

# Bifunctional electroluminescent and photovoltaic devices using bathocuproine as electron-transporting material and an electron acceptor

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## Abstract

Electroluminescence (EL) devices, using 4, 4', 4''-tris (2-methylphenyl- phenylamino) triphenylamine (m-MTDATA) as hole-transporting material and bathocuproine (BCP) as an electron-transporting material, were fabricated, which emitted bright green light peaked at 520 nm instead of the emission of m-MTDATA or BCP. It was attributed to the exciplex formation and emission at the interface of m-MTDATA and BCP. EL performance was significantly enhanced by a thin mixed layer (5 nm) of m-MTDATA and BCP inserted between the two organic layers of the original m-MTDATA/BCP bilayer device. The trilayer device showed maximum luminance of 1,205 cd/m<sup>2</sup> at 8 V. At a luminance of 100 cd/m<sup>2</sup>, the power efficiency is 1.64 cd/A. Commission International De L'Eclairage (CIE) color coordinates of the output spectrum of the devices at 8 V are  $x = 0.244$  and  $y = 0.464$ . These devices also showed photovoltaic (PV) properties, which were sensitive to UV light. The PV diode exhibits high open-circuit voltage ( $V_{oc}$ ) of 2.10 V under illumination of 365 nm UV light with 2 mW/cm<sup>2</sup>. And the short-circuit current ( $I_{sc}$ ) of  $92.5 \times 10^{-6}$  A/cm<sup>2</sup>, fill factor (FF) of 0.30 and power conversion efficiency ( $\eta_c$ ) of 2.91% are respectively achieved. It is considered that strong exciplex emission in an EL device is a good indicator of efficient charge transfer at the organic interface, which is a basic requirement for good PV performance. Both the bilayer and trilayer devices showed EL and PV properties, suggesting their potential use as multifunction devices.

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## 1. Introduction

Photoelectron device based on organic semiconductors is a focus of increasing research effort motivated by the possibility to realize large area, lightweight, and low-cost flexible electroluminescence (EL) devices, solar cells [1–5], photodetectors [6,7], optical sensor, taking advantage of the processability of organic materials. The devices of bifunctional [8–10] EL and photovoltaic (PV) have been widely investigated because of using organic materials on both PV and EL diodes. It is well known that organic PV devices is related closely to the interface between the two

organic layers [11], and exciplex formation takes place mostly between the two organic layers or two organic molecules because interaction between molecules or organics of a hole-transporter with lower ionization potential (IP) and an electron transporter with larger electron affinity (EA) would take place through bringing instantaneous charge-transfer excited state [12]. Generally speaking, an intermolecular excited-state complex is identified as an exciplex when electron donor is in the excited state and electron acceptor is in the ground state [13].

Based on above proposition, we use 4, 4', 4''-tris- (2-methylphenyl phenylamino) triphenylamine (m-MTDATA), which have a low IP of 1.9 eV [14], as an electron donor and bathocuproine (BCP), which have a high EA of 7.0 eV [15], as an electron acceptor, respectively. Moreover,

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BCP, whose electron mobility [16,17] is  $6 \times 10^{-7} \text{ cm}^2/\text{V/s}$  at an electric field of  $7 \times 10^5 \text{ V/cm}$ , was used as efficient hole or exciton blocking material in both PV cells [3–5] and EL devices [18]. So m-MTDATA and BCP were respectively used as the electron donor and the electron acceptor to construct a PV diode, and we expect the diode will show good EL and PV performances [19]. Copper phthalocyanine (CuPc) has been widely used both as hole-injection material in organic EL devices and PV cells due to its better hole-transporting ability [1–3]. Poly (3,4-ethylene dioxathiophene): poly (styrene sulfonate) (PEDOT: PSS) has been reported to facilitate hole injection and to increase the built-in potential [4]. LiF is used as an electron injector in combination with an aluminum cathode.

## 2. Experiment details

The molecular structures of the organic materials used in this study are shown in Fig. 1. All of the materials were commercially available and used without further purification. A pre-patterned indium-tin-oxide (ITO) coated-glass substrate with a sheet resistance of  $30 \Omega/\square$  was cleaned by acetone, glass detergent sonication and deionized water rinse. After UV ozone treatment, the ITO substrates were overlay with PEDOT: PSS by spin coating then drying in a vacuum oven at  $120^\circ\text{C}$  for 1 hour, and then the ITO substrates loaded in a vacuum chamber. All the organic layers, LiF and Al cathode were sequentially neatly deposited onto the ITO substrates by thermal evaporation at a pressure of  $2 \times 10^{-4} \text{ Pa}$  without breaking the vacuum. The thickness of depositing film of above materials was monitored by a quartz oscillators and controlled at a rate of  $0.2\text{--}0.4 \text{ nm/s}$  for the organic layers and LiF, and  $1.0 \text{ nm/s}$  for the Al layer, respectively. The active area of typical device was  $10 \text{ mm}^2$ . Absorption spectra of all organic films on quartz substrate were measured with a Shimadzu UV-3101PC spectrophotometer. Photocurrent response curves were recorded under a  $40 \mu\text{W/cm}^2$  Xe lamp. The EL spectra of the diodes and the EL emission spectra of the m-MTDATA film, BCP film and m-MTDATA/BCP (1:1) blending film were measured with a Hitachi MPF-4 Fluorescence Spectrophotometer. All measurements were carried out in ambient air at room temperature without being especially pointed out.

## 3. Results and discussion

The fabricated device structures as follows:

- ITO/PEDOT: PSS/m-MTDATA (30 nm)/BCP (30 nm)/LiF/Al.
- ITO/PEDOT: PSS/CuPc (5 nm)/m-MTDATA (30 nm)/BCP (30 nm)/LiF/Al.
- ITO/PEDOT: PSS/CuPc (5 nm)/m-MTDATA (30 nm)/m-MTDATA: BCP (1:1), (5 nm)/BCP (30 nm)/LiF/Al.

Fig. 2 indicates the PL emissions from m-MTDATA, BCP and mixed film (m-MTDATA: BCP), as well as the

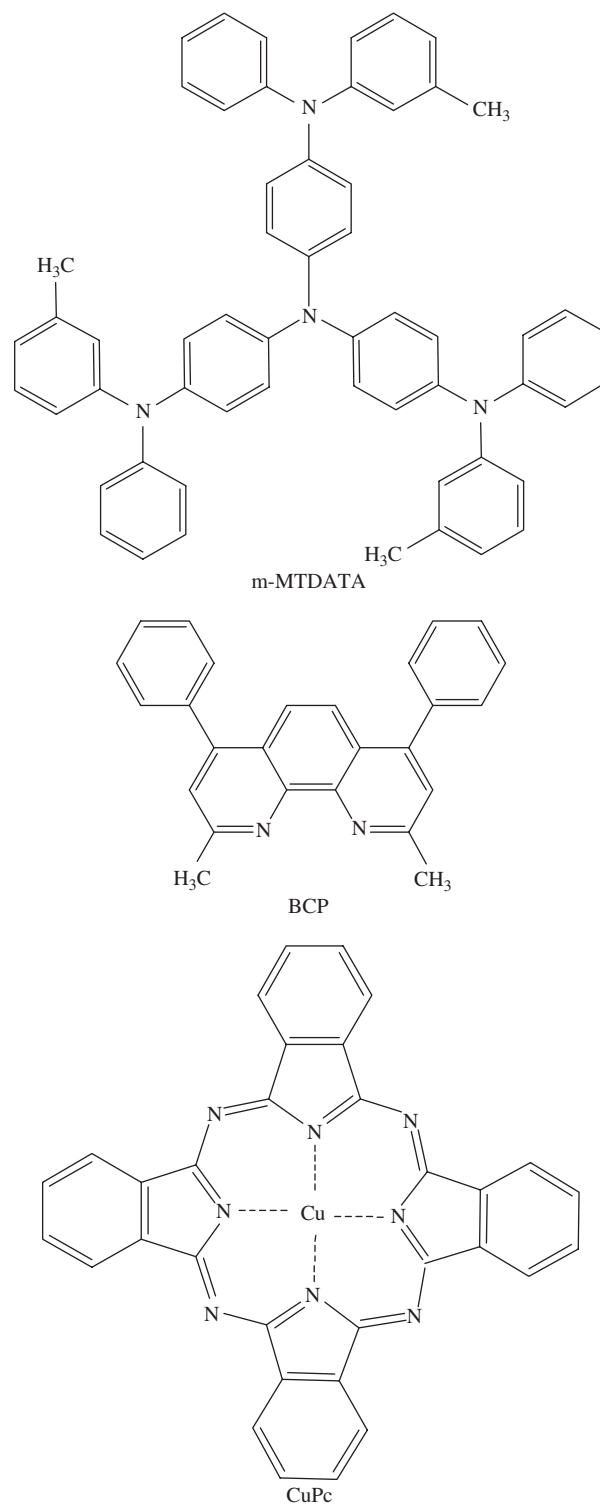


Fig. 1. Chemical structure of organic materials used in this study.

EL emission from the bilayer device (a) and trilayer device (c). We can conclude that the EL spectrum of the device, which is from neither m-MTDATA (peaked at  $424 \text{ nm}$ ) nor BCP (peaked at  $385 \text{ nm}$ ), peaked at  $520 \text{ nm}$  at  $8 \text{ V}$  is attributed to emission the interfacial exciplex.

We noticed that the emission of the exciplex is stronger with the insertion of CuPc as shown in Fig. 3, which shows

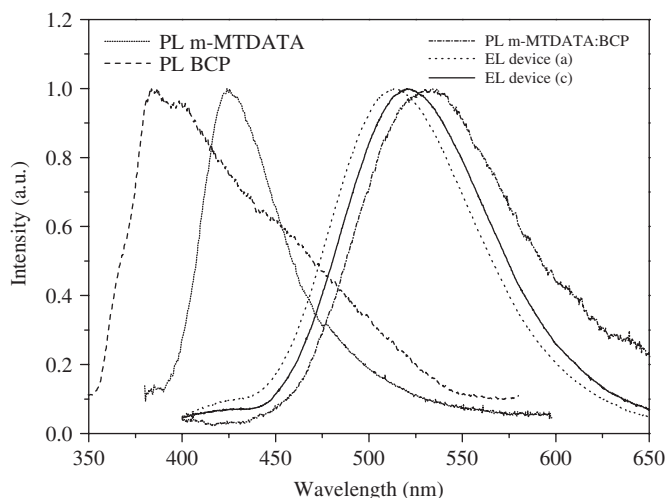


Fig. 2. PL emission from m-MTDATA film, BCP film and m-MTDATA:BCP (1:1) mixed film, and EL emission from bilayer and trilayer devices.

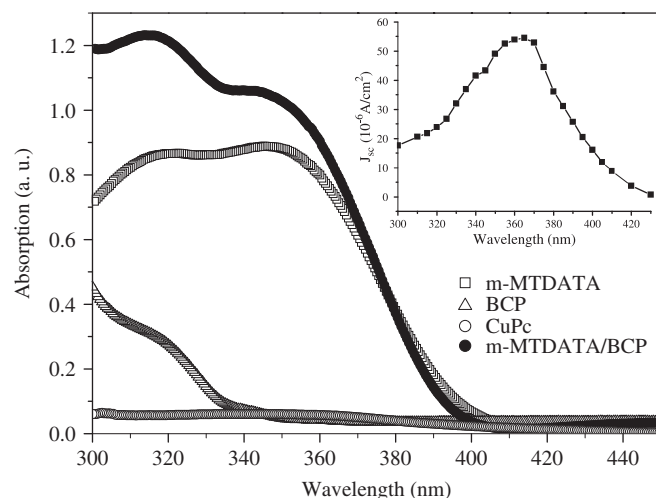


Fig. 4. Absorption spectra of m-MTDATA film, BCP film and m-MTDATA/BCP film. Inset: Photocurrent response curve of the bilayer device.

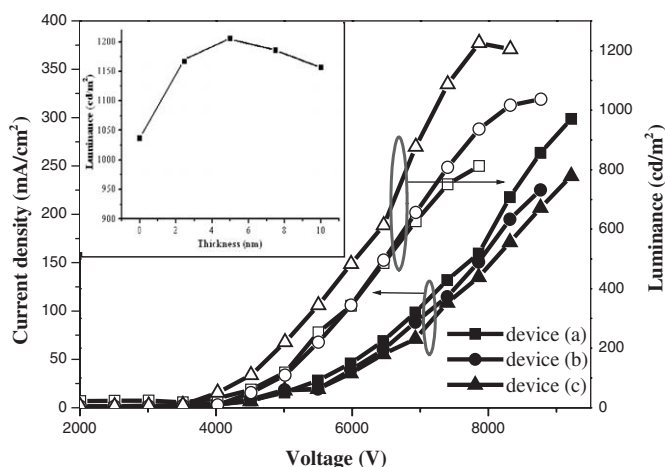


Fig. 3. Luminance–voltage and current–voltage characteristics of three devices. Inset: variation of device luminance with thickness of m-MTDATA:BCP mixed layer.

the current–voltage and luminance–voltage properties of three devices. In order to obtain better intermolecular contact of the m-MTDATA and BCP compounds, a thin mixed (m-MTDATA:BCP) layer was inserted between the m-MTDATA and BCP, as shown in device (c), and it is noticed that thickness of mixed layer is up to 5 nm (see Fig. 3, inset), the EL properties of the diode was intensively enhanced. The trilayer device showed maximum luminance of 1205  $\text{cd}/\text{m}^2$  at 8 V. At a luminance of 100  $\text{cd}/\text{m}^2$ , the power efficiency is 1.64  $\text{cd}/\text{A}$ . Commission International De L'Eclairage (CIE) color coordinates the output spectrum of the devices at 8 V are  $x = 0.2440$  and  $y = 0.4641$ .

Besides, EL emissions of device (c) at 6, 10 and 12 V are located at 512, 510 and 509 nm, respectively, that is blue shift compared with emission at 8 V, as a result of the

change of exciton combination area. EL emission of device (c) comprises both emission of m-MTDATA and that of exciplex, and the combination of hole and electron is confined to the mixed layer (m-MTDATA:BCP) at 8 V, the emission of m-MTDATA is weak. But at higher voltage, the combination area is moved to the interface of mixed layer/m-MTDATA, the emission of m-MTDATA becomes strong, which leads to the blue shift.

It is surprising that our diode also displayed PV performances. Fig. 4 indicates the absorption spectra of the organic material films from which we noticed that the maximum absorption is mainly located from 300 to 400 nm peaked at 315 nm. Photocurrent response curve of bilayer device is also located on UV region peaked at 365 nm (see the inset), so UV light of 365 nm was selected as the wavelength of incident light.

The photocurrent–voltage character of the three devices are shown in Fig. 5. It can be seen that device (c) indicates much better PV performance than device (a) and (b). Under 2  $\text{mW}/\text{cm}^2$ , 365 nm UV illumination, device (a) with the m-MTDATA/BCP bilayer showed an open-circuit voltage ( $V_{oc}$ ) as high as 2.05 V, a short-circuit current ( $I_{sc}$ ) of  $58.5 \times 10^{-6} \text{ A}/\text{cm}^2$  and fill factor (FF) of 0.26, which corresponds to the maximum power conversion efficiency ( $\eta_e$ ) of 1.83%. For device (b), inserting CuPc between anode and m-MTDATA layer,  $I_{sc}$  increased little, which is correlative with the absorption of CuPc.

Comparing device (b) and (c), we can see that a thin mixed layer (m-MTDATA:BCP) in device (c) was added between electron donor and acceptor. Device (c) achieves better PV property, that is  $I_{sc}$ ,  $V_{oc}$  and  $\eta_e$  were increased considerably to  $92.1 \times 10^{-6} \text{ A}/\text{cm}^2$ , 2.10 V and 2.91%, respectively. It is demonstrated that the thin mixed layer plays a important role for improving PV performance through increasing the contact area between m-MTDATA and BCP molecules and providing a better exciton dissociation zone than the simple interface between

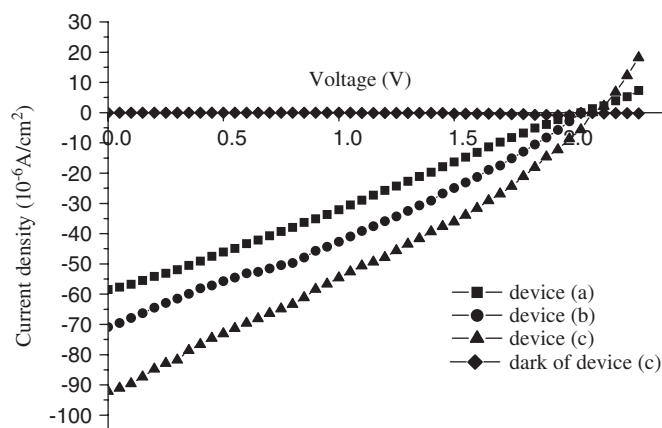


Fig. 5. I–V characteristics of the devices under dark and UV illumination.

m-MTDATA/BCP. The more active intermolecular interface would be provided for excitons decompose, the better PV diode would perform, which were higher than results reported previously [9].

Besides it is also approved from this work that EL and PV characters improved synchronously when CuPc was introduced into the mixed layer device, and probably demonstrated that, increasing PV properties could contribute increased UV CuPc absorption and enhancing EL emission should result from controlling recombination of electron and hole because hole mobility of m-MTDATA considerably larger than that of electron mobility of BCP. CuPc can restrain the hole transport to the mixing layer emitting zone so that efficient exciplex emission controlled to form in the thin mixing layer (m-MTDATA: BCP).

In addition, such a thin mixing (m-MTDATA: BCP) layer played respectively important role for improving the EL emission and PV effect of the bifunctional diode [12,20]. Under the bias, the hole is injected from ITO anode into the HOMO of m-MTDATA, when it meets the injected electron in the LUMO of BCP from the Al cathode, then recombine as an exciplex. This will give an emission far from the emission of m-MTDATA and BCP. When the device was under illumination of a UV light from glass/ITO side, [m-MTDATA] molecule is excited to be [m-MTDATA]\* that is a good electron donor to the acceptor BCP in its ground state, leading to an exciplex forming at the intramolecular interface, a photoinduced electron transfer process of [m-MTDATA\* + BCP] → [m-MTDATA<sup>+</sup>...BCP], that is, donor–acceptor (D–A) pair is assumed to occur [8]. At the same time, photogeneration excitons are formed in m-MTDATA layer, and then migrate to D–A interface where exciton dissociation is known to be efficient. An exciton is separated by mixing exciplex, creating electron in the A layer and holes in the D layer at the interface, respectively. The charges should be removed by transfer toward the opposite collection electrode [3,21]. According to the above argument, the

EL and PV effects are proposed to associate with the exciplex formation, and this is another method to choose suitable material system to design a efficient EL and PV diode [8].

#### 4. Conclusions

In conclusion, BCP-containing organic bifunctional diodes with light to electricity and electricity to light conversions have been achieved. The obtained EL emission originates from recombination of electrons and holes coming from the electrodes, and the PV effect is ascribed to exciplex formation at the interface between the two organic films. The UV light sensitizing PV diode is presumed to apply an optical sensor due to its high-voltage signal under illumination. This kind of device can be used to produce energy, which can be stored and used for the EL emission when the additional power supply cannot be required.

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