Hydration effect on the electronic transport properties of oligomeric phenylene ethynylene molecular junctions*

Li Zong-Liang(李宗良)†, Li Huai-Zhi(李怀志)‡, Ma Yong (马 勇), Zhang Guang-Ping(张广平), and Wang Chuan-Kui(王传奎)§

Physics and Electronics College, Shandong Normal University, Jinan 250014, *China*

(Received 23 October 2009; revised manuscript received 30 December 2009)

A first-principles computational method based on the hybrid density functional theory is developed to simulate the electronic transport properties of oligomeric phenylene ethynylene molecular junctions with H_2O molecules accumulated in the vicinity as recently reported by Na *et al.* [*Nanotechnology* **18** 424001 (2007)]. The numerical results show that the hydrogen bonds between the oxygen atoms of the oligomeric phenylene ethynylene molecule and H_2O molecules result in the localisation of the molecular orbitals and lead to the lower transition peaks. The H_2O molecular chains accumulated in the vicinity of the molecular junction can not only change the electronic structure of the molecular junctions, but also open additional electronic transport pathways. The obvious influence of H_2O molecules on the electronic structure of the molecular junction and its electronic transport properties is thus demonstrated.

Keywords: hydration effect, electronic transport properties, oligomeric phenylene ethynylene, molecular junction

PACC: 7360R, 7115A, 0560, 3640

1. Introduction

Searching for single organic molecules to design functional devices has attracted considerable attention.[1−4] For experimental works, many technologies, such as those of mechanically controllable break junctions,[5] scanning tunneling microscopy,[6] atomic force microscopy,[7] have been developed. By these means, various kinds of single-molecule junctions or molecular monolayer junctions have been formed and their electronic properties measured.[8−11] At the same time, theories also have been developed to understand and explain electronic transport properties of the molecule junctions. To date, one knows that the electronic transport properties and dynamic properties of the molecular junctions are influenced by many factors,[12−23] for instance, molecular structure,[18] contact configuration,[19] positions of the terminal atoms on the metal surfaces,[10] distance between the electrodes,[20] pressure of the electrodes,[21] and ambience.[22−24] When molecular devices are exposed in air, the influence of water on their electronic properties is expected because of possible formation of hydrogen bonds between organic compounds and water molecules.

Recently, Na *et al.* have investigated experimentally the electronic transport properties of oligomeric phenylene ethynylene (OPE) molecule terminated with thioacetate functionalities.[22,23] They found that the real-time conductivity measured through the junction was sensitive to the ambient conditions, and changed persistently over several days of exposure. In order to understand the mechanisms for ambient influence on the electronic transport properties of the molecular junctions, we provide a theoretical study on the current–voltage features of the molecular junctions by considering the hydration effect. The numerical results are qualitatively consistent with the experimental measurements.

2. Computational details

The molecular systems consist of two semi-infinite electron reservoirs, namely the source (S) and the drain (D), connected by a molecule (M) or molecular clusters. Based on the general Green's function

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10804064 and 10674084).

†Corresponding author. E-mail: lizongliang@sdnu.edu.cn

‡Present address: Frist Senior School of Xintai, Xintai 271200, Shandong Province, China

§E-mail: ckwang@sdnu.edu.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

formalism of Mujica *et al.*,[25] for a three-dimensional electrode, the net current density of molecular junction from source to drain can be written as[20,26]

$$i_{\rm SD} = \frac{4em^*k_{\rm B}T}{\hbar^3}\int_{eV}^{\infty}\ln\frac{1+\exp\left(\dfrac{E_{\rm f}+eV_{\rm SD}-E_z}{k_{\rm B}T}\right)}{1+\exp\left(\dfrac{E_{\rm f}-E_z}{k_{\rm B}T}\right)} \times |T(E_z)|^2\, n^{\rm S}(E_z)n^{\rm D}(E_z)\,{\rm d}E_z, \quad (1)$$

where $V_{\rm SD}$ is the external bias, m^* is the electron effective mass, $E_{\rm f}$ is the Fermi level, $n^{\rm S}$ and $n^{\rm D}$ are the density of states of the source and drain respectively. And

$$T(E_z) = \sum_J\sum_K V_{J{\rm S}}V_{{\rm D}K}\sum_n \frac{\langle J|n\rangle\langle n|K\rangle}{(E-E_n)+{\rm i}\Gamma_n} \quad (2)$$

is the transition matrix element from the source to the drain, where $|n\rangle$ is the eigenstate of the Hamiltonian (H) of a finite system that consists of the molecule sandwiched between two clusters of metal atoms. J runs over all the atomic sites, which are denoted as 1, 2, ... , N; sites 1 and N are two end sites of the molecules that connect with two electron reservoirs. And S(D) runs over the atomic sites of the reservoirs (source and drain). $V_{J{\rm S}}(V_{{\rm D}K})$ represents the coupling between an atomic site $J(K)$ and the reservoir S(D), and is written as follows:

$$V_{J{\rm S}} = \langle J|\,H\,|{\rm S}\rangle = \sum_{n,\alpha,i} C^J_{n\alpha}\langle J_\alpha|\,H\,|{\rm S}_i\rangle\, C^{\rm S}_{ni},$$
$$V_{{\rm D}J} = \langle {\rm D}|\,H\,|K\rangle = \sum_{n,\beta,j} C^{\rm D}_{nj}\langle {\rm D}_j|\,H\,|K_\beta\rangle\, C^K_{n\beta}, \quad (3)$$

where $C^J_{n\alpha}$ ($C^K_{n\beta}$) is the expansion coefficient of the orbital $|n\rangle$ on the atomic orbital $|\alpha\rangle$ ($|\beta\rangle$) of the atom $J(K)$ and $C^{\rm S}_{ni}$ ($C^{\rm D}_{nj}$) is on the orbital $|i\rangle$ ($|j\rangle$) of the gold atom cluster S(D). The coupling between the molecule (M) and a reservoir S(D) is thus written as

$$V_{\rm MS} = \langle {\rm M}|\,H\,|{\rm S}\rangle = \sum_J V_{J{\rm S}},$$
$$V_{\rm DM} = \langle {\rm D}|\,H\,|{\rm M}\rangle = \sum_K V_{{\rm D}K}. \quad (4)$$

Then the current is obtained by $I_{\rm SD} = Ai_{\rm SD}$, where A is the contact area. The conductance is $G = \partial I_{\rm SD}/\partial V_{\rm SD}$.

In our calculations, the middle of highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the metal–molecule–metal cluster is chosen as the Fermi level, and the nonequilibrium transport is considered by simply lining up the Fermi energy of the extended molecule and bulk metals.[26]

There are three steps in our simulations. Firstly, considering that only the nearest atoms have evident interaction with the OPE molecule, we construct molecular junctions by sandwiching OPE molecules between two gold clusters. In the numerical simulation, each gold cluster consists of three gold atoms with equilateral triangle configuration. The Au–Au bond length is fixed to be 0.288 nm. The terminal sulfur atoms of the molecule are set on the hollow positions of the gold triangles.[27] Then, we perform structure optimisations at the B3LYP level with Lan2DZ basis set implemented in Gaussian03 package.[28] Finally, on the basis of our generalized elastic scattering Green's function theory in QCME codes,[29] we calculate and analyse the electronic transport properties of the molecular junctions in different ambient conditions.

3. Results and discussion

In order to analyse the hydration effect on the electronic transport properties, we construct several hyper-molecular configurations to simulate the molecular junctions in different ambient conditions (Fig. 1). Firstly, we investigate the electronic transport properties of an OPE molecular junction without consideration of hydration effects (system 1). Secondly, considering that the oxygen atoms of an OPE molecule tend to form a hydrogen bond with H_2O molecules in the ambient air, we add one H_2O molecule to form a hydrogen bond with each oxygen atom of the OPE molecule (system 2). The molecular dynamics simulations that we carry out also show that each oxygen atom of the OPE molecule is connected with one H_2O by a hydrogen bond. Geometric optimizations are performed for both of these two configurations. As predicted in Ref. [23], for longer times the water vapour accumulated in the junction region may lead to additional current pathways. Therefore, we set many H_2O molecules around the OPE molecular junctions and some of the H_2O molecules connect with each other and form chains. In fact, molecular dynamics simulations are needed here in order to consider the influence of more H_2O molecules around an OPE molecule. However, due to the limitation of the computational capacity, it is almost impossible to perform molecular dynamics simulations to imitate the experiment. And the geometric optimizations are also impossible for the OPE molecular junctions with many H_2O molecule around. Therefore, the other configurations are constructed empirically. In this work, 13, 20, 23, 26, 36,

38, 40 and 42 H_2O molecules in the vicinity of the OPE molecular junctions are taken into account. For simplicity, two configures with 23 and 36 H_2O molecules are shown here (systems 3 and 4).

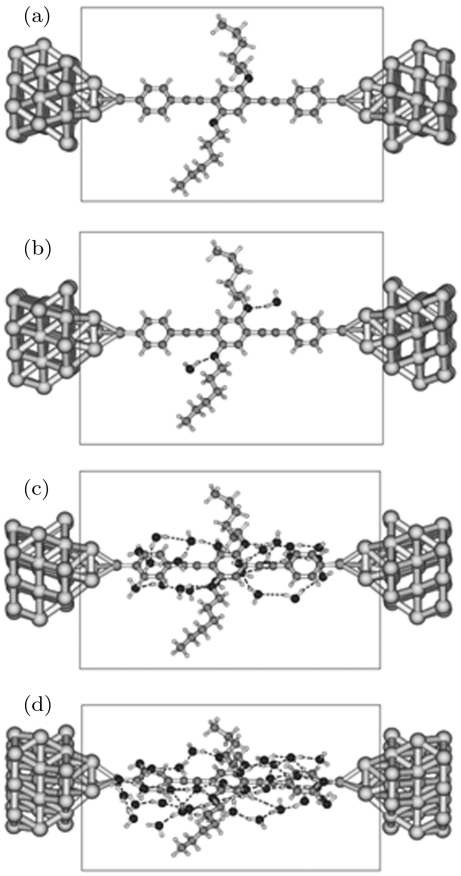


Fig. 1. Schematic structure of OPE molecular junctions for (a) system 1, (b) system 2, (c) system 3, (d) system 4.

In system 1, the geometric optimization shows that the distance between the two electrodes is about 2.5 nm, and the distances from sulfur atoms to gold surfaces are about 0.23 nm, which is consistent with the results in our previous works.[20,26,30] The C–S bonds are normal to the gold triangles. Each oxygen atom of the OPE molecule shows negative net charge of about –0.30 e. While in system 2, the net charge of each oxygen atom of the OPE molecule is about –0.38 e. We also find that each H_2O molecule connected to the OPE molecule by a hydrogen bond shows a positive charge of about 0.015 e. One can find that upon the formation of the hydrogen bond, the oxygen atoms of the OPE molecule obtain electrons from H_2O molecules. And by the influence of the hydrogen bond, more electrons in the OPE molecule are moved to the oxygen atoms. This result can be understood that, since the H atoms of the H_2O molecule show positive charge, when the H atoms approach the oxygen atoms of the OPE molecule, they can attract electrons to gather around the oxygen atoms from the OPE molecule. At the same time, the oxygen atoms are strong electronegative, they also attract electrons from H_2O molecules. The larger number of electrons attracted by the oxygen atoms will result in the localization of the molecular orbital, which plays a negative role to the electronic transport through the molecular junctions.

Figure 2 shows the transition intensity of the molecular junctions with different numbers of H_2O molecules accumulated in the vicinity. For the molecular junction without H_2O molecules (Fig. 2(a)), one can find that there are two transition peaks for the electrons with energy lower than 1 eV. However, there is only one transition peak for the OPE molecular junction with two H_2O molecules (Fig. 2(b)), and its intensity is much weaker than those in Fig. 2(a). When more H_2O molecules are accumulated, a transition peak located at about 0.18 eV appears. In addition, with the increase of H_2O molecules, the intensity of the other two peaks is increased and their positions are shifted to a lower energy region. These peaks will have an obvious contribution to the electronic transport at lower bias compared with the cases of systems 1 and 2. The reason is that the H_2O molecules are connected into one or more chains, by which the electronic transport ability is enhanced.

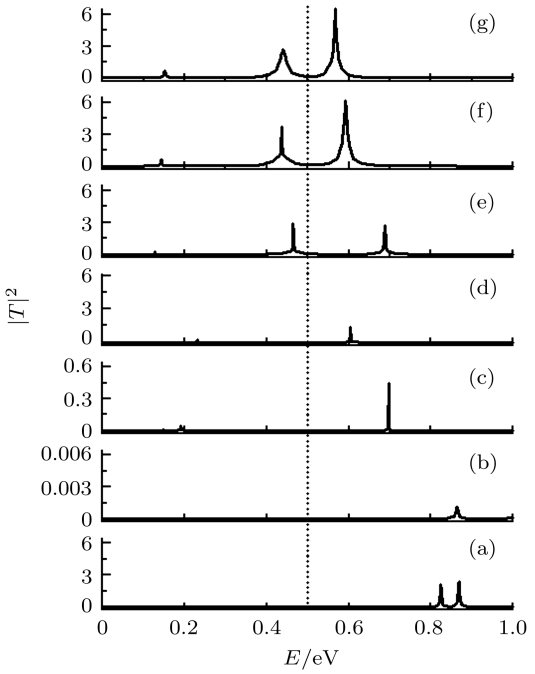


Fig. 2. Transition spectrum of OPE molecular junctions with (a) 0, (b) 2, (c) 13, (d) 23, (e) 36, (f) 40, and (g) 42 H_2O molecules.

Current values of all the molecular junctions at 0.5 V bias voltage are given in Fig. 3. The figure

shows that, for the configuration with only two H_2O molecules connected with OPE molecule (point B) by hydrogen bonds, the current value is much smaller than that of the bare OPE molecular junction (point A), which displays a negative role of the hydrogen bonds to the electronic transport. When the OPE molecule is exposed to air very briefly, the current of the OPE molecular junction may show a decrease, as indicated by the experimental observation.[23]

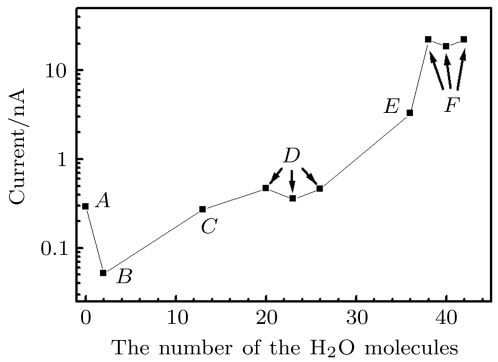


Fig. 3. Current of OPE molecular junctions with different numbers of H_2O molecules in the vicinity at external bias voltage of 0.5 V.

The other points in Fig. 3 can be divided into four groups of C, D, E and F as the figure shows, which correspond to one, two, three and four H_2O molecular chains formed in the super-molecular systems, respectively. It shows that more H_2O molecular chains formed in the molecular junction will result in higher currents. When a H_2O molecular chain is formed, one more H_2O molecule has little influence on the current because the H_2O molecule is far away from the molecular junction and thus has little contribution to the electronic transport. Once enough H_2O molecules are accumulated and a new H_2O molecular chain is formed, the current of the molecular junction is obviously enhanced. Furthermore, when the H_2O molecular chains reach a saturation condition, one can expect that the current trends to a limit value. The numerical simulation qualitatively explains the effect of long-term storage environments on the current change of the OPE-linked gold nanoparticle dimers.[23]

In order to gain a deep understanding of the electronic transport properties of the molecular junctions, we illustrate some molecular orbitals in Fig. 4. The orbital analysis shows that, for the bare OPE molecular junction (system 1), the LUMO and the LUMO + 1 are localized molecular orbitals, which have little contribution to the electronic transport. However, the LUMO+2 and the LUMO+3 are good delocalized molecular orbitals (Figs. 4(a) and 4(b)), which are

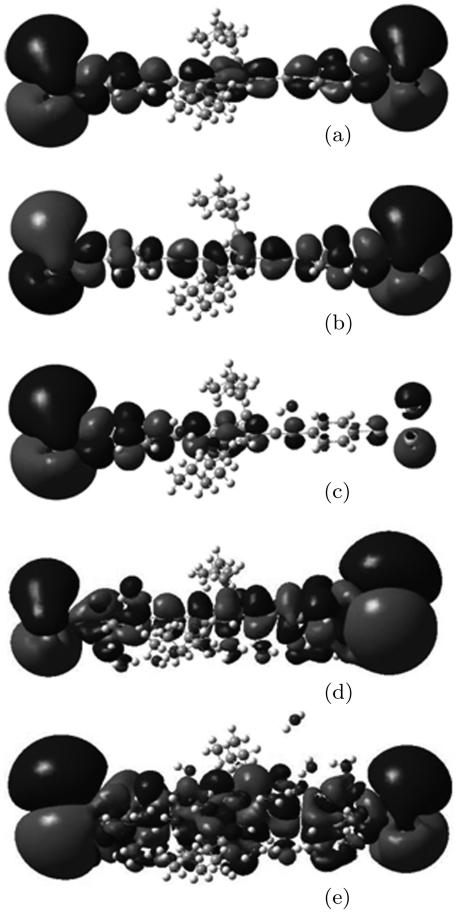


Fig. 4. Molecular orbitals of OPE molecular junctions. (a) LUMO+2 (0 H_2O), (b) LUMO+3 (0 H_2O), (c) LUMO+1 (2 H_2O), (d) LUMO+1 (13 H_2O), (e) LUMO (40 H_2O).

related to the two peaks of the curve in Fig. 2(a) and make an obvious contribution to the electronic transport. For system 2, in the range of curve shown in Fig. 2(b), only the LUMO+1 which is related to the peak at about 0.85 eV (Fig. 4(c)) has a small contribution to the electronic transport. When some H_2O molecular chains have formed with the increase of the amount of H_2O molecules, the numerical results show that the H_2O molecular chains not only open additional electronic transport pathways but also influence the electronic structure of OPE molecular junction and lead to new delocalized molecular orbitals. For example, when there are thirteen H_2O molecules in the vicinity of the OPE molecular junction, the H_2O molecular chain makes a considerable contribution to the LUMO+1 and results in a low transition peak near 0.2 eV (Fig. 4(d)). For the OPE molecular junction with 40 or 42 H_2O molecules accumulated in the vicinity, the LUMO, LUMO+2 and LUMO+3 are delocalized all over the OPE molecular junction including

the H_2O molecular chains. The LUMO (Fig. 4(e)) is related to the first peaks of the curves of Figs. 2(f) and 2(g), and the LUMO+2 and LUMO+3 are related to the second and the third peaks. They all make a great contribution to the electronic transport. The difference between these two configurations is that the two more H_2O molecules of the configuration with 42 H_2O molecules are a little further away from the OPE junction than the other H_2O molecules, which seems to suggest that only the H_2O molecules near the OPE junction and especially those connected into chains can exert obvious influence on the electronic structures of the molecular junctions and have obvious contribution to the electronic transport. This is confirmed by our further computations.

Based on our theory, the coupling constant, especially the coupling constants between the terminal atoms of the molecule and the electrodes, is another factor that influences the height of the transition peaks as well as the current flow. For the bare OPE molecular junction, the coupling constants between the terminal sulfur atoms and the gold electrodes are about 0.75 eV. However, for the molecular junction with 13 H_2O molecules, the coupling constants are larger than 1 eV. And the coupling constants have an increasing trend with the increase of H_2O molecules in the vicinity of the OPE molecular junction. According to formula (2), the height of the transition peaks and also the current are approximately proportional to the second power of the coupling constants. Since the LUMO+1 of system 2 is just a delocalized orbital to some extent (Fig. 4(c)), and the coupling constants between OPE molecule and the electrodes are approximately equal to that of system 1, the transition peaks and the current are obviously smaller than others.

4. Conclusion

In summary, based on density functional theory, the electronic transport properties of OPE molecular junctions with H_2O molecules accumulated in the vicinity are investigated by applying our generalized elastic scattering Green's function theory. The simulations explain the experimental results qualitatively. The numerical results show that the hydrogen bonds between the oxygen atoms of the OPE molecule and the H_2O molecules result in the localization of the molecular orbitals and lead to the lowered transition peaks and weaker current value. The H_2O molecular chains accumulated in the vicinity of the molecular junction can not only open additional electronic transport pathways, but also change the electronic structure of the molecular junctions, which result in large coupling constants and higher transition peaks. Only the H_2O molecules near the OPE junction and especially those connected into chains can have obvious influence on the electronic transport properties of the molecular junctions.

References

[1] Reddy P, Jang S Y, Segalman R A and Majumdar A 2007 *Science* **315** 1568

[2] Zhao A D, Li Q X, Chen L, Xiang H J, Wang W H, Pan S, Wang B, Xiao X D, Yang J L, Hou J G and Zhu Q S 2005 *Science* **309** 1542

[3] Venkataraman L, Klare J E, Nuckolls C, Hybertsen M S and Steigerwald M L 2006 *Nature* **442** 904

[4] Solomon G C, Gagliardi A, Pecchia A, Frauenheim T, Carlo A D, Reimers J R and Hush N S 2006 *J. Chem. Phys.* **125** 184702

[5] Reed M A, Zhou C, Muller C J, Burgin T P and Tour J M 1997 *Science* **286** 252

[6] Nazin G V, Qiu X H and Ho W 2003 *Science* **302** 77

[7] Cui X D, Primak A, Zarate X, Tomfohr J, Sankey O F, Moore A L, Moore T A, Gust D, Harris G and Lindsay S M 2001 *Science* **294** 571

[8] Guo W, Hu Y B, Zhang Y Y, Du S X and Gao H J 2009 *Chin. Phys.* B **18** 2502

[9] Bannani A, Bobisch C and Möller R 2007 *Science* **315** 1824

[10] Beebe J M, Engelkes V B, Miller L L and Frisbie C D 2002 *J. Am. Chem. Soc.* **124** 11268

[11] Long Y Z, Yin Z H, Li M M, Gu C Z, Duvail J L, Jin A Z and Wan M X 2009 *Chin. Phys.* B **18** 2514

[12] Emberly E G and Kirczenow G 2002 *Chem. Phys.* **281** 311

[13] Heurich J, Cuevas J C, Wenzel W and Schön G 2002 *Phys. Rev. Lett.* **88** 256803

[14] Wang C K, Fu Y and Luo Y 2001 *Phys. Chem. Chem. Phys.* **3** 5017

[15] Luo Y, Wang C K and Fu Y 2002 *J. Chem. Phys.* **117** 10283

[16] Li Z L, Wang C K, Luo Y and Xue Q K 2005 *Chin. Phys.* **14** 1036

[17] Brandbyge M, Mozos J L, Ordejón P, Taylor J and Stokbro K 2002 *Phys. Rev.* B **65** 165401

[18] Müller K H 2006 *Phys. Rev.* B **73** 045403

[19] Reichert J, Ochs R, Beckmann D, Weber H B, Mayor M and Löhneysen H V 2002 *Phys. Rev. Lett.* **88** 176804

[20] Jiang J, Lu W and Luo Y 2004 *Chem. Phys. Lett.* **400** 336

[21] Engelkes V B, Beebe J M and Frisbie C D 2004 *J. Am. Chem. Soc.* **126** 14287

[22] Na J S, Ayres J, Chandra K L, Chu C, Gorman C B and Parsons G N 2007 *Nanotechnology* **18** 035203

[23] Na J S, Ayres J, Chandra K L, Gorman C B and Parsons G N 2007 *Nanotechnology* **18** 424001

[24] Cao H, Jiang J, Ma J and Luo Y 2008 *J. Am. Chem. Soc.* **130** 6674

[25] Mujica V, Kemp M and Ratner M A 1994 *J. Chem. Phys.* **101** 6849

[26] Li Z L, Zou B, Wang C K and Luo Y 2006 *Phys. Rev.* B **73** 075326

[27] Bae S J, Lee C R, Choi I S, Hwang C S, Gong M S, Kim K and Joo S W 2002 *J. Phys. Chem.* B **106** 7076

[28] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Montgomery J A, Vreven T, Kudin K N, Burant J C, Millam J M, Iyengar S S, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson G A, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox J E, Hratchian H P, Cross J B, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Ayala P Y, Morokuma K, Voth G A, Salvador P, Dannenberg J J, Zakrzewski V G, Dapprich S, Daniels A D, Strain M C, Farkas O, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Ortiz J V, Cui Q, Baboul A G, Clifford S, Cioslowski J, Stefanov B B, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin R L, Fox D J, Keith T, Al-Laham M A, Peng C Y, Nanayakkara A, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Gonzalez C and Pople J A 2003 *GAUSSIAN 03*, Revision D.1, Gaussian Inc., Pittsburgh, PA

[29] Jiang J, Wang C K and Luo Y 2005 *QCME-V1.0* (Quantum Chemistry for Molecular Electronics), Royal Institute of Technology, Sweden

[30] Su W Y, Jiang J and Luo Y 2005 *Chem. Phys. Lett.* **412** 406