Organic Electronics 26 (2015) 176–180

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Length enhancement of thermoelectric effects in DNA duplex chains due to quantum interferences

Yao-Jun Dong [a], Xue-Feng Wang [a,b,*], Yu-Shen Liu [c], Xue-Mei Wu [a,b]

[a] College of Physics, Optoelectronics and Energy, Soochow University, Suzhou 215006, China
[b] State Key Laboratory of Functional Materials for Informatics and Key Laboratory of Terahertz, Solid-State Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, 865 Changning Road, Shanghai 200050, China
[c] College of Physics and Engineering, Changshu Institute of Technology and Jiangsu Laboratory of Advanced Functional materials, Changshu 215500, China

ARTICLE INFO

Article history:
Received 31 March 2015
Received in revised form 1 July 2015
Accepted 20 July 2015

Keywords:
DNA
Charge transfer
Seebeck coefficient
Thermoelectric performance

ABSTRACT

The thermoelectric performance of DNA duplex chains (G:C)–(T:A)$_n$–(G:C)$_3$ is studied by a tight-binding ladder model. The quantum interferences due to intra- and inter-strand couplings can greatly enhance the thermopower effect in long systems. The peak value of Seebeck coefficient increases exponentially with n while the charge transfer rate remains almost constant for $n > 3$ as previously measured. Big figure of merit (ZT) might be available for large n. This result is applicable to other wire molecules having similar structure.

1. Introduction

Searching for thermoelectric materials of high performance to make efficient energy conversion devices has been one of the main scientific and technological activities in the last decade. The successful measurement of Seebeck coefficients in atomic and molecular junctions [1–3] has inspired rapid theoretical development on thermoelectric properties of these systems [4–8]. Thermoelectric devices based on these nano junctions have great application potential. For example, they can be integrated into chip sets to assist the stability of devices by converting the accumulated waste heat into usable electric energy. One-dimensional (1D) systems have been demonstrated having high figure-of-merit (ZT) because the phonon induced thermal conductivity therein can be greatly reduced [9,10]. The experimental and theoretical results have shown that the Seebeck coefficient can increase linearly with the length of a wire molecule while the corresponding conductance decreases quickly [1,3,11,12]. DNA is a natural 1D nano material with perfect self-assembling [13] and self-recognition [14] properties and can be artificially assembled in arbitrary base-pair sequences. It has been considered as a potential multi-functional material in molecular devices. However, few studies have focused on thermoelectric properties of DNA. Employing a tight-binding chain model, E. Maciá studied thermoelectric properties of some synthetic DNA oligonucleotides ten years ago and suggested that they can be used as nanoscale thermoelectric cells [15]. The dimension effects on charge transport and thermopower performance of DNA based molecular junctions were briefly studied as well [16]. Recently, Nestorova and Guilbeau proposed that thermoelectric properties can be used for sequencing DNA at low cost [17].

On the other hand, charge transfer in DNA has been the interest of many experimental [18–23] and theoretical [24–29] studies in the past decades. In one widely notified experiment, Giese et al. measured that charge transfer rate of DNA molecules of sequences (G:C)–(T:A)$_n$–(G:C)$_3$ with the number of (T:A) base pairs $n = 1, 2, 3, \ldots, 15$. The charge transfer rate decreases exponentially with n as expected by chain models at $n < 3$ but then shows a very weak distance dependence in longer molecules [18]. This behavior can be understood by the two-strand ladder model where each base instead of base-pair is treated as a transport unit. The number of transport channels increases with the molecule length due to inter-strand coupling and compensate the decrease of transfer rate in each channel [22,26].

In this paper, we study the thermoelectric behavior of double strand DNA (G:C)–(T:A)$_n$–(G:C)$_3$. High ZT values and Seebeck coefficients are found and they increase with the DNA length at room temperature. The result suggests that double-strand DNA can be a very good thermoelectric material for efficient energy conversion devices. Our analysis is also suitable for other molecule wires with similar structures.

---

* Corresponding author at: College of Physics, Optoelectronics and Energy, Soochow University, Suzhou 215006, China.

E-mail address: wxf@suda.edu.cn (X.-F. Wang).

http://dx.doi.org/10.1016/j.orgel.2015.07.043
1566-1199/

2. Models and methods

We consider a DNA duplex chain of N Waston–Crick base-pairs connected to four semi-infinite 1D electrodes with one for each end of the first and the second strand as illustrated in Fig. 1. Holes in the highest occupied molecular orbit (HOMO) states usually work the carriers responsible for charge transfer in DNA. The tight-binding Hamiltonian of the system reads

$$\begin{aligned} H = \; & 2\sum_{s=-\infty}^{\infty}[\varepsilon_s c_s^\dagger c_s - t_{s,s+1}(c_s^\dagger c_{s+1} + c_{s+1}^\dagger c_s)] \\ & +2\sum_{s=-\infty}^{\infty}[u_s d_s^\dagger d_s - h_{s,s+1}(d_s^\dagger d_{s+1} + d_{s+1}^\dagger d_s)] \\ & -2\sum_{s=1}^{N}\lambda_s(c_s^\dagger d_s + d_s^\dagger c_s) \end{aligned}$$

Here $c_s^\dagger$ ($d_s^\dagger$) is the creation operator of holes in the first (second) strand on site s of the DNA chain (for $1 \leqslant s \leqslant N$), the left electrodes ($s \leqslant 0$), and the right electrodes ($s \geqslant N+1$). The on-site energy of site s in the first (second) strand is denoted by ε_s (u_s), which is equal to the HOMO energy of the base on this site in the DNA chain or the center of conduction band in the electrodes. The coupling parameter of the first (second) strand $t_{s,s+1}$ ($h_{s,s+1}$) is equal to the intrastrand coupling parameter t_d between neighboring sites s and $s+1$ of the DNA for $1 \leqslant s \leqslant N-1$, one-fourth of the conduction bandwidth in the electrodes t_m for $s \leqslant -1$ and $s \geqslant N+1$, and the coupling strength t_{dm} between the electrodes and the DNA strands for $s = 0$ and $n = N$. The interstrand coupling between sites in the same Watson–Crick base pair is described by λ_s. The factor 2 multiplied to each sum in the Hamiltonian arises from the spin degeneracy.

The transport properties can be evaluated by the transfer matrix method [28–30]. For an open system, the secular equation is expressed as a group of infinite number of equations of the form

$$\begin{aligned} & t_{s-1,s}\Psi_{s-1} + (\varepsilon_s - E)\Psi_s + \lambda_s\Psi_s + t_{s,s+1}\Psi_{s+1} = 0 \\ & d_{s-1,s}\Phi_{s-1} + (u_s - E)\Phi_s + \lambda_s\Phi_s + h_{s,s+1}\Phi_{s+1} = 0 \end{aligned}$$

with Ψ_s (Φ_s) the wave function of the first (second) strand on site s. The wave functions of the sites $s+1$ and s are related to those of the sites s and $s-1$ by transfer matrix $\hat{M}$,

$$\begin{pmatrix} \Psi_{s+1} \\ \Phi_{s+1} \\ \Psi_s \\ \Phi_s \end{pmatrix} = \hat{M}\begin{pmatrix} \Psi_s \\ \Phi_s \\ \Psi_{s-1} \\ \Phi_{s-1} \end{pmatrix},$$

with

$$\hat{M} = \begin{bmatrix} \frac{(E-\varepsilon_s)}{t_{s,s+1}} & \frac{-\lambda_s}{t_{s,s+1}} & \frac{-t_{s-1,s}}{t_{s,s+1}} & 0 \\ \frac{-\lambda_s}{t_{s,s+1}} & \frac{(E-\varepsilon_s)}{h_{s,s+1}} & 0 & \frac{-h_{s-1,s}}{h_{s,s+1}} \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$$

The transmission can be calculated by assuming the plane waves propagating in the electrodes. Here we are interested in the DNA of sequence (G:C)–(T:A)$_n$–(G:C)$_3$ as used in one of the experiments. Because the HOMO energy of base G is much lower than that of base C at the ends of the DNA, the charge transfer between the DNA and the electrodes via base C is negligible and we neglect electrodes L$_2$ and R$_2$. Holes are injected from electrode L$_1$ to base G in the first strand. The hole wave functions in electrode L$_1$ is $\Psi_s = (Ae^{ik_L sa} + Be^{-ik_L sa})$ $(s \leqslant 0)$ and in electrode R$_1$ is $\Psi_s = Ce^{ik_R sa}$ $(s \geqslant N+1)$. The distance between two neighboring bases along any DNA strand is $a = 3.4$ Å. We express the output wave amplitude C in terms of the input wave amplitude A and evaluate the transmission τ and conductance σ between electrodes L$_1$ and R$_1$ as

$$\tau(E) = \frac{|C|^2\sin(k_R a)}{|A|^2\sin(k_L a)} \tag{1}$$

At finite temperature the charge current through the system can be estimated by

$$I = \frac{2e}{h}\int_{-\infty}^{\infty} dE\tau(E)[f_R(E) - f_L(E)] \tag{2}$$

where $f_X = \{1 + \exp[(E-\mu_X)/(k_B T)]\}^{-1}$ denotes the Fermi–Dirac distribution function in electrode X = L or R and μ is the chemical potential. We define the voltage bias between the two electrodes $V = \mu_R - \mu_L$ and derive the linear electric conductance

$$\sigma(\mu, T) = \left.\frac{\partial I}{\partial V}\right|_{V=0} = \frac{2e^2}{h}K_0 \tag{3}$$

At low temperature we have $\sigma \cong \sigma_0\tau(\mu) = 2e^2\tau(\mu)/h$ with σ_0 the conductance quantum and $K_\nu(\mu, T) = \int dE(-\partial f/\partial\varepsilon)(E-\mu)^\nu\tau(E)$ with $\nu = 0$, 1, or 2.

The Seebeck coefficient indicates the voltage difference created by unit temperature difference between the electrodes and can be obtained by [31]

$$S(\mu, T) = -\lim_{\Delta T\to 0}\frac{\Delta V}{\Delta T} = -\frac{1}{eT}\frac{K_1(\mu, T)}{K_0(\mu, T)} \tag{4}$$

At low temperature, S is approximately proportional to the slope of conductance spectrum and the inverse of conductance at the chemical potential and reads

$$S \approx -\frac{\pi^2 k_B^2 T}{3e}\frac{\tau'(\mu)}{\tau(\mu)} \tag{5}$$

The energy-conversion efficiency of thermoelectric device, measured by the dimensionless parameter ZT, can be calculated by the following formula:

$$ZT(\mu, T) = \frac{S^2\sigma T}{\kappa_{el} + \kappa_{ph}} \tag{6}$$

where κ_{el} (κ_{ph}) is the electron (phonon) thermal conductance. A large value of ZT might result from a large value of S, a large σ, or a low thermal conductance ($\kappa_{el} + \kappa_{ph}$).

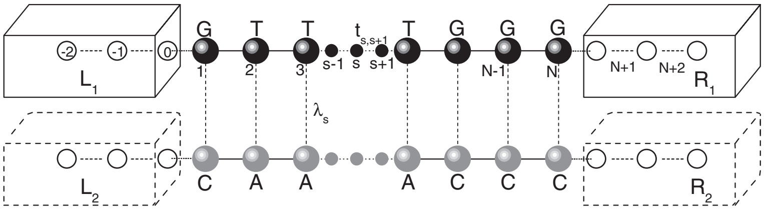

Fig. 1. Schematic illustration of the DNA ladder model. The first strand (●) has a DNA base sequence G(T)$_n$GGG and the second strand (●) a sequence C(A)$_n$CCC. The four cuboids indicate the four electrodes connected to the DNA chain.