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## High efficient organic ultraviolet photovoltaic devices based on gallium complex

### Zisheng Su<sup>a,b</sup>, Bei Chu<sup>a</sup>, Wenlian Li<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China <sup>b</sup> Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

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1. Introduction

#### ABSTRACT

High efficient organic ultraviolet (UV) photovoltaic devices comprising 4,4',4"-tri-(2-methylphenyl phenylamino) triphenylamine (m-MTDATA) and tris-(8-hydroxyquinoline) gallium (Gaq<sub>3</sub>) as the electron donor and acceptor, respectively, are demonstrated. The m-MTDATA/Gaq<sub>3</sub> bilayer device shows a short-circuit current density of 59.3  $\mu$ A/cm<sup>2</sup>, a open-circuit voltage of 1.85 V, a fill factor of 0.41, and a power conversion efficiency of 3.74% under illumination of a 1.2 mW/cm<sup>2</sup> 365 nm UV light. And this power conversion efficiency is superior than that of the device based on tris-(8-hydroxyquinoline) aluminum with the same device structure, which is attributed to the high electron mobility of Gaq<sub>3</sub> and the low exciton loss via radiation decay and hence more exciton dissociation in m-MTDATA/Gaq<sub>3</sub> device.

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In the past two decades, there is a growing interest on organic electronic devices, including light-emitting diodes [1], photovoltaic (PV) devices [2], thin film transistors [3], etc., due to their light weight, low cost, and compatibility with flexible substrates compared to inorganic counterparts. Since the demonstration of high efficient exciton dissociation in the donor–acceptor (D–A) heterojunction interface [4], PV devices have drawn particular attention owing to their potential applications in solar cells and photodetectors [5–9]. The PV effect involves the formation of excitons under illumination, the diffusion of excitons to the D–A interface, the dissociation of excitons into electrons and holes, and the collection of electrons and holes at opposite electrodes. To achieve a maximum efficiency, many methods have been adopted to optimize all the four processes involved in the generation of photocarriers [10–12].

The major ultraviolet (UV) radiation reaching the surface of the earth covers wavelength from 300 to 420 nm, and a lot of diseases, such as skin cancer, would be caused by long-term exposure to the UV radiation. Thereby it is necessary to detect the UV radiation intensity for human health. On the other hand, UV PV devices have the potential applications for UV curing monitors, solar astronomy, missile plume detection, and space-to-space transmission. Thus, they are attracting much attention recently. UV PV devices comprising a lot of materials have been reported, such as rear-earth complexes [13–15], Cu(I) complexes [16], and polymer/inorganic

hybrids [17]. Hong et al. [18] reported that PV devices with 4,4',4"-tri-(2-methylphenyl phenylamino) triphenylamine (m-MTDATA) and tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) acted as the electron donor and acceptor, respectively. Tris-(8-hydroxyquinoline) gallium (Gaq<sub>3</sub>) has analogous molecular structure and photophysical properties to that of Alq<sub>3</sub>. The photoluminescent (PL) quantum efficiency of Gaq<sub>3</sub> is demonstrated to be a quarter of that of Alq<sub>3</sub> [19,20]. Low PL efficiency of the donor and the acceptor is usually considered as one criterion to obtain high power conversion efficiency  $(\eta_{\rm P})$  in PV devices due to the competitive processes of the exciton radiation and exciton dissociation. Moreover, the electron mobility of Gaq<sub>3</sub> is higher than that of Alq<sub>3</sub> [19,21]. In view of these, Gaq<sub>3</sub> may offer superior performance compared to Alg<sub>3</sub> in the PV devices. In this paper, UV PV devices with m-MTDATA as the electron donor and Gag<sub>3</sub> as the electron acceptor, respectively, were fabricated. The m-MTDATA/Gag<sub>3</sub> bilayer device shows a short-circuit current ( $I_{SC}$ ) of 59.3  $\mu$ A/cm<sup>2</sup> and a  $\eta_{\rm P}$  of 3.74%. And the performance is better than that of Alq<sub>3</sub> with the same device structure, which is attributed to the high electron mobility of Gaq3 and low exciton loss due to radiation and hence more exciton dissociation in the m-MTDATA/Gaq<sub>3</sub> interface.

#### 2. Experimental

Devices were fabricated on precleaned indium tin oxide (ITO)coated glass substrates with a sheet resistance of 25  $\Omega$ /sq. A 50 nm 3,4-polyethylenedioxythiophene:polystyrenesulfonate (PED-OT:PSS) was spin-coated on ITO, followed by drying at 120 °C for





<sup>\*</sup> Corresponding author. Tel./fax: +86 431 86176345. *E-mail address:* wllioel@yahoo.com.cn (W. Li).

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60 min in vacuum. The PEDOT:PSS layer serves to planarize the ITO, thereby preventing shorts through the thin donor and acceptor layers [22]. Then, m-MTDATA and Gaq<sub>3</sub>, which acted as the electron donor and acceptor, respectively, were thermal evaporated in vacuum chamber at  $3 \times 10^{-4}$  Pa, followed by a 0.5 nm LiF and 100 nm Al cathode. The molecular structures of m-MTDA-TA and Gaq<sub>3</sub> are shown in Fig. 1. Two devices were fabricated with configurations as follows:

Device A: ITO/PEDOT:PSS/m-MTDATA (30 nm)/Gaq<sub>3</sub> (30 nm)/ LiF /Al Device B: ITO/PEDOT:PSS/m-MTDATA (30 nm)/Alq<sub>3</sub> (30 nm)/ LiF/Al

Deposition rates and thickness of the layers were monitored using oscillating quartz monitors. The evaporating rates were kept at 0.5–1 Å/s for organic layers and LiF layer and 10 Å/s for Al cathode, respectively. Absorption spectra of all organic films on quartz substrates were measured with a Shimadzu UV-3101 PC spectro-photometer. PL spectra were measured with a Hitachi F-4500 spectrophotometer. Photocurrent response curve was obtained under irradiance of a 40  $\mu$ W/cm<sup>2</sup> Xe lamp. Current density-voltage (*I–V*) curves were measured by a Keithley 2400 source meter under illumination of 365 nm UV light (1.2 mW/cm<sup>2</sup>) or AM 1.5 solar simulator (100 mW/cm<sup>2</sup>). All the measurements were carried out at room temperature under ambient conditions.

#### 3. Results and discussion

Fig. 2 shows the absorption spectra of 30 nm m-MTDATA, 30 nm Gaq<sub>3</sub>, 30 nm Alq<sub>3</sub>, and 30 nm m-MTDATA/30 nm Gaq<sub>3</sub> blend films on quartz substrates. A broad absorption band in the range of 300 to 400 nm in the absorption spectrum was found in the m-MTDATA/Gaq<sub>3</sub> bilayer film, which is a simple superposition of the absorptions of m-MTDATA and Gaq<sub>3</sub>, indicating that the absorptions of m-MTDATA and Gaq<sub>3</sub> are responsible for the photo-induced carrier generation. For reference, the absorption spectrum of 30 nm Alq<sub>3</sub> measured with the same conditions is also presented in Fig. 2. Gaq<sub>3</sub> and Alq<sub>3</sub> have almost the same absorption spectra in the range investigated, although the absorption coefficiency of Alq<sub>3</sub> is a little lower than that of Gaq<sub>3</sub>. The photocurrent response curve of Device A is shown in Fig. 3, which reveals a maximum response in the region of 360–370 nm. Thus, a 365 nm UV light was selected as the illumination source for the PV devices.



Fig. 2. Absorption spectra of 30 nm m-MTDATA, 30 nm Gaq<sub>3</sub>, 30 nm Alq<sub>3</sub>, and 30 nm m-MTDATA/30 nm Gaq<sub>3</sub> films on quartz substrates.



Fig. 3. Photocurrent response of Device A under illumination of a Xe lamp.

Fig. 4 plots the *I–V* characteristics of Devices A and B under irradiation of a 365 nm UV light with the intensity of 1.2 mW/cm<sup>2</sup>.



Fig. 1. Molecular structure of m-MTDATA and Gaq<sub>3</sub>.

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