CHIN. PHYS. LETT. Vol. 36, No. 12 (2019) 127201

Hole Injection Enhancement of MoO_3/NPB/Al Composite Anode *

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(Received 10 September 2019)

An ultra-thin molybdenum(VI) oxide (MoO_3) modification layer can significantly improve hole injection from an electrode even though the MoO_3 layer does not contact the electrode. We find that as the thickness of the organic layer between MoO_3 and the electrode increases, the hole injection first increases and it then decreases. The optimum thickness of 5 nm corresponds to the best current improvement 70%, higher than that in the device where MoO_3 directly contacts the Al electrode. According to the 4,4-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPB)/MoO_3 interface charge transfer mechanism and the present experimental results, we propose a mechanism that mobile carriers generated at the interface and accumulated inside the device change the distribution of electric field inside the device, resulting in an increase of the probability of hole tunneling through the injection barrier from the electrode, which also explains the phenomenon of hole injection enhanced by MoO_3/NPB/Al composite anode. Based on this mechanism, different organic materials other than NPB were applied to form the composite electrode with MoO_3. Similar current enhancement effects are also observed.

PACS: 72.80.Ga, 72.20.Jv, 72.80.Le DOI: 10.1088/0256-307X/36/12/127201

High injection barrier between a metal electrode and an organic layer always limits carrier injection severely and reduces current and luminous efficiency of organic light-emitting diodes (OLED). Therefore, improving carrier injection is one of the important topics for organic light emitting. Introducing a thin hole injection layer between an anode and a hole transport layer is a simple option. MoO_3, as a representative of transition metal oxides, is a typical and widely used hole injection layer material.[1] Many studies[2–8] have shown that inserting nanometer-thick MoO_3 (or other transition metal oxides) layer into the anode/organic interface (i.e., MoO_3 directly contacts the electrode) can effectively improve the hole injection current, reduce the threshold voltage and significantly improve the luminescence efficiency of OLED devices. In addition, MoO_3 (or other transition metal oxides) as an anode interface buffer layer has been reported to improve the performance of organic solar cells[9,10] and organic field-effect transistors.[11,12]

Recently, it was reported that in some top-emitting OLED devices, MoO_3 was also used to modify metal materials such as Al, Ag, and significantly increased their work function, resulting in reduction of hole injection barrier between hole transport materials and metal electrode. Therefore, these modified materials can be made as anode to realize hole injection.[13–15]

According to the enhancement of hole injection current by a MoO_3 layer at the electrode interface, it is believed that MoO_3 helps forming an ohmic hole contact with organic materials,[16] because it can completely or partially eliminate the hole injection barrier at the electrode/organic interface. Further studies with UPS, XPS, etc. have shown that charge transfer or energy band bending could be observed at the interface between the transition metal oxide and the electrodes or organic materials.[4,9,11,16,17] That is to say, the high work function (WF) of MoO_3 may lift the highest occupied molecular orbital (HOMO) level of the contact organic materials, which reduces the interface potential barrier and facilitates the hole extraction at the interface.[4,5,11,18] Therefore, in the past two decades, since Tokito *et al.*[1] reported that MoO_3 can be used as a hole injection layer, almost all researches on transition metal oxides focused on the applications at the interface between electrode and organic layer, while the insertion of MoO_3 into the organic layer (away from the electrode) has rarely been reported.

However, in Ref. [19] it was found that the current of the hole-only device ITO/CuPc(100 nm)/Al under negative bias can be greatly enhanced (mainly manifested by the increase of reverse hole injection current of metal cathode) by inserting a MoO_3 doping layer located at 20 nm away from both the electrodes (i.e., MoO_3 does not contact the electrodes directly). Similarly, Zhao *et al.* introduced a MoO_3 layer into the organic transport layer of OLED at 30 nm away from the anode, and also obtained a significant increase of device current and luminous efficiency.[20] These works showed that MoO_3 modified organic/organic interface could improve the device current even without direct contact between MoO_3 and the electrode. However, in these modified structures, since MoO_3 did not connect organic material to the electrode any more, the mechanism for forming ohmic contact or energy level alignment between the two materials would no longer be applicable. Although the devices with MoO_3 inserted in the organic layer showed significant current increase compared to those without MoO_3, the optimum position of the MoO_3 for the maximum current enhancement might be considered a priori or intuitively as it

*Supported by the National Natural Science Foundation of China under Grant Nos 11874007 and 11574049.
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directly contacts the electrodes.

In this work, it is found that a thin NPB modification layer inserted into the hole-only device ITO/NPB (active layer, 100 nm)/MoO_3(5 nm)/Al between MoO_3 and Al electrode can lead to the hole current injected by the Al electrode further to increase. The maximum current enhancement by 70% compared to the case that MoO_3 directly contacts Al is due to the 5-nm-thick NPB modification layer. Further experiments using a thin Bphen layer inserted at the interface to separate the NPB active layer from MoO_3 show that the charge transfer characteristic of the NPB/MoO_3 interface would be the key factor to enhance the hole current. Therefore, we propose a mechanism that mobile carriers generated at the interface and accumulated inside the device change the distribution of electric field inside the device, resulting in increase of the probability of hole tunneling through the injection barrier from the electrode. Furthermore, instead of NPB, we employ CuPc or Bphen to insert between MoO_3 and the Al electrode as the modification layer, similar hole current enhancement effect is observed, confirming the mechanism proposed.

In our experiment, the substrate glass used was covered with a 120-nm-thick film as the ITO transparent electrode with square resistance of about 15 Ω/square. The substrate glass was ultrasonically cleaned with detergent and deionized water successively, followed by surface ozone treatment. Organic and inorganic thin films were deposited layer by layer onto the substrate by vacuum thermal evaporation, and strip metal electrode was grown with shadow mask to make the device effective area of 3 mm × 4 mm. The chamber pressure during the thermal evaporation was below 10^{-5} Pa, and growth rate of the material (organic material ∼0.1 nm/s, metal material ∼0.5 nm/s) was monitored by a crystal oscillator. Keithley 236 Source Measure Unit was used to measure the I–V characteristics of the devices at room temperature in a dark nitrogen glove box. It should be noticed that the positive applied voltage is defined between the Al anode and the ITO cathode, different from most publications. During the whole process of growth and measurement, the device was not exposed to the atmosphere.

Thin film hole-only devices ITO/NPB/MoO_3/Al were fabricated with thin modification layers of NPB (in thickness x = 0, 3, 5, 8, 10 nm) inserted at the MoO_3/Al interface. The device structure was ITO/NPB(active layer, 10 nm)/MoO_3(5 nm)/NPB(modification layer, x nm)/Al and the current-voltage characteristics of the devices (with Al electrode as the anode) are shown in Fig. 1. For comparison the current-voltage characteristic of the device without MoO_3 (ITO/NPB(100 nm)/Al) is also shown as the black curve in the figure. Due to the high injection barrier at the interface between the Al electrode and NPB, current density of the devices without MoO_3 was only 0.46 μA/cm^2 under the applied bias voltage of 5 V. Inserting a 5-nm-thick MoO_3 layer in direct contact with the Al electrode made the current density of the ITO/NPB(100 nm)/MoO_3(5 nm)/Al device significantly improved by more than five orders of magnitude, reaching 74.5 mA/cm^2 under bias voltage of 5 V. It is proved that the MoO_3 layer directly contacted the electrode has really improved hole injection of the device. This is in good agreement with the results reported previously.[1,6,20] However, when a 3-nm NPB modification layer was inserted between MoO_3 and the Al electrode (i.e., the MoO_3 layer was separated from the Al electrode and no longer directly contacted the electrode), the device current density would unexpectedly increase to 96.9 mA/cm^2. The device current density even increased to 125.8 mA/cm^2 for x = 5 nm, but then dropped to 35.4 mA/cm^2 for x = 8 nm and further dropped to 13.0 mA/cm^2 for x = 10 nm. The inset of Fig. 1 shows the dependence of the forward current density (the hole current injected by the Al electrode) on the thickness x (nm) of the NPB modification layer under different bias voltages 3, 4, and 5 V, respectively. It can be seen that the device current density changed non-monotonically with x. With the increase of x, the device current density first increased and then decreased. The maximum enhancement was at x = 5 nm, where the device current density not only increased by about five orders of magnitude compared with that of the device without MoO_3 (black line), but also increased by about 70% compared with that of the device with direct contact between MoO_3 and the Al electrode (red line). These results clearly show that MoO_3 contacted Al electrode can greatly enhance the hole injection of the Al electrode. It modified the Al electrode, which is usually used as a cathode, and enabled the MoO_3/Al electrode to be used as anode. However, surprisingly the hole injection of the Al electrode was further improved by inserting a 5-nm NPB modification layer at the MoO_3/Al interface, which separated MoO_3 from the Al electrode.

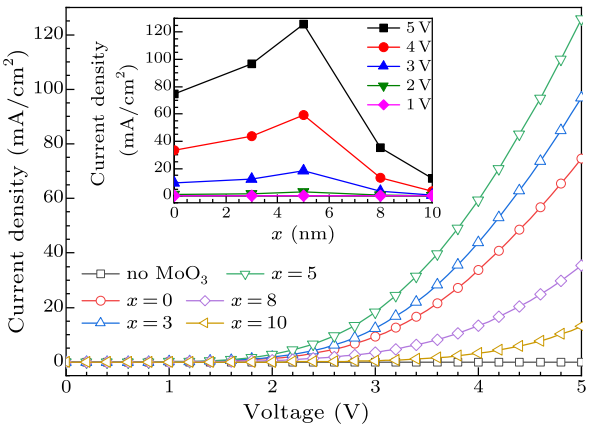

Fig. 1. Current-voltage characteristics of devices with structure ITO/NPB(100 nm)/MoO_3(5 nm)/NPB(x nm)/Al and ITO/NPB(100 nm)/Al. Inset: current density versus thickness x (nm) of NPB inter-layer for different bias voltages (3 V, 4 V, and 5 V).

It should be emphasized that most previous researches about the current enhancement by the MoO_3 layer as a hole injection buffer were based on the direct contact between MoO_3 and the electrode. How-

ever, in this work, the MoO_3 layer is inserted into the organic layer NPB, rather than direct contact to electrodes, while the device current is still enhanced. Therefore, this new phenomenon cannot be explained by the mechanisms like interface level arrangement[5] or interface ohmic contact suggested previously.[16]

In addition, Zhao *et al.* reported the current enhancement by insertion of the MoO_3 layer near the ITO electrode in a hole-only device,[20] and they attributed the enhancement to the co-evaporated layer structure formed by the diffusion of MoO_3 into the organic layer during the deposition. However, in the present work, the deposition sequence is reversed and the NPB modification layer is grown after MoO_3 to avoid the diffusion of MoO_3 into it. Therefore, the physical mechanism of hole injection by the MoO_3/NPB/Al composite anode would be obviously different from what has been already reported. Since this composite anode consists of multiple interfaces, the interface influence on the increase of hole injection current should be considered.

Many researchers have accepted that the interface between transition metal oxides and organic materials or the co-evaporated layer can produce mobile holes in organic materials due to the effect of electron transfer from organic materials to transition metal oxides. Moreover, this charge-producing co-evaporated layer containing MoO_3 was often used in tandem OLEDs as intermediate connector.[21–25] Previously, our group also reported the charge generation mechanism in the CuPc:MoO_3 co-evaporated layer.[19,26] It was suggested that electrons can transfer from organic molecules to MoO_3 molecules to form charge transfer (CT) complexes. This means that MoO_3 obtains electrons while organic materials lose electrons, leaving behind the positively charged holes (forming CT complexes with electrons on MoO_3). The CT complexes can be dissociated into free carriers with the help of an applied electric field.[26,27] Based on those studies, it can be considered that field-induced mobile carrier generation at the NPB (active layer)/MoO_3 interface could be a key factor for the great enhancement of hole current by the MoO_3/NPB/Al composite anode.

In the present case, the formation of CT complexes at the interface of NPB (active layer)/MoO_3 can be inhibited by inserting a thin bathophenanthroline (Bphen) layer between the NPB active layer and MoO_3. A series of devices with structures of ITO/NPB(100 nm)/Bphen(x nm)/MoO_3(5 nm)/NPB(8 nm)/Al (where x = 0, 1, 2, 3) were then prepared and the I–V characteristics are shown in Fig. 2.

Without the Bphen layer, the current density of the ITO/NPB(100 nm)/MoO_3(5 nm)/NPB(8 nm)/Al device (black line) under applied bias voltage 5 V is 35.4 mA/cm^2 (not shown in the figure). Insertion of the 1-nm-thick Bphen layer between the NPB active layer and MoO_3 results in the reduction of current density of ITO/NPB(100 nm)/Bphen(1 nm)/MoO_3(5 nm)/NPB(8 nm)/Al device (red line) to 1.13 mA/cm^2, one order of magnitude lower than the case without Bphen inserted. With the increasing thickness of Bphen, the device current density further decreases to 0.36 mA/cm^2 for x = 2 nm (blue line) and 0.12 mA/cm^2 for x = 3 nm (green line), about two orders of magnitude smaller than that of the device without Bphen insertion.

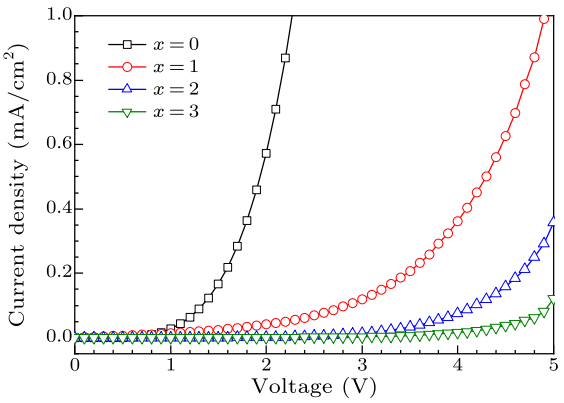

Fig. 2. Current-voltage characteristics of the devices with structure ITO/NPB(100 nm)/Bphen(x nm)/MoO_3(5 nm)/NPB(8 nm)/Al.

This experimental result shows that in the devices using MoO_3/NPB/Al composite anode, the mobile carriers generated at the NPB (active layer)/MoO_3 interface have a definite effect on the hole current enhancement of the device. In other words, the physical mechanism for further enhancement of hole current by insertion of MoO_3 into the organic layer NPB must be closely related to the CT complexes (or charge transfer characteristic) at the NPB (active layer)/MoO_3 interface.

Therefore, we propose a mechanism that mobile carriers generated at the interface and accumulated inside the device change the distribution of electric field inside the device, resulting in increase of the probability of hole tunneling through the injection barrier from the electrode, as shown in Fig. 3. As described above, we sign the NPB active layer of 100 nm as NPB$^{(1)}$ and the NPB modification layer of x nm as NPB$^{(2)}$. The NPB$^{(1)}$/MoO_3 interface generates mobile carriers (holes) under external electric field, holes generated transport through the NPB$^{(1)}$ layer and then be collected by the ITO electrode, while electrons on the other side of the interface continue to accumulate inside MoO_3 due to the effective electron blocking effect of NPB$^{(2)}$.[28] Meanwhile, a certain amount of holes would accumulate at the interface between the Al electrode and NPB$^{(2)}$. Then the accumulation of opposite charges at the interfaces on the two sides of NPB$^{(2)}$ enhances the local electric field in this layer, resulting in the redistribution of the electric field inside the device. As shown in Fig. 3, the electric field in NPB$^{(1)}$ (thicker NPB layer on the ITO electrode side) is decreased while the electric field in NPB$^{(2)}$ (thinner NPB layer on the side of the Al electrode) is increased. According to the widely accepted carrier injection mechanism, the tunneling model proposed

by Parker in 1994,[29] the enhancement of the local electric field in the NPB$^{(2)}$ decreases the interface triangular barrier between NPB$^{(2)}$ and the Al electrode. As a result, the probability of holes tunneling from the Al electrode to the NPB$^{(2)}$ increases (or the tunneling probability of the electrons accumulated inside MoO_3 through the NPB$^{(2)}$ increases). Consequently, the hole injection is increased, which further increases the device current.

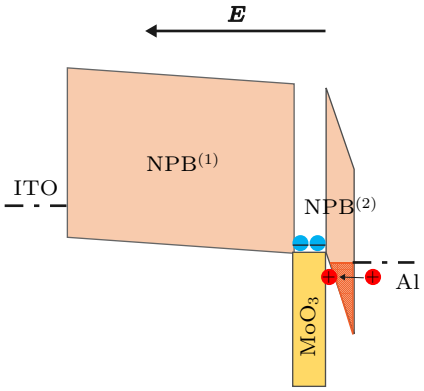

Fig. 3. Schematic energy-band diagram of the device under bias voltage (with the Al electrode as the anode)

Based on this physical mechanism, the non-monotonic dependence between the device hole current and the thickness of NPB$^{(2)}$(x nm) given in Fig. 1 can be understand.

According to the experimental result that the hole current of the device was further improved by inserting a thin modification layer of NPB ($x \leq 5$ nm) between MoO_3 and the Al electrode, it can be speculated that the direct contact between MoO_3 and the Al electrode would not be completely ohmic. Actually, previous work[2] has also pointed out that the contact between MoO_3 and the Al electrode is not completely ohmic through theoretical simulation and fitting of I–V data. This means that some mechanism must exist to prevent carrier transporting through the interface. For example, it has been proved by XPS that a redox reaction occurs between Al and Mo with +6 valence when MoO_3 was deposited onto Al via thermal evaporation.[30] That is, the aluminium oxide thin layer on the interface may be one of the factors limiting the electron extraction.

However, as shown in Fig. 3, NPB$^{(2)}$ not only prevents the redox reaction on the interface, but also effectively blocks the electrons in MoO_3 and the holes in the Al electrode. The built-in field brought by carrier accumulation reduces the difference between the Fermi levels of MoO_3 and Al on the two sides of NPB$^{(2)}$, resulting in the reduction of hole injection barrier between Al and MoO_3 (or the electrons extraction barrier between them). Li also reported in 2016 that a band bending of about 0.40 eV in the MoO_3 layer can be obtained by the shift of MoO_3 HOMO, which was verified by the XPS data when contacting with NPB.[18]

In this case, first, increase of NPB$^{(2)}$ thickness would cause larger potential difference under the same amount of charge accumulated, and make the Fermi level of the Al electrode closer to or even higher than the Fermi level of MoO_3. Accordingly, when a thin layer of NPB$^{(2)}$ ($x \leq 5$ nm) is inserted between MoO_3 and the Al electrode, hole current of the devices increases rather than decreases in comparison with the case that MoO_3 directly contacts Al. The hole current increases with NPB$^{(2)}$ thickness.

Second, in the case of thicker NPB$^{(2)}$ ($x > 5$ nm), the hole injection current decreases with the NPB$^{(2)}$ thickness increasing because the additional barrier introduced by NPB$^{(2)}$ (between MoO_3 and NPB$^{(2)}$ or between NPB$^{(2)}$ and Al) increases with thickness,[29] depressing the carrier transport.

Therefore, hole current of the device increases first and then decreases with x increasing, which is quite similar to the modification mechanism based on tunneling effect reported in previous works on different electrode buffer layers.[31–34]

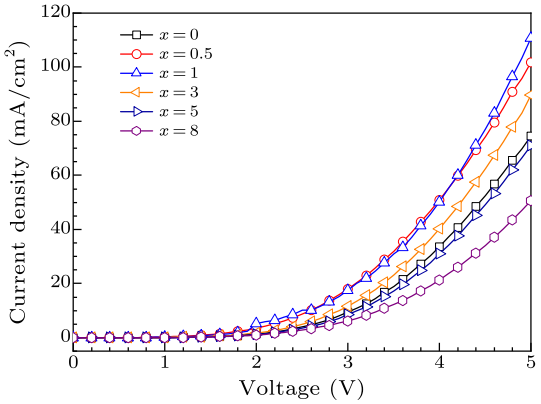

Fig. 4. Current-voltage characteristics of the devices with the structure ITO/NPB(100 nm)/MoO_3(5 nm)/Bphen(x nm)/Al.

According to this physical mechanism, it can be concluded that the charge redistribution effect on both the sides of NPB$^{(2)}$ is a necessary condition for increasing the hole injection current of the device. Therefore, it can also be inferred that other organic materials with the same charge accumulation effect as NPB could also help to increase the hole injection current from the Al electrode. As is expected, similar experimental phenomena are obtained when Bphen or copper phthalocyanine (CuPc) is selected to replace the NPB modification layer in the composite anode MoO_3/NPB/Al. The I–V characteristic of the ITO/NPB(100 nm)/MoO_3(5 nm)/Bphen(x nm)/Al device is shown in Fig. 4, in which the electron transport material Bphen is used instead of the hole transport material NPB$^{(2)}$. In this experiment, the similar phenomenon that the hole current of the device from the Al electrode increases first and then decreases with the increasing Bphen inter-layer thickness x is observed. For example, introduction of 0.5 nm Bphen increases the current density of the device from 74.5 mA/cm^2 (black line) to 101.7 mA/cm^2 (orange line) at bias voltage of 5 V. Bphen of 1 nm results in the maximum current density of 110.8 mA/cm^2. Then the current decreases with further increase of x, but in the range of 0.5 nm $\leqslant x \leqslant$ 3 nm, the device per-

formance is obviously superior to the device with the MoO_3 layer directly contacting to the Al electrode.

The experimental results show that Bphen also has the effect of increasing the hole injection current of the Al electrode. The optimum thickness of the organic modification layer in the composite anode may be different. This could be originated from the different barrier of the electrodes dues to different energy levels of different organic materials. This has been discussed in many previous works and the interfacial tunneling injection mechanism was considered to play a decisive role.[1,28,29,35–37] The variation of the equilibrium between these two mechanisms results in the change of the optimum thickness of the organic modification layer. The non-monotonic variation of current with the thickness of both Bphen and CuPc (shown by Fig. S1 in the Supplementary Material), as well as that in the device applied ITO/NPB/MoO_3 composite anode (shown by Fig. S3 in the Supplementary Material), further confirms the physical mechanism proposed.

The results also show that the MoO_3/NPB/Al composite anode proposed in our work is similar in structure to some charge generation layers (such as MoO_3-modified PEN/C_{60}-based CGL[38]), but different in work function. According to our mechanism, holes are generated not inside MoO_3/NPB/Al but on the interface between the composite anode and the active layer, which is outside the composite anode. The composite anode here is only responsible for transporting these holes. In other words, the composite anode may be used to modify the charge generation layer to further enhance the carrier transport and injection in the devices.

In conclusion, a schematic approach for modifying the Al electrode (or other metal electrode with low work function) by using MoO_3(5 nm)/NPB(x nm) composite layer is proposed, which can overcome the hole injection barrier of the device effectively and modify the electrode material with lower work function to be used as the anode of the device. Meanwhile, it shows potential application flexibility that a variety of organic materials instead of NPB could be used to lead to similar results, indicating the rationality of the proposed mechanism that mobile carriers generated at the interface and accumulated inside the device change the distribution of electric field inside the device, resulting in increase of the probability of hole tunneling through the injection barrier from the electrode. This composite anode could be widely used for design of organic electronic devices, especially for the design of inverted top-emitting OLED devices.

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Supplementary Material: Hole Injection Enhancement of MoO_3/NPB/Al Composite Anode

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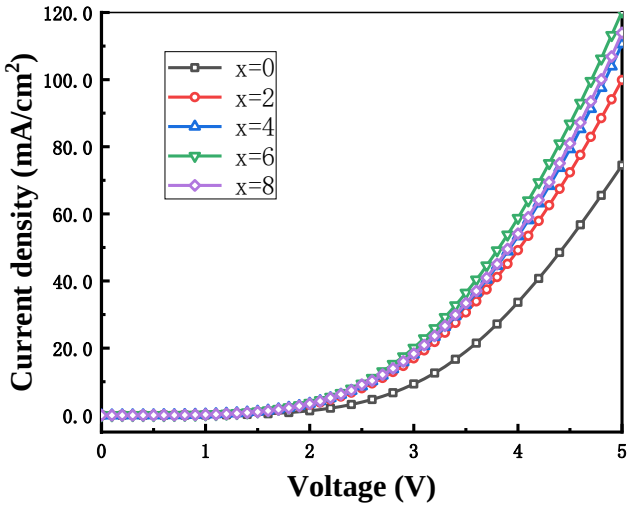

Fig. S1. Current–voltage characteristics of devices with structure ITO/NPB (100 nm)/MoO_3 (5 nm)/CuPc (x nm)/Al.

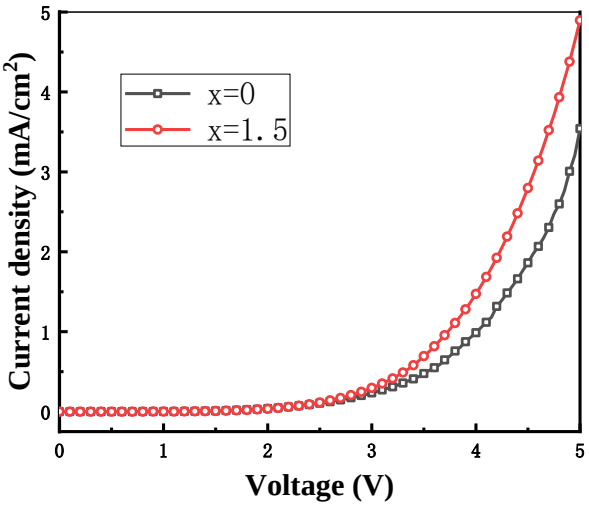

Fig. S2. Current–voltage characteristics of devices with structure ITO/TAPC (100 nm)/MoO_3 (5 nm)/NPB (x nm)/Al.

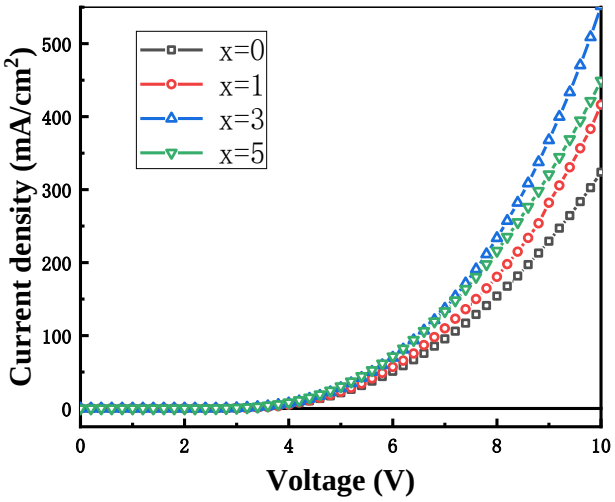

Fig. S3. Current–voltage characteristics of devices with structure ITO/NPB (x nm)/MoO_3 (5 nm)/NPB (100 nm)/Al.