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Surface modification of metal oxide using ionic liquid molecules in hybrid organic–inorganic optoelectronic devices†

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We demonstrate enhanced device performance by surface modification of n-type ZnO using ionic liquid molecules (ILMs) in hybrid organic–inorganic polymeric light-emitting diodes (HyPLEDs) and solar cells (HySCs). Spontaneously aligned dipole polarization within the thin ILMs layer reduces the electron injection barrier, and significantly enhances the electron injection efficiency in HyPLEDs and the open-circuit voltage (V_{OC}) in HySCs.

Organic/polymer-based optoelectronic devices have been investigated extensively over the past two decades for display, energy harvest, solid-state lighting and flexible electronic devices.^{1–4} For commercial applications, so much effort has been devoted in the hope of improving device efficiency and lifetime in organic/polymer light emitting diodes (LEDs). Among various device configurations, hybrid organic–inorganic polymeric light-emitting diodes (HyPLEDs) using metal oxides (ZnO, TiO₂, ZrO₂, HfO₂, and MoO₃) as charge injection/transporting layers have been regarded as promising candidates due to high device performance and exceptional air-stability.^{5–14} Nevertheless, considerable room for improvement of device performance remains due to unbalance of electron and hole carriers transfer.

One way to solve the problem of the unbalance of electron and hole carriers transfer is to control the band gap of each contact through the surface modification for an ohmic contact. Especially, the interfacial engineering between the organic semiconductor and the inorganic electrode is critical in the performance of organic electronic devices, and the work function between the contact layers greatly affects the carrier injection and transport in organic semiconductors. For hybrid solar cells (HySCs), electrical contact between the active layer and metal oxide is critical for charge transfer in bilayer structure. The contact resistance between layers must be minimized

for high device performance. For HyPLEDs, balanced charge carrier injection and transport are needed to obtain highly efficient device performance. However, the operational mechanism of the device in HyPLEDs is hole-dominated using a MoO₃ hole injection layer; hence electron injection is poor compared to hole injection due to the large energy barrier difference between the conduction band of ZnO (~4.0 eV)¹³ and the lowest unoccupied molecular orbital (LUMO) of an active layer such as poly(phenylvinylene): super yellow (SY) (~2.7 eV).⁷ For optimized device performance of HyPLEDs, enhanced electron injection at the counter electrode is crucial in order to balance the charge injection and, finally the electroluminescence efficiency can be improved.

Several approaches have been suggested to efficiently promote electron injection and transfer by modifying the interfaces between the electrodes and the active polymer layers using cesium carbonate (CS₂CO₃),^{5,7} lithium fluoride,¹⁵ conjugated polyelectrolytes,¹⁶ ionic polymers,¹⁷ and self-assembled dipole monolayer (SADM).^{11,13,18}

Here we present a direct method to notably enhance the device performance by surface modification of the ZnO layer using ionic liquid molecules (ILMs) such as 1-benzyl-3-methylimidazolium chloride (benmim-Cl).

Fig. 1(a) shows the complete device architecture of HyPLEDs and HySCs. The hybrid devices were fabricated by successive deposition

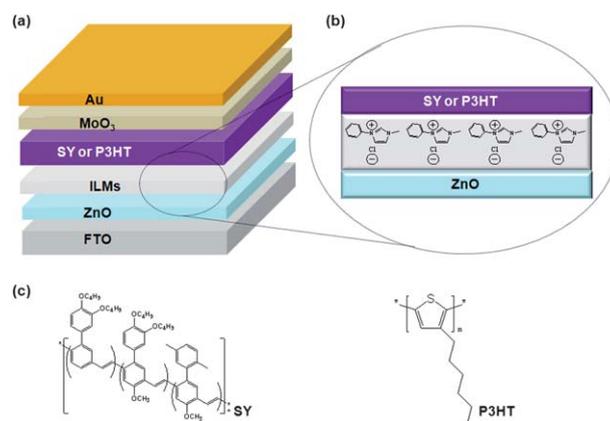


Fig. 1 (a) Device structure of P3HT and SY : ZnO-based hybrid devices with ILMs layer. (b) Schematic illustration of cations and anions of ILMs between ZnO and active layer. (c) Chemical structures of poly(phenylvinylene), super yellow and poly(3-hexylthiophene), P3HT.

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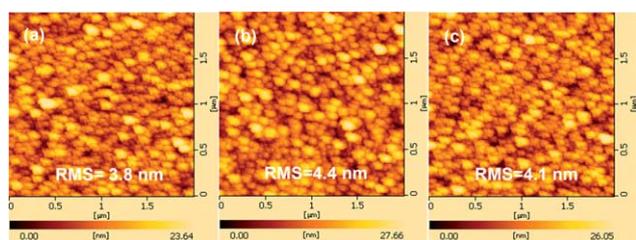


Fig. 2 AFM images (a) without modification of ZnO layer, with surface modification of ZnO layer using (b) SADM (BA-CH₃) and (c) ILMs.

of FTO as transparent cathode, ZnO, ILMs, an active layer (SY (Merck Co., $M_w = 1\,950\,000\text{ g mol}^{-1}$), or poly(3-hexylthiophene) (P3HT, Rieke Metal inc., $M_w = 50\,000\text{ g mol}^{-1}$, ~95% regio-regularity)), MoO₃ and Au as the anode. An 80 nm thick n-type ZnO layer was prepared by spray pyrolysis method from 80 mg mL⁻¹ zinc acetate dihydrate/methanol precursor solutions at 400 °C. For the ILMs modified ZnO layer, an ionic liquid solution dissolved in water (0.1 wt%) was spin-coated at 5000 rpm onto a ZnO layer and then annealed at 120 °C for 10 min to remove residual water. The preparation method of the SADM (BA-CH₃) layer was shown in ref. 13. The SY (Fig. 1(c)) solution dissolved in chlorobenzene (0.7 wt%) was spin-cast at 2000 rpm on top of the buffer layer and annealed at 80 °C for 30 min to obtain a 150 nm thick SY layer in HyPLEDs, whereas P3HT (Fig. 1(c)) solution dissolved in chlorobenzene (1.0 wt%) was spin-cast at 700 rpm on top of the buffer layer and annealed at 150 °C for 10 min to obtain a 100 nm thick P3HT layer in HySCs.

In Fig. 2, atomic force microscopy (AFM) images of ZnO surface layers are preserved even after coating the SADM and ILMs on the ZnO layers; the roughness values of the three sample surfaces are similar (rms roughness = 3.8, 4.4, and 4.1 nm respectively). However, the contact angles of the ZnO layer with (b) SADM and (c) ILMs modification are quite different from that without modification, as shown in Fig. S1†. The combined results confirm the formation of uniform monolayers of ILMs and SADM on the ZnO layers.

The ZnO/SY interface has a significant electron injection barrier (~1.3 eV) compared to the MoO₃/SY interface. Consequently, the electron and hole injections are severely unbalanced. We modified the ZnO interface by inserting buffer layers such as SADM or ILMs. The ILMs used in this work are cationic 1-benzyl-3-methylimidazolium with chloride counter ions. The insertion of charged ILMs between the ZnO and the emissive layer brings spontaneous dipolar polarization within the layer, as shown in Fig. 1(b). While hydrophilic Cl anions prefer an inorganic ZnO interface, hydrophobic cations spontaneously prefer an organic SY interface. This spontaneous dipole polarization was readily stabilized with an

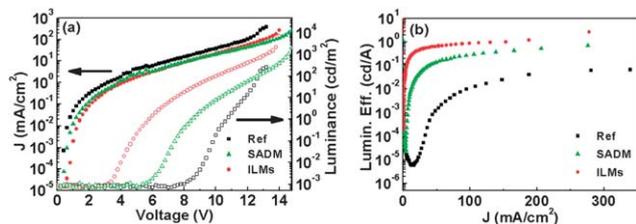


Fig. 3 HyPLED characteristics of (a) current density vs. applied voltage (J - V), luminance vs. applied voltage (L - V); (b) luminous efficiency vs. current density (LE - J) curves with and without surface modification of ZnO layer using SADM (BA-CH₃) and ILMs.

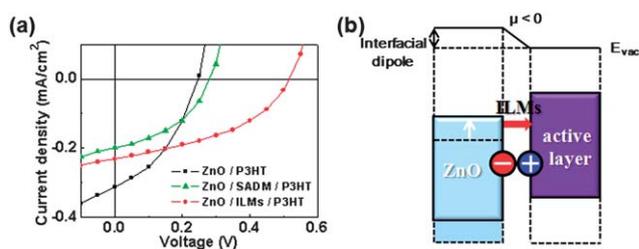


Fig. 4 (a) J - V characteristics of ZnO/P3HT hybrid solar cells with and without surface modification of ZnO layer using SADM (BA-CH₃) and ILMs. (b) Schematic energy diagrams for flat band conditions the ZnO/ILMs/active layer.

annealing process of the active polymer.^{19,20} If the dipoles within ILMs are directed away from the ZnO surface, it causes an upward shift of the vacuum level of ZnO and, thereby, the band edge of ZnO shifts closer to the energy level of SY, as shown in Fig. 4(b). Therefore, the resultant ZnO work function and the electron injection barrier decrease. The BA-CH₃ modified ZnO layer with negative dipoles caused by different electronegativity of functional groups also reduced the electron injection barrier in previous experiments.^{11,13} The difference of ILMs (benmim-Cl) from SADM (BA-CH₃) is that self-aligned dipole polarization of ILMs arises due to the self-aligned distribution of ions within the layers, and the dipole polarization effect of ions on the work function of the ZnO layer is expected to be higher than that of SADM.

The device performances of HyPLEDs with ZnO, SADM-modified ZnO and ILMs-modified ZnO are presented in Fig. 3. We note that all the devices exhibited original green emission of SY, regardless of the SADM and ILMs interfacial modification and applied voltages. Compared to the devices without interfacial modification, those modified with negative dipole SADM and ILMs demonstrated remarkably enhanced PLED performances, as shown in Fig. 3. Especially, devices using ILMs showed greatly enhanced luminance and luminous efficiency, and low turn-on voltage. Table 1 summarizes the detailed device characteristics including luminance, luminous efficiency, and turn-on voltage. The device modified with ILMs shows higher device performance with a luminance of 7500 cd m⁻² (at 14.0 V), and luminous efficiency of 2.7 cd A⁻¹ (at 14.0 V), which correspond to approximately a forty-fold increase compared to the electroluminescence efficiency of an unmodified device. We also compare the turn-on voltages for electroluminescence in Fig. 3(a). The turn-on voltage of a device with an ILMs layer is 3.2 V, whereas the turn-on voltages of devices with SADM layers and without buffer layers are 5.6 V and 8.0 V, respectively. This lower turn-on voltage of devices with ILMs layers confirms that the electron injection barrier is greatly reduced between ZnO/ILMs and SY.

Fig. 4(a) gives current density versus voltage (J - V) characteristics of ZnO/P3HT HySCs with and without a buffer layer, respectively. The photovoltaic characteristics are summarized in Table 2. The J - V curves for devices were measured under AM 1.5G illumination at 100 mW cm⁻². The device without a buffer layer shows short circuit current (J_{SC}) of 0.31 mA cm⁻², open circuit voltage (V_{OC}) of 0.25 V, fill factor (FF) of 0.39, and power conversion efficiency (PCE) of 0.030%. For devices with SADM, we obtained J_{SC} of 0.20 mA cm⁻², V_{OC} of 0.28 V, FF of 0.43, and PCE of 0.024%. The slightly increased V_{OC} is attributed to a change of interfacial energy level due to the molecular dipole of SADM between the P3HT and the ZnO layer, while the decreased J_{SC} is thought to originate from the interference

Table 1 Light-emitting device characteristics of SY : ZnO-based HyPLEDs with and without surface modification of ZnO layer using SADM (BA-CH₃) and ILMs

Device configuration	Maximum luminance/cd m ⁻² (at voltage)	Maximum luminous efficiency/cd A ⁻¹ (at voltage)	Turn-on voltage/V
FTO/ZnO/SY/MoO ₃ /Au	270 (13.2 V)	0.07 (13.4 V)	8.0
FTO/ZnO/SADM/SY/MoO ₃ /Au	2000 (14.8 V)	0.73 (14.8 V)	5.6
FTO/ZnO/ILMs/SY/MoO ₃ /Au	7500 (14.0 V)	2.70 (14.0 V)	3.2

Table 2 Device characteristics of ZnO/P3HT hybrid solar cells with and without surface modification of ZnO layer using SADM (BA-CH₃) and ILMs

Device configuration	J_{SC} /mA cm ⁻²	V_{OC} /V	FF	η (%)
FTO/ZnO/P3HT/MoO ₃ /Au	0.31	0.25	0.39	0.030
FTO/ZnO/SADM/MoO ₃ /Au	0.20	0.28	0.43	0.024
FTO/ZnO/ILMs/P3HT/MoO ₃ /Au	0.23	0.52	0.43	0.051

of the charge transfer from the P3HT to the ZnO by SADM.¹¹ The device with an ILMs layer exhibits J_{SC} of 0.23 mA cm⁻², V_{OC} of 0.52 V, FF of 0.43, and PCE of 0.051%. The remarkable increase in device efficiency results in a two-fold increased V_{OC} compared to that of the reference device, which is attributed to the shift of the band edge of the ZnO closer to the vacuum level of P3HT due to spontaneous dipole polarization within the ILMs layer. Decreased J_{SC} is attributed to hindrance to direct charge transfer from P3HT to ZnO.^{11,20} Fig. 4(b) schematically illustrates the energy band diagrams for the flat band condition of hybrid devices with surface modification using ILMs. A dipole moment pointed away from the ZnO would effectively shift the band edge of the ZnO closer to the vacuum level of the active layer.

To understand the mechanism of interfacial dipoles within ILMs, the time response of L and LE in HyPLEDs with and without surface modification of the ZnO layer using SADM (BA-CH₃) and ILMs was investigated under a continuous bias of 11 V; the values of L and LE did not change significantly, as shown in Fig. S2†. This shows that self-assembled and permanent interfacial dipoles arise between ZnO/ILMs and the active polymer interface, dipoles of which shift the vacuum level at that interface. The results of J - V - L measurements in HyPLEDs and V_{OC} characteristics in HySCs confirm that the ionic dipoles are spontaneously self-aligned at the ZnO/active layer, which reduced the electron transfer barrier and enhanced device performance.

In conclusion, we demonstrated a straightforward way to notably increase the device performance by interfacial modification between ZnO and active polymer layers using ILMs. Ionic dipole polarization effectively influenced the electron injection barrier between the conduction band of ZnO and the LUMO of the active layer and remarkably enhanced the electron injection and transfer in the corresponding device performance of HyPLEDs and HySCs. The modified HyPLEDs using ILMs showed a luminous efficiency of 2.7 cd A⁻¹ (14.0 V) and luminance of 7500 cd m⁻² (14.0 V), which is approximately forty-fold higher than the electroluminescence efficiency of unmodified HyPLEDs. Furthermore, the ionic dipole polarization effect was confirmed by reduction of turn-on voltage of electroluminescence and two-fold increase of the open-circuit voltage (V_{OC}) of photovoltaic devices due to the interfacial modification effect of the ZnO layer using ILMs. This interfacial engineering offers a new design scheme for carrier injection and transfer for organic/

polymeric optoelectronic devices, such as photovoltaic cells and LEDs.

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