Study of CuI thin films properties for application as anode buffer layer in organic solar cells

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After chemico-physical characterization of CuI thin films, the structures indium tin oxide (ITO) /CuI are systematically studied. We show that the morphology of the 3 nm thick CuI film depends on its deposition rate. To obtain smooth homogeneous CuI film, it is necessary to depose it at 0.005 nm/s. After optimization of the deposition conditions of CuI, it is shown that it behaves like a template for the organic layer. For instance, when the organic film is copper-phthalocyanine, the molecules which are usually perpendicular to the plane of the substrate lie parallel to it when deposited onto CuI. In a same way, when the electron donor is a prophyrin derivative, CuI allows to double the power conversion efficiency of the cells based on the heterojunction porphyrin/C60. When CuI is used as anode buffer layer, it increases systematically the short circuit current, the open circuit voltage, thus the efficiency of the organic solar cell. These effects are related, not only to the improvement of the band matching between the ITO and the electron donor, but also to the templating effect of the CuI. Moreover, we show that the beneficial effect of CuI is effective, not only with ITO, but also with fluorine doped tin oxide.

Keywords: Organic solar cells, Anode buffer layer, Templating effect, CuI deposition rate

1 Introduction

The interest devoted to organic photovoltaic cells (OPV cells) is rising very fast, due to continuous efficiency improvement. Recent considerable improvement of the performance of small molecules OPV cells induces a new growing interest for this type of OPV cells. A classical small molecule OPV cell is based on an organic bilayer, sandwiched between two electrodes. One of these electrodes must be transparent and the other highly reflective. The organic bilayer is a heterojunctions between an electron donor (ED) and an electron acceptor (EA). Moreover, one, at least, of the organic material must absorb the light, usually it is the electron donor. About the electrodes one of them must be transparent and the other highly reflective. While aluminium is often used as reflective cathode, it is well known that the transparent conductive anode which gives the best optoelectronic devices is the indium tin oxide (ITO). The holes exchange at the interface ED/anode can greatly influence the device performance. Ideally, the donor’s HOMO (Highest Occupied Molecular Orbital) should match the work function of the anode. Rates of holes collection of the anode must be fast and electron selective. Between the ED and the ITO, an anode a buffer layer (ABL) is usually introduced. About the ABL, we have shown that an ultra thin gold film and/or a thin MoO3 thin film are highly efficient. The use of an ABL allows achieving a good band matching between the work function of the anode and the highest occupied molecular orbital (HOMO) of the ED and numerous works were
determined to this adjustment. For instance, MoO$_3$ is well known as very efficient ABL in optoelectronic devices$^{7,8}$. If an ABL can improve the band matching at the interface anode/ED it can also modify the structure of the ED organic layers. However, the works dedicated to this subject are less numerous, while a structural templating of the organic layer can allow significant modification of the device behaviour$^5$. For instance, some years ago, it was shown that perylene derivatives can be used to modify the orientation of metal phthalocyanines (MPc) such as CuPc (Refs 11-13) and ZnPc (Ref. 14). As a matter of fact, MPc molecules, which are usually perpendicular to the plane of the substrate, become parallel in the presence of this kind of ABL. Such modification allows improving the OPV cells performance. Similar templating effect was obtained using a thin antimony oxide layer$^{15}$ or an organic (hexaazatriphenylene-hexacarbonitrile) layer$^{16}$. Recently, Cul has been proven as an efficient template for metal phthalocyanines (MPc). As a matter of fact, in the same way as in the examples evoked above, when the ED is a MPc, such as CuPc, PbPc or ZnPc (Refs 14, 17, 18), the Cul ABL modifies the orientation of the molecules of MPc, from perpendicular to the plane of the substrate to parallel to this plane. In the present paper having proceeded to a systematic study of the properties of the Cul thin films and of its effect on the properties of organic thin films, we show that its improving effect is not limited to MPc but that it is also very effective for other organic materials.

2 Experimental Details

The chemical materials were provided by Aldrich and they were deposited in thin film form by sublimation under vacuum ($10^{-4}$ Pa). The thickness of thin films and the deposition rates were estimated in-situ using a quartz monitor. The substrates were either bare glass or ITO coated glass. Before thin films deposition, the substrates were scrubbed with soap, rinsed with distilled water, dried and next placed in the vacuum chamber. For the Cul study, the film thickness was varied between 3 to 500 nm, depending on the characterization technique. For the characterization of the structures ITO/Cul, the thickness of the Cul was 3 nm. Since MoO$_3$ is well known as very efficient ABL in optoelectronic organic devices, we also have characterized ITO/MoO$_3$ samples for comparison. Finally, OPV cells were realized. The multi-heterojunction solar cells studied were as follows: ITO/ABL/ED/C$_{60}$/BCP/Al. The fullerene C$_{60}$ was the EA due to its very high efficiency in capturing excited electron of the ED. Bathocuproine (BCP) is used as exciton blocking layer (EBL) at the interface EA/cathode. The insertion of an EBL between the EA and the Al layer was shown to significantly improve the performances of OPV cells$^{19}$. The ABL was either a simple layer of CuI or MoO$_3$, or a double layer MoO$_3$/CuI. In order to assess to gain due to the presence of the different ABL layers, a cell without any ABL was used as reference. The thickness of the layer of C$_{60}$ was 40 nm and that of BCP was 20 nm. Finally, the ED was the CuPc, then we widened the study to others ED. The thickness of the ED layer depends of the material used. That of CuPc film was 35 nm, while that of the others donors was 20 nm. The ITO and the Al film were thick of 100 nm.

When a MoO$_3$ ABL was introduced in the device, its thickness was 3 nm. Following earliest studies, that of the CuI layer$^{17}$ 3 nm. The Cul was deposited by sublimation under vacuum, its deposition rate was varied from 0.0 5 to 0.005 nm, the effective area of each cell was 0.16 cm$^2$.

The main focus of this work was the study of the influence of the Cul ABL on the band matching at the interface anode/ED, on the ED molecular alignment and, finally, on OPV cells performance. To this end, we show that it is effective for numerous ED others than MPc, such as porphyrin derivatives. Firstly, for the Cul films and ITO/Cul structures characterization, different physico-chemical and optical techniques have been used. The thin films structures are analyzed by X ray diffraction (XRD) by a Siemens D5000 diffractometer using K$_\alpha$ radiation from Cu ($\lambda_{K_{\alpha}} = 0.15406$ nm).

The optical measurements were carried out at room temperature using a Carry spectrometer. The film absorbance was measured at wavelengths of 1 to 0.30 $\mu$m. The morphology of the different structures used as anode was observed through scanning electron microscopy (SEM) with a JEOL 7600F at the “centre de microcaractérisation de l’Université de Nantes”. Images in secondary (SEM) and backscattering (BEI) mode have been done. Only the powerful resolution of this field emission SEM with its large angle backscattered detector (LABE) allowed us to obtain images at so high magnification in backscattered mode. The composition of the films is determined by electron probe micro analysis (EPMA).
AFM images on different sites of the film were taken ex-situ at atmospheric pressure and room temperature. AFM microscopy was performed in contact mode using a Pico SPM microscope (Molecular Imaging). For each sample, imaging of the surface was carried out in various places with a maximum scan size of \(6.2 \times 6.2 \, \mu m^2\). The image processing was done using the WSxM program \(^{21}\) which allows, among others, calculation of the roughness of the surface and profilometry. The RMS given in the following has been calculated by averaging the roughness obtained from each images for a given sample.

X-ray photoelectron spectroscopy (XPS) measurements (Leybold LHS12, University of Nantes-CNRS) were performed with a magnesium X-ray source (1253.6 eV) operating at 10 kV and 10 mA. During the measurements, the vacuum was \(10^{-7} \, \text{Pa}\), the pass energy for high resolution spectra was 50 eV. The samples were grounded with silver paste to prevent charge effect. At the surface of the samples air is exposed, there is systematically a carbon-carbon bond corresponding to surface contamination. In the apparatus used, the C1s peak of the C−C bond had a well defined position at 284.6 eV and this carbon value was used as a reference to estimate the electrical charge effect. The quantitative study of CuI films was based on the determination of the I3d\(_{5/2}\) and Cu 2p\(_{3/2}\) peak areas with 6.4 and 5.3, respectively, as sensitivity factors.

The electrical conductivity, at room temperature, was measured using planar structures. The surface of the electrodes was \(2 \times 10 \, \text{mm}^2\), the electrode gap was 2 mm, the thickness of the electrodes was 0.1 µm. The electrodes were covered with silver past, which also allows to past copper wires for electrical measurements.

The characteristics of the photovoltaic cells were measured using a calibrated solar simulator (Oriel 300W) at 100 mW/cm\(^2\) light intensity adjusted with a reference cell (0.5 cm\(^2\) CIGS solar cell, calibrated at NREL, USA). Measurements were performed at an ambient atmosphere. All devices were illuminated through TCO electrodes. The effects of the ABL on the ED film conductivity were investigated using the J-V characteristics of devices with MoO\(_3\) or CuI ABL. These devices were grown using high work-function electrode buffer layers. These devices were fabricated by replacing C\(_{60}\) and Alq\(_3\) EBL by the high work function MoO\(_3\), which is well known as hole injector (collector) and electron blocking layer. The devices were made with the different anodes used in OPV cells. After ABL deposition, a 10 nm ED film was deposited. The organic film was covered with 7 nm of MoO\(_3\) and aluminium was used as top electrode.

A Kruss G40 Contact Angle Measuring System G40 was used to estimate the surface energy of anode surfaces through the sessile drop method. A drop of liquid with known surface tension (water, formamide, ethylene glycol and glycerol) is put on the anode surface and according to the Owens, Wendt, Rabel and Kaelble method, the surface tension, split up into a polar and a disperse fraction, can be deduced from the accurate measure of the angle between the substrate surface and a line tangential to the circumference of the drop \(^{22}\).

### 3 Experimental Results

After characterization of the CuI and ITO/CuI thin film structures, we focused our experimental study on the influence of the CuI ABL on the ED layer properties and on the performances of OPV cells using CuI ABL.

#### 3.1 Structural, chemical, optical and electrical properties of CuI films

In Fig. 1 the XRD pattern of CuI films thick of 50 nm is presented. The peaks visible in the diagram \(^{23}\) indicate it is Q-CuI (JCPDS: 060246). Only two peaks are visible in the XRD diagram of the CuI thin film. They can be identified as (111) and (222), indicating that the CuI films are textured with crystallites preferentially oriented along the (111) direction. The full width at half maximum (FWHM) of the main diffraction peak is 0.2 degree.

The Scherrer’s formula was used to estimate the crystallite size \(D\):

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

![Fig. 1 — X-ray diffraction diagram of a CuI thin film (thickness 50 nm)](image-url)
where $K$ is a constant ($K = 0.9$); $\lambda$ the X-ray wavelength (0.1548 nm for Cu K\(\alpha1\)), $\theta$ the diffraction angle and $\beta$ the FWHM $\beta^2 = \beta'^2 - \beta_0^2$. $\beta'$ is the measured line width in radian and $\beta_0$ the line width of the apparatus ($\beta_0$ of the used apparatus, is 0.14 degree). The averaged value of the crystallite deduced from the Scherrer’s formula is 55 nm. It means that the height of the crystallites is of the same order of magnitude that the CuI film thickness.

The (111) peak is situated at $2\theta = 25.51$ degrees, which corresponds, using the Bragg’s formula, $d_{111} = 3.489\text{Å}$, value in good agreement with the expected value\(^{24}\) for CuI.

Figure 2 shows the transmission spectrum of a CuI film thick of 50 nm. The CuI thin film is highly transparent below the threshold energy of around 400 nm. The absorption coefficient, $\alpha$, in the high absorption domain deduced from the optical measurements has been used to estimate the optical band gap $E_g$. CuI is a direct band gap semiconductor, therefore $E_g$ can be obtained from the relation: $(\alpha h\nu)^2 = A(h\nu-E_g)$ in which $h\nu$ is the photon energy. The inset in Fig. 2 shows that the optical band gap $E_g$ deduced from the high absorption domain is 3.16 eV. This value is in good agreement with reported values\(^{24,25}\).

We proceeded to XPS measurements of thin (3 nm) and thick (50 nm) CuI films deposited onto ITO. In the case of thick films, the substrate is not detected by XPS and we can consider that the CuI film behaves as bulk material. The C1s peak of the carbon surface contaminant is situated at 284.6 eV, which shows that there is no charge effect. The I3d and Cu2p photoelectron peaks are shown in Fig. 3. The I3d\(5/2\) peak appears at a binding energy of 619.5 eV, which is close to the values given in the literature\(^{25}\). For Cu2p\(3/2\), the peak appears at 932.3 eV. This corresponds to the expected value\(^{26}\) for Cu\(^+\) of CuI. As it can be seen in Fig. 3, each peak could be fitted with a single component, indicating that only one type of iodine and copper are present in the CuI film. Moreover, in the case of copper, the shape of the oxidized copper peak is typical\(^{27}\) and very different from that visible in Fig. 3(b). Moreover, the O1s peak binding energy is 531.5 eV, which corresponds to oxygen surface contamination and not to copper oxide\(^{27}\), which is situated at 530.5-530.5 eV.

It can be concluded from the XPS study that Cu is bonded to I only, even in the surface region. This gives evidence for the high chemical stability of the CuI deposited by Joule heating under vacuum. The relative atomic concentration of the surface of the CuI films is around 52% of I and 48% of Cu. The same values have been measured by microprobe analysis, which shows that the films are homogeneous since XPS is a surface analysis while the microprobe analyses the whole thickness of the film. The electrical conductivity of thick (50 nm) CuI films has been estimated to be around $10^{-3}$ Schm\(^{-1}\).
3.2. ITO/Cul layers characterisation

The morphology of the ABL has a strong influence on the shunt resistance of the OPV cells\(^4\) and it is known that the CuI thin film morphology depends on its deposition conditions. As a matter of fact we have shown above that, in the case of thick CuI thin films (50 nm) the crystallite thickness corresponds to the film thickness. Actually, CuI crystals tend to grow perpendicularly to the substrate\(^9\). So we checked the variation of the surface morphology of the CuI/ITO anodes when CuI is deposited at different deposition rates. The CuI ABL being thick of 3 nm, we measured the XRD diagram of these very thin layers deposited onto ITO. As it can be seen in Fig. 4, the shape of the curve is quite different from that of the 50 nm thick film. As a matter of fact, while the films are very thin, when deposited at 0.05 nm/s, some diffraction features are visible. The intensity of these features is smaller when CuI is deposited at 0.01 nm/s while, for the smaller deposition rate (0.005 nm/s), such features are not visible.

The surface visualization of these ITO/CuI structures is shown in Fig. 5. It can be seen that a lot of small grains are randomly distributed on the surface the film when the CuI layer is deposited at 0.05 nm/s [Fig. 5(a)], no such grains are visible when the film is deposited at 0.005 [Fig. 5(b)].

Because the average atomic number of CuI is higher than the one of ITO, the backscattering mode allowed us to obtain qualitative information on the chemical homogeneity of the film [Fig. 6(a)]. It can be seen that the small grains visualized in the secondary mode are white, which means that they are constituted, on average, by atoms heavier than those constituting the film itself. Therefore, they correspond probably to CuI grains.

The scanning electron microscope being equipped with a PGT X-ray microanalysis system, we have proceeded to microprobe mapping of the visualized surfaces (Fig. 7).

Figure 7(b) shows the map of the distribution of Cu in the film. It is clear that the bright spots of the image of the Fig. 6(a) are due to high Cu concentration, which confirm that the white spots of Fig. 6 are due to CuI grains. The spectra of Fig. 6(c) correspond to a white spot (line) and to the whole film surface (grey curve). They show that, the Cu concentration is the highest in the white spots, while the grey curve testifies that there is Cu all over the surface of ITO. In order to estimate the rate coverage of the ITO films by CuI grains we have used the software ImageJ\(^30\). Indeed, as said above, the backscattering mode allowed us to obtain well contrasted pictures for further treatment by the software ImageJ. The powerful resolution of the field emission SEM with

![Fig. 4 — X-ray diffraction diagram of CuI thin films (thickness 3 nm), deposited at 0.05 nm/s (—) and 0.005 nm/s (- -)](image)

![Fig. 5 — Surface morphology of CuI thin films deposited at (a) 0.05 nm/s and (b) 0.005 nm/s](image)
its large angle backscattered detector (LABE) allowed us to obtain images of high magnification in backscattered mode [Fig. 6(a)]. The software ImageJ allows improving the exploitation of the images themselves. SEM backscattered images were first filtered to reduce the noise then converted to binary image by threshold operation to see the area covered by CuI grains (in black in Fig. 6b) and that of the substrate (in white). Then ImageJ can measure this covering\(^\text{11}\). From Fig. 6, the first objective was to evaluate the rate of covering of the thin ITO film by the CuI grains. To achieve this goal, we have looked for a higher contrast adjustment than usual when we took backscattered images with the SEM to facilitate the ImageJ job, making black and white image (Fig. 6b). According to the calculation, the coverage of the ITO substrate by CuI grains is only 2%. When CuI is deposited at 0.01 nm/s, the density of grains at the surface of the films is too small to be quantified.

In order to check the SEM results, the CuI layers thick of 3 nm deposited at 0.05 nm/s and 0.005 nm/s were studied by AFM. Figure 8 shows that the surface of the CuI films can be described as columnar structure, mainly when it is deposited at 0.05 nm/s. As a matter of fact the rms surface roughness, deduced from a 6.2 \(\mu\text{m}\times6.2 \mu\text{m}\) surface, is only 0.6 nm when the CuI is deposited at 0.005 nm/s, while it is 1.1 nm when deposited at 0.05 nm/s.
Fig. 8 — Three dimensions TM-AFM images of ITO/CuI structures, CuI deposited at 0.005 nm/s (a) and 0.05 nm/s (b)

More precisely, when the CuI is deposited at 0.005 nm/s, the surface of the anode is homogeneous (Fig. 8a), but when deposited at 0.05 nm/s, some crystal like features are present at the surface of the ITO covered with 3 nm of CuI (Fig. 8b). The CuI crystals present onto the anode are as high as 100 nm (Fig. 9). The presence of these peaks leads to an increase of the overall surface roughness. If those are not taken into account, the rms surface roughness is 0.8 nm, comparable to that of films deposited at 0.005 nm/s.

Therefore, the XRD, SEM and AFM results are in good agreement, and they all lead to conclude that when the CuI films are deposited too fast, a lot of CuI grains are present on the surface of the films. However, after optimisation of the deposition conditions of the CuI ABL, the roughness of the ITO/CuI structures is small and the films are more homogeneous.

It is known that the presence of inhomogeneities, at the anode surface could decrease the performances and the life time of the OPV cells, due to small shunt resistance\textsuperscript{28}. As a matter of fact, the CuI crystals present onto the anode are as high as 100 nm (Fig. 9), which means that they are as thick as the whole OPV cell. Therefore, the vacuum deposition of organic films could be dramatically affected by «shadow effect». If the top of the anode becomes too rough, through the peaks discussed above, it would be rather difficult to cover uniformly the anode with the organic layer and, due to large thickness variations of the organic layers, large current leakage and small shunt resistance are obtained.

So, in line with above results, we used layers of CuI deposited at 0.005 nm/s for the realization of the OPV cells.

Finally, since MoO\textsubscript{3} is a well-known efficient ABL in OPV cells, we proceeded to the measurement of the surface energy of the anode covered with CuI or MoO\textsubscript{3}. The surface energies are very different, as shown in Fig. 10 where it can be seen that the MoO\textsubscript{3} surface is hydrophilic, while that of CuI is hydrophobic. It means that the surface energy of MoO\textsubscript{3} is higher than that of CuI, more precisely the polar component of the surface energy deduced from the accurate measure of the angles between the substrate surface and a line which is tangential to the circumference of the drops varies from 59.3 mJ/m\textsuperscript{2} with MoO\textsubscript{3} ABL to only 26.3 mJ/m\textsuperscript{2} with CuI ABL.

3.3 Effects of the CuI ABL on the properties of CuPc films and OPV cells, comparison with MoO\textsubscript{3} ABL

In the present work, the sample studied corresponds to those used to achieve OPV cells i.e. the same ITO coated substrate and the same CuPc thickness
(35 nm), the films studied are deposited directly onto ITO/MoO₃ or ITO/CuI substrates. It was already shown that the optimum CuI thickness⁷ is around 3 nm. Therefore, all the results presented in this chapter have been achieved using CuI ABL thick of 3 nm. For comparison, MoO₃ ABL thick of 3 nm has been also used because it is well known as a very efficient abl.

It was already shown that CuI ABL modifies strongly the orientation of the CuPc films, from perpendicular to the plan of the substrate when deposited onto MoO₃ ABL to parallel to this substrate when deposited onto CuI⁷. Therefore, firstly, - we checked the molecule orientation of the CuPc films. Actually, in the X-ray diffraction spectra of ITO/MoO₃/CuPc and ITO/CuI/CuPc (not shown here) the contribution of CuPc to the spectra depends strongly on the ABL. A peak centred in 2θ = 6.8° is visible in the case of ITO/MoO₃ substrates, while a peak centred in 2θ = 27.8° is visible in the case of ITO/CuI, that situated at 6.8° having completely disappeared. The peak situated at 2θ = 6.8° can be attributed to the (200) direction of the α-CuPc, that situated at 27.8° corresponds to an interlayer separation of 0.32 nm. As discussed earlier¹¹, these results indicate that onto CuI, the CuPc molecules lie down parallel to the plan of the substrate, while onto MoO₃ they stand up perpendicular to the substrate.

In a similar way, the optical density of the CuPc film depends strongly on the anode configuration. In the visible region, the absorption band corresponding to the Q band (π*-π* transition) shows two peaks located at 622 nm and 695 nm, which is expected for α-CuPc films³¹. When deposited onto CuI ABL there is a broadening and a red shift of 5 nm of the second peak. At half maximum, the Q peak width of films deposited onto MoO₃ is 160 nm, while it is 200 nm when the films are deposited onto CuI. This effect is attributed to a decrease of the intermolecular separation¹⁸. The main information is that the Q band surface increases significantly, which will increase the absorption and therefore, probability of free carrier formation in OPV cells.

We have probed the influence of the CuI ABL on the performances of the OPV cells: ITO (100 nm)/ABL/CuPc/C₆₀ (40 nm)/BCP (9 nm)/Al(100 nm), with ABL = CuI, MoO₃ or no AB.

The results achieved with CuPc are summarized in Table 1. The values are averaged from a series of 6 OPV cells. When CuI is used as ABL, it can be seen that, compared with the OPV cells using bare ITO as anode, the efficiency is doubled, whereas it is increased by a third with regard to OPV cells using the MoO₃ as ABL. Cheng et al¹², have already shown that the presence of CuI (3 nm), by comparison with reference OPV cells without ABL, results in an increase of the efficiency of about 70%.

However, up to now, the anode used for these studies was systematically ITO. Here we show (Table 1 and Fig. 11) that a similar improvement is induced by the presence of the CuI ABL when the anode is a film of fluorine doped tin oxide (FTO). As a matter of fact, by comparison with bare ITO both ABL increase all the OPV cells parameters. More precisely, by comparison with the MoO₃ ABL, the main positive effect of CuI is a large increase of the short circuit current Jsc and some improvement of the open circuit voltage Voc, while the fill factor FF is smaller.

The increase of Jsc can be attributed to the increase in the absorption of the MPc films deposited onto CuI, this increase being itself due to the modification of the orientation of the MPc molecules. Regarding the increase of Voc, it is known that Voc increases with the difference LUMO_{EA}-HOMO_{ED}, where LUMO_{EA} is the lowest unoccupied molecular orbital of the

Table 1 — Photovoltaic performance data and parasitic resistances under AM1.5 conditions of OPV cells with CuPc as ED, using different ABLs

<table>
<thead>
<tr>
<th>Anode</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Rs (Ω)</th>
<th>Rsh (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>0.44</td>
<td>4.6</td>
<td>42</td>
<td>0.86</td>
<td>209</td>
<td>640</td>
</tr>
<tr>
<td>ITO/MoO₃</td>
<td>0.48</td>
<td>5.8</td>
<td>60.5</td>
<td>1.68</td>
<td>3.7</td>
<td>1900</td>
</tr>
<tr>
<td>ITO/CuI</td>
<td>0.52</td>
<td>7.7</td>
<td>48</td>
<td>1.91</td>
<td>13</td>
<td>490</td>
</tr>
<tr>
<td>ITO/MoO₃/CuI</td>
<td>0.53</td>
<td>6.71</td>
<td>57</td>
<td>2.01</td>
<td>9.5</td>
<td>4650</td>
</tr>
<tr>
<td>FTO</td>
<td>0.35</td>
<td>4.5</td>
<td>38.5</td>
<td>0.64</td>
<td>11.5</td>
<td>290</td>
</tr>
<tr>
<td>FTO/MoO₃</td>
<td>0.44</td>
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<td>60</td>
<td>1.22</td>
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</tr>
<tr>
<td>FTO/CuI</td>
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<td>6.5</td>
<td>45</td>
<td>1.33</td>
<td>11</td>
<td>334</td>
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<tr>
<td>ZnO</td>
<td>0.43</td>
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<td>0.56</td>
<td>204</td>
<td>440</td>
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<td>ZnO/CuI</td>
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<td>4.94</td>
<td>40</td>
<td>0.91</td>
<td>14</td>
<td>590</td>
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<tr>
<td>ZnO/MoO₃/CuI</td>
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<td>4.65</td>
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<td>1.2</td>
<td>5.5</td>
<td>665</td>
</tr>
</tbody>
</table>
electron acceptor. It has been shown that the HOMO of organic thin films is modified by the molecules orientation. In the case of CuPc, it varies from 4.75 to 5.15 eV when the molecules orientation changes from perpendicular to the plan of the substrate to parallel to it. Therefore, the higher value of \( V_{oc} \) obtained with CuI than with MoO\(_3\) as ABL can be attributed to the larger value of LUMO\(_{EA}\)-HOMO\(_{ED}\), the CuPc molecules being parallel to the CuI substrate and perpendicular to the MoO\(_3\) substrate.

On the other hand, it can be also seen in Table 1 that the smaller value of the series resistance \( R_s \) and higher value of shunt resistance are achieved with MoO\(_3\), which can explain the difference in FF value for different ABLs. It is known that FF decreases when the series resistance increases and the shunt resistance decreases. Such increase can originate from the interface anode/CuPc. It is known that MoO\(_3\), air exposed or not, allows achieving very good band matching with the electron donors through the creation of a dipole at its interface with the organic material. Therefore, even if CuI improves the band matching ITO/MPc, it is not as efficient as MoO\(_3\). However, the best OPV cells efficiency is achieved with CuI because of the significant improvement of \( J_{sc} \) and \( V_{oc} \). The decrease of the shunt resistance may be due to the surface roughness of the CuI/ITO anode since we have shown that inhomogeneities can be present at the surface of the CuI layer.

In order to prevent these disagreements, we have used double ABL (DABL). As a matter of fact, it was already shown that it is possible to cumulate the advantages of both ABLs by stacking them. In earlier works, CuI was coupled with PEDOT:PSS in order to improve the band matching with PEDOT:PSS and to improve the phase separation of the blend ZnPc:C\(_{60}\) thanks to CuI. In a similar way the DABL MoO\(_3\)/CuI was used in the case of ZnPc/C\(_{60}\) planar heterojunction. Here, CuI improves the cell efficiency through the templating of the ZnPc molecules, while MoO\(_3\) increases its life time by preventing CuI diffusion into the organic material. Actually, we have probed a DABL MoO\(_3\)/CuI and we can see in Table 1 that it allows improving the power conversion efficiency (PCE) of the OPC cell through the FF value. Thus, to test the effect of CuI on others ED, we used systematically this DABL.

3.4 Examples of CuI ABL influence on the properties of porphyrin derivatives films and OPV cells, comparison with MoO\(_3\) ABL

After probing that CuI induces a strong improvement of the efficiency of OPV cells using CuPc thin films as ED we have probed its influence on the efficiency of OPV cells using others ED such as Porphyrin derivatives.

3.5 Effects of the MoO\(_3\)/CuI DABL on the properties of porphyrin derivative films and OPV cells

Different porphyrin derivatives were probed. The tetrakis(bromo), porphyrin (BrP), the zinc(II)-meso-tetrakis(4_bromoPhenyl), porphyrin (BrPhPZn) and the meso-tetrakis (5-bromo- 2-thienyl)porphiryn), (TBrTP) (Fig. 12) were used as new donors in planar heterojunctions.

In all cases the optimum porphyrin derivative thickness is 10 nm. Typical \( J-V \) characteristics, in the case of BrP, are shown in Fig. 13, while a summary of the OPV cells performances for all the porphyrin derivatives probed are presented in Table 2.
It can be seen that there is, systematically, a remarkable improvement of the PCE of the OPV cells. This improvement is due to an increase of $J_{sc}$ and $V_{oc}$. The same specific characterizations of the ITO/MoO$_3$/porphyrin derivative and ITO MoO$_3$/CuI/porphyrin derivative were made for all the porphyrin derivatives probed in order to try to understand the effect of CuI. Similar effects were put in evidence whatever the porphyrin derivative. The XRD study shows that all the porphyrin layers used, whatever the anode configuration is, are amorphous. Therefore, it is not as easy as in the case of MPc to put in evidence a templating effect of the CuI. However, the SEM studies show that the morphology of the layers of all the prophyn derivatives depends on the anode configuration.

An example is shown in Fig. 14 in the case of TBrTP. When deposited onto MoO$_3$ (Fig. 14b), the surface of the film is partly covered by features with “butterfly like” shape, when deposited onto CuI, features cover the entire surface (Fig. 14a). These systematic morphology differences induce some modifications of the optical and/or electrical properties of the porphyrin layers. One can see in Fig. 15 that, as in the case of CuPc, the CuI layer induces an improvement of the absorption of the porphyrin layer, here the BrPhPZn.

Figure 15 shows the expected Soret intense absorption band ($\beta$) in the 400 to 430 nm region, these bands are characteristic for porphyrins and are due to $\pi-\pi^*$ ligand transitions. Beyond 500 nm, 2 bands (Q) can be observed due to zinc insertion in the porphyrin ring. We can see that the absorption of films deposited onto MoO$_3$/CuI is significantly higher.

![Fig. 13 — Typical J-V characteristics of glass/ITO/ABL/BrP/C$_60$/BCP/Al structures, in the dark (full symbol) and under illumination of AM1.5 solar simulation (100 mW/cm$^2$) (open symbol)](image)

![Fig. 14 — Surface morphology of TBrTP thin film deposited onto (a) MoO$_3$/CuI and (b) MoO$_3$](image)

<table>
<thead>
<tr>
<th>Porphyrine derivative</th>
<th>MoO$_3$ (nm)</th>
<th>CuI (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (\Omega)</th>
<th>$R_{sh}$ (\Omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BrP</td>
<td>3</td>
<td>1.5</td>
<td>0.73</td>
<td>3.21</td>
<td>44</td>
<td>1.03</td>
<td>5.3</td>
<td>555</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>-</td>
<td>0.68</td>
<td>1.63</td>
<td>47</td>
<td>0.52</td>
<td>5.25</td>
<td>1102</td>
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<tr>
<td>BrPhPZn</td>
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<td>1.5</td>
<td>0.71</td>
<td>2.9</td>
<td>50</td>
<td>1.03</td>
<td>2.4</td>
<td>680</td>
</tr>
<tr>
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<td>0.57</td>
<td>1.68</td>
<td>45</td>
<td>0.42</td>
<td>0.576</td>
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</tr>
<tr>
<td>TBrTP</td>
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<td>0.56</td>
<td>4.4</td>
<td>54</td>
<td>1.32</td>
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<td>2.5</td>
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</table>
than that of films deposited onto MoO$_3$, through the Soret absorption of the porphyrin, which justifies that, whatever the porphyrin derivative probed, with or without Zn, the absorption increases. These results could justify, at least partly, the improvement of $J_{sc}$ and therefore of the OPV cells efficiencies induced by the double MoO$_3$/CuI ABL.

In the case of the porphyrin, there is also an improvement of the layer conductivity when it is deposited onto CuI. In order to determine the effect of the different ABLs on the BrPhZn layer conductivity, we have investigated the $J$-$V$ characteristics of devices with MoO$_3$ and MoO$_3$/CuI ABL. The devices were made using the same ITO covered glass substrate than those used to grow OPV cells. After deposition of the ABL, a porphyrin film thick of 30 nm was deposited. Then the organic film was covered with a MoO$_3$ film thick of 7 nm. Finally, aluminium was used as top electrode. The $J$-$V$ characteristics of these devices are shown in Fig. 16. Charge transport in these devices is limited to holes. Electron injection from the aluminium electrode can be neglected, due to the large electron barrier due to the MoO$_3$ interlayer. The devices using MoO$_3$/CuI ABL show largest current density at the same driving voltages as compared to the devices using MoO$_3$ ABL. Clearly, the conductivity is enhanced by an order of magnitude when a MoO$_3$/CuI ABL is used on the place of the MoO$_3$ ABL. All the devices display near ohmic transport at low voltage. Actually, in the low voltage range, ohmic contacts can be seen by the linear relation between the current density $J$ and the voltage $V$ at higher current density the slope increases, which corresponds to a transition towards Space Charge Limited Current (SCLC) which is often obtained in such devices\textsuperscript{42}.

As a conclusion, the study dedicated to different porphyrin derivatives shows that the field of effectiveness of the CuI ABL is not restricted to MPc.

Moreover, very recently, an improvement of the cells performance through the use of a MoO$_3$/CuI DABL was also put in evidence when the electron donor used is the 5-[2,6-bis(E-2-{3',4'-di-n-hexy[2,2':5',2'-terthiophen]-5-yl}vinyl)-4H-pyran-4-ylidene]pyrimidine-2,4,6(1H,3H,5H)-trione (TTB)\textsuperscript{43} or the the thienylenevinylene-triphenylamine functionalized with peripheral dicyanovinylene (TDCV-TDA)\textsuperscript{44}. In the case of this last exemple, the OPV cell efficiency change from 1.13% with MoO$_3$ as ABL to 2.5% with MoO$_3$/CuI ABL. Therefore, all these studies show clearly that the effect of CuI on the organic film is not specific to MPc but more general.

4 Discussion

4.1 Templating effect of the CuI ABL

Usually the performances of the OPV cells are improved through the introduction of an ABL between the anode and the ED. The improvement of OPV cells efficiency using these anodes so modified, can be due to an improvement of the band matching at the interface anode/ED, which is often verified, and the improvement of the properties of the organic layer due to the influence of the ABL on the growth of the organic layer. The former effect is related to the surface work function of the modified anode and the latter to its surface properties, such as surface energy and chemical reactivity.

On the other hand, it is possible to modify the properties of the ED film through a templating effect, which, in the present film is due to CuI. For instance, in the case of metal phthalocyanine, with the ITO/MoO$_3$ substrates the CuPc molecular plane is perpendicular to the substrate, while it is parallel for CuI substrate. In the case of porphyrin derivatives, the morphology of the films is clearly modified by the CuI. Theses differences in organic film morphology and structure on different substrates is usually
attributed the different interaction between the organic material and the surface of the substrates. When the interaction organic molecule-substrate is stronger than the molecule-molecule interaction, the films adopt a growth layer by layer (2 dimensions growth of the film). If the molecule-substrate is weak, the molecule-molecule interaction dominates and the films adopt a three dimension growth. Moreover, the chemical reaction at the bottom layer with the organic material has to be taken into account. It is well known that CuI can be used as a reagent in organic synthesis.

About the interaction organic molecule-substrate, it depends on the surface energy of the modified anode. We showed (Figure 10) that the MoO$_3$ surface is hydrophilic, while that of CuI is hydrophobic indicating that the surface energy of MoO$_3$ is much higher than that of CuI. According to the Owens, Wendt, Rabel and Kaelble method, the surface tension, split up into a polar and a disperse fraction. More precisely, in the present study, the polar component of the surface energy varies from 2.19 mJ/m$^2$ for CuI ABL to 52.92 mJ/m$^2$ for MoO$_3$ ABL. It has been shown already that a hydrophobic surface, such as that modified by CuI here, could provide a better compatibility with the subsequent hydrophobic organic material, such as CuPc, TDCV-TPA etc. It is also clearly established that the surface energy of the electrode can modify the arrangement of the molecules on the surface and hence affect the carrier mobility and the trap density in the organic film and the contact resistance between the electrode and the organic material. About CuI interactivity with organic molecules, it is known that CuI catalyses the conversion of ary1, heteroaryl and vinyl bromides into corresponding iodides. Moreover, it was already shown that CuI and other copper halides can interact easily with organic molecules. As a matter of fact, CuI exhibits a high tendency to react with an atom donor of organic molecules (as nitrogen, sulphur and oxygen atoms) they are in contact. Therefore, in the case of the ED studied here, the high interactivity CuI-organic material produces an interfacial complex between them inducing a templating effect of the organic molecules in such a way that the improved properties of the ED allows to achieve systematically higher $J_{SC}$ in OPV cells.

When the double ABL, MoO$_3$/CuI, is used, the OPV cells efficiency is optimum. We assume that the reason for this may be due to the dual function of MoO$_3$ and CuI. Through the modification of the morphology of the different ED layers probed, the CuI improves the optical absorption and/or the conductivity of the organic films, which increases $J_{SC}$, $V_{OC}$ and the PCE of the OPV cells. Nevertheless, we have shown during the presentation of the CuI thin films properties that it is quite difficult to grow homogeneous thin films, which explains that when CuI alone is used as ABL the value of FF is not very high. Therefore, MoO$_3$, which allows achieving high FF value prevents the OPV cells from leakage path formation, which permits achieving better FF values when MoO$_3$/CuI DABL are used.

Another positive effect of MoO$_3$ in the DABL is that it improves the lifetime of the OPV cells by preventing Cu diffusion into the organic layers under UV illumination. As a matter of fact, in agreement with this study, we have shown that while the cells involving MoO$_3$ or MoO$_3$/CuI ABL show similar degradation rates, this rate is significantly larger for CuI ABL.

Actually, it was already shown that CuI can be used as an efficient $p$-dopant in an organic hole transporting material. It was shown that the conductivity of 2TNATA (4,4',4''-tris(N-(2-naphthyl)-N-phenylamino)-triphenylamine) is more than three orders of magnitude higher when 25% mol of CuI is introduced into 2TNATA. In the same way, the performance of top-emitting organic light-emitting diodes was improved by using CuI doped layer. The hole injection from the Ag metal anode to NPB is dramatically enhanced by the formation of charge transfer complex between NPB and CuI. It was also shown that the use of the blend CuI-PVA as electron donor in bulk heterojunction increases the absorption of the electron donor. All these studies show that CuI diffusion into the ED layer, at least in the part near the contact with the organic layer, can justify the improvement of their electrical and optical properties.

5 Conclusions

The nature of the ABL can influence strongly the structural properties of the organic layer deposited onto this ABL, which can modify significantly the performance of OPV cells grown from these structures. CuI modifies the CuPc molecule orientation onto the anode. All this results in a significant improvement of the efficiency of the CuPc based OPV cells using CuI as ABL, optimum results being obtained when a double MoO$_3$/CuI ABL is used. Moreover, we show for the first time that CuI allows improving organic solar cells using others ED

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than MPC. Actually the power conversion efficiency of OPV cells using different porphyrin derivatives is significantly improved when a MoO3/CuI DABL is introduced. This improvement is related to a templating effect of the CuI on the organic layer. The origin of the CuI influence on the structural properties of organic films is discussed in terms of improved surface energy of the modified anode and high reactivity of CuI with atoms donor of organic molecules. At least we report, for the first time, that CuI ABL is efficient not only with ITO anode but also with FTO anode.

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