Uncovering the role of cathode buffer layer in organic solar cells

Boyuan Qi1,2, Zhi-Guo Zhang1 & Jizheng Wang1

1Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China, 2Graduate University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

Organic solar cells (OSCs) as the third generation photovoltaic devices have drawn intense research, for their ability to be easily deposited by low-cost solution coating technologies. However the cathode in conventional OSCs, Ca, can be only deposited by thermal evaporation and is highly unstable in ambient. Therefore various solution processible cathode buffer layers (CBLs) are synthesized as substitute of Ca and show excellent effect in optimizing performance of OSCs. Yet, there is still no universal consensus on the mechanism that how CBL works, which is evidently a critical scientific issue that should be addressed. In this article detailed studies are targeted on the interfacial physics at the interface between active layer and cathode (with and without treatment of a polar CBL) by using ultraviolet photoelectron spectroscopy, capacitance-voltage measurement, and impedance spectroscopy. The experimental data demonstrate that CBL mainly takes effect in three ways: suppressing surface states at the surface of active layer, protecting the active layer from being damaged by thermally evaporated cathode, and changing the energy level alignment by forming dipole moments with active layer and/or cathode. Our findings here provide a comprehensive picture of interfacial physics in devices with and without CBL.

Organic solar cells (OSCs) have attracted a continuously growing interest in the roadmap of clean energy, for their potential to realize ultralow-cost manufacturing and ability to be deposited on various flexible substrates by solution process, such as roll-to-roll coating technology. However there is still a big challenge to overcome for the commercialization of OSCs, i.e., achieving solution processible cathode. In conventional devices the commonly used cathode is thermally evaporated Ca/Al. But Ca is readily oxidized when exposed to the air and moisture, and hence induces large performance drop as time goes on. Therefore cathode buffer layer (CBL), as an inert and solution processible substitute of Ca, is a hot spot in the field of OSCs1–3, and a significant achievement in efficiency (9.2%) has been made promoted by this research interest4. Despite this progress, the precise mechanism by which CBL takes effect in OSCs is still under debate. Currently the most popular strategy of designing CBL molecules is to introduce polar groups into the backbones5–9. These polar groups are intended to alter the energy level alignment between the cathode and active layer, increase the built-in potential, and enhance the open-circuit voltage (\(V_{OC}\)) and power conversion efficiency (PCE) ultimately. However, a different perspective has come out from the recent observations that even treating active layer with methanol (the solvent to dissolve CBL), the \(V_{OC}\) and PCE of device could be improved drastically compared to the control device10–14, indicating the polarity of CBL may be unnecessary.

In this manuscript, we intend to investigate this important issue. By using a fullerene based polar molecule N-methylpiperazine adduct C60 (NMPAC) as CBL in high-performance system thiene [3, 4-b] - thiophene/benzo-dithiophene: [6, 6]-phenyl C71-butyric acid methyl ester (PTB7:PC71BM), \(V_{OC}\) and PCE are found to be enhanced obviously, which is consistent with previous reports10–14. In order to explore the role of molecular polarity, the energy levels of blend surface are measured with UPS. It is observed however that there is no significant change before and after CBL deposition. This implies that NMPAC does not work by means of proving dipole moments to the organic blend. In order to figure out the role of NMPAC, capacitance-voltage (CV) measurements are applied to directly target on the interface between active layer and cathode, and find that the CV plots show a large discrepancy in dark and under illumination in device without CBL. This discrepancy is attributed to the surface states at the interface between active layer and cathode, which lead to a slow kinetics for charge transfer, and as a result non-equilibrium carriers generated under illumination are blocked at the interface. After methanol and CBL treatment, surface states are reduced significantly and discrepancy becomes less with the increasing thickness of CBL. Then the density and energy level of interfacial surface states and lifetime of charge carriers are calculated via CV and impedance measurements. Carriers in devices with CBL treatment suffer less recombination and show longer lifetimes resulting from less surface states. Finally molecular polarity is briefly
discussed with UPS data and previous reports. It is concluded that
dipole moments formed at the interface of blend/CBL and CBL/
cathode both contribute to the overall enhance of $V_{OC}$ on condition
that surface states are supressed.

**Results**

**J-V characterization.** The NMPAC was obtained via facile synthesis
procedures with high yields using eco–friendly reagents according to
the method initially described by Nakamura\textsuperscript{15,16}, while their
application remains largely unknown. Here, our exploration of
NMPAC as the CBL is inspired by its unique virtues of being structurally similar to the conventionally used fullerene acceptors
(such as PCBM) and most importantly possible dipole moments at
the interfaces provided by the four adducted $N$-methyl piperazine
polarity groups. Moreover it has been reported that fullerene based
materials have similar energy levels with PCBM, which makes them
to be energetically favorable for electron extraction\textsuperscript{17–19}. The
configuration of the OSCs is indium tin oxide (ITO)/poly (3, 4-
ethylendioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)/
PTB7:PC\textsubscript{71}BM/CBL (w/wo)/Al (shown in Fig. 1). It should be
noted that NMPAC is dissolved in methanol and spin-coated on
active layer, which means the active layers in our experiments also
have been treated by methanol.

To optimize the thickness of CBL, concentrations of the solution
are chosen as 0.5, 1.0, 1.5 and 2.0 mg/ml with the spin-coating speed
fixed at 3,000 rpm, and thicknesses are 9, 7, 5 and 3 nm, respectively.
The current density-voltage (J–V) characteristics of devices with and
without CBL are shown in Fig. 2. All of the parameters measured are
listed in Table 1, it can be seen that short-circuit current density ($I_{SC}$)
is improved by about 1 mA/cm\textsuperscript{2} from the control device to the optimized
device, and even with methanol treatment the $I_{SC}$ is increased.
This is induced by the enhanced optical absorption in devices, and
can be proved by the increased external quantum efficiency (EQE)
spectra and decreased reflectance spectra shown in Supplementary
Fig. S1.

Meanwhile, even treated by methanol, $V_{OC}$ varies a lot compared
to that of the control device (from 0.519 V to 0.688 V). This can be
explained by the reduced dark current. From the J–V curves in dark,
two parameters characterizing the property of diodes, namely ideal-
ality factor (n) and saturation dark current density ($I_{0}$), can be
extracted by fitting the data into Shockley equation listed below
(fitting scheme is shown in Fig. 2b and details can be found in the
supporting information of ref. 20):

\[
J = \frac{R_{sh}}{R_{sh} + R_{s}} \left( I_{0} \left[ e^{\frac{q(V - J R_{s})}{n k_{B} T}} - 1 \right] + \frac{V}{R_{sh}} \right) - J_{ph} \quad (1)
\]

Here, $q$ is the elementary charge, $k_{B} T$ the thermal energy, $J_{ph}$ the
photocurrent. After simplification, the $V_{OC}$ could be deduced as refs
21, 22:

\[
V_{OC} = \frac{n k_{B} T}{q} \ln \left( \frac{I_{SC}}{I_{0}} \right) \quad (2)
\]

Table 1 shows that $I_{0}$ decreases about 3 orders of magnitude from
control device to device with 1.0 mg/ml CBL. Therefore the $V_{OC}$
could be evidently enhanced according to equation (2).

Shunt resistance ($R_{sh}$) denotes current leakage both from the edge
of the cells and inside the device. It has been reported by several
groups that hot Al atoms during thermal evaporation can cause
damage to the surface of active layer and diffuse inside the blend\textsuperscript{23–25}.
Metal atoms are active centers for carriers’ recombination and as a
result the current loss will increase as reflected by decrease of $R_{sh}$. In
Surface states. In order to explore the effect of polarity of NMPAC, three samples are fabricated and measured by UPS, with the structure of ITO/PEDOT:PSS, ITO/PEDOT:PSS/PTB7:PC71BM and ITO/PEDOT:PSS/PTB7:PC71BM/NMPAC, respectively. Fig. 3a shows the secondary electron cutoff region of the three samples, from which the work function (WF) can be determined. The WF of PEDOT:PSS is deduced to be 5.1 eV, in good agreement with its common value. Interestingly the WF of blend shows little change after CBL spin-coated on its surface, opposite to our initial expectations. This suggests that overall dipole moments provided by the CBL are zero at the interface of blend/CBL, maybe the CBL molecules distribute dispersedly in the film, and therefore the dipole moments are counteracted ultimately.

Then CV measurements are performed on the actual devices in dark, with the results of which the built-in potential can be extracted by fitting CV plots into Mott-Schottky equation. From Fig. 4, it is demonstrated that the built-in potential shows an obvious difference between the devices with and without methanol treatment. Here it is assumed that there are surface sates existed at the interface, leading to lower built-in potential in control device. Generally at the surface of crystal, periodic potential field being broken off, adsorption of other kinds of molecules or existence of oxide film can all induce additional energy levels in the band gap, which are called surface states\(^2\). Similarly disorder at the surface of organic semiconductor can also lead to localized sates into the band gap. What’s more, when hot metal atoms are deposited onto the surface of blends, it may also induce extra surface states.

Table 1 | Device performance and extracted parameters with different CBL under 1 sun illumination

| Device | \(V_{OC} \) [V] | \(J_{SC} \) [mA/cm\(^2\)] | FF [%] | PCE [%] | Avg. PCE [%]* | \(R_s \) [\(\Omega \cdot \text{cm}^2\)] | \(R_{sh} \) [k\(\Omega \cdot \text{cm}^2\)] | \(n\) [n.a.] | \(J_0\) [mA/cm\(^2\)] |
|--------|----------------|----------------|--------|--------|---------------|----------------|----------------|--------|----------------|
| Control | 0.519          | 14.62          | 57.0   | 4.34   | 4.22          | 7.80           | 412.5          | 1.51   | 6.68 \(\times\) 10\(^{-6}\) |
| Methanol | 0.688          | 14.96          | 64.2   | 6.62   | 6.55          | 5.25           | 557.4          | 1.68   | 1.47 \(\times\) 10\(^{-6}\) |
| 0.5 mg/ml | 0.726          | 15.15          | 68.3   | 7.51   | 7.37          | 4.36           | 897.5          | 1.54   | 1.61 \(\times\) 10\(^{-7}\) |
| 1.0 mg/ml | 0.740          | 15.79          | 71.3   | 8.33   | 8.23          | 3.95           | 856.2          | 1.37   | 7.04 \(\times\) 10\(^{-9}\) |
| 1.5 mg/ml | 0.737          | 15.92          | 67.5   | 7.92   | 7.72          | 7.08           | 831.3          | 1.48   | 2.80 \(\times\) 10\(^{-8}\) |
| 2.0 mg/ml | 0.733          | 15.59          | 60.1   | 6.87   | 6.74          | 15.2           | 992.5          | 1.62   | 1.34 \(\times\) 10\(^{-7}\) |

\(V_{OC}\) : open-circuit voltage; \(J_{SC}\) : short-circuit current density; FF : fill factor; PCE : power conversion efficiency; \(R_s\) : series resistance; \(R_{sh}\) : shunt resistance; \(n\) : ideality factor; \(J_0\) : reverse saturation dark current density.

*Avg. PCE is average PCE for 8 devices.

To verify this hypothesis, we apply the CV measurements on devices again under illumination and find the built-in potential decreases under illumination without CBL or methanol treatment, reflected by the left-shift Mott-Schottky plots. Because the Fermi level of surface states lies deep in the bandgap of blends, electrons at the conduction band prefer to fill the surface states at the contact and then the exchange of charge carriers between electrode and semiconductor is mainly accomplished via surface states. But this charge transfer process is slow, carriers will accumulate at the contact and induce undesirable surface recombination and poor extraction property. Especially under illumination photo-generated excitons provides a large amout of non-equilibrium carriers, highly efficient surface recombination is expected to occur at the interfacial layer. Surface states will get more charges with respect to the dark conditions, due to the slow charge transfer kinetics, too. It leads to an

Figure 3 | UPS spectra. UPS spectra of CBL on the surface of (a) active layer and (b) various metals. The spectra show the energy region of the secondary electron cut-off and are normalized to the peaks of ITO/ PEDOT:PSS in (a) and Ag/CBL in (b).
upward of band edges and at the same time the potential drop across the interfacial layer increases. This means the flat-band voltage decreases and could be observed in the Mott-Schottky plots that the position of $V_b$ moves to the left\cite{25,29}. While if surface states are shallow ones in the bandgap, the kinetics of charge transfer will be fast and the displacement of Mott-Schottky plots will be little or none. From Fig. 4 it is observed that without CBL or methanol treatment the $V_b$ varies about 0.14 V, proving that there are surface states at the cathode contact; after the methanol treatment the variation of $V_b$ decreases to only 0.04 V, indicating that surface states could be eliminated effectively by methanol wash; if 1.0 mg/ml NMPAC is used as the CBL, there is no shift of $V_b$ which implies this CBL can protect active layer from being damaged by metal evaporation.

Here we further investigate the surface states by CV and impedance measurements, and discuss it with a well-known device model proposed by Bisquert et al.\cite{30}. Generally the conjugated polymer is p-doped when exposed to air or moisture. After donor and acceptor being blended, the whole active layer is assumed as p-type semiconductor rather than insulator. So the Fermi level of blend is in the vicinity of HOMO level of donor. When low WF metal is deposited onto the surface of active layer, band bending occurs and Schottky barrier is formed (shown in Fig. 5a). Here the contact of anode is seemed as ohmic contact for the similar Fermi levels of blend and PEDOT:PSS layer. From the device model, the height of the built-in barrier is determined by the Fermi level difference between cathode ($\phi_c$) and blend ($E_{F0}$):

$$qV_b = E_{F0} - \phi_c$$

The barrier height could be obtained by applying standard Mott-Schottky analysis to the results of CV measurements. In order to explore the relationship between WF and barrier height of organic blend, we made solar cells with three different metals, Ca, Al and Ag. The structure of the devices is ITO/PEDOT:PSS/blend/metal and their Mott-Schottky plots are shown in Fig. 6. It can be seen $V_b$ changes little with different metals. Especially with Ca and Al as cathode, despite WF varies from 2.7 eV to 4.2 eV, $V_b$ changes only 0.09 V. This is quite opposite to the theory of Schottky that the barrier height is equal to the WF difference between metal and semiconductor. However it has been found that in inorganic devices the barrier height of metal-semiconductor systems is related to the surface states of semiconductor. If the variation of $V_b$ with WF of metals is defined with a slope, $S$, then according to the discussion above, if $S = 1$, there is no surface states; while if $S = 0$, the density of surface states is large and the Fermi level of metal will be totally pinned to 0.09 V.
that of surface states. Assuming that the surface states are distributed in an interfacial layer with thickness of about 0.5 nm, the surface states in this layer can exchange charge carriers with semiconductor and metal and withstand potential drop across itself. In the model of Bisquert, at the flat-band voltage, the depletion area in semiconductor disappears and the charges in the interfacial layer are only provided by the metal. Therefore if we further assume that the density of the surface states is constant (Ds) between the Fermi level of metal and surface states, then Ds could be calculated with the relationship between flat-band voltages and different metal WFs, e.g., S:

\[
S = \frac{1}{\frac{1}{q^2} \delta D_s / \varepsilon_0}
\]

Here \( \delta \) is the thickness of interfacial layer, \( \varepsilon_0 \) the dielectric constant of interfacial layer, \( \varepsilon_0 \) the permittivity of vacuum. The experimental results of Fig. 6 are summarized in the inset, the dashed line is a guide for eyes from which the slope S is calculated to be 0.11. \( \varepsilon_0 \) is 4.36, obtained by the CV measurement under high frequency condition (details are shown in Supplementary Information). Substituting them into equation (4), Ds is deduced to be \( 3.9 \times 10^{14} \text{ cm}^2 \text{ eV}^{-1} \).

Impedance measurement and simulation. Then we apply a combined experimental and simulation approach, impedance spectroscopy (IS), to probe the dynamics of charge transfer and recombination at the interface. IS is a non-destructive tool that has been commonly used in OSCs in the past few years. Because it can distinguish different processes inside the working devices according to their response to the external applied alternating current (AC) signal. The device structure used for IS measurement is ITO/PEDOT:PSS/PTB7:PC71BM/CBL (w/wo)/Al. Cole-Cole plots of the devices under 1 sun illumination and different bias are shown in Fig. 7a and b. It can be seen the impedance responses of these devices are semicircles in the complex plane with lateral axis standing for the real part of the impedance (ReZ) and vertical axis as the negative imaginary part of the impedance (-ImZ). At high frequencies (shown in the inset of Fig. 7), it is noted all the curves intersect with lateral axis at about 25 V, which represents for series resistance of the devices. While at low frequencies, these plots intersect with lateral axis at different points which is related to recombination resistance. When applied bias increases from 0.1 V to the vicinity of Voc, recombination resistance decreases rapidly. This is because under high bias density of carriers inside the device increases significantly, as a result, more recombination events are induced.

In order to extract these constants in impedance response from different processes, equivalent circuits are often established to fit the experimental data. Fig. 8a and b show the equivalent circuits we use for devices with CBL and without CBL. R0 is series resistance, C1 is the geometrical capacitance of the whole device and R1 stands for the charge transport. It is well-known that paralleled combination of resistance and capacitance accounts for the recombination process happened at the interface of donor and acceptor. In the famous transmission line model, infinite R/C circuits are connected in series to represent for recombination processes with different relaxation time. For simplicity, we use R2/CPE to stand for the distribution of relaxation time for different recombination processes. CPE is abbreviation for constant phase element, generally used to denote non-ideal capacitor. In Fig. 8 (b) a third parallel R3||C3 is used to stand for the recombination induced by the surface states.
displays the fitting results for devices with CBL under +0.7 V bias (using model in Fig. 7a) and without CBL under +0.5 V bias (using model in Fig. 7b). The biases are chosen to make the devices work around the flat-band points. It can be seen the fitting lines show good agreement with the measuring data, with the errors under 2% in all cases (provided by the built-in software of our IS equipment).

Capacitance $C_3$ extracted from fitting is about 30 nF from which the density of surface states can be calculated by $\frac{C_3}{q^2A}$ simply. Here $A$ is the area of device, therefore $D_I = 4.5 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$. This value is two orders of magnitude lower than the one calculated by CV measurement, which can be attributed to the rough assumption of parameters in the calculation, such as thickness of interfacial layer, deviation of metal WF deposited in high vacuum and in our experiments, density of surface states being constant and so on.

In addition, from impedance spectra the effective lifetime can be estimated. The peak of the large semicircle in Cole-Cole plot corresponds to a frequency, and the reciprocal of this frequency is the effective lifetime. For device with CBL under +0.6 V bias and device without CBL under +0.4 V (each bias is chosen in the vicinity of maximum power point), the effective lifetime is 7.7 $\mu$s and 4.6 $\mu$s, respectively, indicating the device with CBL suffers less recombination.

**Discussion**

At last we explore the interface of CBL/cathode by UPS. The samples used are: Al, Al/CBL, Ag, Ag/CBL, Au and Au/CBL, respectively and results are displayed in Fig. 3b. It is noted here that the measured WFs of Al and Ag are quite distinct from the common values (4.2 eV for Al, 5.4 eV for Au). This is because the samples are exposed to the air before they are transferred into the chamber of UPS, Al was oxidized and 2.98 eV should be the WF of AlO$_x$; while the common WF of Au can be obtained when measured at clean surface in high vacuum condition, our result indicates the surface of Au layer may be soiled in the air. At this time the WFs of metals show displacement after spin-coating CBL. This indicates that dipole forms at this interface and pulls down the WF of cathode.

In Bisquert’s model, $V_{OC}$ is determined by Fermi level difference of semiconductor and cathode (Schottky barrier). Based on our observations, it is shown however, surface states pin the Fermi level of organic semiconductor to a certain value. This value is independent on the Fermi level of metal used as cathode. That is to say, the energy level of surface states dominates the height Schottky barrier and acts as Fermi level of cathode. Therefore even if CBL can form dipole moments at interfaces of blend/CBL and CBL/cathode, it plays a small part in the whole built-in potential.

While if surface states are suppressed effectively during the spin coating process, the Fermi level of organic semiconductor is unpinned and influence of CBL on $V_{OC}$ is the overall energy level shift between semiconductor and cathode induced by the dipole moments. This has also been observed by other group.

In conclusions, we use a fullerene based polar molecule NMPAC as CBL in OSCs, and investigate its role in enhancing the device performance. It is found that the effect of CBL is originated from three aspects. Both solvent and solute of the CBL solution contribute to the optimized performance. Firstly the solvent, methanol, which is used to dissolve NMPAC, can remove the intrinsic states at the surface of the active layer. As a result, the Fermi level pinning at the surface is relieved and surface recombination is suppressed effectively. Furthermore, an additional layer of NMPAC formed at the surface of blend by spin-coating, can protect the active layer from the damage of hot atoms during cathode evacuation, and the NMPAC layer (owing deep HOMO level) can also block the holes from transferring to the cathode without hindering electrons extraction. Therefore even if deposited cathode induced states at the surface of CBL, there would be less surface recombination due to the lack of holes. Finally the interfacial dipole moments formed at blend/CBL and/or CBL/cathode interface, alter the energy level alignment. It is very meaningful when surface states are eliminated. We believe our study here is of great importance to understanding the role of CBL in OSCs, designing new buffer layer materials and optimizing the device performance.

**Methods**

**Device Fabrication.** P3HT, PC71BM and PTB7 were purchased from Rieke Metals, Nano-C and 1-Materials, respectively. All the materials used were as received. The configuration of the devices is shown in Fig. 1. The pre-cleaned ITO glass substrate was firstly treated by oxygen plasma for 6 min, and then a 30 nm PEDOT:PSS (poly (3, 4-ethylenedioxythio-phene)-poly(styrenesulfonate), Clevios P VPAl 4083, from H. C. Starck) layer was spin-coated on the substrate, followed by thermal treatment at 140 °C for 10 min on a hotplate. The substrate was then transferred into the nitrogen glove box, and all the other processes were done in the glove box unless otherwise stated. PTB7:PC71BM were dissolved in o-dichlorobenzene (o-DCB) to be the active layer with the ratio of 10:15 mg/mL, with 3% volume 1, 8-diiodooctane as the additive. Then the blend was spin-coated onto the substrate at 900 rpm for 90 s. NMPAC was dissolved in methanol with varied concentrations and spin-coated atop

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**Figure 7** | Impedance spectra of devices with and without CBL. Cole-Cole plots of devices under 1 sun illumination and different bias: (a) with 1.0 mg/ml NAMPC as CBL, (b) without CBL. Insets show the high frequency part of the plots from which the series resistances can be extracted.
the active layer at 3,000 rpm for 30 s. Finally, top electrodes were deposited in vacuum at a pressure of about $5.0 \times 10^{-3}$ Pa. The active device area was 4.2 mm$^2$.

The thickness of the interlayer was determined using a Profilometer, combined with extrapolation from an absorbance-thickness curve which assumed a linear dependence of absorbance at 320 nm for NMPAC.

J–V Characterization and EQE. Current density-voltage (J–V) characteristics of the devices were measured with a computer-controlled Keithley 2400 source meter and Newport 6279 NS solar simulator (450 W) with 100 mW/cm$^2$ illumination. The external quantum efficiency (EQE) spectra were collected using Oriel IQE-200TM in the atmosphere. UPS spectra were obtained using a He discharged lamp (He I 21.22 eV).

CV and IS measurements. The capacitance-voltage (CV) and impedance spectroscopy (IS) measurements were performed using a Zahner Zennium electrochemical workstation. The CV measurements were recorded at a frequency of 1 kHz for extracting $V_{th}$ and $N_{th}$, and at a frequency of 1 MHz to calculate the dielectric constant of blend. The impedance spectra were recorded by applying varied AC signal from 10 Hz to 1 MHz. All the AC oscillating amplitudes were set as low as 10 mV (rms) to maintain the linearity of the response.

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**Author contributions**

Z.Z. synthesized the NMPAC and performed cyclic voltammograms experiments. B.Q. performed the experiments and data analysis. B.Q., Z.Z. and J.W. wrote the paper, J.W. supervised the project.

**Additional information**

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