Open-circuit voltage dependency on hole-extraction layers in planar heterojunction organic solar cells

Chandramouli Kulshreshtha,[1] Jin Woo Choi,[1] Jeong-kyu Kim,[2] Woo Sik Jeon,[1] Min Chul Suh,[1,a)] Yougsup Park,[2] and Jang Hyuk Kwon[1,a)]
[1]*Department of Information Display, Kyung Hee University, Dongdaemoon-gu, Seoul 130-701, South Korea*
[2]*Department of Physics, Kyung Hee University, Dongdaemoon-gu, Seoul 130-701, South Korea*

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The open-circuit voltage (V_{oc}) dependency on hole-extraction layers (HELs) with different energy levels and mobility was investigated in a single stack heterojunction subphthalocyanine chloride (SubPc)/C_{60} organic solar cells. The HELs having about 0.2–0.3 eV higher highest occupied molecular orbital (HOMO) level than that of a donor material can significantly enhance the V_{oc} in SubPc/C_{60} device due to a corresponding built-in potential increase. The high mobility of HELs can also increase V_{oc} with increasing J_{sc} according to the simple diode equation. Among all HELs we utilized, *N,N,N′,N′*-tetra(biphenyl-4-yl)biphenyl-4,4′-diamine (TBBD) illustrates a largest increase in V_{oc} (from 0.90 to 1.15 V) with an improvement in efficiency compared to a reference SubPc/C_{60} device without HEL. This increase is mainly attributed to easy and rapid extraction of holes by TBBD due to its proper HOMO level and high mobility. © *2011 American Institute of Physics*. [doi:10.1063/1.3610962]

The growing demand of cost-effective and light weight solar energy technology has led to a significant improvement in power conversion efficiency (PCE) of organic solar cells (OSCs).[1,2] Especially, the increase of open-circuit voltage (V_{oc}) has been recognized as one of the most important factors to improve the performance of OSCs. On that account, there have been lots of reports which explain the decisive factors in determining the enhanced V_{oc} of OSCs (e.g., metal-organic interfaces,[3,4] methods of efficient hole extraction from the donor layer using different surface treatments of indium-tin-oxide (ITO),[5,6] insertion of buffer layer between the ITO and donor layer due to a reduction in dark saturation current[7,8]). Anyhow, those phenomena could be mainly verified by the following equation as previously reported:[9]

$$Voc = \frac{nKT}{q} \ln\left(\frac{J_{sc}}{J_{so}}\right) + \frac{\Delta E_{DA}}{2q}, \tag{1}$$

where J_{SC} is the short-circuit current, J_{SO} is the reverse saturation dark saturation current, n is ideality factor, ΔE_{DA} is the thermal activation energy for charge separation at the donor-acceptor interface. In addition to the factors associated with this equation, the V_{oc} depends linearly on the work function difference ($\Delta\Phi_{electrodes}$) between two electrodes. This built-in potential (V_{bi}) is the voltage required for flat band condition which plays a key role in diffusing the charge carriers to the electrodes. In fact, V_{oc} appears to be quite sensitive to many materials and device parameters that can alter the V_{bi} in the devices. Kumar *et al*. shows that V_{oc} increases with the increase in V_{bi} under illumination.[10] However, the V_{oc} can be raised to a maximum level corresponding to a difference of energy levels between HOMO of donor and lowest unoccupied molecular orbital (LUMO) of acceptor materials under the condition of minimized voltage losses of fabricated device. Given this, one of the possible ways to raise the V_{oc} could be an introduction of hole-extraction layers (HELs) in between ITO and donor layer. Therefore, it is highly important to choose a HEL material with the HOMO level well matched with that of donor material. The HEL is supposed to make an energetically good contact to the ITO and also extract the holes rapidly if it has high hole mobility. In addition, the high LUMO level of HELs can prevent the electron leakage by reducing the dark current, resulting in high performances. However, this approach could cause S-shaped kink type J-V (current density-voltage) characteristics in many cases, which is generally due to charge accumulations at any interfaces of HEL or inside of HEL owing to a large injection barrier or low mobility.[11,12] Therefore, the systematic understanding of HEL in relation to V_{oc} and its dependence on HOMO level, mobility, and dark current is required for further development of new materials and device design.

Here, we report the precise and systematic relation of mobility, energy levels, and dark current with V_{oc} using different HELs in a SubPc/C_{60} heterojunction OSC. A discrete planar heterojunction structure was employed to understand such relationships. In this paper, we compare the effects of five different HELs such as 2-TNATA (4,4,4-tris-N-2-naphthyl-N-phenyl-amino-triphenylamine), TBBD (*N,N,N′,N′*-tetra(biphenyl-4-yl)biphenyl-4,4′-diamine)), TPD (*N,N*-diphenyl-*N,N*-3-methylphenyl-1,1-biphenyl-4,4-diamine), NPB (4,4′-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl), and TAPC (1,1-bis[(di-4-tolylamino)phenyl]cyclohexane in a SubPc/C_{60} OSC. The OSC devices were fabricated on ITO glass having an area of 2×2 mm^2 with a sheet resistance of 10 Ω/square. The photovoltaic devices were fabricated by the evaporation of TBBD, TAPC, NPB, 2-TNATA, TPD, SubPc, C_{60}, bathophenanthroline (Bphen), and Al. The reference stack consists of ITO/SubPc(11.5 nm)/C_{60}(31.5 nm)/Bphen(13 nm)/Al(100 nm). A xenon light source was used to give simulated irradiance of 100 mW/cm^2 (equivalent to an AM1.5 irradiation) at the surface of the device.

[a)]Author to whom correspondence should be addressed. Electronic mail: mcsuh@khu.ac.kr and jhkwon@khu.ac.kr.

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In this study, the basic device structure with optimized HELs has an architecture of ITO/HEL(7.5 nm)/SubPc(9.5nm)/C_{60}(31.5 nm)/Bphen(13 nm)/Al(100 nm). Fig. 1 shows energy level diagram of various HELs fabricated with SubPc/C_{60} device. The space charge limited current (SCLC) method for hole mobility measurement with the structure of ITO/MoO_3(0.75 nm)/HEL(100 nm)/MoO_3(3 nm)/Al was used for all HELs. The thin MoO_3 layer on a metal electrode was inserted to make ohmic contact so that SCLC region can be investigated clearly in the devices.[13] The SCLC hole mobility of HELs evaluated at the 0.3 MV/cm^2 electric field was increased in the following order: 2-TNATA($\sim 6.4\times10^{-5}$ cm^{2}V^{-1}s^{-1}) < NPB ($\sim 2.2\times10^{-4}$ cm^{2}V^{-1}s^{-1}) < TPD ($\sim 1.4\times10^{-3}$ cm^{2}V^{-1}s^{-1}) < TAPC ($\sim 2.5\times10^{-3}$ cm^{2}V^{-1}s^{-1}) < TBBD ($\sim 1.7\times10^{-2}$ cm^{2}V^{-1}s^{-1}). Our measured mobilities for TPD,[14] NPB,[15] and 2-TNATA (Ref. 16) are very similar to those reported previously elsewhere.

The J-V curves shown in the inset of Fig. 2 illustrates the increase in V_{oc} of all devices using different HELs. Table I lists the OSC characteristics, i.e., V_{oc}, J_{sc}, fill factor (FF), and PCE. The SubPc/C_{60} reference device shows the $V_{oc} = 0.90$ V, FF = 54.50, $J_{sc} = 4.80$, and PCE = 2.37%. The insertion of HEL significantly resulted in enhancing the V_{oc} value to 1.15 V (TBBD), 1.14 V (TPD), 1.12 V (NPB), and 1.09 V (TAPC), while 2-TNATA increased V_{oc} very slightly (0.90 → 0.95 V). However, the insertion of HEL gives a lower FF compared to that of reference device due to an increased series resistance although the enhancement of V_{oc} is the great benefit to the OSC devices. The J_{sc} was improved in TBBD device while other HELs show a reduction in performance due to lower values obtained for J_{sc}. In order to evaluate the V_{oc} dependence on hole extraction ability of HELs with SubPc, we investigated the relationship between V_{oc} and ΔE_{HOMO}, which is the energy difference between the HOMO level of SubPc donor and those of HELs. Fig. 2 shows the variation of V_{oc} in accordance with the variation of ΔE_{HOMO}. The highest V_{oc} of 1.15 V was obtained in the OSC devices with TBBD (ΔE_{HOMO}: $\sim$0.3 eV). And, TPD and NPB devices with ΔE_{HOMO} of $\sim$0.2 eV also produced high V_{oc} value (1.14 V for TPD, 1.12 V for NPB, respectively). The device with TAPC with least ΔE_{HOMO} of $\sim$0.1 eV also exhibits a high V_{oc} value (1.09 V). In contrast, 2-TNATA with

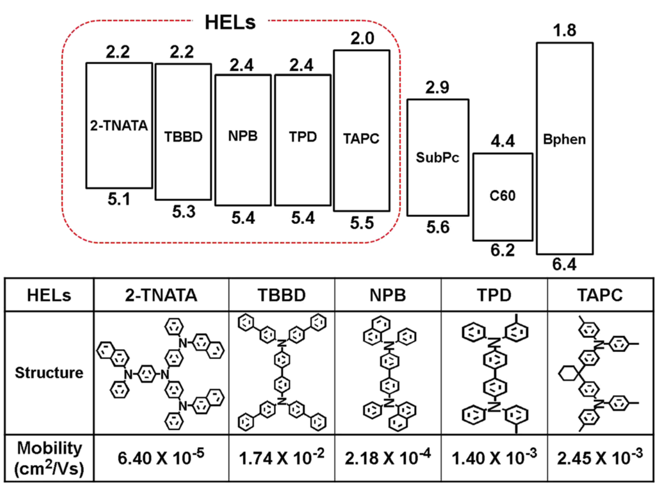

FIG. 1. (Color online) Energy band diagram of SubPc/C_{60} device with HELs such as TAPC, TBBD, NPB, TPD, and 2-TNATA. Table shows the structure and mobility of HEL materials.

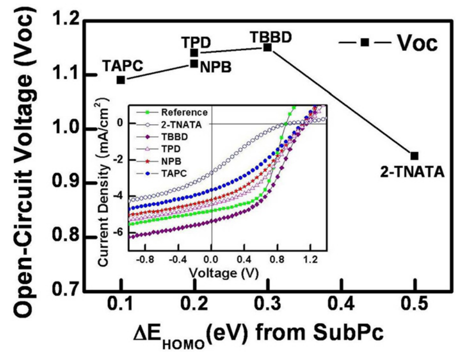

FIG. 2. (Color online) V_{oc} versus HOMO energy level difference (ΔE_{HOMO}) between the HEL and SubPc donor. Inset shows J-V characteristics of ITO/SubPc/C_{60}/Bphen/Al and ITO/HEL/SubPc/C_{60}/Bphen/Al devices.

greatest ΔE_{HOMO} of $\sim$0.5 eV shows a limited increase. This means ΔE_{HOMO} is a very important factor which affects V_{oc} value, and 0.2–0.3 eV of ΔE_{HOMO} is the optimum level to achieve the highest V_{oc}. This V_{oc} increases are considered to have a certain relationship with V_{bi} voltage increase because it is not related to Eq. (1).

In order to observe other effects to V_{oc}, dark saturation current density versus V_{oc} relationship were investigated with different HELs. There was no systematic trend of dark current with respect to LUMO levels, despite dark current could be reduced if the LUMO level is high. Inset of Fig. 3 shows the dark saturation current density as a function of V_{oc} with different HEL incorporated devices. When TAPC, 2-TNATA, and NPB were introduced as HELs, the levels of leakage current density at -0.75 V were decreased about one order of magnitude from $\sim 10^{-3}$ to $\sim 10^{-4}$ mA/cm^2 compared with a reference device. With TPD and TBBD HTLs, these were decreased about three orders of magnitude from $\sim 10^{-3}$ to $\sim 10^{-6}$ mA/cm^2. There was little tendency of V_{oc} increase with reduction of leakage current density. However, it shows less sensitivity in attaining the highest V_{oc} than other factors.

To establish whether the V_{oc} can be affected by mobility of HELs, all the devices including different HEL materials with various mobilities were compared (shown in Fig. 3). The TBBD HEL with a highest mobility produced the largest V_{oc} (1.15 V) while the other HELs with lower mobility values exhibited smaller V_{oc} value, except for TAPC device. Almost similar trend of J_{sc} was noticed. As J_{sc} increases, V_{oc} also increases. This is well commensurate with a simple diode equation (1). In this equation, the impact of mobility on carrier extraction is directly observed in enhancing J_{sc}, resulting in the influence on V_{oc}.

An interesting increase in V_{oc} with the introduction of HELs in our OSC devices was observed with relationship to

TABLE I. Comparative performances of ITO/SubPc/C60/Bphen/Al reference device and ITO/HELs/SubPc/C60/Bphen/Al devices.

HELs	V_{oc} (V)	FF	J_{sc} (mA/cm^2)	Efficiency (%)
Reference	0.90	54.50	4.80	2.37
2-TNATA	0.95	20.01	2.71	0.50
TBBD	1.15	41.97	5.47	2.65
TPD	1.14	37.82	4.43	1.92
NPB	1.12	35.57	4.18	1.66
TAPC	1.09	33.62	3.64	1.34

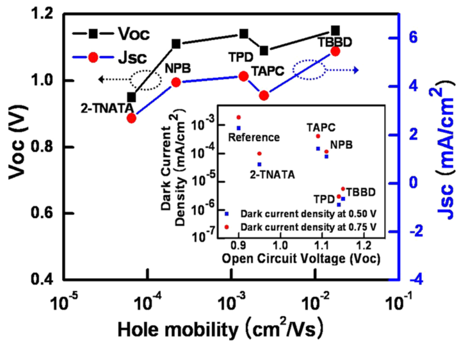

FIG. 3. (Color online) Hole mobility versus V_{oc} and J_{sc} behavior of HEL incorporated devices. Inset shows dark current behavior with respect to V_{oc} of all devices.

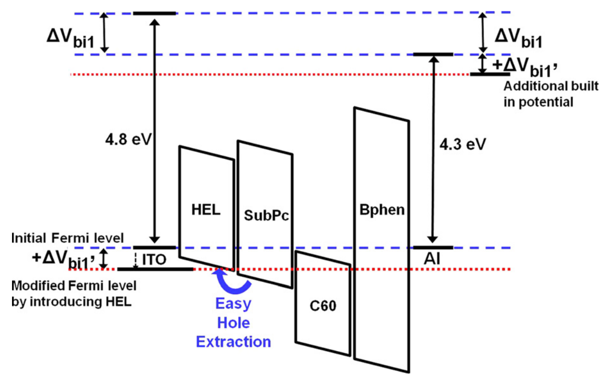

FIG. 4. (Color online) Schematic illustration of V_{bi} increase under illumination when ΔE_{HOMO} is 0.2-0.3 eV.

HEL mobilities and ΔE_{HOMO} values. The V_{oc} increase by high mobility in HEL with a proper HOMO level could be understood from the diode equation. High mobility HTLs can extract holes easily from the donor layer if there is no barrier because of better hole carrier mobilities than SubPc ($\sim 10^{-5}$ $cm^2V^{-1}s^{-1}$),[17] which results in increase of J_{sc} with V_{oc}. On the other hand, the V_{oc} increase by the ΔE_{HOMO} value in our OSCs could be explained by the following reasons: (1) a proper HOMO level with respect to donor material can extract hole carriers at the interface between HEL and donor layers, (2) a low hole density at this interface can generate a different electrical filed, and (3) finally it gives increased built-in electric field in the devices.[18,19] Fig. 4 shows V_{bi} increase by a new electrical field generation through the efficient hole extraction by HEL. Hancox *et al.* formulated a similar hypothesis to explain about the increase in V_{oc} in non-planar phthalocyanines using MoO_x as HEL.[20] They explained increase in V_{oc} by increased V_{bi} because MoO_x generate a gap state between the MoO_x and donor interface. The highest V_{oc} of 1.15 V achieved in TBBD incorporated device is equivalent to a difference of the HOMO level of SubPc donor and LUMO level of C_{60} acceptor. This value, which is raised by 0.25 V compared to that of reference, corresponds to the maximum of possible increase in V_{bi} inside. For the increase of V_{bi}, a similar HOMO level between HTL and donor layer is not good energetically because hole density is decreased when extraction force for the hole carrier movement is existed with high hole carrier mobility. Hence, a little lower HOMO level compared to that of donor material may be better energetically for the easy hole extraction. About 0.2-0.3 eV of ΔE_{HOMO} seems to be good for easy hole extraction. In a view of built-in potential (V_{bi}), TPD, NPB, TBBD, and TAPC devices are better than the 2-TNATA device. Therefore, their V_{oc} values were higher than 2-TNATA, respectively. The ability to extract holes energetically was better for TPD, NPB, and TBBD devices than TAPC device. Thus TAPC does not seem to provide sufficient V_{oc} and J_{sc} performances.

For promoting the high V_{oc} from the donor through HELs, high mobility of HEL can also suppress the voltage losses and produce a maximum V_{oc}. The devices with TPD and NPB exhibit similar behavior to that of device with TBBD. However, a slightly smaller V_{oc} in NPB and TPD devices is caused by a difference in the mobility driven photo-current. The TBBDs high mobility is very useful to attain very high J_{sc} with high PCE due to its efficient charge collection at the electrodes. The 2-TNATA device shows a very low J_{sc} and S-shaped kink owing to imbalanced mobility in the device caused by its low mobility, which makes the hole-extraction almost impossible. Therefore, a space charge built-up inside 2-TNATA increases the possibility of carrier recombination in the device, leading to a low fill factor resulting in an S-shaped kink.[12]

In conclusion, the effect of HELs on SubPc/C_{60} OSC was demonstrated with the idea to generate large V_{oc} in the devices to improve performances in solar applications. Using HELs, we investigated that V_{oc} (1) varies with the HOMO energy difference between donor and HEL materials, (2) depends on mobility of the HELs, and (3) does not have any systematic relationship with dark current. A very high mobility HEL material with its proper HOMO level is very important to improve the solar cell performance significantly.

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