Energy transfer ultraviolet photodetector with 8-hydroxyquinoline derivative-metal complexes as acceptors*

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We choose 8-hydroxyquinoline derivative-metal complexes (Beq, Mgq, and Znq) as the acceptors (A) and 4,4',4"-tri-(2-methylphenyl phenylamino) triphenylaine (m-MTDATA) as the donor (D) respectively to study the existing energy transfer process in the organic ultraviolet (UV) photodetector (PD), which has an important influence on the sensitivity of PDs. The energy transfer process from D to A without exciplex formation is discussed, differing from the working mechanism of previous PDs with Gaq [Zisheng Su, Wenlian Li, Bei Chu, Tianle Li, Jianzhuo Zhu, Guang Zhang, Fei Yan, Xiao Li, Yiren Chen and Chun-Sing Lee 2008 *Appl. Phys. Lett.* **93** 103309)] and REq [J. B. Wang, W. L. Li, B. Chu, L. L. Chen, G. Zhang, Z. S. Su, Y. R. Chen, D. F. Yang, J. Z. Zhu, S. H. Wu, F. Yan, H. H. Liu, C. S. Lee 2010 *Org. Electron.* **11** 1301] used as an A material. Under 365-nm UV irradiation with an intensity of 1.2 mW/cm^2, the m-MTDATA:Beq blend device with a weight ratio of 1:1 shows a response of 192 mA/W with a detectivity of 6.5×10^{11} Jones, which exceeds those of PDs based on Mgq (146 mA/W) and Znq (182 mA/W) due to better energy level alignment between m-MTDATA/Beq and lower radiative decay. More photophysics processes of the PDs involved are discussed in detail.

Keywords: organic photodetector, energy transfer, ultraviolet

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1. Introduction

A number of synthesized organic materials exhibit semiconducting properties and they generate free electron–hole pairs when thermally or photon excited and they allow carrier transport. The interest in these materials as possible substitutes of inorganic semiconductors, like Si, GaAs or others, has constantly increased, owing to their mechanical flexibility, luminescence in the visible range, possibility to cover large surfaces, and relatively easy fabrication. In recent years organic ultraviolet (UV) photodetectors (PDs) having scientific, industrial, and commercial applications, such as in astrophysics, chemical/biological sensing, and UV meters for various electronic products, have been widely studied as a complementary alternative to the inorganic ones. The manufacturing of inorganic PDs is rather complicated and expensive, and is unsuitable for large-area applications.[1–8]

8-hydroxyquinoline derivative-metal complexes (Mq) have been extensively studied in analytical chemistry and used as emitting materials emitting fluorescence.[9–12] Among them tris-(8-hydroxyquinoline) aluminum (Alq) is excellent for its highly stable film formation, high carrier transport, and good heat resistance.[13–17] Recently, organic UV PD with using N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) and Alq as the donor (D) and acceptor (A) materials, respectively, provided a low responsivity (30 mA/W), and it had a high working bias (up to −12 V).[18] We have determined a highly efficient UV PD with aluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate(BAlq) as the D material.[6] There is an exciplex formation process between D and A materials and it is demonstrated that exciplex emission competes with the photocurrent obtained. Another case is that there is no exciplex emission between D and A materials, that is, energy transfer from D to A does occur;[18,19] however, there is rarely study on this. In this paper, we demonstrate organic UV PDs with energy transfer process with using two-ligand complexes Beq, Mgq, and Znq as the acceptors and 4,4',4"-tri-(2-methylphenyl phenylamino) triphenylaine (m-MTDATA) as the donor material. m-MTDATA is chosen as the A component due to its lower IP (1.9 eV) and higher hole mobility of 3×10^{-5} cm^2/Vs.[20,21]

2. Experimental details

The PDs were fabricated on cleaned glass substrates pre-coated with a conducting indium-tin-oxide (ITO) an-

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ode with a sheet resistance of 25 Ω/sq and the substrates were treated by UV ozone in a chamber for 15 min after solvent cleaning. The device structure was ITO/m-MTDATA:Mq(1:1, 80 nm)/LiF(1 nm)/Al(150 nm). The organic films were thermally evaporated in a high vacuum ($<10^{-6}$ Torr, 1 Torr = 1.33322×10^{2} Pa) using previously calibrated quartz crystal monitors to determine the deposition rate and the film thickness. The organic layers and Al cathode were deposited at a rate of 2 Å/s and 10 Å/s respectively. The absorption spectra and photoluminescence (PL) spectra of the organic films on quartz substrates were measured with a Shimadzu UV-3101 PC spectrophotometer and a Hitachi F-4500 spectrophotometer, respectively. The current–voltage (I–V) curves of the devices were recorded in darkness and under the illumination of 365-nm UV light through the ITO anode. The device area was about 0.03 cm^2. All the measurements were carried out at room temperature under ambient conditions.

3. Results and discussion

Figure 1 shows the molecular structure of the complex, and the energy level alignment of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the donor and acceptor materials. The LUMOs and HOMOs of Mq are determinated by cyclic voltammetry.[22] It has been recognized that energy level offset at the heterojunction is essential to the operation of the organic detector and the most efficient exciton dissociation in organic material occurs at the D/A interface because of the fundamental nature of the photogeneration process in organic material. From Fig. 1 we can see that m-MTDATA with a low ionization potential (IP) forms a heterojunction with Mq with high electron affinity (EA). Depending on the alignment of the energy levels of the donor and acceptor materials, the dissociation of the strongly bound excitons can become energetically favorable at such an interface.[23,24]

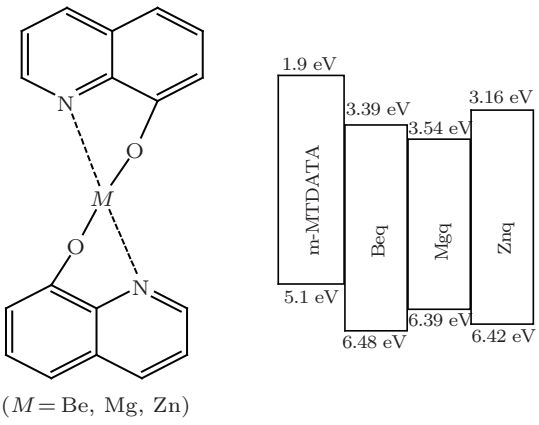


Fig. 1. Molecular structure of the complex and the LUMOs and HOMOs of donor m-MTDATA and acceptor materials.

Figure 2 shows the absorption spectra of 40-nm thick pristine films of Mq and 80-nm thick blend films with 1:1 weight ratio of m-MTDATA:Mq on quartz substrates, respectively. It demonstrates that the three blend absorption spectra appear to have almost the similar absorption spectra and a broad absorption band in a range of 300 nm–375 nm. It can be seen that the absorption peaks and valleys respectively lie at around 350 nm and 410 nm, similarly for three blend films. Znq blend film has the maximum absorption intensity at 365 nm for the stronger monomer absorption of Znq as shown by the line with a triangle in Fig. 2.

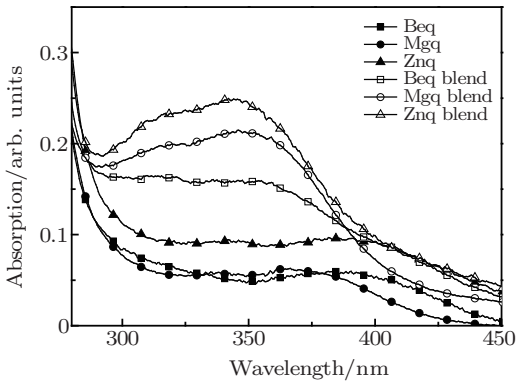


Fig. 2. Absorption spectra of 40-nm-thick pristine films of Mq and 80-nm-thick blend films of m-MTDATA:Mq with 1:1 weight ratio on quartz substrates, respectively.

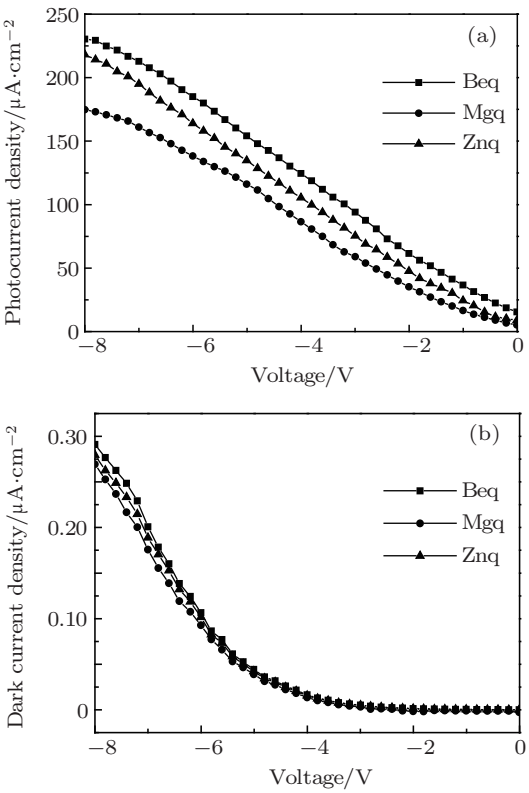


Fig. 3. Variations of (a) dark-corrected photocurrent density and (b) dark current density with reverse biase for Mq-based PDs (Beq, Mgq, and Znq) under the illumination of 365-nm UV light with an intensity of 1.2 mW/cm^2.

Figure 3(a) describes the dark-corrected photocurrent density as a function of reverse bias for Mq-based PDs (Beq, Mgq, and Znq) under the illumination of 365-nm UV light

with an intensity of 1.2 mW/cm^2. The response R is measured from the following relation:

$$R = \frac{J_p - J_d}{P_0}, \tag{1}$$

where P_0 is the incident light intensity, J_p and J_d are respectively the photo- and the dark-current densities at a certain reverse bias. The photocurrent densities of PDs based on Beq, Mgq, and Znq at −8 V are 230.4, 174.8, and 218.2 μA/cm^2, corresponding to the responses of 192, 145.7, and 181.8 mA/W, respectively.

The dark currents of the devices are extremely low compared with the photocurrents due to the rectifying I–V characteristics of the devices shown in Fig. 3(b). For example, the dark currents are only 0.292, 0.265, and 0.279 μA/cm^2 for the PDs based on Beq, Mgq, and Znq at −8 V, respectively. Figure 4 shows the response spectra of three kinds of PDs based on Beq, Mgq, and Znq as acceptor materials. It describes that the PDs each have an excellent function for UV detection.

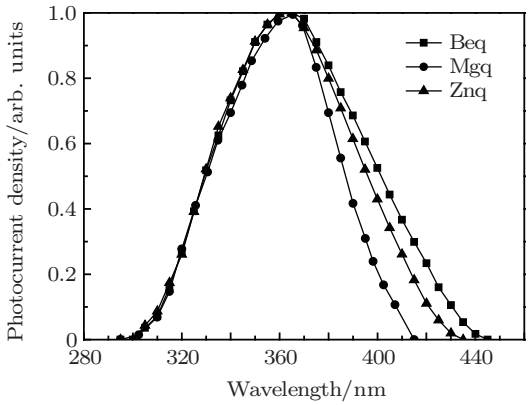


Fig. 4. Photocurrent response spectra for Mq-based PDs.

As a photodiode figure of merit, the noise equivalent power (NEP) is defined as the minimum impinging optical power that a detector can distinguish from the noise,[25] which can be shown as follows:

$$NEP = (A\Delta f)^{1/2}/D^*, \tag{2}$$

where A is the effective area of the photodiode in cm^2, Δf is the electrical bandwidth in Hz, and D^* is the detectivity measured in units of Jones. For a reverse biased photodiode, the contributions from the Johnson noise and thermal noise can be neglected and the shot noise for dark current is proposed to be the dominant component, and then D^* can be shown as follows:

$$D^* = R/(2qJ_d)^{1/2}, \tag{3}$$

where q is the absolute value of electron charge (1.6×10^{-19} C). A high D^* indicates the ability to detect lower levels of radiant power and produces a figure of merit which is area-independent. At −8 V, the detectivities calculated from Eq. (3) are $D^* = 6.5 \times 10^{11}$, 5×10^{11}, and 6.1×10^{11} Jones respectively for Beq-, Mgq-, and Znq-based PD under 365-nm illumination with an intensity of 1.2 mW/cm^2, which are comparable to those for inorganic PDs.[26–28]

PL spectra of 40-nm-thick neat films of m-MTDATA and Mq as well as 80-nm-thick m-MTDATA:Mq blend films with 1:1 ratio under the excitation of 365-nm UV light, are shown in Fig. 5 respectively. In all the blend films, no trace of emission from m-MTDATA is observed. The emission of the m-MTDATA:Mq blend film comes from Mq and its intensity is much higher than that of the pristine Mq film. The pristine film emissions of Beq, Mgq, and Znq concentrate at 520, 510, and 525 nm respectively. No emission of m-MTDATA in the blend films proves that the energy transfers from m-MTDATA to Mq, which has the same phenomenon as those in the cases of blend film of TPD and Alq.[18]

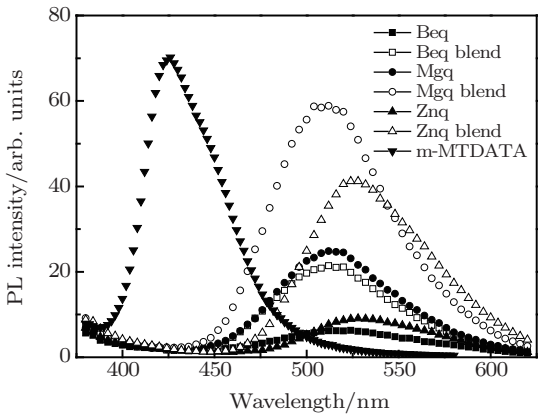


Fig. 5. PL spectra of 40-nm-thick neat films of m-MTDATA and Mq as well as 80-nm-thick m-MTDATA:Mq blend films with 1:1 ratio under the excitation of 365-nm UV light.

The work process of a PD diode is proposed in which an exciton is generated by photon absorption, the exciton diffuses to the D/A interface, the exciton is dissociated by charge transfer at a D/A interface, and the free charge carriers are collected at the electrodes under reverse bias. From the absorption, it has been seen that Znq blend film has the strongest absorption for 365-nm UV light. However, from the PL spectra as shown in Fig. 5 we see that the PL intensities of both pristine and blend film of Znq are much stronger than those of Beq, which leads to the fact that the PD based on Beq has better performance than that based on Znq. In order to understand the effect of the radiative decay on the performance of the PD, the photophysics involved should be explored. Figure 6 shows the schematic process for the present photophysics of the PD device on the assumption that geminate electron–hole pairs at D/A interface can dissociate totally. Process 1 describes the energy transfer from

D to A, that is, $D^*+A \rightarrow A^*+D$. Electron transfer from the donor to the acceptor forms the geminate electron-hole pairs, which is process 2, that is, $D^*+A \leftrightarrow (D^+-A^-)^*$. Process 3 presents $A^*+D \leftrightarrow (D^+-A^-)^*$. The excited state of the acceptor changes into the ground state by radiative decay, which is referred to as process 4. The dissociation of the geminate electron–hole pairs generates free charge carriers, which is named process 5. Thereby the formation of such a geminate electron–hole pair competes with the bulk emission of the acceptor. Although the device based on Znq blend film has the highest optical absorption, the larger loss via radiative decay leads to a lower photocurrent. The superior performance of PD based on Beq is attributed to the lowest loss of the photogenerated excitons which finally form the photocurrent.

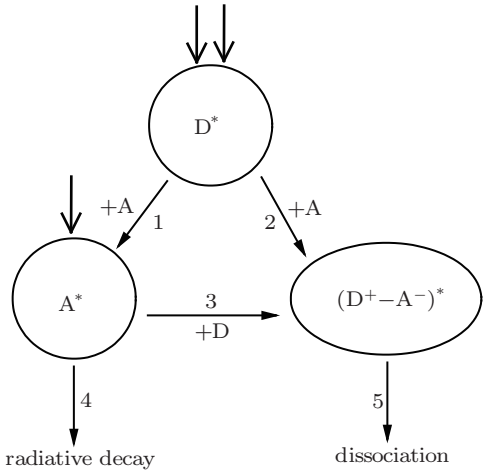


Fig. 6. Schematic diagram of PD work process for the present photophysics. The thick-line arrows represent the incident light absorbed by the donor and acceptor materials.

In order to obtain a high photosensitivity, efficient exciton dissociation is needed. The IPs and EAs of Beq and Znq are 6.48 eV and 3.39 eV and 6.42 eV and 3.16 eV, respectively. On the basis of the principle of designing a PD diode structure, a larger band-edge offset between D/A interface favors the dissociation of the strongly bound excitons energetically at such an interface, leading to a free electron polaron in the acceptor material, and a free hole polaron in the donor. The higher IP and EA of Beq than those of Znq are energetically favorable for the dissociation of the excitons for the PD using m-MTDATA as the donor material, which is another reason for the superior performance of Beq-based PD.

4. Conclusions

In this paper, we demonstrate organic UV PDs with an energy transfer process by using m-MTDATA as the donor and Beq, Mgq, and Znq as the acceptors, respectively. There is competition between the formation of geminate electron–hole pair and the bulk emission of the acceptor. Under 365-nm UV irradiation, the m-MTDATA:Beq blend device with 1:1 weight ratio shows a maximum response of 192 mA/W with a detectivity of 6.5×10^{11} Jones due to good energy level alignment between m-MTDATA/Beq and its lower radiative decay, analysed by the photophysics process of the PD involved. It is expected that the selections and/or syntheses of the D and A materials with more UV absorptions, proper energy offset, and high charge transfer would be a promising approach to achieving a higher responsivity of UV photodetectors.

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