

Efficient hybrid organic-inorganic light emitting diodes with self-assembled dipole molecule deposited metal oxides

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We investigate the effect of self-assembled dipole molecules (SADMs) on ZnO surface in hybrid organic-inorganic polymeric light-emitting diodes (HyPLEDs). Despite the SADM being extremely thin, the magnitude and orientation of SADM dipole moment effectively influenced the work function of the ZnO. As a consequence, the charge injection barrier between the conduction band of the ZnO and the lowest unoccupied molecular orbital of poly(9,9'-dioctylfluorene)-co-benzothiadiazole could be efficiently controlled resulting that electron injection efficiency is remarkably enhanced. The HyPLEDs modified with a negative dipolar SADM exhibited enhanced device performances, which correspond to approximately a fourfold compared to those of unmodified HyPLEDs. © 2010 American Institute of Physics. [doi:10.1063/1.3453759]

The challenging demand for ultrathin, mechanically flexible displays has stimulated research attention on polymer light-emitting diodes (PLEDs).¹ Among various device architectures, hybrid organic-inorganic polymeric light-emitting diodes (HyPLEDs) that utilize metal oxides as charge transporting and injection layers are promising candidates for low-cost, high-performance, and solution-processible flexible displays. HyPLEDs exhibit high luminance, low turn-on voltages, and exceptional air stability, largely owing to the attractive properties of metal oxide layers, such as high electrical conductivity, tunable refractive index, excellent air stability, and high optical transparency.²⁻⁷ Nevertheless, considerable room for the enhancement of the device performances of HyPLEDs still remains. As an example, n-type metal oxide such as ZnO is frequently used as an electron injection layer for a poly(9,9'-dioctylfluorene)-co-benzothiadiazole (F8BT) emissive layer.^{3,7} However, injection barrier between the conduction band of the ZnO (~ 4.0 eV) (Ref. 8) and the lowest unoccupied molecular orbital (LUMO) of the F8BT (~ 3.0 – 3.5 eV) (Ref. 9) hinders efficient electron injection.

Recent work on HyPLEDs has demonstrated that MoO₃ provides an unprecedented Ohmic contact to the high ionization potential of F8BT, which is a widely used, air-stable, and highly efficient green-light-emitting polymer. Owing to the idealized electric contact, an extremely high injection current density of holes can be generated.^{6,10} Consequently, electron and hole injection from each electrode is seriously unbalanced such that the recombination probability of electrons and holes is significantly deteriorated. For optimized device performance of HyPLEDs employing a MoO₃ hole injection layer, enhanced electron injection at the counter electrode is crucial to balance the charge injection. To date, several approaches have been exploited to promote electron

injection by interfacial modification between the electron injection layer and emissive polymer layers. Electrodes with cesium carbonate (Cs₂CO₃),^{2,4} metal fluoride,¹¹ conjugated polyelectrolytes,¹² ionic polymers,¹³ and radiative surface treatment of electrodes¹⁴ have been reported to improve electron injection so far.

Here we present a straightforward strategy to remarkably enhance the electron injection efficiency of HyPLEDs by surface modification of n-type metal oxide using self-assembled dipole molecules (SADMs).

The complete device architecture of HyPLEDs with a single F8BT layer and the chemical structures of carboxylic acid based SADMs employed in this work are presented in Fig. 1. The HyPLEDs were prepared by the sequential deposition of fluorine doped tin oxide, ZnO, SADM, F8BT, MoO₃, and Au layers [Fig. 1(a)]. An 80 nm thick n-type ZnO layer was prepared by spray pyrolysis deposition from 80 mg mL⁻¹ zinc acetate dihydrate/methanol precursor solutions. The surface of the ZnO layer was modified with a few nanometer thick SADM layer by spin-coating from 7 mM

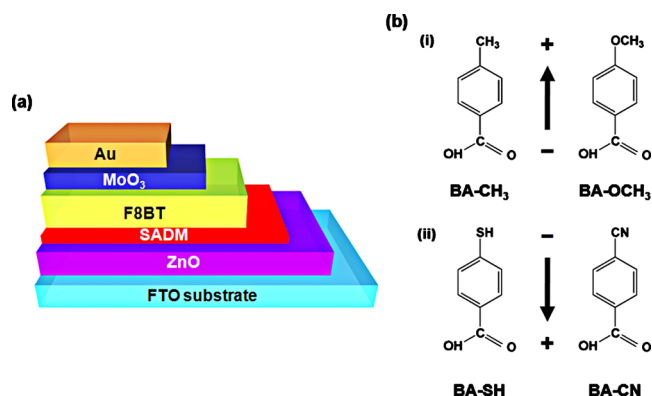


FIG. 1. (Color online) (a) Device architecture of single F8BT layer HyPLEDs with SADMs on a ZnO surface. (b) Chemical structures of carboxylic acid based SADMs: (i) negative dipole molecules: BA-CH₃, and BA-OCH₃, (ii) positive dipole molecules: BA-SH and BA-CN.

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ethanol solutions. The carboxylic acid based SADMs consisting of (i) negative dipoles containing an electron-donating group and (ii) positive dipoles containing an electron-withdrawing group are well-known interfacial modifiers for hydroxyl ($-\text{OH}$) terminated metal oxides [Fig. 1(b)].^{15,16} A uniform SADM layer was readily formed on the ZnO surface through the covalent bonding between the carboxyl group ($-\text{COOH}$) of the SADM and the hydroxyl group ($-\text{OH}$) of the ZnO. The formation of an SADM layer was confirmed by contact angle measurement. A 100 nm thick F8BT emissive layer was spin cast from 20 mg mL⁻¹ p-xylene solutions onto the SADM-modified ZnO surface, and then thermal annealing was performed at 155 °C for 1 h under a nitrogen atmosphere.¹⁷ A 10 nm thick p-type MoO₃ layer and a 60 nm thick Au layer were subsequently evaporated on the F8BT layer to complete the device fabrication.

The presence of adequate molecular dipoles at the interface between ZnO and polymer emissive layer plays a crucial role in enhancing the charge injection within devices. The carboxylic acid based SADMs employed in this study have two types of dipole moments (μ). One is pointing away from the ZnO surface (BA-CH₃ and BA-OCH₃) and another is pointing toward the ZnO surface (BA-SH and BA-CN), as described in Fig. 1(b). In accordance with the dipole moments of SADMs, the expected variation in the ZnO work function ($\Delta\Phi$) is given as follows:¹⁸

$$\Delta\Phi = eN \left(\frac{\mu_n}{\epsilon_{\text{SADM}}\epsilon_0} \right), \quad (1)$$

where N is the surface density of the molecules, μ_n is the molecular dipole moment normal to the surface, ϵ_{SADM} is the dielectric constant of the SADM, and ϵ_0 is the permittivity of free space. According to the previously reported literature values, the dielectric constant of aromatic molecules is assumed to be $\epsilon_{\text{SADM}}=5.3$. The sign of μ_n depends on the direction of the dipoles. The negative dipole ($\mu_n < 0$) indicates that the dipole moment points away from ZnO surface, whereas the positive dipole ($\mu_n > 0$) corresponds to the dipole moment points toward the ZnO surface. It is worth noting that the surface coverage, N , is also an important parameter in determining the magnitude of $\Delta\Phi$.

Figures 2(a)–2(c), schematically illustrate the energy band diagrams for flat band conditions of HyPLEDs without or with SADM modification.^{15,16} A dipole moment pointed away from the ZnO [Fig. 2(b)] would effectively shift the band edge of the ZnO closer to the vacuum level of the F8BT. Accordingly, the work function of ZnO and the energy barrier to electron injection would decrease from those without SADM interface modification [Fig. 2(a)]. In contrast, a dipole moment pointing toward the ZnO surface [Fig. 2(c)] would conversely shift the band edge of the ZnO away from the local vacuum level of the F8BT and increase the work function and the energy barrier for electron injection.

In order to clarify the effect of the molecular dipoles on the ZnO work function, ultraviolet photoemission spectroscopy (UPS) measurements were performed. Figure 2(d) shows the variation in the experimentally measured work functions of the ZnO (Φ_{ZnO}) as a function of the SADM dipole moments (μ_{SADM}). The μ_{SADM} values were confirmed by calculation using CHEM3D ULTRA software. As expected, negative dipoles effectively lowered the work function of the

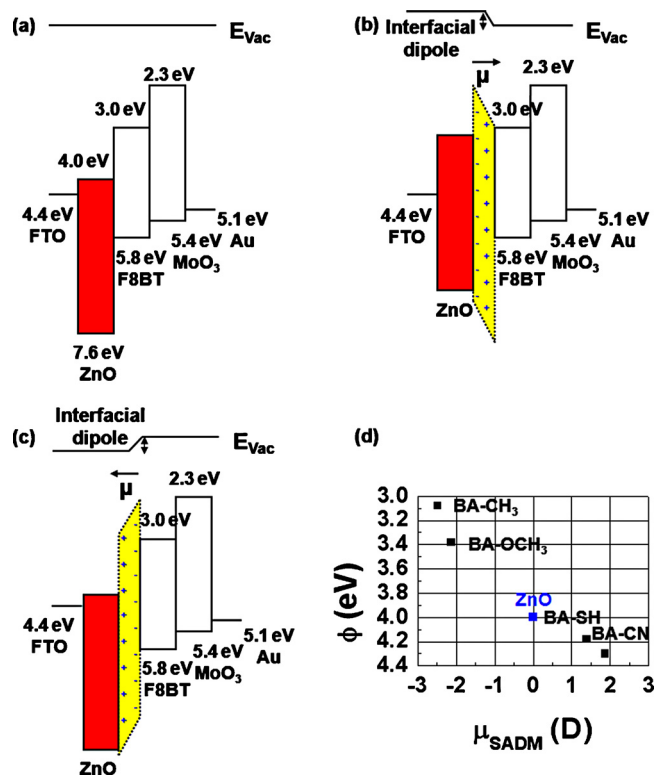


FIG. 2. (Color online) Schematic energy diagrams for flat band conditions of HyPLEDs with (a) unmodified ZnO, (b) negative, and (c) positive SADM modified ZnO. (d) Experimentally measured work functions of ZnO as a function of the μ_{SADM} using UPS.

ZnO: 3.08 eV for BA-CH₃-modified ZnO, and 3.38 eV for BA-OCH₃-modified ZnO, while 4.0 eV for unmodified ZnO. Positive dipoles raised the work function: 4.18 eV for BA-SH-modified ZnO and 4.3 eV for BA-CN-modified ZnO.

The device performances of HyPLEDs with SADM-modified ZnO are presented in Fig. 3. The device perfor-

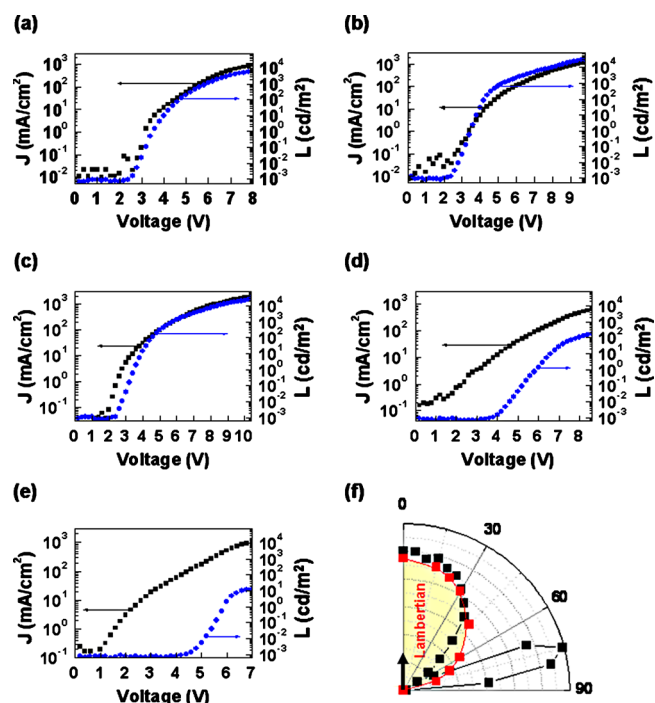


FIG. 3. (Color online) J-V-L characteristics for SADM-modified ZnO layer in HyPLEDs.

TABLE I. Detailed device characteristics of HyPLEDs without or with SADM modification of ZnO.

Device configuration	Maximum luminance (cd/m ²) (at voltage)	Maximum luminous efficiency (cd/A) (at voltage)	Turn on voltage (V)
ZnO/F8BT	11 000 (9.4 V)	0.7 (8.0 V)	2.4
ZnO/BA-CH ₃	38 000 (9.8 V)	2.8 (9.6 V)	2.2
ZnO/BA-OCH ₃	38 200 (10.4 V)	2.1 (10.0 V)	2.4
ZnO/BA-SH	200 (8.8 V)	0.01 (8.6 V)	4.0
ZnO/BA-CN	15 (7.6 V)	0.001 (6.8 V)	4.6

mances were evaluated by the current density and luminance versus applied voltage (J-V-L) measurements in atmospheric conditions without further encapsulation. Figures 3(a)–3(e) show the J-V-L characteristics of the devices employing an SADM-modified ZnO layer. We note that all the devices exhibited the original green emission of the F8BT, regardless of the SADM interfacial modification and applied voltages. In comparison to the devices without interfacial modification [Fig. 3(a)], those modified with negative dipole SADM, such as BA-CH₃ [Fig. 3(b)] and BA-OCH₃ [Fig. 3(c)], demonstrated remarkably enhanced PLED performances. They demonstrated greatly enhanced luminance and luminous efficiency and low turn-on voltages. In contrast, the devices modified with positive dipole SADM, such as BA-SH [Fig. 3(d)] and BA-CN [Fig. 3(e)], showed significant deterioration of device performances. Table I summarizes the detailed device characteristics including luminance, luminous efficiency, and turn-on voltages. The devices modified with the negative dipole molecules of BA-CH₃ shows the best device performance with a luminance of 38 000 cd/m² (at 9.8 V), luminous efficiency of 2.8 cd/A (at 9.6 V), and turn-on voltage of 2.2 V, which correspond to approximately a fourfold increase in desirable characteristics compared to unmodified devices. We note that all of the characteristics elucidated in Table I were corrected with the correction factor of 1.2. Since the metal oxide has a high refractive index ($n_{r-\text{ZnO}} \approx 2$), optical wave-guiding and non-Lambertian edge emissions occurred in these HyPLEDs. These effects resulted in angle dependent electroluminescent emission that considerably deviated from the Lambertian emission patterns of conventional PLEDs [Fig. 3(f)]. In our measurement setup, a photodetector is located in the forward direction with the luminance output calculated assuming a Lambertian emission. Thus, the correction of luminance and luminous efficiency was required for the exact evaluation of device performances. For the measurement of angular dependence of luminescence, a reference Si photodetector was rotated to detect the luminance output as a function of external viewing angle. A correction factor of 1.2 was obtained by comparing the two integrated values of measured emission patterns.³

The influence of SADM interfacial modification upon electron injection was also confirmed by electron-only device performance as shown in Fig. S1(a) (see section 1 in Ref. 19). As observed in J-V-L and electron-only device characteristics, the negative dipoles acted as molecular electron-injection layers, which reduced the injection barrier

for electrons and facilitated the electron transporting and injection within HyPLEDs.

In summary, we have demonstrated that straightforward surface modification using SADM remarkably enhances the electron injection efficiency of a metal oxide and the corresponding device performance of HyPLEDs. Despite the SADM being extremely thin, the magnitude and orientation of SADM dipole moment effectively influenced the work function of the ZnO layer. As a consequence, the charge injection barrier between the ZnO conduction band and the F8BT LUMO could be efficiently controlled. Our approach is potentially useful for advanced optoelectronic devices, such as electrically pumped organic laser diodes with enhanced electron injection efficiency of minority carriers, recombination opportunity, and reduced excited state optical absorption associated with injected carriers.

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- ¹R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, and W. R. Salaneck, *Nature (London)* **397**, 121 (1999).
- ²K. Morii, T. Kawase, and S. Inoue, *Appl. Phys. Lett.* **92**, 213304 (2008).
- ³D. Kabra, M. H. Song, B. Wenger, R. H. Friend, and H. J. Snaith, *Adv. Mater.* **20**, 3447 (2008).
- ⁴H. J. Bolink, E. Coronado, J. Orozco, and M. Sessolo, *Adv. Mater.* **21**, 79 (2009).
- ⁵N. Tokmoldin, N. Griffiths, D. D. C. Bradley, and S. A. Haque, *Adv. Mater.* **21**, 3475 (2009).
- ⁶Y. Nakayama, K. Morii, Y. Suzuki, H. Machida, S. Kera, N. Ueno, H. Kitagawa, Y. Noguchi, and H. Ishii, *Adv. Funct. Mater.* **19**, 3746 (2009).
- ⁷M. H. Song, D. Kabra, B. Wenger, R. H. Friend, and H. J. Snaith, *Adv. Funct. Mater.* **19**, 2130 (2009).
- ⁸H. J. Bolink, E. Coronado, D. Repetto, and M. Sessolo, *Appl. Phys. Lett.* **91**, 223501 (2007).
- ⁹L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus, and R. H. Friend, *Nature (London)* **434**, 194 (2005).
- ¹⁰M. Kröger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, and A. Kahn, *Org. Electron.* **10**, 932 (2009).
- ¹¹L. S. Hung, C. W. Tang, and M. G. Mason, *Appl. Phys. Lett.* **70**, 152 (1997).
- ¹²F. Huang, L. Hou, H. Wu, X. Wang, H. Shen, W. Cao, W. Yang, and Y. Cao, *J. Am. Chem. Soc.* **126**, 9845 (2004).
- ¹³T. W. Lee and O. O. Park, *Adv. Mater.* **13**, 1274 (2001).
- ¹⁴M. G. Mason, L. S. Hung, C. W. Tang, S. T. Lee, K. W. Wong, and M. Wang, *J. Appl. Phys.* **86**, 1688 (1999).
- ¹⁵C. Goh, S. R. Scully, and M. D. McGehee, *J. Appl. Phys.* **101**, 114503 (2007).
- ¹⁶H.-L. Yip, S. K. Hau, N. S. Baek, H. Ma, and A. K. -Y. Jen, *Adv. Mater.* **20**, 2376 (2008).
- ¹⁷C. L. Donley, J. Zaumseil, J. W. Andreasen, M. M. Nielsen, H. Sirringhaus, R. H. Friend, and J.-S. Kim, *J. Am. Chem. Soc.* **127**, 12890 (2005).
- ¹⁸S. Khodabakhsh, D. Poplavskyy, S. Heutz, J. Nelson, D. D. C. Bradley, H. Murata, and T. S. Jones, *Adv. Funct. Mater.* **14**, 1205 (2004).
- ¹⁹See supplementary material at <http://dx.doi.org/10.1063/1.3453759> for more information (Section S1).