

Efficient Electron Injection into Organic Semiconductors Induced by Hydrogen Bonds

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Keywords: Electron injection, Hydrogen bond, Flexible OLED

ABSTRACT

It was found that stable bases widely used in organic syntheses as catalysts can lower the electron injection barrier in organic light-emitting diodes. In contrast to conventional n-doping, the reduction of the injection barrier caused by adding bases is induced by the formation of hydrogen bonds between hosts and bases.

1. Introduction

Flexible devices such as displays and sensors can be easily achieved by preparing organic thin films and electrodes on flexible substrates such as plastic films [1–7]. The most important issue remaining for the practical application of these flexible devices is their poor environmental stability owing to the use of unstable electron-injection materials [8,9]. In carrier-injection-type devices such as organic light-emitting diodes (OLEDs), it is generally difficult to inject electrons from the cathode since there is a large injection barrier between the work function (WF) of the cathode and the lowest unoccupied molecular orbital (LUMO) of organic compounds, as illustrated in Fig. 1(a). To enhance electron injection, n-type dopants have been applied to most present-day OLEDs. The electron injection using conventional n-type dopants has mainly been achieved by electron transfer from dopants to hosts; however, the low ionization

potential (IP) required for these dopants generally renders them unstable, as illustrated in Fig. 1(b). In early studies and even now, alkali metals capable of donating electrons to the LUMO of hosts have been widely used, even though the reactivity of alkali metals is extremely high. For the realization of stable n-type dopants, many molecular n-type dopants with low IP have been evaluated [10–13]. Most of the host materials used in n-type doping processes with molecular n-type dopants have been materials with a high electron affinity (EA) of about 4 eV, which are used in organic solar cells and organic thin-film transistors. On the other hand, reports on n-type doping processes using hosts with a lower EA are limited. Thus, the development of stable n-type dopants that can enhance electron injection has been hindered by the requirement for energy level matching between the host and the dopant, since the stability is compromised by the low IP. For this reason, a strategy that can reduce the electron injection barrier independently of the energy levels is desirable. If such a new electron injection strategy is realized, the practical application of flexible organic devices will be accelerated since the environmental stability of devices without the use of unstable materials is higher than that of devices using unstable materials.

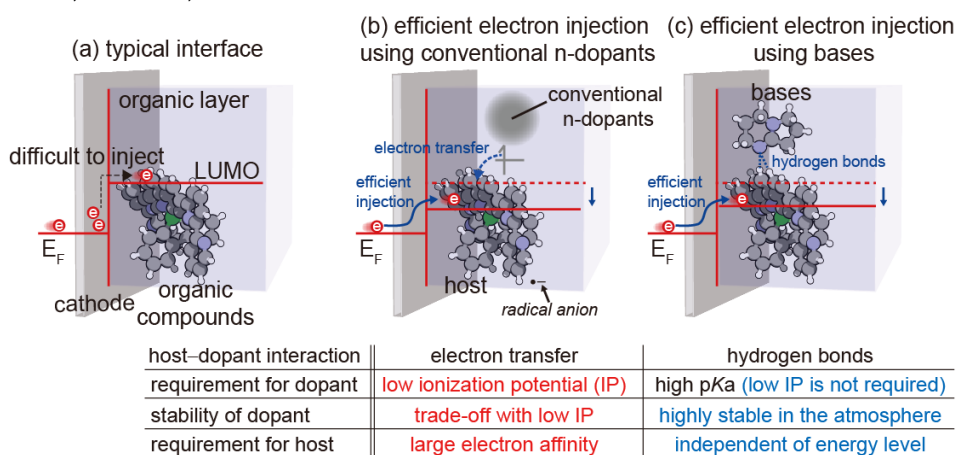


Figure 1: Schematic illustration of the carrier injection mechanism and characteristics in (a) typical cathode/organic interfaces, (b) interfaces using conventional n-type dopants and (c) interfaces using bases.

Here, we report a novel strategy for efficient electron injection into organic semiconductors, which is realized by forming hydrogen bonds (H-bonds) between host semiconductors and bases [14]. The differences between efficient electron injection using conventional n-type dopants and that using bases are summarized in Figs. 1(b) and (c). The injection efficiency is mainly determined by the basicity (pK_a) of bases, whereas it is independent of the energy levels of the hosts and bases. The effect of bases on the injection efficiency was examined by adding them into the interlayer in inverted OLEDs (iOLEDs). In addition, several phenomena related to H-bonds were investigated such as the change in energy levels and the polarization between hosts and bases.

2. Improvement in electron injection efficiency in various devices using bases

The effect of bases on electron injection efficiency was investigated by adding them into the interlayer of iOLEDs, as shown in Fig. 2(a). Since the characteristics of iOLEDs strongly depend on the electron injection/transport property of the interlayer, information about the improved electron injection efficiency resulting from the addition of bases can be extracted from the base-dependent iOLED characteristics [15]. A mixed solution containing spB-BPy₂

and the base, which can be prepared easily owing to the high air stability of each base, was spin-coated to form the interlayer. Then, the other layers, including the emitting layer, which consists of an electron-transporting host, i.e., bis[2-(2-hydroxyphenyl)benzothiazolato]zinc(II) [Zn(BTZ)₂], and a red phosphorescent emitter, that is, tris[1-phenylisoquinolino-C2,N]iridium(III) [Ir(piq)₃], were subsequently deposited.

The current density (J)–voltage (V) characteristics of the iOLEDs were improved by adding bases into the interlayer as shown in Fig. 2(b). The electron injection efficiency was found to be inversely related to the pK_a of the bases, as depicted in Fig. 2(c), where the luminance data is also shown. Thus, bases with stronger basicity exhibited higher electron injection efficiency. Among the bases tested, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) afforded iOLEDs that exhibited the best characteristics. The bases with high pK_a provided effective electron injection, thereby circumventing the need for air-sensitive alkali metals. In addition, some of the iOLEDs with base-added interlayers exhibited higher operational stability than those with the pristine spB-BPy₂ [Fig. 2(d)], which suggests that the operational stability of these bases is also high.

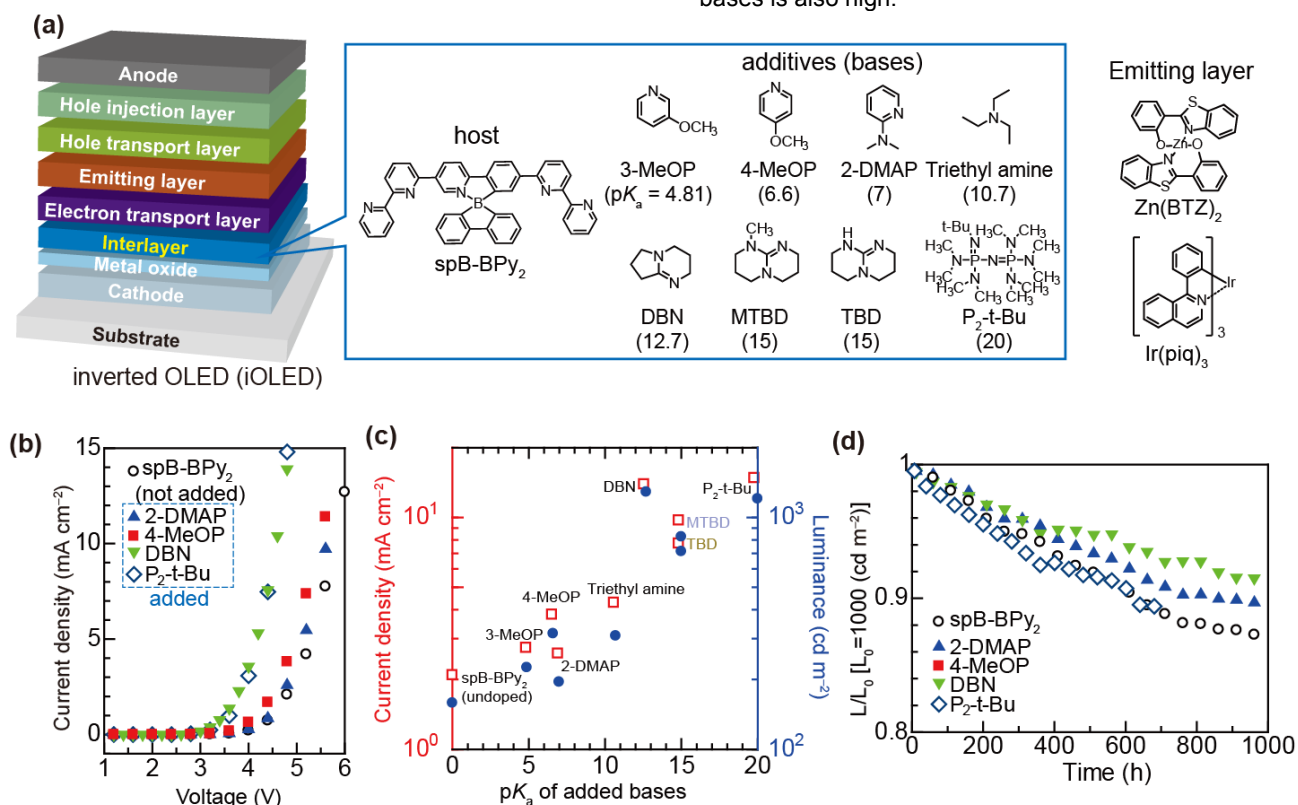


Figure 2: (a) Multilayer structure of an iOLED and chemical structure of the materials used in the interlayer and the emitting layer. (b) Current density–voltage characteristics of iOLEDs prepared using various interlayers. (c) Summary of the relationship between current density (left vertical axis, red squares) and luminance (right vertical axis, blue circles) of iOLEDs at a voltage of 4.8 V and the pK_a of the added bases. (d) Luminance–time characteristics of iOLEDs under a constant dc with an initial luminance of 1,000 cd m⁻².

3. Mechanism of efficient electron injection using bases

Next, the mechanism of the efficient electron injection resulting from adding bases using DBN was investigated. We performed ultraviolet photoelectron spectroscopy (UPS) on spB-BPy₂ spin-coated on ITO/ZnO with or without added DBN as summarized in Fig. 3(a). Upon mixing spB-BPy₂ with DBN, the line shapes of the spectra did not change substantially (not shown), whereas a shift toward a higher binding energy and a change in the surface work function were detected. A reduction of the electron injection barrier similar to that in the conventional n-type doping system was observed. The energy diagram is consistent with the characteristics of iOLEDs. However, the mechanism of the electron injection enhancement by adding bases is most likely entirely different from that of efficient electron injection using conventional n-type dopants for the following two reasons: (1) The bases cannot donate electrons directly to the LUMO state of spB-BPy₂ because the EA of spB-BPy₂ is smaller than 3 eV [16], and the IP of the bases is expected to be larger than the EA of spB-BPy₂; and (2) no formation of a radical anion was observed in the DBN-added spB-BPy₂ film, as confirmed from electron spin resonance spectra and UV-vis-near-IR spectra (not shown).

Since the bases are likely to interact with hydrogen, we confirmed the possible interaction of DBN with hydrogen

atoms of the host by recording the ¹H nuclear magnetic resonance (NMR) spectra. It was confirmed from the ¹H NMR spectra that H-bonds formed between the N atom of DBN and the H atoms in spB-BPy₂, as illustrated in Fig. 3(b). To evaluate the effect of H-bonds on the electron injection barrier, the charge distribution between the two molecular systems was calculated on the basis of density functional theory (DFT). Although no spB-BPy₂ anion is formed in the base-added layer, it was demonstrated by DFT calculation that there is polarization between spB-BPy₂ (δ⁻) and the base (δ⁺), as illustrated in Fig. 3(b). It was confirmed from UPS and DFT calculation results that almost all negative charges induced by H-bonds are transferred from spB-BPy₂ to ITO/ZnO through gap states to achieve thermodynamic equilibrium as illustrated in the center of Fig. 3(c) [17–19]. As a result, not only does the chemical potential of spB-BPy₂ shift upwards, as shown in Fig. 3(a), but also an interface dipole effective for lowering the injection barrier is formed, as illustrated in Fig. 3(a) and on the right of Fig. 3(c) [20]. From these results, a novel strategy for efficient electron injection, H-bond-induced electron injection utilizing air-stable bases, is summarized in Fig. 3(c). In general, there is a large electron injection barrier at cathode/organic layer interfaces. However, the injection barrier can be reduced by forming H-bonds, and electrons can be effectively injected.

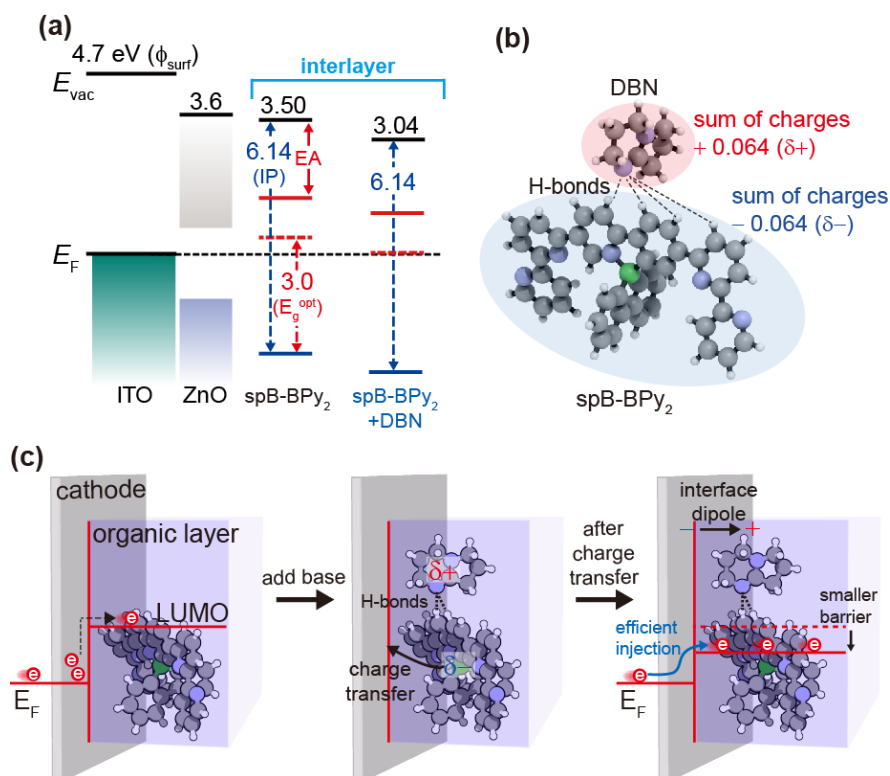


Figure 3. (a) Energy diagram of pristine and DBN-added interlayers, showing reduction of the electron injection barrier after adding DBN. (b) Geometries of spB-BPy₂ and DBN expected from the ¹H NMR results. The negative charge induced by the formation of H-bonds is also illustrated. (c) Schematic illustrations of electron injection from the cathode to the organic layer enhanced by the formation of H-bonds.

4. Wide applicability of electron injection strategy utilizing H-bonds

On the basis of the capability of the bases to enhance electron injection independently of the energy levels of the host, we next examined the applicability of this electron injection strategy in other organic semiconductors. We evaluated the interlayer-dependent characteristics of an iOLED having the device configuration depicted in Fig. 1(a), employing various hosts either by themselves or with DBN. The chemical structures of the hosts are shown in the inset of Figs. 4(a) and (b), PIC-TRZ is a bipolar material and PTAA is a hole-transporting material [21,22]. The luminance–voltage characteristics of the two iOLEDs were significantly improved by adding DBN. Most notably, electrons were injected effectively from the hole-transporting material PTAA, whose EA is lower than 2 eV, upon adding DBN, whereas no luminance was observed from the iOLED prepared using pristine PTAA. Therefore, this electron injection strategy utilizing H-bonds can also be applied to systems in which the electron transfer from the additive to the host has been considered unfeasible owing to energy level limitations.

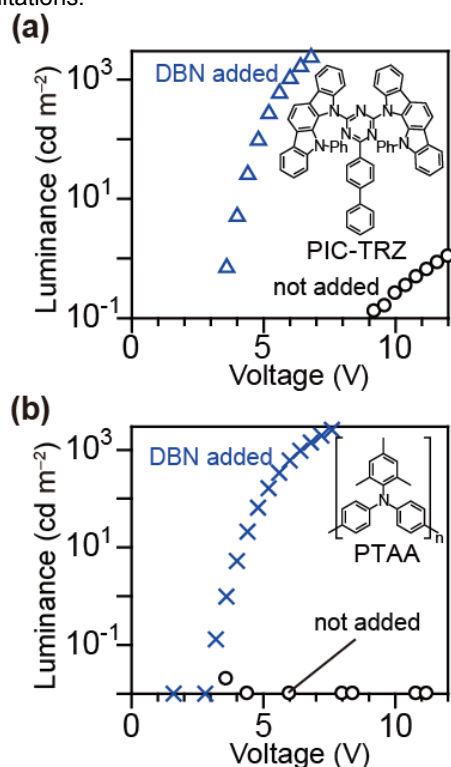


Figure 4. (a), (b) Luminance–voltage characteristics of iOLEDs prepared using various base-added and pristine interlayers. Inset: chemical structure of the host material used in the interlayer.

5. Conclusion

We have reported a novel strategy for efficient electron injection into organic semiconductors that can be induced by the formation of H-bonds between organic compounds

and stable bases. The electron injection technique utilizing bases has many advantages over the use of conventional n-type dopants, such as its independence of energy level, easy availability, high stability, and processability in solution and vacuum. These findings can be envisaged as an innovative achievement in many fields, including organic electronics, the physics of organic semiconductors, and chemistry. The results of this research are expected to pave the way toward a new research field of controlling the electronic behavior in organic devices without using conventional unstable n-type dopants.

iOLED is a trademark of Nippon Shokubai Co., Ltd.

REFERENCES

- [1] Z. B. Wang *et al.*, Nat. Photon. Vol. 5, p. 753 (2011).
- [2] T.-H. Han *et al.*, Nat. Photon. Vol. 6, p. 105 (2012).
- [3] M. S. White *et al.*, Nat. Photon. Vol. 7, p. 811 (2013).
- [4] C. M. Lochner *et al.*, Nat. Commun. Vol. 5, p. 5745 (2014).
- [5] A. K. Bansal *et al.*, Adv. Mater. Vol. 27, p. 7638 (2015).
- [6] T. Yokota *et al.*, Sci. Adv. Vol. 2, p. e1501856 (2016).
- [7] A. Steude *et al.*, Sci. Adv. Vol. 2, p. e1600061 (2016).
- [8] J. McElvain *et al.*, J. Appl. Phys. Vol. 80, p. 6002 (1996).
- [9] C. Charton *et al.*, Thin Solid Films Vol. 502, p. 99 (2006).
- [10] X. Lin *et al.*, Nat. Mater. Vol. 16, p. 1209 (2017).
- [11] B. Lüssem *et al.*, Chem. Rev. Vol. 116, p. 13714 (2016).
- [12] P. Wei *et al.*, J. Am. Chem. Soc. Vol. 132, p. 8852 (2010).
- [13] C. Gaul *et al.*, Nat. Mater. Vol. 17, p. 439 (2018).
- [14] H. Fukagawa *et al.*, Adv. Mater. doi.org/10.1002/adma.201904201 (2019).
- [15] H. Fukagawa *et al.*, Adv. Mater. Vol. 30, p. 1706768 (2018).
- [16] H. Yoshida *et al.*, Org. Electron. Vol. 20, p. 24 (2015).
- [17] J.-P. Yang *et al.*, J. Phys. D: Appl. Phys. Vol. 50, p. 423002 (2017).
- [18] T. Kanagasekaran *et al.*, Appl. Phys. Lett. Vol. 107, p. 043304 (2015).
- [19] H. Fukagawa *et al.*, Adv. Mater. Vol. 19, p. 665 (2007).
- [20] Y. Zhou *et al.*, Science Vol. 336, p. 327 (2012).
- [21] A. Endo *et al.*, Appl. Phys. Lett. Vol. 98, p. 083302 (2011).
- [22] J. H. Heo *et al.*, Nat. Photon. Vol. 7, p. 486 (2013).