

High response organic ultraviolet photodetector based on a novel phosphorescent Cu (I) complex

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The authors demonstrate high response organic ultraviolet (UV) photodetector (PD) utilizing 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine (m-MTDATA) and a novel phosphorescent Cu (I) complex [Cu(1,2-bis(diphenylphosphino)benzene)(4,7-diphenyl-1,10-phenanthroline)]BF₄ (CuDB), to act as the electron donor and acceptor, respectively. CuDB behaves better electron transport ability compared with that of tris-(8-hydroxyquinolino) aluminum (Alq₃) and the PD is highly sensitive to UV light while it has almost no response to the visible light. The optimized PD offers a photocurrent up to 253 $\mu\text{A}/\text{cm}^2$ at -10 V , corresponding to a response of 331 mA/W under an illumination of 365 nm UV light with power of 0.691 mW/cm^2 . We attribute the high response to the high electron transport ability of CuDB, the suppression of radiative decay of m-MTDATA and efficient charge transfer from m-MTDATA to CuDB. The working mechanism of the PD is also discussed in terms of the performance and device structures.

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1. Introduction

In the past decades, organic ultraviolet photodetectors (UV-PDs) have received much attention due to their potential practical use in military counter measures, solar astronomy, missile plume detection and sterilization monitors [1–4]. UV-PDs are conventionally implemented with wide band gap, such as GaN and SiC [5,6]. However, those UV-PDs have not been suitable for large area applications because of their rather complicated manufacturing processes, high cost, and so on. In recent years, organic UV-PDs based on photovoltaic (PV) diodes developed rapidly thanks to their advantages of low fabrication cost, simple manufacturing process, large-area scalability and variety in substrates, etc. This has result in an increased understanding and interest in the photophysics of these materials [7-10]. Except the absorption wavelength and coefficient of photoresponsive materials, the responsivity of organic UV-PDs was mainly determined by the exciton dissociation and the carrier collecting by electrodes, which rely intensively on the carrier mobilities of donor (D) and acceptor (A) materials, the level alignment of the highest occupied molecular orbital (HOMO)/the lowest unoccupied molecular orbital (LUMO) of the D/A pair and the device configuration. Previous reports in organic UV-PDs primarily aim at small molecular materials and polymers [11,12]. Though organic UV-PD with a peak responsivity of 30 mA/W was reported [11], its responsivity was very low may be due to

strong luminescence of Alq₃ as the acceptor. Similarly, a low response of PD with 135 mA/W was also attributed to exciplex emission [13]. The photoresponse of the PD showed a narrow band centered at 364 nm with a full width at half maximum of only 26 nm, which used ZnO nanorods and poly-N-vinylcarbazole as the electron acceptor and donor, respectively. However, its responsivity was only 110 mA/W [9]. Double wavelength ultraviolet light sensitive organic photodetector was realized by utilizing 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine (m-MTDATA) and 1,3,5-tris(N-phenylbenzimidazol-2-yl)-benzene (TPBi) as D and A. This work presented more valuable application anticipation in ultraviolet astronomy, such as solar-blind detection [14]. Highly efficient UV-PD with a peak photoresponse of 338 mA/W was obtained by employing m-MTDATA and tris-(8-hydroxyquinoline) gallium as D and A, respectively [12]. Unfortunately, the photoresponse covers blue visible spectrum zone which will affect the accurate detection of UV light.

4,7-diphenyl-1,10-phenanthroline (Bphen) was widely used as efficient hole or exciton blocking material in organic light-emitting diodes (OLEDs) and organic photovoltaic devices to improve the device performance due to its high electron mobility and high ionization potential (IP) [15,16]. Additionally, Bphen was also used as a potential organic ligand to compose metal complexes which were confirmed as highly efficient electrophosphorescent and organic ultraviolet optical

sensor materials [17–19]. Recently, our group had obtained high response of UV-PDs based on a Cu (I) complexes, [Cu(1,2-bis(diphenylphosphino)benzene)(bathocuproine)]BF₄ (CuBB) to act as the electron acceptor. The optimized UV-PD behaves the responsivity of 251 mA/W due to high electron mobility and efficient charge transfer between the m-MTDATA and Cu (I) complex [7]. Additionally, we also reported another UV-PD with response of 186 mA/W using [Cu(DPEphos)(bathocuproine)]BF₄ (CuPB) as the electron acceptor [20].

In this paper, we demonstrate highly sensitive UV-PDs based on [Cu(1,2-bis(diphenylphosphino)benzene)(4,7-diphenyl-1,10-phenanthroline)]BF₄ (CuDB) in which Bphen acts as the first ligand and 1,2-bis(diphenylphosphino)benzene (BDPB) instead of bis[2-(diphenylphosphino)phenyl]ether (DPEphos) previously utilized in phosphorescent Cu (I) materials functions as the second ligand. m-MTDATA was chosen as the donor in the study owing to its high hole mobility, low IP and feasible level alignment with CuDB. The PDs with a structure of ITO/m-MTDATA/m-MTDATA:CuDB/CuDB/LiF/Al were fabricated with different blend layer thicknesses. The optimized PD shows a photocurrent of 253 $\mu\text{A}/\text{cm}^2$ at -10 V, corresponding to a response of 331 mA/W under an illumination of 365 nm UV light. The high response could be ascribed to the excellent electron transport ability of CuDB, the suppression of radiative decay of m-MTDATA as well as the efficient charge transfer from the D to the A. The performances of these devices make them a useful building block for molecular organic ultraviolet photonic integrated circuits.

2. Experimental

m-MTDATA, Bphen were purchased from Aldrich Chemical Co. and used as received. CuDB was prepared from [Cu(NCCH₃)₄]BF₄, BDPB and Bphen in CH₂Cl₂ at room temperature[21].

Devices were fabricated on cleaned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 25 Ω/sq , and the substrates were treated by UV ozone in a chamber for 10 min after solvent cleaning. Organic layers were deposited by thermal evaporation in a vacuum chamber at a pressure of 5×10^{-4} Pa. The organic layers were deposited at a rate of 0.2–0.4 nm/s. The evaporating rate of LiF and Al cathode were controlled to be 0.5 and 1 nm/s with the thickness of 1 and 100 nm, respectively. The mixture films in various devices separately formed by heat coevaporating from two sources. A 365 nm UV light with a power of 0.691 mW/cm² was employed to illuminate both types of diodes at zero bias and various reverse biases. 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. Electroluminescence (EL) spectra were measured with a Hitachi MPF-4 fluorescence spectrophotometer. 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 PDs 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.

3. Results and discussion

To obtain better intermolecular contact of the m-MTDATA and CuDB compounds, a thin mixed layer was inserted between the m-MTDATA and CuDB. Three kinds of PDs with the structure of ITO/m-MTDATA (40 nm)/m-MTDATA:CuDB (10–30 nm)/CuDB (40 nm)/LiF (1 nm)/Al with different blend layer thicknesses of 10, 20 and 30 nm for A, B and C were fabricated. About 1 nm LiF was inserted between electrodes and the photoresponsive layer to increase device photoresponses [22]. Fig. 1 depicts the chemical structure of m-MTDATA, crystal structure of CuDB and the schematic energy level diagram of the UV-PDs based on CuDB. Relative alignment of energy levels of CuDB was estimated from results of cyclic voltammetry and absorption spectroscopy.

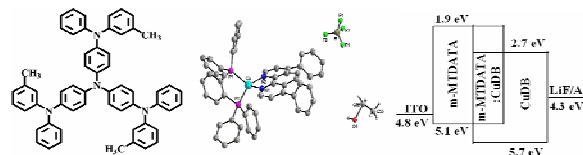


Fig. 1. Chemical structure of m-MTDATA, crystal structure of CuDB and schematic energy level diagram of UV-PDs based on CuDB.

Fig. 2 plots the normalized absorption of 40 nm pristine films of m-MTDATA, CuDB, 80 nm 1:1 blend films of m-MTDATA:CuDB on quartz substrates. All exhibit strong UV absorption with an apparent tail around or below 410 nm. On the other hand, absorption spectra of blend films of m-MTDATA:CuDB is roughly weighted sum of the individual characteristics, indicating no sign of absorption peak due to charge transfer complex.

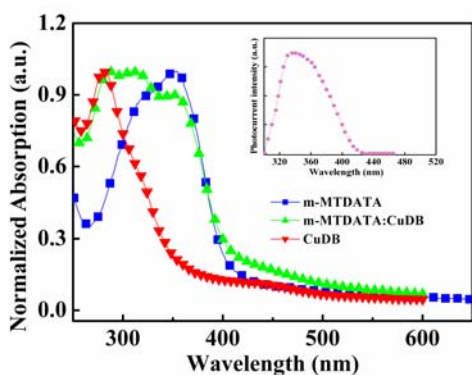


Fig. 2. Normalized absorption spectra of pristine films of *m*-MTDATA, CuDB and *m*-MTDATA:CuDB (1:1) blend films on quartz substrates. The inset shows the photocurrent spectral response of PDs based on CuDB.

As presented in the insert of Fig. 2, CuDB based devices offer the photocurrent spectral responses located at the band from 300 to 410 nm, which is just at the visible-blind UV spectral position.

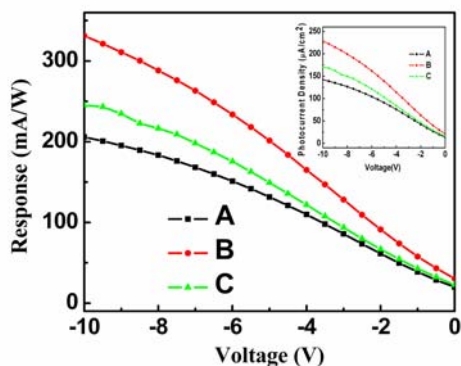


Fig. 3. Dark-corrected photoresponse as a function of various reverse biases for the different structure detectors. The inset shows the photocurrent of PDs based on CuDB.

Fig. 3 depicts dark-corrected photoresponse as a function of different reverse biases for CuDB based UV-PDs. Photoresponses of all PDs increase with the reverse bias and saturate at higher voltages. The photoresponses of CuDB based devices A, B and C at zero bias are 20, 30 and 23 mA/W, respectively, and increase significantly with the reverse bias up to 206, 331, and 245 mA/W at -10 V, respectively. It can be noted that the photoresponse of device B is higher than that of GaN (230 mA/W at 356 nm) [5] and SiC (130 mA/W at 270 nm) [6] based UV-PDs.

Superior performance of CuDB based PDs can be attributed to the higher electron transport ability of CuDB, substantial emission quenching of *m*-MTDATA and efficient charge transfer from the D to the A.

CuDB was demonstrated with high electron transport ability when applied in OLEDs. EL spectra of devices based on CuDB and Alq₃ with the configuration of ITO/NPB/CuDB or Alq₃/LiF/Al at different biases were illustrated in Fig. 4. Devices based on Alq₃ exhibited the same intrinsic Alq₃ luminescence peaking about 524 nm at different biases, while the CuDB based devices showed strong NPB emission and broadened peak toward a longer wavelength resulting from the exciplex formed at the interface between the NPB layer and CuDB layer.

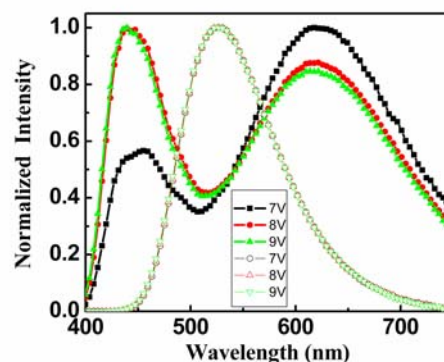


Fig. 4. EL spectra of devices based on CuDB (filled) and Alq₃ (blank) with the structure of ITO/NPB/CuDB or Alq₃/LiF/Al at different biases.

Fig. 5 describes the PL spectra of 40 nm neat *m*-MTDATA, 80 nm (1:1) mixed films of *m*-MTDATA:CuDB and CBP:CuDB. The emission of CuDB can not be observed in neat film due to the severe concentration quenching. But, when doped in CBP, yellow emission from CuDB with maximum at 547 nm along with strong blue emission from CBP can be observed obviously. This behavior could be attributed to well-conjugated ligand BDPB which encourages π - π stacking interaction between CuDB molecules, and this plays an effective role in boosting the electron transport ability of CuDB. Yet, in PL spectrum of *m*-MTDATA:CuDB blend film, blue emission from *m*-MTDATA is completely quenched, being replaced with a weak and largely red-shifted yellow emission from CuDB. The complete quenching of PL from component chromophores, is a signature of efficient photoinduced electron transport from *m*-MTDATA to CuDB as well as the exciton formation on CuDB molecules [23]. The favorable electron transport is supported by the relative alignment of energy levels of the D/A chromophores, as shown in Figure.1. In the present D/A systems, upon application of reverse bias, geminate hole-electron pairs and the excitons of *m*-MTDATA and CuDB dissociated into free carriers followed by efficient carrier transport thanks to the high electron transport ability of CuDB and being collected by electrodes, thus, yielding the outstanding performance in CuDB based PDs.

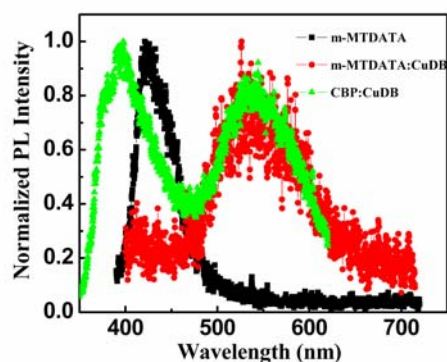


Fig. 5. PL spectra of 40 nm pristine films of *m*-MTDATA, 80 nm *m*-MTDATA:CuDB (1:1) and CBP:CuDB (1:1) blend films on quartz substrates.

4. Conclusions

We demonstrate highly response UV-PDs based on a novel Cu (I) complex. The higher rigidity of BDPB ligand compared to traditional DPEphos significantly enhanced the electron transport ability of CuDB. The excellent performances of PDs can be rationalized in terms of high electron transport ability of CuDB, substantial PL quenching of *m*-MTDATA and efficient charge transfer between the D and the A. The overlap of the spectral response with the UV range and highly efficient performances of CuDB based PDs offer them potential application in near-UV region as low-cost optical switches or photodetectors.

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