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Electrochemical and optical studies of 1,4-diaminoanthraquinone for solar cell applications

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Summary

Organic microelectronic devices performances are strongly dependant on the energy level alignment of their different constituents (electrode/organic, organic/organic). The cyclic voltammograms (CV) of 1.4-diaminoanthraquinone (1,4-DAAQ) have been measured. The CV curves of 1,4-DAAQ show a one electron reversible reduction and oxidation wave. The energy levels corresponding to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the 1,4-DAAQ have been determined from the first oxidation and reduction potential respectively. The electrochemical energy gap deduced from these measures (E_g=LUMO-HOMO = 1.76 eV) agrees well with the optical energy gap (Eg ~ 1.8 eV). 1,4-DAAQ thin film has been used as electron acceptor in ITO/PEDOT:PSS/ZnPc/acceptor/LiF/Al solar cells. Perylene 3,4,9,10-tetracarboxylicdianhydre (PTCDA) has also been used as electron acceptor. The open circuit voltage value varies with the acceptor, which is in good agreement with their different HOMO values.

Introduction

Nowadays, application of organic materials (conjugated polymers, dyes, pigments) as the active element in microelectronic devices is broadly investigated. Organic light emitting diodes (OLED) are now on the market [1] and significant progress have been done in the field of organic photovoltaic [2]. The success obtained in the field of organic electroluminescent diode has induced a new interest for organic solar cells [3]. In these devices the concepts of electron donor, D, i.e. hole transporting material (p-type) and electron acceptor, A, i.e. electron transporting material (n-type) are recurrent. They correspond to fundamental material properties for such applications. These properties depend on the ionisation potentials (IP) and electron affinities (EA) of the materials. IP corresponds to the highest occupied molecular orbital (HOMO) and EA corresponds to the lowest unoccupied molecular orbital (LUMO) of the material.

The basic process of OLEDs involves injection type electroluminescence, namely, after injection of holes from the anode and electrons from the cathode, the interaction between oppositely charged carriers induces exciton formation, which desexcitation could be radiative recombination. Therefore, efficient carrier injection from both electrodes is a key factor in the performance of OLED. The band structure of the whole device should be optimized in order to decrease the barriers at the interface electrode/organic material. A good adequation is needed between the Fermi level of the anode and the HOMO of the organic material, usually a hole transporting layer and between the Fermi level of the cathode and the LUMO of the organic, which induces the use of an electron transporting layer because of the highest value of its electron affinity. In the case of solar cells, after photon absorption and exciton creation the efficiency of the photo induced charge separation is a key problem. Whatever the structure used, bilayer or bulk heterojunction, the donor and acceptor should have their relative electron affinity (LUMO) and ionisation potential (HOMO) well adapted. The electron affinity of the donor is smaller than that of the acceptor, while the ionisation potential of the acceptor should be significantly greater than that of the donor. When the donor is excited, the electron promoted to the LUMO will lower its energy by moving to the LUMO of the acceptor. The band offset at the organic heterointerface between the weak electron-donor material and a weak electron-acceptor material tends to separate the exciton diffusing to that interface into an electron in the acceptor and a hole in the donor material. Moreover, the theoretically obtainable open circuit voltage, Voc, is given by the difference between the highest occupied molecular orbital of the electron donor ($HOMO_D$) and the lowest unoccupied molecular orbital of the electron acceptor ($LUMO_A$) that is to say Δ ($HOMO_D$-$LUMO_A$) [4].

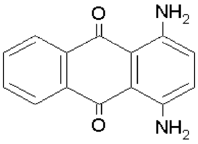
Therefore, whatever the device, the knowledge of the HOMO and LUMO of the organic material is very important, even if others specific properties such as luminescence for OLED or optical absorption for solar cells are also needed. UPS is a performing, but very sophisticated, technique to measure the HOMO and LUMO.

When the organic material shows a one electron reversible reduction and oxidation wave, cyclic voltammetry (CV) is recognised as an important technique for measuring band gaps, electron affinities (LUMO) and potential ionisation (HOMO). The oxidation process corresponds to removal of charge from the HOMO energy level whereas the reduction cycle corresponds to electron addition to the LUMO.

In the present work we have estimated the HOMO and LUMO of 1,4-diaminoanthraquinone (1,4-DAAQ), (schema 1), which absorption spectrum covers, at least partly, the solar spectrum [5]. Then, 1,4-DAAQ thin film has been introduced as an electron acceptor in ITO/PEDOT:PSS/ZnPc/acceptor/LiF/Al solar cells. In order to check the value of the measured HOMO, the Voc of the solar cells obtained with 1,4-DAAQ and with the PTCDA (perylene 3,4,9,10-tetracarboxylicdianhydre) are compared.

Experimental

The 1,4-DAAQ has been purchase to *Aldrich Chem. Co.*, it has been purified by vacuum sublimation.The 1,4-DAAQ has been used for electrochemical measurements, vacuum evaporation and solar cells realisation. The structure of 1,4-DAAQ is presented in scheme 1:



Scheme 1. 1,4-DAAQ

The experimental method to carry out the cyclic voltammetry (CV) has been previously described [6]. As work electrode a polycrystalline platinum disc of 0.24 cm^2 geometric area was used. The reference electrode was Ag/AgCl in solution of tetraethylammonium chloride (Et_4NCl). The potential was adjusted to 0.197 mV with respect to the normal hydrogen electrode (NHE) [7]. As counter-electrode spiral platinum was used in a separated compartment of work electrode by fritted glass. Before each experiment, the work electrode was polished with alumina slurry (particle size 0.3 µm). The data were recorded in a BAS CV-50W system coupled to a PC computer, using one milimolar solutions containing 0.1 M supporting electrolyte, and the scanning rate was 50 $mV \cdot s^{-1}$.

N,N-Dimethylformamide (DMF) (*Mallinckrodt*) as solvent was used. As support electrolyte tetrabutylammonium hexafluorphosfate ($TBAPF_6$) (*Aldrich Chemical Co*) was used. It was dried under vacuum at 60 °C for 24 h.

All solutions were kept under nitrogen during 30 min before each experiment. The gas flux was inverted to keep an inert atmosphere while the electrochemical perturbation was applied.

In the second part of the paper, we report on single junction ITO/PEDOT:PSS/ZnPc/acceptor/LiF/Al solar cells. ITO is the transparent conductive indium tin oxide. ITO has been supplied by SOLEMS SA. PEDOT:PSS is the conductive doped polymer poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid. The organic donor is zinc phthalocyanine (ZnPc). The organic acceptor is 1,4 diaminoanthraquinone (1,4-DAAQ). Perylene 3, 4, 9, 10-tetracarboxylicdianhydre (PTCDA) has also been used as acceptor. X. The upper electrode is a LiF/Al bilayer.

The ITO coated glass substrates have been prepared using the following process. The whole glass substrate (25 mm x 25 mm) was covered with ITO. Therefore, some ITO had to be removed to obtain the electrode. After masking, a strip of ITO broad of 4 mm was etched, along one side of the substrate, by using Zn + HCl as etchant [8]. Then the substrates were cleaned using the RCA treatment [9], a process which involves heating the ITO in a 1:1: 5 solution of $NH_4OH(25\%):H_2O_2(30\%):H_2O$ for 20 min at 80°C, rinsing thoroughly with boiling distilled water, and then drying with a stream of argon gas.

After chemical cleaning, ITO coated glass substrates were spin coated with PEDOT:PSS and annealed in room air at 100°C for 15 min. Layers of ZnPc, 1,4-DAAQ or PTCDA, were deposited by heating in a laboratory made evaporation cell in vacuum (10^{-3} Pa). The deposition rates and film thickness were measured by a quartz monitor.

After organic thin films deposition, the upper electrode was deposited in another vacuum chamber. A thin film of LiF (10 nm) and then an aluminium film (100 nm) were thermally evaporated. A mask was used to determine a well defined shape for the Al electrode, which gives an active area of 2.5 mm^2.

For optical measurements some films of 1,4-DAAQ were deposited onto bare glass substrates. 1,4-DAAQ deposition.

The I-V characteristics of the solar cells have been measured, in room air, in the dark and under illumination, using a solar simulator generating AM 1.5 light (100 mW/cm^2). They were measured using a Lambda power supply as source voltage and Keithley apparatus.

Optical measurements were carried out with a Cary 2300 spectrophotometer from 2 to 0.2 μm.

Results

The electrochemical reduction and oxidation potentials of the 1.4-DAAQ were measured by cyclic voltammetry (CV) (see figure 1). From CV curves, 1,4-DAAQ in DMF showed a one electron reversible reduction and oxidation wave.

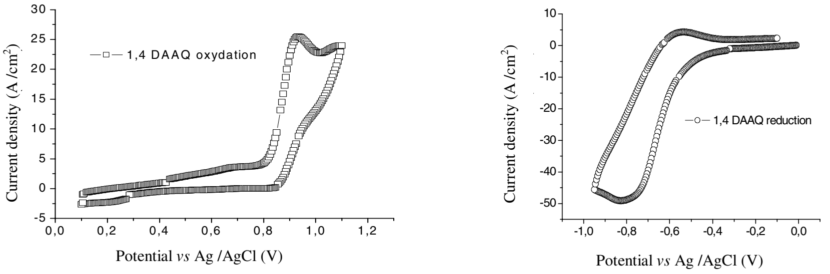


Figure 1. Cyclic voltammograms of 1,4-DAAQ

The HOMO and LUMO energy of 1.4-DAAQ can be determined from the first oxidation and reduction potential respectively. The potential difference Eg = LUMO-HOMO can be used to estimate the energy gap of the dye. The energy level of the normal hydrogen electrode (NHE) is situated 4.5 eV below the zero vacuum energy level [10]. From this energy level of the normal hydrogen and the reduction potential of the reference electrode used in the present work Ag/AgCl i.e. 0.197 V versus NHE, a simple relation can be written which allow to estimate the both energy values:

$$\text{LUMO} = [(-4.5) - (0.197 - E\text{red})] \text{ eV.}$$

$$\text{HOMO} = [(-4.5) - (0.197 - E\text{ox})] \text{ eV.}$$

Relatively to the vacuum level the energy values of HOMO and LUMO levels are -5.63 eV and -3.87 eV respectively. Therefore the band gap estimated from the electrochemical measurements is 1.76 eV.

In figure 2 the transmission spectrum of a thin 1,4-DAAQ film deposited by sublimation onto a glass substrate is reported. It can be seen that the transmission curve exhibits threshold energy around 1.8 eV. It can be estimated roughly that this threshold energy corresponds to the optical band gap of 1,4-DAAQ.

Two solar cells families have been studied, one using 1,4-DAAQ another with PTCDA as electron acceptor.

As said above, for each cell family a thin PEDOT:PSS film (poly(3,4-ethylene dioxythiophene) oxidized (doped) with poly(4-styrenesulfonate)) was deposited by spin coating onto the ITO film before the deposition of the photoactive organic layers. This PEDOT/PSS conductive blend allows to improve the cells performances. The PEDOT:PSS film thickness was around 10 nm.

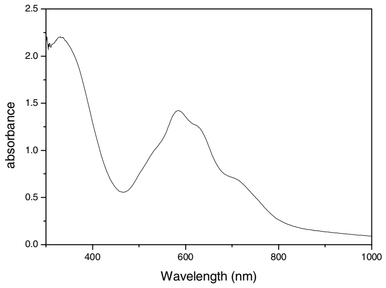


Figure 2. Transmission (optical density) spectrum of 1,4-DAAQ thin film (100 nm) at room temperature

The thickness of the different films of the cell structures were:
ITO (100nm) / PEDOT : PSS (10nm) / ZnPc (45nm) / 1.4-DAAQ (15nm) or
PTCDA (30nm) / Al (150nm).

In the case of heterojunction ZnPC/DAAQ, an effective photovoltaic effect was measured with a short circuit current I_{sc} of $2 \cdot 10^{-2}$ mA and an open circuit voltage, V_{oc} of 0.9 V. It can be seen that, if V_{oc} is large, the short circuit current is small, which induces low efficiencies for the cells ($\eta \cong 10^{-2}$).

In the case of heterojunction ZnPc/PTCDA the short circuit current I_{sc} is $2 \cdot 10^{-1}$ mA and the open circuit voltage V_{oc} is 0.6 V. The results are better. A maximum efficiency $\eta = 2.5 \cdot 10^{-2}$ has been achieved (figure 3).

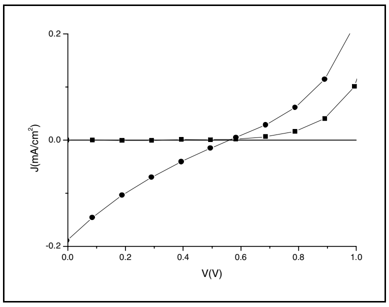


Figure 3. Current-voltage characteristics of an ITO/PEDOT:PSS/ZnPc/PTCDA/LiF/Al cell, (■ in the dark, ● under AM 1.5 light)

Discussion

As shown above, relatively to the vacuum level, the energy values of HOMO and LUMO levels are -5.63 eV and -3.87 eV respectively and the band gap deduced from the electrochemical measurements is 1.76 eV. Since the optical band gap is estimated to be around 1.8 eV, the energy gap calculated from the difference between the LUMO and HUMO energies is quite close to the optical band gap, which testifies to the validity of the electrochemical measurements.

About solar cells, if the HOMO and LUMO of 1.4-DAAQ have been estimated during this work, the corresponding values for ZnPc and PTCDA are available in the literature. Relatively to the vacuum level, in the case of ZnPc we have HOMO = -5.17 eV, LUMO = -3.78 eV [11] and HOMO = -6.8 eV, LUMO = -4.7 eV in the case of PTCDA [12].

As said above, the band offset at the organic heterointerface between the electron-donor material and the electron-acceptor material tends to separate the exciton diffusing to that interface. The different HOMO-LUMO values at the interface ZnPc/acceptor are represented in figure 4. It can be seen that, if effectively 1.4-DAAQ can be used as an electron acceptor, a better exchange should be present at the interface ZnPc/PTCDA than at the interface ZnPc/DAAQ, since, the band offset is 0.8 eV in the former case, while it is only 0.1 eV in the latter case. Therefore, this difference in band offset can justify the higher value of the short circuit current in the former case.

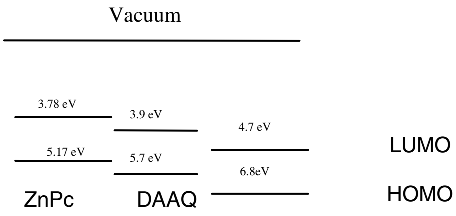


Figure 4. Schematic representation of different HOMO and LUMO energies

The variation of the Voc value with the cell configuration is summarized table 1. The Δ ($HOMO_D$-$LUMO_A$) values are also reported in this table, while HOMO and LUMO values of organic materials are recalled in figure 4. It can be seen in table one that the measured Voc follows qualitatively the variation of Δ ($HOMO_D$-$LUMO_A$). This evolution corresponds to that expected from the theory. The open circuit voltage also depends on others cell parameters, such as parallel resistance, interface states, which justifies that experimental and theoretical values are not equal, however, this result corroborates the validity of the electrochemical estimation of the HOMO and LUMO of 1,4-DAAQ.

Table 1. Variation of Voc with Δ ($HOMO_D$-$LUMO_A$) for ITO / PEDOT : PSS / ZnPc / acceptor (PTCDA or DAAQ) / LiF / Al

Heterojunction	ZnPc/PTCDA	ZnPc/1,4-DAAQ
Δ ($HOMO_D$-$LUMO_A$) (eV)	0.5	1.3
Voc (V)	0.5-0.6	0.9-1

Conclusions

It is well known that the knowledge of the HOMO and LUMO values of organic materials is needed for optoelectronic applications of these materials. In the present paper we show that these values can be estimated with some reliability by electrochemical measurements. Effectively the measured values in the case of 1,4-DAAQ (HOMO = -5.63 eV, LUMO = - 3.87 eV) are corroborated by optical measurements (optical band gap = 1.8 eV, electrochemical band gap = 1.76 eV). The 1,4-DAAQ has been used in solar cells as acceptor. It is shown, here also, that the experimental results obtained corroborate the HOMO and LUMO measured values.

Effectively when the electron acceptor changes (1'4-DAAQ to PTCDA), the Voc and Icc values vary as expected theoretically.

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References

[1] L. S. Hung, C. H. Cheng, *Material Sciences and Engineering*, R39 (2002) 143.

[2] C. Brabec, V. Dyakonov, J. Parisi, N. S. Sariciftci, in "Organic Photovoltaïcs-Concepts and Realization", Materials Sciences 60, Springer, Berlin, 2003.

[3] J. C. Bernède, V. Jousseaume, M. A. del Valle, F. R. Díaz, "From the Organic Electroluminescent Diodes to the New Organic Photovoltaic Cells", Current Trends in Polymer Sciences, Vol. 6 (2001) 135.

[4] E. Kymakis, E. Koudoumas, I. Franghiadakis, *Sol. Ener. Mat.& Sol. Cells*, 90 (2006) 1705.

[5] M. Jamali, J. C. Bernède, C. Rabiller, *J. Solid State Chem.*, 141 (1998) 309.

[6] F. Brovelli, M. A. del Valle, F. R. Díaz, J. C. Bernède, *Bol. Soc. Chil. Quim.*, 46 (2001) 319.

[7] R. Córdova, M. A. del Valle, H. Gómez, R. Schrebler, *J. Electroanal. Chem.*, 377 (1994) 75.

[8] R. G. Gordon, *Mater. Res. Soc. Symp. Proc*. 426 (1996) 419.

[9] J. S. Kim, R. H. Friend, F. Cecialli, *J. Appl. Phys.*, 86 (1999) 2774.

[10] A. J. Bard, L. R. Faulkner, in "Electrochemical Methods. Fundamentals and Applications", Wiley, New York, 1984, p 634.

[11] H. R. Kerp, E. E. van Faassen, *Chem. Phys. Lett.*, 332 (2000) 5.

[12] T. Maruyama, A. Hirasawa, T. Shindow, K. Akimoto, H. Kato, A. Kakizaki, *J. Lum.*, 87-89 (2002) 782.