) we conclude the structure of the examined layer: we recognise it as a system with close contact between carboxylic and amino groups. The resulting complex molecular layer consists of two hydrophobic layers and a hydrophilic layer with the protonic p–n junction which is formed owing to interactions of

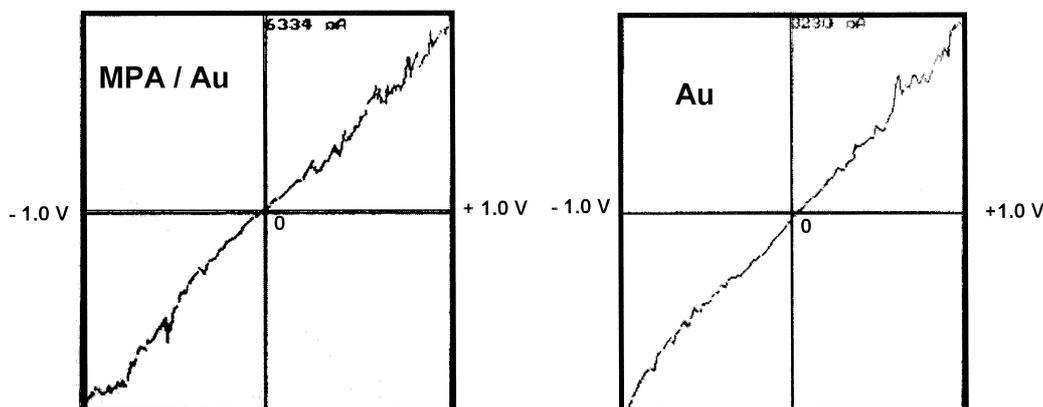


Fig. 4.  $I$ – $V$  characteristics of a clean gold surface and a gold surface modified with MPA monolayer.

$\text{NH}_2$  and  $\text{COOH}$  groups mediated by water molecules [10,11] (the solvent used and the layer have not been protected against water). The presence of water inside the working layer is necessary and it can stabilise the whole system [10,11,15]. The hydrophilic layer is embedded into two hydrophobic layers, which strengthens the hydrogen bonding inside and protects the working layer against environmental perturbations (Figs. 1 and 2a).

STM has been applied to monitor the surface of a sample before and after modification. It enabled us to make a qualitative control over modification process [13]. Imaging was also possible with the aid of a TEM. The monomolecular layer was observed at the edge of the gold film modified with MPA (Fig. 3). The thickness of the layer is about 1.5 nm and corresponds to the structure composed of MPA in a dimeric form (typical for carboxylic acids) which is stabilised by strong hydrogen bonding between carboxylic groups. This makes the layer hydrophobic with SH groups located at the external surface (the contact angle measured for MPA layer is  $39^\circ$ ). The dimers are not stable in contact with basic reagents (as ammonium hydroxide and amino-derivatives) being transformed into MPA monolayer with more or less ionised carboxylic groups at the surface (the contact angle decreases up to  $14^\circ$  after treatment with  $\text{NH}_4\text{OH}$ ).

The most interesting are measurements of current–voltage ( $I$ – $V$ ) characteristics with the use of STM and its high precision positioning system: the current between STM tip and a gold substrate through the MPA-APS layer was measured (Fig. 2a). The experiment enables us to study the electrical properties of nano-scale objects. This is a non-contact technique and we were able to repeat our measurements many times with no damage of the layer. We can also monitor the area examined (STM image operating mode) and recognise the point actually tested. The  $I$ – $V$  diagrams measured are not only typical for a tunnelling gap [16], but what is more important, they are asymmetric with forward and reverse directions typical for a protonic rectifier [10,11]: i.e., for negative and positive polarisation of the STM tip, respectively (Fig. 2b). However, either a clean gold substrate, as well as the layer formed of MPA only, examined at the same conditions, do not work as rectifiers: their  $I$ – $V$  characteristics are symmetric, ohmic and almost linear (Fig. 4). A difference in the work function of the STM tip (Pt/Ir) and the substrate (Au) does not play the essential role in the case of tunnelling and it can be neglected in our experiments.

Our results clearly prove the rectifying behaviour of the layer MPA-APS, examined in many points at its surface. Moreover, taking into account that the STM tip is testing the very limited area of the sample (even as small as a single molecule), we are able to examine the homogeneity of the layer with respect to its rectifying properties and we found a non-uniform structure: rectifying nano-domains of dimensions of about 100 nm [13]. The rectifying domains are embedded into the area of non-rectifying properties, in

some parts electrically conducting. The electrical conductivity can be attributed to conduction through the water layer formed as a result of the capillary condensation effect. The water layer can change the electrical conductivity but not rectifying properties of the MPA-APS layer. We note, that the presence of water is necessary for a protonic rectifier [10,11].

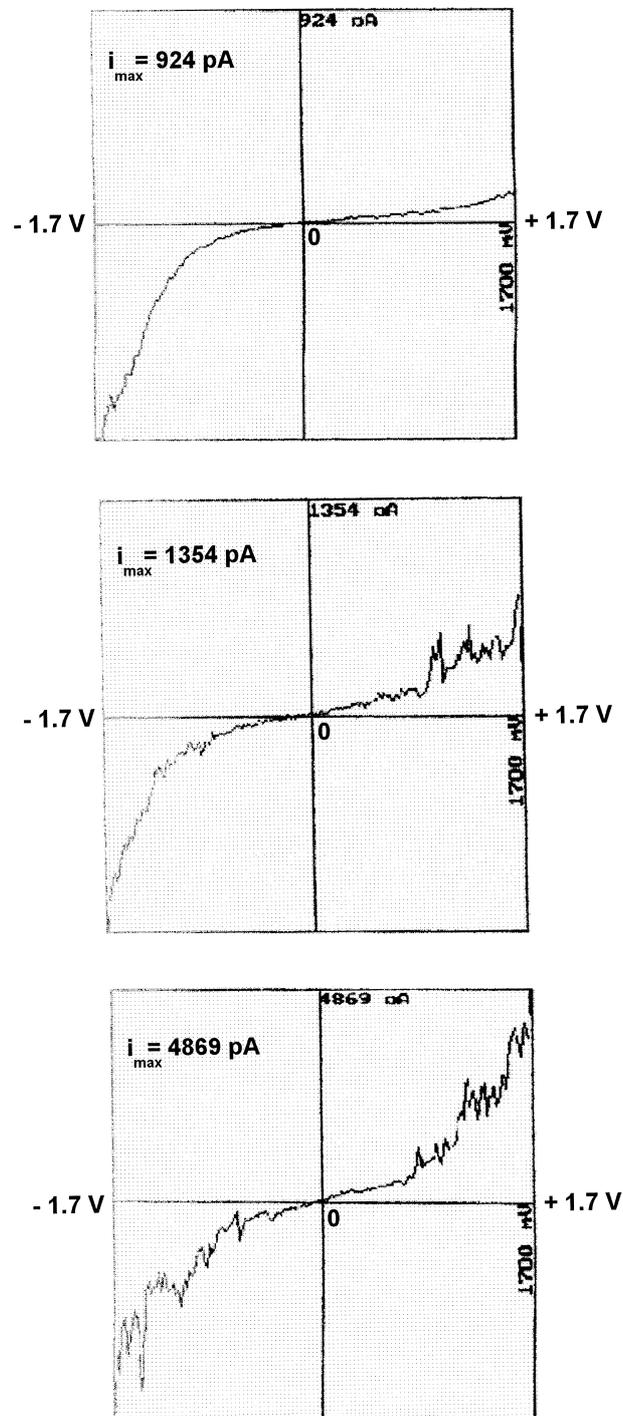


Fig. 5. Three  $I$ – $V$  diagrams for MPA-APS layer measured at different values of the tunnelling current which correspond to different STM tip-gold substrate separation (a low tunnelling current is associated with the large separation).

The structure of the layer appears to be dense and ordered enough to form a microscopic two-dimensional system of strongly interacting protons. This leads to a collective behaviour which results in high electrical conductivity, rectifying properties and a broad absorption in the IR spectrum owing to the hydrogen bonding system. The third dimension, the thickness of the working layer, is of a nanometer (molecular) scale.

We also found that the  $I$ – $V$  diagrams are asymmetric only if a distance between the STM tip and the layer examined is sufficiently large to protect the layer against mechanical disturbance and damage, otherwise, for small distances, i.e., high values of the tunnelling current, we can only observe symmetric diagrams or simply linear  $I$ – $V$  characteristics (Fig. 5), with no short-circuiting.

#### 4. Conclusions

Despite our rectifying diode is an experimental device with the very low current flow, its break down voltage appears to be high enough for practical applications. This is the first protonic rectifier on a molecular scale and one of the smallest electronic devices. (Recently, an electronic unimolecular rectifier of similar dimensions has been prepared by Metzger et al. [17,18]).

On the other hand, the results presented here spot a light on the crucial role of the proton transport in biological systems (membranes, enzymes, bio-macromolecules) which can be controlled in the same way: with an intramolecular or — a more complex — supramolecular protonic p–n junction lattice formed by interacting proton-donor and proton-acceptor amino acid residues in a 3-dimensional protein structure, as we suggested previously [10,11,19].

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