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THERMOELECTRIC PROPERTIES OF CODON DNA BASED MOLECULAR DEVICES

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Abstract. The thermoelectric power of short oligonucleotides connected in between metallic contacts at different temperatures is theoretically studied. The obtained analytical expressions reveal the existence of important resonance effects leading to a significant enhancement of both the electrical conductance and thermoelectric power in the case of trimer codons. This result suggests the possible existence of a thermoelectric signature for different codons of biological interest. The potential of this class of junctions for thermoelectric applications is also discussed.

1. INTRODUCTION

The experimental study of thermoelectric voltage over guanine molecules adsorbed on a graphite substrate, reported by Poler and co-workers using a STM tip [1], opened novel perspectives in the quest for thermoelectric devices based on molecular electronics engineering. In fact, due to the extreme sensitivity of thermopower to finer details in the electronic structure one can think of tailoring the Fermi level position in order to optimize the thermoelectric performance of a given molecular arrangement. Such a possibility has spurred theoretical studies regarding the possible use of suitable organic molecules to design novel thermoelectric devices. Seebeck coefficient values comparable to those observed in experiments (S =18 μV K^{-1} at room temperature [1]) were derived in a theoretical study considering a phenyl-dithiol molecule chemisorbed on a gold surface [2]. Although these figures are too low to be of interest for thermoelectric applications, it is reasonable to expect that the thermoelectric response may be improved by a a proper choice of the molecular junction materials. On the basis of the vast knowledge gained from bioengineering research during the last decade, we have performed a systematic study on the thermoelectric properties of DNA based short molecular arrangements connected to either guanine [3] or graphite leads [4].

Motivated by a recent study discussing the electronic signature of single DNA nucleotides via transverse charge transport [5], in this work we present a comparative study of the Seebeck coefficient, S; and the thermoelectric power factor ($P = S^2G$, where G is the electrical conductance) of different trimer nucleobases connected to platinum leads in order to ascertain for a possible thermoelectric signature of different codons of biological interest. By the light of the obtained results, the possible use of DNA

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based thermoelectric devices at room temperature is also discussed in the context of current search for improved thermoelectric materials.

2. MODEL DESCRIPTION

Generally speaking, the binding of a relatively small organic molecule to the metallic leads can affect the electronic structure of the bonded molecule [6,7]. In the nucleobase case, however, it seems reasonable to assume that weak coupling conditions prevail [8]. Accordingly, the lead-molecule-lead junction will be described in terms of three non-interacting subsystems, given by the single-band tight-binding Hamiltonian [4,9]

$$H = \sum_{n=1}^{N}\left(\varepsilon_n^v c_n^t c_n - t_{n,n+1} c_n^t c_{n+1}\right) - \tau\left(c_N^t c_{N+1} + c_0^t c_1 + h.c.\right) + \sum_{k=0}^{-\infty}\left(\varepsilon_m c_k^t c_k - t_m c_k^t c_{k+1} + h.c.\right) + \sum_{l=N+1}^{+\infty}\left(\varepsilon_m c_l^t c_l - t_m c_l^t c_{l+1} + h.c.\right). \quad (1)$$

The first term in Eq.(1) describes the oligonucleotide, the second term describes the DNA-metal contact, and the last two terms describe the metallic contacts at both sides of the DNA chain, where c_j (c_j^t) is the creation (annihilation) operator for a charge at the *j*-th site in the chain, ε_n^v, with *v* = {G,A,C,T} and *n* = {1;2;3}; are the HOMO energies of the N-methylated G, A, C, and T bases, respectively, $t_{n;n+1}$ is the hopping term between the bases, and τ measures the coupling strength between the leads and the end nucleobases. The leads are modeled as semi-infinite one-dimensional chains of atoms with one orbital per site, where ε_m is the on-site energy and t_m (>τ) is the hopping term. Modelling the geometry and bonding character of the contact at the interface is a very delicate issue, since detailed information on both the metal geometry and DNA chemical bonding at the contacts is poorly known to date. Consequently, in our modelling of the DNA-contact interface, the parameter t is related to the tunneling probability between the frontier orbitals, thus roughly encompassing bonding effects at the interface [10].

3. ANALYTICAL EXPRESSIONS

To evaluate the thermoelectric voltage we make use of expression [2]

$$S_v(T) = -|e|L_0\left(\frac{\partial \ln \mathrm{T}_v(E)}{\partial E}\right)_\mu T, \quad (2)$$

where *e* is the electron charge, $L_0 = \pi^2k^2/3e^2 = 2\times44\cdot10^{-8}$ V^2·K^{-2} is the Lorenz number, $\mathrm{T}_v(E)$ is the transmission coefficient at zero bias as a function of energy, and *T* is the temperature. By considering nearest-neighbors interactions the Schrödinger equation corresponding to the Hamiltonian (1) can be expressed, within the transfer matrix framework, in the form

$$\begin{pmatrix}\psi_{N+1}\\ \psi_N\end{pmatrix} = T_{N+1}T_N\ldots.T_1T_0\begin{pmatrix}\psi_0\\ \psi_{-1}\end{pmatrix}, \quad (3)$$

where ψ_n is the wavefunction amplitude for the energy *E* at site *n* and

$$T_n = \begin{pmatrix}\dfrac{E-\varepsilon_n^v}{t_{n,n+1}} - \dfrac{t_{n,n+1}}{t_{n,n+1}}\\ 1 \qquad 0\end{pmatrix}. \quad (4)$$

Accordingly, the lead-oligonucleotide-lead global transfer matrix corresponding to three nucleobases of energies ε_1^v; ε_2^v, and ε_3^v, respectively coupled with hopping terms $t_{12}\equiv t$ and $t_{23}\equiv \eta t$; takes the form [4]

$$M_v = \prod_{j=4}^{0} T_j = \quad (5)$$
$$c\begin{pmatrix}8K_v\cos^2k - 2\lambda^2\left(J_v + H_v\right)\cos k + 2\lambda^4 x_1^v & \lambda^2 J_v - 4K_v\cos k\\ 4K_v\cos k - \lambda^2 H_v & -2K_v\end{pmatrix}$$

where $c\equiv\lambda^{-2}\mu^{-2}\eta^{-1}$, $\lambda\equiv\tau/t_m$, $\mu=t/t_m$, $K_v=4x_1^v x_2^v x_3^v - x_1^v\eta^2\mu^2 - x_3^v\mu^2$, $J_v=4x_1^v x_2^v-\mu^2$, $H_v=4x_3^v x_2^v-\eta^2\mu^2$, $x_n^v=(E-\varepsilon_n^v)/2t_m$, and $2\cos k = (E-\varepsilon_m)/t_m$ is the metal dispersion relation. From the knowledge of the M_{ij} matrix elements we get [4]

$$\mathrm{T}_{v(E)} = \left[\left(4K_v\cos k - Q_v\right)^2 + \frac{4t_m^2P_v^2}{\left(E-E_-\right)\left(E_+-E\right)}\right]^{-1}, \quad (6)$$

where $Q_v=\lambda^2(J_v+H_v)/2$, $P_v=\lambda^4x_2^v+K_v-Q_v\cos k$ and $E_\pm=\varepsilon_m\pm2t_m$ define the allowed spectral window as determined by the metallic leads bandwidth. From the knowledge of the transmission coefficient given by Eq.(6) the conductance through the lead-oligonucleotidelead is determined using the Landauer formula [11]

$$G_v = \frac{2e^2}{h}\mathrm{T}_v(E_F), \tag{7}$$

where $2e^2/h \approx 1/12906\ \Omega^{-1}$. The corresponding thermopower curve is obtained making use of Eq.(6) into Eq.(2) to obtain

$$S_v(T) = 2|e|L_0 T\Gamma_v F_v, \tag{8}$$

where

$$\begin{aligned} &F_v \equiv t_m^{-1}\left(4K_v f - Q_v\right)\left(8\tilde{K}_v f + 2K_v - \tilde{Q}_v\right) + \\ &P_v \frac{2t_m}{cd}\left(\lambda^4 + 4\tilde{K}_v - 2\tilde{Q}_v f - Q_v + \frac{4t_m^2}{cd}P_v f\right), \\ &\text{with } \tilde{K} = x_1^v x_2^v + x_1^v x_3^v + x_2^v x_3^v - \\ &\mu^2\left(1+\eta^2\right)/4,\ \tilde{Q}_v = \lambda^2\left(x_1^v + 2x_2^v + x_3^v\right) \\ &\text{and } f \equiv \cos k. \end{aligned} \tag{9}$$

4. DISCUSSION

In order to obtain quantitative results we evaluate Eqs. (7) and (8) at room temperature taking ε_G = 7.75 eV, ε_A = 7.95 eV, and $\varepsilon_T = \varepsilon_C$ = 8.30 eV [8]. Depending on the DNA sequence composition, its length and temperature the effective value of parameter t can vary over a relatively broad range from t = 0.01 to t = 0.4 eV [12–15]. In our study we will adopt the values t_{CC} = 0.3 eV, t_{GG} = 0.25 eV, t_{TT} = 0.13 Ev, and t_{AA} = 0.035 eV in the study of homopolymers, and t_{GT} = 0.083 eV, t_{TG} = 0.26 eV, t_{AC} = 0.11 eV, and t_{CA} = 0.37 eV in the study of heteropolymers. These values were derived from ab-initio calculations for 5'-XY-3' intrastrand stacked pairs [16]. The nucleobase-lead electronic coupling strongly depends on the contact geometry between the molecule and the lead at the junction. We will consider values within the range τ = 0.1-0.5 eV for the base-metal electronic coupling, since these figures compare well with a number of experimental results [1,17–19]. Finally, we consider platinum contacts corresponding to the tight-binding parameters t_m = 2.2 eV, and ε_m = 5.4 eV [8], determining the allowed spectral window [-9.8,-1.0] eV.

Homonucleotide codons. In the first place we shall consider the transport properties corresponding to GGG, AAA, CCC, and TTT codon trimers, respectively codifying for glycine, lysine, proline and phenylalanine amino acids in the homo sapiens genetic code. In this case we have η = 1 in Eqs.(6) and (8). In Fig.1a and b we compare the thermopower curves for the different trimers as a function of the Fermi energy. As a general feature, these curves are characterized by two peaks and a crossing point at the resonance energy ε_m = 5.4 eV. The location of the resonance energy is exactly the same for the four trimers, since it does not depend on the chemical nature of the nucleobases, but it is related to contact-dependent effects [10,20]. The crossing point defines two different regimes exhibiting n-type or p-type thermopowers alternatively. This reversal in the sign of the Seebeck coefficient can be understood by considering the topology of the conductance peak shown in Fig.1c by the light of Eq.(2). In fact, when the Fermi level is located at the left (right) of the resonance energy the slope of the transmission coefficient curve $\mathrm{T}_v(E)$ is positive (negative) leading to n-type (p-type) thermopowers, respectively. In addition, the stepper the conductance curve the higher the thermopower value close to the resonance energy, as it can be readily seen by comparing Figs.1a, 1b, and 1c. The thermopower values attained at the peaks are significantly high, and compare well with the values reported for benchmark thermoelectric materials. If the Fermi level is located far from the resonance energy the Seebeck coefficient values rapidly decrease by several orders of magnitude. In Fig.1c we compare the conductance curves of the different codons as a function of the Fermi energy. A well defined, narrow peak is located at the resonance energy determined from the condition $4Kf$-Q = 0 in Eq.(6). Accordingly, the thermopower power factor P vanishes at this energy, but it rapidly increases around ε_m peaking at about P = 0.025 $\mu V^2K^{-2}\Omega^{-1}$, as it is shown in Fig. 1d. Therefore, the overall shape of the power factor is mainly determined by the energy dependence of the Seebeck close to the resonance energy.

Heteronucleotide codons. Now we consider the transport properties corresponding to TGT, CAC and TTG codon trimers, respectively codifying for cysteine, histidine and leucine amino acids in the homo sapiens genetic code. The aim is to compare their properties with those previously obtained for the TTT and AAA trimers in order to see the effects stemming from the change of one of their original nucleobases ($\eta \neq 1$ in this case). In Figs. 2a and 2b we respectively compare the thermopower curves for the TTT/TGT and CCC/CAC trimers as a function of the Fermi energy. We can see that the thermopower is substantially reduced upon the substitution of the central nucleobases in both cases. This is a general feature of the codons obeying the formula XYX. This result strikingly contrasts with

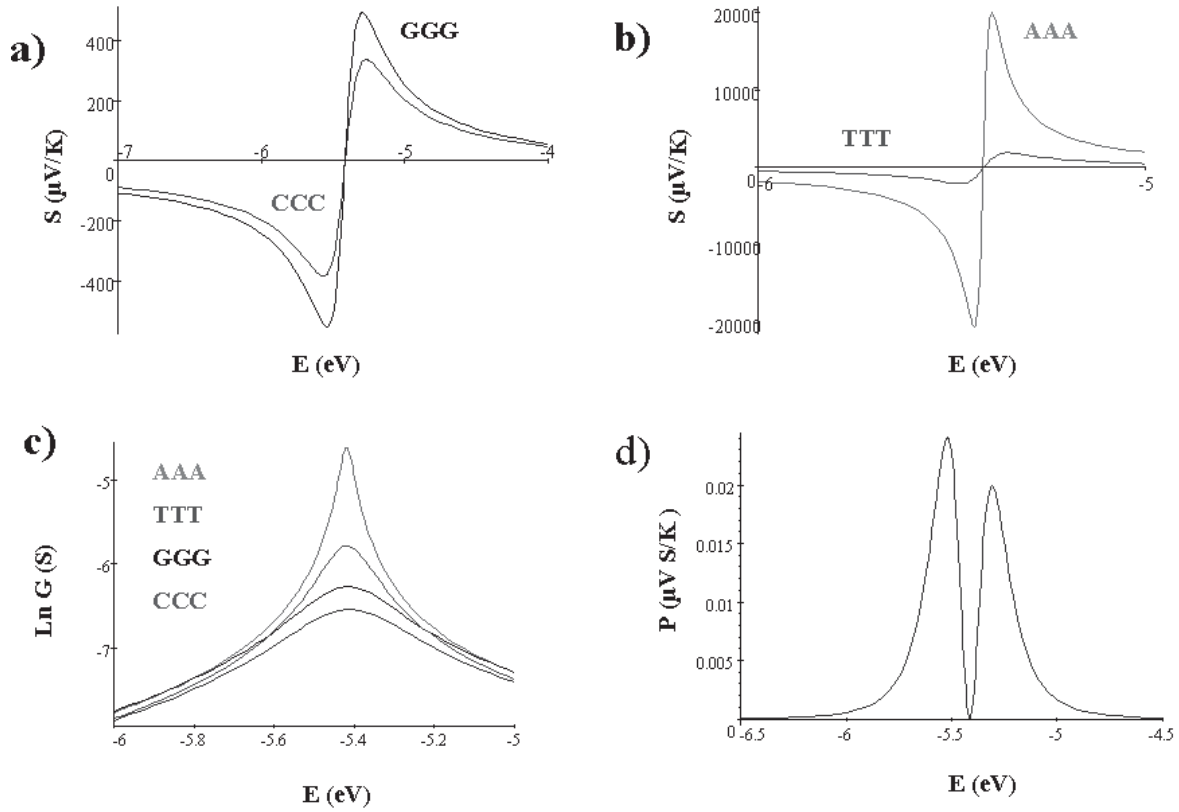

Fig. 1. Dependence of the room temperature thermopower as a function of the Fermi level energy for a) GGG and CCC homonucleotides; b) AAA and TTT homonucleotides connected to platinum leads with τ = 0.5 eV, t_m = 2.2 eV, and ε_m = -5.4 eV. c) Landauer conductance as a function of the Fermi level energy for the different XXX homonucleotides. The curves are labelled in the figure from top to bottom. d) Room temperature dependence of the thermoelectric power factor as a function of the Fermi level energy for a GGG trimer.

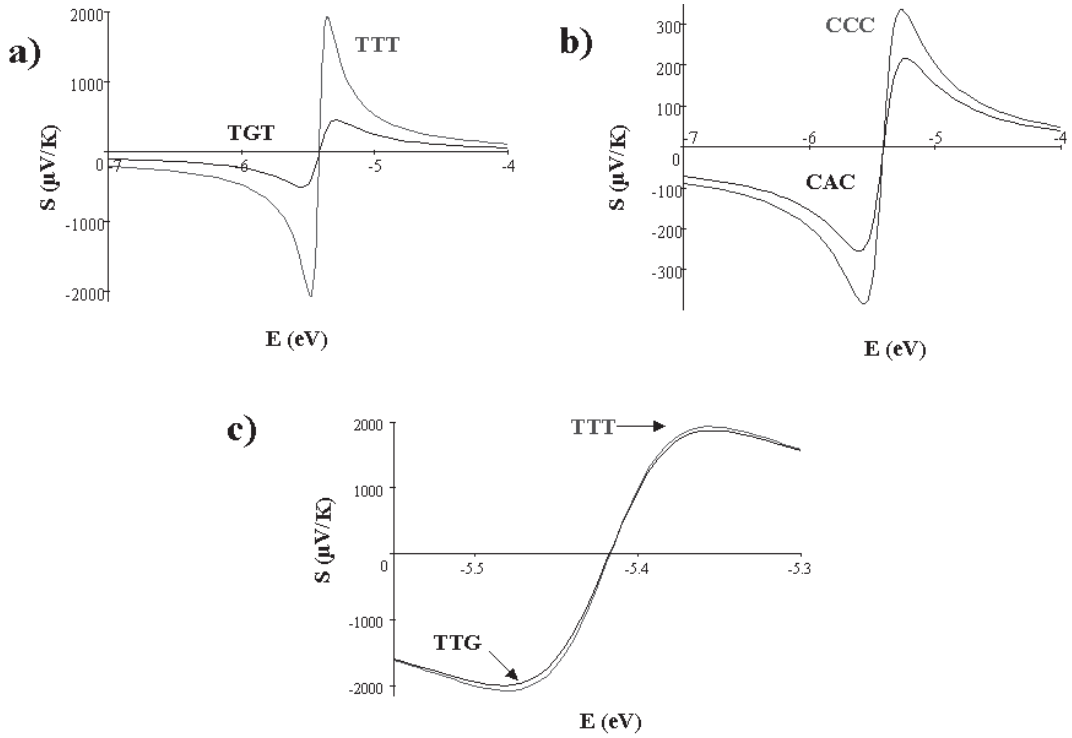

Fig. 2. Dependence of the room temperature thermopower as a function of the Fermi level energy for a) TTT and TGT codons; b) CCC and CAC codons; and c) TTT and TTG codons connected to platinum leads with τ = 0.5 eV, t_m = 2.2 eV, and ε_m = -5.4 eV.

the small effect associated to the substitution of an end nucleobase instead, as it is illustrated in Fig. 2c. Accordingly, the thermoelectric properties of codons obeying the general formula XXY are quite similar to those observed for the corresponding homonucleotides.

5. CONCLUSIONS

In summary, the thermoelectric response of trimer codons connected between two metallic leads strongly depends on the relative position between the metal Fermi level and the trimer molecular levels. Therefore, we can efficiently optimize the *P* power factor by properly shifting the Fermi level position, which plays the role of a tuning parameter. Close to the resonance energy ε_m determined by the metallic contact Fermi energy we obtain very high values for the Seebeck coefficient, suggesting that DNA based molecular junction may be of interest for thermoelectric applications. In addition, the thermoelectric power factor can be significantly enhanced by a judicious choice of the metal-molecule chemical bonding. Since the thermoelectric quality of a material is expressed in terms of the dimensionless figure of merit $ZT = S^2\sigma T/\mathrm{k}$, where k is the thermal conductivity, the potential of these junctions as thermoelectrics ultimately will depend on their thermal transport properties, which to the best of our knowledge, have not yet been fully analysed. By comparing the transport curves corresponding to different types of trimers we have shown that a characteristic thermoelectric signature can be used to identify the XYX type codons from XXX homonucleotide ones on the basis of their different thermoelectric responses. Since the coding properties of DNA introns are closely related to codon triplet associations our preliminary result may enclose some biological relevance well deserving a more detailed study by means of more realistic modelling of both the electronic structure of nucleotides and the codon-lead bonding geometry.

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