

Improvement of Open-Circuit Voltage in Organic Photovoltaic Cells with Chemically Modified Indium-Tin Oxide

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Received August 12, 2013; revised September 13, 2013; accepted September 20, 2013

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ABSTRACT

The possibility of the increase in open-circuit voltage of organic photovoltaic cells based primarily indium-tin oxide (ITO)/rubrene/fullerene/Al structure by changing the work function of ITO anodes and Al cathodes was described in this work. To change built-in potential preferably in order to increase the open-circuit voltage, the work function of ITO should be increased and work function of Al should be decreased. The correlation between the change in work functions of electrodes and performance of the organic photovoltaic cells before and after surface modifications was examined in detail. The enhancement of open-circuit voltage depends on a function of work function change of both ITO and Al electrode. We could show that the built-in potential in the cells played an important role in open-circuit voltage.

Keywords: Open-Circuit Voltage; Chemical Modification; Indium-Tin Oxide

1. Introduction

Organic photovoltaic (PV) cells have been attracted much attention in recent decades due to their potentials as fabrication, low-cost production, and technological advantages of semiconductor materials [1-5]. Since the first report of donor-acceptor heterojunction with a power conversion efficiency (η_p) of about 1% by Tang [6], new materials and device structures have been developed in PV cells [7-15]. After the first report of organic PV cells, the performances of this type of cells have been significantly improved to reach η_p in a range of 3% - 8% [8,9,16,17]. However, such efficiency is not sufficient for practical use, and further improvement is required.

To obtain large open-circuit voltage (V_{oc}), Taima *et al.* introduced a *p*-type semiconductor 5, 6, 11, 12-tetra-phenylnaphthacene (rubrene), which has the HOMO level of 5.4 eV. They obtained the V_{oc} of 0.91 V [18]. Forrest

et al. introduced an excellent *p*-type semiconductor boron subphthalocyanine chloride (SubPc) with a low HOMO level of 5.6 eV [19].

Indium-tin-oxide (ITO) is the most widely used as a transparent anode in organic PV cells due to its high conductivity, work function, and transparency in the visible spectral range [6]. Thus, various surface treatments of ITO have been attempted to change the work function of ITO in order to improve the properties of ITO substrates and control the charge injection barrier height reviewed in previous reports [20,21]. Although a number of groups have shown that chemical modification of ITO can be used to optimize the performance of organic light-emitting diodes (OLEDs) [20,21], there have been limited attempts to use chemical modification or chemically self-assembled monolayers (SAMs) in organic PV cells [22,23].

To investigate the possibility of increase in V_{oc} by controlling the work functions of the electrodes, we report

here the use of chemically modified ITO with different terminal groups (H- and Cl-) of *p*-benzenesulfonyl chlorides and *p*-chlorophenyldichlorophosphate (-P) forming effective monolayers. We examine the correlation between the change in the work function of ITO and the performance of the PV cells by the chemical modification and find that the large increase in V_{oc} . In this work, we selected tris(8-hydroxyquinoline)aluminum (Alq_3) as an electron transport layer (ETL) to substitute for bathocuproine (BCP) in cells based on rubrene (Rub)/buckminsterfullerene (C_{60}) heterojunction. Moreover, to examine the further improvement of V_{oc} , we used a lithium carboxylate (C_6H_5COOLi) [24] as a cathode interface material with low-work function which was inserted between ETL and Al.

2. Experimental

ITO coated glass substrates with a sheet resistance of *ca.* 15 Ω /square (Sanyo Vacuum Industries) were cleaned by sonication successively in two detergents (Extran MA 03, pH 6.8, MERCK and Kontaminon O, pH 10, WAKO), rinsed with deionized water, and stored in isopropanol until being required. After cleaning with acetone and isopropanol (this cleaned ITO will be called hereafter "as-cleaned ITO" with notation of "ac") the ITO substrates were immersed for 5 min in dichloromethane solutions containing 1 mM of (H- and Cl-) of *p*-benzenesulfonyl chlorides (Tokyo Chemical Industry) and *p*-chlorophenyldichlorophosphate (Tokyo chemical industry). The modified ITO anodes were rinsed in pure dichloromethane and then vacuum dried for ~ 1 h.

C_{60} (purity > 99%) (Tokyo Chemical Industry), the sublimed grade rubrene (Aldrich Co.) and Alq_3 (Dojindo Labs), the reagent grade BCP (Kanto Chemical), and lithium benzoate (purity \sim 99%) (Aldrich Co.) were used without further purification. All the materials were deposited using vacuum evaporation under a pressure of $5 - 7 \times 10^{-6}$ Torr at deposition rates of 1 - 1.5 $\text{\AA}/s$ for organic layers and 3 - 4 $\text{\AA}/s$ for Al cathode. The active area for all the cells was defined to be 5×5 mm² by using a shadow mask. The current density-voltage (*J-V*) curves were measured under illumination of a simulated solar light with 100 mW \times cm⁻² (AM1.5G) by a solar simulator (Yamashita Denso, YSS-50). Electric data were taken using an Advantest R6145 DC voltage current source unit at room temperature in ambient atmosphere.

The absorption spectral data for all the thin film were taken using an UV-visible spectrophotometer (UV-265 FW, Shimadzu) at room temperature in ambient atmosphere.

3. Results and Discussions

3.1. Expected Energy Diagrams of PV Cells

For a cell based on exciton dissociation by charge trans-

fer at a donor-acceptor (D/A) interface, η_p is the product of the efficiencies [1] of four sequential steps 1) photon absorption leading to the generation of an exciton, 2) diffusion of the exciton to the D/A interface, 3) exciton dissociation (or charge separation) by charge-transfer (CT) at the D/A interface, and 4) collection of the free charge carriers at electrodes, *i.e.*, charge transport to the anode (holes) and cathode (electrons), to supply a direct current.

Figure 1 shows the interfacial energy diagrams with shifts of vacuum level (Δ) at the interfaces due to dipole layer formation in four types of cells studied in the present work. In general, the work function of metal is changed by covering the metal surface with different materials [25]. First, we will discuss the shift at a C_{60}/Al cathode interface. The photoemission study of the C_{60}/Al interface revealed an abrupt vacuum-level shift of $\Delta = \sim +0.9$ eV [26]. Namely, the work function of the Al electrode (4.2 eV) was increased to 5.1 eV by depositing a C_{60} film on an Al surface. This shift is schematically illustrated in **Figures 1(a)** and **(b)**. The same energy level shift at the C_{60}/Al interface was also reported previously [27]. Another group reported the shift of +0.7 eV for the C_{60}/Al interface and that of +0.9 eV for the $C_{60}/LiF(0.5$ nm)/Al interface [28]. In the latter case, the work function was increased from 3.6 eV (LiF/Al) to 4.5 eV ($C_{60}/LiF/Al$). The increase in the work function for all cases described above is possibly interpreted by partial electron transfer from Al to C_{60} [26-28]. The HOMO and LUMO levels of C_{60} are reported to be 6.2 eV and 3.7 eV, respectively [10]. The increase in the work function of the Al electrode, however, is not preferable to create the built-in potential (V_{bi}) to separate the charge effectively in the PV cells.

In order to decrease the work function of the Al electrode, we have to put another layer of less electron affinity than C_{60} . As such materials, we examined Alq_3 and BCP [10,16,20,29-31] LUMO levels of which are higher (*i.e.*, less electron affinity) than that of C_{60} . In fact, the organic side for these interfaces is charged positively, making this side more comfortable (low energy) for an electron, and making the sign of Δ negative. Taking into account the Δ at Alq_3/Al interface of ~ -1.0 eV [25], the resulting work function of Alq_3/Al is decreased from the value of metallic Al (4.2 eV) [16] down to 3.2 eV as shown in **Figures 1(c)**-**(d)**. The work function of the LiF/Al substrate was also gradually decreased upon Alq_3 deposition, from 3.6 eV to 3.1 eV for Alq_3 film deposition [28,32]. Toyoshima *et al.* reported the electronic structure at the interface between BCP and Al by UV photoemission spectroscopy [33]. Their results for BCP /Al interface were similar to the shift in the work function as observed at Alq_3/Al interface [25,32]. In this way, we constructed the energy diagrams of the Al cathode side as shown in **Figure 1**.

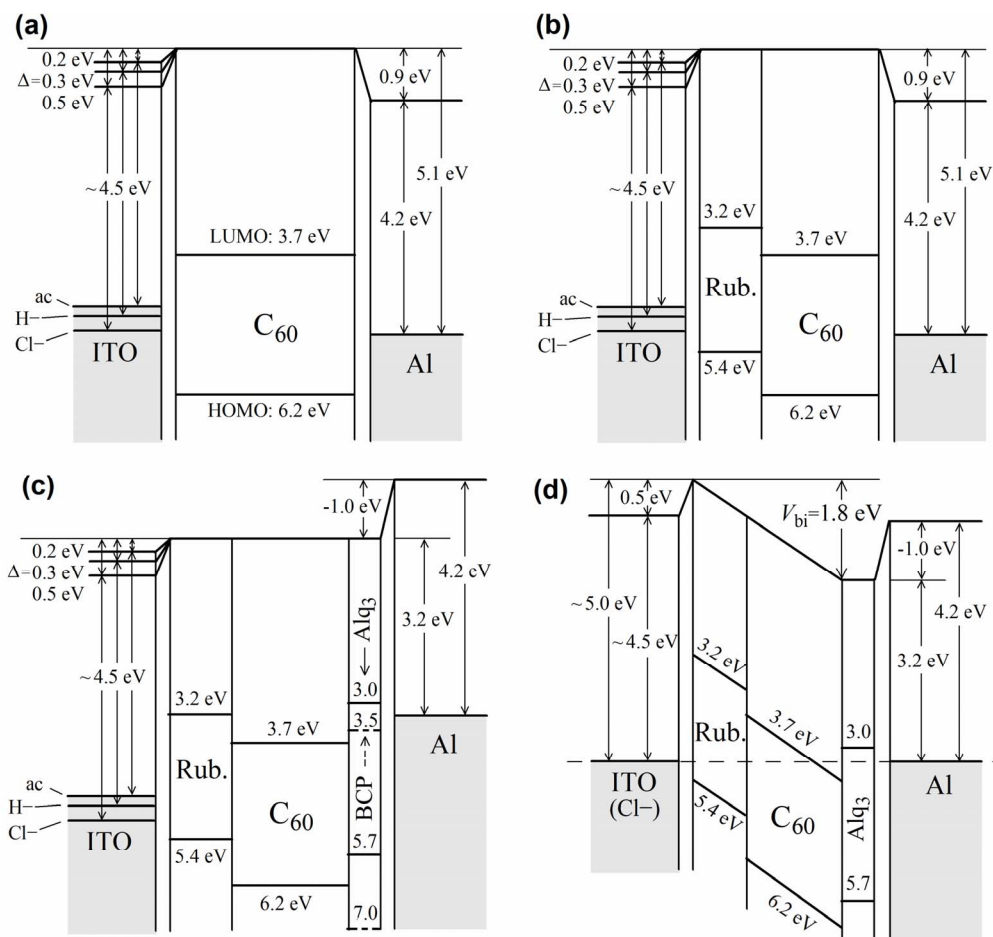


Figure 1. Interfacial energy diagrams with the shifts of vacuum level (Δ) at the interfaces due to dipole layer formation in the PV cells. These lead to buildup of built-in potential (V_{bi}) as shown in (d).

Next, we discuss the work function control of the anode side. The molecular approach allows for fine-tuning the work function using organic molecules on ITO depending upon magnitude and direction of the dipole moment [34]. The effective work functions formed by chemical modification of ITO shown in **Figure 1** were estimated from the contact potential difference (CPD) values [34,35].

An interface dipole with its negative end pointing toward the organic layer and its positive end toward the electrode surface increases the ITO work function (*i.e.*, the Fermi energy is down) and HOMO energy level in the organic layer is relatively up by adding an electrostatic energy [8] as shown in **Figure 1**. When the cells studied have the same cathode material, the changes in V_{bi} obtained for cells with variously modified ITO electrodes are equal to the changes in the ITO work function. This is illustrated on the left side of **Figure 1**, where we consider that the ITO work function is in the range 4.5 - 5.0 eV. The HOMO and LUMO values for rubrene are reported to be 5.4 eV and 3.2 eV, respectively [18]. The work function control at the anode as well the cathode

leads to buildup of a large V_{bi} as shown in **Figure 1(d)**. The dipole layers at interfaces may have a deep impact on the V_{bi} and consequently on the V_{oc} of organic PV cells.

3.2. Characteristics of PV Cells

Figure 2 shows the effect of ITO work function on the current density-voltage (J - V_{bias}) characteristics under 100 $mW \times cm^{-2}$ illumination and in dark of four kinds of the PV cells with various surface treatments of ITO. **Figure 2(a)** shows the room temperature J - V_{bias} characteristics of ITO(variably treated)/ C_{60} (60 nm)/Al single-layer cells with a focus on the dark conduction properties. A linear fitting of the log-log plot (not shown) for these cells shows that the current for forward bias (electrons injection from the top contact) increases much slower (a slope is ~ 1) than the space-charge limited conduction (SCLC) [36]. Conducting charge transfer complex formed on C_{60} /metal interface was studied in previous report [37]. The gap state, pinning the Fermi level close to the LUMO of C_{60} molecules, is originating from the C_{60} -metal complex formation at the interface [37]. The unoccupied

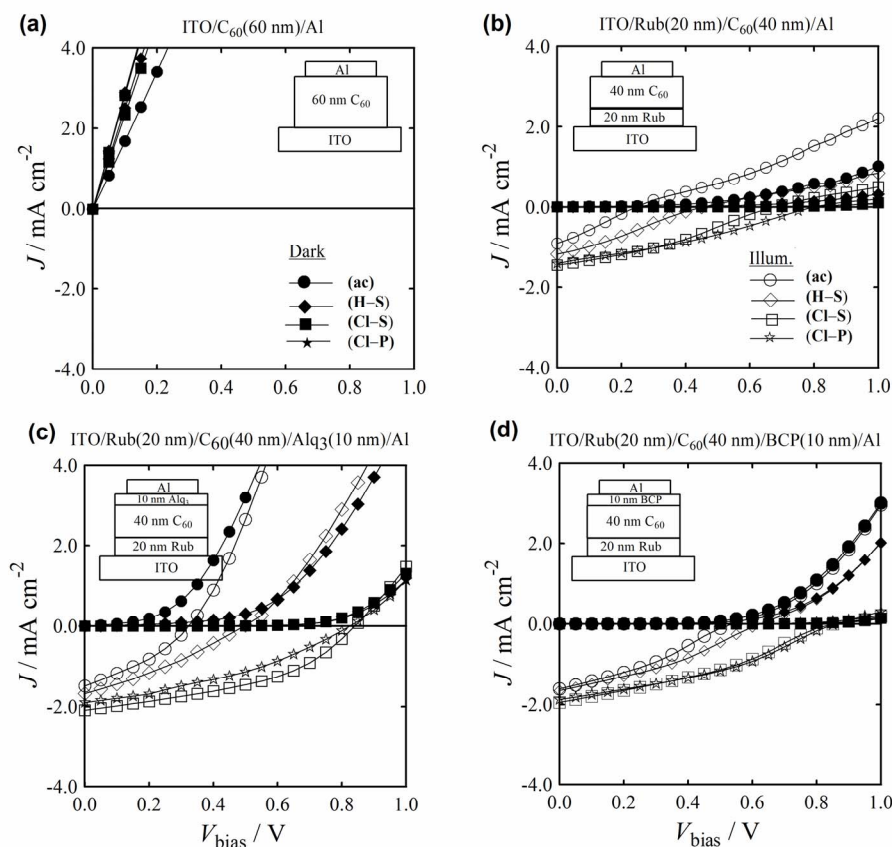


Figure 2. The effect of ITO work function on the J - V_{bias} characteristics under $100 \text{ mW} \times \text{cm}^{-2}$ illumination and in dark of the cells with various surface treatments of ITO: (a) single-layer C₆₀, (b) two-layer Rub/C₆₀, and three-layers (c) with Alq₃, and (d) with BCP.

states of the C₆₀-metal complex appeared between the Fermi level and LUMO of C₆₀ molecules lower the injection barrier which directly explains the improved device characteristics [37]. These states lead to the formation of Ohmic contact at the C₆₀/Al. A thin LiF interlayer inserted between C₆₀ film and Al cathode gave an effective passivation for the contacts by preventing Al oxidation [38]. It appears that a thin interlayer can help to reverse the SCLC in C₆₀ film and cells under exposure to air, by considerably suppressing the oxygen diffusion into the C₆₀ film and reaction at the C₆₀/Al interface [38].

In **Figures 2(b)** and **(c)**, the V_{oc} was most effectively increased when Cl-terminated benzenesulfonyl chloride was used. With ITO modified with H-terminated benzenesulfonyl chloride without any appreciable dipole moment in the para-position, the characteristics of PV cells were much better than those on as-cleaned ITO. From the results, the PV characteristics, in particular the V_{oc} , which were well correlated with the work function change, were dramatically improved by the chemical modification of ITO.

The changes in V_{oc} resulting from changes in the self-assembling dipole molecules used to coat the ITO

surfaces follow the work function changes for the resulting ITO electrodes. Higher work function anodes result in larger values of the V_{oc} in the cells studied in the present work. In **Figure 2(c)**, it can be seen, for example, that the V_{oc} can be increased from 0.35 V (as-cleaned ITO anode) to 0.48 V by grafting benzenesulfonyl chloride onto the ITO electrode. By grafting a monolayer of *p*-chlorobenzenesulfonyl chloride molecules results in a further increase in the V_{oc} to 0.84 V.

A dramatic effect of Alq₃ (10 nm) or BCP (10 nm) as a buffer layer deposited between C₆₀ and Al on the measured J - V_{bias} characteristics is clearly observed in **Figures 2(b)-(d)**. The PV cells with Alq₃ or BCP exhibited the best J - V_{bias} characteristics and gave the typical diode characteristics. BCP is the material selected as an exciton blocking layer [16]. Alq₃ is a good ETL material widely used in OLEDs [34]. It can be seen in **Figures 2(c)** and **(d)** that the cells exhibited similar PV characteristics, indicating that band gaps and LUMO levels of the materials of Alq₃ and BCP have minor effects on the PV performances. As shown in **Figure 1(c)**, while bandgaps and LUMO levels of Alq₃ and BCP are different, the performance of the cells is not significantly changed by dif-

ferent ETL materials (Table 1). This indicates that electron transport in these cells should not be via LUMO levels of these ETL materials. The results suggest that the most important role of Alq₃ or BCP is to establish an Ohmic contact between Al and C₆₀ *i.e.*, a protective film on C₆₀ [39].

While alkali metal-doped organic materials such as Alq₃ have been used as an ETL in OLEDs [40,41] this approach has been not been explored in organic PV cells. Recently, we observed the alkali metal formation by thermal decomposition during vapor deposition of alkali metal carboxylates without post-deposition of Al cathode [42].

The improvement was attributed to the reaction of hot Al atoms with C₆H₅COOLi to form metallic Li during Al vapor deposition [41]. The resulting metallic Li was believed to dope the Alq₃ layer [40] and to alloy with the Al cathode [24]. To examine the influence of induced V_{bi} on the performance of the cells, a 2 nm C₆H₅COOLi as a cathode interface material deposited between C₆₀ or C₆₀/Alq₃ (or C₆₀/BCP) and Al cathode was used. The *J-V_{bias}* characteristics of the ITO (modified with Cl-)/Rub(20 nm)/C₆₀(40 nm)/Al with variously configured cathodes under 100 mW × cm⁻² illumination and in dark are shown in Figure 3. The PV performances of the cells are summarized in Table 1. Among all the cells studied, we found that the large increase in V_{oc} for the ITO (modified with Cl-)/Rub (20 nm)/C₆₀ (40 nm)/Alq₃ (10 nm)/Li/Al cell. We obtained the V_{oc} of 0.92 ± 0.1 V.

In Figure 3 and Table 1, the V_{oc} of cell with the Alq₃/Li/Al is the highest, and followed by the BCP/Li/Al, Alq₃/Al or BCP/Al, Al, and C₆H₅COOLi/Al cells. The results suggest the importance of lower work function of Li (2.9 eV) for the larger V_{oc} [41]. The V_{bi} is increased to larger value, giving an interfacial dipole, which may be attributed to both the alloy formation at the Al cathode [24,41] and doping of Alq₃ with Li [40-43]. The ITO (modified with Cl-)/Rub (20 nm)/C₆₀(40 nm)/Li/Al cell exhibited the lowest V_{oc}. It may be considered, however, from our recent study of quenching by the presence of excess and colored species [44] that the doping of C₆₀

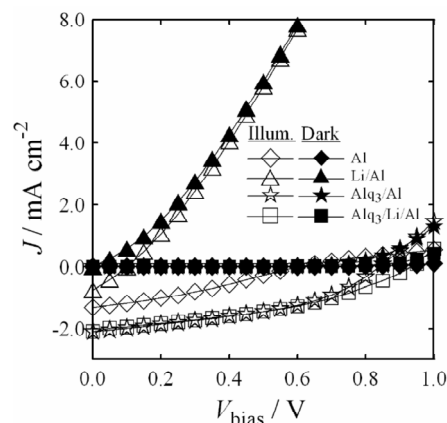


Figure 3. *J-V_{bias}* characteristics of the ITO(Cl-)/Rub/C₆₀/Al with variously configured cathodes under 100 mW × cm⁻² illumination and in dark.

with Li increases exciton quenching and so that more excitons cannot contribute to the generation of electricity. Srdanov *et al.* reported results of an *in-situ* optical absorption study on alkali metal-doped thin films of C₆₀ [45].

Gregg and Hanna proposed that the V_{oc} is controlled by a chemical potential energy gradient of the organic PV cells [46]. The chemical potential gradient is equivalent to the carrier concentration gradient and would depend on the carrier mobility. Based on this idea, V_{oc} is dependent on the hole mobility [47]. The V_{bi} still plays a role in most organic PV cells. Both the chemical potential and the electrical potential must be taken into account [46].

In bilayer cells, the V_{oc} scales linearly with the work function difference, however, with an additional contribution depending on the light intensity. This contribution is due to the accumulation of charge carriers at the D/A interface, giving rise to a diffusion current which must be compensated by a drift current at open circuit [48]. Under illumination, charges are separated across the D/A interface. Due to the concentration gradient, carriers will diffuse away from the interface, leading to a net diffusion current. The effect of diffusion on V_{oc} in single-layer PV cells has been studied by Malliaras *et al.* [49]. The accumulated charges at the interface will create a band-bending, which leads to a reduction of the electric field in the bulk of the cell.

In addition to attempts to optimize the components and composition of the active layer, modification of the electrodes has also lead to an improvement in device performance [50]. It is evident that the work function of the negatively charged electrode is relevant for the V_{oc} of the cells. In the classical metal-insulator-metal (MIM) concept, the V_{oc} is in first order approximation governed by the work function difference of the anode and the cathode, respectively. It should be noted that this only holds for the case where the Fermi levels of the contacts are

Table 1. The performances of organic PV cells with a structure of ITO(Cl-)/Rub/C₆₀/Al with different configured cathodes under 100 mW × cm⁻² illumination.

Cathode structures	<i>J_{sc}</i> (mA × cm ⁻²)	<i>V_{oc}</i> (V)	FF	<i>η_p</i> (%)
Al	1.46	0.68	0.37	0.36
C ₆ H ₅ COOLi/Al	0.80	0.21	0.37	0.06
BCP/Al	1.95	0.85	0.35	0.58
BCP/C ₆ H ₅ COOLi/Al	2.06	0.82	0.43	0.73
Alq ₃ /Al	2.09	0.84	0.45	0.79
Alq ₃ /C ₆ H ₅ COOLi/Al	2.10	0.93	0.40	0.78

within the bandgap of the insulator and are sufficiently far away from the HOMO and the LUMO levels, respectively [51]. In the case of ohmic contacts, meaning that the negative and positive electrodes match the LUMO level of the acceptor and the HOMO level of the donor, respectively, the situation is different; charge transfer of electrons or holes from the metal into the semiconductor occurs in order to align the Fermi level at the negative and positive electrode, respectively [51]. As a result, the electrode work functions become pinned close to the LUMO/HOMO level of semiconductor [50]. Because of this pinning, the V_{oc} will be governed by the energetics of the LUMO of the acceptor and the HOMO of the donor. Indeed, in bilayer cells, a linear correlation of the V_{oc} with the reduction potential of the acceptor has been reported [52].

For cells with non-ohmic contacts, the observed V_{oc} is in agreement the expected values [50]. In this case, the V_{oc} is determined by the work function differences of the electrodes. However, for the Ohmic contact the measured value is lower than the predicted value, possibly due to the energetic disorder of the charge transport levels [50]. Furthermore, generation of free charges is enhanced by an electric field in the appropriate direction. Possible mechanism by which balance between electron and hole escape currents can be maintained in the steady state is by the build-up of a net charge density within the cell. This acts to reduce the electric field (and hence suppress the generation of free charges) at one electrode and increase it at the other [53]. Snaith *et al.* found that a charge injection barrier from electrodes into the polymer film helps to retain a high V_{oc} in the blend cell [53].

4. Conclusion

We have studied the use of chemically modified ITO with 4-chlorophenyldichlorophosphate and different terminal groups (H- and Cl-) of *p*-benzenesulfonyl chlorides forming effective monolayers to control work function of ITO for enhancing the V_{oc} in organic PV cells. We have examined the correlation between the change in the work functions of electrodes and the performance of the PV cells before and after the surface modification and found that there is a large increase in V_{oc} for the ITO (modified with Cl-)/Rub(20 nm)/C₆₀(40 nm)/Alq₃(10 nm)/C₆H₅COOLi (2 nm)/Al. We obtained the V_{oc} of 0.92 ± 0.1 V. Controlling the work functions of electrodes by surface modification at the interfaces is a key parameter, which is useful for interpreting the origin of the open-circuit voltage and leads to improvements in the J - V_{bias} characteristics of the cells.

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