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High response organic ultraviolet photodetector based on blend of 4,4′,4″-tri-(2-methylphenyl phenylamino) triphenylaine and tris-(8-hydroxyquinoline) gallium

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The authors demonstrate high response organic ultraviolet (UV) photodetector (PD) using 4,4′,4″-tri-(2-methylphenyl phenylamino) triphenylaine (m-MTDATA) and tris-(8-hydroxyquinoline) gallium (Gaq_3) to act as the electron donor and acceptor, respectively. The m-MTDATA:Gaq_3 blend device shows a photocurrent of 405 μA/cm^{-2} at −8 V, corresponding to a response of 338 mA/W under an illumination of 365 nm UV light with an intensity of 1.2 mW/cm^2. The high response is attributed to the enhanced dissociation of geminate hole-electron pairs in the distributed heterojunction of the blend and suppression of radiative decay. Photophysics of the PD involved is also discussed in terms of the performance and device structures. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2980025]

Organic semiconductors with photovoltaic (PV) properties are regarded as promising candidates for applications in solar cells and photodetectors (PDs) due to their unique merits of light weight, low cost, and compatibility with flexible substrates.[1–9] The PV process involves the formation of excitons under illumination, the dissociation of excitons into electrons and holes, and the collection of electrons and holes at opposite electrodes. Ultraviolet (UV) PDs have drawn particular attention due to their potential applications as UV curing monitors, sterilization monitors, etc. Much effort on the UV-PDs has been focused on inorganic semiconductors with wide band gap such as GaN (Ref. 10) and SiC.[11] However, the inorganic semiconductor based PDs require complicated manufacturing processes, high cost, and so on. Thus, organic UV-PDs are considered as a complementary alternative for the inorganic ones. Recently, organic UV-PD based on N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD) and tris-(8-hydroxyquinoline) aluminum (Alq_3) was reported.[12] Its performance, however, is obviously lower than the inorganic ones.[10,11]

With low ionization potential (IP) and electron affinity (EA),[13] 4,4′,4″-tri-(2-methylphenyl phenylamino) triphenylaine (m-MTDATA) has been generally used as a donor in UV sensitive PV diodes.[14] In previous works, we have demonstrated that m-MTDATA/Alq_3 and m-MTDATA/tris-(8-hydroxyquinoline) gallium (Gaq_3) based PV devices show power conversion efficiencies of 2.97% and 3.74%, respectively, under an illumination of 365 nm UV light. For the prototypical copper phthalocyanine (CuPc)/C_{60} PV devices, Xue *et al.*[5] demonstrated that by mixing CuPc and C_{60} to form a distributed heterojunction, the device performance can be substantially enhanced due to more efficient exciton dissociation. It is thus of interest to see whether similar enhancement effects can be exploited with other small molecular materials in PDs. In this work, PD using blend of m-MTDATA:Gaq_3, where the former and the latter function as the donor and the acceptor, respectively, was fabricated and shown to have a good response of 338 mA/W under illumination of 365 nm UV light at −8 V bias.

Devices were fabricated on cleaned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 25 Ω/sq. Organic layers were deposited by thermal evaporation in a vacuum chamber at a pressure of 3×10^{-4} Pa, followed by deposition of a 100 nm Al cathode. Three devices were fabricated with configurations as follows; device A: ITO/TPD:Alq_3 (80 nm)/Al; device B: ITO/m-MTDATA:Alq_3 (80 nm)/Al; and device C: ITO/m-MTDATA:Gaq_3 (80 nm)/Al. The blending ratio of the donor and acceptor in all the devices was 1:1 by weight. The deposition rates and thickness of the layers were monitored using oscillating quartz monitors. Absorption 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. Photocurrent responses of the devices were measured under illumination of a 40 μW/cm^2 Xe lamp. Current-voltage (*I-V*) characteristics of the devices were recorded in dark and under illumination of 365 nm UV light with different intensities through the ITO anode. All the measurements were carried out at room temperature under ambient conditions.

Figure 1 shows the absorption spectra of 40 nm pristine films of m-MTDATA, Alq_3, and Gaq_3, as well as 80 nm 1:1 blend films of TPD:Alq_3, m-MTDATA:Alq_3, and m-MTDATA:Gaq_3 on quartz substrates. It can be found that Alq_3 and Gaq_3 show almost the similar absorption spectra in the range of 275–450 nm and there is a broad absorption band in the region of 300–400 nm. On the other hand, absorption spectra of the three blend films are close to simple

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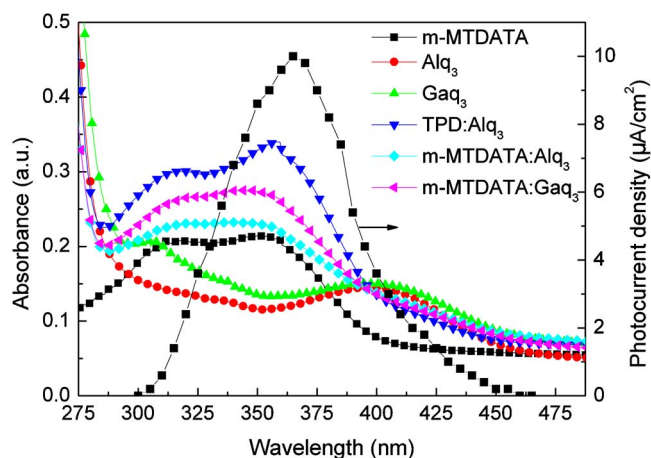
FIG. 1. (Color online) Absorption spectra of 40 nm pristine films of m-MTDATA, Alq_3, and Gaq_3, as well as 80 nm 1:1 mixed films of TPD:Alq_3, m-MTDATA:Alq_3, and m-MTDATA:Gaq_3 on quartz substrates, and the photocurrent response of device C at zero bias.

FIG. 3. (Color online) PL spectra of 40 nm pristine films of Alq_3 and Gaq_3 as well as 80 nm 1:1 mixed films of TPD:Alq_3, m-MTDATA:Alq_3, and m-MTDATA:Gaq_3 on quartz substrates excited by 365 nm UV light.

superposition of the absorption spectra of the individual components with no sign of absorption peak due to charge transfer complexes. As the photocurrent response spectrum of the m-MTDATA:Gaq_3 device (device C) shows a maximum in the range of 360–370 nm, thus a 365 nm UV lamp was used as the illumination source.

Figure 2(a) plots I-V characteristics of devices A, B, and C at reverse bias under illumination of 365 nm UV light with an intensity of 1.2 mW/cm^2. The photocurrent densities of devices A, B, and C at zero bias are 1.1, 18.8, and 20.3 μA/cm^2, respectively. The currents increase significantly with the reverse voltage and reach 107.9, 358.8, and 405.0 μA/cm^2 at −8 V, respectively. Correspondingly, the photocurrent response of devices A, B, and C are 90, 299, and 338 mA/W at −8 V bias, respectively. The dark current of the devices is extremely low compared to the photocurrent due to the rectifying I-V characteristics of the devices. For example, the dark current of device C is only 0.6 μA/cm^2 at −8 V. The response of 338 mA/W corresponds to a quantum yield of 110%; this over unity quantum yield suggests that an avalanche mechanism may be involved.[6] It can be seen that the photocurrent response of m-MTDATA based devices (de-
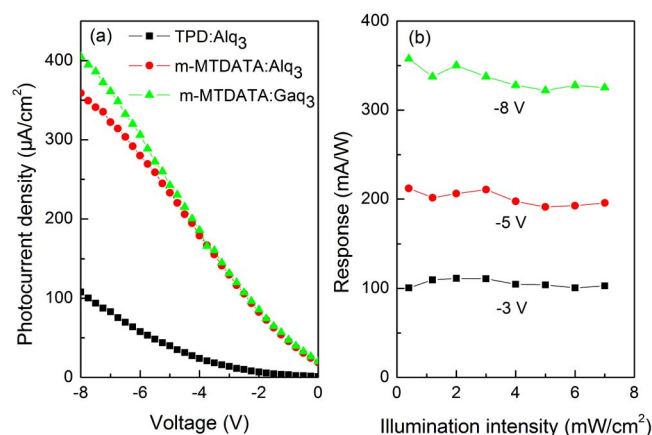
vices B and C) is much higher than that of the TPD based device (device A).

It is worthy to note that the photocurrent of device A is higher than that reported by Ray and Narasimhan[12] with a similar device configuration. The difference could be attributed to the fact that the illumination is through the highly transparent ITO side for our devices while it was through the semitransparent Al cathode in the work of Ray and Narasimhan. Besides, it can be noted that the photocurrent response of device C is higher than that of GaN (150 mA/W) (Ref. 10) and SiC (120 mA/W) (Ref. 11) based UV-PDs.

Figure 2(b) depicts the photocurrent response of device C as a function of the illumination intensity. The responses are 110, 202, and 338 mA/W at −3, −5, and −8 V, respectively, under illumination of 365 UV light with an intensity of 1.2 mW/cm^2. Moreover, the photocurrent response of the device at a given voltage is almost unchanged with the increase in irradiation intensity from 0.4 to 7 mW/cm^2. This suggests that there is no significant buildup of space charge, which can cause derivation from linear dependence of irradiation intensity.

Figure 3 shows the PL spectra of 40 nm pristine films of Alq_3 and Gaq_3 as well as 80 nm 1:1 mixed films of TPD:Alq_3, m-MTDATA:Alq_3, and m-MTDATA:Gaq_3 on quartz substrates excited by 365 nm UV light. In all the blend films, no trace of emission from the donors is observed. The emission of the TPD:Alq_3 blend film comes from Alq_3 and its intensity is much higher than that of the pristine Alq_3 film, indicating that there is an energy transfer from TPD to Alq_3. While the PL spectra of the m-MTDATA:Alq_3 and m-MTDATA:Gaq_3 blend films reveal a redshift and broadening of the emission band compared with the monoemissions of Alq_3 and Gaq_3, such emissions were previously attributed to the hybrid radiations of the monomer and the exciplex.[14,15] Moreover, it is worth noting that the intensities of these hybrid emissions are dramatically lower than those of the monomer emissions of the pristine films.

To further understand the effect of the radiative decays on the performance of the PDs, the photophysics involved should be explored. Under optical excitation, excitons can be formed in the donor molecules in the blend layer. When an

FIG. 2. (Color online) (a) Photocurrent density of devices A, B, and C under illumination of 365 nm UV light with an intensity of 1.2 mW/cm^2. (b) Responses of device C at −3, −5, and −8 V as a function of the UV-light intensity.
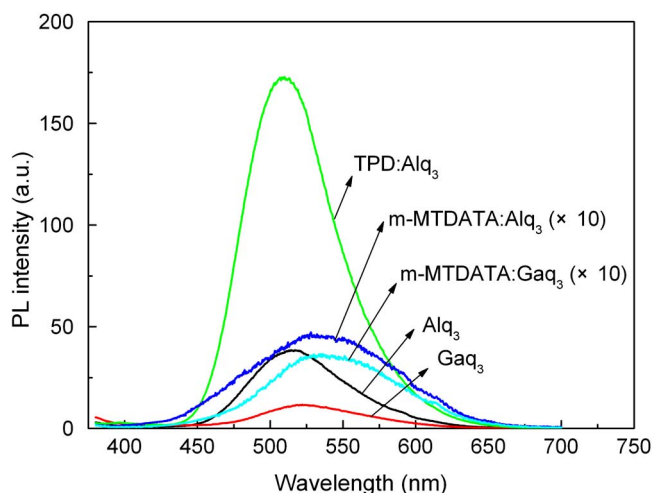
exciton on a donor molecule approaches an acceptor molecule in the blend layer, one of the following processes may occur: (a) energy transfer from the donor to acceptor molecules; (b) transfer of an electron from the donor to acceptor molecule to form a geminate hole-electron pair; or (c) relaxation of the donor exciton to its ground state.[16] Depending on the materials used, the direction of charge and energy transfers can occur in the opposite direction (i.e., from acceptor to donor). In the present cases, the absence of the emission component from the donors in the blend PD films (Fig. 3) suggests that the electron and energy transfers are from the donor to the acceptor. On the other hand, the optical excitation can also form the acceptor excitons. The acceptor excitons, including the directly photogenerated and those formed through energy transfer from the donor, can transfer a hole to the donor molecules and form interfacial geminate hole-electron pairs.[17,18] Morteani *et al.*[19] demonstrated that the geminate hole-electron pair can either dissociate or back-transfer to a bulk exciton from the exciplex via thermally activation. This leads to a circulative transformation of bulk exciton → interfacial geminate hole-electron pair → bulk exciton. Upon application of a reverse bias, the photogenerated free carriers can be more favorably collected, hence increasing the branching ratio of the dissociation of the interfacial geminate hole-electron pair.

The IPs and EAs of TPD and m-MTDATA are 5.5 and 2.4 eV and 5.1 and 1.9 eV,[13] respectively, while Alq_3 (Ref. 13) and Gaq_3 (Ref. 20) have almost the same IP and EA. The lower IP and EA of m-MTDATA compared to those of TPD are energetically favorable for the formation of interfacial geminate hole-electron pairs in m-MTDATA based devices.[3,21] The increased PL emission of $TPD:Alq_3$ blend film compared with that of the pristine Alq_3 film and the low photocurrent of device A imply that most excitons in Alq_3 are radiative decayed to its ground state. Furthermore, the lower PL emissions of the $m-MTDATA:Alq_3$ and $m-MTDATA:Gaq_3$ blend films indicate that in these blends higher proportions of geminate hole-electron pairs can be dissociated in devices B and C. Although device A has the highest optical absorption, the larger loss via radiative decay leads to a lower photocurrent. The superior performance of device C is attributed to the lowest loss of the photogenerated excitons which finally form the photocurrent.

In summary, high response UV-PD based on the blend of $m-MTDATA:Gaq_3$ was demonstrated. The device shows a response of 338 mA/W under an illumination of 365 nm UV light with an intensity of 1.2 mW/cm^2. The investigation reveals that both the radiative decays of the bulk excitons and the exciplex states are unwanted loss channels for the photocurrent. The higher response of the $m-MTDATA:Gaq_3$ device is due to the lower radiative efficiency under illumination. This finding has potential values for further understanding the working mechanism and improving the performance of the PDs.

[1]P. Peumans, A. Yakimov, and S. R. Forrest, J. Appl. Phys. **93**, 3693 (2003).
[2]G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and J. Heeger, Science **270**, 1789 (1995).
[3]M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, and R. H. Friend, Nature (London) **395**, 257 (1998).
[4]P. Peumans, S. Uchida, and S. R. Forrest, Nature (London) **425**, 158 (2003).
[5]J. Xue, B. P. Rand, S. Uchida, and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) **17**, 66 (2005).
[6]G. Yu, K. Pakbaz, and A. J. Heeger, Appl. Phys. Lett. **64**, 3422 (1994).
[7]L. Ouali, V. V. Krasnikov, U. Stalmach, and G. Hadziioannou, Adv. Mater. (Weinheim, Ger.) **11**, 1515 (1999).
[8]H.-W. Lin, S.-Y. Ku, H.-C. Su, C.-W. Huang, Y.-T. Lin, K.-T. Wong, and C.-C. Wu, Adv. Mater. (Weinheim, Ger.) **17**, 2489 (2005).
[9]Y. Kim, M. Ballarotto, D. Park, M. Du, W. Cao, C. H. Lee, W. N. Herman, and D. B. Romero, Appl. Phys. Lett. **91**, 193510 (2007).
[10]J. C. Carrano, P. A. Grudowski, C. J. Eiting, R. D. Dupuis, and J. C. Campbell, Electron. Lett. **33**, 1980 (1997).
[11]P. Sandvik, D. Brown, J. Fedison, K. Matocha, and J. Kretchmer, J. Electrochem. Soc. **152**, G199 (2005).
[12]D. Ray and K. L. Narasimhan, Appl. Phys. Lett. **91**, 093516 (2007).
[13]Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, and K. Imai, Appl. Phys. Lett. **65**, 807 (1994).
[14]Z. R. Hong, C. S. Lee, S. T. Lee, W. L. Li, and Y. Shirota, Appl. Phys. Lett. **81**, 2878 (2002).
[15]K. Itano, H. Ogawa, and Y. Shirota, Appl. Phys. Lett. **72**, 636 (1998).
[16]J. J. M. Halls, J. Cornil, D. A. dos Santos, R. Silbey, D.-H. Hwang, A. B. Holmes, J. L. Brédas, and R. H. Friend, Phys. Rev. B **60**, 5721 (1999).
[17]Y. Liu, M. A. Summers, C. Edder, J. M. J. Fréchet, and M. D. McGehee, Adv. Mater. (Weinheim, Ger.) **17**, 2960 (2005).
[18]M. T. Lloyd, Y.-F. Lim, and G. G. Malliaras, Appl. Phys. Lett. **92**, 143308 (2008).
[19]A. C. Morteani, P. Sreearunothai, L. M. Herz, R. H. Friend, and C. Silva, Phys. Rev. Lett. **92**, 247402 (2004).
[20]L. Wang, X. Jiang, Z. Zhang, and S. Xu, Displays **21**, 47 (2000).
[21]C. Winder and N. S. Sariciftci, J. Mater. Chem. **14**, 1077 (2004).