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Improvement of both efficiency and working lifetime in organic photovoltaic devices by using bathophenanthroline/tin(IV) phthalocyanine dichloride as bilayer exciton blocking layers

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We demonstrate that the improvement of both efficiency and lifetime of organic photovoltaic (OPV) devices by employing thinner bathophenanthroline (Bphen) and thicker tin(IV) phthalocyanine dichloride ($SnCl_2Pc$) as the bilayer exciton blocking layers (EBLs), where Bphen and $SnCl_2Pc$ acts as the photogenerated exciton blocking layer and optical spacer, respectively. The thicker $SnCl_2Pc$ layer can be adopted due to its high electron mobility and aligned lowest unoccupied molecular orbital with the acceptor. The OPV device with such a bilayer EBL leads to an increase by 27% in power conversion efficiency compared to the device with a traditional bathocuproine EBL. Moreover, the lifetime is also improved due to the superior oxygen and moisture diffusion blocking effect of the thick $SnCl_2Pc$ layer. The operation mechanism for the improvement in PCE and lifetime was also discussed. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4729146]

Organic photovoltaic (OPV) devices have gained considerable attention due to their potential as low-cost and flexible energy conversion devices. Significant efforts have been devoted in recent years to improving the power conversion efficiency (PCE), such as an exciton blocking layer (EBL), a bulk heterojunction and a tandem device structure, etc.[1–3] However, there are relatively few studies that develop ways to improve device stability,[4,5] which is also a huge problem restricting the application of OPV devices. Therefore, there is great interest in introducing useful structures into OPV devices to gain both high performance and long-term lifetime.

Previous studies have shown that the predominant degradation mechanism in OPV devices is a result of the entrance of ambient gases such as moisture and oxygen entering into the device,[6–9] and the major route for ambient gas diffusion is through the top electrode instead of via the edge sides of the devices.[10,11] And generally, we know that a thick spacer layer can be optimally designed to position highest incident light intensity at the active interface for exciton dissociating, which leads to increase in the photocurrent.[12,13] Thus, introducing a thicker EBL interposed between organic layer and cathode functioning as an optical spacer and a gas diffusion barrier should be one simple and effective way to improve both PCE and lifetime of OPV devices. The most commonly used EBLs, such as bathocuproine (BCP) and bathophenanthroline (Bphen), are wide energy gap semiconductors that transport carriers via cathode metal-deposition-induced damage (shown in Fig. 2(a)), which make them unsuitable as thick EBLs.[13,14] Rand *et al.* have employed a tris-(acetylacetonato) ruthenium(III) [Ru(acac)$_3$] layer as an effective thick EBL.[12] In this case, the holes from the cathode are transported along the highest occupied molecular orbital (HOMO) of Ru(acac)$_3$ to recombine with electrons at the acceptor/EBL interface. However, the OPV device with such a thick Ru(acac)$_3$ EBL do not offer a better performance compared to the device with a conventional thin BCP EBL.

In this work, we report on a bilayer EBL based on thinner Bphen layer and thicker tin(IV) phthalocyanine dichloride ($SnCl_2Pc$) layer. $SnCl_2Pc$ is an n-type semiconductor with good air stability (the molecular structure shown in Fig 1(a)) and also shows high electron mobility.[15] Besides the lowest unoccupied molecular orbital (LUMO) of $SnCl_2Pc$ is aligned with that of the acceptor (C_{60} in this work). Therefore, using $SnCl_2Pc$ as a thick EBL can achieve low-resistance electron transport from acceptor to cathode via LUMO of $SnCl_2Pc$. In the Bphen/$SnCl_2Pc$ EBL, the thinner Bphen layer acts as an effective exciton diffusion barrier while the thicker $SnCl_2Pc$ layer is used as an electron transporting optical spacer. By using such an EBL, not only the PCE but also the lifetime of the OPV device is considerably enhanced.

All devices were fabricated on cleaned glass substrates precoated with conducting indium-tin-oxide (ITO) anode with a sheet resistance of 20 Ω/sq. The organic materials for fabrication were procured commercially and were used without further sublimation. Prior to deposition, the ITO surface was cleaned in a series of solvents and then treated by ultraviolet-ozone in a chamber for 15 min. The organic films were thermally evaporated in high vacuum ($\sim 5 \times 10^{-4}$ Pa) using previously calibrated quartz crystal monitors to determine the deposition rate and film thickness. The organic

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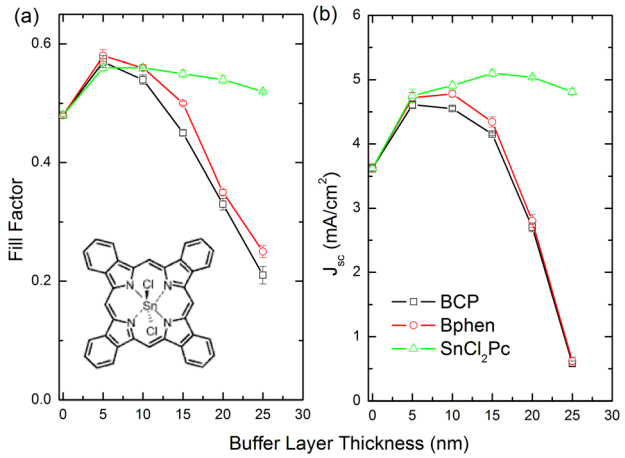

FIG. 1. (a) FF, (b) short-circuit photocurrent (J_{sc}) under 1 sun, AM 1.5G illumination for devices with BCP (square), Bphen (circle), and $SnCl_2Pc$ (triangle) EBLs as a function of thickness. Inset: the molecular structure of $SnCl_2Pc$.

layers were deposited at a rate of 0.1–0.2 nm/s. After the deposition of the organic layers, Al cathode (100 nm) was deposited by thermal evaporation using a shadow mask that defined an active device area of 0.1 cm^2. In this work, different types of devices were fabricated with a structure of ITO/CuPc (20 nm)/C60 (40 nm) /EBL (x nm)/Al (100 nm). The current-voltage characteristics were measured using a programmable source meter (Keithley 2400) in the dark and under illumination of 100 mW/cm^2 with AM 1.5G simulated solar spectrum from a solar simulator. The light intensity was measured with a calibrated Si detector. All measurements were carried out at room temperature and under ambient conditions without encapsulation.

The performance of OPV devices by using the $SnCl_2Pc$ EBL has been studied and then compared with other EBL devices. Figs. 1(a) and 1(b) show that fill factor (FF) and short-circuit photocurrent (J_{sc}) as a function of the EBL thickness for BCP, Bphen, and $SnCl_2Pc$, respectively. It is seen that the open-circuit voltage (V_{oc}) depends on the interfacial energy gap between the donor and acceptor[16,17] and is from 0.49 to 0.51 V, independent of the EBL composition and thickness. The 5 nm BCP EBL based OPV device offers the optimal FF = 0.56 ± 0.01, J_{sc} = 4.6 ± 0.1 mA/cm^2, and PCE = 1.29% ± 0.05%. As the thickness of BCP layer increases, both FF and J_{sc} decline sharply which is ascribed to the limited depth of damage-induced transport states extending into the film from the surface.[18] And because there presents the same mechanism of electrons transporting in both BCP and Bphen EBL, a similar trend of the photovoltaic response is observed in Bphen devices, with peak FF, J_{sc}, and PCE of 0.58 ± 0.01, 4.7 ± 0.1 mA/cm^2, and 1.34% ± 0.05% at the thickness of 5 nm, respectively. In contrast, the device with $SnCl_2Pc$ EBL exhibits FF = 0.56 ± 0.01 at x = 5 nm, with an only small reduction as EBL thickness increases, confirming the low resistance transport in the thick $SnCl_2Pc$ EBL. The optimized device with 15 nm $SnCl_2Pc$ shows FF, J_{sc}, and PCE of 0.55 ± 0.01, 5.1 ± 0.1 mA/cm^2, and 1.37% ± 0.05%, respectively.

In term of the previous results, the HOMO and LUMO energies of C60 are 6.2 eV and 3.7 eV, respectively,[19] while $SnCl_2Pc$ has corresponding energies of 5.3 eV and 4.0 eV.[20] Differing from the high LUMO level of BCP (1.7 eV) or Bphen (2.9 eV)[21] which causes a large barrier to electron extraction at the cathode, the LUMO level of $SnCl_2Pc$ is a little lower than that of C_{60} and therefore electrons from the active interface can easily transport via LUMO of $SnCl_2Pc$ to the cathode (shown in Fig. 2(b)). Such an effective way of electron transport and high electron mobility in $SnCl_2Pc$ film[15] together ensure that devices with a much thicker $SnCl_2Pc$ EBL can maintain a low electron transport resistance.

In Fig. 1(b), it can be seen that as EBL thickness increases, the $SnCl_2Pc$ EBL based devices keep a high J_{sc} without remarkable drop, which is attributed to not only the effective mechanism of the electron transport but also the appropriate absorption spectrum of $SnCl_2Pc$, which has little overlap with that of CuPc and C_{60}.[22,23] In addition, the peak of J_{sc} for devices with $SnCl_2Pc$ EBL occurs at the thickness of 15 nm with 5.1 ± 0.1 mA/cm^2, which is approximately 10% higher than J_{sc} at a thickness of 5 nm. This enhancement of J_{sc} can be explained by optical field adjustment, which has been reported previously in the device with similar structure.[24] In this case, the low resistant $SnCl_2Pc$ layer is thick enough to serve as a spacer that can be adjusted to maximize the optical field at the donor-acceptor junction through optical interference effects. As a result, more excitons can be generated in the vicinity of the donor-acceptor interface and consequently larger photocurrent for the device is gained.[23] The calculated distributions of optical electric field inside the OPV devices with 5 nm and 15 nm $SnCl_2Pc$ EBLs are shown in Figs. 3(a) and 3(b), respectively, using the transfer matrix approach that includes the optical constants of the

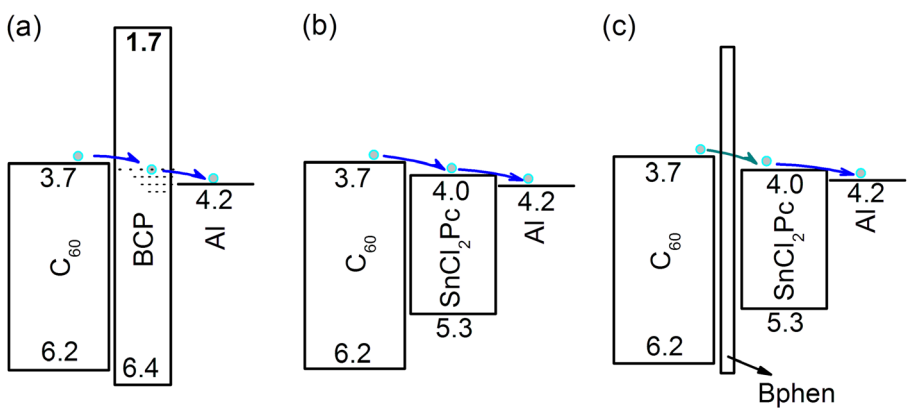

FIG. 2. Schematic energy-level diagram for electrons transport process of OPV device using (a) BCP, (b) $SnCl_2Pc$, and (c) 2 nm Bphen/15 nm $SnCl_2Pc$ EBLs. Electrons are shown as filled circles.

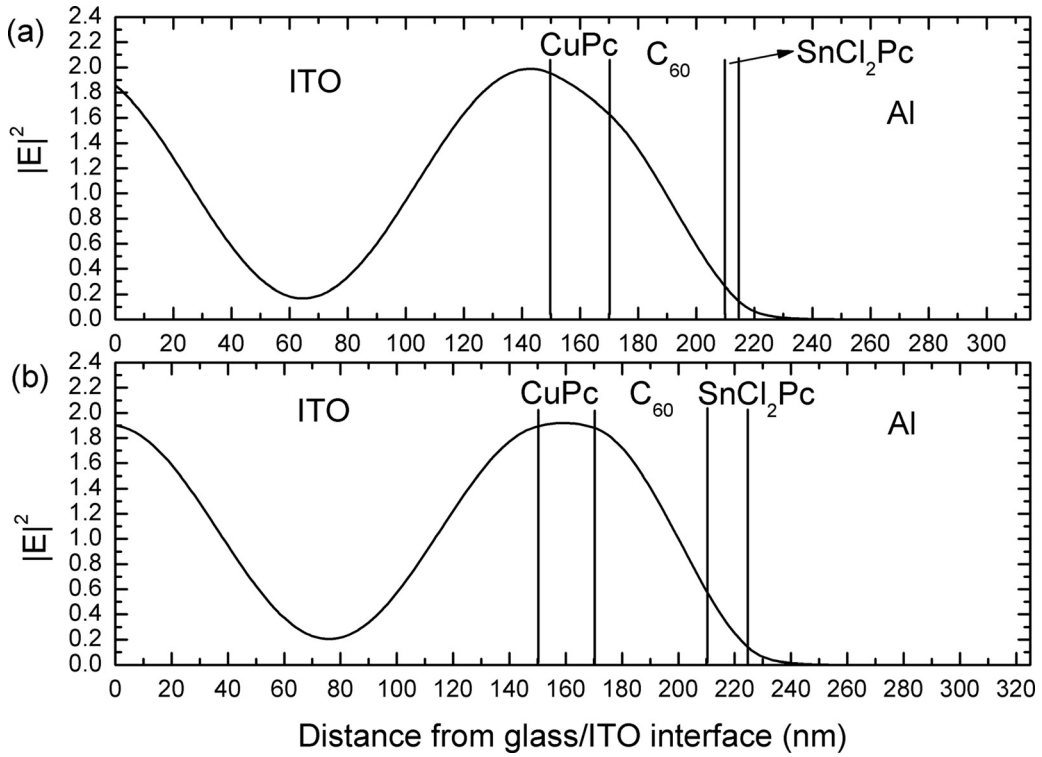

FIG. 3. Calculated distribution of the normalized modulus squared of the optical electric field $|E|^2$ inside the OPV device with (a) 5 nm $SnCl_2Pc$ and (b) 15 nm $SnCl_2Pc$ at a wavelength of 600 nm.

various films.[25] It can be seen that the peak of optical field is much closer to the donor-acceptor junction inside the device with 15 nm $SnCl_2Pc$ layer than the device with 5 nm $SnCl_2Pc$ layer. Thus, we demonstrate that the thicker $SnCl_2Pc$ EBL acts as an optical spacer in the device;[26] and as a result, the photocurrent was improved.

I–V characteristics for optimized devices with BCP, Bphen, $SnCl_2Pc$ EBLs under 1 sun, AM 1.5G illumination are shown in Fig. 4 and the corresponding OPV performance parameters are summarized in Table. I. We note that the optimized $SnCl_2Pc$ based device displays a slightly improved PCE of $1.37\% \pm 0.05\%$ compared to $1.29\% \pm 0.05\%$ for BCP and $1.34\% \pm 0.05\%$ for Bphen due to the limited enhancement of J_{sc}. Given the smaller energy gap of $SnCl_2Pc$ in comparison with C_{60}, we see the $SnCl_2Pc$ layer alone is unable to effectively block excitons generated in the acceptor and prevent them quenching at the Al cathode surface.[27] Therefore, the J_{sc} loss caused by exciton quenching may be the reason limiting the improvement of J_{sc}. For reducing the J_{sc} loss caused by exciton quenching, a simple way is to insert a large band gap semiconductor layer between C_{60} and $SnCl_2Pc$.[13] Bphen is a wide energy gap material with great electron conductivity, so it should be suitable for this design.[14] However, taking into account the large barrier of electron transport at C_{60}/Bphen interface, inserting a thinner Bphen layer between C_{60} and $SnCl_2Pc$ should be better because it seems to be more feasible for electrons tunneling through thinner (~2 nm) layer.[20,28,29]

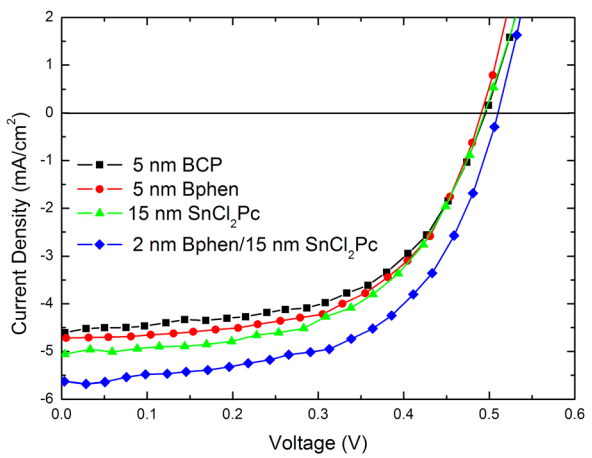

FIG. 4. I–V characteristics under 1 sun, AM 1.5G illumination for optimized devices with 5 nm BCP (square), 5 nm Bphen (circle), 15 nm $SnCl_2Pc$ (triangle), and bilayer 2 nm Bphen/15 nm $SnCl_2Pc$ (diamond).

As shown in Fig. 4, the device with 2 nm Bphen/15 nm $SnCl_2Pc$ EBL achieves an enhanced $J_{sc} = 5.6 \pm 0.1$ mA/cm^2, demonstrating the efficient excitons blocking of the inserted thin Bphen layer. Besides, the quite high $FF = 0.57 \pm 0.01$ indicates that the inserted layer hardly obstructs the electrons transport from C_{60} to $SnCl_2Pc$. Thus, it seems that the electrons can pass through 2 nm Bphen layer efficiently by tunneling mechanism,[23,29] as shown in Fig. 2(c). Consequently, the optimized device with bilayer 2 nm Bphen/15 nm

TABLE I. OPV performance for devices with different EBLs under simulated 1 sun, AM 1.5G illumination.

EBL	Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
BCP	5	0.50	4.6	0.56	1.29 ± 0.05
Bphen	5	0.49	4.7	0.58	1.34 ± 0.05
$SnCl_2Pc$	15	0.49	5.1	0.55	1.37 ± 0.05
Bphen/$SnCl_2Pc$	2/15	0.51	5.6	0.57	1.64 ± 0.06

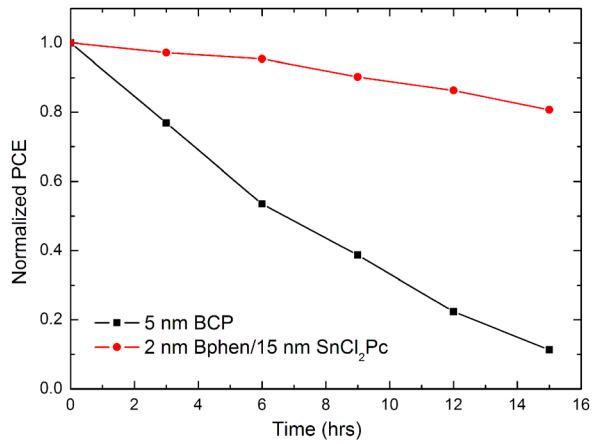

FIG. 5. Decline in device performance as a function of time for devices with 5 nm BCP (square) and bilayer 2 nm Bphen/15 nm $SnCl_2Pc$ (circle) EBLs, which were kept under a constant illumination of a fluorescent lamp with an illumination power of 20 mW/cm^2.

$SnCl_2Pc$ EBL shows PCE = 1.64% ± 0.06% under 1 sun, AM 1.5G illumination and an PCE enhancement by about 27% over the device with traditional 5 nm BCP EBL is obtained.

Using the optimized Bphen and $SnCl_2Pc$ layer thickness, the environmental stability of the OPV device with the Bphen/$SnCl_2Pc$ EBL is also investigated. Fig. 5 shows the normalized PCE as a function of time for devices with 5 nm BCP and 2 nm Bphen/15 nm $SnCl_2Pc$ bilayer EBL which were kept under a constant illumination of a fluorescent lamp with an illumination power of 20 mW/cm^2. The device performance was measured under 1 sun, AM 1.5G illumination. The device with BCP has a half-life of only 6 h, which is close to the typical lifetime reported.[30] By contrast, about 80% of the initial PCE is retained even after 15 h in the Bphen/$SnCl_2Pc$ based device, confirming that this 2 nm Bphen/15 nm $SnCl_2Pc$ EBL can greatly improve the environmental stability and lifetime of the OPV device, which should be due to the introduction of the 15 nm $SnCl_2Pc$ layer functioning as an effective diffusion barrier of ambient gases. The detailed mechanism of enhanced stability is under studying.

In summary, we have demonstrated that the improvement of both PCE and lifetime of the OPV devices by using a bilayer EBL of 2 nm Bphen/15 nm $SnCl_2Pc$. The $SnCl_2Pc$ layer can achieve a large thickness due to its high electron mobility and lower LUMO level. With the thick $SnCl_2Pc$ layer to adjust the optical field and the thin Bphen layer to prevent excitons from quenching at the cathode surface, the OPV device with such a bilayer EBL leads to an increase by 27% in PCE compared to the device with a traditional BCP EBL. And because the diffusion of ambient gases can be avoided efficiently by using the thick $SnCl_2Pc$ layer, the long-term lifetime of the device with Bphen/$SnCl_2Pc$ EBL is also greatly improved. This design of the bilayer EBL provides a route for increasing PCE and extending lifetime of OPV cells.

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