



Communication

Enhancing and optimizing electronic transport in biphenyl derivative single-molecule junctions attached to carbon nanotubes electrodes

J.C. Reis-Silva^{a,b}, D.F.S. Ferreira^{a,b}, J.F.P. Leal^{b,*}, F.A. Pinheiro^c, J. Del Nero^{d,e}^a Pós-Graduação em Engenharia Elétrica, Universidade Federal do Pará, 66075-900 Belém, PA, Brazil^b Departamento de Ciências Naturais, Universidade do Estado do Pará, 68745-000 Castanhal, PA, Brazil^c Instituto de Física, Universidade Federal do Rio de Janeiro, 21941-972 Rio de Janeiro, RJ, Brazil^d Departamento de Física, Universidade Federal do Pará, 66075-110 Belém, PA, Brazil^e Department of Physics and Quantum Theory Project, University of Florida, 32611 Gainesville, FL, USA

ARTICLE INFO

Keywords:

A. Carbon nanotubes electrodes

A. Phenyl derivatives

C. NEGF/DFT methodology

D. Enhanced transport property

ABSTRACT

We investigate, by means of *ab initio* calculations based on non-equilibrium Green's function method coupled to density function theory, electronic transport in molecular junctions composed of biphenyl (BP) and biphenyl within (-2H⁺) defect (BP2D) molecules attached to metallic (9,0) carbon nanotubes. We demonstrate that the BP2D junction exhibits unprecedented electronic transport properties, and that its conductance can be up to three orders of magnitude higher than biphenyl single-molecule junctions. These findings are explained in terms of the non-planar molecular conformation of BP2D, and of the stronger electronic coupling between the BP2D molecule and the organic electrodes, which confers high stability to the junction. Our results suggest that BP2D attached to carbon nanotubes can be explored as an efficient and highly stable platform in single-molecule electronics with extraordinary transport properties.

1. Introduction

Since the pioneer work by Aviram and Ratner, understanding and optimizing electronic transport properties of single molecules attached to electrodes has been a major challenge to the implementation of molecular scale electronics [1,2]. In the past decade, intense theoretical and experimental work has shown that this is a complex task, as the transport characteristics in single-molecule junctions depend on many factors: the intrinsic molecular properties, such as their geometrical conformation and length, the nature and details of the contacts, environment (e.g. temperature, stress, UHV), the energy gap between the HOMO and the LUMO, and the relative position of this gap to the contact's Fermi level. The precise control of all these factors is usually difficult, so that the majority of experiments in single-molecule transport recur to a statistical treatment [3–9]. One important strategy to extract information about single-molecule junctions from ensemble measurements is that of “molecular families”, in which a systematic variation of a single element of the junction (e.g. molecular length and conformation, electronic structure, anchoring group) is carefully performed and analyzed (see Ref. [10] and references therein).

Among all these parameters the nature of the contacts is crucial for stability of the single-molecule junctions. This fact has motivated intense research on the various “clip-alligator” molecules that are

employed to attach the central molecule to the electrodes [11–14]. In order to obtain better electronic coupling to the leads, organic electrodes have been proposed. Probably the most successful example is the carbon nanotube (CNT). Indeed, CNTs have been demonstrated to be an ideal material for electrodes in single-molecule devices [15–17], as they exhibit many advantages in comparison to ordinary metallic contacts: they show higher conductivity [18], allow for better contact to organic molecules [17], and reduce the screening of the gate electric fields due their smaller size [16]. In addition, recent advances in nanofabrication techniques permit a precise control of the gap size in between the CNT leads [19], which is crucial in the development of single-molecule junctions. For these reasons single-molecule junctions with CNTs as electrodes have been recently addressed [20,21].

The aim of the present paper is to theoretically investigate novel single-molecule junctions attached to CNTs in order to obtain large electrical conductivity with high electronic stability [20–23]. In particular we have focus on biphenyl (BP) and biphenyl within (-2H⁺) defect (BP2D) molecules attached to all symmetrical single-wall (9,0) CNTs. In contrast to previous studies on similar systems (metal-biphenyl derivative-metal) [9,10,24–27], we consider metallic CNT contacts, i.e. all-organic electrodes constituted by the same chemical species (carbon) as the molecular bridge. By means of Density Functional Theory calculations coupled with Non-Equilibrium Green's Functions (DFT

* Corresponding author.

E-mail address: jfpleal@uepa.br (J.F.P. Leal).

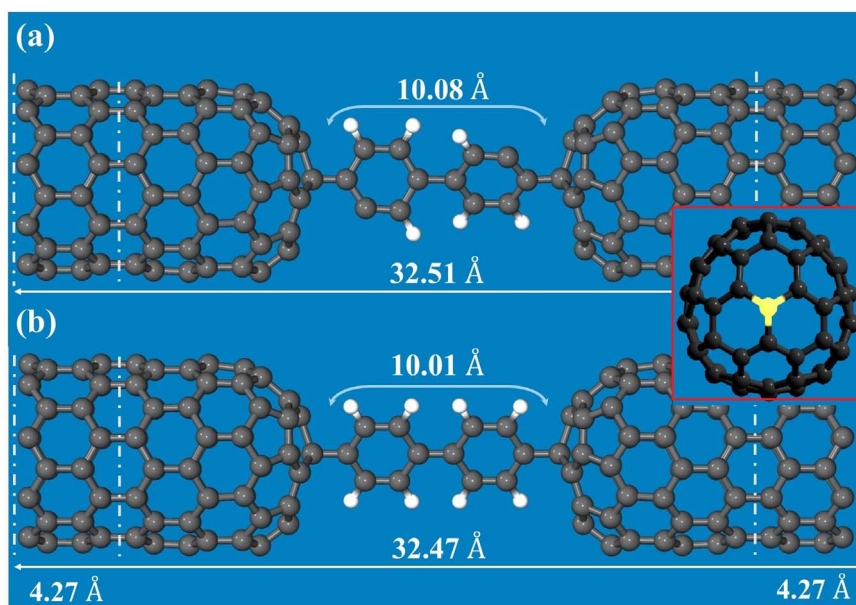


Fig. 1. All-symmetrical metallic (9,0) carbon nanotubes (CNTs) as contact attached to (a) biphenyl within (-2H⁺) defect (BP2D) and to (b) biphenyl (BP) molecule. The bond between CNT and biphenyl is done exactly in the central Carbon atom. In inset is presented the view of end-capped all-symmetrical metallic (9,0) carbon nanotube. The color difference (online version) is only a guide-view and all atoms represent Carbon atoms. The biphenyl bond in the central Carbon atom (yellow) is shown. Also, the diedral angle between phenyl rings are $\approx 43^\circ$ and $\approx 0^\circ$ for BP2D and BP, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

+NEGF) formalism, we investigate electronic transport in BP and BP2D junctions to demonstrate that conductance in the BP2D junction can be up to three orders of magnitude higher than biphenyl ones. These findings are explained in terms of the non-planar molecular conformation of BP2D, and of the stronger electronic coupling between the BP2D molecule and the organic electrodes.

This paper is organized as follows. In Section 2 we describe the electronic transport calculations and detail the methodology used. Section 3 is devoted to the main results and discussions, whereas Section 4 is reserved for the conclusions.

2. Methodology

The 6–311G** basis set was implemented in DFT B3LYP level [28–31] for junctions optimization presented in Fig. 1 to find the ground state in molecules attached (or not) to carbon nanotubes [32].

Full geometric optimization were utilized, resulting in a diedral distortion $\approx 43^\circ$ and $\approx 0^\circ$ for BP2D and BP conformations, respectively. The electric current is calculated by means of Non-Equilibrium Green's (NEGF) functions formalism coupled to *ab initio* though the molecular junction after the ground state optimization [22]; a calculations utilizing similar transport procedure has been performed out in Ref. [33–35].

The atoms from the leads into a semi-infinite region were translated by modeling the molecular junction with DFT. The BP molecule has 20 atoms and BP2D molecule has 18 atoms (but both systems are the same number of electrons. The difference raises in the two removed hydrogen protons); whereas carbon nanotubes has 103 atoms in each sides. Hence the supercell consists of molecule bridging the gap between two all-symmetrical metallic (9,0) carbon nanotubes electrodes.

The gap value is set in 1.50 Å and after optimization the final result shows small difference and it is as: 1.46 Å and 1.48 Å, respectively. Double- ζ + polarization basis set was utilized for all atoms of the junction with a norm-conserving pseudo-potentials and local density approximation [33–35]. The optimization process was very tight permitting relaxation in all atoms including a force field less than 0.10 eV/Å.

To achieve self-consistency in electric transport calculation is necessary to calculate the charge density through the integration of scattering states between left and right chemical potentials. The temperature is adjusted to 300 K. The optimization process by self-consistency is reached after relaxing charge density maps. The electric current is calculated using NEGF method by applying bias between leads after complete molecular relaxation. The current through all system is given by Landauer-Buttiker/Keldish equation [36–38]:

$$I(V_e, \theta) = \frac{2e}{h} \int_{U_L}^{U_R} T(E, V_e, \theta) f(E)_{RL} dE, \quad (1)$$

where $T(E, V_e, \theta)$ is the transmission coefficient at energy E and at torsion angle θ ; $f(E)_{RL}$ is the difference between the Fermi-Dirac functions of the right and left electrodes with $f(E)_{R/L} = \left[1 + e^{\frac{E - \mu_{R/L}}{k_B T}}\right]^{-1}$ and $\mu_{R/L}$ and T are the chemical potentials and electrodes temperature, respectively; $U_R(V_e)$ and $U_L(V_e)$ are the energies corresponding to the left and right leads, respectively.

3. Results and discussion

In Fig. 2 the current I and the conductance $G = dI/dV$ calculated NEGF formalism coupled to DFT, are shown as a function of the external bias V for both BP2D (panels (a)) and BP (panels (b)) junctions. Fig. 2 reveals that electronic transport is astoundingly enhanced in the case of BP2D in comparison to the case of the BP junction. Indeed, Fig. 2 demonstrates that the current is approximately three orders of magnitude larger in the BP2D case. This result shows that a molecular junction composed of a BP2D attached to carbon nanotubes, a system that at the best of our knowledge has never been considered in the context of single-molecule electronics, has unique electronic transport properties that could be applied in the development of new single-molecule junctions. In addition to high conductance, this systems is expected to be highly stable, as the molecular backbone is attached to electrodes made of the same atomic species [20–23], which offers better electric stability and does not require the employment of clip-alligator molecules to mediate the connection of junction to the (inorganic) leads, as it often the case in single-molecule

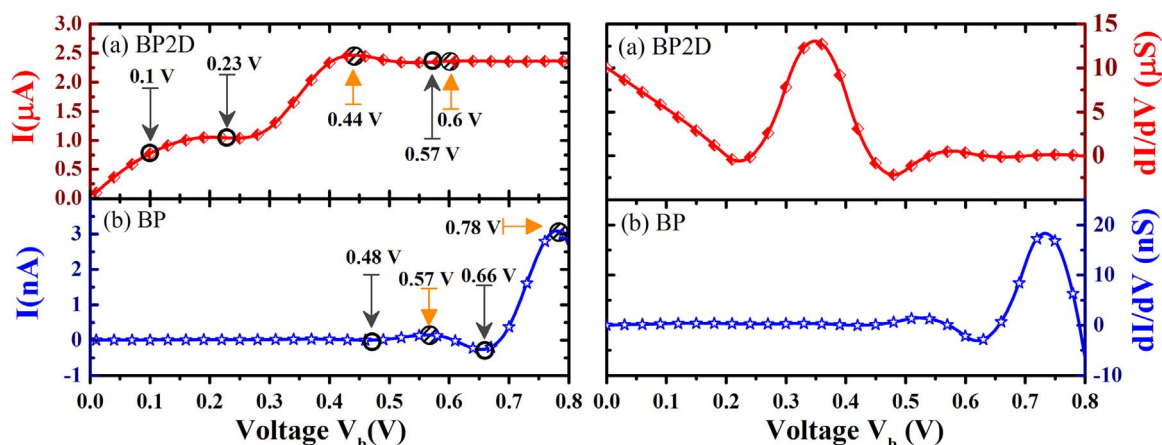


Fig. 2. (Left panel) Current vs. voltage for (a) BP2D and (b) BP presenting specific voltage values where the density of states presents significant changes. (Right panel) Conductance versus voltage for (a) BP2D showing NDR for 0.23 V and 0.47 V and (b) BP showing NDR for 0.62 V. The main difference in the behavior presented in BP and BP2D raised up when the voltage for BP reaches 0.61 V provoking changes to a negative polarization up to 0.65 V where saddle point is achieved then returning to positive polarization. In the inset is possible to see the transmission probability and density of states as a proof of preceding finds. Corroborating the transmission probability present $0.707 | \text{HOMO}-1 \rightarrow \text{LUMO} >$ and $0.011 | \text{HOMO}-3 \rightarrow \text{LUMO} + 1 >$ as main transitions for this region. This corroborate the hole as the main player for transport in these biases and the σ - π orbitals mixing is evidenced.

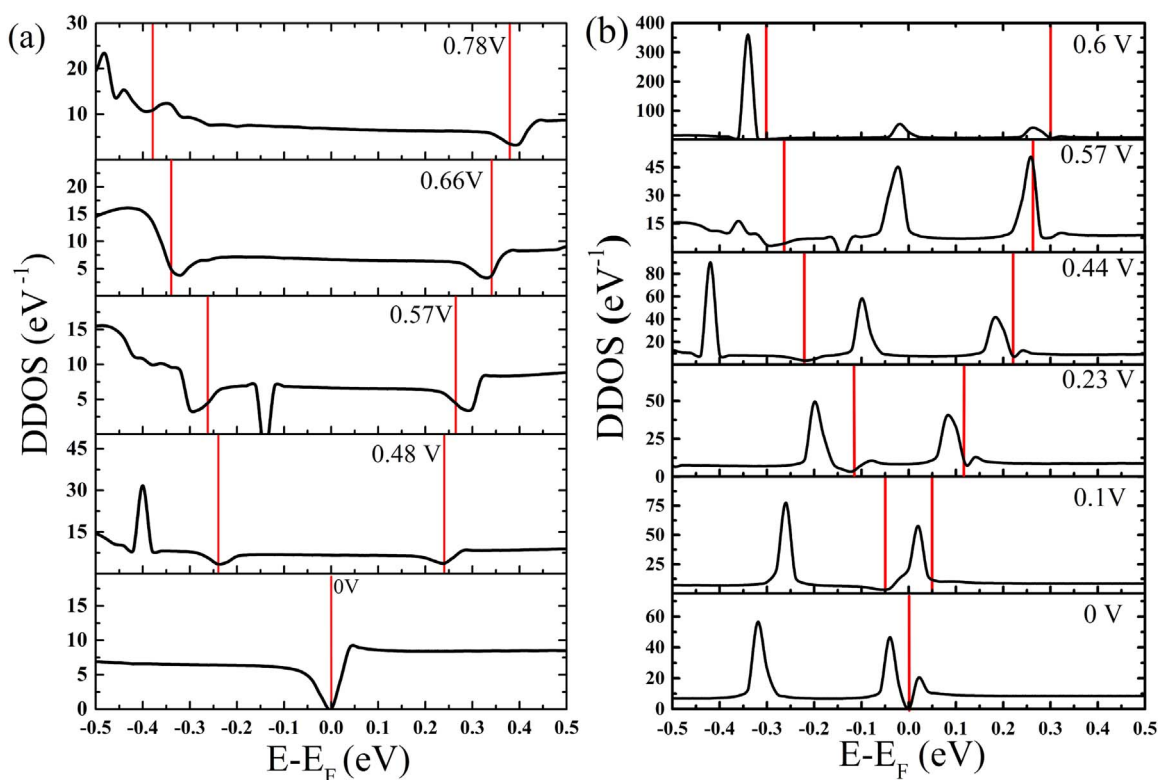


Fig. 3. The electronic density of states spectra (DDOS) for the corresponding devices presented in Fig. 1 for (a) BP2D and (b) BP. The (red) full line indicates the Fermi level position for different values of external applied bias. For BP2D three regions are detected: (i) increase of narrow band up to 0.23 V when the device reaches the resonance (by Fig. 2) provoking a new operational window; (ii) lost of states when the maximum current and conductance is obtained for 0.44 V; and (iii) creation of conduction band in the Fermi level region and a metallic regime is achieved. For BP a very different bandwidths for the Fermi level region as direct consequence between the twisted and flat geometries when compared with BP2D showing two almost symmetrical localized gap states corroborated by zero transmission probability possibility in bias window (Fig. 4). The device begins conduction process at 0.60 V and larger bands in the Fermi level region appears as well non-zero transmission probability.

electronics. Fig. 2 also shows the bias voltages for which resonances (full circles) and negative differential resistance [(NDR) dotted circles] occur, i.e. the situation where the current decreases as the bias voltage increases. The analysis of Fig. 2 reveals that the values of the bias voltage required to excite molecular resonances are generally considerably larger for the BP junction than that of the BP2D one. The evidence for this feature is clear in Figs. 3 and 4 combined as follow.

The role of resonant transport is investigated in Fig. 3, where the Density Of States (DOS) is shown as a function of energy is shown for

both BP2D and BP single-molecule junctions. Vertical red lines indicate selected values of the applied bias window. Fig. 3 confirms that different frontier molecular orbitals participate in electronic transport through the BP2D junction. Indeed, in Fig. 3(a) it is possible to identify that resonances indicated in Fig. 2 correspond to the situation where a molecular resonance of the BP2D junction enters in the bias window. In contrast, for the BP junction the excitation of molecular junctions only occurs for larger values of the bias voltages. In these cases, however, the DOS is significantly smaller than in the BP2D

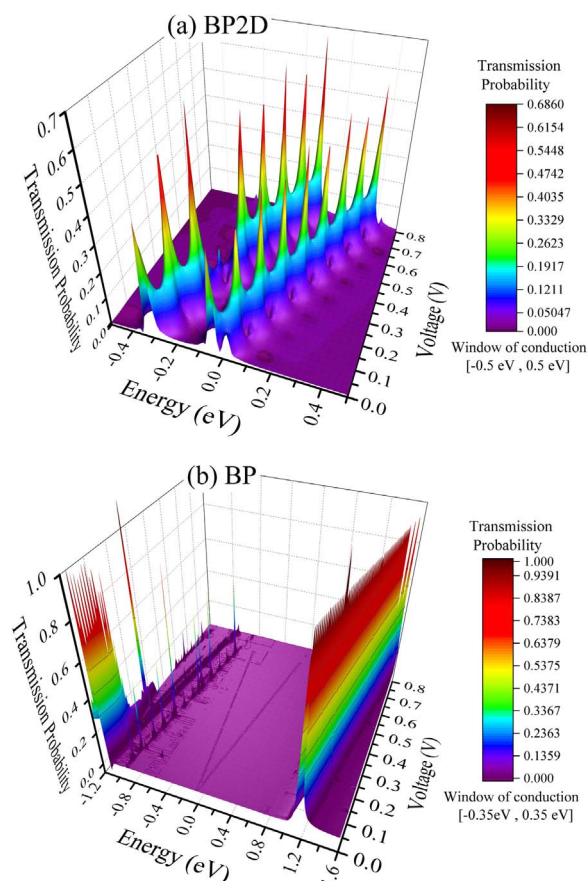


Fig. 4. (3D and 2D transmission probability for the (a) BP2D and (b) BP junctions attached in longitudinal CNTs as a function of energy for several different values of the external applied voltage V . The (yellow) arrows for 2D plot are the operational windows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

junction. In addition, in the latter case the DOS at the Fermi is significantly higher than in the BP junction for all values of the external bias considered.

In Fig. 4 the transmission probability is shown as a function of energy and external bias voltage for both the BP2D [panel (a)] and BP junctions [panel (b)]. Fig. 4(b) shows there are no transmission probability peaks within the bias window in the case of the BP junction.

In contrast, Fig. 4(a) demonstrates that several transmission probability peaks occur within the bias window, contributing to enhance electronic transport through the molecular junction. These results further explain why electronic transport in the BP2D junction is greatly enhanced in comparison to the BP one.

In order to completely characterize electronic transport properties of both systems the spatial distribution of frontier molecular orbitals are shown in Figs. 5 and 6, which corresponds to the BP and BP2D junctions, respectively. Fig. 5 shows the frontier molecular orbitals corresponding to the BP lie within the molecular backbone. On the other hand, in the BP2D junction, the frontier molecular orbitals lie out of the plane defined by the molecular backbone, as it can be seen from Fig. 6. These results are related to the different molecular conformation of these two systems, as BP2D is not a planar junction as the BP. In view of these facts, the enhanced electronic transport of the BP2D junction relative to the BP contrasts to the common belief in single-molecule electronics that transport is optimized in planar junctions [7,39,40]. In addition, Figs. 5 and 6 unveils that the electronic overlap between frontier molecular orbitals of the central region and the electrodes orbitals is much more pronounced in the BP2D junction. This result, together to the out of plane molecular conformation of the BP2D molecule, contributes to overall huge enhancement of electronic transport of this system with respect to the BP junction.

4. Conclusions

In conclusion we investigate, by means of *ab initio* calculations based on non-equilibrium Green's function method coupled to density function theory, electronic transport in molecular junctions composed of BP and BP2D molecules attached to metallic carbon nanotubes. The idea is to consider organic electrodes (Carbon atoms), which facilitates the mismatch between the Fermi level of the leads and the frontier molecular orbitals of the central molecule (Carbon atoms), dispensing the use of a clip-alligator molecule to mediate the coupling as a cooperative effect. We demonstrate that the BP2D junction has extraordinary electronic transport properties, and that its conductance can be up to three orders of magnitude higher than biphenyl single-molecule junctions. We completely characterize electronic transport processes in both junctions to conclude that these results can be explained in terms of: (i) strong electronic coupling of molecule with metallic carbon nanotubes; (ii) extended electronic overlap for LUMOs molecular orbitals and electrodes orbitals (comparing Figs. 5 and 6); (iii) Finally, these cooperative effects raise an huge increase of transmission probability (Fig. 4). Our findings pave the way for

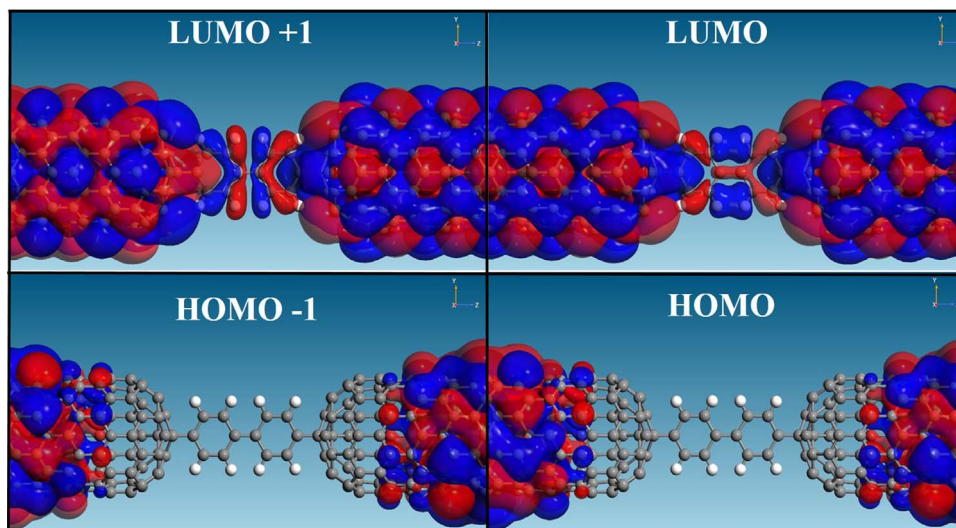


Fig. 5. LUMO+1, LUMO, HOMO and HOMO-1, respectively, for the BP system with no applied bias.

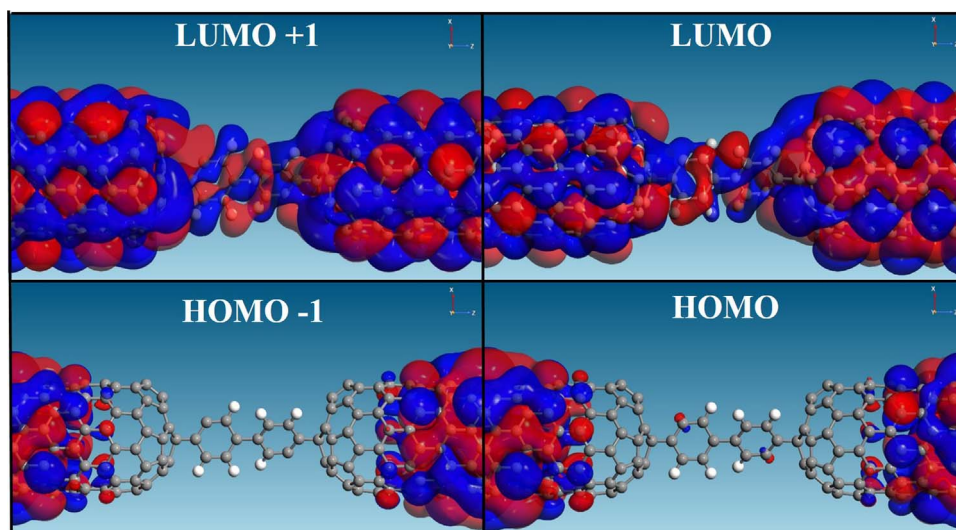


Fig. 6. LUMO+1, LUMO, HOMO and HOMO-1, respectively, for the BP2D system with no applied bias.

applications of BP2D attached to carbon nanotubes as a novel, efficient, and highly stable platform in single-molecule electronics with unprecedented transport properties.

Acknowledgments

JCR-S, DFSF and JFPL acknowledge CNPq and FAPESPA for financial support. FAP acknowledges The Royal Society through the Newton Advanced Fellowship (NA150208), CAPES (BEX 1497/14-6), and CNPq (303286/2013-0) for financial support. JDN acknowledges CNPq (PDE/233320/2014-8) for financial support.

References

- [1] A. Nitzan, M.A. Ratner, *Science* 300 (2003) 1384. <http://dx.doi.org/10.1126/science.1081572>.
- [2] N.J. Tao, *Nat. Nanotechnol.* 1 (2006) 173. <http://dx.doi.org/10.1038/nnano.2006.130>.
- [3] M.T. Gonzalez, S.M. Wu, R. Huber, S.J. van der Molen, C. Schnenberger, M. Calame, *Nano Lett.* 6 (2006) 2238. <http://dx.doi.org/10.1021/nl061581e>.
- [4] M. Kiguchi, O. Tal, S. Wohlthat, F. Pauly, M. Krieger, D. Djukic, J.C. Cuevas, J.M. van Ruitenbeek, *Phys. Rev. Lett.* 101 (2008) 046801 (doi: <https://doi.org/10.1103/PhysRevLett.101.046801>)).
- [5] B.Q. Xu, N.J. Tao, *Science* 301 (2003) 1221. <http://dx.doi.org/10.1126/science.1087481>.
- [6] C. Li, I. Pobelov, T. Wandlowski, A. Bagrets, A. Arnold, F.J. Evers, *J. Am. Chem. Soc.* 130 (2008) 318. <http://dx.doi.org/10.1021/ja0762386>.
- [7] L. Venkataraman, J.E. Klare, C. Nuckolls, M.S. Hybertsen, M.L. Steigerwald, *Nature* 442 (2006) 904. <http://dx.doi.org/10.1038/nature05037>.
- [8] X.D. Cui, A. Primak, X. Zarate, J. Tomfohr, O.F. Sankey, A.L. Moore, T.A. Moore, D. Gust, G. Harris, S.M. Lindsay, *Science* 294 (2001) 571. <http://dx.doi.org/10.1126/science.1064354>.
- [9] A. Mishchenko, D. Vonlanthen, V. Meded, M. Brkle, C. Li, I.V. Pobelov, A. Bagrets, J.K. Viljas, F. Pauly, F. Evers, M. Mayor, T. Wandlowski, *Nano Lett.* 10 (2010) 156. <http://dx.doi.org/10.1021/nl903084b>.
- [10] M.S. Hybertsen, L. Venkataraman, J.E. Klare, A.C. Whalley, M.L. Steigerwald, C. Nuckolls, *J. Phys.: Condens. Matter* 20 (2008) 374115 (doi: <http://iopscience.iop.org/article/10.1088/0953-8984/20/37/374115/meta>)).
- [11] M.G. Reuter, T. Seideman, M.A. Ratner, *J. Chem. Phys.* 134 (2011) 154708. <http://dx.doi.org/10.1063/1.3581097> (doi: <http://dx.doi.org/10.1063/1.3581097>)).
- [12] H. Häkkinen, *Nat. Chem.* 4 (2012) 443. <http://dx.doi.org/10.1038/nchem.1352>.
- [13] J.M. Seminario, A.G. Zacarias, J.M. Tour, *J. Am. Chem. Soc.* 121 (1999) 411. <http://dx.doi.org/10.1021/ja982234c>.
- [14] R.P. Kaur, R.S. Sawhney, D. Engles, *J. Multiscale, Modelling* 04 (2012) 4. <http://dx.doi.org/10.1142/S1756973712500151>.
- [15] K. Horiuchi, T. Kato, S. Hashii, A. Hashimoto, T. Sasaki, N. Aoki, Y. Ochiai, *Appl. Phys. Lett.* 86 (2005) 153108 (doi: <http://dx.doi.org/10.1063/1.1899251>)).
- [16] A.J.P. Qi, M. Rolandi, Q. Wang, E. Yenilmez, H.J. Dai, *J. Am. Chem. Soc.* 126 (2004) 11774. <http://dx.doi.org/10.1021/ja045900k>.
- [17] X.F. Guo, J.P. Small, J.E. Klare, Y. Wang, M.S. Purewal, I.W. Tam, B.H. Hong, R. Caldwell, L. Huang, S.O. Brien, J.M. Yan, R. Breslow, S.J. Wind, J. Hone, P. Kim, C. Nuckolls, *Science* 311 (2006) 356. <http://dx.doi.org/10.1126/science.1120986>.
- [18] H.J. Li, W.G. Lu, J.J. Li, X.D. Bai, C.Z. Gu, *Phys. Rev. Lett.* 95 (2005) 086601 (doi: <https://doi.org/10.1103/PhysRevLett.95.086601>)).
- [19] D.C. Wei, Y.Q. Liu, L.C. Cao, Y. Wang, H.L. Zhang, G. Yu, *Nano Lett.* 8 (2008) 1625. <http://dx.doi.org/10.1021/nl080283+>.
- [20] C.A.B.S.Jr, S.J.S. da Silva, E.R. Granhen, J.F.P. Leal, J.D. Nero, F.A. Pinheiro, *Phys. Rev. B*, 82, 2010, 0854021. doi: <http://dx.doi.org/10.1103/PhysRevB.82.085402>.
- [21] C.A.B.S.Jr., S.J.S. da Silva, J.F.P. Leal, F.A. Pinheiro, J.D. Nero, *Phys. Rev. B*, 83, 2011, 245444. doi: <http://dx.doi.org/10.1103/PhysRevB.83.245444>.
- [22] W.Y. Kim, S.K. Kwon, K.S. Kim, *Phys. Rev. B* 76 (2007) 033415. <http://dx.doi.org/10.1103/PhysRevB.76.033415>.
- [23] C.A.B. da Silva, J.F.P. Leal, V.F.P. Aleixo, F.A. Pinheiro, J.D. Nero, *Phys. Chem. Chem. Phys.* 16 (2014) 19602. <http://dx.doi.org/10.1039/C4CP00016A>.
- [24] L. Venkataraman, Y.S. Park, A.C. Whalley, C. Nuckolls, M.S. Hybertsen, M.L. Steigerwald, *Nano Lett.* 7 (2007) 502. <http://dx.doi.org/10.1021/nl062923j>.
- [25] W. Haiss, C.S. Wang, R. Jitchati, I. Grace, S. Martin, A.S. Batsanov, S.J. Higgins, M.R. Bryce, C.J. Lambert, P.S. Jensen, R.J. Nichols, *J. Phys.: Condens. Matter* 20 (2008) 374119. <http://dx.doi.org/10.1088/0953-8984/20/37/374119>.
- [26] F. Pauly, J.K. Viljas, J.C. Cuevas, G. Schön, *Phys. Rev. B* 77 (2008) 155312. <http://dx.doi.org/10.1103/PhysRevB.77.155312>.
- [27] C.M. Finch, S. Sirichantaropass, S.W. Bailey, I.M. Grace, V.M. Garcia-Suarez, C.J. Lambert, *J. Phys.: Condens. Matter* 20 (2008) 022203 (doi: <http://iopscience.iop.org/article/10.1088/0953-8984/20/02/022203/meta>)).
- [28] A.D.J. Becke, *J. Chem. Phys.* 98 (1993) 1372 (doi: <http://dx.doi.org/10.1063/1.464304>)).
- [29] J.P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* 105 (1996) 9982 (doi: <http://dx.doi.org/10.1063/1.472933>)).
- [30] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098 (doi: <http://dx.doi.org/10.1103/PhysRevA.38.3098>)).
- [31] S.H. Vosko, L. Wilk, M. Nusair, *J. Phys.* 58 (1980) 1200. <http://dx.doi.org/10.1139/p80-159>.
- [32] N.A. Bruque, M.K. Ashraf, G.J.O. Beran, T.R. Helander, R.K. Lake, *Phys. Rev. B* 80 (2009) 155455 (doi: <http://dx.doi.org/10.1103/PhysRevB.80.155455>)).
- [33] K. Stokbro, J. Taylor, M. Brandbyge, *J. Am. Chem. Soc.* 125 (2003) 3674. <http://dx.doi.org/10.1021/ja028229x>.
- [34] J. Taylor, M. Brandbyge, K. Stokbro, *Phys. Rev. Lett.* 89 (2002) 138301 (doi: <http://dx.doi.org/10.1103/PhysRevLett.89.138301>)).
- [35] Z.K. Qian, S.M. Hou, R. Li, Z.Y. Shen, X.Y. Zhao, Z.Q. Xue, *J. Comput. Theor. Nanosci.* 5 (2008) 671 (doi: <http://dx.doi.org/10.1166/jctn.2008.035>)).
- [36] R. Landauer, *IBM J. Res. Dev.* 1 (1957) 223. <http://dx.doi.org/10.1147/rd.1.0223>.
- [37] M. Buttiker, *Phys. Rev. Lett.* 57 (1986) 1761 (doi: <http://dx.doi.org/10.1103/PhysRevLett.57.1761>)).
- [38] A. Hernandez, V.M. Apel, F.A. Pinheiro, C.H. Lewenkopf, *Physica A* 385 (2007) 148 (doi: <http://dx.doi.org/10.1016/j.physa.2007.06.032>)).
- [39] L. Wang, Y. Guo, C.F. Tian, X.P. Song, B.J. Ding, *Phys. Lett. A* 374 (2010) 4876. <http://dx.doi.org/10.1016/j.physleta.2010.09.068>.
- [40] E. Chikayama, Y. Shimbo, K. Komatsu, J. Kikuchi, *J. Phys. Chem. B* 120 (2016) 3479. <http://dx.doi.org/10.1021/acs.jpcc.5b12748>.