Optical and electronic proprieties of thin films based on (Z)-5-(4-chlorobenzylidene)-3-(2-ethoxyphenyl)-2 thioxothiazolidin-4-one, (CBBTZ) and possible application as exciton-blocking layer in heterojunction organic solar cells

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Abstract. In this work, organic thin film solar cells with structures based on CuPc/C60 bulk heterojunctions, have been fabricated and characterized. The effect of introducing an exciton blocking layer (EBL) between the active layer and the metal layer in the solar cell was investigated. For that (Z)-5-(4-chlorobenzylidene)-3-(2-ethoxyphenyl)-2-thioxothiazolidin-4-one, that we called (CBBTZ) has been synthesized, characterized and probed as EBL. It was shown that optimized structures containing EBLs resulted in an improvement in solar cell conversion efficiencies. The energy levels corresponding to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the CBBTZ have been determined from the first oxidation and reduction potential respectively, using cyclic voltametric (CV) measurements. From CV curves, CBBTZ in dichloromethane showed a one electron reversible reduction and oxidation waves. The values of its HOMO and LUMO have been estimated to be 6.42 eV and 3.42 eV respectively. Such values show that CBBTZ could be probed as EBL in organic solar cells based on the ED/EA couple copper phthalocyanine(CuPc)/fullerene (C60). The photovoltaic solar cells have been obtained by sequential deposition under vacuum of the different films where their thicknesses were measured in situ by a quartz monitor. When obtained, the averaged efficiency of the cells using the CBBTZ is higher than that achieved without EBL layer.

1 Introduction

Efficient photovoltaic conversion in a heterojunction organic solar cell was first demonstrated by Tang [1] and have recently been more intensively investigated due to their potential as flexible, light-

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weight, and low-cost devices [2,3,4]. The main challenges in organic solar cell research are currently to improve the device efficiency and lifetime [5,6]. For that a variety of interfacial treatments have been applied to both the cathode/organic and the anode/organic interfaces, different more or less thin buffer layers have been placed at these interfaces, resulting in varying degrees of devices improvement in term of charge exchange [6]. Because metal electrodes are suspected to quench excitons in the electron acceptor layer (C_{60} in our case), exciton-blocking layers were introduced in devices between the metal cathode and the electron acceptor layer. Additionally, these transparent spacer layers allow to shift the active layer toward the maximum of the electric-field intensity distribution of the light in these devices[11]. As a matter of fact, significant efficiency improvements of layered cells, based on an electron donor/electron acceptor junction, have been achieved through the introduction this buffer layer at the interface electron acceptor/cathode. It has been proposed that this layer blocks exciton transport towards the cathode, which avoids exciton quenching at the contact organic/ cathode and protects the electron acceptor layer during the cathode deposition by evaporation [8].

In the present manuscript we studied the optical and electronic proprieties of CBBTZ ((Z)-5-(4-chlorobenzylidene)-3-(2-ethoxyphenyl)-2-thioxothiazolidin-4-one) thin films and we have tested it as an exciton blocking layer in CuPc/C60 heterojunction solar cells.

2 Experimental

2.1 CBBTZ experimental characterization

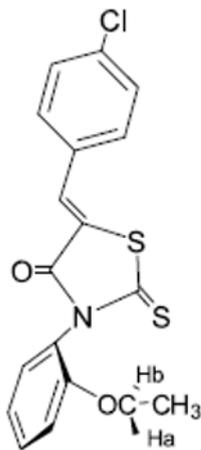Fig. 1 shows the chemical structures of CBBTZ used in this study.

Fig. 1. (Z)-5-(4-chlorobenzylidene)-3-(2-ethoxyphenyl)-2-thioxothiazolidin-4-one, (CBBTZ)

The HOMO and LUMO of the CBBTZ have been estimated by cyclic voltammetry (CV). The experimental method to carry out the CV has been previously described [8].

A three-compartment three-electrode glass cell was used to carry out this experiment. A Pt disc of 0.07 cm^2 geometric area was used as work electrode. A Pt gauze of large geometrical area and a Ag/AgCl in tetramethylammonium chloride (Me_4NCl) were used as counter and reference electrodes, respectively. All the potentials are referred to the saturated calomel electrode (SCE) [9].

Dichloromethane anhydrous (CH_2Cl_2) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were used as solvent and support electrolyte, respectively. A solution of CBBTZ 0.001 mol l^{-1}, $TBAPF_6$ 0.1 mol l^{-1} and CH_2Cl_2 was used in this experiment.

To warrant a minimum content of water (below 0.5 mmol L^{-1}) CH$_2$Cl$_2$ was stored under dry argon atmosphere, on molecular sieves (3 ˚A), and handled with a syringe.

The potential range from 0 to 2.5 V and potential range from −1.5 to 0 V (scan rate 0.008 Vs−1) were used to determine the HOMO and the LUMO, respectively. The experiment was performed on a Radiometer (Model PGP-201) potentiostat connected to a computer for data acquisition and analysis.

Optical measurements were carried out with a Cary 2300 spectrophotometer from 0.8 μm to 0.4 μm.

2.2 Organic cells realisation and characterisation

The device structure used in this study was: ITO/Au (0.5 nm)/CuPc (35 nm)/C$_{60}$/BL/Al.

The multi-layer heterojunction structure has indium tin oxide (ITO) as bottom anode. We have shown that the hole barrier often present at the interface ITO/organic electron donor can be systematically avoided by evaporating an ultra thin gold layer between the ITO and the organic layer [10,11], therefore ITO/Au (0.5 nm) anode structures have been used.

The ITO coated glass substrates used in this study were commercially obtained from the SOLEMS. Since ITO covered the whole glass substrates, some ITO must be removed to obtain the under electrode. After masking a broad band of 30 mm by 20 mm, the ITO was etched by using Zn powder + HCl (N/10) [12]. After carefully scrubbing, with alcohol and then soap, these substrates were rinsed in running deionised water. Then the substrates were dried and immediately loaded into a vacuum chamber (10^{-4} Pa).

The chemical products (CuPc, C60, BCP, Alq3, butyl-PBD) have been provided by Aldrich. The CBBTZ has been synthesized by the LSOA team (Université d'Oran Es-Sénia). The synthesis of the CBBTZ is described in a previous paper [13].

The chemical products were used without any purification. It has been shown that, using the same charge in the evaporation crucible, there is an "auto purification" of the product after approximately five thin film depositions. The main impurity in CuPc-95% is H$_2$Pc [14]. The melting point of H$_2$Pc (300 ◦C) being less than that of CuPc (360 ◦C), H$_2$Pc is removed from the source during the initial deposits [15]. Therefore, our experiment has shown that, in the experimental conditions used in the laboratory, the deposition of 300 nm of CuPc, before cells realisation, are necessary to be sure to achieve performing devices.

All the thin films of the structures have been deposited in the same run in a vacuum of 10^{-4} Pa. The thin film deposition rates and thickness were estimated in situ with a quartz monitor. The deposition rate and final thickness were 0.05 nm/s and 35 nm in the case of CuPc, 0.05 nm/s and 40 nm in the case of C60. These thicknesses have been chosen after optimisation.

In the case of the exciton blocking layer, the known optimum thickness has been used, 8–9 nm for BCP [3], while it has been varied from 5 to 15 nm in the case of the new material CBBTZ.

After organic thin film deposition, the aluminium top electrodes, through a mask with 2 mm × 8 mm active areas, and an approximately 100 nm encapsulating layer of amorphous selenium (Se-a) were thermally evaporated, without breaking the vacuum. The selenium protective coating layer has been proved to be efficient to protect the under layers from oxygen and water vapor contamination [16], at least during the first hours of room air exposure [7].

3 Results and discussion

3.1 CBBTZ characterization

The HOMO and LUMO values of CBBTZ have been measured following the process described in the experimental section. From CV curves (Fig. 1), CBBTZ in CH2Cl2 show the oxidation (Fig. 1a) and reduction (Fig. 1b) waves. The energy levels (in electron volts, eV), i.e. HOMO and LUMO

energies of CBBTZ can be determined adding 4.4 eV to values of the first oxidation (Ep) and reduction (En) potentials, respectively [17]. Therefore, $E_{HOMO} = -e(E_p + 4.4)$, and $E_{LUMO} = -e(E_n + 4.4)$.
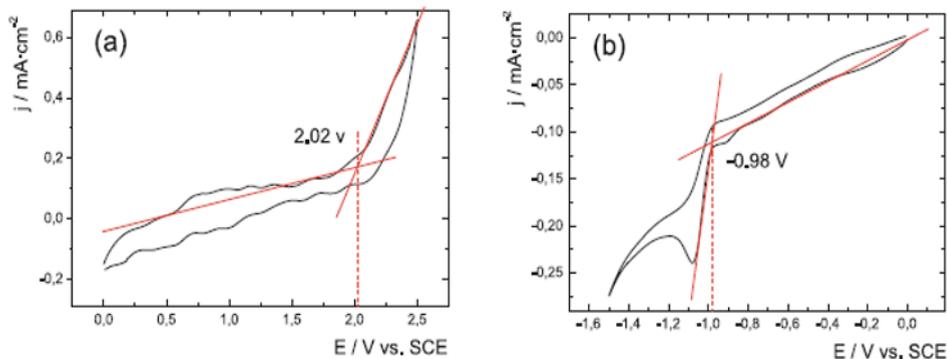

Fig. 2. Cyclic voltammetric profiles of CBBTZ in CH_2Cl_2. (a) Between $Ec = 0$ and $Ea = 2.5$ V. (b) Between $Ec = -1.5$ V and $Ea = 0$ V. Interface: Pt| 0.001 mol l^{-1} CBBTZ + 0.1 mol l^{-1} TBAPF$_6$. Scan rate 0.008 Vs^{-1}

The potential difference $Eg = E_{LUMO} - E_{HOMO}$ can be used to estimate the energy gap (Eg) of the dye.

Relatively to the vacuum level the energy values of HOMO and LUMO levels are -6.42 eV and -3.42 eV respectively. Therefore the band gap estimated from the electrochemical measurements is 3.0 eV.

In Figure 3 the transmission spectrum of a thin CBBTZ film deposited by sublimation onto a glass substrate is reported.
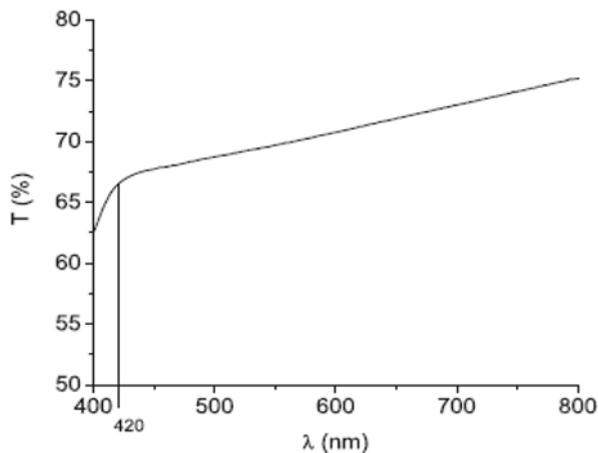

Fig. 3. Transmission (optical density) spectrum of CBBTZ thin film (100 nm) (at room temperature)

It can be seen that the transmission curve exhibits threshold energy around 2.95 eV. It can be estimated roughly that this threshold energy corresponds to the optical band gap of CBBTZ, which is in good agreement with electrochemical study.

3.2 Organic solar cells study

The characterization of the CBBTZ has shown that it exhibits the properties expected to be used as exciton blocking layer in organic solar cells.

In a first time, the optimum CBBTZ exciton blocking layer thickness has been determined by probing different devices with a EBL thickness varying from 5.5 nm to 15 nm, which is given in Figure 4. It can be seen that the optimum thickness (8–9 nm) is similar to that of the BCP EBL used in the present work, [3,7].
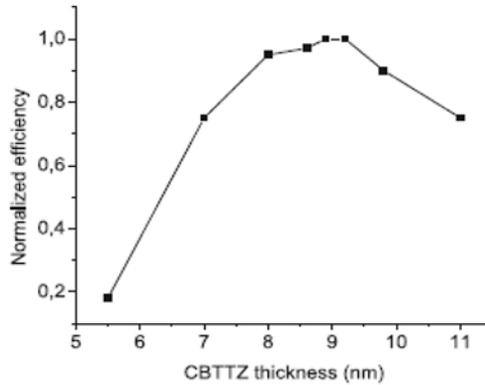

Fig. 4. Variation of the energy conversion efficiency of the cells with the thickness of the CBBTZ buffer layer thickness

In a second time, we have studied the results achieved with different EBL in solar cells deposited in the same run, using the optimum thickness. The results have been checked by successive runs.

Typical results are presented in Table 1 and Figure 5. It appears that the introduction of an exciton blocking layer at the interface C_{60}/Al permits achieving better energy conversion efficiency, More precisely, the fill factor and the short circuit current of these cells are significantly improved.
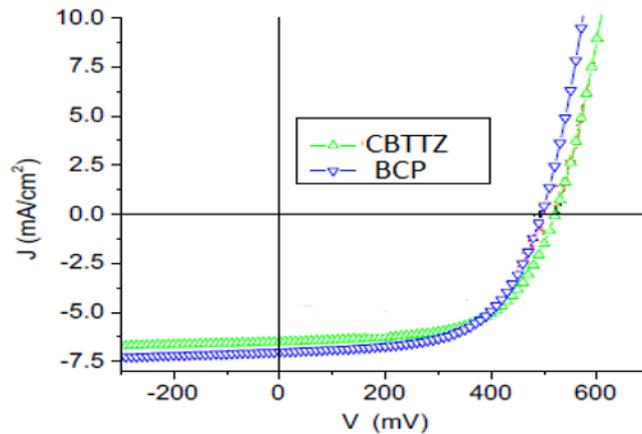

Fig. 5. (Color online) Typical *I-V* characteristics of organicsolar deposited at the same time, using different buffer layersat the interface electron acceptor/electron donor

Table 1. Typical parameters of organic solar cells with, or not, different buffer layers

Buffer layer	Voc (V)	Jcc (mA/cm2)	FF	(%)
No EBL	0.37	2.00	0.36	0.27
CBTTZ	0.525	6.35	0.60	1.99
BCP	0.505	6 .70	0.59	2.07

In an organic solar cell, after photon absorption and exciton formation, this exciton should reach a dissociation site i.e. usually a donor/acceptor interface. Exciton diffusion range in organic materials

before desexcitation is only 10–20 nm, while the thickness of the absorbing organic film should be around 100 nm to absorb efficiently the solar light. It has been shown that one way for circumventing the diffusion length limitation is to use cells with multiple interfaces. Peumans et al. [3] have shown that the introduction of a thin large band gap organic material allows improving significantly the device performances. They called electron blocking layer (EBL) this thin film, because its band gap is substantially larger than that of the organic donor and acceptor, which block excitons in the organic semiconducting layer far from the cathode avoiding any quenching effect at the interface cathode/organic. For vapor deposited multiplayer structures, a significant increase in efficiency occurs upon the insertion of the exciton blocking layer interfacial layer, the cathode and the electron acceptor film. Bathocuproine (BCP) is often used as exciton blocking buffer layer [3].

Accordingly to the above discussion, the results of the present work can be, at least partly, explained by the band scheme of the different structures used. To act as efficient exciton blocking layer, its HOMO absolute energy value should be greater than the HOMO value of the electron accepting organic layer, as it can be seen in Figure 8. It can prevent exciton quenching at the acceptor/cathode interface and therefore justifies the higher short circuit current and fill factor values.
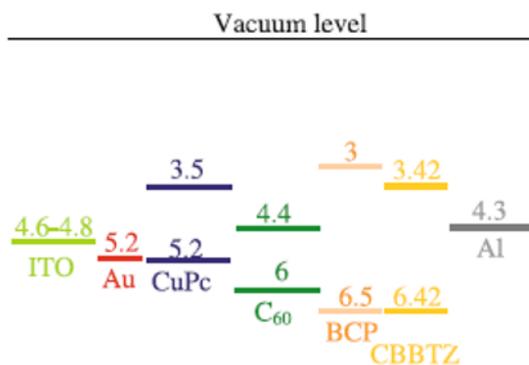

Fig. 8. Band scheme before contact of the organic solar cells with the different buffer layers probed at the interface cathode/organic material.

If the EBL blocks the excitons and should be thick enough to protect the electron accepting layer, it should not block all charge carriers. Therefore the EBL should be chosen so that it allows electrons collection at the cathode. However, as the offset energy of the HOMO of the electron donor (often the fullerene) and the EBL (see Fig. 8) is large and the optimum EBL thickness is around 8nm, which is too tick to allow high tunneling current, the electrons must overcome a large energy barrier to reach the Al cathode in case of electron transport via LUMO levels. The offset energy value of the LUMO level at the interface C_{60}/EBL is significantly smaller with CBBTZ, which can explain a better electron transmission towards the cathode and therefore the higher short circuit current.

4 Conclusion

After optical, and electrochemical characterization a new material, the CBBTZ, has been probed as exciton blocking layer in organic solar cells.

When the CBBTZ is introduced as EBL in ITO/Au (0.5 nm)/CuPc (3.5 nm)/C60/EBL/Al devices, it allows achieving efficiencies of the same order of magnitude than those achieved with BCP. The different behaviours are discussed with the help of the different hypothesis proposed to explain the effects of EBL. As a conclusion, the EBL blocks the excitons far from the cathode where they can be quenched, and prevent the electron acceptor film from damage, during cathode deposition.

It should be transparent to the solar spectrum to act as a spacer between the photoactive region and the metallic cathode and it must transport electrons to avoid high series resistance.

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