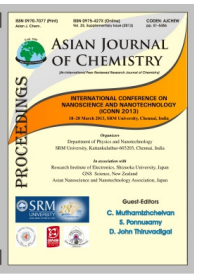
Asian Journal of Chemistry; Vol. 25, Supplementary Issue (2013), S445-S448

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Effect of Different Metallic Electrodes on Transport Properties of a Carbon-Dimer Based Molecular Devices†

R.M. HARIHARAN and D. JOHN THIRUVADIGAL*

Center for Materials Science and Nanodevices, Department of Physics and Nano Technology, SRM University, Kattankulathur, Chennai-603 203, India

*Corresponding author: Tel: +91 44 27417835 Extn-2751; E-mail: john.d@ktr.srmuniv.ac.in

AJC-12901

By using non-equilibrium Green's function in combination with density functional theory, we study the electronic transport properties of carbon dimer with two different anchoring atoms Se and N sandwiched between various metallic electrodes made of different metals such as Au, Ag and Pt. The electron transport of the molecular system is systematically studied by analysis of transmission function and current-voltage characteristics of the systems. The results exhibit that, depending on metallic electrodes and the anchoring groups the current varies considerably under the same bias. We find that Ag and Pt make better electrical electrodes for Se and N anchoring atom than Au. The zero-bias conductance is found to be greatest for Ag, followed by Pt than Au for Se and N anchoring atom. Thus it reveals the importance of electrodes in molecular devices.

Key Words: Electrode effect, Electronic transport, First-principle, I-V Characteristics, Transmission spectra.

INTRODUCTION

Over the past decade, molecular devices have received significant attention owing to their great potential practical applications in atomic-scale circuits[1]. Many interesting physical properties of molecular devices have been predicted theoretically and verified experimentally, such as single-electron characteristics[2], negative differential resistance (NDR)[3,4], molecular rectification[5] and field-effect characteristics[6], *etc*. An important objective in molecular electronics is to study and control electron transport through a molecule attached to two electrodes. From the first-principles calculations, it is clear that the chemical nature of the metal electrodes may have strong effect on the conductance of a molecular junction. Hence, in studying the electron transport properties through a single molecule, it is important to design an appropriate molecule-electrode contact, because the contact plays a decisive role on the electron transport process through the molecule[7,8]. One way to optimize the molecule-electrode contacts is to select supreme metallic electrode and anchoring group at the two ends of a molecule so that they can bind to the electrodes and in the meantime, provide efficient electronic coupling between the molecule and the electrodes[9]. Gold is known to make good chemical contact with the thiol end groups but the ρ of Au is relatively low because of its sp state characteristics. Therefore, the Au-S bond is not always the best anchoring group for the single molecular junction with high conductivity. It is important to develop a pair of metals group other than Au-S to establish highly conductive single molecular-junctions[10]. Therefore, the extensive and profound understanding of these effects in molecular devices is quite necessary. Using DFT + NEGF method, Zeng *et al.*[11] performed transport calculations on carbon dimer sandwiched between Au electrodes, with anchoring groups, H, Cu and S.

In this present work, we focus our concentration on the effect of electrode in molecular devices. Specifically, we study the transport properties of a carbon-dimer C_2 cluster sandwiched between different metallic electrodes such as Au, Ag and Pt[12-16]. The anchoring groups connecting the cluster and the electrodes are chosen as the atoms Se and N respectively. Thus, equivalently, we study the transport properties of two different molecules C_2Se_2 and C_2N_2, sandwiched between three different metallic electrodes Au, Ag and Pt. These six systems are denoted as Au/C_2Se_2/Au, Ag/C_2Se_2/Ag, Pt/C_2Se_2/Pt, Au/C_2N_2/Au, Ag/C_2N_2/Ag and Pt/C_2N_2/Pt respectively. Reason for choosing selenium and nitrogen as anchoring atoms, are because they serve as efficient alligator clip other than sulfur[17-19]. In this paper we show that junctions with different metal electrodes result in qualitatively different conduction characteristics.

†International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

Modeling and method

The simulation model adopted in this work is presented: a C_2 molecule is sandwiched between two Au(III) bulk electrodes *via* different anchoring atoms. In the present work, the central sandwiched molecules are C_2Se_2 and C_2N_2, which are all linear and symmetrical molecules. The C-C and C-Se bond lengths in C_2Se_2 molecule and C-C and C-N bond lengths in C_2N_2 molecule are obtained by fully optimizing the respective molecules. For the left and right electrodes, we select a 3 × 3 unit cell in the x and y directions to avoid the interaction between the molecules and their mirror images. The terminating atoms of the molecules are located symmetrically at the hollow sites above the Au(III), Ag(III) and Pt(III) surface respectively. By full optimization, we obtain the equilibrium distances between the central molecules and the electrodes.

In the NEGF theory, the transmission function T (E, V)[20] of the system is the sum of transmission probabilities of all channels available at energy E under external bias voltage V:

$$T(E,V) = Tr[\Gamma_L(E,V)G^R(E,V)\Gamma_R(E,V)G^A(E,V)] \quad (1)$$

where $G^{R/A}$ are the retarded and advanced Green's functions and coupling functions $\Gamma_{L/R}$ are the imaginary parts of the left and right self-energies, respectively. Self-energy depends on the surface Green's functions of the electrode regions and comes from the nearest-neighbor interaction between the extended molecule region and the electrodes.

The I-V characteristics of the two probe system can be obtained by using the Landauer-Buttier formula[11], the current is the integration of the transmission function over the bias window around the Fermi level:

$$I = \frac{2e}{h}\int_{\mu_1}^{\mu_2} T(E,V)[f(E-\mu_1) - f(E-\mu_2)]dE \quad (2)$$

where T (E, V) is the transmission function through the device at energy E and funcion f (E - $\mu_{1/2}$) are the Fermi distribution functions of electrons in the left/right electrodes. $\mu_{1,2} = E_f \pm \frac{eV}{2}$ are the chemical potentials of the left/right electrodes, with μ the Fermi level of the electrodes in equilibrium and V the bias applied to the device.

Our calculations are carried out using the Atomistix Toolkit (ATK 11.8.2 version)[21] program which combines density functional theory (DFT) and non-equilibrium Green's functions (NEGF) method to simulate the transport properties of two-probe systems. The exchange-correlation functional is described by generalized gradient systems. The exchange-correlation functional is described by generalized gradient approximation (GGA) in the form of the Revised Perdew-Burke-Ernzerh (revPBE) in the present calculations. The valence wave functions are expanded by localized numerical atomic orbital (LNAO), with the single zeta plus polarization basis set (SZP) for Au, Ag and Pt element and the double zeta plus polarization basis set (DZP) for C, Se and N atoms. The Brillouin zone of the leads is sampled by 1 × 1 × 80 k points in the directions of x, y and z (z is the electron transport direction), which is enough to produce the results.

RESULTS AND DISCUSSION

The current through the optimized molecule junctions of two systems contains C_2Se_2 and C_2N_2 molecules, sandwiched between Au, Ag and Pt electrodes respectively, is calculated and presented in Fig. 1. At each bias, both electronic structure and current are determined self-consistently under the non-equilibrium condition. As can be seen from Fig. 1, the current for C_2Se_2 linearly increases with the voltage increasing from 0.0 to 2.0 V for Ag electrodes whereas it increases nonlinearly for Au and Pt electrodes. On the whole, the magnitude of the current of C_2Se_2 molecule with three different electrodes varies over more than three times of magnitude. For example, when the bias is 0.5 V, the currents are 9590 nA for Au/C_2Se_2/Au, 27914 nA for Ag/C_2Se_2/Ag and 13908 nA for Pt/C_2Se_2/Pt, respectively. In case of C_2N_2 molecule, when the bias is 0.5 V,

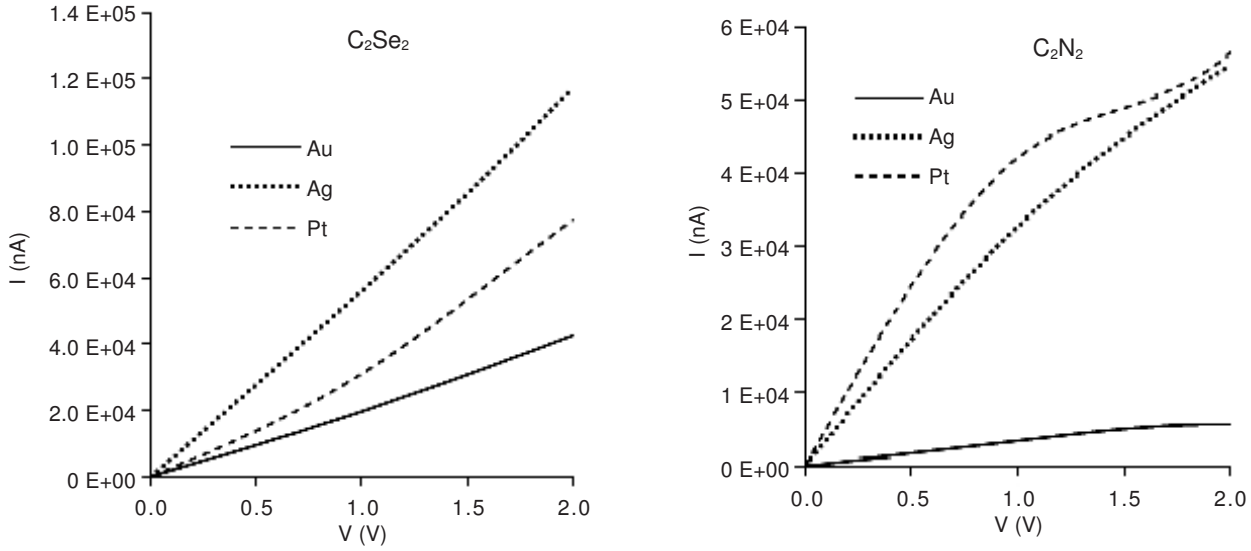


Fig. 1. The I-V characteristics of C_2Se_2 (left) and C_2N_2 (right) molecules, sandwiched between Au, Ag and Pt electrodes respectively

the currents are 1678 nA for Au/C_2N_2/Au, 17327 nA for Ag/C_2N_2/Ag and 24654 nA for Pt/C_2N_2/Pt, respectively. On the whole, the magnitude of the current of C_2N_2 molecule with three different electrodes varies over more than two times of magnitude. But at higher bias, there is very less variation in current for Ag/C_2N_2/Ag and Pt/C_2N_2/Pt. Obviously, this result is originated from the different metallic electrodes and the anchoring atoms. We show that Ag electrode has better conductance followed by Pt than Au electrodes. Therefore, in order to better understand the big difference in the I-V characteristic curves of C_2Se_2 and C_2N_2 molecules, we show the transmission spectra at zero bias for Au/C_2Se_2/Au, Ag/C_2Se_2/Ag, Pt/C_2Se_2/Pt, Au/C_2N_2/Au, Ag/C_2N_2/Ag and Pt/C_2N_2/Pt, respectively in Fig. 2. The magnitude of transmission varies greatly with electrode, which leads to the change in conductance. In the case of C_2Se_2 molecule, for Ag/C_2Se_2/Ag, there is a large platform near the Fermi level, so the current is very big when the bias voltage is applied to the device. While for Au/C_2Se_2/Au, the transmission function is characterized by small peaks which lead to the very small current. For Pt/C_2Se_2/Pt, since the Fermi level is at the tail of a big peak in the transmission spectra, its current magnitude lies between Ag/C_2Se_2/Ag and Au/C_2Se_2/Au. And in C_2N_2 molecule, for Ag/C_2N_2/Ag, magnitude of the transmission function increases greatly with an increase in the bias voltage. For Pt/C_2N_2/Pt, there are peak on the either side of the transmission spectra, so initially it has large transmission, leads to high current which decreases at higher bias. While for Au/C_2N_2/Au, the transmission function is characterized by large gap between the peaks at -2.2 eV and 0.6 eV which lead to the very small current. In order to further understand the difference in the transmission functions, density of states (DOS) for the two molecules C_2Se_2 and C_2N_2 with Au, Ag and Pt electrodes, are calculated under zero bias and shown in Fig. 3. We notice in particular that while for Au the density of states are rather flat and for Pt the density of states are small, whereas, the density of states are rapidly increasing near their Fermi energy for Ag. The higher conductance of Ag/C_2Se_2/Ag and Ag/C_2N_2/Ag is the result of a higher density of states in the adjacency of the Fermi level, than Pt and Au electrodes. These are effects imposed by the electrodes.

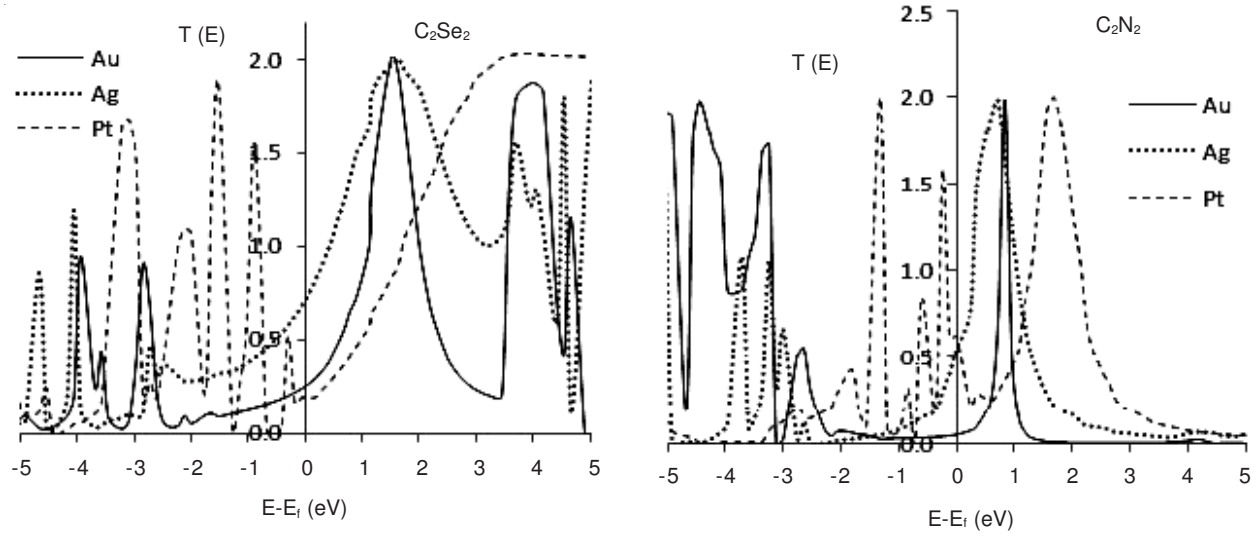


Fig. 2. Transmission spectra of C_2Se_2 (left) and C_2N_2 (right) molecules at zero bias, sandwiched between Au, Ag and Pt electrodes respectively.

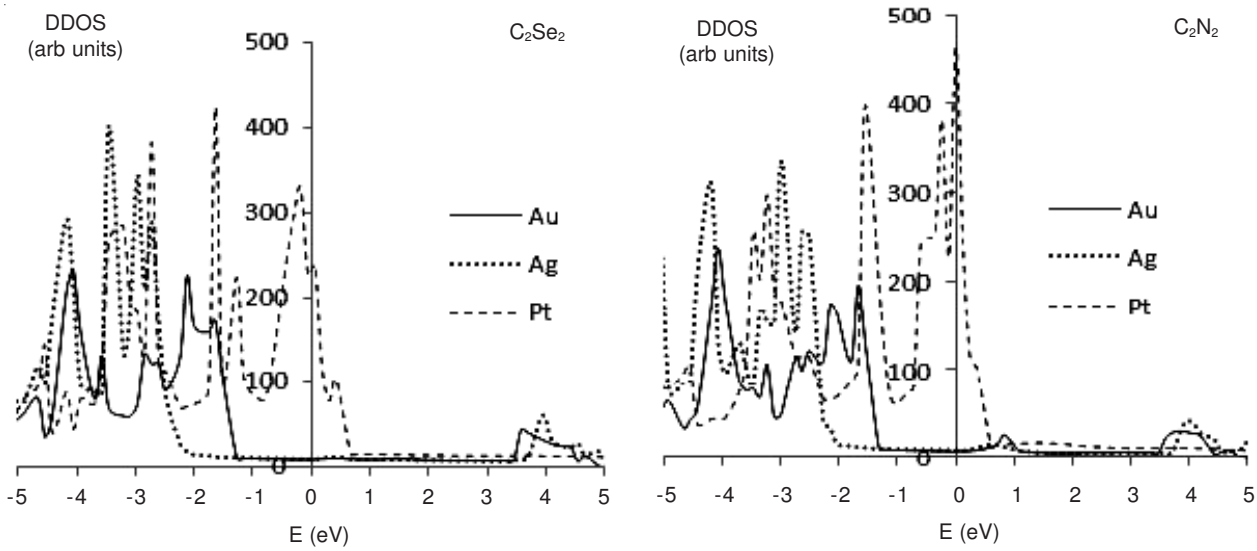


Fig. 3. Density of states spectrum of C_2Se_2 (left) and C_2N_2 (right) molecules at zero bias, sandwiched between Au, Ag and Pt electrodes respectively

Conclusion

Using the density functional theory combined with a non-equilibrium Green's function approach, the electron transport properties of molecular junctions containing carbon dimer molecule with two different anchoring groups Se and N, connected to Au, Ag and Pt electrodes were calculated. The current with Ag electrodes varies by more than two times of magnitude under the same bias range than Au electrodes, closely followed by Pt electrodes. It is, due to large transmission near the Fermi level for Ag electrodes. So the zero-bias conductance is found to be greatest for Ag, followed by Pt than Au for Se and N anchoring atom. We find that Ag and Pt make better electrical electrodes for Se and N anchoring atom than Au. Thus in this paper we investigated that changing the electrode material, would efficiently improve the characteristics of a metal-molecule-metal junction.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support for this project from DST-FIST, Government of India (Ref. No. SR/FST/PSI-010/2010).

REFERENCES

1. C. Joachim, J.K. Gimzewski and A. Aviram, *Nature*, **408**, 541 (2000).
2. H.W.C. Postma, T. Teepen, Z. Yao, M. Grifoni and C. Dekker, *Science*, **293**, 76 (2001).
3. J. Chen, W. Wang, M.A. Reed, A.M. Rawlett, D.W. Price and J.M. Tour, *Appl. Phys. Lett.*, **77**, 1224 (2000).
4. M.Q. Long, K.Q. Chen, L. Wang, B.S. Zou and Z. Shuai, *Appl. Phys. Lett.*, **91**, 233512 (2007).
5. A. Aviram and M.A. Ratner, *Chem. Phys. Lett.*, **29**, 277 (1974).
6. J. Lu, S. Yin, L.M. Peng, Z.Z. Sun and X.R. Wang, *Appl. Phys. Lett.*, **90**, 052109 (2007).
7. Y.C. Cho, W.Y. Kim and K.S. Kim, *J. Phys. Chem. A*, **113**, 4100 (2009).
8. W.T. Geng, J. Nara and T. Ohno, *Appl. Phys. Lett.*, **85**, 24 (2004).
9. M. Kiguchi, *Appl. Phys. Lett.*, **l95**, 073301 (2009).
10. F. Chen, X.L. Li, J. Hihath, Z.F. Huang and N.J. Tao, *J. Am. Chem. Soc.*, **128**, 15874 (2006).
11. R.N. Wang, X.H. Zheng, Z.X. Dai, H. Haoa, L.L. Song and Z. Zeng, *Phys. Lett. A*, **375**, 657 (2011).
12. J.W. Lawson and C.W. Bauschlicher Jr, *Phys. Rev. B*, **74**, 125401 (2006).
13. C.-H. Ko, M.-J. Huang, M.-D. Fu and C.-H. Chen, *J. Am. Chem. Soc.*, **132**, 756 (2010).
14. S. Jalili and A. Pangh, *Int. J. Mod. Phys. B*, **23**, 5657 (2009).
15. C.F. Fang, B. Cui, Y.Q. Xu, G.M. Ji, D.S. Liu and S.J. Xie, *Phys. Lett. A*, **375**, 3618 (2011).
16. G.H. Ma, L.L. Sun, R.X. Zhang, Z.Y. Shen and S.M. Hou, *Chem. Phys.*, **375**, 67 (2010).
17. J.M. Seminario, A.G. Zacarias and J.M. Tour, *J. Am. Chem. Soc.*, **121**, 411 (1999).
18. M.-J. Li, H. Xua, K.-Q. Chen and M.-Q. Long, *Phys. Lett. A*, **376**, 1692 (2012).
19. S. Jalili and R. Ashrafi, *Physica E*, **960**, 43960 (2011).
20. Y.-P. An, Z.Q. Yang and M.A. Ratner, *J. Chem. Phys.*, **135**, 044706 (2011).
21. Atomististix Tool Kit Version 11.2.8, www.quantumwise.com.