

Visible-blind organic ultraviolet photodetectors based on [Cu(DPEphos)(bathocuproine)]BF₄

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We demonstrate organic ultraviolet photodetectors (UV-PDs) based on a novel Cu(I) complex, [Cu(DPEphos)(bathocuproine)]BF₄(CuPB) (DPEphos = Bis[2-(diphenylphosphino)phenyl]ether). UV-PDs with the structure of ITO/m-MTDATA/m-MTDATA:CuPB(1:1)/CuPB/TPBi/LiF/Al were fabricated, in which m-MTDATA, CuPB and 1,3,5-tris(N-phenyl-benzimidazol-2-yl) benzene (TPBi) act as the electron donor, acceptor and exciton blocking layer, respectively. The optimized UV-PD exhibits the current density of 128 $\mu\text{A}/\text{cm}^2$ at -12V under an illumination of 365 nm UV light irradiation with an intensity of 0.691 mW/cm², corresponding to a responsivity of 186 mA/W.

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1. Introduction

Over the past decade, organic ultraviolet photodetectors (UV-PDs) have attracted much attention due to their unique features, such as light weight, low cost, easy fabrication and so on, as well as their potential applications in astronomy/astrophysics, medical instruments, environmental monitoring and sterilization monitors [1-9]. The responsivity of UV-PDs is strongly determined by the absorption wavelength and charge carrier transfer of donor (D) and acceptor (A) as well as the charge carrier collecting by electrodes. Strong UV absorption of photoresponsive materials is a significant characteristic of UV-PDs which can insure the accurate qualitative and measurable determination of UV light [10-12]. Organic UV-PD based on tris-(8-hydroxy quinoline) aluminum (Alq₃) and N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) with a responsivity of 30 mA/W was reported [13]. We consider that the low responsivity may be attributed to the strong luminescence of the Alq₃. Similarly, a low response of PD with 135 mA/W was also due to the high exciplex emission [14]. Efficient UV-PD with a peak photoresponse of 338 mA/W was realized by using m-MTDATA and tris-(8-hydroxyquinoline) gallium as donor and acceptor [15]. However, the photoresponse covers blue visible spectrum zone which can influence the accurate detection of UV light. Currently, great achievements have been acquired in application of Cu(I) complexes as emitters in organic light emitting diodes [16-18]. Whereas, the report on Cu(I) complexes in UV-PDs was scarce. In this study, we used m-MTDATA and a novel Cu(I) complex, [Cu(DPEphos)(bathocuproine)]BF₄(CuPB) (DPEphos= Bis[2-(diphenyl phosphino)phenyl]ether) as the electron donor and acceptor to fabricate the UV-PDs. 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBi) was utilized as the exciton blocking layer due to its low ionization potential (IP) and high electron mobility [19]. The

optimized PD offers a peak responsivity of 186 mA/W.

2. Experimental

In this study, CuPB was prepared from DPEphos, [Cu(NCCH₃)₄]BF₄ and Bathocuproine (BCP) in CH₂Cl₂ at room temperature. m-MTDATA, BCP and TPBi were purchased from Aldrich Chemical Co. We fabricated the UV-PDs with the structure of ITO/m-MTDATA/m-MTDATA:CuPB(1:1)/CuPB/TPBi/LiF/Al, in which m-MTDATA, CuPB acted as the electron donor and acceptor, TPBi was used as the exciton blocking layer, respectively. Energy levels of CuPB were estimated from results of cyclic voltammetry. Fig. 1 shows the chemical structures of organic materials.

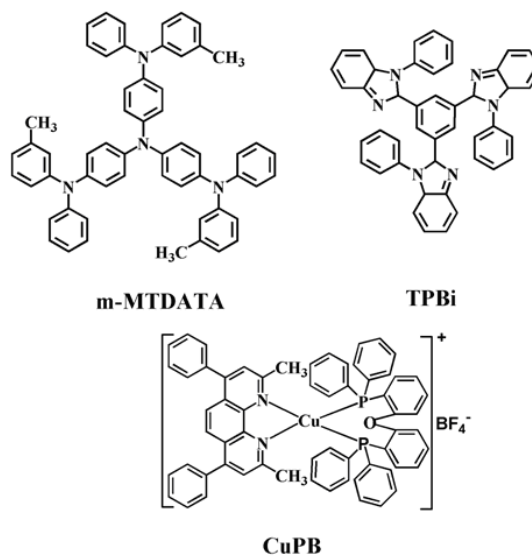


Fig. 1. The chemical structures of organic materials.

All devices were fabricated on cleaned glass substrates precoated with conducting indium–tin-oxide (ITO) anode with a sheet resistance of $25 \Omega/\text{sq}$, and the substrates were treated by UV ozone in a chamber for 10 mins after solvent cleaning. The organic films were thermally evaporated in high vacuum ($<10^{-6}$ Torr) using previously calibrated quartz crystal monitors to determine the deposition rate and the film thickness. The organic layers were deposited at a rate of $2 \text{ \AA}/\text{s}$. The evaporating rate of LiF and Al athode were controlled to be 0.5 and $10 \text{ \AA}/\text{s}$ with the thickness of 1 and 200 nm, respectively. The mixture films in various devices separately formed by heat coevaporating from two sources. Photocurrent responses of the devices were measured under illumination of a $40 \mu\text{W}/\text{cm}^2$ Xe lamp. Current–voltage (I – V) characteristics of active area of $2 \text{ mm} \times 2 \text{ mm}$ based devices were recorded in dark and under illumination of 365 nm UV light with different intensities through the ITO anode using a programmable Keithley mode 2601 power source. All the measurements were carried out at room temperature under ambient conditions. This device structure is plotted in Fig. 2.

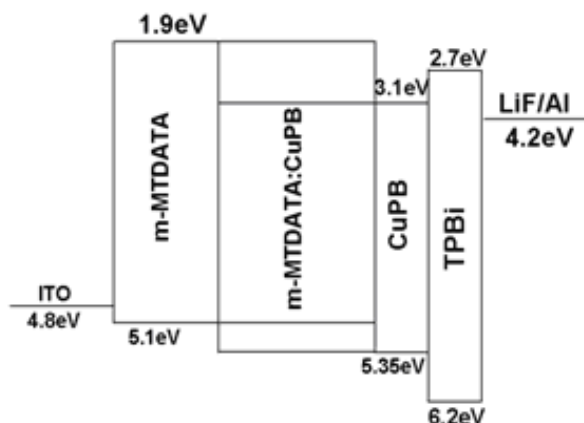


Fig. 2. The device configuration.

3. Results and discussion

To optimize performance, we fabricated three kinds of PDs with different blend layer thicknesses for comparison, device A: ITO/m-MTDATA(40 nm)/ m-MTDATA:CuPB(1:1)(20 nm)/CuPB(20 nm)/TPBi(15 nm)/LiF(1 nm)/Al(200 nm); device B :

ITO/m-MTDATA(40nm)/m-MTDATA:CuPB(1:1)(30 nm)/CuPB(20 nm)/TPBi(15 nm)/LiF(1 nm)/Al(200 nm); device C: ITO/m-MTDATA(40 nm)/ m-MTDATA:CuPB(1:1)(40 nm)/CuPB(20 nm)/TPBi(15 nm)/LiF(1 nm)/Al(200 nm). In our study, TPBi was used as exciton blocking layer to confine excitations in active layer effectively and decrease excitations quenching at the CuPB–Al interface.

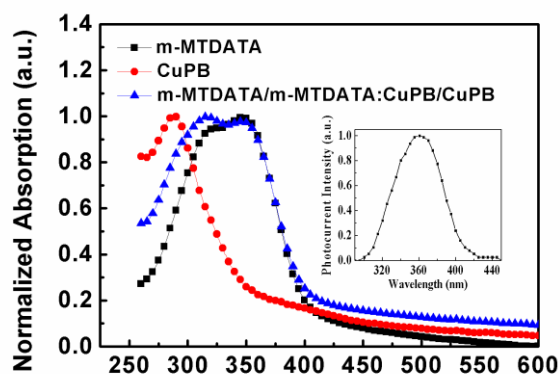


Fig. 3. The normalized absorption spectra of neat films of CuPB, m-MTDATA, and m-MTDATA:CuPB blend film. Inset depicts the photocurrent density response of the device.

Fig. 3 shows the normalized absorption spectra of neat films of CuPB, m-MTDATA, and m-MTDATA:CuPB blend film. The inset depicts the photocurrent density response of the device. It can be seen clearly from Fig. 3 that all exhibit strong UV absorption with an apparent tail around or below 400 nm, and the absorption spectra of blend films of m-MTDATA:CuPB are roughly weighted sum of the individual characteristics, indicating no sign of absorption peak due to charge transfer complex. Absorption of blend film is located at the band from 300 to 400 nm, a peak value is about 365 nm. As shown in the inset of Fig. 3, the photocurrent spectral response overcast the whole ultraviolet region, which is just at the visible-blind UV spectral position. This is important for the exact determination of ultra-violet radiation.

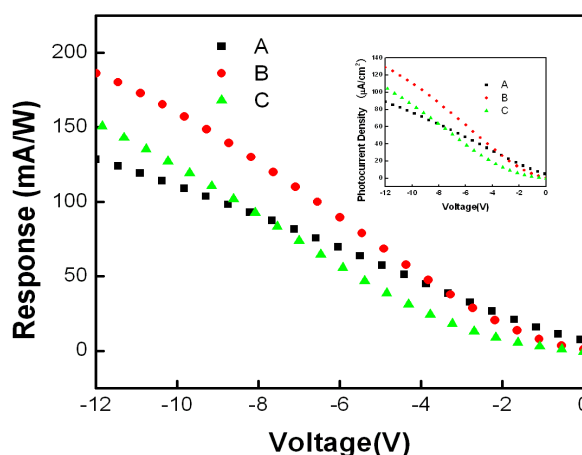


Fig. 4. Dark-corrected photoresponse and photocurrent density (inset) as a function of reverse biases for UV-PDs based on CuPB with different thicknesses.

Fig. 4 plots photocurrent density as a function of different reverse biases for UV-PDs. The photoresponse of devices A, B and C under illumination of 365 nm UV light with an intensity of 0.691 mW/cm² are 128 mA/W, 186 mA/W and 150 mA/W respectively, corresponding to the photocurrent density are 88 μ A/cm², 128 μ A/cm² and 104 μ A/cm². Among these three UV-PDs, the photoresponse of device B is higher than those of A and C, as a result of trade-off between the dissociation interface area and free charge carrier recombination.

As thickness of the mixed layer increases, contact area between m-MTDATA and CuPB molecules increases and a large exciton dissociation zone is formed. So device B shows the better PD performance than that of device A. However, as the thickness of the blend layer further increases to 40 nm, the photoresponse decreases. This can be understood as follows: In the mixing configuration, since separated electrons and holes transport through the same medium in opposite directions on their way toward collection electrodes, there are more chances for carriers to recombine, which, if occurring, some free carriers will be lost and do not contribute to the photocurrent, thus leads to the inferior PD performance of the device C.

4. Conclusions

In summary, we investigate the performance of visible-blind organic ultraviolet photodetector based on [Cu(DPEphos)(bathocuproine)]BF₄ under an illumination of 365 nm UV light with an intensity of 0.691 mW/cm² at -12V. The optimized device displays a peak response of 186 mA/W. This study indicates that the efficient PL quenching of m-MTDATA, feasible energy alignment and efficient charge transfer between the donor and the acceptor are all crucial factors for such high UV photoresponse. This finding has potential value for further understanding of improving the PD performance. Furthermore, the investigation in our study can further expand the application region of Cu(I) complex, and highly efficient visible-blind UV-PDs offer them potential for environmental and biological fields.

Acknowledgements

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