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Open circuit voltage of organic photovoltaic cells using C₆₀ as acceptor: variation with the donor[★]

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Abstract. The open circuit voltage (Voc) of organic photovoltaic cells (OPVs) is an important parameter in terms of OPV performance. In the present work, we check that its value depends on the energy difference between the Lowest Unoccupied Molecular Orbital of the electron acceptor (LUMO_A) and the Highest Occupied Molecular Orbital of the donor (HOMO_D). The electron acceptor is the fullerene, while the electron acceptors are used as parameter. The results show that Voc increases with the value of $\Delta(\text{LUMO}_A\text{-HOMO}_D)$. However, for some molecules, this increase is not linear, which shows that other parameters are also determinant.

1 Introduction

Today, it appears that the different PVC families are not exclusive but complementary, crystalline Si (C-Si) and inorganic thin films solar cells (GaAs, CuInSe₂, etc.) for their high efficiency and stability, perovskite (PVSCs) for its high potential in the near future and organic solar cells (OPVs) for their high potential in the field of semitransparent OPVs.

In the case of organic materials, a specific interest is dedicated to flexible semitransparent OPVs, the aim being integrating OPVs into façade elements to reduce the energy consumption and CO₂ emission of a building. Actually, beside their flexible, lightweight, the most exciting thing about organic semiconductors is that it is possible to design molecules that are colored or quite transparent, which allows growing semitransparent photovoltaic cells. Concerning the pronounced absorption features of various absorber molecules used in organic solar cells, devices can be designed to transmit light in a specific spectral range. Thereby, colored see-through photovoltaic elements (e.g., windows or colored semitransparent curtains) are possible [1]. If some organic molecules are sensitive to humidity and oxygen, it was already shown that an efficient encapsulation allows over passing this problem and a life times of more than 8 yr were already

announced. OPVs are already on the market as semitransparent solar cells into building façades [1] and also as mobile phone chargers [2].

Even if the efficiency of OPVs progresses regularly it is always lower than that of inorganic cells. The main parameters on which the efficiency depends are the short circuit current, J_{sc} , the fill factor, FF, and the open circuit voltage, Voc. The OPVs are based on the organic couple electron donor/electron acceptor, (ED)/(EA) [3]. In the present work, we studied the behavior of Voc when we change the electron donor. It is now well admitted that the Voc maximum value is limited by the difference between the Lowest Unoccupied Molecular Orbital of the acceptor (LUMO_A) and the Highest Occupied Molecular Orbital of the donor (HOMO_D) [4] (Fig. 1). If Voc increases with $\Delta(\text{LUMO}_A\text{-HOMO}_D)$, the light absorption efficiency depends on the band gap value, Eg. The optimum band gap value is: $1.5\text{ eV} < E_g < 2\text{ eV}$. Moreover, the energy difference between the LUMOs (and HOMOs) of the donor and acceptor must be higher than the exciton energy in order to achieve efficient charge separation. All this makes it necessary to find the optimum compromise, to achieve the highest possible efficiency (Fig. 1). In the present study, in order to obtain reproducible experimental conditions, we choose to work on planar-heterojunctions. It was already shown that efficiency as high as 8.4% can be achieved using small molecules [5]. Actually, if, often, OPVs based on bulk-heterojunction (BHJ) achieve highest efficiency, their morphology is difficult to control. Therefore, we used simple stacked layers sandwiched between the ITO anode and the Al cathode [3]. We used fullerene as acceptor, while we used the electron donor as parameter. We show that Voc increases with $\Delta(\text{LUMO}_A\text{-HOMO}_D)$, the slope of the corresponding curve being around 1.

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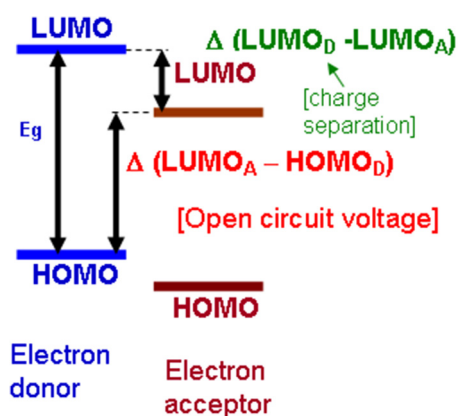


Fig. 1. Band structure of the interface donor/acceptor.

2 Experimental technique

2.1 Organic photovoltaic cells (OPVs) realization

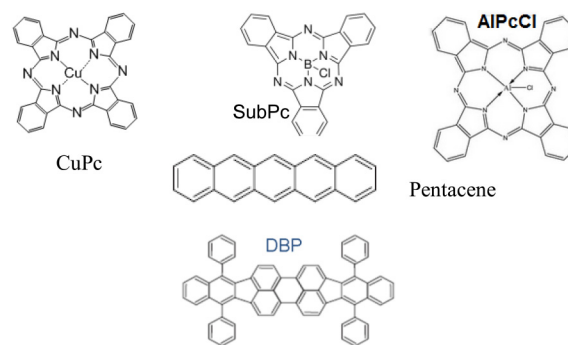
ITO coated glass substrates with a sheet resistance of about $25 \Omega/\text{square}$ were used as anode. After cleaning and drying, the substrates were introduced into a vacuum deposition apparatus. All the layers were deposited by Joule effect without breaking the vacuum. The thickness and the deposition rate of the layers were controlled by a quartz monitor. The hole transporting layer (HTL) and the electron transporting layer (ETL) of all the OPVs were MoO_3/CuI and Alq_3 , respectively [6]. The deposition rate of the organic layer was 0.05 nm/s while their thickness was optimized for each ED/EA couple. Fullerene was used as EA, while different EDs were probed. Al was used as cathode, the active surface of the OPVs was 0.10 cm^2 . Finally the OPVs were as follow: ITO/MoO_3 (3 nm)/ CuI (1.5 nm)/ED (x nm)/ C_{60} (40 nm)/ Alq_3 (9 nm)/Al (120 nm).

2.2 Organic photovoltaic cells (OPVs) characterizations

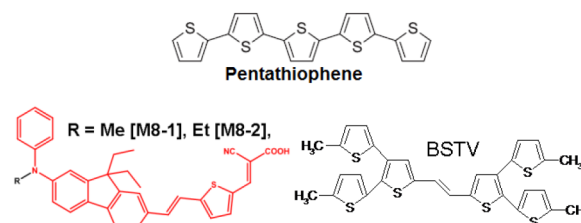
The electrical characterization of the OPVs was performed using a J-V tester, in the dark and under sun global AM 1.5 simulated solar illumination. The ED/EA bilayers were also characterized by X-ray diffraction and optical absorption. The bilayer structures were analyzed by X-ray diffraction (XRD) by a Siemens D5000 diffractometer using $\text{K}\alpha$ radiation from Cu ($\lambda_{\text{K}\alpha} = 0.15406 \text{ nm}$). Optical absorption spectra were recorded on a Carry spectrophotometer from 300 nm to 900 nm. Also, some images of the surfaces were obtained by Atomic Force Microscopy (AFM).

3 Experimental results and discussion

In order to check the variation of V_{oc} with LUMO_D , the LUMO_A being fixed ($\text{LUMO}_{\text{C}_{60}} = 4.4 \text{ eV}$), we used ED with different HOMO values. These ED were either commercial (Phthalocyanine dyes [7], Pentacene [8]; Scheme 1) or synthesized in laboratories (Pentathiophene [8], DBP [9], M8-1 [10], M8-2 [10], BSTV [11]; Scheme 2). Small molecules used in this work are known for their harmless nature. For instance, Phthalocyanine dyes, such as CuPc, are used in gouache paint for children [12].



Scheme 1. Commercial electron donors.



Scheme 2. Laboratory made ED.

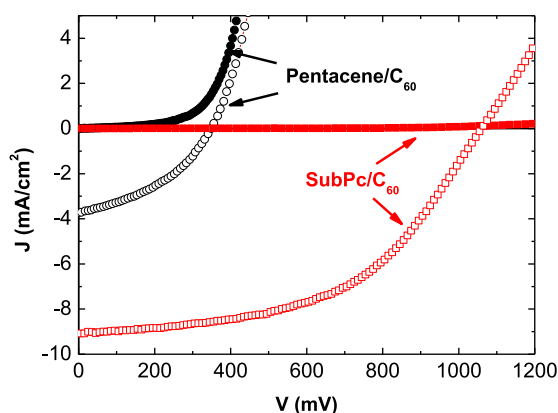
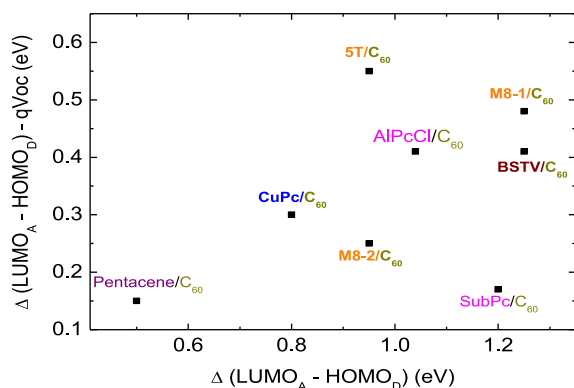
The HOMO_D and the corresponding $\Delta(\text{LUMO}_A - \text{HOMO}_D)$, are given in Table 1. It can be seen that a quite wide range of HOMO_D (from 4.9 eV for pentacene to 5.65 eV for BSTV) and of $\Delta(\text{LUMO}_A - \text{HOMO}_D)$ (from 0.5 eV to 1.52 eV) were probed. The experimental values of V_{oc} are also reported in Table 1. It must be noted that the highest efficiency was obtained with the couple SubPc/ C_{60} ($V_{oc} = 1.03 \text{ V}$; $J_{SC} = 8.31$; $\text{FF} = 54.5\%$ and $\eta = 4.66\%$), while the worst result is obtained with the couple pentacene/ C_{60} ($V_{oc} = 0.35 \text{ V}$; $J_{SC} = 3.74$; $\text{FF} = 40\%$ and $\eta = 0.52\%$) (Fig. 2).

It can be seen immediately in Table 1 that the value of V_{oc} has a determining effect on the efficiency of the cell since the highest efficiency corresponds to the largest V_{oc} and the lowest to the smallest V_{oc} .

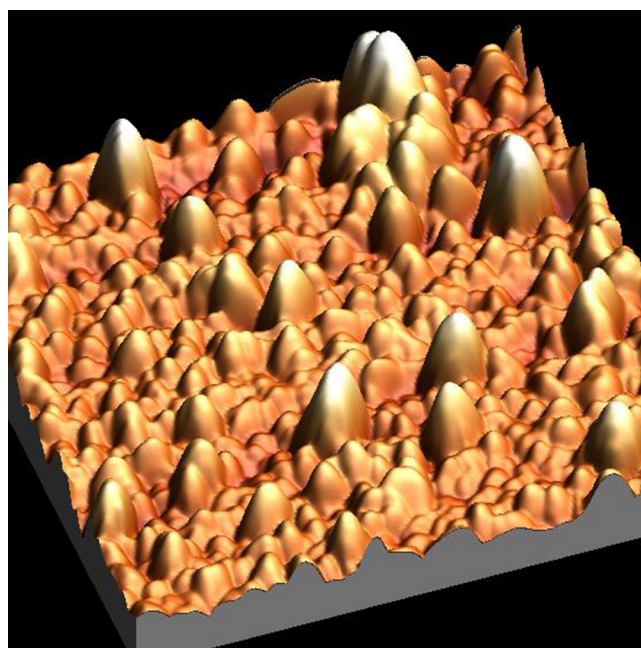
As expected, V_{oc} increases with the value of $\Delta(\text{LUMO}_A - \text{HOMO}_D)$. Nevertheless, as shown in Figure 3, some scattering is observed depending on organic material. For instance, if the difference between the maximum theoretical value of V_{oc} , i.e. $\Delta(\text{LUMO}_A - \text{HOMO}_D)$, and the experimental value can be smaller than 0.2 eV, it can also be higher than 0.5 eV (Fig. 3). We have focused our attention on the two ED/EA couples giving the extreme values in Figure 3, namely, Pentathiophène/ C_{60} for the maximum difference between the theoretical and experimental value and SubPc/ C_{60} for the minimum value. Concerning the couple Pentathiophène/ C_{60} , V_{oc} is only 0.4 eV, while $\Delta(\text{LUMO}_A - \text{HOMO}_D)$ is 0.95. Such small V_{oc} can be due the presence of leakage current. The R_s and R_{sh} values calculated from the J-V curves were $R_s = 3 \Omega$ and $R_{sh} = 300 \Omega$ for Pentacene/ C_{60} while they were 4Ω and 575Ω , respectively, in the case of SubPc/ C_{60} . It was already shown that V_{oc} decreases when R_{sh} decreases, while the saturation current I_s of the diode increases.

Table 1. Parameters and Voc for different electron donors.

ED	Table column head		
	Voc V	HOMO _D	$\Delta(\text{LUMO}_A - \text{HOMO}_D)$
Pentacene	0.35	4.9	0.5
CuPc	0.50	5.2	0.8
AlPcCl	0.70	5.35	0.95
SubPc	1.03	5.6	1.2
Pentathiophene	0.40	5.35	0.95
M8-1	0.77	5.22	1.25
M8-2	0.63	5.44	1.04
BSTV	0.84	5.65	1.25
DBP		5.5	1.1

**Fig. 2.** J–V characteristics of OPVs with Pentacene/ C₆₀ and SubPc/C₆₀ active couple.**Fig. 3.** Variation of $(\Delta(\text{LUMO}_A - \text{HOMO}_D) - qVoc)$ with $\Delta(\text{LUMO}_A - \text{HOMO}_D)$

Such leakage current can be due to some inhomogeneities of the organic films. Therefore, we proceeded to AFM characterizations. The image of a pentathiophene layer is shown in Figure 4. It can be seen that the layer is quite rough, which can initiate some leakage path. The rms deduced is 18 nm. In relation to this result, the dark current of the diode Pentathiophene/C₆₀ under a polarization of 100 mV is $6.4 \cdot 10^{-4} \text{ mA/cm}^2$, which is

**Fig. 4.** 3D image of a pentathiophene layer with thickness 70 nm.

much higher than that obtained with the SubPc/C₆₀ couple which is only $1.4 \cdot 10^{-4} \text{ mA/cm}^2$. Actually, the surface rms of the SubPc layer is only 5 nm [6], which is significantly smaller than that of the pentathiophene layer and can justify the smaller leakage current and therefore the smaller difference between the theoretical and the experimental value of Voc.

Moreover, the reduced dark current obtained with SubPc demonstrates that carrier recombination is weak at the interface SubPc/C₆₀ [13]. All this results in a nearly optimum Voc value.

4 Conclusion

To date, it is well admitted that Voc depends on the energy difference $\Delta(\text{LUMO}_A - \text{HOMO}_D)$. However, this value is the maximum theoretical value that can be reached.

The difference between this theoretical value and the experimental Voc value is more or less large depending on the properties of the ED/EA interface such as the roughness of the bottom layer and charge recombination, some of them being incompressible [14] so that the value of Voc is well described by:

$$qV_{oc} = \Delta(\text{LUMO}_A - \text{HOMO}_D) - x. \quad (1)$$

It was shown that, in the case of BHJ [15] the x value is at least 0.6 eV when the fullerene derivative, PCBM, is used as EA. In the case of PHJ, when C₆₀ is used as EA, we have shown that, after optimization of the layer thicknesses, x is smaller than 0.6 eV. This makes that, by choosing ED and EA molecules with large $\Delta(\text{LUMO}_A - \text{HOMO}_D)$ value, OPVs with high efficiency could be achieved, even if the exciton charges separation is not as efficient as in the case of BHJ.

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