Absorption spectra and transition states for new organic dye sensitizers based on anthracene

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Abstract

Anthracene is the backbone of three suggested organic compounds in present work. Our calculations depending on DFT and TD-DFT take on B3LYP hybrid function using the basis sets 6-31g to carry out some properties at the ground state electronic and photovoltaic properties for the studied compounds. The relax structures show all the compounds have quasi planar conformation. The results showed that Homo and Lumo are little different, suggesting that be different structures play substantial characters to increase an electron acceptance. The result of (Lumo-Homo) gap and the voltage of open circuit are the factors operating to refining the quality for devices of solar cells. Furthermore, due to the high probability of the process for an electron injection of the organic structure in the TiO₂ conduction band, where the energy of maximum absorption and the wavelength are occur in the range spectrum of the solar.

Keywords: Open circuit voltage, Transition states, Molecular orbital character and energy gap.

Introduction

The solar cell energy has high significant due to increasing energy requirements in all the world[1, 2]. A number of inorganic and organic materials have been applied in solar cells[3-7]. O. Regan and Gratzel was at first technologically advanced the solar cell using dye sensitized [8]. Polymers with small band gap which are considered to enhanced solar production have been considered, a number of research groups have been studied some Polymers with thiophene derivatives such as alternating di-thiophene and thiadiazolothienopyrazine [9]. Sanyin Qu et al. [10] have developed new materials based on diketo-pyrrolopyrrole for the applications of solar cell. Many theoretical studies have been considered to form a significant basis of appreciated data which accompaniments the experimental data, by this means donating for respectful of electronic structure of the molecules in addition to both emission and absorption [11]. Dye-sensitized cells are inexpensive, have a high efficiency of photo-electric conversion and hey have high probable applications in coating and fabrication technology [12-14]. A small prohibited band material with a new electronical structure can achieved by linking the donor part with acceptor part and can affect the hybridization of the Homo level of the high donor and the acceptor low level. On the other hand, the importance in organic dyes without metal as a substitute to complexes of noble metal has improved in recent years due to its diversity of molecular structures, its high molar extinction coefficients, its simple synthesis and its properties, its low cost. Tian et al. It is believed that a number of structural organic donor-acceptor π bridge acceptor dyes (DA-π-A) have linked
benzothiadiazole in the structure of triphenylamine, causing a red shift in absorption and failure of the effect of deprotonating in TiO₂-Film useful for light collection [15]. Our work, a theoretical study focuses on photo-voltaic properties for new organic materials using the time dependent density function theory TD-DFT method, electronical structure for compounds were investigated by introducing different electron subgroups.

Method

Three suggested organic complexes were drawn and examined in the Gauss View 5.0.8 software package. To obtain their optimize structures, they are relax using the Lee-Yang-Parr three parameters B3-L-Y-P with basis ses 6-31g. Our calculations included ground states and the properties of the excited states, which are done in the Gauss 09 software package [16]. Relaxation of the studied compounds was found at virial ratio equal to (-2.0056) without any imaginary frequency for all three compounds. The band gaps were calculated directly from the two frontier molecular orbitals (Lumo and Homo). Other ground properties were calculated according to theory of Koopmans [17].

Results and discussion

Relaxation and geometrical parameters

The relax structures of the compounds under study were illustrated in Figure 1, the anthracene molecule is the base of all compounds connected to the rings of phenylene at both ends of anthracene. The delocalization of the π electrons between the molecular units and the aromatic cycles is clear. The compounds are designed to look at the effect of asymmetry and symmetry configurations, so the conclusion of the groups that accept and donate electrons is examined. The relaxation structures show that all compounds have a quasi flat conformation.

The result showed that the geometrical parameters for the cyclic carbon compounds of the DFT calculations in the present work match up with those obtained from the X-ray data. The results showed that the successive parts make sure similar to angles of dihedral (180° to -180°) and C-C distances are about 1.421Å with about 120° is the angle of C-C-C [18].
Electronic properties

Table 1 listed some electronic properties for the studied compounds. The total energy $E$ is independent of the location of the similar subgroups in the compounds and be determined by only the total of electrons. It is inversely proportional to the number of electrons.

**Table 1: $E_a$, Homo, Lumo, and $E_{Gap}$ for the compounds.**

| Specie | $E_a$, u | Homo [eV] | Lumo [eV] | $E_{Gap}$ [eV] | $V_{oc/TiO_2}$ [eV] |
|--------|---------|-----------|-----------|--------------|-------------------|
| 1      | -1611.62170 | -4.0614 | -2.0256 | 2.0358 | 1.3015 |
| 2      | -1644.77659 | -4.0285 | -2.1015 | 1.927 | 1.3837 |
| 3      | -1644.77426 | -4.2425 | -2.0722 | 2.1703 | 1.3428 |
| TiO$_2$ |         | -5.928 | -3.900 |          |                  |

Table 1 also shows the calculated the energies of frontier orbitals, the energy difference Lumo-Homo $E_{Gap}$ and open circuit voltage $V_{oc}$, since TiO2 is a good acceptor of the investigated compounds. The results showed that these compounds show a de-stabilization of Lumo and a stabilization of Homo. The resultant observed that the effect of symmetry in addition to distribution of the aromatic rings on the Homo and Lumo energies cannot be ignored, since Homo and Lumo are little different and this proposes that many structures play an important key in the electronic properties and increase the acceptance of electrons. The Lumo energy of our compounds is in the rank $2 <3 <1$.

The lowering of Lumo which leads to reducing the energy gaps, which is because of occurrence of sub-groups of electronic attraction in the compounds. On other hand, the decrease in the energy gap may come from destabilization of Lumo energies due to triple and double CC bonds [3]. The order of calculated energy gaps is as: $2 (1.927 \text{ eV}) <1 (2.0358 \text{ eV}) <3 (2.1703 \text{ eV})$. Compound 2
has a lowest energy gap comparing with others by reason of the para state of subgroups in the terminal ends of the compound. In general, the three compounds appear small energy gaps. Injecting the C-C triple bonds as linking the anthracene and the rings of phenylene in donor and acceptor sides leads increasing the length of conjugation of the compound and can then accomplished the transfer properties well. Figure 2 shows Lumo-Homo difference.

![Figure 2: Lumo-Homo gap of the compounds.](image)

Figure 3 shows the distribution forms of the FMO edges molecular orbitals (Homo and Lumo). The contribution of Homo and Lumo represents the core contribution to the definition of the states separated by the charge in the structure. As can be seen, all organic dyes were examined in very different electronic states. We showed a strong de-localization of Lumo in the bridges between the subunits, which emphasize the flow of electron density along the strength of the compounds, where the density of electrons for Lumo is mainly in acceptable units and a strong localization of Homo occurs in phenyl donor subunits.
Global quantum parameters

Some global quantum parameters included the electrochemical hardness $H$, electronic softness $S$ and electrophilicity $W$ were calculated for the studied compounds and listed in Table 2.

Table 3: The $X$, $H$ and $W$ for the compounds.

| Compound | $H$ (eV) | $S$ (1/eV) | $W$ (eV) |
|----------|----------|------------|----------|
| 1        | 1.0179   | 0.4912     | 1.8365   |
| 2        | 0.9635   | 0.5189     | 4.8282   |
| 3        | 1.0851   | 0.4607     | 4.5391   |

As shown in Table 2, the test compounds have low total electrochemical hardness values because the electrons in the test compounds have a great tendency to escape, the reduction in hardness is 1 future as an indication of the band gap of compounds that are said to be softer and an indication that the resistance of connections to electron loss should be reduced. The calculated values of electronic softness showed the compounds in present study have high ability for an electron transfer, the ranking of highly soft (small band gap) compound is as: $2 > 1 > 3$. Figures 4 and 5 illustrate the hardness and softness for the compounds, respectively.

Figure 3: Homo (left) and Lumo (right) shapes distribution of the compounds.
Figure 4: Global electrochemical hardness of the compounds.

Figure 5: Global electronic softness of the compounds.

Figure 6 shows electrophilicity $W$ for the test compounds. The result showed that these compounds have a high capacity for electron transfer, since the electrophilic index is a decisive factor for the ability of the molecule to interact with other molecules or species. Compound 2 has the heist ability to interacting with the surrounding species, as seen in Figure 6.
Figure 6: Electrophilicity of the compounds.

Ultraviolet spectra

Figure 7 shows the ultraviolet spectra of the compounds which were examined using the TD-SCF method with the same basic and functional hybrid sets. The absorption spectrum is the key factor for connections as photovoltaic materials. From the result of the electronic transitions, we showed the compounds have absorption energy between (2.568-2.078) eV. Compound 1 has absorption energy equals 2.568 eV corresponding to absorption wave length 485.5 nm with oscillator strength 0.27, the electronic transition in compound 1 is directly Homo→Lumo and molecular orbital character 99%. Compound 2 appeared Uv-vis spectrum with peak at 2.078eV(568.2 nm) with oscillator strength 0. 0023 and directly electronic transition Homo→Lumo (100%). While compound 3 has the character of 2.165 eV, 558.45nm, oscillator strength 1.127 and electronic transition Homo→Lumo (97%). The above result shows that the transition from Homo to Lumo to intra-molecular charge transfer from the donor units to the subgroups in the contracts over the conjugated bridge between the two sides. These compounds include energy related to its absorption and wavelength, which corresponds to the solar spectrum, which can be used as sensitizers for organic dyes for solar cells. The main reason for this result is that these connections belong to electronegativity zones and that the electrostatic potential slides in the zones with high electronegativity.
Conclusions

The results showed that the relax structures display all compounds have quasi planar conformation. Homo and Lumo suggests that various structures show substantial characters in order to improve the acceptance of the electrons. The result of (Lumo-Homo) gap and the voltage of open circuit are the factors operating to refining the quality for devices of solar cells. Furthermore, due to the high probability of the electron injection process of the compounds in the TiO\textsubscript{2} conduction band, where the energy of maximum absorption and the wavelength are occur in the range spectrum of the solar.

References

1. Grätzel, M., *Phil. Trans. R Soc A.* 365 (2007) 993-1005.
2. Katzenstein, W., Apt J. Environ. Sci. Technol. 43(2009) 253-258; Schafer, A. I., Broeckmann, A., Richards, B. S., *Environ. Sci. Technol.* 41 (2007) 998-1003.
3. Tang, C. W., *Appl. Phys. Lett.* 48 (1986) 183-185.
4. Liu, R., *J. Phys. Chem. C.* 11 (2009) 9368-9374.
5. Prezhdo, O. V., Duncan, W. R., Prezhdo, V., *Acc. Chem. Res.* 41 (2008) 339-348.
6. Peumans, P., Bulovic, V., Forrest, S. R., *Appl. Phys. Lett.* 76 (2000) 2650-2652.
7. Yu, G., Gao, J., Hummelen, J. C., Wudl, F., Heeger, A. J., *Science.* 270 (1995) 1789-1791; Halls, J. M., Walsh, C. A., Greenham, N. C., Marsiglia, E. A., Friend, R. H., Moratti, S. C. et al., *Nature.* 376 (1995) 498-500; Jenekhe, S. A., Yi, S., *Appl. Phys. Lett.* 77 (2000) 2635-2637.
8. O’Regan, B., Grätzel, M., *Nature.* 353 (1991) 737-740; Grätzel, M., Nature. 414 (2001) 338-344.
9. Wienk, M. M., Turbiez, M. G. R., Struijk, M. P., Fonrodona, M. J., Rene, Janssen, A. J., *Appl. Phys. Lett.* 88 (2006) 153511; Bundgaard, E., Krebs, F. C., *Sol. Ener. Mater. & Sol. Cells.* 91 (2007) 1019-1025.
10. Qu, S., Wang, B., Guo, FA., Li, J., Wu, W., Kong, C., Long, Y., Hua, J., *Dyes and Pigments,* 92 (2012) 1384-1394.
11. Bouzakraoui S., Bouzzine S.M., Bouachrine M., Hamidi M., *Energy Mater. Sol. Cells.* 90 (2006) 1393-1402; Bouzakraoui S., Bouzzine S. M., Bouachrine M., Hamidi M., *J. Mol. Struct. (Theochem).* 725 (2005) 39-44; Zgou H., Bouzzine S.M., Bouzakraoui S., Hamidi M., Bouachrine M., *Chin. Chem. Lett.* 19 (2008) 123-126; Bouzzine S.M., Makayssi A., Hamidi M., Bouachrine M., *J. Mol. Struct. (Theochem).* 851 (2008) 254-262; Mondal, R., Becerril, H. A., Verploegen, E., Kim, D., Norton, J.E., Ko S., Miyaki N., Lee S., Toney M.F., Bredas J.-L., McGeehee, M. D., Bao, Z., *J. Mater. Chem.* 20 (2010) 5823-5834.
12. Gratzel M., *Nature* 414 (2001) 338–344.
13. Gratzel M., *J. Photochem. Photobiol. C* 4 (2003) 145–153.
14. Argazzi R., Iha N.Y.M., Zabri H., Odobel F., Bignozzi C.A., *Coord. Chem. Rev.* 248 (2004) 1299–1316.
15. Zhu W., Wu Y., Wang S., Li W., Wang Z., Tian H. *Adv. Funct. Mater.* 21 (2010) 756-63.
16. 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. Jr., 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, 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, GAUSSIAN 09, Revision B.04, Gaussian, Inc. Pittsburgh PA, 2009.
17. Becke A. D., J. Chem. Phys. 98 (1993) 5648-5653; Ditchfield R., Hehre W.J., Pople J. A., IX. J. Chem. Phys. 54 (1971) 724-729.
18. Faeq A. Mohammed and Hamid I. Abbood, Structural and Electronic Properties of Cis-platin Metal Complex: B3LYP-SDD/DFT Calculations, International Journal of Advanced Engineering Research and Science (IJAERS), Vol -4, Issue-7, July- 2017.
19. Hussein N. Najeeb, Mohammed A. ALshareefi and Hamid I. Abbood, Structural and DFT/TD-DFT Investigation of New Rhenium Metal Complexes, IOP Publishing: Journal of Physics: Conf. Series 1243 (2019) 012058 doi:10.1088/1742-6596/1234/1/012058