Enhancement of both electroluminescent and ultraviolet detective properties in organic optoelectronic integrated device realized by two triplet-triplet annihilation materials

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ABSTRACT

The performance enhancement of organic optoelectronic integrated device (OID) was realized by using a triplet-triplet annihilation (TTA) featured material of 6-(3,5-bis-[9-(4-t-butylphenyl)-9H-carbazol-3-yl]-phenoxy}-2-(4-t-butylphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (CzPhONI) as a host and another TTA featured material of (E)-2-[4-(t-butyl)phenyl]-6-{2-[6-(diphenylamino)naphthalene-2-yl] vinyl}-1H-benzo [de]isoquinoline-1,3(2H)-dione (NA-TNA) as a dopant in a doping system to be an active layer. The result showed that the OID with a doping system had a maximum luminance of 7100 cd/m^2 with a lower turn-on voltage of 2.5 V as OLED. Meanwhile, the NA-TNA doped OID exhibited a high detectivity of 4.5×10^{12} Jones at a bias of -1 V under the UV-350 nm illumination, which was 34.6 folds higher than that of the pristine CzPhONI based device. Based on the analysis of the energy transfer model of devices, it was found that the improved electroluminescent performance of OID was attributed to the TTA process and efficient energy transfer from CzPhONI to NA-TNA. And by analyzing the dark current behavior of device, the high ultraviolet detective property of OID was caused by the merit of the energy band "carrier capture region" when the dopant NA-TNA was added into the active layer, and the energy band "carrier capture region" contributed to reducing the dark current of OID.

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1. Introduction

Organic optoelectronic devices have attracted lots of research interests such as organic light-emitting diodes (OLEDs), organic photovoltaic devices (OPVs), organic photodetectors (OPDs) and organic thin film transistors, which have potential to provide low cost, flexible, and large-area devices [1–7]. Among them, OLED has been widely used in solid-state lighting and full-color flat-panel display [6–8]. Simultaneously, OPD has drawn wide interests in the past decades due to the broad applications in biological/chemical sensing, ozone detection, smoke/fire monitoring and missile warning [6–10]. Nowadays, organic optoelectronic integrated device (OID) with OLED and ultraviolet-OPD (UV-OPD) dual functions [12] (or OLED-OPV [9]) becomes an important part of organic optoelectronics, since the state-of-the-art OID shows great potential applications in many fields, e.g., intelligent control, interior decoration and wearable device [11,13].

The OID has two working modes, e.g., OLED mode under forward voltage bias and UV-OPD mode when applying reverse voltage bias. When the OID operates in OLED mode, electrons and holes are separately injected from cathode and anode to form excitons, which radiatively recombine yielding electroluminescence (EL) property [14]. As for the OPD mode, the photo-activated excitons in the active layer will dissociate into holes and electrons, which would be collected by the cathode and anode under the reverse bias [15]. It can be seen that the transport directions of electrons and holes in the two modes are opposite. Thus, it seems contradictory to construct an OID with excellent OLED and UV-OPD properties simultaneously. Even in such a difficult situation, Li reported an OID with a detective response of 135 mA/W and a brightness of 4182 cd/m^2 [21]. Narasimhan also reported an OID based on a fluorescent dye with a photovoltaic response of 77 mA/W and an EL internal quantum efficiency (IQE) of 64% [19].

However, there is still space to improve the luminance and detectivity of OID for practical application [18].

Recently, the delayed fluorescence materials, containing of thermally activated delayed fluorescence (TADF) material and triplet-triplet annihilation (TTA) material, were not only widely adopted to fabricate highly efficient OLED, but also used as the active layer to realize high performance OID [16,18]. However, further improvement of OID performance is refrained by the low energy transfer efficiency and photoluminescence (PL) quenching in the active layer with only one kind of delayed fluorescence material [15]. In TTA-OLEDs, if both the hosts and guests are TTA materials, triplet excitons could be harvested not only through host compounds, but also through guest compounds if the doping levels are relatively high. Although it is an effective strategy to overcome exciton quenching and improve EL performance of OLED by utilizing the model of energy transfer between the host and dopant materials [22–25], there are few works to apply this method for realizing high performance OID. Thus, a study of doping system in the OID, correlating with the energy transfer between the host and the dopant, is imperative [26].

In this work, a TTA featured material of 6-(3,5-bis-[9-(4-*t*-butylphenyl)-9*H*-carbazol-3-yl]-phenoxy)-2-(4-*t*-butylphenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (CzPhONI) as a host and another TTA featured material of (*E*)-2-[4-(*t*-butyl)phenyl]-6-{2-[6-(diphenylamino)naphthalene-2-yl] vinyl}-1*H*-benzo [*de*]isoquinoline-1,3(2*H*)-dione (NA-TNA) as a dopant were used as the active layer in a doping system to fabricate a high performance OID, and the EL and UV detective properties of the device were studied. To analyze the reason for the improvement of both EL and UV detective properties, the mechanism of spectral alterations, energy transfer, doping density, UV-light absorption of the doping system were also discussed.

2. Experiment details

Before the deposition of organic functional layers, indium tin oxide (ITO) coated glass substrates were successively cleaned by detergent, deionized water, acetone, ethanol, for 10 min at each ultrasonic step. Then ITO substrates were treated with oxygen plasma for 5 min to increase the work function of ITO. Organic materials were deposited under a pressure of 2.0×10^{-4} Pa [27] with a deposition rate of 0.5–2 Å/s. After that, without breaking the vacuum, metallic cathode, Mg: Ag (weight ratio is 10:1) cathode was deposited on the organic layer with a shadow mask under a vacuum pressure of 1.5×10^{-3} Pa forming a device area of 0.2 cm^2. Film thickness and deposition rate were monitored by oscillating quartz thickness monitor. The OIDs were fabricated with a basic structure of ITO/MoO$_3$ (8 nm)/1,1-bis((di-4-tolylamino)phenyl) cyclohexane (TAPC) (5 nm)/CzPhONI:NA-TNA (6 wt% in weight)/bathophenanthroline (Bphen) (30 nm)/Mg:Ag (100 nm). The device structure, molecular structures of CzPhONI and NA-TNA were shown in Fig. 1.
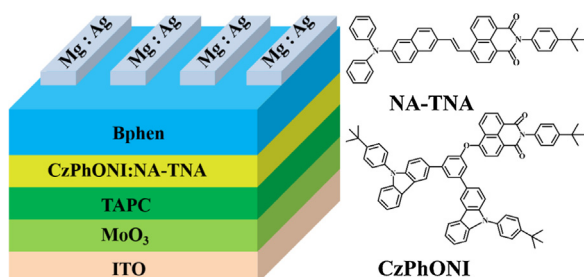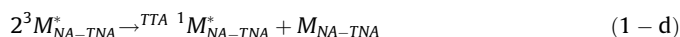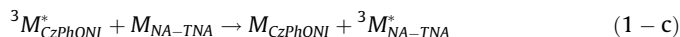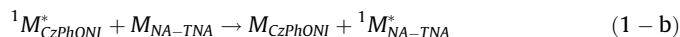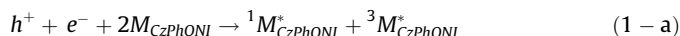

Fig. 1. Structure of NA-TNA doped device, and molecular structures of CzPhONI and NA-TNA.

Current density-voltage-luminance (*J-V-L*) characteristics were tested by combining a spectrometer with a Keithley 4200 semiconductor characterization system. EL spectra of the devices were measured with an OPT-2000 spectrometer. Ultraviolet-visible (UV–vis) absorption spectra were characterized with a Shimadzu UV-1700 spectrophotometer. The current density-voltage (*J-V*) characteristics in dark and under illumination were measured with Keithley 4200 [17]. The 350 nm UV light source with a power of 0.2 mW/cm^2 was used as the illumination source. All devices were tested in the atmospheric environment and all measurements were carried out at room temperature without device encapsulation [29]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the organic materials were calculated according to cyclic voltammetry data and the lowest-energy absorption edge of the UV–vis absorption spectrum.

3. Results and discussion

When OID operates in an OLED mode, as shown in Fig. 2(a), the light emission process can be illuminated as Eqs. (1a–e):

$$h^+ + e^- + 2M_{CzPhONI} \rightarrow {}^1M^*_{CzPhONI} + {}^3M^*_{CzPhONI} \qquad (1-a)$$

$$ {}^1M^*_{CzPhONI} + M_{NA-TNA} \rightarrow M_{CzPhONI} + {}^1M^*_{NA-TNA} \qquad (1-b)$$

$$ {}^3M^*_{CzPhONI} + M_{NA-TNA} \rightarrow M_{CzPhONI} + {}^3M^*_{NA-TNA} \qquad (1-c)$$

$$ 2 {}^3M^*_{NA-TNA} \xrightarrow{TTA} {}^1M^*_{NA-TNA} + M_{NA-TNA} \qquad (1-d)$$

$$ {}^1M^*_{NA-TNA} \rightarrow h\nu + M_{NA-TNA} \qquad (1-e)$$

where the ground state and the excited state of NA-TNA (or CzPhONI) are marked as M and M^*, ${}^1M^*$, and ${}^3M^*$ represent singlet and triplet excitons, respectively. The above energy transfer process can be described in the following 4 steps: (1) Holes and electrons are separately injected into anode and cathode from the external circuit. (2) Holes and electrons transport to the emission layer (EML) through TAPC hole transport layer (HTL) and Bphen electron transport layer (ETL). (3) Holes and electrons form both singlet and triplet excitons in the EML. (4) The excitons recombine to the ground states and generate light emission [30].

As both of the host and dopant materials possess TTA characteristic, triplet excitons are utilized not only by the host, but also by the dopant through TTA process [15]. Fig. 3(a) shows the PL and EL spectra of CzPhONI, NA-TNA and CzPhONI: NA-TNA films. It can be seen that the EL and PL peaks of CzPhONI are 505 nm, 493 nm and NA-TNA are 623 nm, 632 nm, respectively. The CzPhONI: NA-TNA film has a blue shifted emission peak at 570 nm comparing with pristine NA-TNA film, which is due to the low doping effect of NA-TNA. For the charge transfer (CT) feature of CzPhONI and NA-TNA, the EL and PL spectral of them are closely related to the polarity of the solvents, along with the increase of polarity of the solvents, the spectral will has a red-shift for the positive solvent effect. Similarly, in the doped film, the polarity of the host (or dopant) has a great impact on the spectral of the dopant (or host). As the polarity of dopant is larger than that of the host, with the increase of the dopant concentration (the ratio increase of NA-TNA in the doped film), the PL and EL spectral of the doped film will also have a red-shift compared to pristine CzPhONI film. Thus the PL and EL spectral of the doped film will locate