Electronic transport through oligopeptide chains: An artificial prototype of a molecular diode

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Using an effective tight-binding model, together with a transfer matrix technique, we investigate the electronic transport through an oligopeptide chain composed by two amino acid pairs alanine–lysine (Ala–Lys) and threonine–alanine (Thr–Ala), respectively, sandwiched between two platinum electrodes. Our results show that factors such as the oligopeptide chain length and the possible combinations between the amino acids residues are crucial to the diode-like profile of the current–voltage (I–V) characteristics, whose asymmetric curves were analyzed using the inverted rectification ratio (IRR).

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1. Introduction

The ability to integrate man-made solid-state nanostructures with biological structures (including biomolecules) is opening up revolutionary means for the electrical and optical characterization of biomolecular processes, with the consequent impact on a wide variety of medical and biological applications. Nanostructure–biomolecule complexes must be biocompatible in a way that the properties of their interface are critical to the development of new types of biological device, including the bioelectronic one. New ways to interface physical electronics with biological systems are being developed, leading to the possibility to fabricate new classes of biomedical devices, which make use of organic materials in place of conventional semiconductors. Accordingly, nanostructure–biomolecule complexes including quantum dots (QDs) and carbon nanotubes (CNTs), and important classes of biomolecules, like oligopeptides, proteins, and the nucleic acids RNA and DNA, have been designed, fabricated, modeled, and characterized. Their main advantages are their lower current and power operation, cheaper and simpler fabrication, versatility in usage, and mechanical flexibility, which allows the devices to be incorporated into flexible plastic structures. The main disadvantages, however, are their low life time due to degradation, as well as their reactivity with water and other substances, which necessitate the design of effective packaging systems (for reviews see [1–3] and the references therein).

Encompassing all the properties summarized above, the so-called molecular electronics technologies offer nowadays a viable alternative to overcome the difficulties arising from the biological materials, as well as those associated to the continuing shrinking of electronic devices in the silicon-based technology. Usually, molecular electronics takes full advantage of the unique properties of its molecular components, leading to applications that may be complementary to conventional electronics, instead of trying to replace it. This complementarity, indeed, points to applications much more diversified than the simple miniaturization of electronic circuits. The possibilities include mainly the connection of traditional electronics to biological tissues, allowing the creation of neural chips, implants, prostheses and devices designed to extend the capabilities of the human body, among many other possibilities [4,5].

The idea of replacing electronic components by molecules is not new. In 1974, Aviram and Ratner [6] were the first to suggest an organic molecular system showing current rectification, composed by a donor and an acceptor group attached by a carbon bridge with single bonds. Since then, several works have been done in the fields of molecular electronics and nanoelectronics (for a recent review see Ref. [7]).

A diode or rectifier is an important component in conventional electronics, allowing an electric current to flow in one direction, but blocks it in the opposite direction. Building diodes using single molecules has been pursued by many groups (for a recent review see Ref. [8]). The basic structure of early molecular diodes consists of a donor and an acceptor separated by a σ-bridge, with σ being some saturated covalent bond linking the donor

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and acceptor, providing a tunneling barrier between them. In this “donor–σ–acceptor” structure, the diode behavior was expected to occur as a consequence of different thresholds at positive and negative bias voltages.

On the other hand, amino acids are important organic compounds composed of amine (–NH₂) and carboxylic acid (–COOH) functional groups, along with a side-chain specific to each of them. Their key elements are carbon, hydrogen, oxygen, and nitrogen, though other elements are found in their side-chains. Besides, amino acids are the basic units of proteins, performing several important functions such as neurotransmitters, formation of hormones, drugs, methylation, etc. Short chains of amino acid monomers, whose covalent chemical bonds are formed when the carboxyl group of one amino acid reacts with the amino group of the other, are known as oligopeptide.

Results of several electron-transfer studies through oligopeptides and proteins suggest that the efficiency of electron transport is strongly influenced by the length of the peptide, the nature of the scaffold, and the amino acid sequence [9–12]. The presence of hydrogen bonding also influences the electron-transfer rates [13–16].

Our motivation to study electron transport through a molecule is based on the fact that it may be controlled electrically, magnetically, optically, mechanically, chemically and electrochemically, leading to various potential device applications. To reach the ultimate goal in device applications, experimental techniques to fabricate an electrode|molecule|electrode junction, and theoretical methods to describe the electron transport properties are being developed nowadays.

In this work, we report a numerical study of the electronic transport through oligopeptide chains formed by the combination two by two of three amino acids: alanine (Ala), lysine (Lys) and threonine (Thr). The two oligopeptide chains studied are the Ala–Lys and Thr–Ala, in their neutral and non-solvated conformation (see Figure 1a). These amino acids were gathered in groups of four building blocks each, in a linear molecular geometry of non-equilibrium, forming oligopeptide chains with 8, 16, 24 and 32 amino acids, covalently linked to two platinum electrodes (see Figure 1b and c). The current–voltage (I–V) characteristics and properties are discussed as a function of the intra (inter)-chain electronic coupling in the electrode|oligopeptide|electrode junction, taking into account their on-site energies, the intra (inter)-chain hopping between the

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**Figure 1.** (a) The three amino acids used in this work: alanine (Ala), lysine (Lys) and threonine (Thr), with their corresponding 3D structures. (b) The oligopeptide chains obtained by juxtaposing two building blocks A, B, meaning the Ala, Lys and Thr, Ala amino acids, respectively. The length of these chains varies from 8 to 32. (c) Schematic illustration of the oligopeptide chains (Ala–Lys and Thr–Ala) sandwiched between two electrodes, mimicking the second sequence in (b), each of them with 16 amino acids in the total.
amino acid residues, the type of electrode, the oligopeptide chain length and the possible combinations between the amino acids residues.

2. Computational methods

The electronic transport properties of a molecular-junction are usually described by two approaches: ab initio calculations and model-based Hamiltonians (for a recent review see [7]). The former can provide a detailed description but is currently limited to relatively short molecules, while the latter is less detailed but allows for describing systems of realistic length. Here, as our focus is mainly on the qualitative properties of a protein-nano-junction, we choose a mathematical framework based on an effective tight-binding model, together with a transfer matrix technique, employed to simplify the algebra which can be otherwise quite involved, as described in our previous work [17], without any environment or complex contact related effects. In this way, keeping the formalism as simple as possible, the total Hamiltonian of the structure can be written as (see Figure 2):

$$H_{\text{total}} = H_{\text{oligopeptide}} + H_{\text{electrode}} + H_{\text{coupling}}.$$ \hspace{1cm} (1)

The first term of Eq. (1) describes the intrachain charge propagation through the oligopeptide chain, and it is given by:

$$H_{\text{oligopeptide}} = \sum_{n=1}^{N} \left[ \varepsilon_n^a |n, 1\rangle \langle n, 1| + \varepsilon_n^b |n, 2\rangle \langle n, 2| \right]$$
$$+ \sum_{n=1}^{N} \varepsilon_n^c \left[ |n, 1\rangle \langle n+1, 1| + |n+1, 2\rangle \langle n, 2| \right]$$
$$+ \sum_{n=1}^{N} \varepsilon_n^d \left[ |n, 1\rangle \langle n+1, 2| + |n, 2\rangle \langle n+1, 1| \right]$$
$$+ |n, 1\rangle \langle n+1, 1|. \hspace{1cm} (2)$$

The energies $\varepsilon_n^{a,b}$ are the on-site ionization energy of the respective base $\alpha, \beta = \text{alanine (Ala), lysine (Lys) and threonine (Thr)},$ at the nth site. The energies $\varepsilon_n^{c,d}$ are chosen from the ionization potential of their respective bases: $\varepsilon_{\text{Ala}} = 9.85,$ $\varepsilon_{\text{Lys}} = 9.50$ and $\varepsilon_{\text{Thr}} = 10.20,$ all units in eV [18–20]. Furthermore, $t_{n,n+1}$ represent the hopping terms between adjacent (next and next-nearest neighbors) amino acids residues $n, n+1$ in the oligopeptide chain, with their values listed as follows: $t_{\text{Ala} \rightarrow \text{Ala}} = 0.317, t_{\text{Ala} \rightarrow \text{Lys}} = 0.139, t_{\text{Lys} \rightarrow \text{Lys}} = 0.079, t_{\text{Lys} \rightarrow \text{Ala}} = 0.168, t_{\text{Ala} \rightarrow \text{Thr}} = 0.214, t_{\text{Thr} \rightarrow \text{Thr}} = 0.205$ and $t_{\text{Thr} \rightarrow \text{Ala}} = 0.239,$ all units in eV. All electronic parameters were derived from molecular orbitals close to the highest occupied molecular orbital (HOMO) or upper valence band edge. We are aware that more reliable estimation of the electronic matrix elements could be obtained if the majority of valence and conduction band edge states contribution were taken into account, including structural fluctuation effects, but this is beyond the scope of this work. These results were obtained by first principles calculations using the software Gaussian 09 within the Density Functional Theory (DFT) framework [21] through:

$$t_{n,n+1} = 0.5(E_{\text{HOMO}} - E_{\text{HOMO} - 1})^2 - (E_n - E_{n+1})^2)^{1/2}, \hspace{1cm} (3)$$

where the two-state model based on the energetic splitting between the HOMO and HOMO–1 in a system of two amino acids was employed [22–24]. The $E_{\text{HOMO}}$ and $E_{\text{HOMO} - 1}$ are, respectively, the first and second highest occupied molecular orbitals energies calculated for each base combination formed by $n, n+1$ amino acids residues of the oligopeptide chain. For these amino acids, the individual site energies $E_n$ and $E_{n+1}$ (vertical ionization energies) were determined experimentally and reported in the literature [18–20]. When the difference in the above square brackets is negative, we adopted the expression [25]:

$$t_{n,n+1} = 0.5(E_{\text{HOMO}} - E_{\text{HOMO} - 1}) \hspace{1cm} (4)$$

Furthermore, recent studies show that the conventional DFT functionals, commonly used to model charge transport in organic materials, underestimate the values of the hopping terms in comparison with long-range corrected density functional [26,27]. Due to that, a new density functional, a Coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP), has recently been developed specifically to properly predict molecular charge-transfer spectra. It is a skilled Coulomb-attenuation scheme able to solve charge-transfer excitations in the zincbacteriochlorin–bacteriochlorin complex [28] and in the dipeptides model [29]. It has also been successfully applied in the intermolecular charge-transfer transitions [30], predicting the occurrence of charge-transfer bands in the porphyrins and chlorophylls [31], and identification of an unexpectedly large capacity of the aliphatic bridge to electronically connect the ary lamines [32]. To take into account the above remarks, we used here the CAMB3LYP functionals with Dunning’s correlation consistent basis sets (cc-pVDZ), to optimize the structures of the oligopeptides and to calculate their HOMO energies [33,34]. Lastly, the interchain hopping between the amino acid bases is considered to be $w = 0.1 t,$ in eV.

The second term of Eq. (1) is related with the two semi-infinite metallic electrodes

$$H_{\text{electrode}} = \sum_{n=-\infty}^{0} \sum_{m=1}^{2} [\varepsilon_{n}^{e} |n, m\rangle \langle n, m| + t_{f} |n, m\rangle \langle n+1, m|]$$
$$+ \sum_{n=1}^{\infty} \sum_{m=1}^{2} [\varepsilon_{n}^{f} |n, m\rangle \langle n, m| + t_{f} |n, m\rangle \langle n-1, m|]. \hspace{1cm} (5)$$

Here, $\varepsilon_{n}^{e,f}$ ($t_{f}$) is the ionization energy (hopping term) of the electrode. We consider a platinum electrode whose ionization energy $\varepsilon_{s} = 5.36\text{eV}$ is related to the metallic work function of this metal [35,36], and $t_{f} = 12.0\text{eV}.$
Finally, the third term of Eq. (1) describes the contacts between the oligopeptide and the semi-infinite metallic electrodes, yielding:

\[ H_{\text{coupling}} = \sum_{m=1}^{2} \varepsilon_{c} |0, m\rangle \langle 1, m| + |N, m\rangle \langle N+1, m| , \]

where \( \varepsilon_{c} \approx 0.317 \) eV represents the hopping amplitude between the AC (DC) electrodes and the ends of the oligopeptide, with \( N \) being the number of amino acids residues in the chain considered.

With the tight-binding Hamiltonian given above, one can evaluate the \( I-V \) characteristics by applying the Landauer–Büttiker formulation [37], i.e.:

\[ I(V) = \frac{2e}{h} \int_{-\infty}^{+\infty} T_{N}(E) [f_{\text{DN}}(E) - f_{\text{AC}}(E)]dE, \]

where the Fermi–Dirac distribution is given by:

\[ f_{\text{DC(AC)}} = \left( \frac{1}{\exp \left( \frac{E - \mu_{\text{DN(AC)}}}{k_{B} T} \right) + 1} \right)^{-1}. \]

Here \( \mu_{\text{DN(AC)}} \) is the electrochemical potential of the two electrodes fixed by the applied bias voltage \( V \) as [38]

\[ |\mu_{\text{DN}} - \mu_{\text{AC}}| = eV. \]

The current onset is crucially dependent on the electrochemical potentials of the electrodes, that can be altered by the coupling to molecules [39]. For simplicity, before bias voltage is applied, the electrochemical potential of the whole system is taken to be zero.

### 3. Results and discussion

Current rectification in oligopeptide on the nanoscale can be achieved by the integration of molecules with asymmetric structure, such as \( \alpha \)-helix peptides, into the metal electrode junctions [40]. Current patterns of the helical \( \alpha_{1} \) peptide amino acid sequence \((\text{Leu–Glu–Thr–Leu–Ala–Lys–Ala})_{3}\) and its 5Q and 7Q variants were recently investigated to distinguish the fibrous/not fibrous assemblies associated to them, looking for the development of biosensors to probe the onset of amyloidosis-like diseases [41].

However, secondary structures like the \( \alpha \)-helix of supported or even unsupported PolyAla oligopeptide, depend on factors such as the energy state [42], peptide length [43], terminal charges and proline substitution [44], as well as the temperature and physical state of the peptide [45]. Given the difficulty to deal with this structural complexity, we decided instead to use the approach based on bridging molecules that present rectified current response depending on the relative position of the Fermi level energy of the metal electrodes and energy levels of the molecules [46]. In support to this approach, recent theoretical and experimental works have succeeded in addressing the effects of primary protein structure, i.e., specific amino acid sequences like those used in this work, on conductance [47,48].

Before the bias voltage be applied, the electrochemical potential of the whole system is taken to be zero. After the applied bias voltage \( V \) is effective, the difference between the electrochemical potential of the two electrodes is governed by Eq. (9). By properly locating the Fermi level energy close to some of the characteristic resonances of the electrode–oligopeptide–electrode nano-junction, as the voltage drop is switched on, the transmission coefficient becomes voltage-dependent. This implies the appearance of transmission band shifts, which in turn gives rise to a voltage threshold modulation in energy, leading to a lower current at a given bias. As a result, the turn-on current shows an asymmetric profile, further enhanced in the negative voltage region, as depicted in Figure 3a and b.

The main current–voltage \( (I-V) \) characteristics shown in Figure 3a and b present an insulator region for \( -4 \text{eV} \leq V \leq 4 \text{eV} \), and nonlinear and asymmetric regions indicating transitions toward saturation currents for \( V \leq -4 \text{eV} \) and \( V \geq 4 \text{eV} \). It is easy to see that the general shape of the \( I-V \) curves are clearly asymmetric, depicting a diode-like behavior. Figure 3a shows that the current intensity increases with the applied negative (positive) voltages and reaches a maximum of \(-29.3 \mu\text{A} \) at \( V = -15 \text{V} \) (19.3 \mu\text{A} \) at \( V = 15 \text{V} \), respectively. The same occurs to the \( I-V \) curves depicted in Figure 3b, but now with a lower maximum intensity of \(-5.8 \mu\text{A} \) at \( V = -15 \text{V} \) (2.3 \mu\text{A} \) at \( V = 15 \text{V} \), respectively. In both cases, the maximum values for the current intensities were found for the total number of the amino acids residues in the chain \( N = 8 \). Note that the current intensity is inversely proportional to the length of the oligopeptide chains. Lastly, the insets in Figure 3a and b show the conductance \( (dI/dV \times V) \) of the devices, which are highly nonlinear. In contrast with previous work [47], they do not show negative differential resistance, i.e., \( dI/dV < 0 \). Such phenomenon is a tunneling-related effect which has been originally observed in silicon-based heterostructures [49], and can be masked while the current is still small.

The non-negligible rectified currents, depicted in Figure 3a for the oligopeptide chain Thr–Ala, are 9.9 (\( N = 8 \)), 7.8 (\( N = 16 \)), 7.3 (\( N = 24 \)), and 6.5 (\( N = 32 \)), respectively, all units in \mu\text{A}. For the oligopeptide chain Ala–Lys (Figure 3b) the rectified currents are 3.6 (\( N = 8 \)), 2.9 (\( N = 16 \)), 2.3 (\( N = 24 \)), and 2.1 (\( N = 32 \)), respectively, all units also in \mu\text{A}. Here \( N \) is the total number of the amino acids in the oligopeptide chain. Note that the absolute value of these rectified currents may be changed by varying the electronic hopping integrals, as well as by the way the oligopeptide chains are contacted to the electrodes.

Observe that the \( I-V \) curves present a particular asymmetry, whose shape as a function of the polarity of the applied voltage constitutes the rectification of the current by the molecule. To
quantify the asymmetry of the OF characteristics in Figure 3a and b, we defined the rectification ratio (RR) by \( R(V) = |I(V)|/|I(−V)| \), where \( I(V) \) and \( I(−V) \) represent the forward and reverse currents, respectively. However, because the structures studied in this work display higher current intensity in the region of negative voltage, we use instead an inverted rectification ratio \( IRR = 1/R(V) \), to measure the degree of asymmetry of the oligopeptide chains.

We start from the I–V curves in Figure 3a for each oligopeptide chain, as illustrated in Figure 1b and c. It is found that, in all curves, an obvious rectification is observed with the rectifying direction along the negative bias direction, i.e., the electrons prefer to flow from the alanine group to the threonine one at a negative bias. The (1/R)–V curve shows the maximum value of 1.58 at 6.4 V for the shortest chain (N = 8) as depicted in Figure 4a. We can also observe that in this case the (1/R)–V curves are inversely proportional to the length of the oligopeptide chains, but with very close values. They can be divided into three regions namely: (i) \( 0 \leq V < 6 \) V, (ii) \( 6 \leq V < 15 \) V, and (iii) \( 15 \leq V < 18 \) V. In the first region, the IRR's increase continuously from 0 to 6 V (maximum value), with a very small but progressive separation between them. In the second one, the (1/R)–V curves remain parallel and decrease slowly. The third one is the saturation region.

Figure 4b, which is related to the Figure 3b (Ala–Lys pair), displays the same rectifying direction as those observed in Figure 3a. However, while the current intensity values in Figure 3b are much smaller than those observed in Figure 3a, the (1/R)–V curve depicted a maximum value of 2.59 at 12 V for the chain with \( N = 16 \) (see the inset (a) of Figure 4). Unlike what was observed in Figure 4a, in this case there is no relationship of inverse proportionality between the IRR's and the length of the chains (see the inset (b) of Figure 4).

For the Ala–Lys pair case, the (1/R)–V curves can be divided into two regions of interest: (i) \( 0 \leq V < 12 \) V, and (ii) \( 12 \leq V < 18 \) V. In the first region, they increase continuously from 0 until reaching the saturation value at 12 V (maximum value). The second one is the saturation region. Differently from the previous case, here the curves are practically indistinguishable, suggesting the lack of relationship with the chain length.

4. Conclusions

In summary, by using an effective tight-binding model, we have theoretically investigated the transport properties of a molecular device made up of an oligopeptide chain directly coupled to two platinum electrodes. The I–V characteristics are discussed in terms of their on-site ionization and electrode energies, as well as their different hopping parameters. On the way to get these results, we have derived for the first time the hopping energies among the amino acids residues considered in all oligopeptide chains, using quantum chemistry computations. Our calculations reveal that the asymmetry observed in the I–V curves clearly indicate a diode-like profile in the two structures analyzed in this work. However, the values obtained for the I–V and (1/R)–V curves give quite different aspects for the oligopeptide chains formed by the threonine–alanine (Thr–Ala) and alanine–lysine (Ala–Lys) pairs: while the Thr–Ala pair presents a variation in the maximum current intensity six times greater than the Ala–Lys one, the later has a IRR maximum value nearly two times greater than the former one. Besides, we observed also a proportional relationship between the difference of the ionization energies of the oligopeptide chains (Thr–Ala or Ala–Lys) and the values obtained for the I–V and (1/R)–V curves. Such characteristics make these two oligopeptide chains good candidates for artificial prototype of a molecular diode. We hope strongly that our work may stimulate experimental developments in this sense.

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