Effect of CuPc and MoO_3 co-evaporated layer on the conductivity of organic light emitting diodes*

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Devices with copper phthalocyanine (CuPc):molybdenum trioxide (MoO_3) co-evaporated layer were fabricated and the current–voltage (I–V) and capacitance–voltage (C–V) characteristics were measured. It has been found that for a given voltage, the current of the device with a co-evaporated layer is higher than those without the co-evaporated layer and it reaches the highest value if the ratio of MoO_3 to CuPc is 1:1. Meanwhile, the C–V characteristics showed that only free holes exist in the function layer consisting of pure CuPc. However, charge transfer (CT) complexes exist in the function layer of a CuPc:MoO_3 mixture. The charge transfer complexes do not contribute to the transport of the device efficiently under low applied fields but are disassociated into free carriers rapidly at applied fields higher than 1.7×10^5 V/cm, which greatly increases the conductivity.

Keywords: CuPc, MoO_3, conductivity, capacitance

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1. Introduction

Conductivity is an important factor that can greatly impact the performance of devices, such as organic photovoltaic (OPV), organic light emitting diodes (OLED).[1–5] However, the conductivity of organic small molecular materials is still poor compared with traditional inorganic materials because of their low charge mobility and low carrier density.[6,7] In 2001, Zhou *et al.* found that the conductivity of TDATA can be greatly increased by F4-TCNQ doping.[8,9] Then, in the last decade, transition metal oxides (TMO) as p-type dopants have been proposed to improve the conductivity of organic materials.[10–15] Chang *et al*. showed that the WO_3 is capable of accepting electrons from 2-TANTA to generate free holes, leading to conductivity improvement.[16] Meanwhile, Guan *et al*. measured the UV-vis absorption of doped film and found a red shift of CuPc's absorption peak. They attributed this red shift to the formation of a charge transfer complexes between CuPc and MoO_3, resulting in the conductivity improvement.[17–19] However, they have not shown the mechanism through which the conductivity is improved. Moreover, Qiao *et al*. found that the direction of charge transfer would be inversed if MoO_3 is doped into different materials, so they concluded that charge transfer complexes would not result in the conductivity increase of the doped films.[20] Although many researchers have shown conductivity improvement,[16–22] the mechanism is still a controversial subject. Some researchers believed that charge transfer complexes are really formed in the doping film and others have thought that the doping just increases the amount of the free holes rather than forming charge transfer complexes. In addition, whether the charge transfer complexes impact the mobility or if they participate in conduction directly is still not clear, although some researchers believed that they indeed exist in the devices.

In the present work, devices with CuPc:MoO_3 co-evaporated layer were fabricated and the current–voltage characteristics were measured. For a given voltage, the current of devices with the co-evaporated layer is higher than those without the co-evaporated layer and it reaches the highest value if the ratio of MoO_3 to CuPc is 1:1. To explain this phenomenon, the capacitance–voltage characteristics were also measured and a U-shaped C–V curve has been obtained. The capacitance increases slowly under applied voltages lower than 2.4 V, corresponding to the electric field of 1.7×10^5 V/cm, and it increases rapidly under the voltages higher than 2.4 V, for either bias polarity. The C–V characteristics showed that only free holes exist in the function layer consisting of pure CuPc but charge transfer complexes exist in the function layer of the CuPc:MoO_3 mixture. The charge transfer complexes do not efficiently contribute to the conductivity of a device under low applied fields but would be disassociated rapidly into free carriers at applied fields higher than 1.7×10^5 V/cm to greatly increase the conductivity.

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2. Experiment detail

All of the devices were fabricated on pre-cleaned glass substrates coated with transparent conducting indium tin oxide (ITO) as the anode. The substrates were heated to 150 °C in air after solvent cleaning, and they were then loaded into a high vacuum chamber (5×10^{-5} Pa). Organic films were deposited after cooling down the substrates to room temperature. The deposition rates of the organic layer and Al cathode were 0.5 Å/s–2 Å/s and 3 Å/s, respectively. The co-evaporated layer was deposited with both the CuPc and MoO_3 sources. The prepared devices were all of area 9 mm^2 with a 3-mm-wide ITO strip crossed over by a 3-mm-wide Al bar. Device A of structure ITO/CuPc(20 nm)/function layer(60 nm)/CuPc(20 nm)/Al was used for current–voltage characteristic measurement and device B of structure ITO/Al(5 nm)/Bphen(20 nm)/function layer(100 nm)/Bphen(20 nm)/Al (Bphen is a blocking layer to eliminate the influence of injection on capacitance) was used for capacitance–voltage characteristic measurement. Both structures are shown in Fig. 1. The function layer was a mixture of CuPc and MoO_3, with different ratios of CuPc to MoO_3.

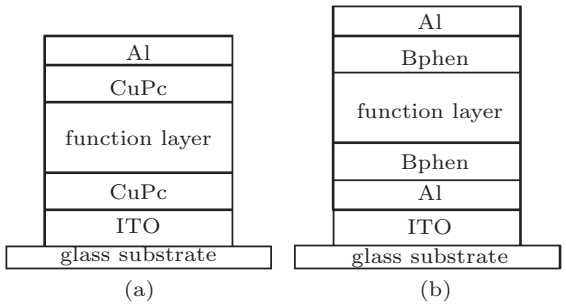


Fig. 1. Structure of the prepared devices. (a) Device A. (b) Device B.

The current–voltage (I–V) characteristics were measured by a Keithley 2440 and capacitance measurements were performed by a Keithley 4200 semiconductor characterization system with 4210-CVU and the ac signal was set as 1 kHz, 50 mV. The positive voltage (forward bias) was defined by a positively biased ITO electrode in all C–V measurements. All of the measurements were carried out in air at room temperature without illumination.

3. Results and discussion

Figure 2 shows the current–voltage characteristics of device A with function layers of different CuPc concentrations (0%, 20%, 30%, 50%, 80%, 90%, and 100%). Inset (a) of Fig. 2 shows the current at 1 V bias and −1 V bias, respectively, for different CuPc concentrations. The current is 0.258 mA (1 V) and 0.065 mA (−1 V), respectively, for 0% CuPc concentration. The current increases with the CuPc concentration if it is lower than 50%. The device with 50% CuPc concentration shows the maximum current both at 1 V and −1 V as 6.536 mA (1 V) and 6.726 mA (−1 V), respectively. Then, the current decreases as CuPc concentration increases further. Finally, for the device with CuPc concentration 100%, the current is 0.108 mA (1 V) and 0.003 mA (−1 V), respectively, which is much lower than that of the doped samples. Namely, the conductivity of CuPc layer would be improved by doping with MoO_3 and most efficiently with a ratio of CuPc to MoO_3 1:1.[18]

Inset (b) of Fig. 2 shows the I–V characteristics of a device with a function layer of pure CuPc or pure MoO_3. The current–voltage characteristic of the device with a pure CuPc function layer shows typical features of rectification. In contrast, the device with a pure MoO_3 function layer will be turned on for either bias polarity. Namely, MoO_3 results in the turning on of the device both at positive and negative biases, while the device without MoO_3 doping can only be turned on under a positive bias. Because the structure of each device A is the same except for different compositions of the function layer, the effects of electrode, CuPc layer, and the interface between them can be disregarded, while the contact of CuPc with MoO_3 must play an important role in this phenomenon.

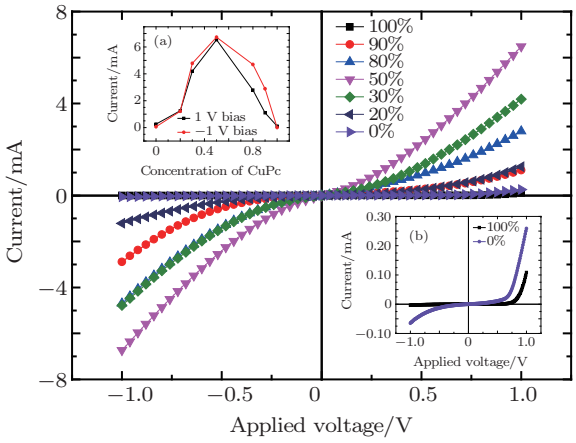


Fig. 2. (color online) Current–voltage characteristics of device A with different CuPc concentrations. The function layer is formed of co-evaporated CuPc and MoO_3. Inset (a) current under 1 V bias and −1 V bias versus CuPc concentration. Inset (b) I–V of devices with a pure CuPc or MoO_3 function layer.

The current–voltage characteristics of OLED with different function layers were measured and are shown in Fig. 3. It can be seen that the current of the device with a co-evaporated layer could reach as high as 90 mA at 11 V bias, while the current of devices with pure MoO_3 or CuPc is only 57 mA and 47 mA, respectively, at the same voltage. The current improvement by mixing CuPc with MoO_3 is obvious. This result demonstrates that doping can indeed improve the conductivity of an OLED.

As mentioned in the introduction, whether free holes or charge transfer complexes would be responsible for the conductivity improvement has not yet been clarified.[16–22] Besides, the real effect of charge transfer complexes is also not clear, although some researchers believe that they really exist in the devices. Here, a mechanism of conductivity improvement that charge transfer complexes existing in the co-evaporated layer would be dissociated by a high-applied electric field is proposed. In order to prove this idea, the capacitance–voltage characteristics of devices with different function layers were measured. Figure 4(a) shows the *C*–*V* curve of the device with a pure CuPc function layer. It is shown that the capacitance reaches a maximum 2.675 nF at a positive bias of 1.5 V. It has been reported that free holes exist in CuPc.[23] The capacitance decreasing away from its peak value could be attributed to the expansion of the space charge region (SCR) in the organic layer.[24] Therefore, the shape of *C*–*V* curve is evidence to show that only free holes exist in the device.

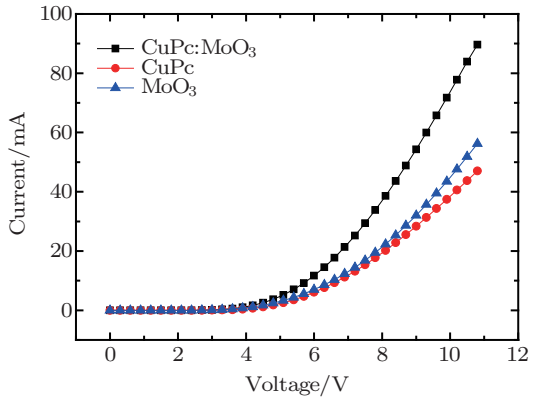


Fig. 3. (color online) Current–voltage characteristics of devices with different function layers and structures of ITO/(function layer, 20 nm) /NPB(20 nm)/Alq3(40 nm)/LiF(1 nm)/Al. Solid squares, solid circles, and solid triangles correspond to the function layers of (CuPc:MoO_3, 1:1), CuPc, and MoO_3, respectively.

Figure 4(b) shows the *C*–*V* curve of the device with a pure MoO_3 function layer. It shows that no obvious relationship exists between capacitance and the applied voltage. The capacitance value fluctuates around 3.87 nF. Compared with the *C*–*V* relation of CuPc, it could be conclude that there are no free carriers existing in the pure MoO_3 layer and the pure MoO_3 layer would not affect the capacitance of the device.

Figure 5 shows the *C*–*V* characteristic of the device with CuPc:MoO_3 co-evaporated layer and a U-shaped relationship was obtained. Basically, the *C*–*V* relation for a positive bias can be divided into two regions. The first region is from 0 V to 2.4 V, where the capacitance increases almost linearly with a slope of about 2.9 nF/V. While under a higher voltage, the capacitance increases sharply with a much higher slope of 28.3 nF/V. The inflection point is at 2.4 V, corresponding to the electric field of 1.7×10^5 V/cm. In addition, the *C*–*V* characteristic shows some polarity symmetry about the applied voltage. This means that the capacitance increasing with the voltage is independent of the direction of the electric field but depends on its magnitude.

With the existence of a blocking layer, no charges can be injected into the device. Therefore, the capacitance of the device changes only when there occurs a charge distribution in the co-evaporated layer.[25,26] In contrast to the result of the pure CuPc function layer, the capacitance was not reduced by the upward bias. Evidently, this rising capacitance is far away from the attributions of pure CuPc. Meanwhile, as shown in Fig. 4(b), no changes in capacitance with the applied voltages from −4 V to 4 V in the device with MoO_3 layer were found, indicating that no charge generates in the MoO_3 layer. In this sense, we attribute the capacitance increase to the mixture of CuPc and MoO_3. Because the highest occupied molecular orbital (HOMO) of CuPc (−5.2 eV) is higher than the lowest unoccupied molecular orbital (LUMO) MoO_3 (−6.3 eV), charges could transfer from CuPc to MoO_3 and form charge transfer complexes, which has been reported in some previous studies.[25,26]

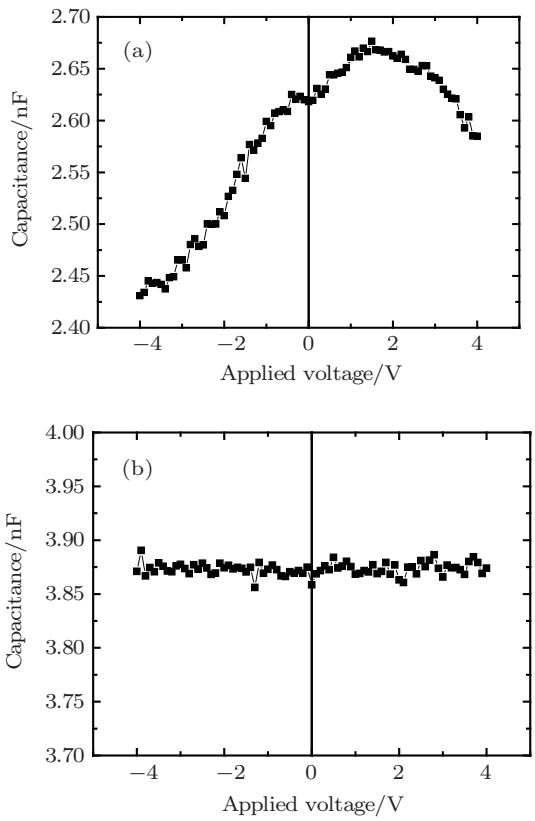


Fig. 4. Capacitance–voltage characteristic of the device with structures (a) ITO/Al(5 nm)/Bphen(20 nm)/CuPc(100 nm)/Bphen(20 nm)/Al (the capacitance peak did not appear at 0 V bias is because the shift of zero point of built-in field) and (b) ITO/Al(5 nm)/Bphen(20 nm)/MoO_3(100 nm)/Bphen(20 nm)/Al.

The electric field induced dissociation of charge transfer complex will lead to a charge accumulation area adjacent to the blocking layers, and thus an increase of capacitance. The slow increase of capacitance under 0 V to 2.4 V bias

indicates that the low electric field cannot dissociate charge transfer complexes efficiently, but the following sharp capacitance increase demonstrates that the charge transfer complexes would be dissociated rapidly under applied fields higher than 1.7×10^5 V/cm.

Overall, the *C*–*V* characteristics indicate that charge transfer complexes are formed between CuPc and MoO_3 and they can be dissociated by a relatively high applied field. When the charge transfer complexes are dissociated, the generated free charges will greatly improve the device's conductivity.

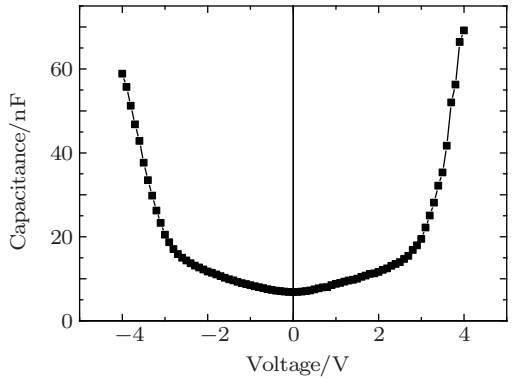


Fig. 5. *C*–*V* characteristic of the device with structure ITO/Al(5 nm)/Bphen(20 nm)/(CuPc:MoO_3, 1:1, 100 nm)/Bphen(20 nm)/Al.

4. Conclusion

In summary, CuPc co-evaporated with MoO_3 is an efficient way to improve the conductivity of an OLED. Charge transfer complexes which can be dissociated by a relatively high applied field are formed between CuPc and MoO_3. When the charge transfer complexes are dissociated, the generated free holes and electrons will improve the device conductivity.

Appendix A

Figure A1 shows the current–voltage characteristic and brightness–voltage characteristic of devices with different function layers. It can be found that the current of the device with a co-evaporation layer reaches 90 mA under 11 V bias but the current of the device with simple MoO_3 or CuPc is just 57 mA and 47 mA, respectively under the same voltage. The improvement of the current is notably. However, the brightness of the device with the co-evaporation layer, MoO_3 layer, and CuPc layer is 11000 cd/m^2, 10000 cd/m^2, and 12800 cd/m^2, respectively. It can be seen that the co-evaporation layer does not improve the brightness of the device, which is mainly caused by the enhanced hole injection and consequent charge imbalance.

Figure A2 shows the capacitance–voltage characteristic of devices with function layers of different CuPc:MoO_3 ratios. It can be seen that all of the curves show a U-shaped relationship. The capacitance increases with the voltage slowly under a small applied voltage but increases rapidly when the voltage goes beyond a higher value. The *C*–*V* characteristic shows the same trend, no matter the change of CuPc:MoO_3 ratio. However, it can be seen that the capacitance of device with CuPc:MoO_3 ratio 1:1 could reach as high as 58 nF at −4 V bias, while the capacitance of devices with CuPc:MoO_3 ratio 0.7:0.3 or CuPc:MoO_3 ratio 0.3:0.7 is only 30 nF and 15 nF, respectively, at the same voltage. This result demonstrates that the amount of free carriers produced by dissociation of CT complexes when the co-evaporated ratio of CuPc:MoO_3 is 1:1 is larger than that when the co-evaporated ratio of CuPc:MoO_3 is 0.7:0.3 or 0.3:0.7. Namely, the CT complexes are produced most efficiently with a ratio of CuPc to MoO_3 1:1. This result is also reflected in the case of the *I*–*V* characteristic.

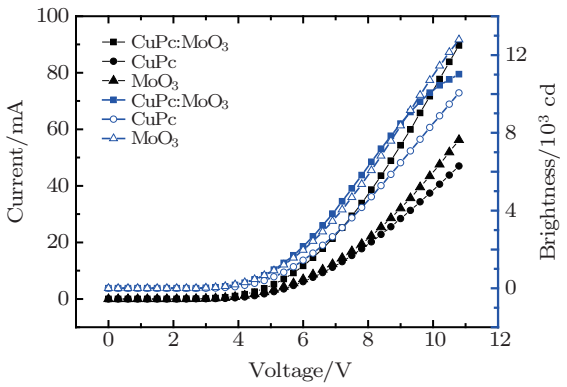


Fig. A1. (color online) The current–voltage characteristic and brightness-voltage characteristic of the devices with different function layers. The structure is ITO/(function layer, 20 nm)/NPB(20 nm)/Alq3(40 nm)/LiF(1 nm)/Al. The solid squares, solid circles, and solid triangles represent the function layers of (CuPc:MoO_3, 1.0:0.7), CuPc, and MoO_3, respectively.

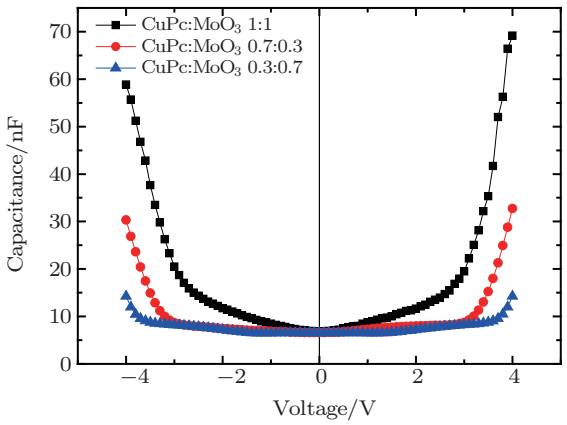


Fig. A2. (color online) *C*–*V* characteristic of the device with structure ITO/Al(5 nm)/Bphen(20 nm)/(CuPc:MoO_3,100 nm)/Bphen(20 nm)/Al. The solid squares, solid circles, and solid triangles represent the CuPc:MoO_3 ratios of 1:1, 0.7:0.3, and 0.3:0.7, respectively.

Figure A3 shows the *C*–*V* characteristic of the device with a NPB:MoO_3 co-evaporated layer and a U-shaped relationship. The capacitance increases with the voltage slowly under a small applied voltage but increases rapidly while the voltage beyonds a higher value. A similar result compared to the case of CuPc:MoO_3 indicates that our theory is also applicable for the case of NPB:MoO_3.

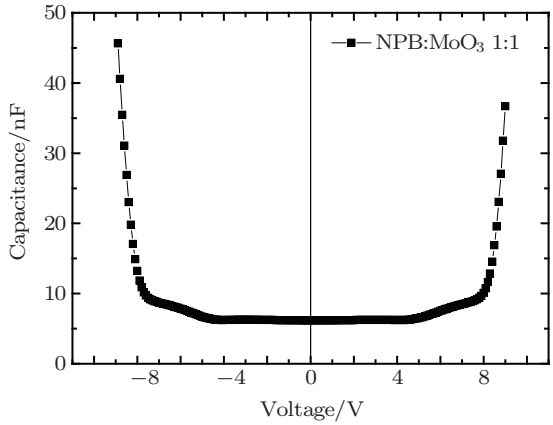


Fig. A3. *C–V* characteristic of the device with structure ITO/Al(5 nm)/Bphen(20 nm)/(NPB:MoO_3, 1:1, 100 nm)/Bphen(20 nm)/Al.

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