

Sains Malaysiana 40(2)(2011): 173–176

Determination of HOMO and LUMO of [6,6]-Phenyl C61-butyric Acid 3-ethylthiophene Ester and Poly (3-octyl-thiophene-2, 5-diyl) through Voltametry Characterization

(Penentuan HOMO dan LUMO Asid [6,6]-Fenil C61-butirik Ester 3-etiltiofena dan Poli (3-oktil-tiiofena-2, 5-diyl) menerusi Pencirian Voltametri)

ASHKAN SHAFIEE, MUHAMAD MAT SALLEH* & MUHAMMAD YAHAYA

ABSTRACT

HOMO and LUMO of organic compounds are basic parameters for the design and fabrication of an organic solar cell. This paper presents a technique to obtain HOMO and LUMO of an n-type polymer of [6,6]-phenyl C61-butyric acid 3-ethylthiophene ester (PCBE) and a p-type polymer of poly (3-octyl-thiophene-2, 5-diyl) (P3OT). The energy of band gap for each material has been calculated using optical absorption spectrum. Cyclic Voltammetry was used to estimate the oxidation potential and energy band diagram consequently. The experiments were carried out in a three-electrode cell consisting of a platinum working electrode, a platinum counter electrode and a SCE reference electrode. P3OT showed energy band gap equal to 1.83 eV with HOMO and LUMO equal to 5.59 eV and 3.76 eV, respectively. PCBE showed energy band gap equal to 1.96 eV with HOMO and LUMO equal to 5.87 eV and 3.91 eV, respectively. Based on energy band diagram that was constructed from this experimental result, the couple materials may be successfully used to fabricate the feasible organic solar cells.

Keywords: Cyclic voltametry; donor-acceptor materials; organic solar cells

ABSTRAK

HOMO dan LUMO adalah parameter asas dalam merekabentuk dan fabrikasi suatu sel suria organik. Kertas ini mengemukakan suatu teknik untuk mendapat HOMO dan LUMO suatu polimer jenis-n, asid [6,6]-fenil C61-butirik ester 3-etiltiofena (PCBE), dan suatu polimer jenis-p, poli (3-oktil-tiiofena-2, 5-diyl) (P3OT). Jurang jalur tenaga tiap-tiap bahan dikira daripada spektrum serapan optik. Voltametri berkitar diguna untuk menganggarkan keupayaan pengoksidaan dan seterusnya gambar rajah jalur tenaga. Uji kaji dijalankan menggunakan sel tiga-elektrod yang terdiri daripada suatu elektrod kerja platinum, satu elektrod lawan platinum dan elektrod rujukan SCE. Bagi P3OT jurang jalur tenaga adalah 1.83 eV dengan HOMO dan LUMO masing-masing berpadanan 5.59 eV dan 3.76 eV. Sementara itu PCBE telah menunjukkan jurang tenaga bersamaan 1.96 eV dengan HOMO dan LUMO masing-masing berpadanan 5.87 eV dan 3.91 eV. Berasaskan kepada gambar rajah yang dibina hasil eksperimen ini, dijangkakan gandingan dua bahan berkenaan dapat difabrikasi untuk menghasilkan sel suria organik yang baik.

Kata kunci: Bahan penderma-penerima; sel suria organik; voltometri berkitar

INTRODUCTION

Discovering the unique properties of organic materials such as polymers and small molecules, opens up a new approach for fabricating the plastic electronic devices rather than conventional inorganic, namely silicon devices. One of the most interesting organic devices, which is a promising energy alternative for the future is organic solar cells (Hagfeldt & Gratzel 2000; Reyes-Reyes et al. 2005; Shaheen et al. 2001; Xue et al. 2005). Organic solar cells have become an interesting research due to their potential for low-cost and flexible power devices (Kietzke 2007). The first step of device fabrication is selecting the appropriate materials for active layer, which is heart of the organic solar cells, and generates the photo-current under illumination of light. In the preparation of organic

solar cells, we desire electron acceptor and electron donor materials, which are fit in the band diagram to fulfill the energy requirements to generate the photo-current (Kietzke 2007). Basically under illumination of light, an electron may be excited from the highest occupied molecular orbital (HOMO) to the lowest un-occupied molecular orbital (LUMO) and leave a hole in HOMO. To generate the photo-current, these band electron-holes (excitons) should be separated to free electron and holes (Hoppe & Sariciftci 2004). After photo-excitation of an electron from HOMO to LUMO, the electron can be achieved to LUMO of the acceptor and be collected by respective electrode, provided that potential difference between ionization potential of the donor and the electron affinity of the acceptor is larger than the exciton binding energy.

Each couple of donor-acceptor materials should be tested to make sure that they fulfill the criteria regarding the energy band diagram energy. There is a possibility that an individual donor or acceptor material shows good properties as a single donor or acceptor but they cannot make a feasible organic solar cell together since they are not matched in terms of energy band diagram.

One of the most accurate methods to characterize the organic materials and estimation about energy band diagram is cyclic voltammetry (CV) (Al-Ibrahim et al. 2005a). The oxidation potentials can be measured by cyclic voltammetry and then the HOMO and LUMO values are calculable (Hwang & Chen 2002).

This experiment can be done using three electrodes consisting of a working electrode, a counter electrode and a reference electrode. Ferrocene is used in this experiment as a known reference to calculate the E_{ox} or E_{red} (Al-Ibrahim et al. 2005a, b). The estimations can be done with the empirical relation $E_{LUMO} = [(E_{red} - E_{1/2(ferrocene)}) + 4.8]$ eV including the ferrocene value of -4.8 eV (Pommerehne et al. 1995). This paper is on the characterization of two potential organic semiconductors to make sure that they may produce feasible solar cells. Optical properties such as absorption were studied. Cyclic voltammetry was employed as an accurate method to measuring the HOMO/LUMO of donor and acceptor.

EXPERIMENTAL METHOD

In this experiment [6, 6]-phenyl C61 -butyric acid 3-ethylthiophene ester (PCBE) and poly (3-octylthiophene-2, 5-diyl) (P3OT) were tested as potential acceptor and potential donor, respectively. The P3OT was purchased from Sigma-Aldrich and PCBE was purchased from American-dye Source and both were used without further purification. Figure 1 shows the chemical structure of the PCBE and P3OT.

Glass slides as substrate were cut with size 25×25 mm² and were cleaned and used for UV-Vis spectrometry. Absorption spectra and E_g of materials, in inkjet printed thin films, were obtained using PerkinElmer LAMBDA 900 UV-Vis spectrophotometer.

For estimation of oxidation potential of P3OT and PCBE, cyclic voltammetry (CV) experiments were carried out in a three-electrode cell consisting of a platinum working electrode, a platinum counter electrode and a SCE reference electrode using a scan rate of 50 mV/s (Solartron 1286). PCBE was dissolved 1×10^{-3} M in toluene/acetonitrile (1:1), while P3OT was measured in films, which was prepared by dipping platinum electrode in solution and drying for 15 min. The supporting electrolyte was 0.1 M TEABF₄ in acetonitrile. The band gap energy was measured from the absorption spectrum. In addition the E_{ox} which was obtained from cyclic voltammetry and E_{HOMO} where the complete band diagram was calculated.

RESULTS AND DISCUSSION

ABSORPTION AND ENERGY OF BAND GAP

Figure 2 shows the absorption spectrum of PCBE. As shown in this Figure the corresponding wavelength to the band gap energy can be calculated from the cross point of absorption onset line and corrected base line (Schlaf et al. 2000). The corresponding wavelength for PCBE is 630 nm and it can absorb the light in the range of 320-480 nm. The 630 nm intercept is equal to 1.96 eV energy band gap.

Figure 3 shows the current-voltage curve for PCBE from the cyclic voltammetry measurements. Based on cyclic voltammetry results, PCBE shows $E_{ox} = 1.48$ V, which is equal to $E_{HOMO} = 5.87$ eV from the equation $E_{HOMO} = [(E_{ox} - E_{1/2(ferrocene)}) + 4.8]$ eV.

Figure 4 shows the absorption spectrum of P3OT. The absorption in the range of 470-620 nm. The corresponding wavelength for P3OT regarding to the absorption spectrum is 675 nm which is equal to 1.83 eV band gap energy.

Figure 5 shows the current-voltage curve for P3OT regarding to cyclic voltammetry measurements. Based on cyclic voltammetry results, P3OT shows $E_{ox} = 1.2$ V. Hence the E_{HOMO} is equal to 5.59 eV.

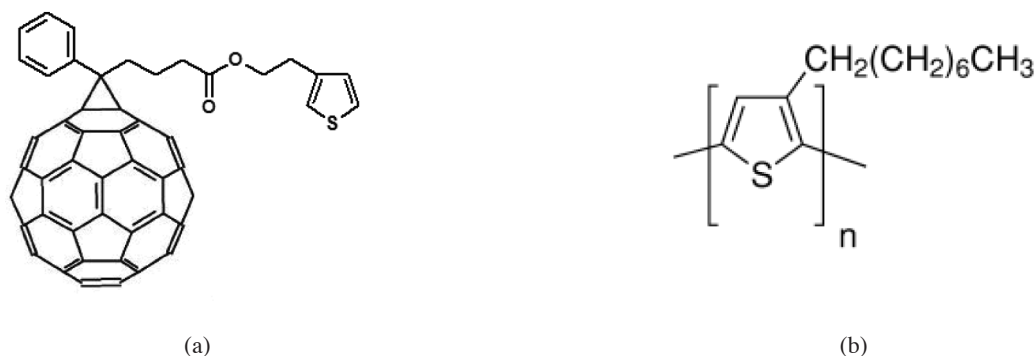


FIGURE 1. (a) PCBE (n-type polymer as acceptor), b) P3OT (p-type polymer as the donor)

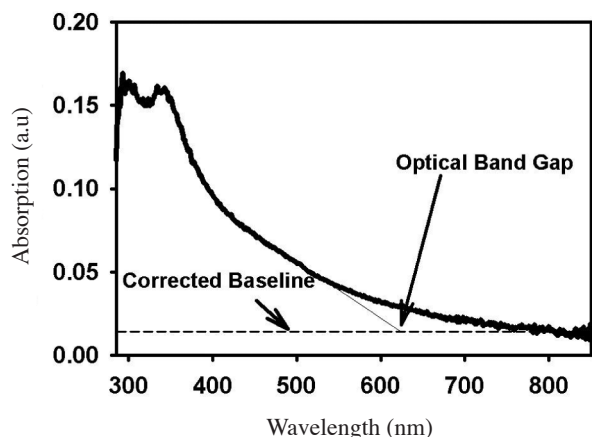


FIGURE 2. Absorption spectrum and optical band gap of PCBE

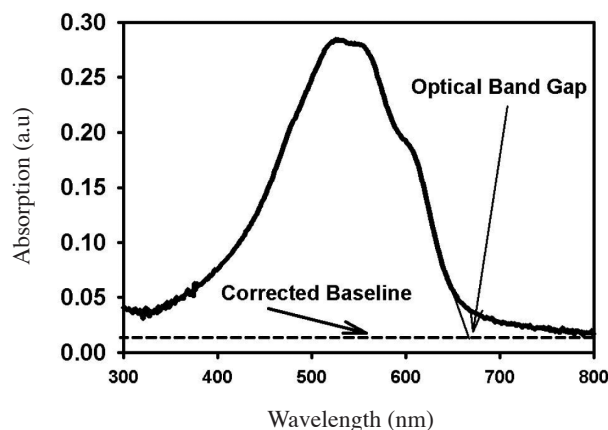


FIGURE 4. Absorption spectrum and optical band gap of P3OT

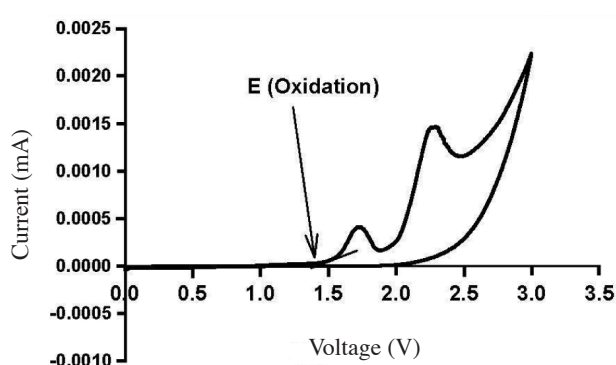


FIGURE 3. Current-voltage curve for PCBE

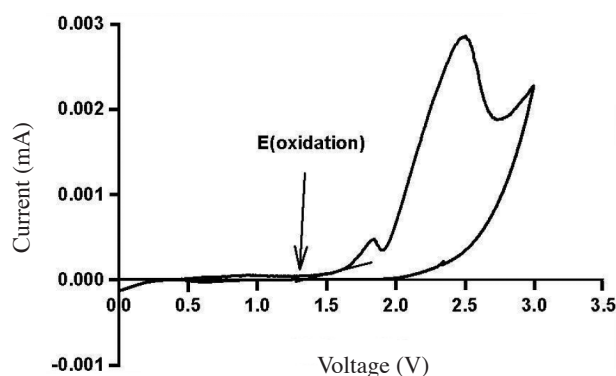


FIGURE 5. Current-voltage for P3OT

HOMO/LUMO ESTIMATION

The corresponding HOMO and LUMO levels were calculated using E_{ox} (onset) for the measurements in film (P3OT) and in solution (PCBE). The estimations were done with the empirical relation $E_{LUMO} = [(E_{red} - E_{1/2(ferrocene)}) + 4.8]$ eV or $E_{HOMO} = [(E_{ox} - E_{1/2(ferrocene)}) + 4.8]$ eV. Ferrocene was used as external standard. It shows two peaks at 0.37 and 0.44 V hence the $E_{1/2(ferrocene)}$ is equal to 0.41 V which can be used in equation to calculate the E_{HOMO} .

Based on cyclic voltammetry results, PCBE shows $E_{HOMO} = 5.87$ eV, $E_{gap} = 1.96$ eV and $E_{LUMO} = 3.91$. Based on the cyclic voltammetry results, P3OT shows $E_{HOMO} = 5.59$ eV, $E_{gap} = 1.83$ eV and $E_{LUMO} = 3.76$ eV.

Figure 6 shows the band diagram with HOMO/LUMO levels of P3OT and PCBE in addition the ITO and Al work functions (Al-Ibrahim et al. 2005 b). This proves that the required energy level for the materials is fulfilled for fabricating organic solar cells using these two materials.

Regarding to the required criteria in selecting material selecting for organic solar cells especially energy concepts, these two materials can be used as a potential active layer for organic solar cells. The fabrication of bulk heterojunction organic solar cells, with these two materials, has been reported (Shafiee et al. 2008, 2009). The devices show a reasonable V_{oc} up to 780 mV, though

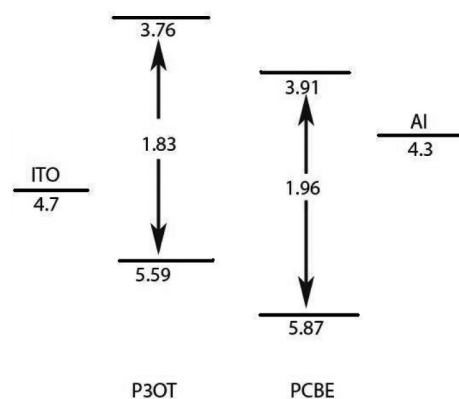


FIGURE 6. Energy Band Diagram of P3OT/PCBE in addition to the work function of ITO and Al

the J_{sc} is still under improvement to enhance the device efficiency.

CONCLUSION

HOMO/LUMO of two organic semiconductors were successfully characterized as potential materials for active layer in the fabrication of bulk heterojunction organic solar cells. Based on cyclic voltammetry studies, in addition to the

absorption and energy band diagram of the materials, viable bulk heterojunction organic solar cells can be fabricated with the combination of these two materials. Open circuit voltage of devices up to 780 mV was obtained with the combination of these materials.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Higher Education of Malaysia for the support under Research University Grant UKM-GUP-BTT-07-26-178.

REFERENCES

- Al-Ibrahim, M., Roth, H.K., Schroedner, M., Konkin, A., Zhokhavets, U., Gobsch, G., Scharff, P. & Sensfuss, S. 2005. The influence of the optoelectronic properties of poly(3-alkylthiophenes) on the device parameters in flexible polymer solar cells. *Organic Electronics* 6: 65-77.
- Al-Ibrahim, Konkin, A., Roth, H.K., Egbe, D.A.M., Klemm, E., Zhokhavets, U., Gobsch, G. & Sensfuss, S. 2005. Phenylene-ethynylene/phenylene-vinylene hybrid polymers: optical and electrochemical characterization, comparison with poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene] and application in flexible polymer solar cells. *Thin Solid Film* 474: 201-210.
- Hagfeldt, A. & Gratzel, M. 2000. Molecular photovoltaics. *Accounts of Chemical Research* 33(5): 269-277.
- Hoppe, H. & Sariciftci, N.S. 2004. Organic solar cells: An overview. *Journal of Material Research Society* 19(7): 1924-1945.
- Hwang, S.W. & Chen, Y. 2002. Photoluminescent and Electrochemical Properties of Novel Poly(aryl ether)s with Isolated Hole-Transporting Carbazole and Electron-Transporting 1,3,4-Oxadiazole Fluorophores. *Macromolecules* 35(14): 5438-5443.
- Kietzke, T. 2007 Recent Advances in Organic Solar Cells. *Advances in OptoElectronics*. Article ID 40285.
- Pommerehne, J., Vestweber, H., Guss, W., Mahrt, R.F., Bassler, H., Prorsch, M. & Daub, J. 1995. Efficient two layer LEDs on a polymer blend basis. *Advanced Materials* 7(6): 551-554.
- Reyes-Reyes, M., Kim, K. & Carroll, D.L. 2005. High-efficiency photovoltaic devices based on annealed poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 blends. *Applied Physics Letters* 87(8): art. no. 083506: 1-3.
- Schlaf, R., Schroeder, P.G., Nelson, M.W., Parkinson, B.A., Merritt, C.D., Crisafulli, L.A., Murata, H. & Kafafi, Z.H. 2000. Determination of interface dipole and band bending at the Ag/tris (8 hydroxyquinolino) gallium organic Schottky contact by ultraviolet photoemission spectroscopy. *Surface Science* 450(1-2): 142-152.
- Shafiee, A., Salleh, M.M. & Yahaya, M. 2008. Fabrication of organic solar cells based on a blend of donor-acceptor molecules by inkjet printing technique. *IEEE International Conference on Semiconductor Electronics, ICSE 2008*: 319-322.
- Shafiee, A., Salleh, M.M. & Yahaya, M. 2009. Fabrication of organic solar cells based on a blend of poly (3-octylthiophene-2, 5-diyl) and fullerene derivative using inkjet printing technique. *Proc. SPIE*, Vol. 7493, 74932D; doi:10.1117/12.843467
- Shaheen, S.E., Brabec, C.J., Sariciftci, N.S., Padinger, F. & Fromherz, T. 2001. 2.5 % Efficient Organic Plastic Solar Cells. *Applied Physics Letters* 78(6): 841-843.
- Xue, J., Rand, B.P., Uchida, S. & Forrest, S.R. 2005. Mixed donor acceptor molecular heterojunctions for photovoltaic applications. II. Device performance. *Journal of Applied Physics* 98(12): art no, 124903, pp. 1-9.

Ashkan Shafiee & Muhamad Mat Salleh*
Institute of Microengineering and Nanoelectronics (IMEN)
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

Muhammad Yahaya
School of Applied Physics
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

*Corresponding author; email: mms@ukm.my

Received: 29 December 2009

Accepted: 9 July 2010