# TERMOELECTRIC PROPERTIES OF AN ARRAY OF MOLECULAR JUNCTIONS

Karl-Heinz Müller

CSIRO Materials Science and Engineering, P.O. Box 218, Lindfield, NSW 2070, Australia
Contact author: karl.muller@csiro.au

Much progress has been made in the area of "molecular electronics" [1] where recently a more detailed understanding has been gained of the thermoelectric properties of single molecules sandwiched between macroscopic electrodes [2]. In this paper we attempt to exploit the unique thermoelectric properties of single molecules in the design of a novel material that is made up of an array of molecular junctions [3]. As shown in Fig. 1, the array of molecular junctions consists of n-doped nanocrystals that are bridged by molecules where the surfaces of the nanocrystals are partially covered with polar molecules. We have estimated by model calculations the thermoelectric properties of such an array of molecular junctions and have calculated the thermoelectric figure of merit $ZT$.

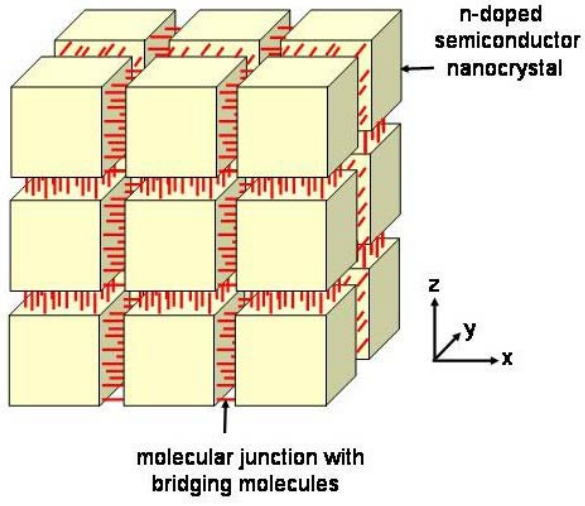


Figure 1: Schematic view of a portion of an array of molecular junctions composed of n-doped semiconductor nanocrystals linked by organic bridging molecules. The nanocrystal surfaces are partially covered with polar molecules.

The figure of merit $ZT$ of a material is given by

$$ZT = \frac{S^2 G}{\kappa} T \quad . \qquad (1)$$

Here $S$ is the material's Seebeck coefficient, $G$ and $\kappa$ the electrical and thermal conductances and $T$ the average temperature. If the temperature drops along the x-direction (Fig. 1), the material can be viewed as being made up of equal building-blocks (BB), where each building block consists of a nanocrystal and a molecular junction in series. If there are L nanocrystals along the x-direction, M along the y-direction and K along the z-direction, then $G = K\,M\,G_{BB}/L$ and $\kappa = K\,M\,\kappa_{BB}/L$. Because $S = S_{BB}$ one finds for the figure of merit

$$ZT = \frac{S_{BB}^2\, G_{BB}}{\kappa_{BB}}\, T \quad . \qquad (2)$$

The building-block conductances $G_{BB}$ and $\kappa_{BB}$ are $G_{BB} = G_C G_J / (G_C + G_J)$ and $\kappa_{BB} = \kappa_C \kappa_J / (\kappa_C + \kappa_J)$, where $G_C$ and $\kappa_C$ are the nanocrystal conductances and $G_J$ and $\kappa_J$ the conductances of a molecular junctions. For the building-block Seebeck coefficient $S_{BB}$ one finds $S_{BB} = (S_C/\kappa_C + S_J/\kappa_J)/(\kappa_C^{-1} + \kappa_J^{-1})$.

For a molecular junction that contains $m$ bridging molecules in parallel, the thermoelectric properties of a molecular junction can be expressed in terms of the thermoelectric properties of its individual bridging molecules. One finds

$$S_J = \sum_{i=1}^{m} S_i\, G_i \;/\; G_J \qquad (3)$$

and

$$G_J = \sum_{i=1}^{m} G_i \quad , \quad \kappa_J = \sum_{i=1}^{m} \kappa_i \quad . \qquad (4)$$

Here $S_i$, $G_i$ and $\kappa_i$ refer to the individual single bridging molecules indexed $i$, and $\kappa_i = \kappa_{e,i} + \kappa_{ph,i}$ where $\kappa_{e,i}$ is the electronic thermal conductance and $\kappa_{ph,i}$ the phononic thermal conductance of a single molecule. Equations (3) and (4) were derived relying on a classical treatment.

In order to calculate $S_i$, $G_i$ and $\kappa_{e,i}$ of a single bridging molecule, we employ the non-equilibrium Green's function theory for electrons from which we obtain expressions for the electrical current $I_{e,i}$ through a bridging molecule. Using a ballistic approach and assuming non-interacting electrons in the nanocrystals and non-interacting electrons in the bridging molecule one obtains [4]

$$I_{e,i} = \frac{2e}{h} \int d\varepsilon \; t_i(\varepsilon) \, [\, f_L(\varepsilon) - f_R(\varepsilon) \,] \quad . \qquad (5)$$

Here $e$ is the electron charge ($e<0$), $h$ the Planck constant, $t_i(\varepsilon)$ the electron transmission coefficient which is a function of the single electron energy $\varepsilon$, and $f_{L/R}$ are the electron Fermi distributions in the nanocrystals to the left (L) and right (R) of a junction. Introducing the functions

$$L_k = \frac{2}{h} \int d\varepsilon \; t_i(\varepsilon) \, (-\frac{\partial f}{\partial \varepsilon})(\varepsilon - \mu)^k \quad , \quad k = 0,1,2 \qquad (6)$$

where $\mu$ is the electron Fermi level, the quantities $S_i$, $G_i$ and $\kappa_{e,i}$ can be expressed in terms of the $L_k$'s as [5, 6]

$$S_i = \frac{1}{eT} \frac{L_1}{L_0} \; , \; G_i = e^2 \, L_0 \; , \; \kappa_{e,i} = \frac{L_2 - L_1^2 / L_0}{T} \qquad . \qquad (7)$$

According to the non-equilibrium Green's function formalism, the transmission coefficient is given by

$$t_i = 4 \; Tr \{ \; \mathrm{Im}\, \mathbf{\Sigma}_L \; \mathbf{G}^+ \; \mathrm{Im}\, \mathbf{\Sigma}_R \; \mathbf{G} \; \} \qquad (8)$$

where $Tr$ is the trace, $\mathbf{\Sigma}_{L/R}$ the electron self-energy operator of the left (L) or right (R) nanocrystal and $\mathbf{G}$ is the electron Green's function operator, which describes the electron propagation along a bridging molecule. The electron Green's function operator is given by

$$\mathbf{G} = (\boldsymbol{\varepsilon} - \mathbf{H} - \mathbf{\Sigma}_L(\varepsilon) - \mathbf{\Sigma}_R(\varepsilon))^{-1} . \qquad (9)$$

Here $\mathbf{H}$ is the single electron Hamiltonian describing the bridging molecule. In order to evaluate $\mathbf{\Sigma}_{L/R}$, the surface Green's function of the nanocrystals has to be evaluated. By choosing a simple electron tight-binding description [7] one finds that only the (1,1) and (N,N) matrix elements of $\mathbf{\Sigma}_{L/R}$ are needed where 1 denotes the most left atom and N the most right atom of the bridging molecule. Assuming symmetric coupling of the bridging molecules to the left and right nanocrystals one finds for $\varepsilon > \varepsilon_{CB}$

$$(\mathbf{\Sigma}_L(\varepsilon))_{11} = (\mathbf{\Sigma}_R(\varepsilon))_{NN} \approx -t_C^2 \sqrt{\varepsilon - \varepsilon_{cb}} \qquad (10)$$

where $\varepsilon_{CB}$ is the conduction band edge of the semiconductor nanocrystals, and $t_C$ is the coupling parameter (tight-binding transfer integral) which is approximately the bond strength between an end atom of the bridging molecule and a surface atom of the nanocrystals. The complete formula for $(\mathbf{\Sigma}_L(\varepsilon))_{11}$ is given in ref. [3].

The electron Hamiltonian $\mathbf{H}$ in Eq. (9) contains the on-site energies, the nearest neighbor interactions and an electrostatic Coulomb term $e\Phi_i(\vec{r})$. This term describes the interaction between electrons along the

bridging molecule $i$ with the charges on the polar molecules that are attached to the surfaces of the nanocrystals. One finds that $e\Phi_i(\vec{r}) \approx p/d$ where $p$ is the polar molecule dipole moment and $d$ the dipole length. This Coulomb interaction is essential to our model as it acts like a "gate-voltage" that shifts the HOMO resonances of the bridging molecules upwards above the conduction band edge $\varepsilon_{CB}$ of the nanocrystals (see Fig. 2), resulting in large electrical conductance values $G_i$ for the bridging molecules [3]. Charge polarization in the nanocrystals, caused by the surface polar molecules, was taken into account in the form of an image potential.

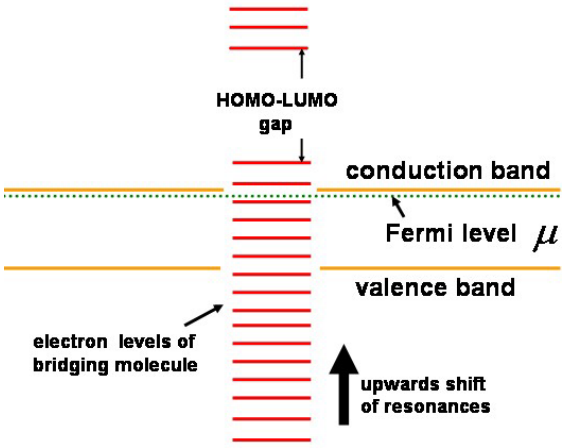


Figure 2: Electron energy diagram showing the molecular resonances shifted upwards into the conduction band of the nanocrystals due to the repulsive interaction with surface polar molecules.

To calculate $e\Phi_i(\vec{r})$, the two opposing surfaces of a molecular junction were covered by a fraction $\eta_P$ with polar molecules where sites were chosen at random on a 2D square surface lattice. The fraction of bridging molecules is $\eta_B$ and $\eta_P + \eta_B \leq 1$. The randomness in site occupations of polar molecules and bridging molecules means that bridging molecules are exposed to different interactions $e\Phi_i(\vec{r})$ causing different molecular resonance shifts. This leads to different $S_i$, $G_i$ and $\kappa_{e,i}$ values for different bridging molecules.

The results shown in the following are for room temperature, $T = 300\,\mathrm{K}$. Figure 3 shows the thermoelectric figure of merit $ZT$ of an array of molecular junctions where the nanocrystals are n-doped silicon and the bridging molecules are trans-polyacethylene molecules with 20 carbon atoms attached to (100) silicon surfaces. The n-doping level is taken such that $(\mu - \varepsilon_{CB})/kT = -2$. The dipole moment of the polar molecules is $p = 6$ Debye with a dipole length of $d = 0.3$ nm, and the coverage of polar molecules is $\eta_P = 0.7$.

Figure 3 shows that $ZT$ decreases with increasing coverage $\eta_B$ of the bridging molecules because for larger coverage the electrical conductance $G_{BB}$ is not only determined by the junction molecules but also by the nanocrystals. Values for $S_C$, $G_C$ and $\kappa_C$ of the n-doped silicon nanocrystals that are needed to evaluate $S_{BB}$, $G_{BB}$ and $\kappa_{BB}$, were taken from experimental data [8, 9]. Figure 3a indicates that $ZT > 1$ can be achieved if the phononic thermal conductance $\kappa_{ph,i}$ of a single bridging molecule is less than about $3 \times 10^{-12}\,\mathrm{W/K}$. As shown in Fig. 3b, increasing the coupling strength to $t_C = -5\,\mathrm{eV}$ results in $ZT > 1$ if $\kappa_{ph,i} < 3 \times 10^{-11}\,\mathrm{W/K}$ and the model calculation predicts a large value of $ZT \approx 10$ for $\kappa_{ph,i} < 10^{-12}\,\mathrm{W/K}$.

Finally, Fig. 4 shows the power factor $S_{BB}^2 G_{BB}/l$ as a function of the position of the Fermi level. The power factor increases with coverage $\eta_B$ because the electrical conductance $G_{BB}$ increases. The very low bridging molecule coverage value of $\eta_B = 6 \times 10^{-3}$ in Fig. 4 corresponds to only one bridging molecule per junction.

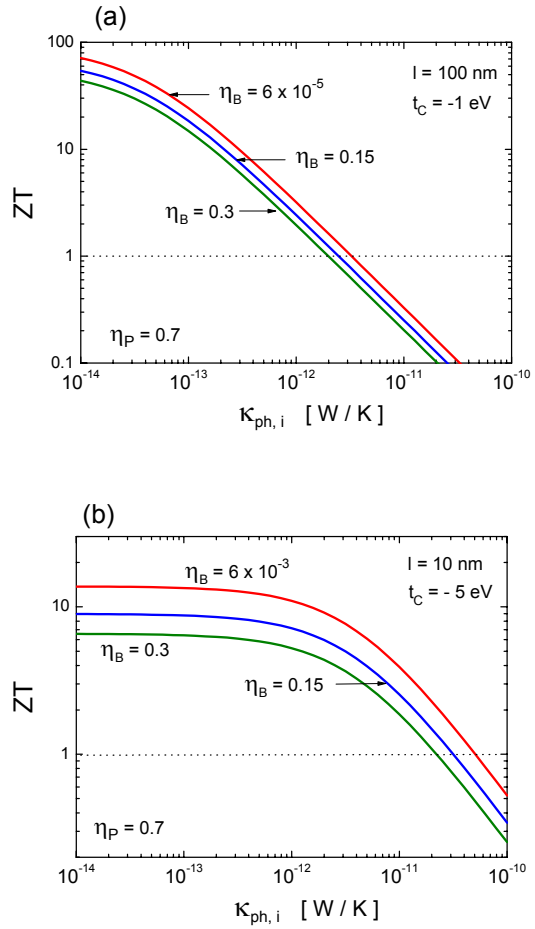


Figure 3: $ZT$ versus the phononic thermal conductance $\kappa_{ph,\,i}$ of a bridging molecule for different bridging molecule coverages $\eta_B$. The nanoparticle size $l$ and coupling strength $t_C$ are different in (a) and (b) as given in the figures.

Our model calculation demonstrates that very large $ZT$ values can be achieved as long as the phononic thermal conductance of the bridging molecules is sufficiently small. Recent calculations by us, using the method proposed in ref. [10], indicate that the phononic thermal conductance of a single molecule can be made rather small by choosing non-matching phonon spectra for the bridging molecule and the nanocrystals, and by choosing appropriate bending and stretching force constants between the end atoms of the bridging molecules and the atoms on the surface of the nanocrystals. Self-assembly methods

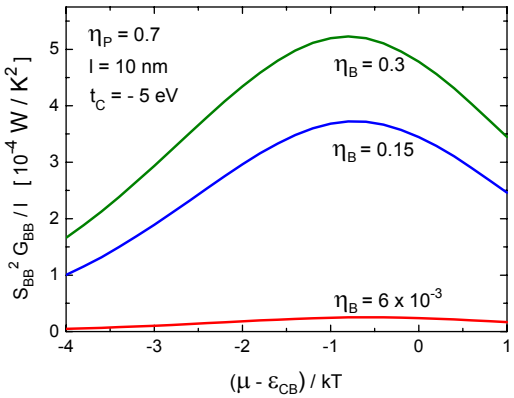


Figure 4: Power factor versus the Fermi level for different coverage of bridging molecules.

would appear most likely to allow synthesis of such a material [11].

References:


1. Heath, J.R. and Ratner, M.A., Physics Today 56 (2003) 43.
2. Reddy, P., Jang, S.-Y., Segalman, R. and Majumdar, A., Science 315 (2007) 1568.
3. K.-H. Müller, J. Chem. Phys. 2008 (in press).
4. Meir, Y. and Wingreen, N.S., Phys. Rev. Lett. 68 (1992) 2512.
5. Ashcroft, N.W. and Mermin, N.D., *Solid Sate Physics* (Holt, Rinehart and Winston, New York, 1995).
6. Esfarjani, K., Zebarjadi, M. and Kawazoe,Y., Phys. Rev. B 73 (2006) 085406.
7. Asai,Y. and Fukuyama, H., Phys. Rev. B 72 (2005) 085431.
8. Pierret, R.F., *Semiconductor Device Fundamentals* (Addison-Wesley, 1996).
9. Brinson, M.E. and Dunstan, W., J. Phys. C: Solid State Phys. 3 (1970) 483.
10. Ozpineci, A. and Ciraci, S., Phys. Rev. B 63 (2001) 125415.
11. Raguse, B., Herrmann, J., Stevens, G., Myers, J., Baxter G., Müller, K.-H., Reda, T., Molodyk, A. and Braach-Maksvytis, V., J. Nanoparticle Res. 4 (2002) 137.