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On the problem of open circuit voltage in metal phthalocyanine/C60 organic solar cells

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ABSTRACT

The open circuit voltage (V_{OC}) plays a crucial role in determining the efficiency of organic solar cells. Models of the V_{OC} based on (i) the energy difference between the LUMO of the acceptor material and the HOMO of the donor material at the heterointerface and (ii) chemical potential gradient which depends on the carrier mobility in a bilayer cell, are inadequate to understand the exact origin of the V_{OC}. In this review article, the V_{OC} in various planar and non-planar metal phthalocyanine/C60 solar cells are analyzed. These results are compared in CuPc/C60 and SubPc/C60 solar cells as a representative case of the planar and non-planar metal phthalocyanine/C60 solar cells, respectively. Regardless of unfavorable characteristics of SubPc films, the V_{OC} value of 0.92 to 0.98V in SubPc (13 nm)/C60 (33 – 32.5 nm) compared to 0.44 to 0.49V in CuPc (20 – 40 nm)/C60 (40 – 30 nm) solar cells was noticed. It is suggested that the structure, morphology, and absorption properties of the evaporated film of the donor materials and the efficient separation of charges at the donor/acceptor interface in bilayer planar and non-planar metal phthalocyanine/C60 solar cells are also imperative in determining the V_{OC}. Copyright © 2011 VBRI press.

Keywords: Organic solar cells; metal phthalocynaine/C60 structure; open circuit voltage (V_{OC}).

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Contents

1. Introduction

In recent years, new approaches for the development of sustainable and clean energy sources have acquired the center stage. The solar energy offers a great potential due to its unlimited and natural source of energy. Solar cells which absorb solar photon and convert them into electrical energy are composed of semiconducting materials with electrical contacts and protective layers. Polycrystalline Si is the most commonly used semiconductor, however others include single-crystal Si, the thin film materials-amorphous Si, CdTe, and CuIn(Ga)Se_2 [**1, 2**]. The first inorganic solar cell based on Si and developed at Bell Laboratories in 1954 had an efficiency of 6% [**3**]. Over the years the efficiency has been improved to 24% for crystalline Si solar cells in the laboratory [**4**].

Solar cells based on *organic semiconducting materials* have the potential to compete with more mature crystalline and thin film based Si photovoltaic technologies in the future, primarily due to the significantly reduced manufacturing costs and facile processing [**5**]. The roll-to-roll manufacturing process involving the low temperature of deposition or printing techniques is expected to reduce the cost and boost their commercial attractiveness. In addition, the favorable attributes of organic solar cells are flexibility, light weight, and not fragile which makes them particularly suitable for transportation and portable electronics applications. In the early 1960s, the conducting properties of many common dyes such as methylene blue were discovered [**6**] and later these dyes among the first organic materials were used to demonstrate the photovoltaic effect [**7**]. In the 1980s, the first polymers solar cells based on dyes or polymers yielded limited power conversion efficiencies, typically below 0.1% [**8**]. In 1986, the first bilayer solar cell consisting of two conjugated small molecules organic layers was reported by Tang [**9**]. The power conversion efficiency of about 1% was achieved in this bilayer solar cell. Organic photovoltaics (OPV) based on the polymer and the small molecule materials with donor-acceptor active layer have become a highly popular research topic during the last 10 years [**10 – 13**].

The two main categories of organic solar cells, the polymer bulk heterojuction and the small molecule heterojunction, are displayed in **Fig. 1**. The bulk heterojunction solar cell is composed of the phase separated blends of electron-donating semiconducting polymer and the electron withdrawing fullerene derivatives as active layers [**10**], while the small molecule heterojunction solar cells usually employ the metal phthalocynaines as a donor and the fullerene C60 as an acceptor [**14**].

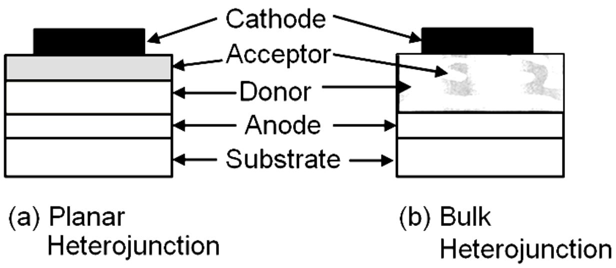

Fig. 1. Schematics of two main configurations of organic solar cells.

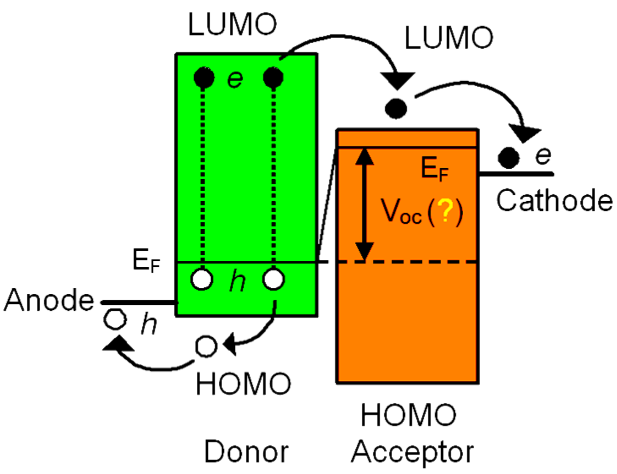

Fig. 2. Energy levels of D-A heterojunction organic solar cell.

A single donor-acceptor (DA) heterojunction organic thin film solar cell consists of two layers of semiconducting materials sandwiched between a transparent and reflecting electrode [**9**]. **Fig. 2** shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the organic molecules. With the absorption of the solar photon by the organic semiconducting thin film, the localized Frenkel or charge transfer excitons are formed [**15, 16**]. These excitons travel to the DA interface via exciton diffusion (see **Fig. 2**). Once an exciton reaches the interface between donor and acceptor, it will (i) dissociate to a bound polaron pair (ii) generate free polarons (i.e. free electron in the acceptor and free hole in the donor) after overcoming the barrier of polaron pair binding energy, (iii) free electrons and holes charge carriers become mobile and transport in the $LUMO_A$ of the acceptor and the $HOMO_D$ of the donor materials, respectively. The dissociation of photogenerated excitons into free charges is often a critical process, limiting the overall efficiency of OPV devices [**12**].

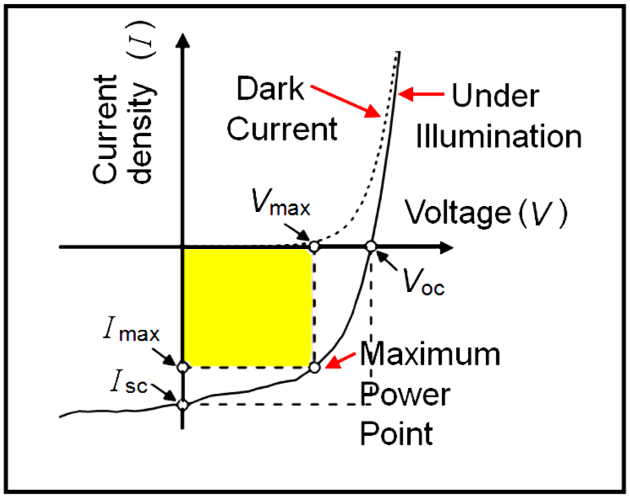

Fig. 3. Current-Voltage characteristic of a typical bilayer solar cell in the dark (dashed line) and in the light (solid line).

The key factors in determining the performance of a solar cell are to measure the current density as a function of the voltage across the cell and determine the power conversion efficiency, η, under the conditions of illumination equivalent to the sunlight. The current-voltage (*I-V*) characteristic of a typical solar cell is shown in **Fig. 3**. As depicted in **Fig. 3**, the *I-V* characteristic under the illumination conditions shifts downward by an amount of -I_{SC} when the applied voltage V = 0 (short circuit current) as compared with the dark current characteristic. This downward shift in the *I-V* characteristic causes the voltage V to have a nonzero value, V_{OC} (open circuit voltage) when the current in the device is zero. The most important parameters to be extracted from the *I-V* characteristic are the short-circuit current (I_{SC}), the open circuit voltage (V_{OC}) and the fill factor, FF.

The fill factor is given by the ratio of maximum power (yellow rectangle in **Fig. 3**) to the product of open circuit voltage and short circuit current (white rectangle). The FF accounts for all deviations from the ideality due to losses. The electrical power produced by the solar cell is:

$$P_{out} = FF \times J_{SC} \times V_{OC}, \text{ ----------- } \mathbf{(1)}$$

where J_{SC} is a short circuit current density. A larger product, $J_{SC} \times V_{OC}$ at the maximum power point, implies the higher output power from the device. The power conversion efficiency is the ratio of the maximum output power, P_{out} to the incident radiant power, P_{inc}:

$\eta = P_{out}/P_{in} = FF \times J_{SC} \times V_{OC}/P_{inc}$. ----------- (**2**)

Recently, Institute of Applied Photo-Physics, Technical University of Dresden and Heliatek GmbH, Dresden has achieved an efficiency of 7.7% over an active area of 1.1 cm² in polymer-fullerene bulk heterojunction solar cells as a part of a joint research project [**17**]. In order to adopt the organic solar cells for wide-spread applications, a power conversion efficiency of 10% is desirable. Dominating opinions support the prediction of commercializing a device with 10% level efficiency by 2015. Although the commercialization is expected to be realized in the near future, the wide-spread acceptance of organic solar cells crucially depends on the efficiency of power conversion, sufficient lifetime, and cost.

Indeed, the open circuit voltage is a critical factor in determining the efficiency of organic solar cells as displayed in equation (2) and is still an open issue. To date, no review report on the V_{OC} studies in small molecule organic solar cells is available. Therefore, the present investigation is focused on the analysis of the V_{OC} in small molecule planar and non-planar metal phthalocyanine/C60 heterjunction solar cells deposited by the vacuum processing. It is proposed that the structure, morphology, and absorption properties of the evaporated film of the donor materials and the efficient separation of charges at the donor/acceptor interface in bilayer planar and non-planar metal phthalocyanine/C60 solar cells are also crucial in determining the V_{OC} value.

2. Open-circuit voltage models

The power conversion efficiency in organic solar cells could be improved by raising the value of V_{OC} and increasing the short circuit current, I_{SC}. It is argued that the V_{OC} of the heterojunction cell is equal to the difference between the Fermi levels of the donor and acceptor organic materials. However, the exact origin and factor limiting its value are still debated. Earlier, the V_{OC} was determined by considering the work function difference between the anode and cathode contact electrodes [**18, 19**]. However, Brabec et al. have shown that the V_{OC} is independent of the choice of cathode [**20**]. Several recent reports on planer heterojunction [**21 – 23**] as well as bulk heterojunction [**24 – 26**] solar cells have shown that the V_{OC} is strongly dependent on the difference between the HOMO or Ionization potential of the donor and the LUMO or electron affinity of the acceptor materials. Some studies suggested that the V_{OC} of organic solar cells varies linearly with the LUMO level of the acceptor material [**20, 27**] and HOMO of the donor material [**23, 25, 28**]. Recently, Li et al. have shown the enhancement of open circuit voltage due to the reduced dark current [**29**].

Gregg and Hanna [**16**] argued that the separation of charge carriers across the DA interface gives rise to a powerful chemical potential gradient that promotes the photovoltaic effect. The chemical potential gradient is equivalent to the carrier density gradient and depends on the carrier mobility. Based on this idea, the open circuit voltage V_{OC} is dependent on the charge carrier mobility.

According to Chenyns Model [**30**], the analytical expression for the V_{OC} of organic planar heterojunction solar cells depends on the (i) free charge carriers at the interface between donor and acceptor, (ii) injection barrier voltage at cathode and anode electrodes, and (iii) does not depend on the work function of the cathode. For a model of moving one electron and one hole from the donor and acceptor interface toward the electrodes, the V_{OC} is:

$V_{OC} = E_L^A - E_H^D + (kT/q) \ln (p_i/N_D) + (kT/q) \ln (n_i/N_A) + \Delta_{low} (F_{c,D}) + \Delta_{low} (F_{c,A})$ ----------- (**3**)

where $E_L^A - E_H^D = |HOMO_D| - |LUMO_A|$ = energy difference between the HOMO of the donor and LUMO of the acceptor materials, k = Boltzmann constant, T= Temperature in K, q is the electronic charge, p_i = hole carrier concentration at the interface which depends on the incident light intensity, n_i = electron carrier concentration at the interface, N_D = effective density of states of the donor, N_A = effective density of states of the acceptor, $\Delta_{low} (F_{c,D})$ = effective reduction in the barrier on the donor contact side, and $\Delta_{low} (F_{c,A})$ = effective reduction in the barrier on the acceptor contact side. The V_{OC} is limited by the effective energy offsets between the HOMO of the donor and the LUMO of the acceptor and is always lower.

Using Koopman's theorem with the single particle energy, Riede et al. [**31**] arrived the open circuit voltage of optimized solar cells as:

$q V_{OC} = E_L^A - E_H^D - (0.3 \text{ to } 0.7)$ eV. ----------- (**4**)

Wurfel proposed the concept of quazi Fermi levels for holes and electrons in donor –acceptor materials to determine the V_{OC} [32, 33]. These quazi Fermi levels pick up at the metal contacts to avoid losses. The V_{OC} is determined by the difference of the quazi Fermi levels at the contacts.

Using this concept of quazi Fermi levels, Hains et al. has obtained a simple and more realistic expression for V_{OC} as [**34**]

$q V_{OC} = E_L^A - E_H^D - 2kT \ln(100) = E_L^A - E_H^D - 0.24$ eV ----------- (**5**)

These results suggest that the V_{OC} is dependent on the energy difference between the LUMO of the acceptor and the HOMO of the donor materials at the heterointerface in a bilayer cell and/or is controlled by a chemical potential gradient which depends on the carrier mobility.

3. Metal phthalocyanines

The synthesis of phthalocyanine was discovered by accident in 1907 [**35**]. Braun and Tcherniac, at the South Metropolitan Gas Company in London, while examining the properties of a cyanobenz amide which they made from the reaction of phthalamide and acetic anhydride, found a trace amount of a blue substance after heating o-cyanobenzamide, cooling, dissolving in alcohol, and filtration. This substance undoubtedly was a phthalocyanine. Metal phthalocyanines have a wide range of applications as colorants for plastics, inks, fabrics, and automobile paints due to their chemical and thermal stability, nonlinear optical behavior, high conductivity [**36 – 38**], and economical and easy to be synthesized. In recent years, metal phthalocyanines have attracted much attention owing to applications in photovoltaics, electrophotography, and chemical sensors [**39 – 48**].

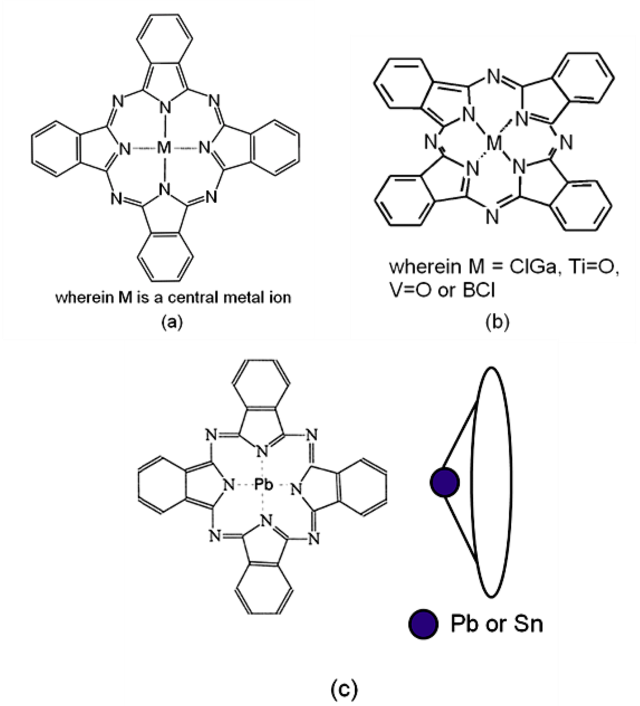

Fig. 4. The molecular structure of (**a**) planar metal phthalocyanine, (**b**) nonplanar phthalocyanine with AlCl or V=O, and (**c**) nonplanar phthalocyanines such as lead phthalocyanine (PbPc) top view (left) and side view (right).

Phthalocyanines, classified as a p-type of semiconductor, with different electronic and optical properties can be synthesized by varying the centered metal atom in the phthalocynaine ring [**49**]. **Fig. 4(a)** show the molecular structure of the planar metal phthalocyanine such as CuPc or ZnPc, while the molecular structures of non-planar metal phthalocyanines such as VOPc or AlClPc and SnPc or PbPc are depicted in **Fig. 4(b)** and **(c)**, respectively. Earlier, it was shown that the issue of the planarity and/or non-planarity of the divalent metal phthalocyanines was strongly related to the size of the metal ion which can be accommodated in the cavity of the phthalocyaninato(2-) ring. It has been long accepted that the metal(II) phthalocyaninato(2-) complexes are planar if the ionic radius of metal is not greater than 0.8 Å. Tetra or tri-valent phthalocynanines (TiOPc or AlClPC) have the same phthalocyanine ring with different central metal atoms inside. The photochemical and photophysical properties of these phthalocyanines depend partly on the central metal atoms [**50 – 53**].

The molecular structures of the evaporated planar and non-planar metal phthalocyanines are displayed in **Fig. 5**. The crystalline planar metal phthalocyanine has a herringbone type structure and molecules crystallize in the solid state as a close packed adlayer with a high molecular packing density due to the strong molecule-molecule interaction [**54**]. The planar molecules arrange with their planes parallel to the substrate surface. On the other hand, the non-planar metal phthalocyanines have a cone-shaped (or pyramid type) structures as seen in **Fig. 5(b)** and molecules show a unique orientation with the central atom looking “up” from the substrate surface or both possible orientations “up” and “down” present on the substrate surface [**55**]. The non-planar metal phthalocyanines lead to a loosely packed adlayer with a low molecular packing density due to a weak molecule-molecule interaction. As a result, a high quality film in planar phthalocyanines is formed, while the crystalline quality film of non-planar phthalocyanine is relatively poor due to an irregular arrangement of the deposited molecules on the glass substrates [**56**]. Depending on the nature of the central metal atom, metal phthalocyanines based solar cells exhibit markedly different device performance due to different optimal layer thickness, fluorescence spectra, diffusion length of photoelectrically generated exciton [**57**].

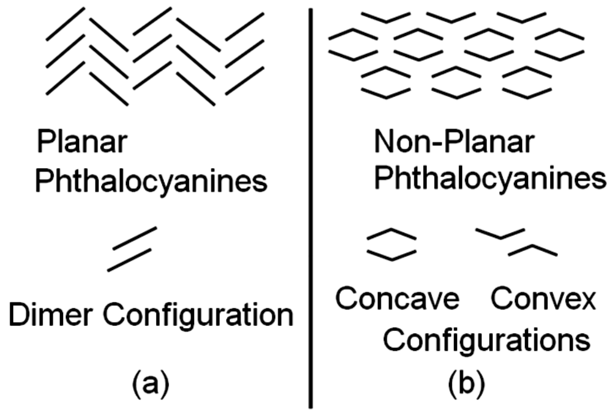

Fig. 5. Crystal structure of (**a**) planar metal phthalocyanine (Herringbone type) and (**b**) non-planar metal phthalocyanine (cone type).

4. Analysis of open circuit voltage, V_{OC}

The V_{OC} values in planar and non-planar metal phthalocyanine/C60 solar cells are compared for the one sun standard at room temperature. Although the V_{OC} is very different for different devices and simply hard to compare as it depends on different contacts, and C60 and donor thicknesses, but the analyzed results give confident relative trends.

4.1. Planar metal phthalocyanine/C60 solar cells

The first organic solar cell with a metal phthalocyanine (MgPc) sandwiched between two glass electrodes was reported in 1958 with a photovoltage of 200 mV [**58**]. Later in 1964, the photovoltaic voltage was measured in copper phthalocyanines placed between two different metal electrodes [**59**]. In 1979, the first bi-layer OPV device consisting of the copper phthalocyanine and the perylene derivative with a photo conversion efficiency of 1% was demonstrated [**60**]. Subsequently, the planar metal

Table 1. Open circuit voltage $V_{OC,expt}$ in various planar metal phthalocyanine/C60 solar cells with one sun standard, AM 1.5G.

Sl. No.	**Structure**	**$E_L^A - E_H^D$ diff. (eV) Expt.**	**$V_{OC,expt}$ (V)**	**η^* (%)**	**Ref.**	**$V_{OC,est.}$ (V) using Eq.(5)**	**$\Delta = \lvert V_{OC,est.} - V_{OC,expt} \rvert$ (V)**
1	CuPc/C60	0.70	0.45	4.2 (4-12 sun)	**[61]**	0.46	0.01
2	CuPc(20)/C60(40)	0.30	0.44	1.02	**[62]**		
3	CuPc (40)/C60(40)	0.70	0.52	1.42	**[57]**	0.46	0.06
4	CuPc/C60	0.70	0.45		**[63]**	0.46	0.01
5	CuPc(40)/C60(30)	0.30	0.49	0.33	**[48]**		
6	CoPc(40)/C60(30)	0.43	0.39	0.17	**[48]**	0.19	0.20
7	NiPc (20)/C60(40)	0.66	0.44	0.64	**[57]**	0.42	0.02
8	NiPc(40)/C60(30)	0.18	0.40	0.21	**[48]**		
9.	ZnPc (40)/C60(40)	0.78	0.55	1.77	**[57]**	0.54	0.01
10	ZnPc(40)/C60(30)	0.25	0.52	0.33	**[48]**		
11	PEDOT:PSS/ZnPc(25) /C60(25)	0.60	0.44	3.6	**[64]**	0.36	0.08
12.	H2Pc(40)/C60(30)	0.36	0.51	0.34	**[48]**	0.12	0.39
13	FePc(40)/C60(30)	0.28	0.13	0.14	**[48]**	0.04	0.08
14	FePc (40)/C60(40)	0.50	0.16	0.07	**[57]**	0.26	0.10

**power conversion efficiency*

Table 2. Open circuit voltage $V_{OC,expt}$ in various non-planar metal phthalocyanine/C60 solar cells with one sun standard, AM 1.5G.

Sl. No.	**Structure**	**$E_L^A - E_H^D$ diff. (eV) (Expt.)**	**$V_{OC,expt}$ (V)**	**η^* (%)**	**Ref.**	**$V_{OC,est.}$ (V) using Eq.(5)**	**$\Delta = \lvert V_{OC,est.} - V_{OC,expt} \rvert$ (V)**
1	AlPcCl(20)/C60(40)	0.80	0.84	1.86	**[62]**	0.56	0.28
2	AlPcCl(13)/C60(40)	0.90	0.64	1.00	**[66]**	0.66	0.02
3	ClAlPc(20)/C60(40)	0.90	0.68	2.10	**[67]**	0.66	0.02
4	SubPc(13)/C60(33)	1.10	0.92	3.00	**[66]**	0.86	0.06
5	SubPc(13)/C60(32.5)	1.10	0.98	2.10	**[68]**	0.86	0.12
6	PbPc(20)/C60(50)	0.70	0.46	1.95	**[69**	0.46	0.00
7	TiOPc(20)/C60 (40)	1.40	0.59(I) 0.57(II)	2.60 4.20	**[70]**	1.16	0.57
8	TiOPc/C60	1.10	0.62	1.60	**[63]**	0.86	0.24
9	SnPc(10)/C60(40)	0.70	0.16	2.10	**[29]**	0.46	0.30

**power conversion efficiency*

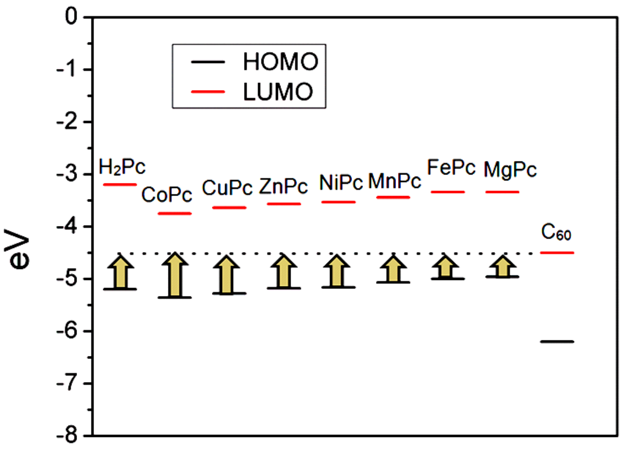

Fig. 6. HOMO and LUMO energy levels of Donor planar metal phthalocyanines and acceptor C60.

phathalocyanine/C60 bilayer structure solar cells with high efficiency have been demonstrated by several researchers as illustrated in **Table 1** [**48, 61 – 64**]. The HOMO and LUMO energies of planar metal phthalocynines and C60 are displayed in **Fig. 6**. The obtained $V_{OC,expt.}$ values in these bilayer structures are much smaller than the HOMO-LUMO gap of the donor metal phthalocynines as well as the ($E_L^A - E_H^D$) energy gap. Not all the absorbed energy is converted in to the electrical energy. **Table 1** also shows the estimated value of the V_{OC} obtained using the equation (5). The experimentally measured value of ($E_L^A - E_H^D$) energy difference was used to estimate the V_{OC}. The absolute values of the difference between the $V_{OC,expt.}$ and $V_{OC,est.}$ (Δ) are determined and listed in the **Table 1**. Results show that the ($E_L^A - E_H^D$) energy difference and $V_{OC,expt.}$ values in CuPc/C60 configuration are in the range from 0.3 to 0.7 eV and 0.44 to 0.49 V, respectively. In some metal phthalocyanine/C60 structures, the Δ value differs by the significant amount as depicted in **Table 1**. Since almost consistent results of $V_{OC,expt.}$ are noticed in CuPc/C60 configuration, these are used for comparison with the V_{OC} values in non-planar solar cells. Furthermore, it is interesting to investigate whether other factors are also influencing the V_{OC} value in bilayer solar cells.

A very recent comparative study on the performances of CuPc based solar cells indicates the V_{OC} value of 0.546V in CuPc/C60 solar cells (where $E_H^D - E_A^L = 5.2 - 4.5 = 0.7$ eV) and 0.612V in CuPc/C70 solar cells (where $E_H^D - E_A^L = 5.2 - 5.0 = 0.2$ eV) [**65**]. Actually, a low value of V_{OC} is expected in CuPc/C70 solar cells due to the lower ($E_H^D - E_A^L$) energy difference as compared to CuPc/C60 solar cells. To our surprise, a high value of V_{OC} is reported in CuPc/C70 solar cells. It seems that electrons and holes charge carriers are efficiently separated at the DA interface in CuPc/C70 solar cells, regardless of ($E_H^D - E_A^L$) energy difference. These results demonstrate that the V_{OC} is not explicitly govern only by the ($E_H^D - E_A^L$) energy difference. Therefore, it is evident from these results that (i) the higher value of V_{OC} is exhibited with the higher ($E_L^A - E_H^D$) energy difference, (ii) the V_{OC} is lower than the ($E_L^A - E_H^D$) energy difference, (iii) equation (5) is not sufficient to estimate the V_{OC}, and (iv) other factors such as absorption properties and morphologies of donor film, charge separation at DA interface, are also influencing the V_{OC} value.

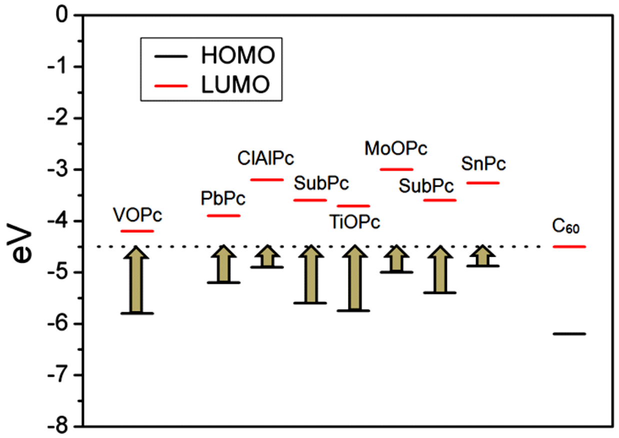

Fig. 7. HOMO and LUMO energy levels of Donor non-planar metal phthalocyanines and acceptor C60.

4.2. Non-planar metal phthalocyanine/C60 solar cells

Fig. 7 shows the HOMO and the LUMO energies of various donor non-planar metal phthalocynines and acceptor C60 materials. The experimental values of V_{OC} and ($E_L^A - E_H^D$) energy difference and the estimated values of the V_{OC} using equation (5) are presented in **Table 2** [**29, 62, 63, 66 – 70**]. As discussed earlier, (i) the large value of $V_{OC,expt.}$ is exhibited with the higher ($E_L^A - E_H^D$) energy difference, (ii) the $V_{OC,expt.}$ is lower than the ($E_L^A - E_H^D$) energy difference, and (iii) no specific relationship between the V_{OC} the ($E_L^A - E_H^D$) is noticed. Results on the V_{OC} in non-planar metal phtalocyanine/C60 solar cell structures, presented here, confirm the earlier argument of V_{OC} dependence on multiple factors as discussed in section 4.1 for planar phthalocyane/C60 configuration. Since the V_{OC} results are more consistent in SubPc/C60 configuration, it is selected as a representative of the non-planar metal phthalocyanine/C60 solar cell for the further analysis.

5. Discussion

The models as discussed in section 2 [**16, 30, 31, 34**] are inadequate to understand the exact origin of the V_{OC}. Although no specific relation between the V_{OC} and the ($E_L^A - E_H^D$) is noticed (see **Fig. 8**), the $V_{OC,expt.}$ observed in various planar and non-planar metal phthalocyanine/C60 solar cells offers imperative fact to understand its association with the ($E_L^A - E_H^D$) energy difference and other factors, if any. The values of the V_{OC} in all configurations are small compared to the HOMO-LUMO donor-acceptor energy gap. Further, it is evident from **Fig. 8** that the V_{OC} value is small in planar metal phthalocyanine/C60 compared to the non-planar metal phthalocyanine/C60 solar cells. By comparing the results in planar and non-planar solar cells, the 0.7 eV and 0.45 V values of ($E_A^L - E_H^D$) and V_{OC} in the CuPc/C60, while 1.1 eV and 0.98 V in SubPc/C60 solar cells were noticed, respectively.

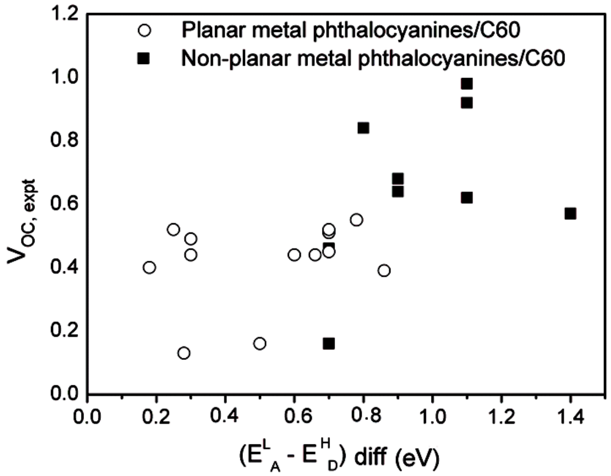

Fig. 8. Variation of $V_{OC,expt}$ with the ($E_A^L - E_H^D$) energy diff. in various metal phthalocyanine/C60 bilayer solar cells.

Indeed, the better value of V_{OC} in SubPc/C60 as compared to CuPc/C60 solar cells is observed. These results may be explained as follows. The non-planar SubPc organic material is characterized by (i) the hole injection/collection barrier of 0.8 eV ($HOMO_D - \phi_{ITO} = (5.6 - 4.8)$ eV), (ii) the short exciton diffusion length of ~ 8.0± 0.3 nm in amorphous film [**71**]. However, Gommans et al. reported the long exicton diffusion length of 28 nm [**72**], and (iii) the low molecular packing density [**55**] in SubPc films. It seems that the charge carrier mobility, exciton diffusion length, and packing density of donor organic materials thin films are definitely playing important roles in achieving the high performance of bilayer solar cells, including the V_{OC} value. Earlier, Tsuzuki et al. reported that the solar cell fabricated using the crystalline α-TiOPc film exhibits much higher conversion efficiency than the devices fabricated using amorphous TiOPc films [**73**]. Very recently, Cho et al. found that the SubPc film shows a significant disorder compared to the CuPc and ClAlPc films [**74**]. The variation in (E_A^L – E_H^D) energy difference with the orientation of ClAlPc molecules relative to the ITO substrate was also observed. Since the SubPc molecules on ITO substrate forms disordered film, a much thin layer of SubPC may be required to achieve the optimal performance of solar cells. Earlier, Gommans et al. had reported the molecular disorder of SubPc on ITO substrate on the basis of microscopy studies [**75**]. Really, the SubPc has inferior attributes as compared to the CuPc organic films. Regardless of unfavorable characteristics of SubPc films, the high value of the V_{OC} (0.92 – 0.98 V) in SubPc(13 nm)/C60(33 – 32.5 nm) compared to the 0.44 – 0.49V in CuPc (20 – 40 nm)/C60 (40 – 30 nm) solar cells was noticed. This difference may be attributed to the film morphologies of the planar and non-planar metal phthalocyanines and charge separation abilities at the DA interface, in addition to (E_A^L – E_H^D) energy difference.

6. Conclusion

To date, two models of V_{OC} based on (i) the energy difference between the LUMO of the acceptor-like material and the HOMO of the donor-like material at the heterointerface in a bilayer cell and (ii) the chemical potential gradient which depends on the carrier mobility, exist. The V_{OC} does not reflect the total energy of the photons absorbed and that some energy must be lost during the power conversion process. The maximum value of V_{OC} could be equal to the (E_A^L – E_H^D) energy gap. However, a very recent study on the performances of CuPc/C_{60} and CuPc/C_{70} solar cells indicates that the V_{OC} is not explicitly govern only by the (E_H^D – E_A^L) energy difference. In conclusion, the results analyzed in this review article indicate that the V_{OC} is also significantly dependent on the structure, morphology, strength and width of the absorption spectrum of the evaporated film of the donor materials and the efficient separation of charges at the donor/acceptor interface in bilayer planar and non-planar metal phthalocyanine/C60 solar cells.

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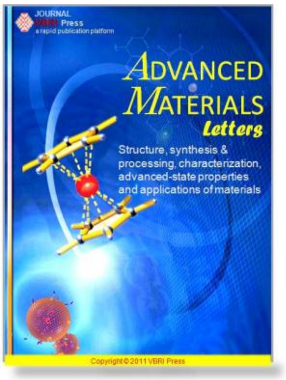
8. Abbreviations

V_{OC} open circuit voltage, **OPV** Organic photovoltaics, **DA** donor-acceptor, **HOMO** highest occupied molecular orbital, **LUMO** lowest unoccupied molecular orbital, **$LUMO_A$** LUMO of the acceptor material, **$HOMO_D$** HOMO of the donor material, **I_{SC}** short-circuit current, **FF** fill factor, **(E_L^A – E_H^D)** HOMO-LUMO energy difference of donor and acceptor materials.

References

1. Rogol, M.; Doi, S.; Wilkinson, A. "*Sun Screen: Solar Power Sector Outlook*" CLSA Asia Pacific Market **2004**, website: http://www.sunenergy.com.au/pdf/CLSA1.pdf
2. Shah, A. *Thin-Film Silicon Solar Cells*, EPFL Press, Switzerland **2010.**
3. Chapin, D. M.; Fuller, C. S.; Pearson, G. L. *J. Appl. Phys.* **1954**, *25*, 676. **DOI:** 10.1063/1.1721711
4. Green, M.A.; Emery, K.; Igari, S.; Warta, W. *Prog. Photovolt. Res. Appl.* **2003**, *11*, 347. **DOI:** 10.1002/pip.499
5. Spanggaard, H.; Krebs, F.C. *Solar Energy Materials & Solar Cells* **2004**, *83*, 125. **DOI:** 10.1016/j.solmat.2004.02.021
6. Bube, R.H. *Photoconductivity of Solids*, Wiley, New York, **1960**. pp 169.
7. Chamberlain, G. A. *Solar Cells*. **1983**, *8*, 47. **DOI:** 10.1016/0379-6787(83)90039-X
8. Kanicki, J.; Skotheim, T. A. *Handbook of Conducting Polymers*, *Vol.* ***1*****,** Marcel Dekker, New York, **1985**.
9. Tang, C. W. *Appl. Phys. Lett*. **1986**, *48*, 183. **DOI:** 10.1063/1.96937
10. Yu, G.; Gao, J.; Hummelen, J.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. **DOI:** 10.1126/science.270.5243.1789
11. Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature (London)* **1995**, *376*, 498. **DOI:** 10.1038/376498a0
12. Peumans, P.; Yakimov, A.; Forrest, S. R. *J. Appl. Phys.* **2003**, *93*, 3693. **DOI:** 10.1063/1.1534621
13. Potscavage Jr, W. J.; Sharma, A.; Kippelen, B. *Accounts of Chem. Res.* **2009**, *42*, 1758. **DOI:** 10.1021/ar900139v
14. Rand, B. P.; Genoe, J.; Heremans, P.; Poortmans, J. *Prog. Photovolt.* **2007**, *15***,** 659. **DOI:** 10.1002/pip.788
15. Pope, M. *Electronic Processes in Organic Crystals (Oxford University Press, Oxford)*, **1982**.
16. Gregg, B. A. *J. Phys. Chem. B* **2003**, *107***,** 4688. **DOI:** 10.1021/jp022507x
17. Rodehau, T. *German Energy Blog*: Posted on **April 14, 2010**, website: http://www.germanenergyblog.de/?p=2402
18. Ramsdale, C. M.; Barker, J. A.; Arias, A. C.; MacKenzie, J. D.; Friend, R. H.; Greenham, N. C. *J. Appl. Phys*. **2002**, *92*, 4266. **DOI:** 10.1063/1.1506385
19. Mihailetchi, V. D.; Blom, P. W. M.; Hummelen, J. C.; Rispens, M. T. *J. Appl. Phys.* **2003**, *94***,** 6849. **DOI:** 10.1063/1.1620683
20. Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T.; Rispens, M. T.; Sanchez, L.; Hummelen, J. C. *Thin Solid Films* **2002**, *403*, 368. **DOI:** 10.1016/S0040-6090(01)01586-3
21. Kietzke, T.; Egbe, D. A. M.; Horhold, H.-H.; Neher, D. *Macromolecules* **2006**, *39***,** 4018. **DOI:** 10.1021/ma060199l
22. Rand, B. P.; Burk, D. P.; Forrest, S. R. *Phys. Rev. B* **2007**, *75***,** 115327. **DOI:** 10.1103/PhysRevB.75.115327
23. Gadisa, A.; Svensson, M.; Andersson, M. R.; Inganas, O. *Appl. Phys. Lett.* **2004**, *84***,** 1609. **DOI:** 10.1063/1.1650878
24. Deng, X.; Zheng, L.; Yang, C.; Li, Y.; Yu, G.; Gao, Y. *J. Phys. Chem. B* **2004**, *108***,** 3451. **DOI:** 10.1021/jp036649i
25. Scharber, M. C.; Muhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789. **DOI:** 10.1002/adma.200501717
26. Kooristra, F. B.; Knol, J.; Kastenberg, F.; Popescu, L. M.; Verhees, W. J. H.; Kroon, J. M.; Hummelen, J. C. *Org. Lett.* **2007**, *9*, 551. **DOI:** 10.1021/ol062666p
27. Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T.; Sanchez, L.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 374. **DOI:** 10.1002/1616-3028(200110
28. Schueppel, R.; Schmidt, K.; Uhrich, C.; Schulze, K.; Wynands, D.; Bredas, J. L.; Brier, R.; Reinold, E.; Bu, H.-B.; Baeuerle, P.; Maenning, B.; Pfeiffer, M.; Leo, K. *Phys. Rev. B* **2008**, *77*, 085311. **DOI:** 10.1103/PhysRevB.77.085311
29. Li, N.; Lassiter, B. E.; Lunt, R. R.; Wei, G.; Forrest, S. R. *Appl. Phys. Lett.* **2009**, *94*, 023307. **DOI:** 10.1063/1.3072807
30. Cheyns, D.; Poortmans, J.; Heremans, P.; Deibel, C.; Verlaak, V.; Rand, B. P.; Genoe, J. *Phys. Rev. B* **2008**, *77*, 165332. **DOI:** 10.1103/PhysRevB.77.165332

31. Riede, M.; Muller, T.; Tress, W.; Schueppel, R.; Leo, K. *Nanotechnology (IOP Publishing)* **2008**, *19,* 424001.
    DOI: 10.1088/0957-4484/19/42/424001
32. Wurfel, P. *Physics of solar cells: From Principle to new concepts*, Weinheim, Wiley-VCH, **2004**.
    DOI: 10.1002/9783527618545.ch6
33. Wurfel, P. *Photovoltaic Principles and Organic Solar Cells, Chimica* **2007**, *61*, 770.
    DOI: 10.2533/chimia.2007.770
34. Hains, A. W.; Liang, Z.; Woodhouse, M. A.; Gregg, B. A. *Molecular Semiconductors in Organic Photovoltaic Cells, Chem. Rev.* **2010.**
    DOI: 10.1021/cr9002984
35. Braun, A.; Tchernaic, J. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2709.
36. Snow, A. W.; Barger, W. R. *Phthalocyanines: Properties and Applications*, VCH Publishers, Weinhein, Germany, edited by C.C. Leznoff, A.B.P. Lever, **1989**, Chapter 5, pp 343.
37. Shirota, Y. *J. Mat. Chem.* **2000**, *10*, 1.
    DOI: 10.1039/a908130e
38. Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449.
    DOI: 10.1021/cr00017a020
39. Ioannides, A.; Dodelet, J. P. *J. Phys. Chem. B* **1997**, *101*, 5100.
    DOI: 10.1021/jp970112l
40. Pan, Y. L.; Wu, Y. J.; Chen, L. B.; Zhao, Y. Y.; Shen, Y. H.; Li, F. M.; Shen, S. Y.; Huang, D. H. *Appl. Phys.* **1998**, *A6*, 569.
    DOI: 10.1007/s003390051203
41. Winter, G.; Heckmannan, H.; Haisch, P.; Eberhardt, W.; Hanack, M.; Luer, L.; Egelhaaf, H.-J.; Oelkrug, D. *J. Am. Chem. Soc.* **1998**, *120*, 11663.
    DOI: 10.1021/ja981644y
42. Povovic, Z. D.; Iltaf Khan, M.; Atherton, S. J.; Hor, A.-M.; Goodman, J. L. *J. Phys. Chem. B* **1998**, *102*, 657.
    DOI: 10.1021/jp973188q
43. Xu, M. S.; Xu, J. B.; Tian, D. X.; Ji, Z. G.; Chem, H. Z.; Wang, M.; Que, D. L. *Thin Solid Films* **2001**, *384*, 109.
    DOI: 10.1016/S0040-6090(00)01685-0
44. Metzger, R. M. *Chem. Rev.* **2003**, *103*, 3803.
    DOI: 10.1021/cr020413d
45. Inabe, T.; Tajime, H. *Chem. Rev.* **2004**, *104*, 5503.
    DOI: 10.1021/cr030649x
46. Kong, X.-H.; Wang, M.; Lei, S.-B.; Yang, Y.-L.; Wang, C. *J. Mater.* **2006**, *16*, 4265.
    DOI: 10.1039/b609804e
47. Kao, P. C.; Chu, S.-Y.; Liu, S.-J.; You, Z. X.; Chuang, C.-A. *J. Electrochemi. Soc.* **2006**, *153*, H122.
    DOI: 10.1149/1.2189267
48. Terao, Y.; Sasabe, H.; Adachi, C. *Appl. Phys. Lett.* **2007**, *90*, 103515.
    DOI: 10.1063/1.2711525
49. Mckeown, N. B. *Phthalocyanines materials: synthesis, structure, and functions;* Cambridge University Press, Cambridge, United Kingdom, **1998**.
50. Rogers, D.; Osborn, R. S. *J. Chem. Soc. D: Chem. Commun.* **1971**, 840.
    DOI: 10.1039/C29710000840
51. Klofta, T. J.; Danziger, J.; Lee, P.; Pankow, J.; Nebesny, K. W.; Armstrong, N. R. *J. Phys. Chem.* **1987**, *91*, 5646.
    DOI: 10.1021/j100306a030
52. Saito, T.; Sisk, W.; Kobayashi, T.; Suzuki, S.; Iwayanagi, T. *J. Phys. Chem.* **1993**, *97*, 8026.
    DOI: 10.1021/j100132a036
53. Mitzuguchi, J.; Rihs, G.; Karfunkel, H. R. *J. Phys. Chem.* **1995**, *99*, 16217.
    DOI: 10.1021/j100044a004
54. Simone, J.; Andre, J. J. *Molecular Semiconductors,* Springer-Verlag, N.Y., **1985**, pp 81.
55. Gopakumar, T. G.; Lackinger, M.; Hietschold, M. *Jpn. J. Appl. Phys.* **2006**, *45*, 2268.
    DOI: 10.1143/JJAP.45.2268
56. Manaka, T.; Taguchi, K.; Ishikawa, K.; Takezoe, H. *Jpn. J. Appl. Phys.* **2000**, *39*, 4910.
    DOI: 10.1143/JJAP.39.4910
57. Bruder, I.; Schoneboom, J.; Dinnebier, R.; Ojala, A.; Schafer, S.; Sens, R.; Erk, P.; Weis, J. *Org. Electron.* **2010**, *11*, 377.
    DOI: 10.1016/j.orgel.2009.11.016
58. Kearns, D.; Calvin, M. J. *Chem. Phys.* **1958**, *29*, 950.
    DOI: 10.1063/1.1744619
59. Delacote, G. M.; Fillard, J. P.; Marco, F. *Solid State Commun.* **1964**, *2*, 373.
    DOI: 10.1016/0038-1098(64)90185-1
60. Tang, C. W. U.S. Patent 4164431, **1979**.
61. Xue, J. ; Uchida, S. ; Rand, B. P. ; Forrest, S. R. *Appl. Phys. Lett.* **2004**, *84*, 3013.
    DOI: 10.1063/1.2924771
62. Kim, D.-Y.; So, F.; Gao, Y. *Solar Energy Materials & Solar Cells* **2009**, *93*, 1688.
    DOI: 10.1016/j.solmat.2009.04.003
63. Brumbach, M.; Placencia, D.; Armstrong, N. R. *J. Phys. Chem. C* **2008**, *112*, 3142.
    DOI: 10.1021/jp0772171
64. Taima, T.; Sakai, J; Yamanari, T.; Saito, K. *Jpn. J. Appl. Phys.* **2006**, *45*, L995.
    DOI: 10.1143/JJAP.45.L995
65. Xi, X.; Li, W.; Wu, J.; Ji, J.; Shi, Z.; Li, G. *Solar Energy Mater. & Solar Cells* **2010**, *94*, 2435.
    DOI: 10.1016/j.solmat.2010.08.008
66. Gommans, H.; Aernouts, T.; Verreet, B.; Heremans, P.; Medina, A.; Claessens, C. G. Torres, T. *Adv. Funct. Mater*. **2009**, *19*, 3435.
    DOI: 10.1002/adfm.200900524
67. Bailey-Salzman, R. F.; Rand, B. P.; Forrest, S. R. *Appl. Phys. Lett.* **2007**, *91*, 013508.
    DOI: 10.1063/1.2752992
68. Mutolo, K. L.; Mayo, E. I.; Rand, B. P.; Forrest, S. R. *J. Am. Chem. Soc*. **2006**, *128*, 8108.
    DOI: 10.1021/ja0616550
69. Dai, J.; Jiang, X.; Wang, H.; Yan, D. *Appl. Phys. Lett.* **2007**, *91*, 253503.
    DOI: 10.1063/1.2824836
70. Placencia, D.; Wang, W.; Shallcross, R. C.; Netensy, K. W.; Brumbach, M. Armstrong, N. R. *Adv. Funct. Mater.* **2009**, *19*, 1913.
    DOI: 10.1002/adfm.200801723
71. Lunt, R. R.; Giebink, N. C.; Belak, A. A.; Benziger, J. B.; Forrest, S. R. *J. Appl. Phys.* **2009**, ***105***, 053711.
    DOI: 10.1063/1.3079797
72. Gommans, H.; Schols, S.; Kadashchak, A.; Hermans, P. *J. Phys. Chem. C* **2009**, *113*, 2974.
    DOI: 10.1021/jp809802q
73. Tsuzuki, T.; Kuwabara, Y.; Noma, N.; Shirota, Y.; Wills, M. R. *Jpn. J. Appl. Phys*. **1996**, *35*, L447.
    DOI: 10.1143/JJAP.35.L447
74. Cho, S. W.; Piper, L. F. J.; DeMasi, A.; Preston, A. R. H.; Smith, K. E. *J. Phys. Chem. C* **2010**, *114* (4), 1928.
    DOI: 10.1021/jp910504a
75. Gommans, H.; Cheyns, D.; Aernouts, T.; Girotto, C.; Poortmans, J.; Heremans, P. *Adv. Funct. Mater.* **2007**, *17*, 2653.
    DOI: 10.1002/adfm.200700398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