

# BULK AND BILAYER INVERTED ORGANIC SOLAR CELLS (OSCs) EXHIBITING D-A AND A-D-A DONORS WITH 2,2'-BI[3,2-*b*]THIENOTHIOPHENE UNITS AND PC<sub>61</sub>BM OR C<sub>70</sub> ACCEPTORS

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**ABSTRACT.** Inverted bilayer and inverted bulk heterojunction OSCs were fabricated and investigated using D-A and A-D-A donors with bi[3,2-*b*]thienothiophene units and PC<sub>61</sub>BM or C<sub>70</sub> acceptors. The cells were optimized by varying the donor/acceptor ratios, the thickness of the layers and the conditions for the spin-coating deposition of the active materials.

**Keywords:** organic solar cells, inverted bilayer structure, inverted bulk heterojunction, 2,2'-bi[3,2-*b*]thienothiophene donors

## INTRODUCTION

2,2'-Bi[3,2-*b*]thienothiophene ([3,2-*b*]-TT) derivatives show a plethora of applications, in emerging fields as medicinal chemistry, [1-3] non-linear optic devices [4,5], materials with liquid crystal behavior [6,7] and conducting (co)polymers. [8–10]. Due to their special opto-electronic properties they were also employed for the fabrication of efficient OSCs (as building blocks in donor molecules [11–16] or non-fullerene acceptors [17–22]) or dye-sensitized solar cells (DSSCs) [23–26].

The replacing of a thiophene ring or a bithiophene unit either in acceptors (**A**) (e.g., [18]) or in donors (**D**) (e.g., [12]) with a [3,2-*b*]-TT moiety

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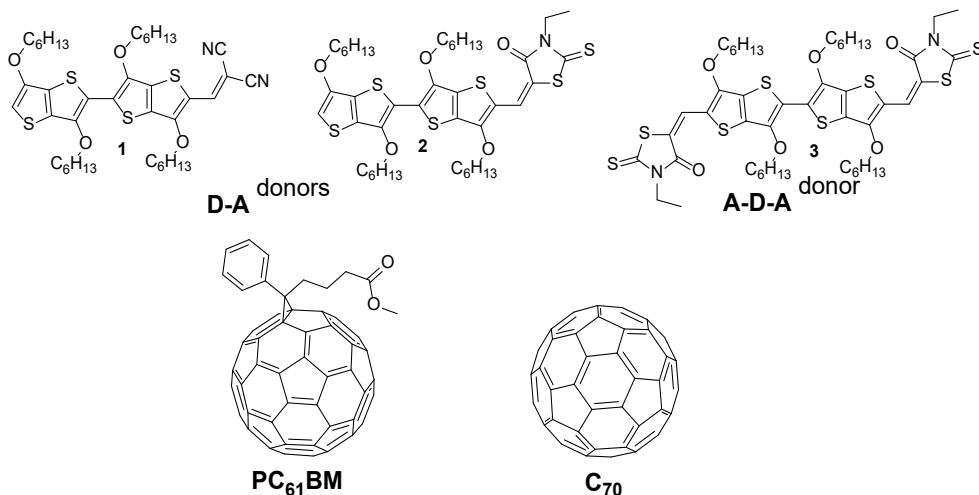
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indicated an improvement in the efficiency of the OSCs exhibiting the modified donors and/or acceptors. In order to develop our research in the field of molecules with exciting optoelectronic properties [27–31] and considering the outstanding properties of [3,2-*b*]-TT derivatives, in a recent work [32] we reported the synthesis and characterization of novel 2,2'-bi[3,2-*b*]thienothiophene derivatives as possible donors for OSCs with **D-A** or **A-D-A** systems.

The fabrication of OSCs can be carried out by vacuum deposition of bilayer planar heterojunction (PHJ) and using solution-processed bulk heterojunction solar cells (BHJ). [33-35] BHJ cells are fabricated at ambient temperature by spin-casting blend films from solutions of donor (**D**) and acceptor (**A**) materials. More stable cells could be obtained in the so called inverted structures of OSCs in which solution-processed layers of ZnO and PVD (Physical Vapor Deposition) deposited MoO<sub>3</sub> are inserted between the electrodes and the active materials, replacing the air and moisture sensitive PEDOT : PSS layer used in the so called direct cells. The active layer in this case can be deposited by spin-casting or PVD technique. The literature in the field underlines the higher efficiency and stability of inverted cells. [33, 35-39]

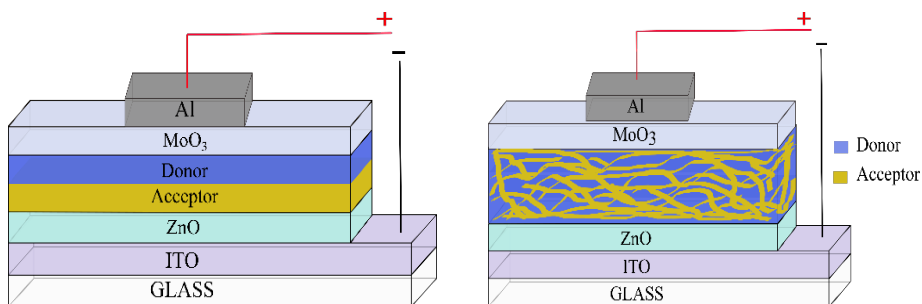
In this context we considered of interest to fabricate and investigate inverted bilayer and inverted bulk heterojunction OSCs using **D-A** (**1** and **2**, Figure 1) and **A-D-A** (**3**, Figure 1) donors with bi[3,2-*b*]thienothiophene units (unexplored in OSCs) and **PC<sub>61</sub>BM** (Figure 1) or **C<sub>70</sub>** (Figure 1) acceptors. Donors **1-3** are new compounds and we recently reported their synthesis and structure determinations.



**Figure 1.** Chemical structures for donors (**1**, **2** and **3**) and the acceptors (C<sub>70</sub> and PC<sub>61</sub>BM)

## RESULTS AND DISCUSSIONS

The simplified structures of inverted-bilayer and inverted-BHJ OSCs are shown in Figure 2. For both structures (bilayer and bulk), two buffer layers were used: one of ZnO with high capability to conduct electrons to the ITO electrode and one of MoO<sub>3</sub> to increase hole-mobility to the Al electrode. At the same time, the MoO<sub>3</sub> presents very good properties for the encapsulation of the cells, protecting the active layer from the outside environment. Layers like C<sub>70</sub>, MoO<sub>3</sub> and the Al were always deposited in the vacuum by PVD (Physical Vapor Deposition) technique. The active layer in the case of the BHJ structures was deposited by spin-coating from solution and for the bilayer structures, the donors **1** and **2** were deposited by PVD (donor **3** decomposed during the PVD deposition).



**Figure 2.** Simplified representations of OSC structures: inverted-bilayer (left) and inverted-BHJ (right)

### *Inverted-BHJ structure (ITO/ZnO/Donor:PC<sub>61</sub>BM/MoO<sub>3</sub>/Al)*

We started to test out the OSC capabilities of the three compounds in inverted bulk architectures, by using a donor-acceptor (Donor: PC<sub>61</sub>BM) ratio of 1:1 (w:w) and different film thicknesses.

**Table 1.** Inverted-bulk solar cell efficiencies using Donor-Acceptor (Donor - PC<sub>61</sub>BM) ratio of 1:1 (w:w) in different active film thicknesses

Film Thickness [nm]	PCE [%]		
	Donor 1	Donor 2	Donor 3
25	0.52	0.49	1.78
<b>35</b>	<b>0.62</b>	<b>0.59</b>	<b>2.28</b>
60	0.36	0.33	1.37

The active film deposition thickness was controlled by the spin-coater speed, to obtain 60 nm, 35 nm, and 25 nm layers.

Having established the optimum film thickness we further investigated the three compounds in different donor: acceptor ratios. The efficiencies measured through these experiments are presented in Table 1, and show that the optimum thickness of the active layer should be 35 nm for all three compounds.

In the first step, we increased the ratio D:A to 1:2 (w:w). Based on the efficiency results of this experiment (Table 2), donors **1** and **2** showed a decrease in efficiency, and donor **3** an increase in efficiency in comparison to the 1:1 ratio. Thus, in the next step we evaluated the efficiency of donors **1** and **2** in a donor:acceptor ratio of 2:1 (w:w) and for compound **3** in a ratio of 1:3 (w:w). These experiments revealed (Table 2) the optimum donor:acceptor ratio of 1:1 (w:w) by the use of donors **1** and **2** with a maximum Power Conversion Efficiency (PCE) value of 0.6% and a ratio of 1:2 for donor **3** with a maximum PCE value of 2.5%.

**Table 2.** Inverted-bulk solar cell efficiencies using different Donor-Acceptor (Acceptor: PC<sub>61</sub>BM) ratios for the 35 nm active layer thickness

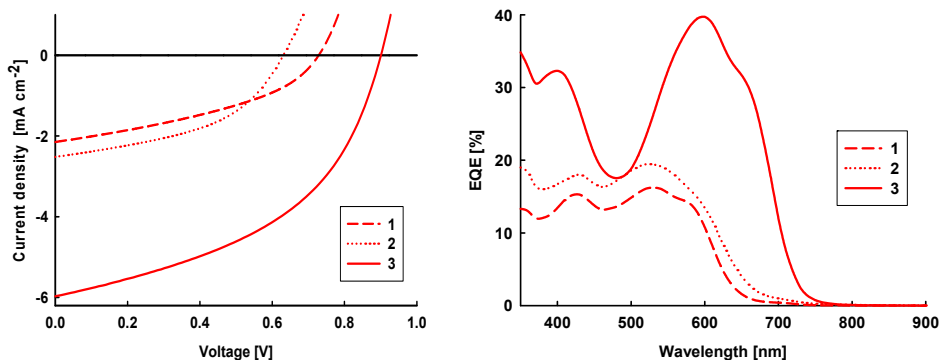
Donor:Acceptor ratio (w:w)	PCE [%]		
	Donor 1	Donor 2	Donor 3
2:1	0.20	0.24	-
1:1	<b>0.62</b>	<b>0.59</b>	2.28
1:2	0.55	0.48	<b>2.5</b>
1:3	-	-	1.42

The electrical characteristics of the best cells and highest PCE values from Table 2, are presented in detail in Table 3 and the J<sub>sc</sub>-V<sub>oc</sub> (current density- open circuit voltage) and EQE (external quantum efficiency) characteristics are plotted in Figure 3, where FF stands for fill-factor.

**Table 3.** Electrical characteristics of the cell with the best efficiencies and the average value of the efficiencies on a batch of six cells

Comp.	Voc [V]	Jsc [mA/cm <sup>2</sup> ]	FF [%]	PCE [%] best cells	Average PCE [%]
1	0.73	2.15	39.75	0.62	0.61
2	0.65	2.66	34.42	0.59	0.57
3	0.90	5.97	46.53	2.5	2.47

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**Figure 3.** Current density vs voltage curves (left) and EQE curves (right) for best inverted-BHJ cells using donors **1**, **2** and **3**.

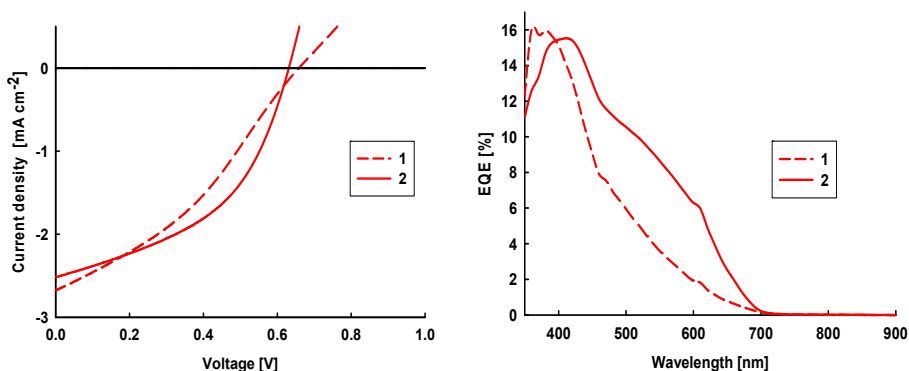
*Inverted-bilayer structure (ITO/ZnO/C<sub>70</sub>/Donor/MoO<sub>3</sub>/Al)*

The investigation of the OSC capabilities using the three compounds in inverted bilayer architecture was undertaken in a standard configuration of film stacking of 30 nm of the acceptor (C<sub>70</sub>) and 20 nm of the donor (**1**, **2**, **3**). The deposition of the layers was fully taken in a vacuum chamber using PVD (physical vapor deposition) technique. The experiments revealed good evaporation for compounds **1** and **2** and a high degradation for compound **3**. Thus, the bilayer structure is well suited for donors **1** and **2**. The electrical characteristics of the best cells are summarized in Table 4 and the J<sub>sc</sub>-V<sub>oc</sub> and EQE characteristics are plotted in Figure 4.

**Table 4.** Electrical characteristics of the best cells in inverted-bilayer structure and the average value of the efficiencies on a batch of six cells

Comp.	V <sub>oc</sub> [V]	J <sub>sc</sub> [mA/cm <sup>2</sup> ]	FF [%]	PCE [%] best cells	Average PCE [%]
1	0.66	2.68	34.87	0.62	0.57
2	0.63	2.52	46.49	0.74	0.68
3	NA	NA	NA	NA	NA

\*NA- does not apply



**Figure 4.** Current density vs voltage curves (left) and EQE curves (right) for the best inverted-bilayer cell using donors **1** and **2**.

## CONCLUSIONS

**D-A** donors with bi[3,2-*b*]thienothiophene units **1** and **2** were successfully used in the fabrication of inverted bilayer planar heterojunction (PHJ) OSCs using C<sub>70</sub> as acceptor and PVD deposition and solution-processed bulk heterojunction solar cells (BHJ OSCs) having PC<sub>61</sub>BM as acceptor. The average PCE values (Power Conversion Efficiency) obtained for these OSCs were similar for the two donors in both types of cells (BHJ **1**, PCE = 0.61 %; BHJ **2**, 0.57 %; PHJ **1**, 0.57% and PHJ **2**, 0.68 %), while the average PCE value obtained for the **A-D-A** donor in BHJ inverted cells (PC<sub>61</sub>BM as acceptor) were considerably higher (2.47 %) proving that the symmetric **A-D-A** donor with bi[3,2-*b*]thienothiophene units is considerably more efficient than the **D-A** donors with the same building blocks. The high electrical parameter values (V<sub>oc</sub>, J<sub>sc</sub> and FF) push a superior efficiency for the inverted-BHJ cells using donor **3** compared to the other cells with the use of donors **1** and **2**. The efficiencies of these cells are comparable to those of the BHJ cells obtained with PC<sub>61</sub>BM and PC<sub>71</sub>BM as acceptors and classic donors with di- and triarylamine [40-42] or 2,1,3-benzothiadiazole [43] moieties.

## EXPERIMENTAL SECTION

### *Materials and equipment*

The cells were obtained using commercially available ITO-coated glass substrates of 24×25 mm. These substrates were sonicated for 10 minutes in

distilled water, ethanol (10 min), isopropanol (10 min) and finally using an UV Ozone Cleaner for 20 minutes.

PC<sub>61</sub>BM, MoO<sub>3</sub>, CHCl<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>Cl and Al were commercially available. The active material and ZnO were prepared accordingly to the literature data. [18] The deposition of different layers of the cells was carried out either using a classic spin-coater or a high vacuum deposition equipment (MANTIS DEPOSITION- model QUBE). The characterization of the cells was performed for the electrical parameters (current density, open circuit voltage, fill factor, power conversion efficiency) with the system formed by the small area solar simulator Newport Oriel LCS-100 (94011A-ES) and the Keithley 2400 source measure unit, for external quantum efficiency parameter the Newport IQE 200B quantum efficiency system (350-1100nm wavelength range), while the thickness of the layers was measured using the Tencor Alpha-Step D500 profilometer. The absorption spectra of the film were analyzed by UV-VIS 1900 Shimadzu spectrometer.

### **General procedure for the fabrication of inverted BHJs**

A layer of 30 nm ZnO was deposited by spin-casting [ $S = 3000$  rpm,  $t = 40$  s) on clean ITO plates and then the plates were heated at 150°C for 20 min. The films of **donor** : PC<sub>61</sub>BM were spun-cast ( $t_1 = 40$  s,  $S_1 = 4500$  rpm,  $t_2 = 1$  s,  $S_2 = 500$  rpm) on top of ZnO layer. The hole transporter layer (HTL) consisting in a 13 nm thick MoO<sub>3</sub> layer and the Al electrodes (100 nm) were deposited by thermal evaporation under high vacuum at 10<sup>-6</sup> mbar.

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