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Influence of the highest occupied molecular orbital energy level of the donor material on the effectiveness of the anode buffer layer in organic solar cells

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Efficiency of organic photovoltaic cells based on organic electron donor/organic electron acceptor junctions can be strongly improved when the transparent conductive Anode is coated with a Buffer Layer (ABL). Here, the effects of a metal (gold) or oxide (molybdenum oxide) ABL are reported, as a function of the Highest Occupied Molecular Orbital (HOMO) of different electron donors. The results indicate that a good

matching between the work function of the anode and the highest occupied molecular orbital of the donor material is the major factor limiting the hole transfer efficiency. Indeed, gold is efficient as ABL only when the HOMO of the organic donor is close to its work function Φ_{Au} . Therefore we show that the MoO₃ oxide has a wider field of application as ABL than gold.

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1 Introduction During the last few years, the efficiency of organic photovoltaic cells (OPV cells) has gained rapid progress [1, 2]. Power conversion efficiencies (PCE) higher than 8% have been announced, while efficiency of 7.4% has been reported [3]. Since the breakthrough of Tang [4] OPV are based on a couple electron donor (ED)/electron acceptor (EA). Since this work, two OPV families have been developed depending on the ED/EA interface geometry, the planar heterojunction (PHJ) and the bulk heterojunction (BHJ). PHJ are based on the superposition of thin films of donor and acceptor materials sandwiched between two electrodes, while in BHJ the active layer is constituted of interpenetrated networks of the two organic materials (ED and EA).

The PCE of OPV depends of the efficiency of four steps, exciton generation by light absorption, exciton diffusion to

an ED/EA interface, charge separation giving free holes and electrons and finally, carrier transport and collection. Therefore, in OPV, besides good photoactive materials, the properties of the interfaces between the organic layers and the electrodes are crucial for achieving high carrier collection efficiency and high PCE. Optoelectronic devices require at least one transparent electrode. Therefore, transparent conductive oxide (TCO) thin films have attracted considerable attention for their application as electrode in optoelectronic devices. Electrode contacts play a critical role in determining the device efficiencies. Rates of charge collection at the electrodes must be fast and selective. Contact selectivity is often achieved using buffer interlayers interposed between the electrodes and the organic materials. Efficiency of OPV cells, based on organic donor/acceptor heterojunctions can be strongly improved

when the transparent conductive anode, is covered with an anode buffer layer (ABL). Currently, indium-tin oxide (ITO) is the most widely used transparent electrode for organic optoelectronic [5]. Here, the effects of a metal or oxide ABL onto the ITO anode are studied using different couples of ED and EA with different HOMO and LUMO (Lowest Unoccupied Molecular Orbital) levels are used. The results indicate that a good matching between the work function of the anode and the HOMO of the organic electron donor is the most important factor limiting the hole transfer efficiency. It is shown that the MoO_x oxide has a wider field of application as ABL than gold.

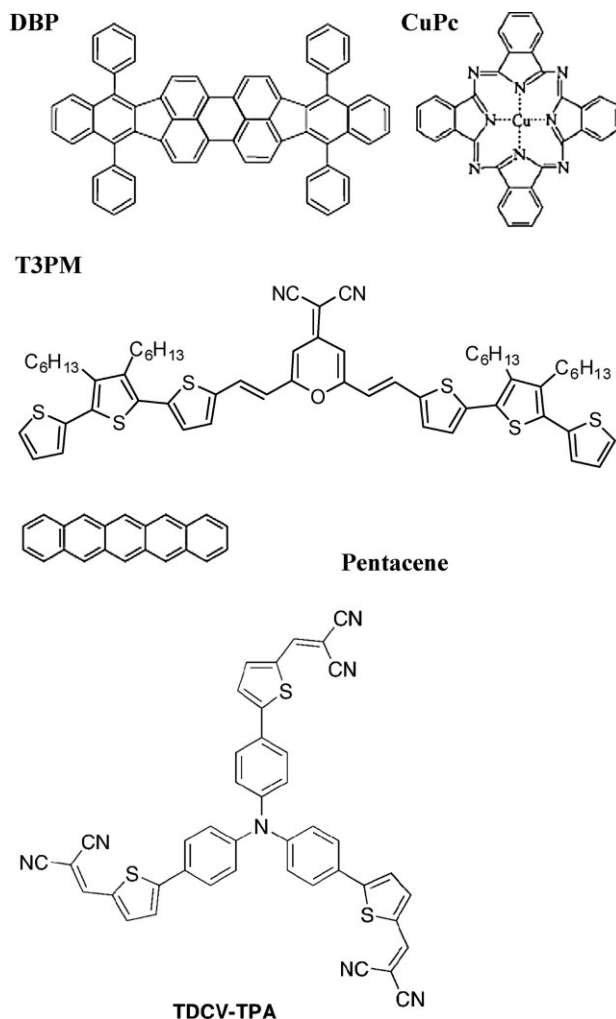
2 Experimental ITO-coated glass substrates with standard substrate dimensions of 25 mm x 20 mm were purchased from SOLEMS. After masking a 20 mm x 20 mm band, ITO was etched using $\text{Zn} + \text{HCl}$ [6]. After scrubbing with soap, these substrates were rinsed in running deionised water, dried with an argon flow and loaded into a vacuum chamber (10^{-4} Pa). The thickness of the ITO films was around 100 nm, its ohm square resistance about $15 \Omega/\square$. The mean averaged transmission in the visible, between 400 and 1000 nm, is higher than 90%. As shown by AFM measurements, the root mean square (rms) roughness measured over an area of $4 \mu\text{m}^2$ was 0.8 nm [7].

In the present work, we focus on the contact between the anode and the electron donor (ED). For sake of simplicity, we have used OPCs with PHJ configuration. It is known that, in PHJ, a buffer layer, between the acceptor and the cathode strongly increases the cell performances. This interlayer introduced at the acceptor/cathode interface is called 'exciton blocking layer' (EBL). Bathocuproine (BCP), a widely used performing EBL [8] has been chosen in the present work. The cathode is a thin aluminium film.

Fullerene is the most often used electron acceptor (EA). However, in order to discriminate between the ED and EA influence on the OPV performance when the ABL is modified, we have used also another EA, perylenetetracarboxylic bisbenzimidazole (PTCBI). To study the influence of the HOMO level of the organic material on the effectiveness of the anode buffer layer (ABL) different ED have been probed: pentacene, copper phthalocyanine (CuPc), tetraphenyldibenzoperiflanthene (DBP), terthiophene-pyran-malonitrile (T3PM) and thienylenevinylene-triphenylamine functionalized with peripheral dicyanovinylene groups [9] (TDCV-TPA) with HOMO levels of 5.0, 5.2, 5.5, 5.7 and 5.8 eV, respectively (Scheme 1).

The ITO contact plays a critical role and the introduction of a thin ABL between the ITO and the ED induces a significant improvement of the device efficiency [10]. For instance, we have shown that simple vacuum deposition of an ultra-thin film of gold [7] or a thin film of MoO_x [11] allow achieving this goal, film when CuPc is the ED. In this work these two ABLs are probed with different ED and EA.

Typical OPV structures were: glass/ITO/ABL/ED/EA/BCP/Al. All layers were deposited by vacuum evaporation at a pressure of 10^{-4} Pa. The thicknesses were 40, 30, 9 and



Scheme 1 Chemical structure of the electron donors used.

130 nm for C_{60} , PTCBI, BCP and Al, respectively. The ABL thicknesses were 0.5 nm [7] and 3.5 nm [11] for Au and MoO_3 , respectively. The thickness of the different ED layers have been optimized to 35 nm for CuPc, 25 nm for pentacene and 20 nm for DBP, T3PM and TDCV-TPA. In the case of TDCV-TPA the BCP film was covered by a 1 nm thick LiF film [9]. The thickness and deposition rate of the layers were monitored by quartz. The deposition rate of the organic material was 0.05 nm/s. The active area of the devices was 0.2 cm^2 . All chemicals have been provided by Aldrich excepted for DBP provided by LUMTEC. T3PM, TDCV-TPA and PTCBI have been synthesized in the laboratories of SSSCU-IIS of Bangalore (India), MOLTECH-Anjou (France) and UCC of Santiago (Chile), respectively and they were used without any purification. Indeed, it has been shown that, using the same charge in the evaporation crucible, there is an 'auto purification' of the product [12].

Electrical characterizations were performed with an automated I - V tester, in the dark and under sun global AM 1.5 simulated solar illumination. Performances of photovoltaic cells were measured using a calibrated solar

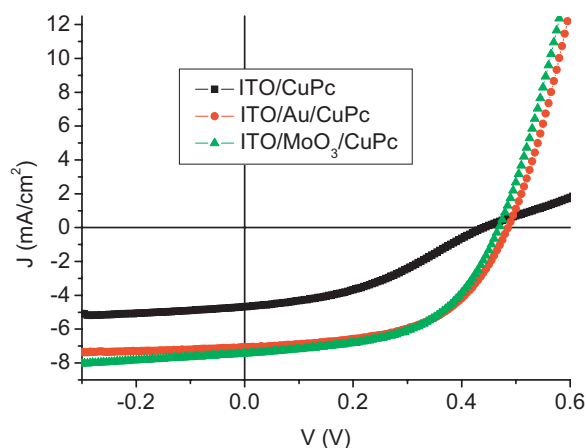


Figure 1 (online color at: www.pss-a.com) J - V characteristics of solar cells, using CuPc as donor, under AM 1.5 illumination with different anode configurations.

simulator (Oriel 300W) at 100 mW/cm^2 light intensity adjusted with a PV reference cell (0.5 cm^2 CIGS solar cell, calibrated at NREL, USA). Measurements were performed in ambient atmosphere. All devices were illuminated through TCO electrodes [13].

3 Experimental results and discussion Typical current density–voltage (J - V) characteristics of the OPV cells with CuPc and DBP as ED are shown in Figs. 1 and 2, respectively.

It can be seen that, while Au buffer layer is very efficient in the case of CuPc, it is not for DBP. On the contrary, MoO_x is efficient for both. These ED differ essentially by their HOMO levels. Therefore, in order to check the origin of the different behaviours of the ABL, we have probed three other EDs, pentacene, with a HOMO level close to that of CuPc and T3PM and TDCV-TPA with a HOMO level close to that of DBP. Corresponding short-circuit current densities (J_{sc}), open-circuit voltages (V_{oc}), calculated fill factors (FF)

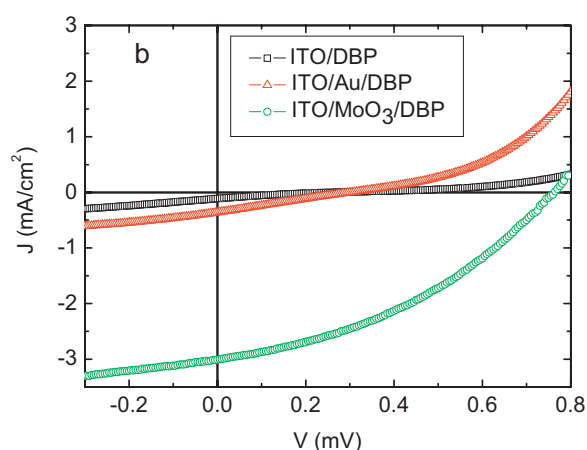


Figure 2 (online color at: www.pss-a.com) J - V characteristics of solar cells, using DBP as donor, under AM 1.5 illumination with different anode configurations.

and power conversion efficiencies (η) are summarized in Table 1.

It can be seen that while MoO_x is efficient for all the ED probed, Au is efficient only for CuPc and pentacene.

We have also checked the effect of a different EA on the efficiency of the ABL. Figure 3 and Table 2 show that as expected, the efficiency of the ABL depends only on the HOMO of the ED and not on the EA.

It should be noted that it is currently accepted that after simple soap-water cleaning, the work function value of the ITO anode is about $\Phi_{\text{ITO}} = 4.4 \text{ eV}$ [14, 15] to 4.8 eV [16, 17]. This implies that Φ_{ITO} is sensibly lower than the HOMO levels of the various investigated ED that are all $\geq 5.0 \text{ eV}$. It is known that the difference between work function (Φ_{M}) of the anode and the HOMO of the ED has strong influence on the flat band conditions of optoelectronic devices [18, 19]. Even if, in the case of organic/metal interface, the effect of this difference on the electrical characteristics of the devices is often modulated by a dipole (Δ) formation at the interface, it

Table 1 Photovoltaic characteristics under AM1.5 conditions of devices, with different anode configurations, using Pentacene, DBP, CuPc, T3PM and TDCV-TPA as electron donor and C_{60} as electron acceptor.

electron donor HOMO (eV)	anode configuration	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
pentacene (5)	ITO	2.35	0.29	24	0.16
	ITO/Au	6.22	0.35	47	1.02
	ITO/ MoO_x	6.6	0.33	45	0.94
DBP (5.5)	ITO	0.055	0.25	22	0.003
	ITO/Au	0.18	0.3	24	0.013
	ITO/ MoO_x	3.01	0.76	38	0.88
CuPc (5.2)	ITO	4.70	0.44	38	0.80
	ITO/Au	7.70	0.49	54	1.91
	ITO/ MoO_x	7.48	0.47	54	1.90
T3PM (5.7)	ITO	0.36	0.02	25	0.0018
	ITO/Au	0.92	0.07	30	0.02
	ITO/ MoO_x	3.26	0.30	35	0.34
TDCV-TPA (5.8)	ITO/Au	1.96	0.64	26	0.33
	ITO/ MoO_x	2.55	0.94	47	1.13

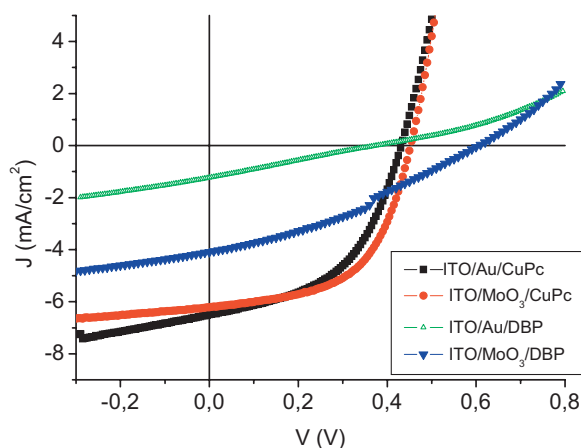


Figure 3 (online color at: www.pss-a.com) J - V characteristics of solar cells, using PTCBI as electron acceptor, under AM 1.5 illumination with different anode configurations.

is admitted that the difference between the HOMO of the ED and the Φ_M of the anode provides a hole injection barrier, in the case of organic light emitting diode (OLED) and a hole collection barrier in the case of OPV [20]. These barriers increase the operating voltage for OLEDs and decrease J_{sc} , FF and therefore the PCE of OPV cells. This barrier effect can be minimized by engineering the interface in order to achieve the alignment of the energy levels of the organic layer and the anode through the introduction of a buffer layer [21]. Although such an engineering of the organic active film/anode interface has been carried out [10, 15, 22], the operation mechanism of these ABL is still in debate.

We have seen above that, whatever the EA used, the efficiency of the different ABL depends on the ED. As a matter of fact, a desired hole-extraction contact should provide a good energy-level alignment with the adjacent ED layer. Many studies have shown that a strong correlation exists between the anode work function and the hole collection barrier at the anode/ED interface. In the Mott-Schottky model, if ϕ_M is the work function of the metal, we will have Φ_B the barrier for holes at the interface:

$$\Phi_B = \phi_M - \text{HOMO}_{ED} \quad (1)$$

However, the Mott-Schottky limit is rarely observed, since an interfacial dipole Δ is often formed at the interface between the anode surface and the organic molecules, which

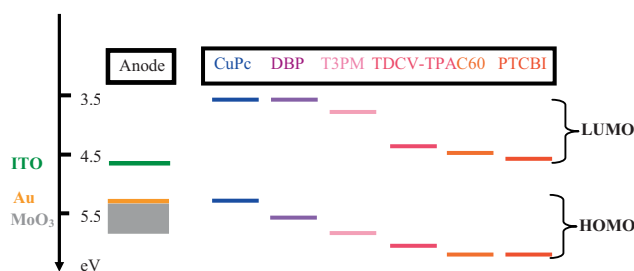


Figure 4 (online color at: www.pss-a.com) Energy level diagram of materials used.

tends to pin the Fermi level and the effective barrier height is [16]:

$$\Phi_B = \Phi_B^0 - \Delta = (\phi_M - \text{HOMO}_{ED}) - \Delta \quad (2)$$

The value of the dipole is proportional to the amount of charge transferred, which is due to energy difference between the metal Fermi level and the organic charge neutrality level (CNL) [23].

In the present work we have used different ABL to increase the anode work function. The experimental results let appear that the work function of the ABL is a key parameter to adjust the work function of the anode to the HOMO of the organic material. As said above, the work function of ITO is around 4.6 ± 0.2 eV, which is much lower than the HOMO level of the ED. Therefore, the energy conversion efficiency of the OPV cells, whatever the ED, is very poor. In the case of Au, where the work function Φ_{Au} is 5.2 eV, good efficiencies are achieved with pentacene and CuPc, the HOMO levels of which are 5.0 and 5.2 eV, respectively. On the contrary very low efficiencies are achieved when the ED is DBP, T3PM or TDCV-TPA, because their HOMO levels, 5.5, 5.7 and 5.8 eV, respectively, are far higher than Φ_{Au} (Fig. 4). Therefore, it appears clearly that Au is not a universal ABL, since a good matching between the ABL metal work function and the HOMO of the ED is necessary.

Indeed, the work functions of the electrodes determine whether the contact with the organic material is ohmic or blocking. Au, above the ITO substrate, improves the work function of the anode up to 5.2 eV (the ITO/Au system is regarded as ‘anode’), providing a better matching with HOMO_{ED} energy level of similar value.

In the case of CuPc and Pentacene, since the work function of Au lies between the work function of ITO

Table 2 Photovoltaic characteristics under AM1.5 conditions of devices, with different anode configurations, using DBP and CuPc, as electron donor and PTCBI as electron acceptor.

electron donor HOMO (eV)	anode configuration	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	η (%)
DBP (5.5 eV)	ITO/Au	1.25	0.377	24.5	0.114
	ITO/MoO _x	4.10	0.605	34.4	0.85
CuPc (5 eV)	ITO/Au	6.5	0.432	49.3	1.39
	ITO/MoO _x	6.2	0.453	55.55	1.32

(4.7 eV) and the HOMO level of the ED, Au can facilitate hole extraction from the photoactive layer, which justifies that the achieved efficiencies are better than those observed with bare ITO. However, when the HOMO level of the donor is much higher than the work function of Au, it is necessary to tune the surface work function of the anode.

So, for the first time we show that a metallic layer will be effective only for organic materials with a HOMO level corresponding to the work function of the metal, whereas the MoO_3 is of wider utility.

Actually, we show that MoO_3 is efficient whatever the HOMO of the ED used. It has been often said that the valence band of MoO_x is 5.3 eV [24], however, nowadays, a debate is open concerning the band structure of MoO_x [19, 25, 26]. Initial studies of thermally evaporated MoO_x layers indicated that the valence band and conduction band are at 5.3 and 2.3 eV, respectively [27]. Recent results report far greater values, ranging between 9.37–9.70 and 6.18–6.70 eV, respectively [24, 28, 29]. These discrepancies for MoO_x energy level are due to the sensitivity of UPS (ultra violet photoelectron spectroscopy) or other measurements to surface states, deposition techniques, material purity and post-treatment [26].

In some works based on UPS it has been proposed that MoO_x [24, 28] is strongly n-doped. This is not the case of our $\text{MoO}_{2.7}$ films, we have checked by electrical measurements (hot probe technique and conductivity measurements) that our films are nearly insulating and slightly n-doped. Nevertheless, whatever the MoO_3 used, thermally evaporated, or electrochemically deposited [30], it is efficient as buffer layer independently of the HOMO level of the organic molecule, at least from 5.0 to 5.7 eV. This shows that, beyond the variety of used oxides, the properties of MoO_3 leads to systematically improved cell performances.

A simple Metal-Insulating-Semiconductor (MIS) model can be proposed as one contribution to explain the functions of MoO_x . Indeed, ITO is a degenerated semiconductor, while MoO_x and ED are typical insulator and organic semiconductor, respectively [10]. In such structure, after contact, the Fermi level must be constant throughout the metal/insulating layer/semi-conductor [31]. This Fermi level alignment is achieved through charge accumulation on both sides of the insulating layer, which induces the dipole Δ_1 formation and therefore the presence of this layer can significantly decrease the barrier value at the interface through the dipole Δ_1 [32]. Recently, Irfan et al. [33] have shown that, while most of the electronic levels of MoO_3 films remained intact, there is a large work function reduction for air exposed films. Such large variation for small air exposition can explain the discrepancies for MoO_x energy level reported in the literature.

4 Conclusion In conclusion, this experimental study allowed us to bring to light directly that an ultra thin metallic film is efficient as buffer layer at the anode/electron donor interface, only if its work function is of the of magnitude of the HOMO level of the electron donor, independently of the

used electron acceptor. When the ABL is a ultra thin film of gold, this goal is achieved with CuPc and pentacene, the HOMO level of which is around 5.0–5.2 eV, while the gold work function Φ_{Au} is 5.2 eV. When the ED HOMO level is around 5.5 eV, there is not anymore good band matching at the anode/organic interface and the PCE improvement is quite small. In the case of the MoO_x layer, due to the above discussed interface dipole effects, more efficient hole-extraction is achieved thanks to the more favourable electronic energy level alignment at the hole-extracting electrode.

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