

# Optimization of 1, 3, 5-tris (2-N-phenylbenzimidazolyl) benzene (TPBI) to increase the lifetime of organic device

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## ABSTRACT

Organic solar cells have an important development potential in achieving low cost modules for the production of domestic electricity. These cells have many advantages: low predictable cost in case of large-scale manufacturing, unlimited original material, ease of implementation, low temperature technology, large surfaces, flexible devices... but the lifetime of organic solar cells is a big problem to resolve before these devices can reach the market. This problem can be solved using one of different strategies is inserting a buffer layer before the cathode. In this study we use the 1,3,5-tris(2-N-phenylbenzimidazolyl) benzene (TPBI) as a buffer layer between the active layer and the cathode. Inserting a thin (TPBI) buffering layer between the active layer (CuPc:C<sub>60</sub>) and the cathode (Al) increases the lifetime from 255 minutes with 2.5nm of TPBI to 900 minutes with 8 nm of TPBI.

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## I. INTRODUCTION

Due to a growing interest in organic semiconductor based devices in general [1,2] and the need for renewable energy in particular [3], organic solar cells have been the object of increasing development during the last decade [4, 5]. Organic photovoltaic (OPV) cells have potential advantages over their inorganic counterparts of light weight and low-cost [6]. Unfortunately, the power conversion efficiency ( $\eta_e$ ) [7 - 15] and lifetime [16 - 21] of OPV cells are far from satisfactory. For the cells based on copper phthalocyanine (CuPc)/fullerene (C<sub>60</sub>) heterojunction structures, a very likely reason for their degradation is the decrease of conductivity of C<sub>60</sub> upon permeation [16, 20, 22]. Recently, the best efficiency of organic solar cells with bathocuproine (BCP) organic buffer has reached 5.7%, which shows a great potential for commercial applications [16, 23]. However the lifetime of organic solar cells with BCP buffer is unsatisfactory. In air and without encapsulation it takes only 20 min for the efficiency of the cells to decrease to half the initial value [24].

A small-molecule OPV cell with the structure ITO/donor(CuPc)/acceptor(C<sub>60</sub>)/buffer layer/Al, lifetime improvement results probably from the reduced permeability of oxygen and moisture into the active layer due to the buffer layer such as 1,3,5-tris(2-N-phenylbenzimidazolyl) benzene (TPBI). In addition, the buffer layer blocks the diffusion of cathode atoms into the active layer during deposition. We found that the incorporation of BCP buffer, for example, accelerates degradation of the current and consequently the shelf life of the cells, due to crystallization of BCP, as demonstrated by polarised light microscopy. However, it was shown that performance of these cells improves when TPBI is used as a buffer [25].

The encapsulation of organic solar cells minimizes the diffusion of oxygen and water through the side walls of the active layer. But the encapsulating structure does not prevent the diffusion of aluminum atoms to the organic active layer during thermal deposition of the cathode or the reactions of aluminum with the active layer during the aging process. The only way to avoid the inherent degradation at the cathode is to insert a buffer layer between the organic layer and the cathode:

- ✓ Improve the contact aluminum / organic layer.
- ✓ Avoid the reaction among the atoms of aluminum and the molecules of the organic layer;
- ✓ Protect the organic layer of hot aluminum atoms during thermal deposition;
- ✓ Improve the performance of these cells in terms of aging.

The buffer layer inserted between the cathode and the C<sub>60</sub> layer are often called EBL (exciton blocking layer). First this layer allows the transport of loads of the active layer to the electrode and also protects the active layer of the reaction between aluminum and C<sub>60</sub>. However BCP crystallizes quickly and degrades the active layer-cathode interface during the operation of the cells in the open air. We tried to replace this layer of BCP by TPBI layer also should allow the blocking of excitons and extraction of electrons from the cathode.

In this paper, we discuss the optimization of different cells by varying the thickness of TPBI, of un-encapsulated cells with the structure ITO(100nm)/PEDOTPSS( 30nm)/CuPc(25nm)/C<sub>60</sub>(40nm)/TPBI/Al(100nm), and an active layer surface of 25 mm<sup>2</sup>, is discussed. The similar cells were evaluated in air under illumination using AM1.5 solar simulator (100 mw/cm<sup>2</sup>).

## II. EXPERIMENTAL

All cells were fabricated on indium tin oxide (ITO) coated glass substrates with a sheet resistance of 20Ω/square. The substrates were cleaned in an ultrasonic bath with detergent, deionied-water, acetone, isopropanol and deionied-water successively 5 minutes. After being dried in a laboratory oven, the ITO anode layers were obtained by ion beam sputtering (IBS) using a target made up of a mixture of In<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub> (90% and 10% by weight respectively). The targets were bombarded by argon ions accelerated at 6 keV with a current density of 1mA/cm<sup>2</sup> [26] at a pressure of 5.10-6 mbar. Active layers of CuPc-C<sub>60</sub>-based cells were prepared as follows: A 30nm-thick layer of PEDOT-PSS, (Baytron PH from H.C. Starck) was deposited on the anode by spin coating, acting as a hole transport layer and as a barrier layer to prevent oxygen diffusion from ITO into the active layer [27, 28].

CuPc (Aldrich), fullerene C<sub>60</sub> (MER Corp., USA), and TPBI, used as an exciton blocking layer [29] prior to deposition of the aluminum cathode, were used without further purification.

The consecutive vacuum sublimation of CuPc and C<sub>60</sub> was performed using a co-evaporation setup (by Joule effect) [30] built in house. The temperature of 3 cells dedicated to sublimation of organic molecules was monitored by a Eurotherm 2700 process regulator which allows a minimum growth rate, according to the quartz monitor sensitivity of 0.5Ås-1. Vacuum sublimation was operated at a pressure of 10-6 mbar, and for all the experiments of this study, the growth rates were kept at 0.08nm/s and 0.1nm/s for CuPc and C<sub>60</sub> respectively. The aluminum cathode was deposited in an in situ confined bench, through a shadow mask delimiting a 0.25cm<sup>2</sup> diode area. Illumination was done using an AM1.5G solar simulator calibrated for 100 mW/cm<sup>2</sup>.

We performed three organic photovoltaic cells without such encapsulation heterojunction with an active surface layer of 25 mm<sup>2</sup>, and ITO structure (visionTeck) / PEDOT-PSS (30 nm) / CuPc (25 nm) / C<sub>60</sub> (40 nm) / TPBI (x nm) / Al (100 nm) where x is the thickness of TPBI which takes the values 2.5 nm, 6 nm and 8 nm (Figure 1). The goal is to find a compromise between the performance of these cells and their lifetime by varying the thickness of the buffering layer TPBI.

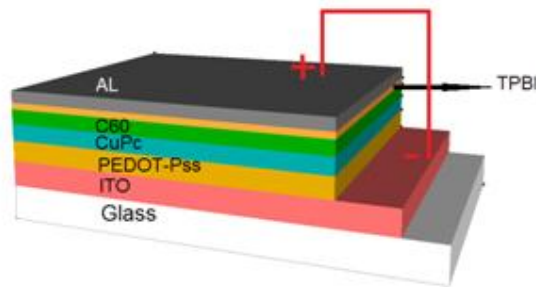


Fig. 1: Device structure of an organic solar cell

The gap bands HOMO and LUMO of TPBI are placed at 6.2 eV and 2.7 eV (Figure 2-a) relative to the vacuum level. The gap band of TPBI is therefore appropriate to make this material a blocking layer for excitons between the layer of C<sub>60</sub> and the Al cathode in solar cells heterojunction. The layer of TPBI reduces excitons dissociation from the active layer toward the cathode and reduces the diffusion of aluminum atoms from the cathode to the organic layer [29].

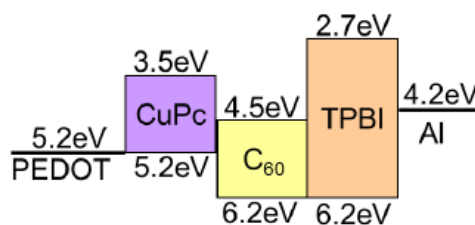
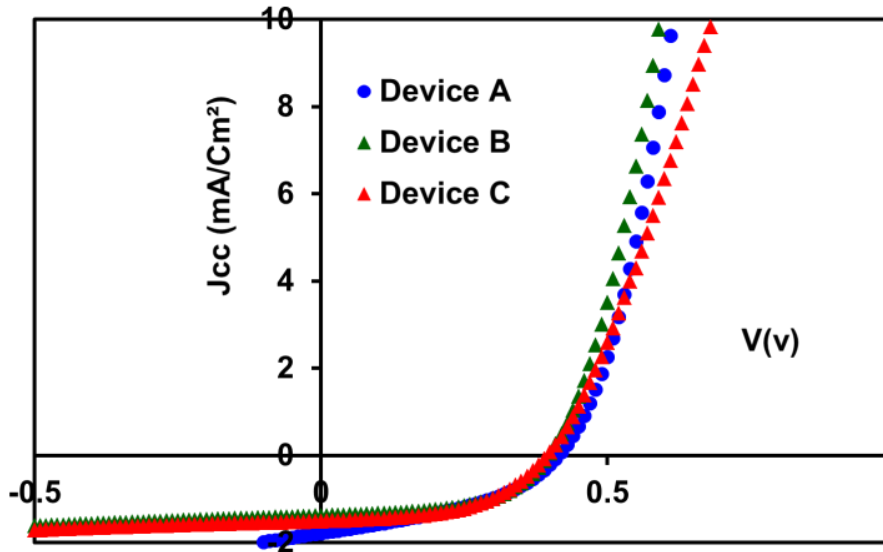


Fig. 2: Energy diagram of photovoltaic device

**Table I: Different Thickness of Buffer Layer T<sub>pbi</sub> of Different Device**

Device	Thickness of TPBI (nm)
Device A	2.5
Device B	6
Device C	8



**Fig. 3: J(V) characteristics under 100 mW/cm<sup>2</sup> illumination of (anode/PEDOT-PSS(30 nm)/CuPc(25 nm)/C<sub>60</sub>(40 nm)/TPBI(x nm)/Al(100 nm))**

Figure 3 shows the I-V characteristics of all cells with different thickness of TPBI measured under illumination (AM1.5 100mW/cm<sup>2</sup>); the photovoltaic parameters are as follows: fill factor (FF), power conversion efficiency ( $\eta_e$ ), open circuit voltage ( $V_{oc}$ ), short circuit current ( $J_{cc}$ ), series resistance ( $R_s$ ) and shunt resistance ( $R_{sh}$ ) (Table 2). Table 2 : Photovoltaic parameters for the various organic solar cells extracted from J(V) characteristics of Figure 3 under illumination.

**Table II Photovoltaic Parameters For The Various Organic Solar Cells Extracted From J(V) Characteristics Of Figure 3 Under Illumination.**

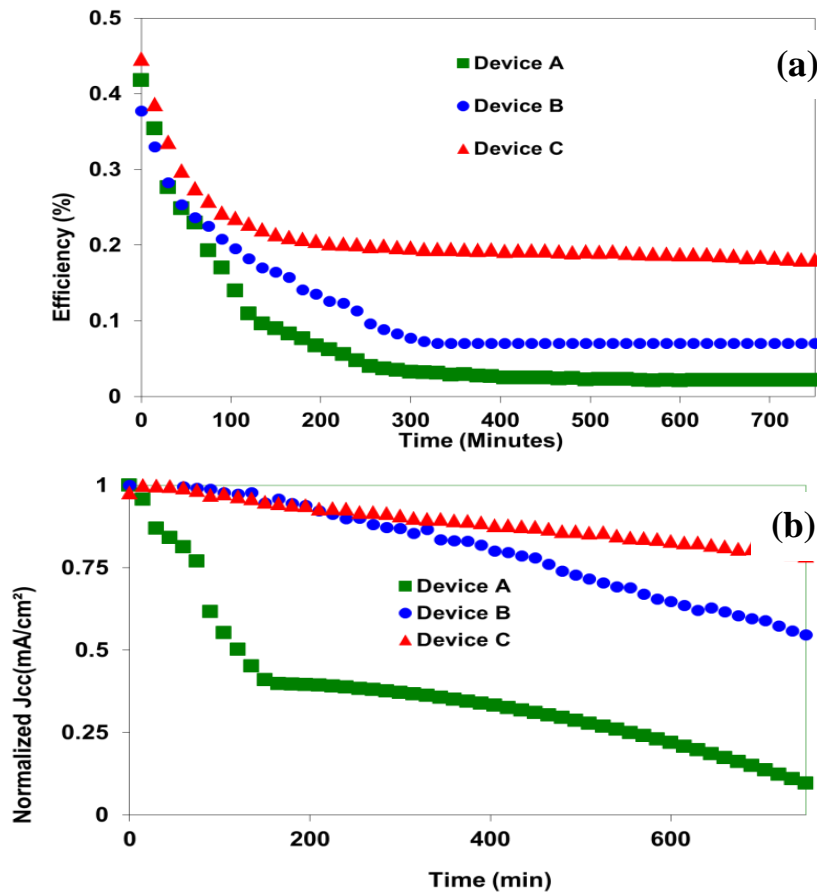
TPBI (nm)	$\eta_e$ (%)	FF	$V_{oc}$ (V)	$J_{cc}$ (mA/cm <sup>2</sup> )	$R_s$ (K $\Omega$ )	$R_{sh}$ (K $\Omega$ )
Device A	0.32	0.4	0.42	1.8	0.243	2
Device B	0.35	0.5	0.41	1.6	0.205	4.7
Device C	0.33	0.5	0.40	1.5	0.247	1.5

The increasing thickness of TPBI reduces the value of  $J_{cc}$  from 1.783mA/cm<sup>2</sup> with 2.5 nm of TPBI to 1.5mA/cm<sup>2</sup> with 8nm of TPBI. This may be because TPBI works not only as cathode buffer layer, but also as whole blocking layer, which can efficiently prevent the recombination of excitons at the cathode Al. Therefore, the performance of the PV devices is further improved.

The photovoltaic parameters show that the thickness of TPBI has much less influence on the series resistance ( $R_s$ ) remains goshawks from 200 to 250  $\Omega$ . Thereby power conversion efficiency ( $\eta_e$ ) varies only slightly in function of the thickness of TPBI.

### III. RESULTS AND DISCUSSION

For organic solar cells based on CuPc/C<sub>60</sub>, one of the most important factors responsible for lifetime reduction is the permeation of oxygen into C<sub>60</sub>. In the conventional structure of ITO/PEDOT-PSS/CuPc/C<sub>60</sub>/Buffer layer/Al, after permeation through the thin buffer layer, oxygen diffuses into C<sub>60</sub> first, then into CuPc. We noted the evolution of the characteristic J(V) of previous cells every 15 minutes for more than 750 minutes in continuous illumination under AM1.5 of 100 mW / cm<sup>2</sup> in air.



**Fig. 4: Evaluation of photovoltaic parameters under continues illumination in air for the three cells with different thickness of TPBI , (a) normalized Jcc (mA/cm<sup>2</sup>) sheet resistance and (b) power conversion efficiency.**

The Figure 4 shows the variations of the normalized short circuit current and power conversion efficiency as a function of time. The sheet resistance ( $R_s$ ) in first cell “Device A” (2.5nm of TPBI) showed a significant increase of its value in function of time: after 300 minutes of operation it reached 16 k $\Omega$ . The evolution of the  $R_s$  the two other cells “Device B” and “Device C” (6 nm and 8 nm of TPBI) shows a sharp increase during the first two hours of operation (up to 3.5 k $\Omega$ ). After this rapid degradation heading,  $R_s$  becomes almost stable (around 4.5 k $\Omega$  after 14 hours) in the case of the thick layer of TPBI (8 nm) or undergoes a slower increase in function of time ( $\approx 9 \Omega$  after 14h) in the case of the middle layer of TPBI (6 nm).

We can conclude that the time for the oxygen and water to penetrate through the cathode (Aluminium layer) and the sidewalls of the active layer increases with the thickness of the layer TPBI.

The Figure 4-a shows that the cell thickness 2.5 nm, 6 nm and 8 nm TPBI have lost more than 90%, 80% and 60% of the initial value of their performance after respectively 255, 840 and 900 minutes in the open air and under illumination. However, it is encouraging to note that the performance remains relatively stable after the first rapid degradation phase of the first two hours of operation in the case of the thickest layer TPBI. This trend is similar to the augmentation of the sheet resistance. We can conclude that the most important degradation mechanism for these cells remains one of the interfaces while the slow deterioration of the active layer by oxygen and water seems less sensitive to these cells.

TPBI is more stable than the BCP [30] whereas the half-life of the cell made with BCP buffer layer does not exceed 60 minutes in the open air under illumination AM1.5 of 100 mW / cm<sup>2</sup>, the duration of half-life of cells with 6 or 8 nm TPBI exceeds 200 minutes under the same operating conditions.

However, the behavior of cell with 8nm of TPBI indicates that penetration of oxygen and moisture is lessened when TPBI is used, which was shown not to crystallize in air as is the case for BCP, as was demonstrated by polarized light microscopy. As a result, electrons from the dissociated excitons can pass through TPBI more easily due to the absence of gaps, and thus lead to an improved shelf life to more than 135 min for cell with 8 nm of TPBI. The fast decrease of FF is probably related to oxidation of the Al electrode at the interface with the TPBI [31]. Though TPBI is more stable, oxygen can still penetrate into the C<sub>60</sub> layer after its penetration through Al and TPBI buffer resulting in an irreversible

decrease of conductivity of  $C_{60}$ . This result indicates that TPBI is a more effective buffer than either BCP or Alq3.

## CONCLUSION

We investigate in this study that the lifetime of organic photovoltaic cells loses 40% (for all cells) of the initial efficiency value during the first 75 minutes of operation under illumination in open air. This degradation, which essentially affects the quality of the interface active layer/electrode becomes negligible after one hour of operation with respect to the slower degradation mechanism of the active layer by oxygen and water vapor.

The evolution of photovoltaic parameters in functions of time for the cells having a TPBI buffering layer shows that:

- ✓ TPBI is more stable than the BCP in the presence of O<sub>2</sub> and H<sub>2</sub>O.
- ✓ The stability of the cells increases with increase in the thickness of the buffer layer.
- ✓ Cells with thicker buffer layers of TPBI (8 nm) lose 60% of the initial value of their performance after 840 minutes of operation in the open air and under continuous illumination of AM1.5 100 mW / cm<sup>2</sup>.
- ✓ The duration of half-life of the cells (50% of the initial efficiency value) is more than 120 minutes with TPBI(8 nm).

From all the characterizations under illumination depending on time in the open air, we decided to choose a TPBI buffer layer (8 nm). This choice, however, remains dependent on a performance/stability of solar cells and we opted for the stability of the cells. Indeed the characteristics with a thickness of 8 nm of TPBI showed only modest performance, the hard point is the high series resistance of the device.

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