Research Article

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Materials for D-D-A ternary organic solar cells: an absorption model study

Abstract: Heterojunction solar cells based on ternary blends of two donors (absorbers and one acceptor) were investigated using modeling. The Tauc-Lorentz model and experimental absorption spectra of selected compounds were used in the simulations. The optimization process was carried out in this way to maximize the absorption of the system. Poly(3-hexylthiophene-2,5-diyl) (PEHT) was investigated as a first donor, which was mixed respectively with poly(3-octylthiophene-2,5-diyl) (P3OT), coumarin 153, purpurin, fluorescent brightener 184, N-chloroethylene carbazole, and 1,3,6,8 tetrachloro 9n amylocarbazole. Simulations were also performed for the Tauc-Lorentz model.

Keywords: absorption; efficiency; ternary solar cells.

1 Introduction

Besides hydro and wind power, photovoltaic energy is an important source of renewable energy. Three generations of solar cells (mono/polycrystalline silicon [1] and other semiconductor materials [2, 3] without an n-p junction) are constantly being refined for various ecological reasons and the growing demand for energy. The advantages of the third generation make its prospects very good. These cells are lightweight, flexible, and inexpensive to manufacture [4, 5]. Dyes [6], organic solar cells [7], perovskites [8] and tandem/hybrid [9, 10] solar cells demonstrate increasing quantum efficiency and stability. Organic solar cells are continually being developed and are currently a hot topic in physics, with one of the trends being ternary solar cells [11].

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The mechanism of organic solar cells is based on optical absorption, which is also the starting point. The active layer consists of a donor mixture and usually a highly conductive fullerene, the acceptor. Photon absorption triggers the excitation of an electron from a donor, the creation of a hole and the formation of an exciton. The next stages are the diffusion of the exciton, exciton separation, the transport of the charges, and the collection of charges on the electrodes. The efficiency of the whole photovoltaic process η depends on the efficiency of individual processes.

$$\eta = \eta_{abs} \cdot \eta_{dyf} \cdot \eta_{mob} \cdot \eta_{col}$$

With ternary organic solar cells, the idea is to enrich a typical mixture for an active layer with an extra donor [12, 13] or extra acceptor [14, 15]. The work discussed in this paper was performed with two donors and one acceptor. The use of two donors is motivated by widening the absorption spectrum and the ability to generate the cascade charge [16]. Unabsorbed photons definitely limit the available number of carriers in the cell. Covering the full spectrum of solar radiation is therefore a primary task in the design of solar cells.

However, the issue of optimization is complex. It can apply to both optical optimization and the approach associated with charge transport, in addition to other significant aspects [17–20]. In applying materials, it is essential to determine the proportion between donor materials and the thickness of the active layer in the bulk heterojunction solar cell arrangement. The aim here is to optimize the donors' arrangement, which is based on the donor's absorption spectra.

2 Calculations

Assuming, as Felekidis et al. do in [21], the internal quantum efficiency (IQE) = 0.85 and including the AM 1.5 standard spectrum, the normalized absorption was defined as:

$$\dot{\eta} = \frac{1}{L_{div}} \int \frac{AM\,1.5(\lambda) \cdot IQE \cdot A(\lambda)}{E_{photon}} \, d\lambda.$$

The reference solar spectrum AM 1.5 is a standardized representation of illumination conditions [the total irradiance is 100 mW/cm², including tilt above the horizon, atmospheric conditions and carbon dioxide (CO_2) level]. Due to the bandgap of polymer semiconductors starting from 2.0 eV (about 600 nm), we were interested in absorption in the 300–600 nm band. Device absorption (a bulk heterojunction organic cell with device thickness L_{div}) is defined as:

$$A(\lambda) = 1 - \exp\left(-\frac{L_{div}}{L_{eff}(\lambda)}\right).$$

In the formula, L_{eff} means device absorption. An effective absorption mixture is defined using attenuation lengths L_{D10}, L_{D20}. Effective absorption also includes a fraction f_{D10} (percentage content) of donor 1.

$$L_{eff}(\lambda) = \frac{L_{D10} \, L_{D20}}{L_{D20} G_{D1}(\lambda) \cdot f_{D10} + L_{D10} G_{D1}(\lambda) \cdot (1 - f_{D1})}$$

3 Results

3.1 Materials

Calculations to obtain the real absorption spectra of selected chemical compounds (Figure 1, Table 1) were performed. The substances were provided by Merck KGaA, Darmstadt, Germany. We investigated poly(3-hexylthiophene-2,5-diyl) (P3HT) [22], [23] as a first donor. This was respectively mixed with poly(3-octylthiophene-2,5-diyl) (P3OT) [24], [25], coumarin 153 [26, 27], purpurin [28], fluorescent brightener 184 [29, 30], N-chloroethylene carbazole and 1,3,6,8 tetrachloro 9n amylocarbazole [31, 32]. Selected materials of organic photovoltaics must show certain properties – good solubility and photochemical and thermal stability. They should also show luminescence properties as confirmation of the possibility of creating a stable excited state. P3HT and P3OT were selected because they are some of the most popular materials used as donors. The others were chosen based on absorption
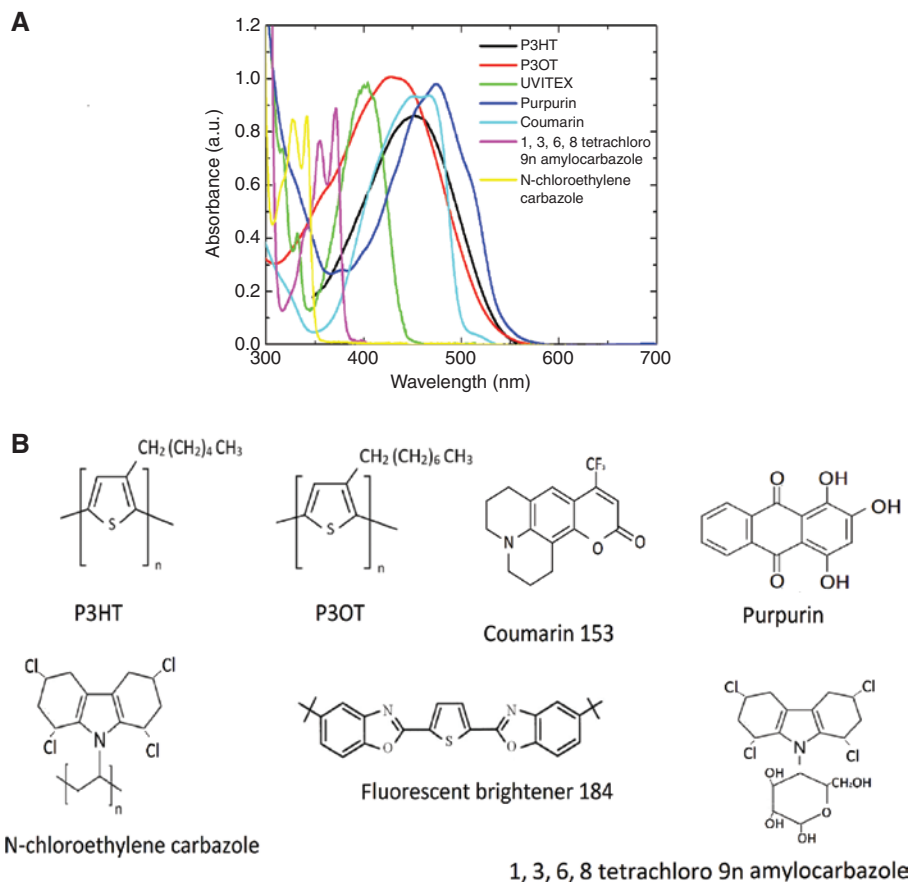

Figure 1: (A) Absorption spectra used in simulations. (B) Chemical formulas of compounds used in simulations.

Table 1: Overview of parameters for compounds.

Substance	Ld [nm]	Eg [nm]	Γ [nm]
P3HT	504	451	103
P3OT	625	430	126
Coumarin 153	469	455	91
Purpin	431	472	97
1,3,6,8 tetrachloro 9n amylocarbazole	274	355;371	10;10
N-chloroethylene carbazole	353	326; 343	10;10
Fluorescent brightener 184	481	403	52

P3HT, Poly(3-hexylthiophene-2,5-diyl); P3OT, poly(3-octylthiophene-2,5-diyl).

optimization because they have different absorption spectra, more specifically different absorption bands, and because they show desirable properties.

Absorption spectra measurement was performed using the Ocean Optics HR4000CG-UVNIR spectrometer (Ocen Optics, Dunedin, FL, USA), and chloroform (solution) was used as a reference. Sample preparation and measurement were carried out at room temperature.

The maximum absorption of E_{max} is associated with E_g; the distribution functions are shown in Figure 2. If, as a reference, pure P3HT (donor 1:donor 2 P3HT:P3HT) is included, a quantum efficiency improvement occurs for a mixture with purpurins. However, for P3OT, coumarin 153, and fluorescent brightener 184, there is a decrease of 8.5%, 9.8%, and 10.3%, respectively. Moreover, efficiency decreased for P3OT. It also decreased for N-chloroethylene carbazole and 1,3,6,8 tetrachloro 9n amylocarbazole by 1.6% and 16.3%, respectively. Considering the energy gaps determined by absorption spectra, these are expected and justified conclusions.

In the second part of the research, we started looking for a more general model. In [21], an optimization model based on the Schockeley-Queisser distribution was presented (specifically, the relationship between HOMO/LUMO levels and efficiency). However, a typical absorption distribution is described by the Breit-Wigner distribution. In optics, it is also called the Lorentz(ian) formula, and in the theory of probability it is referred to as the Cauchy distribution. In this case, there is a dependence on maximum absorption energy and full width at half maximum (FWHM). The Lorentz oscillator is not suitable for describing all real absorbing materials. To include quantum effects, such as an energy gap for amorphous and semiconductor substances, Lorentz equation extensions have been used. Ferlauto et al. [33] included the models of Cody-Lorentz and Tauc-Lorentz, which we found [34] to be most suitable:

$$G_T(E) = \frac{(E - E_g)^2}{E^2}.$$

Based on the algorithm above, calculations for donor 1 and donor 2 were performed, dependent on bandgap value E_g. Figure 3 shows three-dimensional (3D) graphs (normalized) for these systems. The results versus the donor 1 fraction, the thickness of the active layer and efficiency curves depending on the donor 1 concentration are presented in Figures 3 and 4.

In systems of two donors with the same optical bandgap, the results obtained are apparent; the only optimization option reduces the thickness of the active layer. The best results are expected for the thinnest layers. This has been tested experimentally for bulk heterojunction cells [35, 36]. For various donors' bandgaps,
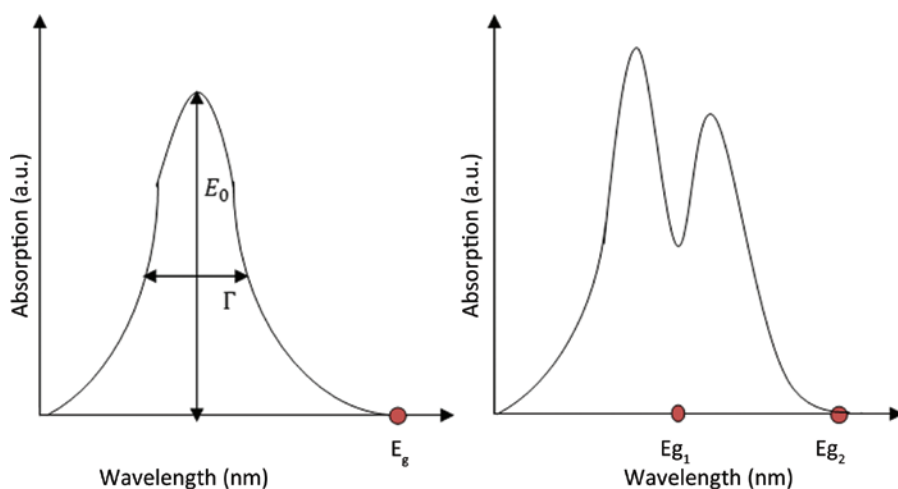
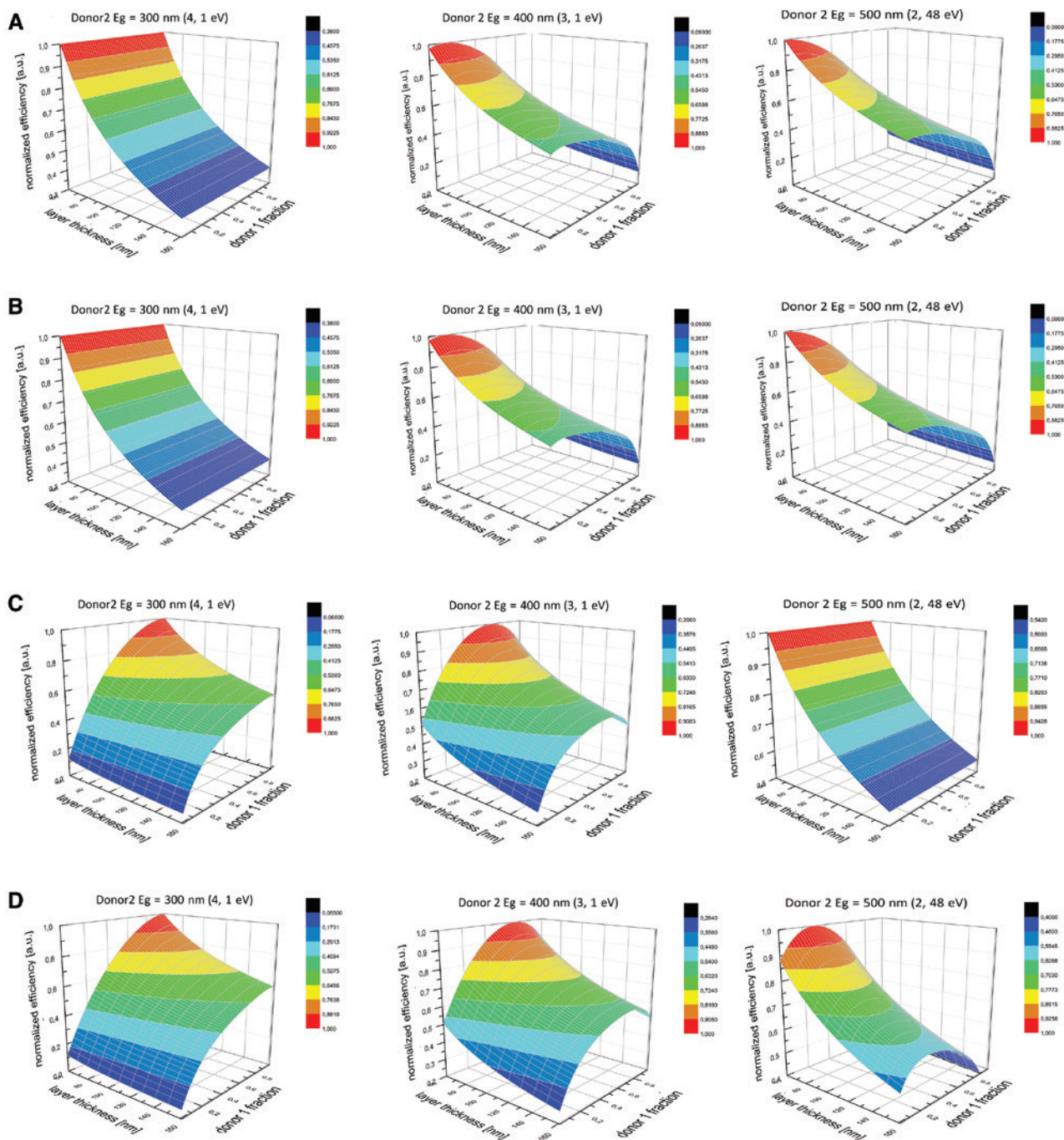**Figure 2:** Parameters describing the absorption spectra used in the study.

Figure 3: Calculated normalized efficiency vs. active layer thickness vs. donor 1 concentration for a donor with E_g value of (A) 300 nm (4.1 eV), (B) 400 nm (3.1 eV), (C) 500 nm (2.48 eV) and (D) 600 nm (2.0 eV).

the dependency functions of the layer thickness and the proportion of donors begin to indicate the maximum efficiency.

Due to the normalization of absorption and arbitrary acquisitions of IQE, performance results can only be determined comparatively. The best arrangement of bandgaps is donor 1 $E_g = 2.48$eV and donor 2 $E_g = 2.1$ eV (500 nm/600 nm) if we compare the maximum values

for different arrangements. Increasing the efficiency of compounds with these maxima of absorption was done experimentally by Shi et al. [37] and for small molecules by Qiu et al. Next in terms of efficiency value is the combination 3.1eV/2.5 eV (400 nm/500 nm) combination and with almost identical 3.1/2.1 eV (400 nm/600 nm) performance. Absorption was normalized, so no quantum efficiency is relative.
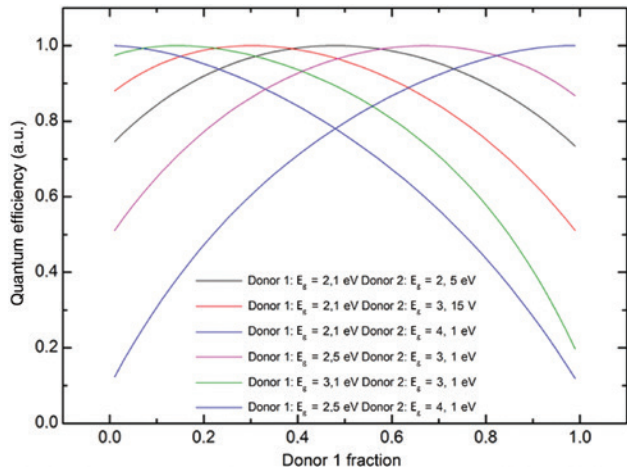
Figure 4: The dependence of quantum efficiency on the amount of donor 1 for an active layer with a thickness of 60 nm.

Figure 6: Current density–voltage characteristics for (A) one donor: acceptor; (B) donor 1 $E_g = 2.48$ eV and donor 2 $E_g = 2.1$ eV: acceptor; (C) donor 2 3.1 eV, donor 1 $E_{1g} = 2.5$ eV: acceptor; (D) donor 2 $E_g = 3.1$, donor 1, $E_{2g} = 2.1$ eV: acceptor.

Absorption spectra with a greater number of absorption maxima were analyzed. Due to the presence of compounds with two or more absorption maxima a donor mixture with two maxima (such as donor 1) and a donor with one absorption maxima (such as donor 1), as the most common (most often, donor 2 is implemented with P3HT) were considered. The 3D graph is shown in Figure 5. For different combinations, the shape is preserved; only the maximum efficiency changed.

The best performance was achieved for donor 2 $E_g = 2.5$ eV, donor 1 $E_{1g} = 3.1$ eV, and $E_{2g} = 2.76$, similarly for donor 2 $E_g = 2.48$ eV, donor 1 $E_{1g} = 3.1$ eV, $E_{2g} = 2.76$ eV. Using $E_g = 2.0$ eV as donor 2 meant that the efficiency was half that of the mixtures.

The presentation of current-voltage performance differences is possible in relation to the basic donor system
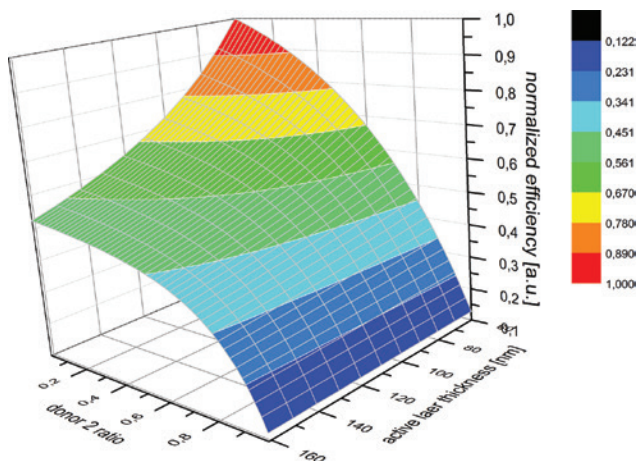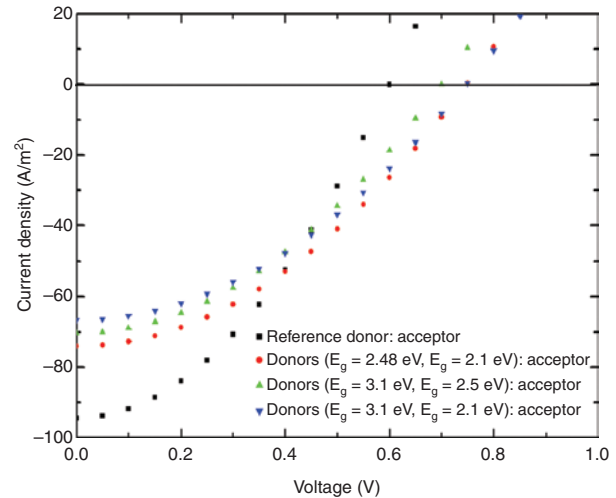
– acceptor P3HT: PCBM (PCBM is [6,6]-phenyl-C61-butyric acid methyl ester, soluble fullerene derivative [38, 39]) – presented by Saunders and Turner [40]). The efficiency of such a system is approximately 5%. The graph in Figure 6 shows the simulation results (input power Pin 1000 W/m² and fill factor at the level of 0.6 was assumed) for the performance of the above-mentioned donor-acceptor combinations.

4 Summary

The model functions well and is applicable. The method can be useful when modeling compounds for photovoltaic applications. Active layer donor mixtures for which performance has been improved are presented. The results of our experiments [41] thus far are consistent with the simulations. The basic conclusion is to deny the possibility of enriching only the absorption; ternary systems like donor 1:donor 2:acceptor should be considered systems for improving electrical conductivity and collecting charges.

Figure 5: Calculated normalized efficiency vs. active layer thickness vs. donor 1 concentration for two-maxima spectrum.

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