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Hind Lamkaouane[1,4], Hajar Ftouhi[1,2], Guy Louarn[1], Yamina Mir[4], Mustapha Morsli[3], Mohammed Addou[2], Linda Cattin[1], Jean Christian Bernède[5*]

1- Institut des Matériaux Jean Rouxel (IMN), CNRS, UMR 6502, Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, France
2-Laboratoire des nanomatériaux et couches minces, FST, Université Abdelmalek Essaadi de Tétouan, FST de Tanger BP 416 – Tanger, Morocco
3- Université de Nantes, Faculté des Sciences et des Techniques, 2 rue de la Houssinière, BP 92208, Nantes, F-44000 France.
4-Laboratoire de la Matière Condensée et des Energies Renouvelables, Faculté des Sciences et des Techniques, Université Hassan II de Casablanca, B.P 5366 Maarif, Casablanca, Maroc
5- MOLTECH-Anjou, CNRS, UMR 6200, Université de Nantes, 2 rue de la Houssinière, BP 92208, Nantes, F-44000 France.

Corresponding Author

Jean Christian Bernède, Université de Nantes, CNRS, MOLTECH-Anjou, F-44000 Nantes, France
E-mail: Jean-christian.bernede@univ-nantes.fr

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Abstract

We present a study of performances of organic photovoltaic cells (OPVs) using a wide variety of small molecules. These OPVs use two or three molecules to form binary or ternary cells, i.e. consisting of two or three flat stacked layers. Different ternary OPVs designs for efficient light harvesting and energy band structure combinations are studied. Molecules have been chosen to study all possible energy band structure alignments in ternary configuration. We discuss various parameters limiting their efficiency, such as carrier mobility, organic layer morphology, energy band structure alignment. Special attention has been paid to understand the device behavior. It is shown that, if light absorption domains, carriers mobility, energy band structure alignment are decisive for achieving performing OPVs, the geometry of the molecules is also decisive. In ternary OPVs, the third organic layer, intercalated between the electron donor and the electron acceptor, must serve as a bridge in the energy levels of the outer layers, which permits an energetic cascade

effect. For this effect to be positive it is necessary that this intermediate layer facilitates creation and transport of charge carriers, but also that it allows transport of energy, all leading to an improvement of the performance of the OPVs.

1. Introduction

Today, due to the need to develop renewable energies, there is a great interest in photovoltaic energy. Among the different photovoltaic cells under study, due to their lightness, flexibility, semi-transparency... organic cells are among the most studied [1, 2]. For efficient organic photovoltaic cells (OPVs) it is necessary to use at least two organic materials, an electron donor (D) and an electron acceptor (A). Two typical geometries of the active layer are possible. It may consist of a blend of D and A, this configuration is called bulk heterojunction (BHJ). The second possibility consists in a stacking of layers, where the active layer is made of at least two films, D/A; it is called planar-heterojunction (PHJ) [3, 4]. Concretely, depending on the roughness of the layers, intermediate geometries are also possible. In recent times, dramatic advances of the performances of OPVs have been achieved using new promising molecules and polymers [5-7]. Nevertheless, the synthesis of these new materials is not trivial which means that the commercialization of solar panels using them is not feasible in the near future. It is therefore interesting to study the performances of cells using small molecules, although less efficient, but easier to obtain with perfectly controlled synthesis and reproducible properties [8-11]. The efficiency of binary OPVs, *i.e.* using two different organic materials as active layer, is limited by the narrow absorption spectra of the organic materials. Ternary OPVs with two acceptor or donor materials allow over-passing this limitation [12-14]. The third material, which must be ambipolar (DA), can bridge the energy levels of the electron donor and the electron acceptor, which can facilitate charge transport through energy cascade effect. Its light absorption must be complementary to that of others organic materials present in the active layer. If these conditions are fulfilled it can significantly improve the efficiency of the OPVs. However, adjusting the relative thickness of the different layers and understanding the electronic processes present at their interface remains a challenge. More precisely, the relative values of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the organic molecules used must fulfil certain rules (Supporting information Fig. S1). In a couple D/A, to obtain efficient separation of the exciton charges, the offset ΔHOMO and/or ΔLUMO must be higher than the

exciton binding energy ΔExc [15-17]. Therefore, in the case of ternary OPVs, HOMO and LUMO energy levels must be progressively offset in form of cascade heterojunctions, in such a way that the central DA layer carries out exciton dissociation on the donor and acceptor side. Moreover, to be efficient, the carrier's mobility of both types, electron and hole, of the DA must be high enough to obtain an acceptable current. On the other hand, it is now well admitted that the maximum value of the open circuit voltage, Voc, follows the energy difference between the LUMO of A and the HOMO of D (See Fig. S1). Therefore, in order to avoid any decrease of Voc, in the case of ternary OPV, it can be desirable to use a DA with same HOMO (or LUMO) than D (or A). Moreover, the amount of light harvested by the OPV depends on the good agreement between the absorption domain of the organic materials used and the solar spectrum. Prerequisites for the absorption domains of organic materials, *i.e.* their band gap, the Voc value and the offset ΔHOMO and/or ΔLUMO value for efficient exciton charge separation make that it is necessary to determine the optimum trade-off between these different values [18]. After light absorption and exciton generation, two mechanisms can take place, charge transfer or energy transfer. On one hand, after exciton diffusion towards an interface D/A, the exciton dissociation induces charge carriers generation and then their diffusion towards the electrodes. To be efficient, in ternary OPVs, it would be desirable that the excitons can be dissociated at the interfaces D/DA and DA/A. On the other hand, energy transfer must be effective in addition to the charges transfer. Usually, in organic material, this transfer is due to Förster resonance energy transfer (FRET), issued from coulombic interaction between organic materials. This FRET is at the origin of two step exciton dissociation: first, exciton diffusion by long scale FRET from D to DA, then, dissociation at interface DA/A. FRET, to be efficient, needs an overlapping between the D emission spectrum and the DA absorption spectrum [19-20]. This second migration route, added to the classical charge transfer, allows expecting for better efficiencies for ternary OPVs compared to corresponding binary OPVs [21]. All these constraints, which must be respected to obtain performing ternary OPVs, makes that ternary OPVs often show limited success relative to binary OPVs. Actually, added to stresses concerning band structure, carrier mobility's must be high enough, mainly in the case of the DA which must be ambipolar and FRET must be possible. Moreover some difficulties due to the morphology of some layers may exist due to specific grow properties of certain organic materials. Nevertheless some promising results were already obtained. Therefore, in the present work, based on new results and complemented by already published results, we sought to determine general

rules that can help us in the choice of new molecules for future performing cells. Thus we analyze the results obtained with ternary cells made up of different molecules whose specific properties allow exploring the effect of energy band structure, carriers mobility's, morphology… Although BHJ-OPVs are most often studied due to their highest efficiency, we chose the PHJ-OPV configuration due to the fact that it consists in a stacking of layer, which made that it is easier to discriminate between the various effects encountered and to determine the molecule from which they originate. The different molecules have been chosen with sufficiently different properties in order to be able to study the influence of the mobility of the carriers, of their energy band structure and of their geometry. PHJ-OPVs are easy to implement by deposition under vacuum, through sublimation of the small organic molecules, which provides an additional purification step. We must not forget that one of the most successful companies in the field of OPVs is Heliatek which realizes all of its solar panels by vacuum deposition and PHJ-OPVs appear as promising option [22-23]. We show that if, as expected, the energy band structure configurations, the carriers mobility, the light absorption ranges are fundamentals to achieve efficient PHJ-OPVs, the geometry of the small organic molecules may be also determinant.

2. Experimental

2.1 Organic molecules

The vast majority of molecules used for this work are available on the market, only a few relatively easy synthesis molecules have been made in the laboratory [24-27]. For this work, CODEX-International (France) was our primary supplier. The chemical structures of the small molecules are shown in supporting information, Fig. S2, while their energy diagrams are reported in Fig. S3, The HOMOs and LUMOs values have been checked by cyclic measurements (S5.8). It should be emphasized that the choice of molecules was guided by the fact that we wanted to study all possible alignments of energy band structures (Fig. 1).

2.2 Organic photovoltaic cells realization and characterization

It is well known that if the composition of the organic active layer is primordial for performances of OPVs, it is also necessary to ensure that carriers are collected after separation, which implies the use of adequate electrodes with interfaces organic material/electrode efficient. Of course one of the electrodes must be transparent to visible light. ITO (indium tin oxide) is the transparent electrode

the most often use due to its high conductivity and transparency. The second electrode must behave like a mirror to reflect the unabsorbed light which thus passes through the layer a second time. Al is often used for this purpose. To obtain efficient interfaces it is necessary to insert buffer layers between electrodes and organic materials. From the anode side, the introduction of a thin hole transporting layer (HTL) increases the work function (W_F) of ITO, which decreases the energy barrier between ITO and D, W_F of ITO being around 4.7 eV, while the HOMO of D is around 5 eV or more (Supporting information Fig. S1). This HTL increases significantly the OPVs performance. Even if it has been shown that hybrid HTL can be highly effective, we chose in the present work to used simple HTL, MoO_3, due its simplicity which permits to improve the reproducibility of the results and due to the fact that MoO_3 is well known as efficient HTL [28]. From the cathode side, in small molecule PHJ-OPVs, the insertion of a buffer layer called exciton buffer layer (EBL), with large band gap to block excitons, improves substantially the OPV efficiency. If bathocuproine is widely used as EBL, it was shown that Alq_3 allows obtaining equivalent but more stable performances, so we used Alq_3 as EBL [29]. Therefore, the binary and ternary PHJ-OPVs consisted of stacks according to ITO/MoO_3/D/A/Alq_3/Al and ITO/MoO_3/D/DA/A/Alq_3/Al (Fig. S4), respectively. During this work C_{60} (fullerene) was the A of all the ternary OPVs. SubPc (Boron subphthalocyanine chloride), which is well admitted as ambipolar material [30-31], was used as DA material. As in the case of organic materials, donor or acceptor character is relative, according to the respective positions of the HOMO and LUMO levels, to be able to achieve all possible alignments of energy band structures we used some molecules, more known as electron donors, as ambipolar layer. As a result, AlPcCl (Aluminum phthalocyanine chloride) was used as D or as DA, while MD2 (2-((5-(4(diphenylamino)phenyl)thiophen-2-yl)methylene) malononitrile) [27] and BDP (tetraphenyldibenzoperiflanthene) were used as ambipolar layer. Pentacene, M8-1 ((E)-2-cyano-3-(5-((E)-2-(9,9-diethyl-7-(methyl(phenyl)amino)-9H -fluoren-2-yl)vinyl)thiophen-2-yl)acrylic acid) [26], CuPc (Copper phthalocyanine), BSTV ((E)-bis-1,2-(5,5’’-Dimethyl-(2,2’:3’,2’’-terthiophene)vinylene) [25] and 5T (Pentathiophene) [24] were used as D (Fig. 1).

The manufacturing of binary and ternary PHJ-OPVs, previously described in other publications, is quickly recalled in the supporting information S4. In the same way, the characterization techniques used during this work are presented in the supplementary information S5 [24-25].

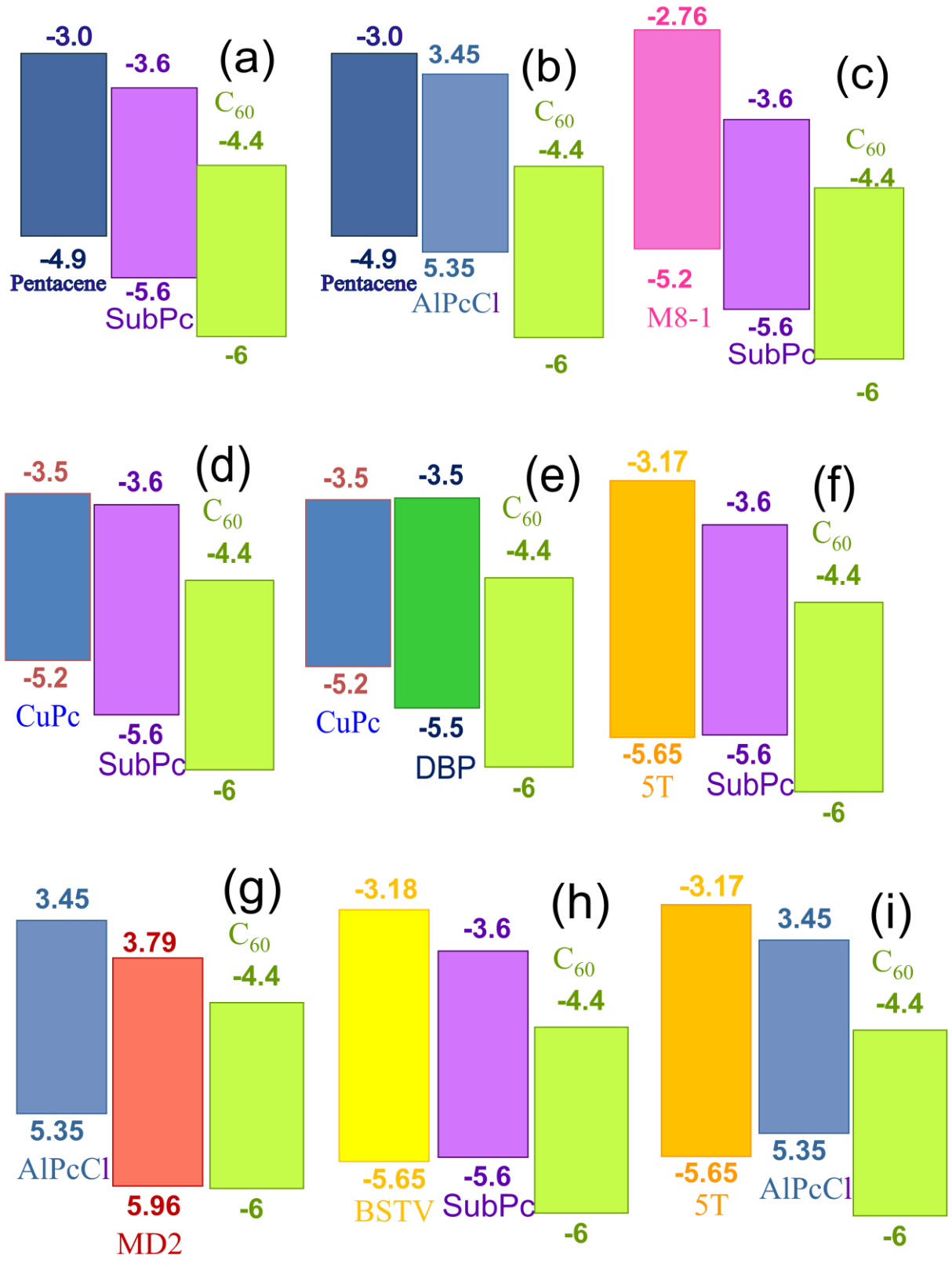


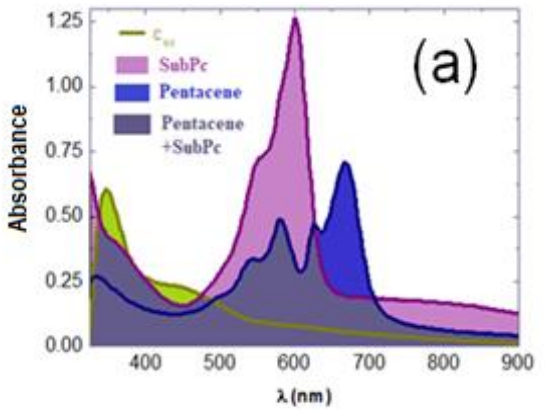
Figure 1. Energy levels alignments for the different ternary OPVs configurations studied.

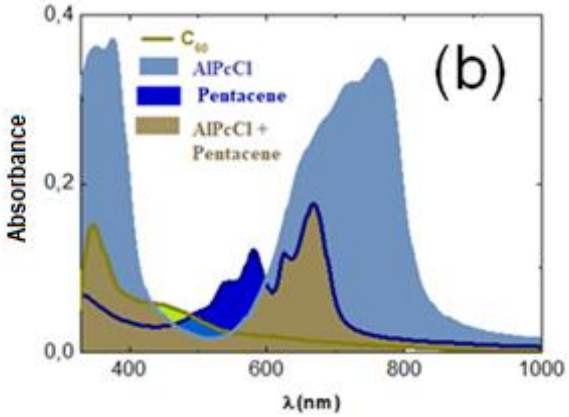
3. Results

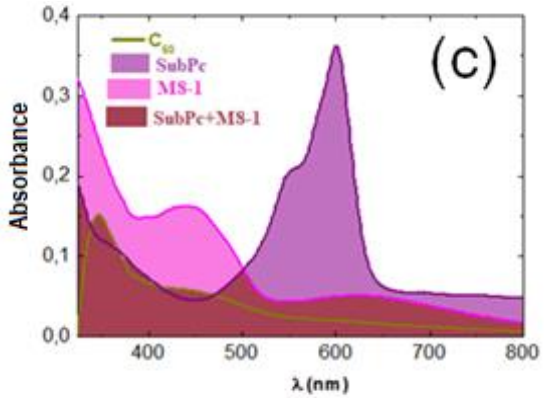
The idea of present work was to realize and study all possible combinations of alignment of energy band structure in ternary OPVs. All of these configurations are shown in Fig. 1.

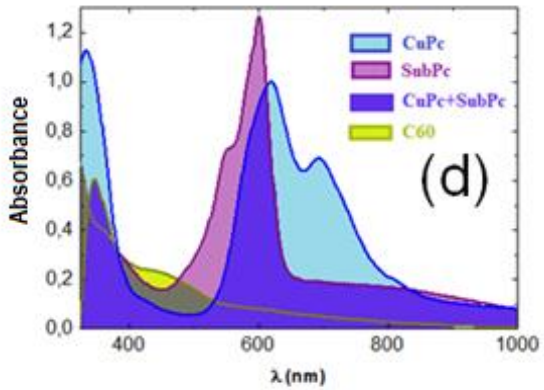
They are presented in a specific order, first the classical "ideal" energy cascade structures (Fig. 1a-c), then the structures having two components of the same LUMO (Fig. 1d, e), then those having two same HOMO (Fig. 1f-h), finally a last unconventional configuration (Fig. 1i). To refine this study, some energy band structure configurations have been repeated but using molecules with different properties such as carrier mobility, photoluminescence or morphology of layers. Thereby, some configurations are similar but with different molecules which allows to see that parameters, such as carrier mobility, layer morphology..., others than the energy band structure configuration are determinant. The UV-vis absorption spectra of the nine ternary PHJs of Fig. 1 are shown in Fig. 2. It can be seen that all the configurations result in a significant widening of the absorption domain.

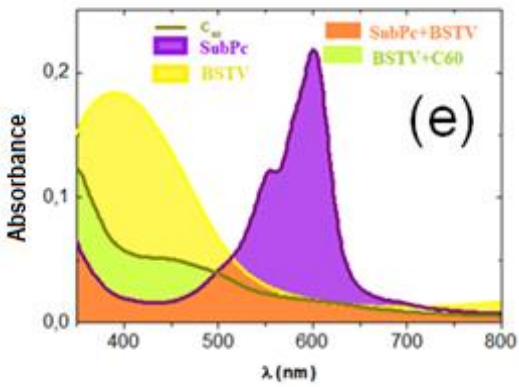
We present firstly the study of the ternary OPV using CuPc as D, SubPc as DA and C_{60} as A (Fig. 1d), due to the fact that they are often chosen as active molecules in PHJ-OPV. The goal of the purpose of producing ternary OPVs was to surpass the efficiencies obtained with binary OPVs, thus we compare the results obtained with the couples CuPc/C_{60}, SubPc/C_{60} and CuPc/SubPc with those obtained with the ternary OPV CuPc/SubPc/C_{60}. The results, obtained after optimisation, are presented in Fig. 3 and are summarized in Table 1. The optimisation of the OPV performances through the variation of the thickness of the different layers is presented in supporting information S6 (Table S6).

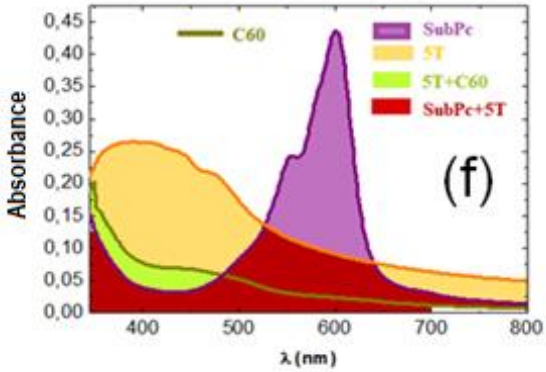

(a)
C60
SubPc
Pentacene
Pentacene +SubPc
Absorbance
λ (nm)

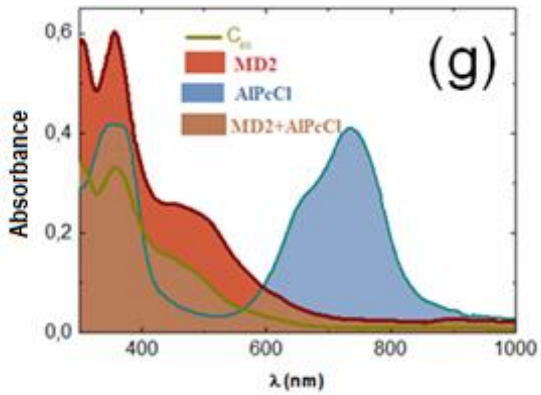

(b)
C60
AlPcCl
Pentacene
AlPcCl + Pentacene
Absorbance
λ (nm)

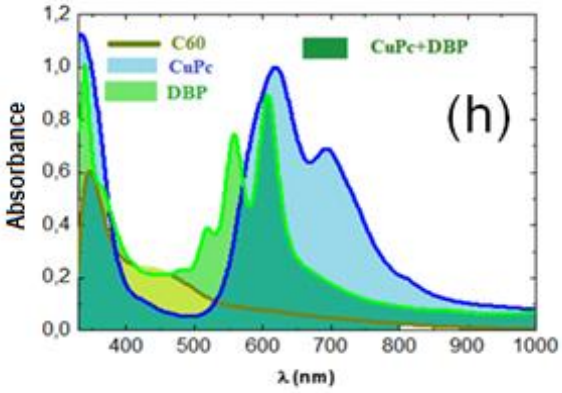

(c)
C60
SubPc
MS-1
SubPc+MS-1
Absorbance
λ (nm)


(d)
CuPc
SubPc
CuPc+SubPc
C60
Absorbance
λ (nm)


(e)
C60
SubPc
BSTV
SubPc+BSTV
BSTV+C60
Absorbance
λ (nm)


(f)
C60
SubPc
5T
5T+C60
SubPc+5T
Absorbance
λ (nm)


(g)
C60
MD2
AlPcCl
MD2+AlPcCl
Absorbance
λ (nm)


(h)
C60
CuPc
DBP
CuPc+DBP
Absorbance
λ (nm)

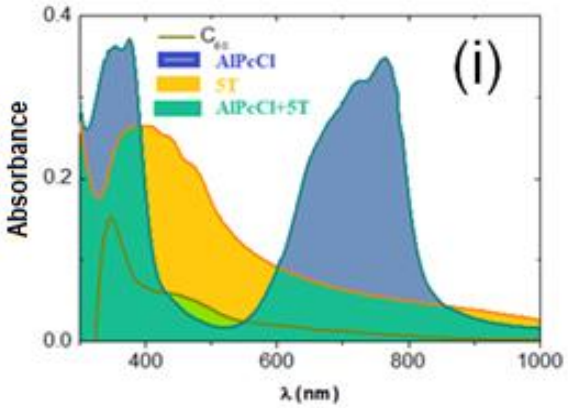


Figure 2. UV-vis absorption spectra of the nine ternary PHJs of Figure 1.

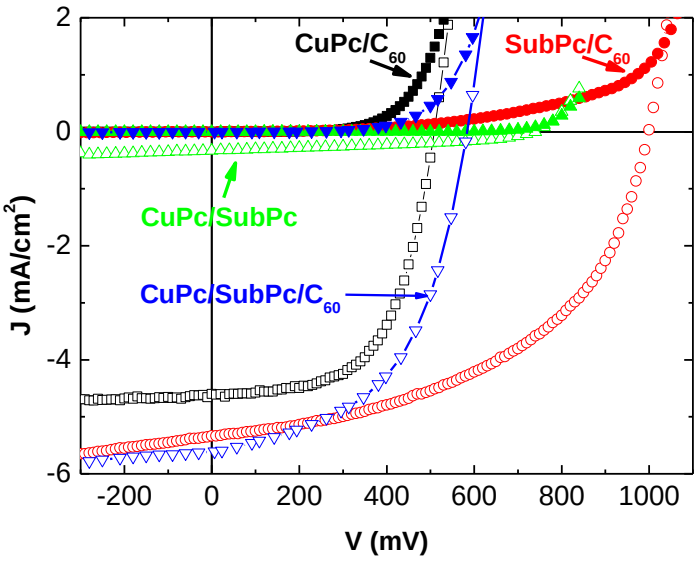


Figure 3. J-V characteristics of binary and ternary OPVs: ITO/MoO_3/active layers/Alq_3/Al, the active layer being CuPc/C_{60} (■), SubPc/C_{60} (●), CuPc/SubPc (▲) and CuPc/SubPc/C_{60} (▼), (the filled symbols correspond to dark conditions while the open symbols correspond to light AM 1.5 conditions).

Table 1. Parameters of the OPV family using CuPc, SubPc and C_{60}.

Active layer (thickness-nm)	Voc (V)	Jsc (mA cm^{-2})	FF (%)	η (%)
CuPc (30)/C_{60} (40)	0.50	4.68	60	1.42
SubPc (20)/C_{60} (40)	1.00	5.33	50	2.63
CuPc (30)/SubPc (15)	0.74	0.33	41	0.09
CuPc (30)/SubPc (15)[a)]	0.75	0.48	33	0.12
CuPc (30)/SubPc (15)/C_{60} (40)	0.58	5.54	55	1.77

[a)] HTL MoO_3/CuI and not MoO_3 alone.

The optimum efficiency of the ternary OPV, CuPc/SubPc/C_{60} is only 1.77%, which is higher than that of the binary OPV based on CuPc/C_{60}, but smaller than that of SubPc/C_{60}. On one hand, the short circuit current, Jsc, of the ternary OPV, overpass that of all the binary OPVs of the family, which was expected since, as visible in Fig. 2d, the insertion of SubPc between CuPc and C_{60} widen the absorption domain of the OPV. Unfortunately, on the other hand, as predicted by the theoretical maximum value of the open circuit voltage (Fig. S1 and Fig. 1d), Voc, of the ternary OPV far is smaller than that of the couple SubPc/C_{60}. Moreover, the success of the attempt to improve the efficiency of the OPVs by moving from 2 to 3 layers in the active organic layer also depends on the efficiency of the D/DA and DA/A interfaces. Fig. 3 and Table 1 show that the binary OPV based on CuPc/SubPc underperforms with very small Jsc and small Fill Factor (FF). In order to check the activity of the interface CuPc/SubPc we proceeded to External Quantum Efficiency (EQE) (see S5.2).

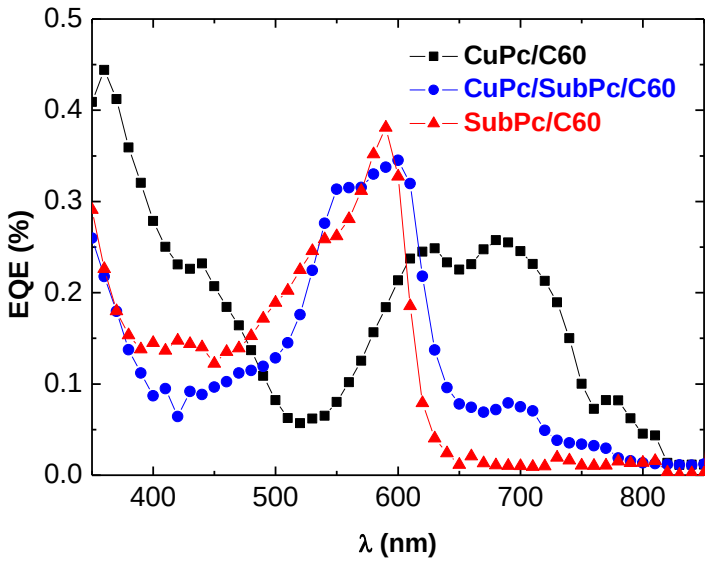


Figure 4. EQE spectra of OPV with different active layers: (■) CuPc/C_{60}, (▲) SuPc/C_{60} and (●) CuPc/SubPc/C_{60}.

First of all, it must be noted that we were unable to measure the EQE spectrum of the OPVs based on the couple CuPc/SubPc, the photocurrent being too small. In the Fig. 4, the EQE spectra, in the case of CuPc/C_{60} and SubPc/C_{60} reproduce clearly the absorption spectra of CuPc and SubPc respectively (Fig. 2d), with a small contribution of C_{60}. On the contrary, the shape of the EQE spectrum of the CuPc/SubPc/C_{60} active layer is quite different from the light absorption of these superposed three layers. In fact, the shape of the EQE spectrum is similar to that of SubPc/C_{60}. It means that the main contribution to the photocurrent in the ternary cell is due to the couple SubPc/C_{60}, with a very small contribution of CuPc between 650 nm and 750 nm. It can be concluded from the electrical study that the contribution of CuPc to the photocurrent is very small, which explains that the efficiency of the ternary OPV is smaller than that of the binary OPV based on the SubPc/C_{60} couple.

On the other hand, it is known that, when deposited by sublimation under vacuum, the films of CuPc are crystallized. Usually, the CuPc molecules are perpendicular to the plan of the substrate. Nevertheless, when specific substrates, such as CuI, are used, the molecules are parallel to the substrate [32]. Generally, the organic molecule layers are amorphous. It is possible that the crystallized surface of CuPc layers disturbs the interface CuPc/organic layer according to the

orientation of the CuPc molecules. Moreover, it is important to note that the energy level of the small molecules strongly depends on the molecular orientation. For instance, in the case of CuPc, it has been shown that the value of the HOMO depends on this orientation [33]. In absolute value it is 4.75 eV for the standing-up CuPc and 5.15 eV when the molecules are the parallel to the substrate. Therefore, since when deposited onto MoO_3 the CuPc are perpendicular to the plan of the substrate while they are parallel when they are deposited onto CuI, we have studied the properties of ITO/MoO_3/CuI/CuPc/SuPc/Alq_3/Al OPVs. Unfortunately, as shown in Table 1, the results are similar to those obtained with MoO_3 alone as HTL. It means that the failure of the CuPc/SubPc interface is not related to the orientation of the CuPc molecules.

We have verified another possibility of trouble. The band gap of SubPc is significantly wider than that of CuPc. Therefore, since in the classical configuration, the light crosses first the CuPc layer, it may penalize the light harvesting by SubPc. So, we have checked this possible trouble by probing inverted OPVs. In inverted OPVs, the ITO is used as a cathode, which corresponds presently to OPVs such as ITO/Alq_3/SubPc/CuPc/MoO_3/Al, so that the light crosses SubPc before CuPc, *i.e.* large band gap material before small band gap. Unfortunately, the results obtained are even worse than those obtained with classical OPVs (supporting information Table S6). Actually, this result is in good agreement with the EQE spectrum of the ternary OPV which shows that the main contribution to the photocurrent is due to SubPc, which means that its interaction with light was not penalized by the fact that CuPc was crossed by light before SubPc itself.

In order to explain the inefficiency of the interface CuPc/SubPc, we had to investigate the specific properties of these materials which may be involved in their electronic exchanges: charge carriers mobility's, surface roughness, optical density, photoluminescence. As it will be interesting to know these properties for the other molecules used during this work we have proceeded to a systematic experimental study of these for all the molecules concerned. We draw up a balance table of the properties of the different materials used.

Table 2. Diverse parameters of the organic layers used.

Molecule	μ_{e^-} ($cm^2\ v^{-1}\ s^{-1}$)	μ_h ($cm^2\ v^{-1}\ s^{-1}$)	RMS[b] (nm)	O. D. Absorption range (nm)	PL[c] Emission range (nm)
Pentacene	-	$7.5\ 10^{-3}$	4-7	500-700	660-700 ; 730-950
CuPc	$5.8\ 10^{-3}$	$1.1\ 10^{-3}$ [a]	3	550-800 ; 300-400	1075-1175
M8-1	$1.6\ 10^{-9}$	$6\ 10^{-7}$	3.5	530-580 ; 300-530	525-750
BSTV	-	$9.5\ 10^{-6}$	1.55	350-500	500-650
5T	-	$1.7\ 10^{-4}$	18	350-600	475-625
AlPcCl	$6.9\ 10^{-4}$	$4\ 10^{-5}$	6	800-600 ; 400-300	660-720 ; (770)
DBP	$1.6\ 10^{-4}$	210^{-4}	-	500-650 ; 300-450	-
SubPc	$8\ 10^{-3}$	$1.7\ 10^{-5}$	-	500-650 ; 430-300	-
MD2	$1.5\text{-}3\ 10^{-7}$	$1\ 10^{-5}$	-	500-300	-

[a] When deposited onto CuI the hole mobility of CuPc is $2\ 10^{-3}\ cm^2v^{-1}s^{-1}$

[b] Values measured for the organic bottom layer D.

[c] From luminescence spectra shown in Fig. S7 or extracted from the bibliography: 5T [35], Pentacene [38], AlPcCl [39], and CuPc [40].

Thus, in Table 2 the electron and hole mobility of the different molecules are enumerated. The values reported have been measured using the space charge limited current technique (SCLC; Supporting information S5.3). The experimental values are of the same order of magnitude than those found in the literature, for instance $2\ 10^{-4}\ cm^2v^{-1}s^{-1}$ for the hole mobility of DBP to be compared to $1\ 10^{-4}\ cm^2v^{-1}s^{-1}$ encountered in earlier publication [34] and $7.5\ 10^{-3}\ cm^2v^{-1}s^{-1}$ Pentacene, what is, as expected, the highest mobility measured (Table 2) [35]. About CuPc, if better results were published, $2.1\ 10^{-2}\ cm^2v^{-1}s^{-1}$, [36], the measured value, $2\ 10^{-3}\ cm^2v^{-1}s^{-1}$ is situated in the range of purified CuPc according to Rhonda F. Salzman et al. [37].

In addition, it is known that in PHJ-OPV the roughness of the bottom organic layer, when too high, may induce leakage currents which results in Voc and FF decrease, so the root mean square (RMS) roughness is noted in the Table 2. In the same way, we have seen that FRET, to be efficient, needs a clear overlapping between the D photoluminescent spectrum (PL) and absorption spectrum of the DA layer, so the PL domain of the D layer and the absorption domain of the DA layer are schematically reported in Table 2.

About the couple CuPc/SubPc, the Table 2 shows that μ_h of CuPc is among the highest of the Table, while the μ_e of SubPc is high enough to use it as ambipolar material. Also, the RMS of CuPc is of the same order of magnitude as that measured for most D layers. Nevertheless, there is no overlapping between the PL spectrum of CuPc and the absorption of SubPc, which makes that energy transfer (FRET) appears improbable, which may be a start to explaining the poor results obtained.

In order to look more carefully for the origin of the trouble we have substituted DBP to SubPc. As shown in Fig. 1 the band scheme d and e are nearly similar. The obtained results are summarized in Table 3.

Table 3. Parameters of the OPV family using CuPc, DBP and C_{60}.

Active layer (thickness-nm)	Voc (V)	Jsc (mA cm^{-2})	FF (%)	η (%)
DBP (20)/C_{60} (40)	0.76	3.01	38	0.88
CuPc (30)/C_{60} (40)	0.50	4.68	60	1.42
CuPc (30)/DBP (15)	0.24	1.02	25	0.06
CuPc (30)/DBP (10)/C_{60} (40)	0.30	1.59	40	0.20

It can be seen that the result are worst than those obtained with SubPc. Nevertheless, the electron mobility of DBP, μ_e = 1.6 10^{-4} cm^2 v^{-1} s^{-1} (Table 2), if not very high, is not so bad and cannot justify the very bad performance of the OPV based on the couple CuPc/DBP. However, one can see in table 2 that, here also, there is no overlapping between the PL spectrum of CuPc and the absorption of DBP.

In front of these results, we propose possible hypotheses of interpretation.

About the ternary PHJ-OPVs with CuPc as donor, it appears that, whatever the ambipolar layer, SubPc or DBP, there is no overlapping between the PL spectrum of CuPc and the absorption range of the DA layer. About the PL spectrum of CuPc Chuan-Hui Cheng et al. measured a small near-infrared electrophosphorescence at 1.1 μm [40]. Even if the PL signal is small, others studies confirm that the emission range of CuPc is around 1.1 μm [41, 42]. It can be concluded that there is no overlapping between the PL spectrum of CuPc and the absorbance of SubPc or DBP, which excludes the possibility of energy transfer (FRET) from CuPc to the central

ambipolar layer. Such absence can explain the disappointing results obtained with the ternary PHJ-OPVs CuPc/SubPc/C_{60} and CuPc/DBP/C_{60}. Similarly, it was shown that, while there was an efficient energy transfer (FRET) from P3HT to C_{60} via TPD (N,N'-diphenyl-N,N'—bis (3-methylphenyl)[1,1'-bisphenyl]-4,4'-diamine), there is not in the case of CuPc/TPD/C_{60} devices, which was attributed to the fact that FRET is a function of the photoluminescence quantum yield of D and the degree of overlap between the A absorption spectrum and the D emission spectrum [43].

On the other hand, it must be noted that the CuPc molecules are plane and their films are crystallized, while those of SubPc (Fig. S2) and DBP (See Fig. S8.1) are not plane and their films are amorphous. Such differences in structures can lead to some disorder at the interface and consequently poor interface properties. Actually, it is well known for a long time that PTCBI, in the same way that C_{60}, allows obtaining efficient OPVs based on the couple CuPc/PTCBI [44] and it turns out that the PTCBI molecules are plane. In fact perylene molecules such as PTCBI, PTCDA, PTCDI-C_7H_{15} are plane as shown in supporting information Fig. S8.2. To explore this hypothesis, we have probed binary OPVs based on couple CuPc/perylene. It can be seen in supporting information S9 (Table S9 and Fig. S9) that all the couples probed, CuPc/PTCBI, CuPc/PTCDI-C_7H_{15} and CuPc/PTCDA give far better results than those obtained with the couples CuPc/SubPc or CuPc/DBP, even in the case of PTCDA despite its small carrier mobility. These results reinforce our hypothesis regarding the possible influence of molecular geometry on cells performance, via the activity, or not, of the interface donor/acceptor.

In order to achieve more information about the effect of the CuPc/A (C_{60} or SubPc) interface on the PHJ-OPV performances, we proceeded to deeper analysis of the J–V characteristics of the binary OPVs based on CuPc/C_{60} and CuPc/SubPc. The variation of the photocurrent density, J_{ph}, with the effective voltage, V_{eff}, has been studied with:

$$J_{ph} = J_L - J_D \quad (1)$$

$$V_{eff} = V_0 - V_a \quad (2)$$

where J_L is the current density under AM 1.5 light, J_D is the current density in dark and V_0 corresponds to the voltage when J_{ph} is equal to zero, while V_a is the applied voltage. It can be seen in Fig. 5 that, if, as expected [12], a saturation state is achieved at about 1 V in the case of the OPV with CuPc/C_{60} as active layer, there is no visible tendency to saturation in the case of OPV with CuPc/SubPc. The absence of visible saturation in this last case indicates that there is

high recombination loss at the interface CuPc/subPc which confirms the bad properties of this interface.

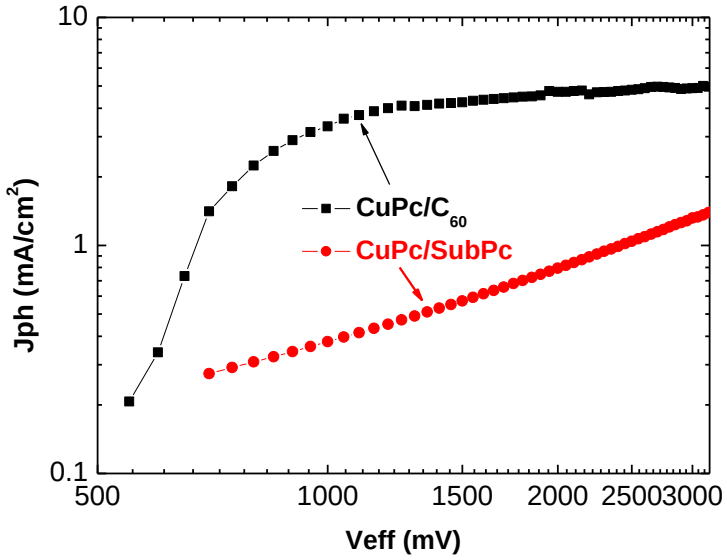


Figure 5. J_{ph}-V_{eff} curves of OPVs with different active layers (■) CuPc/C_{60} and (●) CuPc/SubPc.

Therefore, the absence of transfer energy (FRET) and the bad interface properties due, possibly, to poor geometrical compatibility, explain, the limited performances of the PHJ-OPVs using CuPc as donor when coupled with SubPc or DBP.

In order to pursue the investigation of the effect of energy band structure configurations on the performances of PHJ-OPVs, we have studied cascade energy levels configuration, such as those corresponding to Fig. 1a,b,c. When Pentacene is used as D, its high electron mobility allows using quite thick layer (60 nm). This allows more light to be absorbed which results in a higher photocurrent. Unfortunately, as shown in Fig. 1a, b, the energy difference between the HOMO of pentacene and the LUMO of C_{60} is small, which limits drastically the Voc value (Fig. S1) [45]. For instance, in the case of the Pentacene, SubPc and C_{60} family, for the ternary OPV (Pentacene (60nm)/SubPc (15nm)/C_{60} (40nm)), the efficiency is limited to 2.90%, while Jsc is 12.40 mA cm^{-2} and FF = 51%, due to the fact that Voc is only 0.46 V. In the same way, if we substitute AlPcCl to SubPc, the maximum efficiency of the pentacene (60nm)/AlPcCl (15nm)/C_{60} (40nm) ternary OPV is 2.05%, with Jsc = 12 mA cm^{-2}, FF = 47%, but Voc = 0.37 V. By comparison with the Voc of SubPc/C_{60} or AlPcCl/C_{60} which are 1V and 0.70 V respectively, it is clear that, due to

its HOMO value, -4.9 eV, the efficiency of the OPVs using Pentacene is significantly penalized. Nevertheless, the shape of the EQE spectra of the ternary OPVs pentacene/SubPc/C_{60} and Pentacene/AlPcCl/C_{60} (See S10) follow the corresponding optical density spectra (Fig. 2a, b). Clearly the three organic molecules of each OPV contribute to the photocurrent (Fig. S10) and it can be said that, contrarily to the case of CuPc/SubPc/C_{60}, both interfaces D/DA and DA/A are active. This justifies that the efficiency of the ternary OPVs is higher, at least slightly, than that of the corresponding binary OPVs, only by 0.5% in the case of pentacene/AlPcCl/C_{60}, but 10% in the case of Pentacene/SubPc/C_{60}. Nevertheless, as said above, the performances are limited by the HOMO of prentacene. Actually, the third cascade structure of Fig. 1d, allows us to confirm the effect of the HOMO value on the Voc value. Due to its HOMO at -5.2 eV, M8-1, in the M8-1/SubPc/C_{60} ternary OPV, permits achieving a Voc of 0.73 eV, which corroborates the fact that the Voc value increases with $\Delta(LUMO_A\text{-}HOMO_D)$. Sadly, the hole mobility of M8-1 is very small (Table 2) and the resulting OPV efficiency is limited to 0.8%.

The maximum theoretical value of Voc is equal to the difference between the LUMO of A and the HOMO of D. Therefore, in the case of ternary cells, to avoid a loss in the value of Voc, it can be desirable to use materials of which two of them have the same HOMO or LUMO. Since the results obtained by using D and DA with same LUMO (Fig. 1d and 1e) were disappointing, we decided to probe ternary OPVs using D and DA with the same HOMO value, BSTV/SubPc/C_{60} (Fig. 1h) and 5T/SubPc/C_{60} (Fig. 1f). The Fig. 1 shows that both ternary structures exhibit the same energy band structure, the main difference consists in the higher hole mobility of 5T compared to that of BSTV (Table 2). A previous study, but with a different HTL, has already shown that very good results can be achieved with BSTV [46], which is not the case with 5T [47]. Nevertheless, to increase the reliability of the comparison of the results obtained, we repeated the study, each of the molecules being from the same batch. Moreover, for simplicity, we used a simple HTL, MoO_3 alone and not MoO_3/CuI. The results reinforce, those obtained previously, namely with an increase in efficiency of 20 % in the case of the ternary OPV using the BSTV as D (Fig. 6).

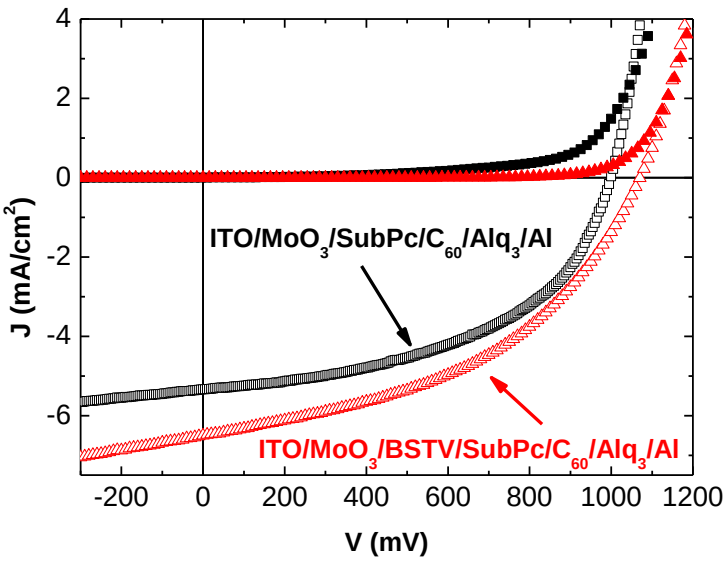


Figure 6. *J-V* characteristics of binary and ternary OPVs: ITO/MoO_3/active layers/Alq_3/Al, the active layer being SubPc/C_{60} (■), BSTV/SubPc/C_{60} (●), (the filled symbols correspond to dark conditions while the open symbols correspond to light AM 1.5 conditions).

The parameter of the champion OPV (BSTV (16 nm)/SubPc (12.5)/C_{60} (40nm)) are Voc = 1.07 V, Jsc = 6.6 mA cm^{-2}, FF = 45% and η = 3.14% to compare with the parameters of the binary OPV SubPc/C_{60} in Table 1. This good result can be associated to the fact that the Förster resonance energy transfer from the BSTV layer to the SubPc layer is highly probable since the PL spectrum of BSTV (Fig. S7.2) overlaps the absorption spectrum of SubPc (Fig. 2, Table 2). Moreover, the hole mobility of BSTV is of the same order of magnitude than that of SubPc (Table 2), while the absorption range of both molecules are complementary (Fig. 2e).

As regards 5T, which HOMO and LUMO values are similar to those of BSTV, unexpectedly, while its hole mobility is higher than that of BSTV, the obtained performances were very poor. In the case of ITO/MoO_3/CuI/5T/SubPc/C_{60}/Alq_3/Al ternary OPV, the maximum efficiency achieved was only 0.80%, to compare with the 0.81% obtained with the couple 5T/C_{60}. This disappointing result was correlated to the small Voc value, 0.38 V, while in the case of BSTV/SubPc/C_{60}, Voc = 1.07 V. It was shown that this small Voc value was due to the too high surface roughness of the 5T layer, high RMS which induces high leakage current and therefore small Voc value [47]. In fact, about the effect of the roughness of organic material interface, two

contradictory effects occur. The first effect is positive, as said by Kjell Cnops et al [48], the high surface roughness of the underlying donor layer increases the interface area compared with the projected area, which permits most excitons generated in the acceptor layer to reach the D/A interface, resulting in high Jsc values. On the other hand, the second effect is due to the fact that, a too high roughness induces leakage currents, which results in a decrease of Voc and FF [49]. For instance, as shown below, in the case of 5T layers, the maximum height of the peak-to-valley (PV) profile is of the same order of magnitude than the whole organic active layer (Fig. 8). Such high roughness induces shunt paths, which may induce some performance limitation via an increase in the leakage current. Therefore, increase in interface roughness improves Jsc through the increase the interface area D/A, but it decreases the Voc and FF value through leakage currents and it is necessary to determine the optimum trade-off between these different effects. In the present case of 5T, it appears that the negative effect of induced leakage current overpass largely the positive effect of the interface area increase. Nevertheless, as shown in the case of CuPc for instance, it is known that CuI modifies strongly the morphology of the organic layer which is deposited on it. Therefore, to circumvent the effect of CuI as template, the 5T layers were deposited onto MoO_3 HTL layer and not as previously on MoO_3/CuI. Nevertheless, as shown by the SEM study, a high density of grains is visible at the surface of the 5T layer deposited onto MoO_3 (Fig. 7a). Some grains seem nearly perpendicular to the substrate, what is confirmed by the cross-section shown in Fig. 7b. The inset in Fig. 7b corresponds to the cross section of a 5T layer deposited onto MoO_3/CuI. The grain visible in this inset is similar to that visible in the 5T film deposited onto MoO_3. This shows that the roughness of the 5T layers is more or less similar whether the layer is deposited on MoO_3 or MoO_3/CuI. This hypothesis is comforted by the AFM study. In Fig. 8, we can see an AFM image, 10 μm x 10 μm, of a 5T layer deposited on ITO/MoO_3. The RMS deduced from this image is 18 nm. Even if this RMS is smaller than that obtained when 5T is deposited on ITO/MoO_3/CuI (30 nm), it stays far higher than the value encountered in the case of the others D (Table 2). Moreover, some high features are visible at the surface of the ITO/MoO_3 anode. As shown by the profile issued from the AFM image, these features are as high as 90 nm, which means that they are nearly as thick as the whole PHJ-OPV cell. Actually, it can be seen in Fig. S11 that the leakage current in the case of the ternary OPV 5T/SubPc/C_{60} is far higher than that measured in the case of BSTV/SubPc/C_{60}, which justifies the measured large difference in Voc values, 0.38 V with 5T and 1.07 V with

BSTV, while they have similar band scheme configurations. Therefore, the surface of the anode being too rough, large leakage currents is obtained. It follows that, the same causes having the same effects, the performances of the OPVs based on 5T/SubPc/C_{60} are limited due to the small Voc value obtained, whatever the HTL, MoO_3/CuI or MoO_3.

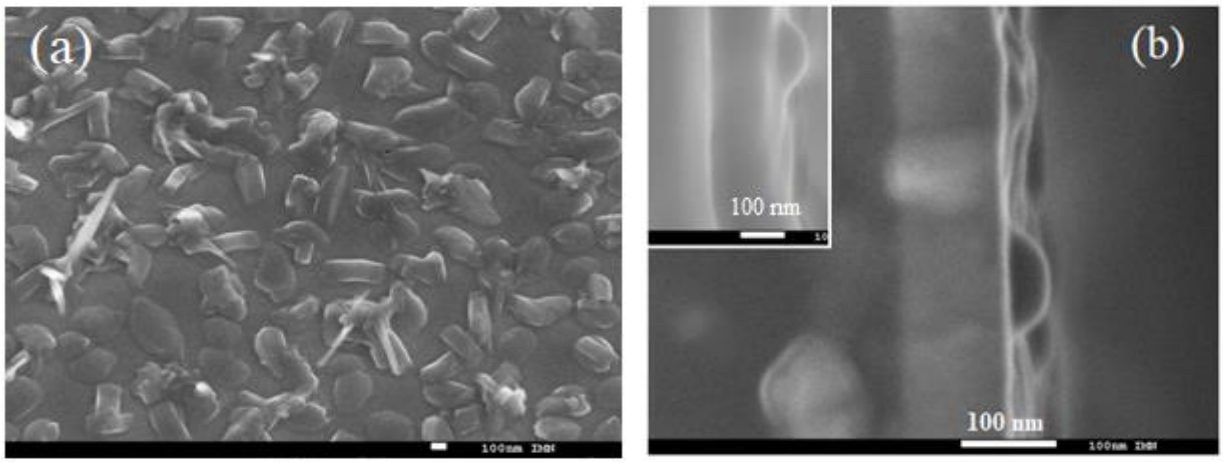


Figure 7. (a) Surface visualization of a 5T layer deposited on MoO_3; (b) Cross section of a structure glass/ITO/MoO_3/5T.
Inset Figure 7b**.** Cross section of a structure glass/ITO/MoO_3/CuI/5T.

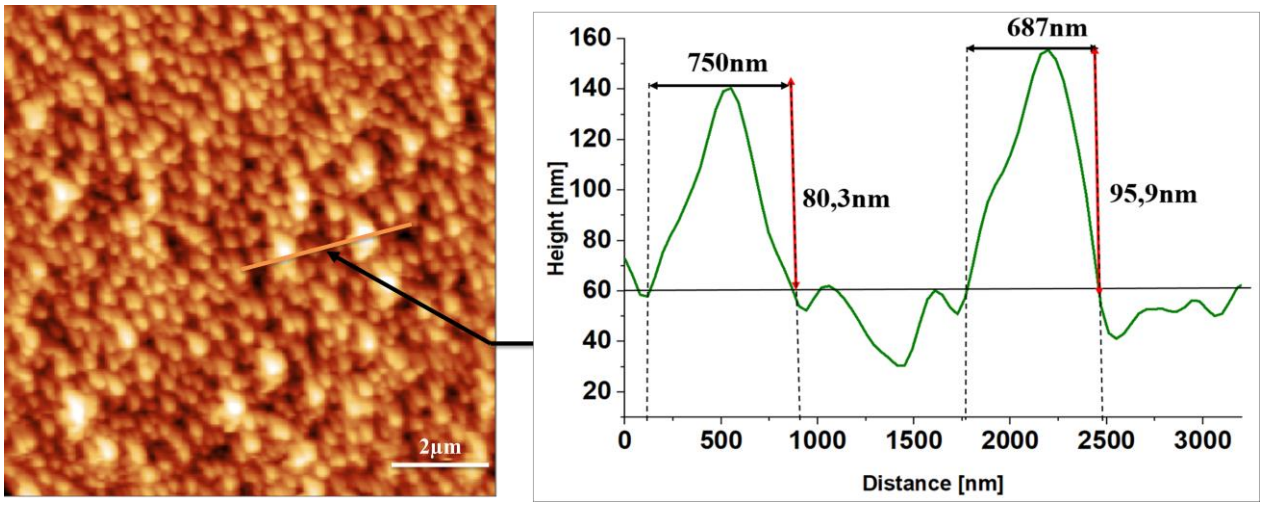


Figure 8. AFM image of a 5T layer and profile of the image following the visualized line.

As part of the study of the effect of the energy band structure alignment on the performances the PHJ-OPVs structure, where DA and A have the same HOMO have been studied, through AlPcCl/MD_2/C_{60} PHJ-OPVs (Fig. 1g) [47].

Here DA and A have the same HOMO whereas in the previous case it was D and DA. The results obtained in a recent study show that this configuration works. However, for the case studied the electron mobility of DA limits the obtained results [47].

There remains a last case for which the configuration is unfavorable to the proper functioning of the PHJ-OPV (Fig. 1i). This study was conducted using the ternary OPV, 5T/AlPcCl/C_{60}. If limited to the case where the intermediate layer is thick enough to be continuous (18 nm) [47], the performance for the 5T/AlPcCl/C_{60} is poor, with a maximum energy conversion efficiency of 0.7%. To explain this small efficiency we have focused our interest to the behavior of the 5T/AlPcCl couple. The optimum efficiency of the corresponding OPV, with 70 nm of 5T and 22 nm of AlPcCl, is η = 0.46% with Voc = 0.40 V, Jsc = 2.95 mA cm^{-2} and 39% as FF. The EQE spectrum of this binary OPV is shown in Fig. 9.

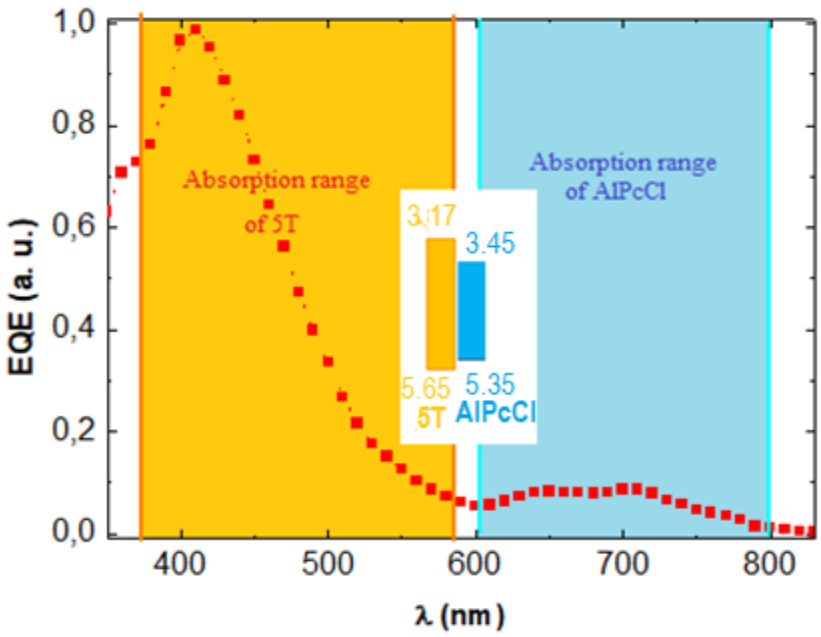


Figure 9. Normalized EQE spectrum of OPV based on 5T/AlPcCl active layer. The absorption ranges of the 5T and AlPcCl molecules are represented schematically as a colored background image.

Inset Fig. 9. Energy band structure of the binary heterojunction 5T/AlPcCl.

The absorption range of each molecule is symbolized by the color of the layer obtained with the corresponding molecules: blue for AlPcCl and orange for 5T (see also Fig. 2i). It is clear that the contribution to the photocurrent of AlPcCl is nearly null. It is due to the fact that, as shown by the Fig. 1i (and recalled by the inset of Fig. 9), the energy band configuration, $\Delta(HOMO_{DA}\text{-}HOMO_{D}) < 0$, is opposed to the passage of holes from AlPcCl to 5T, which impedes the collection of hole issued from the excitons created in the AlPcCl layer.

4. Discussion

Thus, we scanned all possible configurations of energy band structures, using molecules whose mobility of electric carriers and whose geometry were different. This allows us to set out some general rules to be respected in order to hope to achieve efficient ternary PHT-OPVs. Some were expected, some were not. As shown by the study of ternary cells using pentacene as D, but also ternary cells based on BSTV/SubPc/C_{60}, and the set of studied combinations, the Voc value increases with the energy difference between $LUMO_A$ and $HOMO_D$, except when the D layer is too rough which drastically decreases the value of Voc, as shown by the results obtained with 5T which RMS is 18 nm. As expected, the hole mobility of the D M8-1 and the electron mobility of the DA MD2 being very small, the results obtained with the OPVs using these molecules, are quite poor, but their general behavior, Voc value, activity of their interfaces with the other molecules included in the cells, are those expected. The results obtained with the 5T/AlPcCl/C_{60} are bad, which confirms that structure with energy band alignment not in accordance with the cascade energy levels configuration cannot give performing OPV. On the other hand, the study of the ternary OPVs using CuPc as donor shows that, if good band matching is necessary to obtain good performances, it is not sufficient. Actually the absence of transfer of energy by FRET in these OPVs results in disappointing efficiency. Moreover, more unexpected, the study of OPVs using CuPc as D shows that the effect of the molecules geometry on the interfaces properties thus realized must not be neglected. When three-dimensional molecules are deposited on plane molecules regularly oriented (parallel or perpendicular to the substrate) it follows a large disorder at the interface which leads to high losses by recombination of carriers, as shown by the failure to obtain saturation current for Jph. This result, even if the context is different, is not without recalling, those concerning ternary BHJ-OPVs where it has been shown that there too, the quality of BHJ depends heavily on the geometry of molecules introduced [12].

As said above, the review of the results obtained in this study confirms that the *Voc* value depends directly on the energy difference between the acceptor's LUMO and the donor's HOMO. In the case of quality interface, qVoc may be very close to the difference $\Delta(LUMO_A\text{-}HOMO_D)$. However, this value, if it is decisive for the maximum value of Voc, is not the only parameter determining when to its value. The surface roughness of the bottom organic layer of the structure is also decisive. Too high surface roughness dramatically decreases Vo*c* value. The highest Voc value achieved during this work, was obtained from a structure of which D and DA have same HOMO, which avoids the inevitable decrease in the case of stair energy band structure. If a good energy band structure alignment allows to obtain a large Voc value, this of course, is not enough to ensure a high efficiency of the OPV, still it is necessary that the mobility of the carriers of the active layers is sufficient to avoid space charge accumulation that distort the J-V characteristics which results in a S-shaped curve and/or small Jsc and FF. On the other hand, if experience shows that the use of a ternary structure in which D and DA or DA and A have the same HOMO is a good starting point to obtain a performing ternary cell, it remains, that in addition to sufficient charge carriers mobility, it is desirable that, besides conventional charge carrier transfer, via the formation of the exciton then the separation of charges at the level of an interface, there be an efficient transfer of energy by FRET.

FRET energy transfer results in a migration route which consists in two-step exciton dissociation: diffusion from the donor to the acceptor by Föster resonance energy transfer-FRET, over long length scales, then dissociation.

We have shown that ternary OPVs with higher efficiency than that obtained with corresponding binary OPVs fulfill the requirements for effective FRET energy transfer, *i.e*., a significant overlapping between the PL spectrum of D and the absorption spectrum of DA. When all these requirements are fulfilled, good energy band structure configuration, sufficient charge carriers mobility, complementary light absorption domains, overlapping of PL and light absorption, we have shown that there is still an additional requirement to fulfill, the quality of the interfaces must not be perturbed by incompatible geometry of the molecules. When all these requirements are fulfilled, significant efficiency improvement of ternary OPVs by comparison with corresponding binary OPVs. For instance efficiency of the Pentacene/SubPc/C_{60} ternary OPV, by comparison with SubPc/C60 is improved by 10%, while that of BSTV/SubPc/C_{60} is improved by 20%.

5. Conclusion

From this compilation of experimental results a number of rules can be drawn up to be respected if we want to have all the chances of success in the manufacture of ternary cells

-An increase in the RMS induces two opposite effects, one corresponds to an increase of Jsc through the increase of the D/A interface area and the second induces leakage currents and therefore Voc and FF deterioration. Therefore it is necessary to look for the RMS which allows to find the optimum trade-off between these opposite influences.

-When the roughness of the organic layers is less than 5 nm, which is generally the case, the difference between the theoretical maximum value of Voc and the experimental value is small, even less than 0.2, which makes it much lower than measured for BHJ-OPVs.

-The mobility of the carriers, electrons and holes, must be at least 10^{-4} $cm^2/v/s$ and not too different from each other to obtain a homogeneous charge distribution, this especially in the case of the central layer which, of course, must be ambipolar with balanced electron and hole mobilities.

- In addition to the classical process of charge carrier transfer via light absorption, the creation of the exciton, the migration of the exciton to an interface and the separation of charges at that interface, the possibility of energy transfer by FRET must be effective.

-It appears that, beyond the properties of energy band structures, mobility... the geometry of molecules, planar or not, plays a significant role in obtaining high-performance PHJ-OPVs.

As a conclusion it can be said that, using three of organic molecules with suitable properties, *i.e.* complementary light absorption, not too different carrier's mobility, appropriate energy band structure alignment and also compatible molecule morphologies, it is possible to overpass significantly the binary PHJ-OPV efficiency using ternary PHJ-OPV based on the same molecules, for instance the ternary PHJ-OPV based on the active layer BSTV/SubPc/C_{60}, allows to overpass by 20% the efficiency of corresponding binary OPVs such as SubPc/C_{60}.

Supporting Information

Supporting Information is available from the Wiley Online Library.

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Conflicts of interest

There is no conflict of interest to declare.

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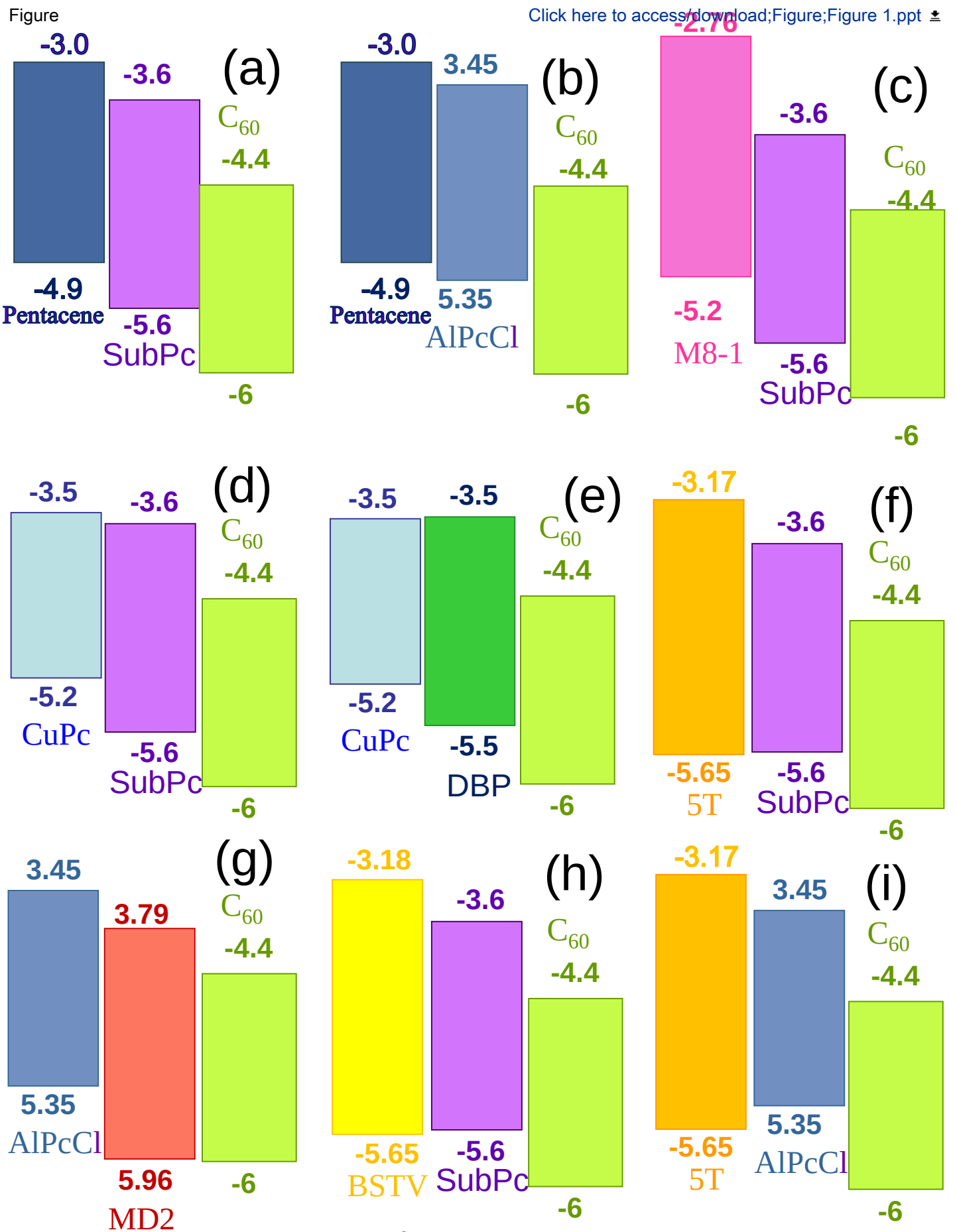

Figure 1.

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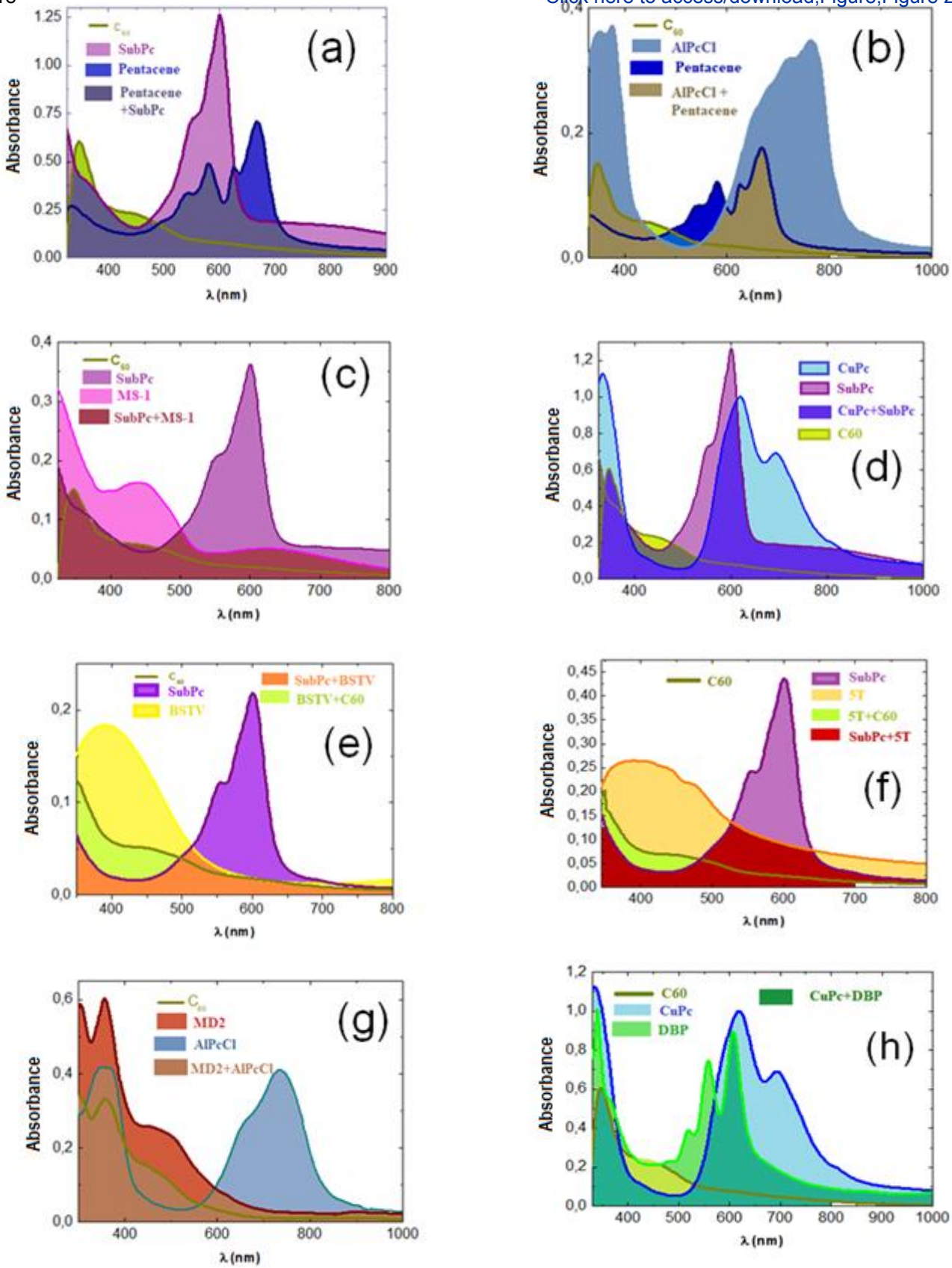

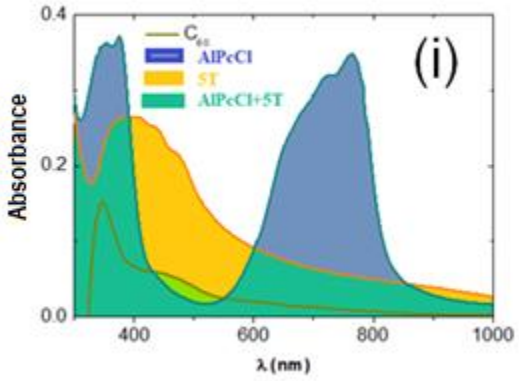
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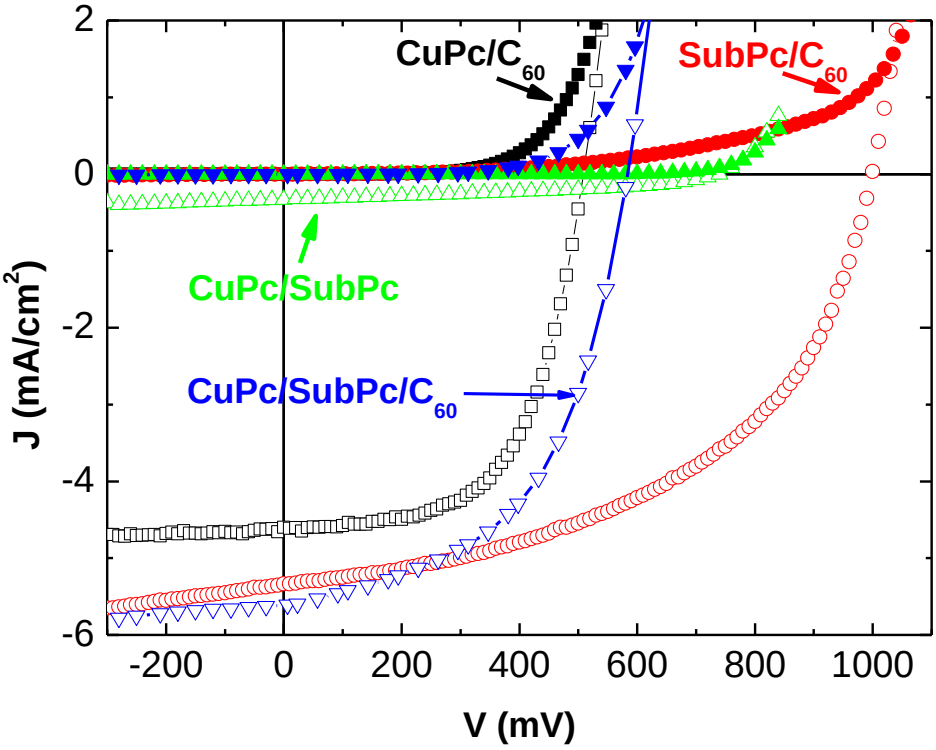
Figure 2



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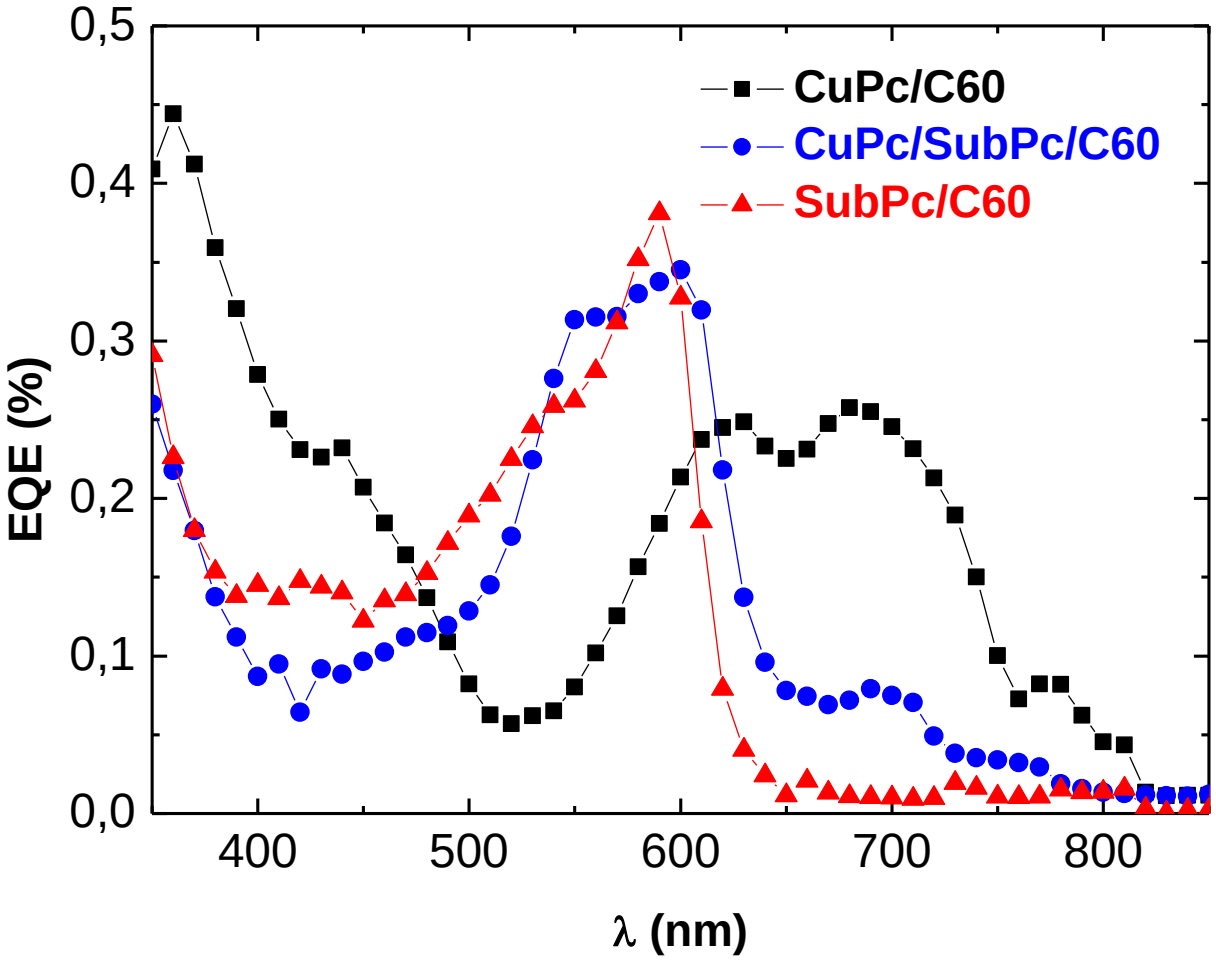

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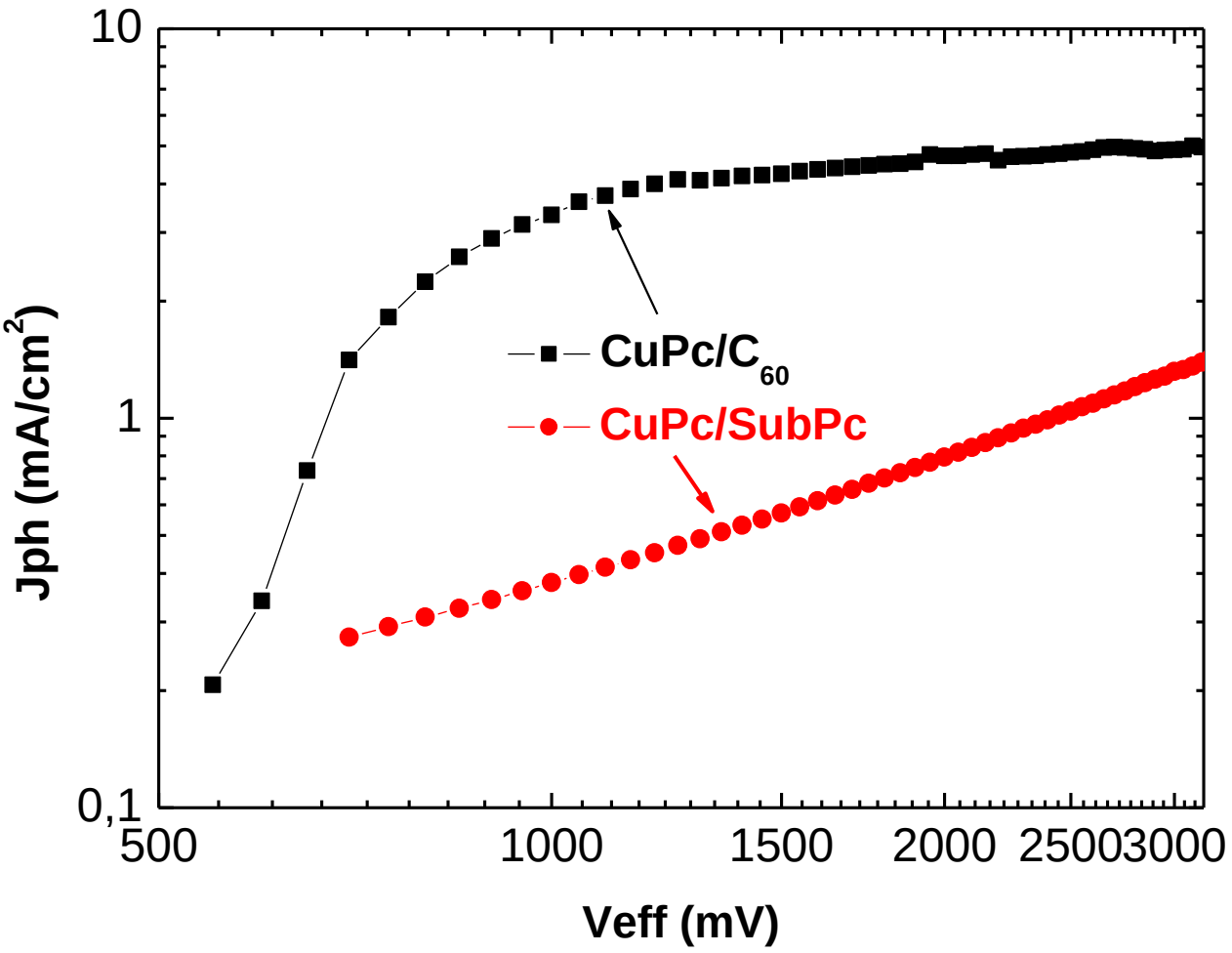

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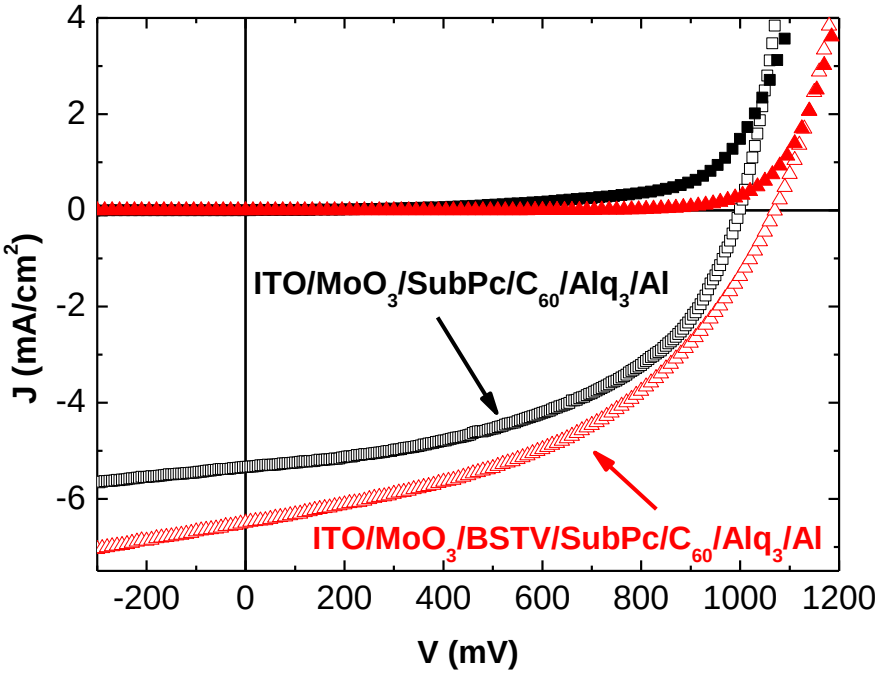

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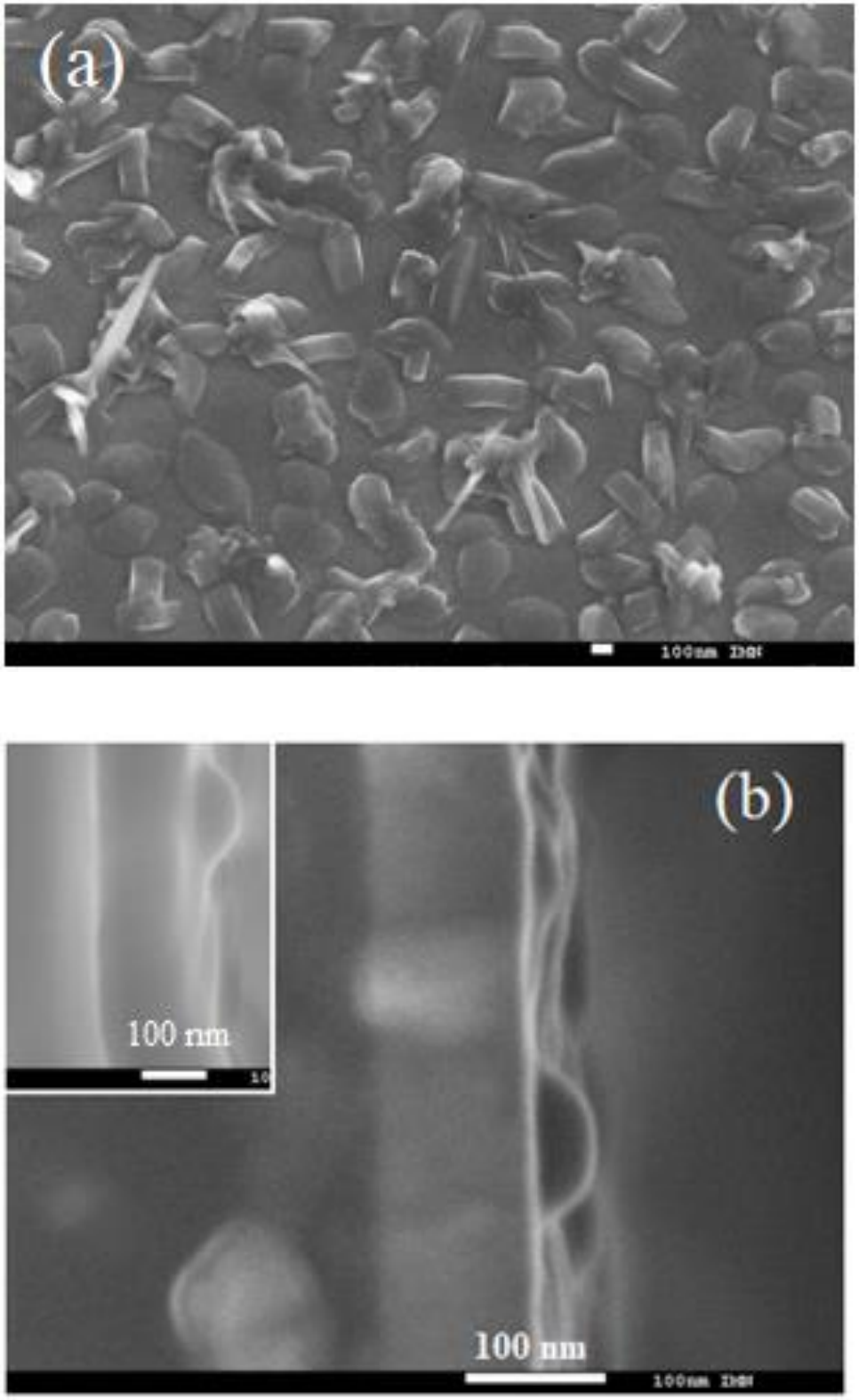

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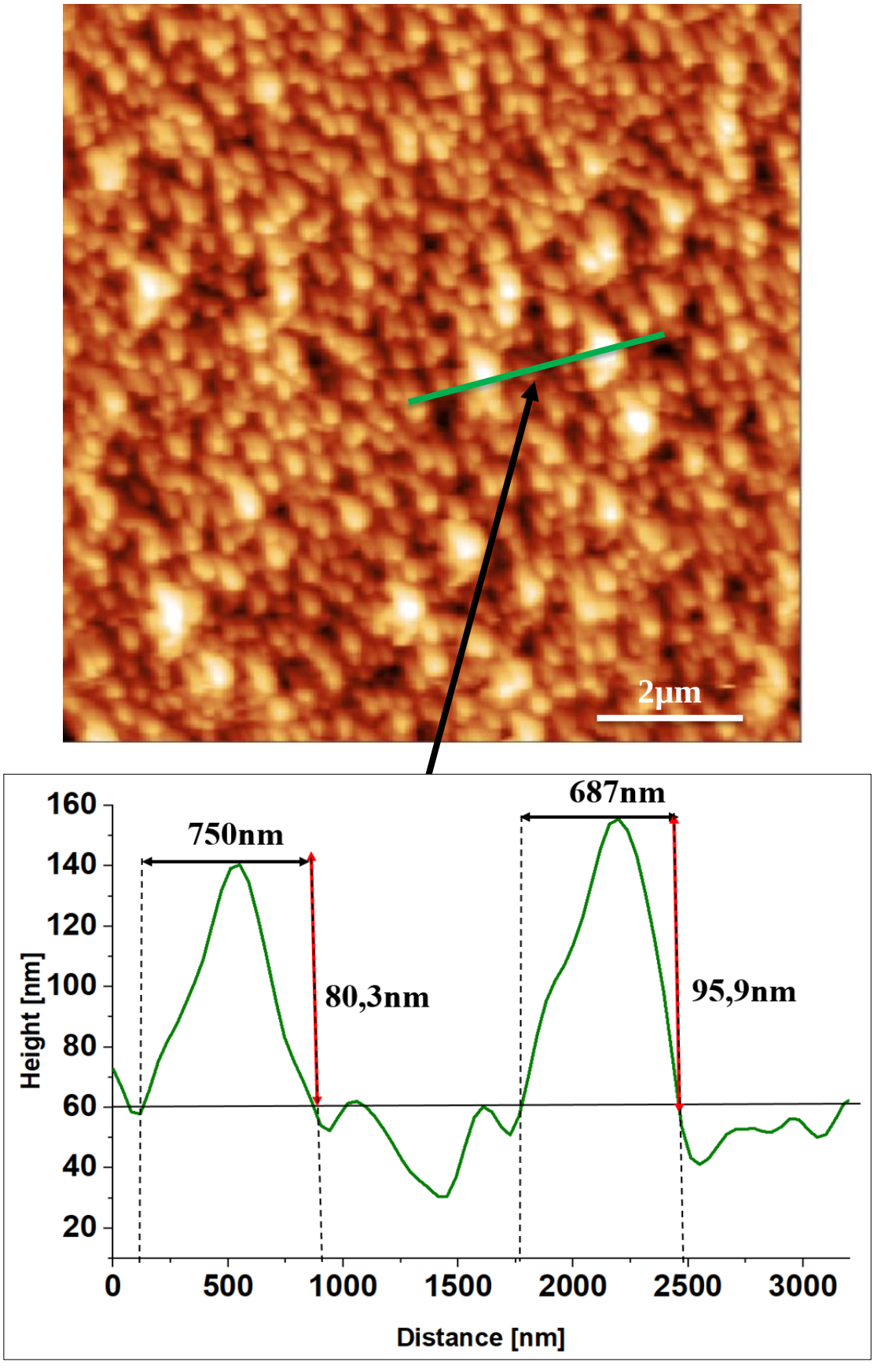

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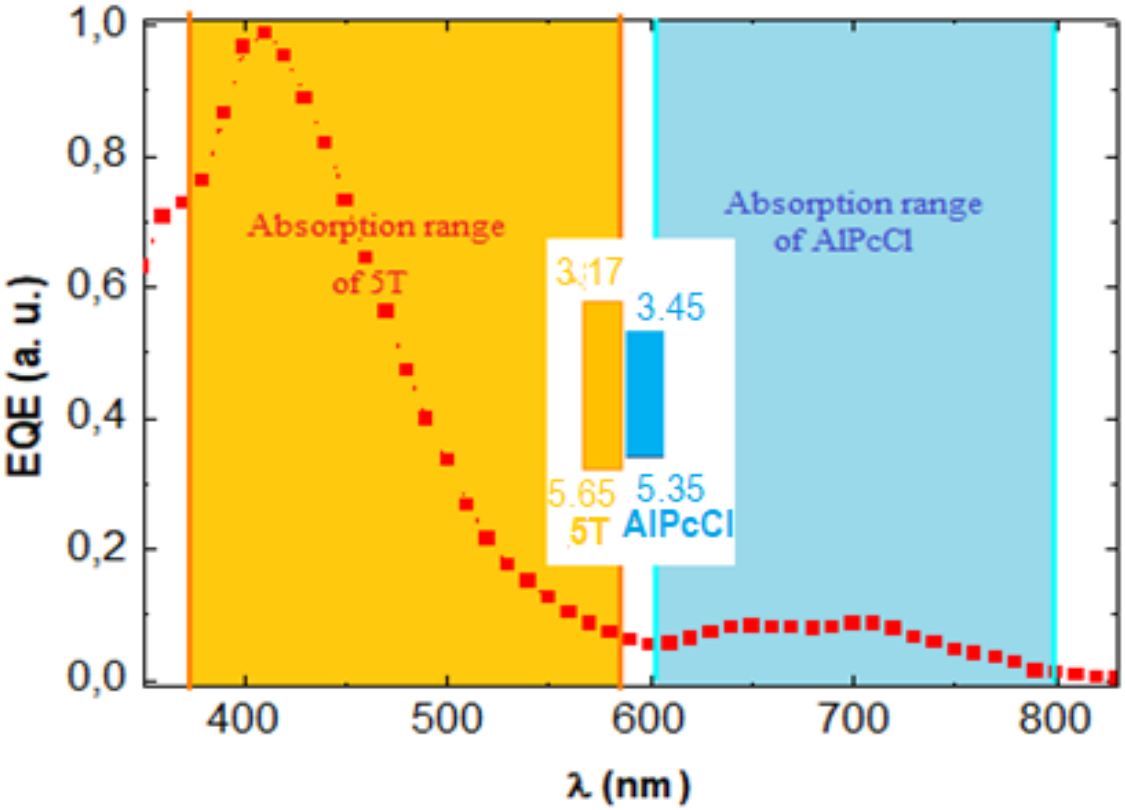

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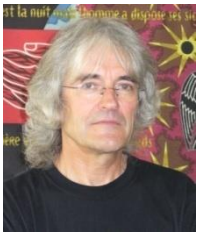

Jean Christian Bernède, Senior Searcher,

Thèse d'Etat, Université de Nantes, France

After working on the thin layer structures of chalcogenides presenting so-called "Ovshinsky" commutations, he turned to the study of photovoltaic cells in thin layer. Firstly, inorganic cells essentially based on $CuInGaSe_2$ (CIGS). Later, he turned to organic electroluminescent diodes (OLED) and organic photovoltaic cells (OPV Cells). He was particularly interested in the interfaces electrode/organic material. Subsequently he extended his field of investigation to the transparent conductive layers alternatives to the ITO.

Author Photo

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Table 1. Parameters of the OPV family using CuPc, SubPc and C_{60}.

Active layer (thickness-nm)	Voc (V)	Jsc (mA cm^{-2})	FF (%)	η (%)
CuPc (30)/C_{60} (40)	0.50	4.68	60	1.42
SubPc (20)/C_{60} (40)	1.00	5.33	50	2.63
CuPc (30)/SubPc (15)	0.74	0.33	41	0.09
CuPc (30)/SubPc (15)[a)]	0.75	0.48	33	0.12
CuPc (30)/SubPc (15)/C_{60} (40)	0.58	5.54	55	1.77

[a)] HTL MoO_3/CuI and not MoO_3 alone.

Table 2. Diverse parameters of the organic layers used.

Molecule	μ_{e^-} ($cm^2\ v^{-1}\ s^{-1}$)	μ_h ($cm^2\ v^{-1}\ s^{-1}$)	RMS[b] (nm)	O. D. Absorption range (nm)	PL[c] Emission range (nm)
Pentacene	-	$7.5\ 10^{-3}$	4-7	500-700	660-700 ; 730-950
CuPc	$5.8\ 10^{-3}$	$1.1\ 10^{-3}$ [a]	3	550-800 ; 300-400	1075-1175
M8-1	$1.6\ 10^{-9}$	$6\ 10^{-7}$	3.5	530-580 ; 300-530	525-750
BSTV	-	$9.5\ 10^{-6}$	1.55	350-500	500-650
5T	-	$1.7\ 10^{-4}$	18	350-600	475-625
AlPcCl	$6.9\ 10^{-4}$	$4\ 10^{-5}$	6	800-600 ; 400-300	660-720 ; (770)
DBP	$1.6\ 10^{-4}$	210^{-4}	-	500-650 ; 300-450	-
SubPc	$8\ 10^{-3}$	$1.7\ 10^{-5}$	-	500-650 ; 430-300	-
MD2	$1.5\text{-}3\ 10^{-7}$	$1\ 10^{-5}$	-	500-300	-

[a] When deposited onto CuI the hole mobility of CuPc is $2\ 10^{-3}\ cm^2v^{-1}s^{-1}$

[b] Values measured for the organic bottom layer D.

[c] From luminescence spectra shown in Fig. S7 or extracted from the bibliography: 5T [35], Pentacene [38], AlPcCl [39], and CuPc [40].

Table 3. Parameters of the OPV family using CuPc, DBP and C_{60}.

Active layer (thickness-nm)	Voc (V)	Jsc (mA cm^{-2})	FF (%)	η (%)
DBP (20)/C_{60} (40)	0.76	3.01	38	0.88
CuPc (30)/C_{60} (40)	0.50	4.68	60	1.42
CuPc (30)/DBP (15)	0.24	1.02	25	0.06
CuPc (30)/DBP (10)/C_{60} (40)	0.30	1.59	40	0.20