

Dedicated to Professor A. Simashkevich on the occasion of his 80th birthday

DETERMINATION OF THE OPTIMAL BANDGAP OF A POLYMER IN BULK HETEROJUNCTION SOLAR CELLS

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Abstract

The aim of this paper is to determine the optimal bandgap of a polymer used as a photoactive material in bulk heterojunction solar cells in order to maximize the power conversion efficiency of the device. We have considered an ideal absorption profile for the photoactive material and we calculated the maximum current output of the device as a function of the polymer bandgap. Since the open circuit voltage depends on the position of the frontier orbitals of the donor and the acceptor, we also took in account acceptors with different LUMO levels.

1. Introduction

In the last years, there was an increasing interest in photovoltaic solar cells based on polymer materials [1-3] because they have the potential for processing easiness, mechanical flexibility and low cost of fabrication [4, 5]. In the last years, the most explored electron donor polymer was the regioregular poly(3-hexylthiophene) (P3HT). Using a bulk heterojunction (BHJ) [6, 7] of this polymer with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), a power conversion efficiency (PCE) surpassing 5% has been demonstrated [8]. However, to competitively use these devices in commercial applications, a PCE greater than 10% is desirable.

The PCE of a photovoltaic cell is directly proportional to the short circuit current density (J_{sc}), the open circuit voltage (V_{oc}), and the fill factor (FF). Since the J_{sc} is a function of the light absorbed by the photoactive material, the utilization of a polymer with a lower bandgap can produce an increase in the current output of the device. On the other hand, the maximum V_{oc} of BHJ solar cells with ohmic contacts is related to the difference between the highest occupied molecular orbital (HOMO) of the electron donor and the lowest unoccupied molecular orbital (LUMO) of the electron acceptor [9-11]. Since the bandgap of a polymer is related to the difference between the energy position of the HOMO and LUMO levels, when the bandgap is lowered, a shift in the HOMO or LUMO levels (or both) is also present. The increase in the HOMO level can produce also a decrease in the V_{oc} of the device. This means that the use of a polymer with a low bandgap is not a guarantee to achieve better PCE in the corresponding device.

The aim of this paper is to determine the optimal bandgap of the donor polymer in order to find the maximum PCE achievable for polymer solar cells. We considered virtual donor polymers having different bandgaps; the absorption profile was assumed to be ideal (every photon with energy higher than the bandgap is absorbed). Since the LUMO level of the acceptor plays a crucial role in the V_{oc} of the polymer cells, we considered in our calculations, as an electron acceptor, the widely used PCBM molecule and an ideal acceptor with a suitable LUMO level (i.e., optimized for the LUMO level of the donor polymer).

2. Modelling of the device

In Fig. 1, we report a schematic representation of the investigated device structure together with the energy diagram for the donor and acceptor materials.

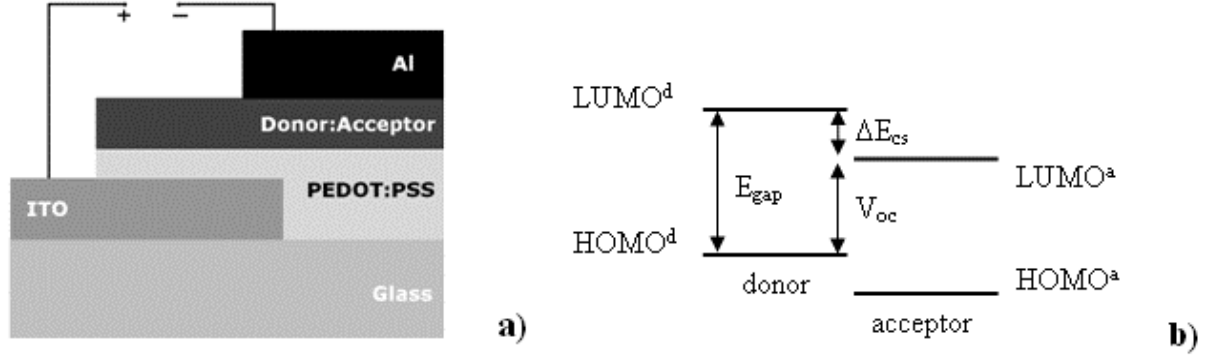


Fig. 1. Schematic device structure of the investigated polymer bulk heterojunction solar cells (a) and energy level diagram for the donor and acceptor materials (b).

Considering that the fill factor (FF) for the best devices realized till now is less than 70%, we used this value as a practical limit in our calculations.

2.1. Modelling of the open circuit voltage

The V_{oc} of polymer BHJ solar cells is directly proportional to the energy difference between the LUMO level of the acceptor and the HOMO level of the donor. This relation holds only for devices with ohmic contacts; instead, for non-ohmic contacts, the V_{oc} is in agreement with the work function difference of the electrodes as expected from the MIM model [12]. In the first case, the V_{oc} of a polymer-fullerene device can be estimated by the following equation [13]

$$V_{oc} = \frac{1}{q} [HOMO(D) - LUMO(A)] - \frac{kT}{q} \ln \left[\frac{(1-P)N_c^2}{PG_M} \right], \quad (1)$$

in which q is the elementary charge, k is the Boltzmann constant, T is the temperature, P is the dissociation probability of a bound electron-hole pair into free charge carriers, N_c is the Langevin recombination constant, G_M is the generation rate of the bound electron-hole pairs, and N_c is the effective density of states.

In addition, for an efficient charge transfer from the donor polymer to the acceptor fullerene, the relative position of donor LUMO and acceptor LUMO is also crucial (an energy difference of 0.3 eV is required [14]). As a general rule, to maximize the V_{oc} in BHJ solar cells, it is necessary to find the appropriate acceptor for each used donor polymer.

In our calculations, we approximated the V_{oc} to the energy difference between the donor HOMO and acceptor LUMO levels: this value should be considered as an upper limit.

If the LUMO of the acceptor is optimized for the LUMO of the donor (i.e., it is 0.3 eV more negative), the V_{oc} of the device decreases lowering the bandgap of the polymer (Fig. 2).

If we consider the solar cells based on a blend of P3HT and PCBM, the energy difference between the LUMO levels of donor and acceptor is around 1.1 eV, hence there is still room to increase the V_{oc} . In this case, using an acceptor with an higher LUMO level, it can be possible to increase the V_{oc} of the device and, therefore, the PCE.

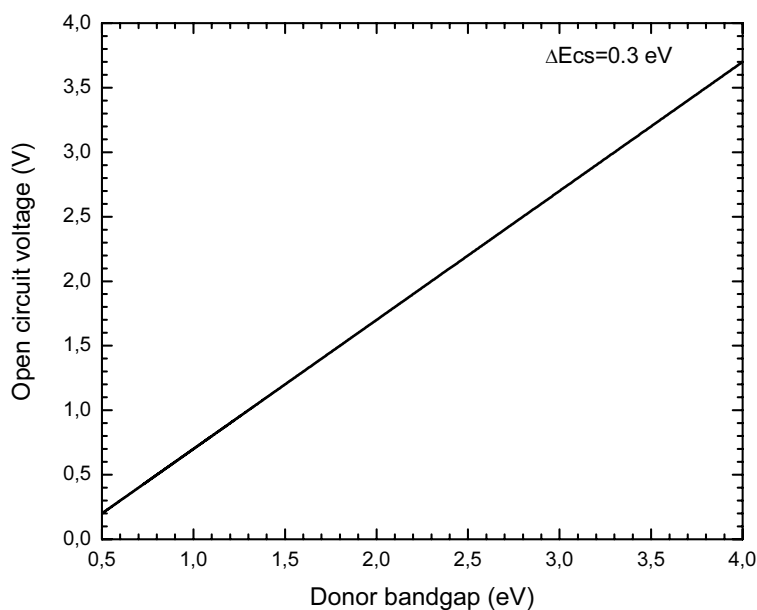


Fig. 2. Maximum value of the V_{oc} as a function of the polymer bandgap in the condition that the acceptor LUMO is 0.3 eV more negative than the donor LUMO.

2.2. Modelling of the short circuit current

The J_{sc} of polymer-fullerene solar cells is a function of the bandgap of the donor polymer if we neglect any contribution to the absorption from the acceptor fullerene is neglected. This is a good approximation when the fullerene used is a derivative of C_{60} , like the commonly used PCBM. Instead, the derivatives of C_{70} and other higher fullerenes have a significant absorption in the visible range and they can effectively contribute to the J_{sc} of the corresponding devices [15]. We considered an ideal absorption for the donor polymers, i.e. we assumed that all the photons with an energy greater than the polymer bandgap are completely absorbed. In Fig. 3, we show the ideal absorption for a polymer with a bandgap of 1.6 eV.

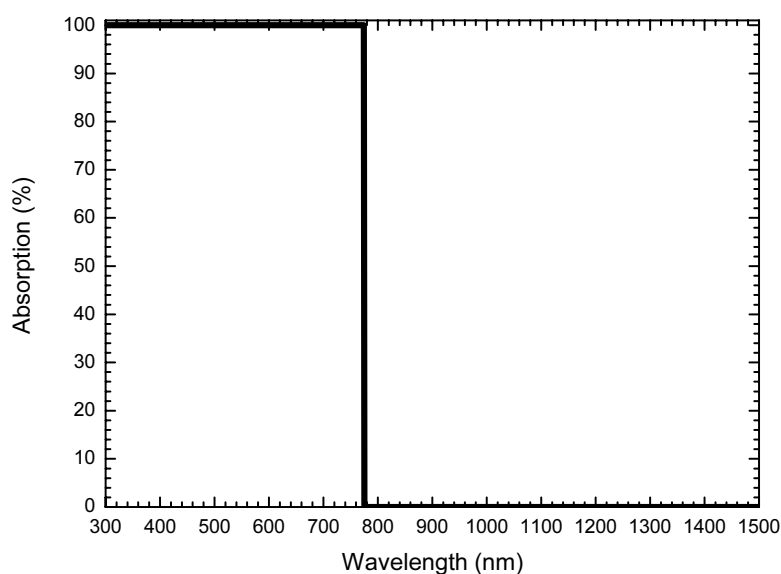


Fig. 3. Ideal absorption for a donor polymer with a bandgap of 1.6 eV.

The maximum J_{sc} can be calculated weighting the absorption of the active layer with the solar irradiance (AM 1.5G spectrum) and integrating this distribution over the wavelengths. Since the electrical losses and the surface roughness were neglected, the calculated J_{sc} can be considered as an upper limit to the real achievable current (Fig. 4).

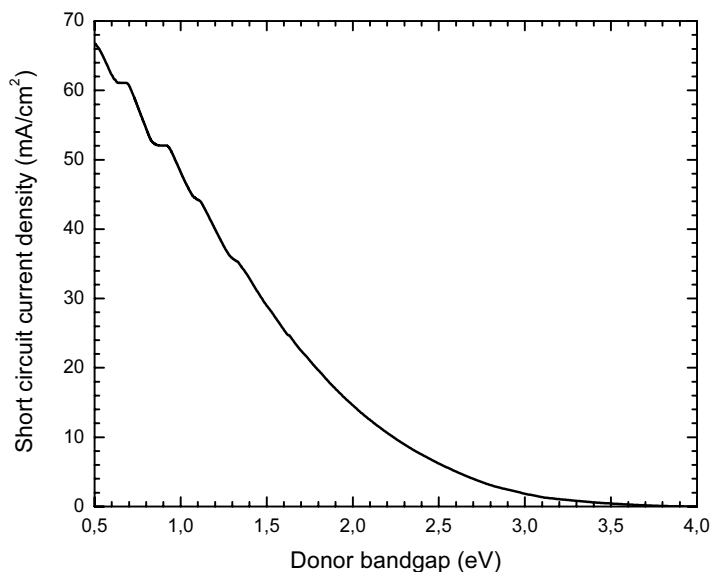


Fig. 4. Maximum J_{sc} as a function of the polymer bandgap.

Since in a real device, not all the photons are absorbed and not all the absorbed photons generate free carriers (i.e., the internal quantum efficiency is less than 100%), we set the external quantum efficiency (for photons with an energy equal or greater than the polymer bandgap) to 70%. This means that only 70% of the incident photons are converted in free carriers.

3. Results and discussion

Using the assumptions described in the previous section, we calculated the theoretical power conversion efficiency of a device as a function of the donor bandgap in the condition that the LUMO level of the acceptor is optimized for the LUMO level of the polymer, namely, the energy difference between these two levels is 0.3 eV. In addition, we considered also the cases where this LUMO-LUMO gap is higher (up to 1.1 eV). All the curves are shown in Fig. 5.

As we can see from Fig. 5, the optimal bandgap is around 1.4 eV and it is shifted to higher values when the gap between the donor and acceptor LUMOs increases.

Since the V_{oc} of a real device is often lower than the value obtained neglecting the third term of equation (1), we calculated the theoretical PCE as a function of the donor bandgap for different V_{oc} correction factors (Fig. 6), while the LUMO of the acceptor was kept 0.3 eV lower than the LUMO of the donor.

Figure 6 shows that the optimal bandgap is shifted to higher values when the V_{oc} of the device is lowered (i.e., when the third term of equation (1) is also taken into account).

If the LUMO level of the acceptor is not optimized for the LUMO level of the donor, like in the above mentioned case, three main scenarios are possible when the polymer bandgap is lowered (for instance when using a new low-bandgap material):

- a) the LUMO level of the polymer decreases;
- b) the HOMO level of the polymer increases;
- c) both HOMO and LUMO levels of the polymer change (i.e., the LUMO decreases and the HOMO increases).

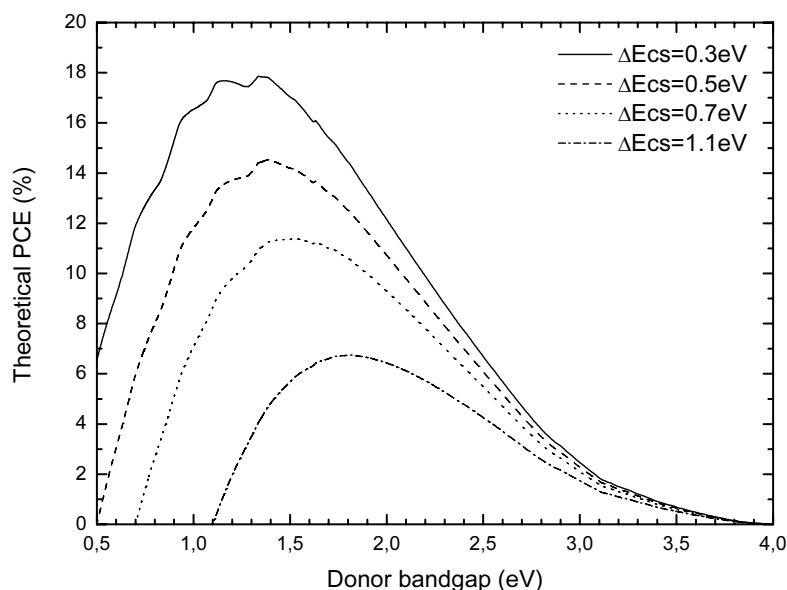


Fig. 5. Theoretical PCE as a function of the donor bandgap using acceptors with a LUMO level ranging from 0.3 to 1.1 eV lower than the donor LUMO.

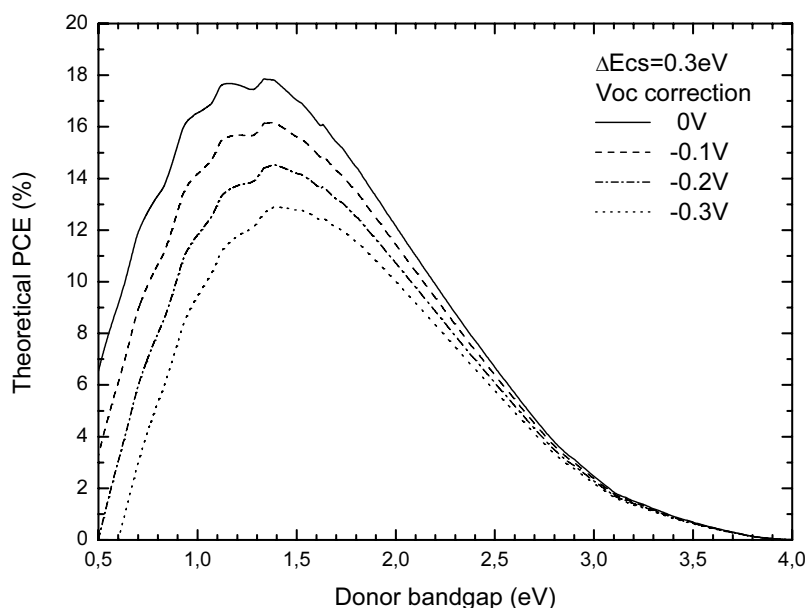


Fig. 6. Theoretical PCE as a function of the donor bandgap using a correction for the V_{oc} .

In Fig. 7, we report the theoretical power conversion efficiency as a function of the polymer bandgap assuming that the donor HOMO is kept constant (i.e., the variation of the bandgap is due only to the variation of donor LUMO). As the electron acceptor, we considered the PCBM (with a LUMO level of -4.3 eV) and as the electron donor, a polymer with a HOMO of -5.1 eV (like P3HT). If the LUMO of the donor polymer is sufficiently higher compared to the LUMO of the acceptor to allow an efficient charge transfer, the V_{oc} of the device remains the same (because the difference between the HOMO of the donor and the LUMO of the acceptor is unchanged) while the J_{sc} increases (due to the reduced bandgap) and the overall PCE increases.

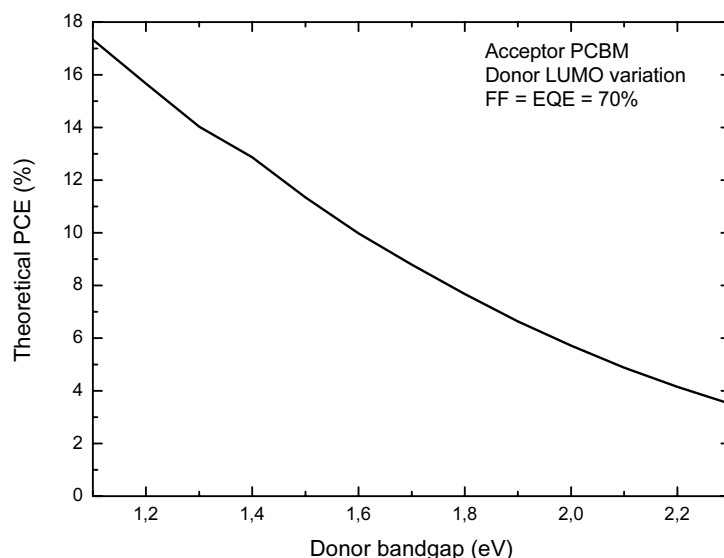


Fig. 7. Theoretical PCE as a function of the donor bandgap shifting only the donor LUMO and using PCBM as an electron acceptor.

In Fig. 8, we report the theoretical PCE as a function of the bandgap of the polymer in the condition that the donor LUMO is kept constant (i.e., the variation is due only to the variation of the HOMO level). Also, in this case, we considered the P3HT:PCBM system and changed the bandgap of the polymer shifting the position of the donor HOMO level. The optimal polymer bandgap is around 1.8 eV (very close to the one of P3HT).

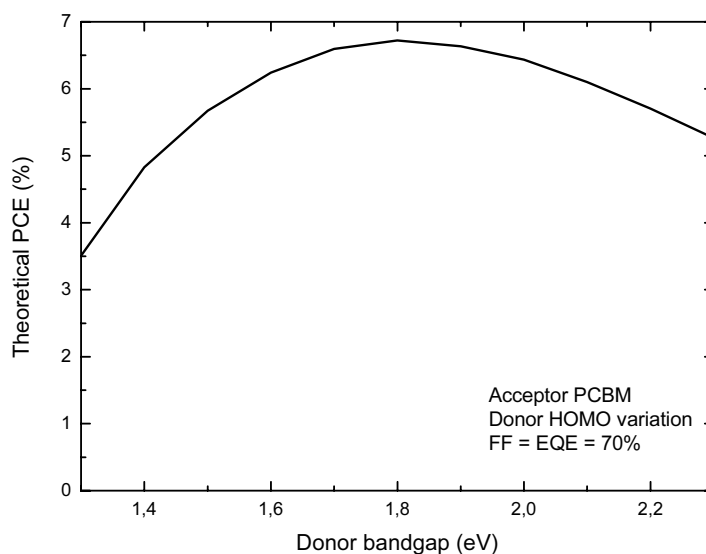


Fig. 8. Theoretical PCE as a function of the donor bandgap shifting only the donor HOMO and using PCBM as an electron acceptor.

In real cases, upon lowering the bandgap of a polymer, both LUMO and HOMO levels can change, and there are competitive factors (decrease of V_{oc} and increase in J_{sc}) that influence the PCE. As a last test case, we considered the variation of the bandgap as a result of a symmetric variation of the HOMO and LUMO levels of the polymer. In Fig. 9, we can see that the optimal bandgap is around 1.4 eV.

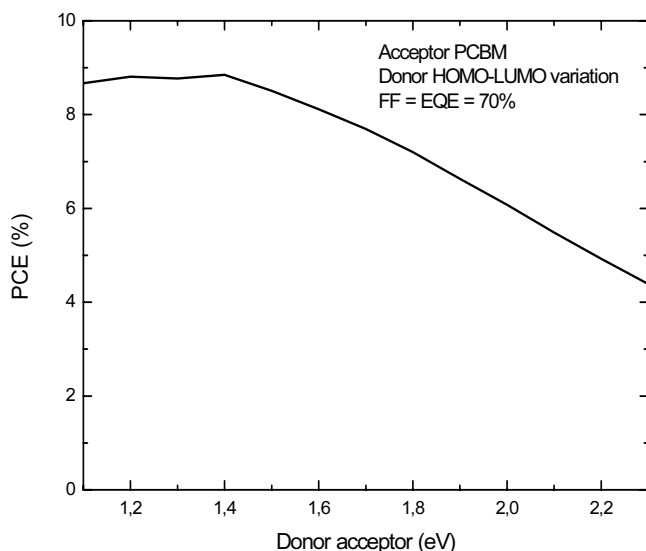


Fig. 9. Theoretical PCE as a function of the donor bandgap shifting both the donor HOMO and LUMO and using PCBM as an electron acceptor.

It should be noticed that if different assumptions are made for the EQE and FF (i.e., values different from 70%), the reported trends for the theoretical power conversion efficiency are shifted to higher values but the optimal bandgap remains unchanged.

4. Conclusions

In the present paper, we have calculated the theoretical power conversion efficiency achievable in BHJ polymer solar cells assuming realistic parameters. We have shown that using proper materials, i.e., polymers with a lower bandgap, a theoretical PCE surpassing 15% is achievable (making this technology more attractive for commercial applications). We also showed that the optimal polymer bandgap is depending on both the energy difference between the donor and acceptor LUMOs and the maximum V_{oc} of the device.

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