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2007 Chinese Phys. Lett. 24 2060

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Photovoltaic and Electroluminescence Bifunctional Devices with Starburst Amine and Rare-Earth-Complexes *

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(Received 8 January 2007)

We fabricate the organic photovoltaic (PV) devices, in which 4,4',4''-tris-(2-methylphenylphenylamino)triphenylamine (*m*-MTDATA) and rare earth (RE) (dibenzoylmethanato)₃(bathohenanthroline) (RE(DBM)₃bath) (RE = Nd or Pr) are used as electron donor and acceptor, and investigate their PV properties. The PV diode fabricated in the optimum processing conditions shows the open-circuit voltage of 1.91 V, short-circuit current of 0.1 mA/cm², fill factor of 0.38, and the overall power conversion efficiency of 1.9% when it is irradiated under UV light (4 mW/cm²). The photocurrent density exhibits an increase of 20% at least when a very thin LiF layer is inserted between the RE-complexes and the Al cathode. A strong electroluminescence from the interface is also observed and the maximum luminance of a yellow emission resulted from the exciplex is 580 cd/m² at 17 V bias.

PACS: 72.40.+w, 78.60.Fi

Considerable interest has been focused on the details of the process in organic electroluminescence (EL) devices in the field of organic electronics for a long history.^[1] Organic photovoltaic (PV) cells have also attracted remarkable attention since reported by Tang in 1986^[2] because the organic PV cells have the potential advantages compared to inorganic PV ones. For example, they can be made lightweight with economical materials and can be deposited on low-cost substrates. Most studies on organic PV devices were mainly focused on conjugated polymers and its derivatives^[3–8] and some small molecular.^[9–12] However, the report about organic PV cell fabricated with rare earth complexes (RE-complexes) is very few compared to those with pure organic materials though there are many EL reports of RE-complexes.^[13–15] An organic-film PV diode with N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and yttrium (acetylacetono)₃(monophenoanthroline) [Y(ACA)₃phen] as electron-donor and acceptor, respectively, was first reported in our group.^[16] PV diodes which were fabricated with other RE-complexes and organic materials as electron-acceptor and donor have been investigated in detail in our lab. The PV performance of the devices with 4,4',4''-tris-(2-methylphenylphenylamino)triphenylamine (*m*-MTDATA) and (RE) (dibenzoylmethanato)₃(bathohenanthroline) (RE(DBM)₃bath) (RE = Nd or Pr) used as electron-donor and acceptor, respectively, were better than that previously reported one. In this Letter,

new PV devices used RE(DBM)₃bath) (RE = Nd or Pr) and *m*-MTDATA as electron materials are fabricated and their PV and EL properties have been investigated. Although improvement of EL performances by inserting LiF between the organic layer and the Al cathode layer is considerably investigated,^[17–19] we also try to introduce this technique in the PV devices and to investigate the effect of LiF on the PV properties.

Nd(DBM)₃bath and Pr(DBM)₃bath were synthesized according to the traditional method in our laboratory.^[20] TPD, *m*-MTDATA and NPB are all commercial products from the Shanghai Chemical Reagent Company of China.

ITO coated glass substrates were pretreated according to Ref. [16]. All of the organic layers and a Mg:Ag alloys (100 nm, 10:1) or a LiF/Al (1 nm/100 nm) cathode were sequentially deposited onto the ITO substrates by thermal evaporation at a pressure of 8×10^{-4} Pa. Deposition of all layers was monitored by quartz oscillators and controlled at a rate of 0.2–0.4 nm/s for the organic layers and 1.0 nm/s for the cathode. The active area of a typical device was 0.15 cm².

The absorption spectra were measured with a Shimadzu UV-3000 spectrophotometer. The EL spectra and CIE colour coordinates of the devices were checked with a Hitachi MPF-4 fluorescence spectrophotometer. The current and the EL brightness were recorded using a C63 type current meter and

* Supported by the National Natural Science Foundation of China under Grant No 90201012, and the University Foundation for Young Doctor Y050429.

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a 1980A spot photometer, respectively. The spectral response curves of the photocurrent of the PV diode were determined by illumination with ultraviolet (UV) light with 3 nm bandwidth generated from a Xe lamp ($40 \mu\text{W}/\text{cm}^2$).

In this work, we mainly focus on investigating the PV performance of diodes with Pr(DBM)₃bath and Nd(DBM)₃bath as electron acceptors, m-MTDATA, TPD and NPB as electron donors respectively, in order to improve the properties of PV diodes.

First, the Pr(DBM)₃bath was fixed up as electron acceptor, m-MTDATA, TPD and NPB were sequentially selected as electron donor under the same conditions in order to compare the PV performance of m-MTDATA-type diodes. Second, the Nd(DBM)₃bath was selected as electron acceptor when m-MTDATA was used as electron donor in the same device structure and fabrication conditions to understand the PV property difference between the Nd-type- and Pr-type-devices. Thus, the PV diode with Nd(DBM)₃bath and m-MTDATA used as electron-acceptor and donor, respectively, was investigated in more detail.

Figure 1 shows the molecular structures of the organic materials used and the configuration of the PV diode. The values of x and y in Fig. 1 are changed to investigate the PV properties. When the values of x and y both reach to 20 nm, the best performance is observed in the PV diode. The spectrum of the diode EL emission and photoluminescence of m-MTDATA (excited at 350 nm) is shown in Fig. 2. The visible emission is not observed in the Nd(DBM)₃bath layer when it is excited by 350 nm UV light.

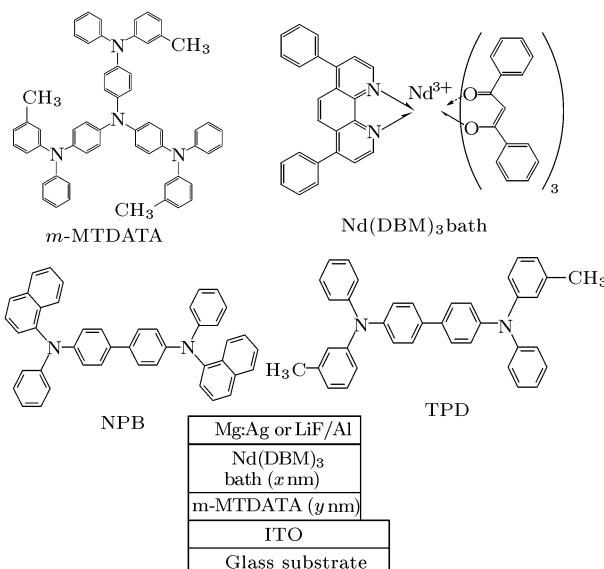


Fig. 1. Configuration of PV diode and the molecular structure of the materials used.

Table 1 lists the CIE colour coordinates of the device at different driving voltages. Figure 3 shows the current-voltage and luminance-voltage proper-

ties of the EL device. The typical device has a maximum luminance of $580 \text{ cd}/\text{m}^2$ at 17V and the threshold voltage is about 3 V. The absorption spectrum of Nd(DBM)₃bath, m-MTDATA and the Nd(DBM)₃bath/m-MTDATA film together with the spectral response curve of the photocurrent of the PV diode is shown in Fig. 4. The spectral response curve of the photocurrent of PV diodes upon illumination in the range between 290 and 430 nm is almost matched to those of the absorptions of Nd(DBM)₃bath, m-MTDATA and the two-layer film. This is remarkably different from that earlier reported result in which the photocurrent is only based on the electron-donor by Chu *et al.*^[16] in our laboratory. The typical parameters, open-circuit voltage V_{oc} , short-circuit current I_{sc} , and fill factor (FF), of the optimum PV cell reach about 1.91 V, $0.1 \text{ mA}/\text{cm}^2$ and 0.38, respectively, and the overall power conversion efficiency is about 1.9% under illumination with 365 nm UV light at $4 \text{ mW}/\text{cm}^2$. The photocurrent density and the overall power conversion efficiency of this PV diode is more than two times of the earlier reported values ($0.46 \times 10^{-3} \text{ mA}/\text{cm}^2$ and 0.7%)^[16] in our group.

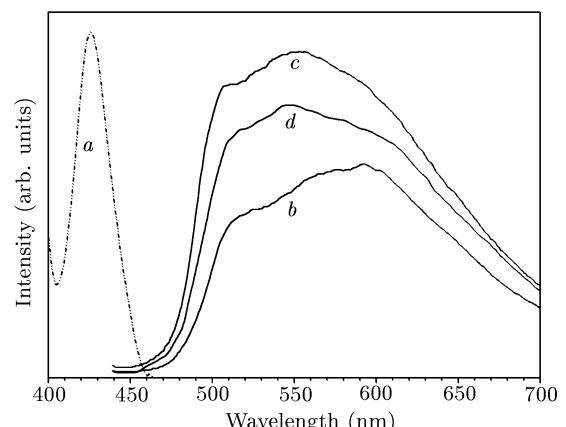


Fig. 2. Photoluminescence spectrum of m-MTDATA (excited at 350 nm) (a) and EL spectra of the device of ITO/m-MTDATA (20 nm)/Nd(DBM)₃bath (20 nm)/LiF:Al (100 nm) driven by different voltages: (b) 5 V, (c) 10 V, (d) 15 V. For comparison, the intensity of (c) and (d) is 1/6 of the original one.

Table 1. CIE colour coordinates of the diode with different driving voltages.

Driving voltage (V)	5	10	15
Colour coordinate x	0.4541	0.4276	0.4260
y	0.5078	0.5173	0.5149

From Fig. 2, it can be found that the EL emission band of the PV device is attributed to neither the m-MTDATA nor the Nd(DBM)₃bath (no visible emission). According to Ref. [16], the emission bands should be assigned to the emission of exciplex formed between m-MTDATA and Nd(DBM)₃bath layers. The exciplex formed from the two organic lay-

ers looks like to play an important role in the PV effects. It is reported that m-MTDATA is easy to form exciplex^[21] due to low solid-state ionization potential (5.1 eV).^[22] The PV effects of the diodes with m-MTDATA are better than those with NPB (or TPD) in our experiment though the hole mobility of the former is poorer than that of the latter,^[23,24] which is similar to the data reported by Hong *et al.*^[25]

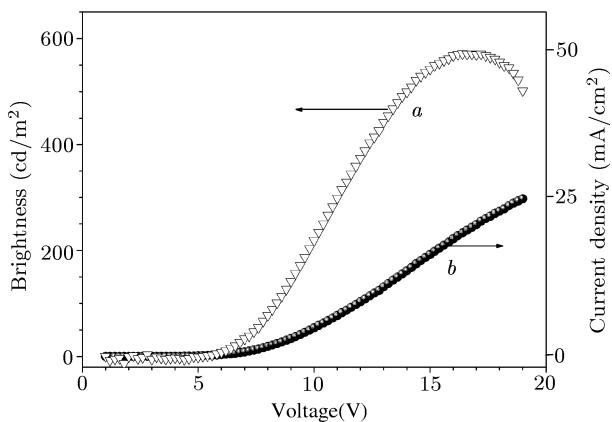


Fig. 3. Luminance–voltage (a) and current–voltage (b) characteristics of the ITO/m-MTDATA (20 nm)/Nd(DBM)₃ bath (20 nm)/LiF:Al (100 nm) device.

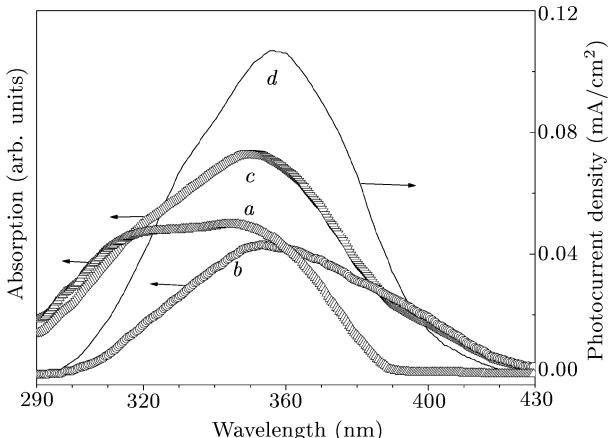


Fig. 4. Absorption spectra of m-MTDATA film (a), Nd(DBM)₃ bath film (b), m-MTDATA/Nd(DBM)₃ bath film (c) and the spectral response curve (d).

Hong *et al.*^[25] have reported that there is some relation between the photocurrent and the emission of exciplex in pure organic PV diode. We also investigate the relationship of photocurrent and the emission of exciplex in RE-complex PV device and find that the result is not fully in agreement with that reported by Hong *et al.*^[25] In our experiment, the change trend of photocurrent of the PV diodes is similar to the intensity of EL emission, but the change between photocurrent and EL intensity is not at the same step. The photocurrent has already been detected though the EL emission of exciplex is not observed in the

Nd(DBM)₃bath system. The most value of photocurrent is obtained when both the thickness of electron-acceptor and donor layers are 20 nm in the PV diode. However, the intensity of EL emission of the device does not reach the most value when the thickness of layers is kept 20 nm. In other words, the optimum conditions in the PV device are not the same as that in the EL device.

When the layers are very thin, the exciplex formed in the interface of layers is very little, thus the value of photocurrent is very low because the photocurrent of the PV device is directly related to the exciplex-formation. When the thickness of the layers is increased, probably the exciplex-formation is also increased and the photocurrent value would increase. The photocurrent decreasing with the increasing thickness further should be attributed to the resistance of the two films. Then, there should be suitable thicknesses of the two films for obtaining good PV performances. The PV diode shows a good PV performance when both m-MTDATA and Nd (DBM)₃bath films are kept 20 nm in our experiment.

Because there have already existed photocurrent in the PV diode when the exciplex emission is not observed, the exciplex formation is not always directly related to its emission. That is, the emission spectrum is only a probe, decay or relaxation from the instantaneous excited states can emit and can also decay to some trap levels or other levels. Thus we can describe that the excited state resulted from exciplex formation can either emit or not emit light.

The exciplex formed by the interaction between the excited singlet-state hole-transport material m-MTDATA and the ground-state electron-transport material Nd(DBM)₃bath. When the exciplex is formed through the UV light irradiation, the photo-generation excitons can be formed in the interface. An exciton is separated by inner field in the exciplex, creating electron in the acceptor layer and holes in the donor layer at the acceptor-donor interface, respectively. The charges should be removed by transfer toward the opposite collection electrode.^[16]

It is well known that the luminance of EL devices can be considerably increased when inserted a LiF film between the organic film and Al cathode.^[17–19] We use only Al metal instead of Mg:Ag alloy as cathode and find that the photocurrent density is not obviously affected. However, when the LiF film is inserted between the Nd(DBM)₃ bath and the Al film, it is found that the photocurrent density increases at least 20%. It is demonstrated that the phenomenon may be attributed to the increasing collection of electrons coming from electron acceptor, i.e. Nd(DBM)₃bath. Because the collecting process is an opposite process with electron-injection of EL, very thin LiF film may also play a ‘channel collection’ role in the PV process.^[26]

In summary, a relatively high efficiency (1.9%) bi-functional PV and EL device has been achieved using Nd(DBM)₃bath and m-MTDATA under the optimum experimental conditions. A relatively strong PV effect is observed from the device which shows exciplex emission. The high efficiency comes from the suitable electron-donor and acceptor materials and the thin LiF film between the RE-complex and Al cathode. The PV effect is ascribed to the exciplex formation at the interface between the organic layers. The PV diode can be used in practice someday by further improving the property because of the relative high efficiency.

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