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Letter

Visible-blind ultraviolet photo-detector using tris-(8-hydroxyquinoline) rare earth as acceptors and the effects of the bulk and interfacial exciplex emissions on the photo-responsivity

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ABSTRACT

A visible-blind ultraviolet (VB-UV) photo-detector (PD) was demonstrated by using tris-(8-hydroxyquinoline) gadolinium (Gdq) as the electron acceptor (A), 1,3,5-tris(3-methyl-phenyl-phenylamino) triphenyamine (m-MTDATA) as the donor (D). For the comparison the PD diodes were also fabricated using other rare earth (RE)-q (REq) complexes (RE = Y, La, Eu, or Lu) as the acceptors. It is found that Gdq-PD diode with 1:1 ratio of m-MTDATA:Gdq offers a maximum photo-responsivity of 230 mA/W at −7.5 V bias. This result is markedly higher than inorganic counterparts and previously organic PD diode (30 mA/W) reported by Ray and Narasimhan [Appl. Phys. Lett. 91 (2007) 093516]. Moreover, the spectral response does not cover visible region. So high responsivity of Gdq-PD was attributed to the presence of dominant dissociation of the geminate carrier pairs at D:A intermolecular contacts. The improvement is the results of the lowest exciplex- and bulk-emissions among the REq-PD diodes and in the various ratio of D:A blend, more detail mechanism was also discussed. Besides degradation tests of the Gdq-PD diode under UV and fluorescent lamp show that the UV detector can suffer from the application conditions.

1. Introduction

In recent years, organic semiconductors are used in various organic optoelectronic devices, such as organic light emitting diodes (OLEDs), photovoltaic (PV) solar cells, and photo-detectors (PDs). Ultraviolet (UV) sensitive PDs, especially visible-blind (VB) UV PD diodes, demonstrate more potential as they are more suitable for applications of solar astronomy, missile plume detection, space-to-space and sterilization monitor and so on [1–9]. It is recognized that the UV photo-response of an organic PD diode represents the photocurrent density property of a PD diode under reverse bias [1]. The PD process involves formation of photo-generated excitons that must firstly be dissociated at the donor and acceptor (DA) interface into their constituent electrons and holes by induced of the larger band-edge offsets at DA interface [1,6]. Comparing with photovoltaic (PV) cell, a working PD diode also needs an additional external electric field that has an identical field direction with the built-in field, which could accelerate the transports of the free carrier resulted from the dissociated excitons towards the two electrodes. The fact that external field was applied at PD diode in its work is because of the difficult transport of the free carriers through molecular blend or multilayered structure for PD diodes [1]. Much effort on

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the UV-PDs has been focused on inorganic counterparts with wide-band gap semiconductor such as GaN (150 mA/W) [10] and SiC (150 mA/W) [11], but these inorganic partners require complicated fabrication technique with high expenses. Since organic UV-PDs have the strongpoint of simple fabrication process, recently organic UV-PDs based on blend of N,N-diphenyl-N,N-bis(3-methylphenyl)-(1,1-biphenyl)-4,4-diamine (TPD) and tris(8-hydroxy-quinoline) aluminum (Alq) was reported, but its UV responsivity is distinctively lower than the inorganic partners [12].

It is recognized that the dissociation of photo-generated exciton must occur at DA interface that needs the D and A species to have low ionization potential (IP) and high electron affinity (EA), respectively, to have as large carrier motilities as possible for both materials. 1,3,5-Tris(3-methylphenyl-phenylamino) triphenyamine (m-MTDATA) presents high hole mobility of 3×10^{-5} cm^2/V s [13] and a low IP of 5.1 eV [14], moreover, it was used as D-material in UV sensitive PV devices [15–17]. Our group has fabricated m-MTDATA/tris(8-hydroxy-quinoline) gallium (Gaq) based UV PD diode by using m-MTDATA as the donor and Gaq as the acceptor [18], but its photo-response spectrum evidently covers visible waveband, i.e., it is not visible-blind, which was attributed to its stronger absorption at visible region of 400–450 nm [18]. Therefore, a new A-material with weaker light absorption at visible spectral region must be selected. Zhang et al. have observed that the absorption peak of the metal-8-hydroxy-quinoline (Mq) complexes is dependent on the metal ion radii, that is, larger ion radii based Mq complex must lead to blue-shift of the absorption peak due to the stronger polarization [19]. We have noted that trivalent Gd (Gd^{3+}) with larger ion radii of 0.11 nm should exhibit weaker absorption at visible spectral region in comparison with Gaq complex due to smaller ion radii of Ga^{3+} (0.047 nm). In addition, Gdq should have larger electron-transporting (ET) property because erbium-q complex (Erq) has higher ET and electrical properties. Moreover, Erq also belongs to one of RE elements and has almost identical ion radii; hence Gdq also seems to exhibit larger ET ability [20,21]. Basing on the argument, it is expected that the PD diode with m-MTDATA/Gdq blend could offer high photo-response and it could be sensitive to the pure UV waveband.

In this letter, we will demonstrate PD diodes using Gdq as the A-material. For comparison, photo-sensitivities of other REq-PD diodes (RE = Y, La, Lu or Eu) were also studied. For the reason that the trivalent RE ions (RE^{3+}) in REq complexes behave inert electric configuration and do not contribute to light radiation from the RE^{3+} ions at UV excitation except for Eu^{3+} ion that emits red luminescence under UV illumination or electrical excitation. It is observed that 1:1 ratio m-MTDATA:Gdq-PD (Gdq-PD) diode exhibits a maximum photo-responsivity of 230 mA/W with VB among the REq-PDs at -7.5 V bias. We have noted that the responsivity considerably related to the exciplex formation of D:A blends and the optical properties of the REq complexes.

2. Experimental

All the REq complexes were synthesized according to methods reported in Refs. [20,21] and function as the A-materials in the PD diode system. Their blend films were thermally deposited on the quartz substrates in a vacuum chamber at the pressure of 5×10^{-4} Pa for the absorption and photoluminescence (PL) measurements. The PD diodes were fabricated on cleaned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 25 Ω/sq in vacuum chamber. The organic layers were deposited at a rate of 2 Å/s; the evaporating rate of LiF and Al cathode were controlled to be 0.5 and 10 nm/s with the thickness of 1 and 200 nm, respectively. All the vacuum chambers were controlled at pressure of 5×10^{-4} Pa; the deposition rates and thickness of the layers were monitored using oscillating quartz monitors. Absorptions and PL spectra of the neat D- and A-material films and their blend films were determined with a Shimadzu UV-3101 PC spectrophotometer and a Hitachi F-4500, respectively. The PD diodes with structures of ITO/m-MTDATA:REq (1:1, 60 nm)/LiF (1 nm)/Al were fabricated, but the m-MTDATA-to-Gdq ratio for Gdq-PD diodes was 1:3, 1:1 and 3:1, respectively. Photocurrent spectral responses of all the PD diodes 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 side. The excited state lifetime of the exciplex emission of (m-MTDATA:Gdq) 1:1 blend film was measured by an F-900 Fluorescence and Phosphorescence lifetime spectrophotometer. All the measurements were carried out at room temperature under ambient condition. Besides, the operational lifetime of the UV PD is about 440 min under a constant illumination of 365 nm UV light with an intensity of a 8 μW/cm^2 Xe lamp and an illumination of a fluorescent lamp with an illumination power of 20 mW/cm^2 for observing its durability.

3. Results and discussion

The absorption spectra of the blend films of m-MTDATA:REq and the neat films of m-MTDATA and Gdq are indicated in Fig. 1(a), respectively. For comparison, the inset indicates relative absorption spectra of 1:1 blend film of m-MTDATA:REq, here RE are Y, La, Gd, Lu and Eu, respectively. We have noted that blue-shifting absorption peak of the Gdq film occurs comparing to Gaq [18], which describes that the photocurrent response of Gdq-PD diode could focus on the pure UV spectrum region. This is attributed to markedly lower absorption intensity of Gdq complex at 400–475 nm comparing with that of Gaq [18]. From the inset it can be seen that the figure of the absorption band of m-MTDATA:Gdq blend film is semblable with the other REq but the absorption intensity of m-MTDATA:Gdq and m-MTDATA:Euq blend films are maximum and minimum, respectively, which will be discussed later. Fig. 1(b) describes the photocurrent spectral responses of REq-PD diodes with 1:1 ratio of m-MTDATA:REq at zero bias, note that the photocurrent response locates almost at 300–400 nm UV spectrum region and Gdq-PD diode offers a maximum photocurrent density.

Fig. 2(a) depicts *I*–*V* characteristics of the five REq diodes at reverse biases under illumination of 365 nm UV

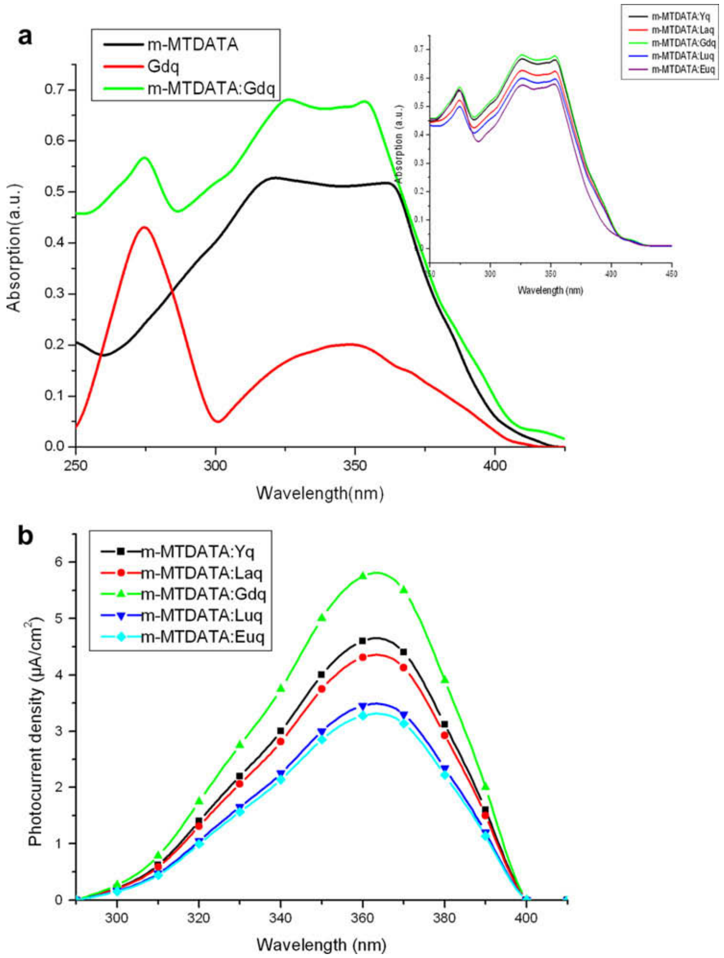

Fig. 1. (a) The absorption spectra of the blend films of m-MTDATA:Gdq and neat films of m-MTDATA and Gdq, the inset: relative absorption spectra of 1:1 blend films of m-MTDATA:REq (RE is Y, La, Gd, Lu and Eu). (b) The photocurrent spectral response of PD diode with m-MTDATA:REq blend with 1:1 ratio at zero bias.

light with a 1.2 mW/cm^2 and *I–V* characteristic of the Gdq-PD at dark, respectively, as well the inset indicates the photo-responses of the five REq-PD diodes as a function of UV light intensity at −7.5 V. It can be seen that current density of the REq-PD diodes significantly increases with the reverse voltage. The dark currents of the Gdq and other REq-PD devices are extremely low, the photocurrent-to darkcurrent ratio is about 260. Fig. 2(b) depicts the photo-responses of Gdq-PD device at −2, −6 and −7.5 V as a function of UV light intensity. It can observe that Gdq-PD diode exhibits a maximum photocurrent density of 276 μA/cm^2 and a peak photo-response of 230 mA/W among the five PD diodes. From Fig. 2(b) we obtained that the photo-sensitivities of Gdq-PD diodes are 64, 169, and 230 mA/W at −2, −6 and −7.5 V under illumination of 365 nm UV light, respectively. We can see that Gdq-PD presents a peak photosensitivity at any irradiation intensity comparing with other REq-PD diodes. Moreover, the photocurrent response of the PD device at a given voltage is almost unchanged with the increase in irradiation intensity from 0.4 to 7.0 mW/cm^2. This suggests that there is no obvious buildup of space charge, which can cause derivation from linear dependence of irradiation. Therefore, achievement of so high photosensitivity for Gdq-PD diode could be explained as below. It is noticed that the photocurrent densities of a PD diode at zero bias is actually short circuit current density (*Isc*) of a PV diode [1,22]. From Fig. 2(a) we also obtained that the photocurrent densities of Gdq, Laq, Yq, Luq and Euq-PD diodes at zero bias are 52.3, 33.1, 32.7, 27.8 and 25.7 μA/cm^2, respectively, and Gdq-PD diode offers a maximum high photocurrent response. That is, if a PV diode could offer higher *Isc*, a higher PD response could be obtained for the same structure PV diode because the PV and photodetection performances of the organic devices are likely to approach at zero bias [1,22]. Note that the five REq-PD diodes have the same structure so the fact that the PV performance increases with the increase in *Isc* would also lead to the same increasing trend of their PD photo-responses at reserve biases.

Fig. 3(a) and (b) depicts the PL spectra of above five blends, neat m-MTDATA and the neat REq films, respec-

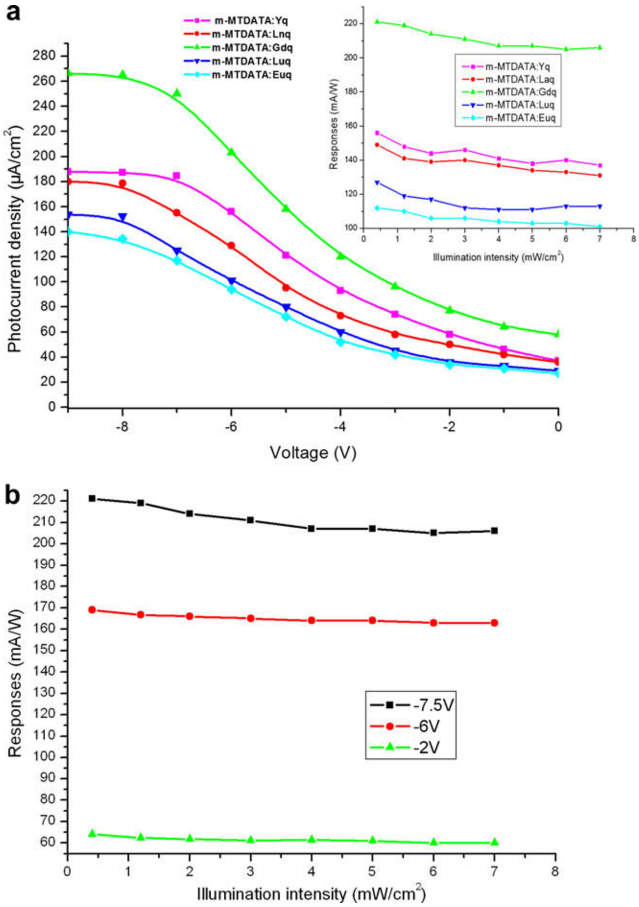

Fig. 2. (a) *I–V* characteristics of PD devices with various REq complexes at changing reverse bias under illumination of a 365 nm UV light with an intensity of 1.2 mW/cm^2. Inset: the photo-responses of the five REq-PD diodes at −7.5 V. (b) The photo-responses of the Gdq-PD device at −2, −6 and −7.5 V, respectively.

tively, as well (c) indicates PL spectra of 3:1, 1:1 and 1:3 blend films of m-MTDATA:Gdq under excitation of an 365 nm UV light, respectively. Comparing Fig. 3(a) and (b) we can seen that the PL spectral peaks are longer for the five blend films than for the five neat REq films, which were ascribed to overlapping of the D:A interfacial exciplex emission bands with the bulk PL. We also observe that PL intensities of the either blend or neat films of Gdq and Euq are, respectively, weakest and strongest among the five REq systems, which are corresponding to their photosensitivity (see Fig. 2(a) and the inset). From Fig. 3(c) we also see that the 1:1 ratio film behaves most low PL intensity among the PL spectra of 3:1, 1:1 and 1:3 blend films of m-MTDATA:Gdq, While both PL spectra of 3:1 and 1:3 blend films composed of not only the intermolecular exciplex emission, but also of the m-MTDATA and Gdq-bulks, the PL emissions of the two blends provide highly stronger than the 1:1 blend film. We note that 1:1 m-MTDATA:Gdq blend based PD diode offers the highest PD response over other two PD diodes based on 3:1 (162.8 μA/cm^2) and 1:3 (193.7 μA/cm^2) blend ratio of m-MTDATA:Gdq. So we can conclude that the photosensitivity is related closely to PL emission of the blend, i.e., the stronger the PL intensity the blend and/or bulk films are, the photosensitivity is the lower.

The findings can also be understood as follows. The geminate electron–hole pairs could be resulted from the intermolecular interface in the m-MTDATA:REq blend film under UV illumination, and thus there would be competition processes between the dissociation and collapse of the geminate carrier pairs [23,24]. We observed that the relative intensity of the exciplex emission of 1:1 ratio m-MTDATA:Gdq blend is the lowest among the three ratio based Gdq diode, and no bulk emissions were almost determined comparing with other REq-PD diodes, as shown in Fig. 3(a) and (b) although neat Gdq film also provides PL (Fig. 3(b)). For m-MTDATA:Euq blend film, both PL emissions of Eu^{3+} center and 8-hydroxyquinoline ligand of the complex occurred, leading to the lowest PD response due to the competition of the PL emission coming from exciplex, Euq and Eu^{3+} centers with the exciton dissociation. Thus the dissociation of the geminate carrier pairs should be less so that Euq-PD diode offers the lowest photocurrent response. The responses of Yq, Laq and Luq-PD diodes are lower than that of Gdq-PD diode due to their stronger bulk PL emissions as well. The competition be-

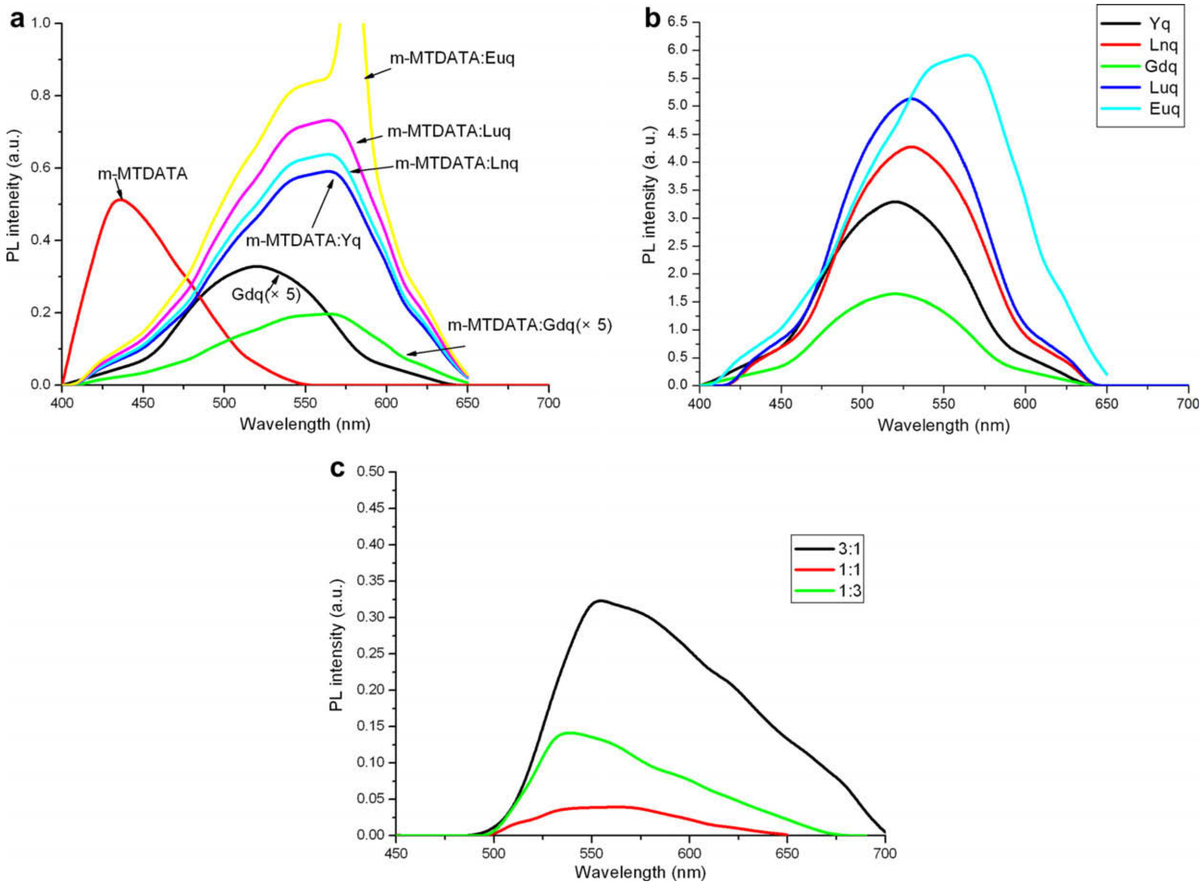

Fig. 3. (a) The PL spectra of above five blends and neat m-MTDATA and Gdq films, (b) the PL spectra of above five RE complexes at excitation by 365 nm UV light and (c) the PL spectra of 3:1, 1:1 and 1:3 blend films of m-MTDATA:Gdq under excitation 365 nm, respectively.

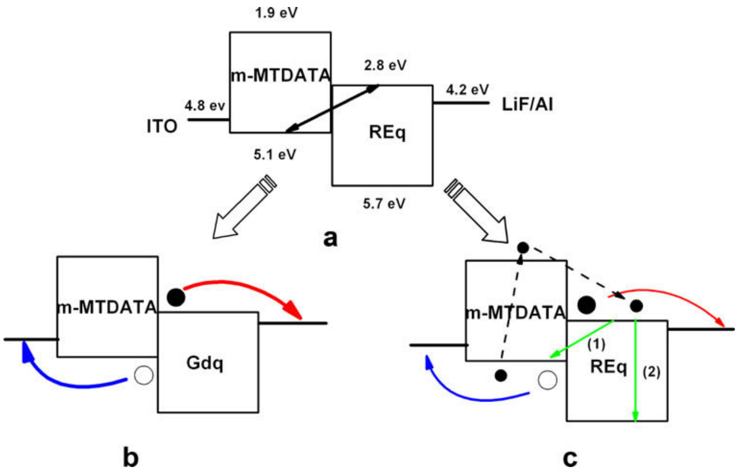

Fig. 4. (a) The geminate charge pair formation at the intermolecular interface of m-MTDATA/REq, (b) the dominant PV (PD) process of m-MTDATA/REq devices at very weak emissions of bulk and/or exciplex, and (c) weaken PV work at intensive emissions of exciplex (1) and/or bulk (2). Double direction arrow: Generated electron–hole pair; ● and ○: electron and hole that are resulted from exciton decomposing at the interface. Red and blue arrows denote the electron and hole transports into the respective electrodes, respectively. Dash arrow: electron transfer processes from HOMO of m-MTDATA to LUMO of REq, green arrow (1) and (2) represent emissions from exciplex and/or bulk of another REq-PD diodes except for Gdq at zero bias. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) levels of REq were cited from Ref. [24] and the LUMO and HOMO of m-MTDATA cited from Ref. [25]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

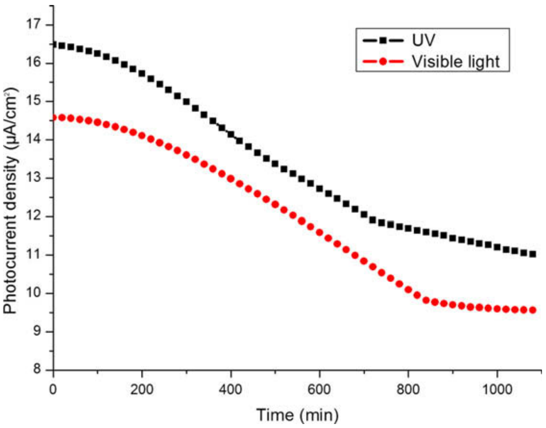

Fig. 5. The dependence of the photosensitivity on the illumination time by 365 nm UV light illumination with a 8 μW/cm^2 Xe lamp and an illumination of a fluorescent lamp with a power of 20 mW/cm^2.

tween dissociation and collapse of the geminate carrier pairs is depicted in Fig. 4. Fig. 4(a) depicts the schematic level diagram of the geminate charge pair formation. It also describes the dominant dissociation process of the geminate carrier pairs forwards into free electrons and holes (Fig. 4(b)) as well as provides the dominant exciplex and/or bulk emission processes which produced from collapse of the geminate carrier pairs (Fig. 4(c)). But the fact that the difference in photocurrent responses among Yq, Laq and Luq-PD diodes is not clearly understood now.

The reason that the photosensitivity is markedly high for Gdq-PD diode than for other REq-PD diodes may be also attributed to the paramagnetic property of Gd^{3+} ion and a very long exited state lifetime (1.3 μs) of PL emission of the exciplex between m-MTDATA:Gdq blend film is different from that of exciplex fluorescence [23], while it is more like to triplet, i.e., phosphorescence exciplex [25], and the more details are under studying. It is well known that organic materials generally are not so much stable under UV illumination, thus we measured the dependence of the photosensitivity on the illumination time by 365 nm UV light illumination and fluorescent lamp, respectively, as described in Fig. 5. We note that the degradation of the photo sensitivity not so much serious, which will be further studied.

4. Conclusion

In conclusion, visible-blind UV photo-detectors (PDs) were fabricated by using series of complexes of RE (RE = Y, La, Gd, Lu or Eu) with 8-hydroxyquinoline (REq) as the A component and m-MTDATA as the D components, respectively. It is discovered that Euq diode offers a maximum bulk PL emission that leads to a small photo-response. The fact is that the peak photosensitivity of Gdq-PD among the REq-PD diodes is attributed to its dominant exciton dissociation process resulted from extreme weak exciplex and bulk emissions and the strongest UV absorption. On the other hand, the realization of visible-blind UV Gdq-PD diode should be resulted from the blue-shift of the absorption band. These findings inspired us to realize that Gdq is an intriguing complex because of its excellent PD performance, and it can be expected that Gdq complex may also be used to design other organic electronic device with high performance. Beside it is believed that the photo-degradation of the Gdq-PD diode is not so much severe the working lifetime of the PD diode will be considerably improved if the PD device will be enveloped to obstruct from atmosphere.

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References

[1] P. Peumans, A. Yakimov, S.R. Forrest, J. Appl. Phys. 93 (2003) 3693.
[2] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, J. Heeger, Science 270 (1995) 1789.
[3] M. Granstrom, K. Petritsch, A.C. Arias, A. Lux, M.R. Andersson, R.H. Friend, Nature (London) 395 (1998) 257.
[4] P. Peumans, S. Uchida, S.R. Forrest, Nature (London) 425 (2003) 158.
[5] J.G. Xue, B.P. Rand, S. Uchida, S.R. Forrest, Adv. Mater. 17 (2005) 66.
[6] G. Yu, K. Pakbaz, A.J. Heeger, Appl. Phys. Lett. 64 (1994) 3422.
[7] L. Ouali, V.V. Krasnikov, U. Stalmach, G. Hadziioannou, Adv. Mater. 11 (1999) 1515.
[8] H.-W. Lin, S.-Y. Ku, H.-C. Su, C.-W. Huang, Y.-T. Lin, K.-T. Wong, C.-C. Wu, Adv. Mater. 17 (2005) 2489.
[9] Y. Kim, M. Ballarotto, D. Park, M. Du, W. Cao, C.H. Lee, W.N. Herman, D.B. Romero, Appl. Phys. Lett. 91 (2007) 193510.
[10] J.C. Carrano, P.A. Grudowski, C.J. Eiting, R.D. Dupuis, J.C. Campbell, Electron. Lett. 33 (1997) 1980.
[11] P. Sandvik, D. Brown, J. Fedison, K. Matocha, J. Kretchmer, J. Electrochem. Soc. 152 (2005) G 199.
[12] D. Ray, K.L. Narasimhan, Appl. Phys. Lett. 91 (2007) 093516.
[13] C. Giebeler, H. Antoniadis, D.D.C. Bradley, Y. Shirota, Appl. Phys. Lett. 72 (1998) 2448.
[14] Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimota, H. Nakada, Y. Yonemoto, S. Kawai, K. Imai, Appl. Phys. Lett. 65 (1994) 807.
[15] L.L. Chen, W.L. Li, M.T. Li, B. Chu, J. Lumin. 122–123 (2007) 667.
[16] H.Z. Wei, W.L. Li, M.T. Li, W.M. Su, Q. Xin, J.H. Niu, Z.Q. Zhang, Z.Z. Hu, Appl. Surf. Sci. 252 (2006) 220.
[17] G. Zhang, W.L. Li, B. Chu, S.Z. Sheng, D.F. Yang, F. Yan, Z.J. Zhuo, Org. Electron. 10 (2009) 352.
[18] Z.S. Su, W.L. Li, B. Chu, T.L. Li, J.Z. Zhu, G. Zhang, F. Yan, X. Li, Y.R. Chen, C.S. Lee, Appl. Phys. Lett. 93 (2008) 103309.
[19] L.G. Zhang, X.G. Ren, D.P. Jiang, A.D. Lu, J.S. Yuan, Spectrosc. Spect. Anal. 17 (1997) 12 (in Chinese).
[20] R.J. Curry, W.P. Gillin, Curr. Opin. Solid State Mater. Sci. 5 (2001) 481.
[21] R.J. Curry, W.P. Gillin, Synth. Met. 111–112 (2000) 35.
[22] P. Peumans, V. Bulović, S.R. Forrest, Appl. Phys. Lett. 76 (2000) 3856.
[23] A.C. Morteani, P. Sreearunothai, L.M. Herz, R.H. Friend, Phys. Rev. Lett. 92 (2004) 247402.
[24] A.C. Morteani, A.S. Anoop, R.H. Friend, Carlos Silva, Adv. Mater. 15 (2003) 1708.
[25] M. Cocchi, D. Virgili, C. Sabatini, J. Kalinowski, Chem. Phys. Lett. 421 (2006) 351.