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Highly sensitive organic ultraviolet optical sensor based on phosphorescent Cu (I) complex

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Ultraviolet light-sensitive organic optical sensor based on photovoltaic diode was demonstrated by using a phosphorescent Cu complex and a diamine derivative as electroacceptor and electrodonor, respectively. The Cu complex is Cu(DPEphos)((Bphen))BF_4, in which DPEphos and Bphen denote 6,7-dicyanodipyrido [2,2-*d*:2′,3′-*f*] quinoxaline and bathophenanthroline. And the diamine derivative, m-MTDATA, is 4, 4′,4″-tris-(2-methylphenyl phenylamino) triphenylamine. The sensor is highly sensitive to UV light band from 300 to 420 nm while it has almost no response to the visible light, and under illumination of 365 nm light with power of 1.7 mW/cm^2, the sensor exhibits an open circuit voltage of 1.86 V, a short circuit current of 105.3 $\mu A/cm^2$, a fill factor of 0.246, and a power conversion efficiency of 2.83%. The dependences of ultraviolet responsive sensitivity on illumination intensity and working temperature were also discussed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2364156]

The major UV irradiation reaching earth's surface from the Sun[1] covers UV-A zone from 300 to 420 nm, and the UV radiation also resulted from bactericidal lamp, astronomy/astrophysics, and so on. It would pollute environment and attaint human health even in small dosage. Therefore, human needs to estimate its intensity by an UV optical sensor that is sensitive to UV radiation while there is almost no response to visible light to prevent the pollution of UV radiation. Inorganic semiconductors with wide band gap, such as III-nitrides and SiC,[2,3] were applied as UV sensors; however, those sensors have not been suitable for large area applications because of their rather complicated manufacturing processes, high cost, and so on. Besides, light responses of organic molecular/polymer or nanocrystal/polymer photovoltaic diodes are mainly in visible and infrared zones,[4–7] and the sensors based on those were applied in visible light[8,9] and infrared light.[10] Organic UV sensor based on photovoltaic (PV) diodes was not widely reported although it has the advantages of low fabrication cost, simple manufacturing process, making use of portable products, etc. In recent years, the UV-sensitized organic PV diodes with fluorescent and phosphorescent materials have been studied in our group. Electron acceptors used most before were fluorescent materials and PV diodes have some responses to visible light,[11,12] therefore, the UV-sensitized organic PV diodes were not very suitable for UV sensors. Because the lifetime of excited state and the exciton diffusing length of phosphorescent materials are much longer than those of fluorescent materials, PV efficiency would be increased.[13] McMillin and co-workers have studied the photochemical and photophysical properties of some Cu complexes[14,15] in detail and found the UV absorption from metal-ligand charge transfer of Cu complexes. During the process of fabricating organic light-emitting diodes (OLEDs) based on our home synthesized Cu (I) phosphorescent materials, we found that the absorption of the materials in visible light is so weak that it has to be omitted and they could be used to architect UV sensors.

In this letter, UV-sensitized optical sensor based on photovoltaic effect was demonstrated in which the electron acceptor and electron donor are copper(dicyanodipyrido [2,2-*d*:2′,3′-*f*] quinoxaline, 6,7- and bathophenanthroline) BF_4, ([Cu(DPEphos)((Bphen))BF4]), and 4,4′,4″-tris-(2-methylphenyl phenylamino) triphenylamine (m-MTDATA), respectively.

The sensors have the structures of ITO/PEDOT:PSS (80 nm)/m-MTDATA (10–70 nm)/Cu complex (10–70 nm)/LiF (1 nm)/Al (100 nm), where PEDOT:PSS is poly (3, 4-ethylene dioxythiophene):poly (styrene sulfonate). Except the Cu complex synthesized in our laboratory, all materials were commercially available without further purification. Relative alignment of energy levels of the Cu complex was determined from the results of cyclic voltammetry and absorption spectroscopy. For the Cu complex, the highest occupied molecular orbital (HOMO) level was estimated to lie at −5.6 eV and the lowest unoccupied molecular orbital (LUMO) level was calculated to be −3.1 eV. A precleaned indium tin oxide (ITO) substrate with a sheet resistance of 20 Ω/sq was first coated with PEDOT:PSS by spin coating and then dried in a vacuum oven at a 100 °C for 120 min. The organic materials were deposited onto the surface of the polymer layer by thermal evaporation in vacuum chamber at 4×10^{-4} Pa, followed by a 1 nm LiF layer and a 100 nm Al cathode in the same vacuum run; the thickness of the func-

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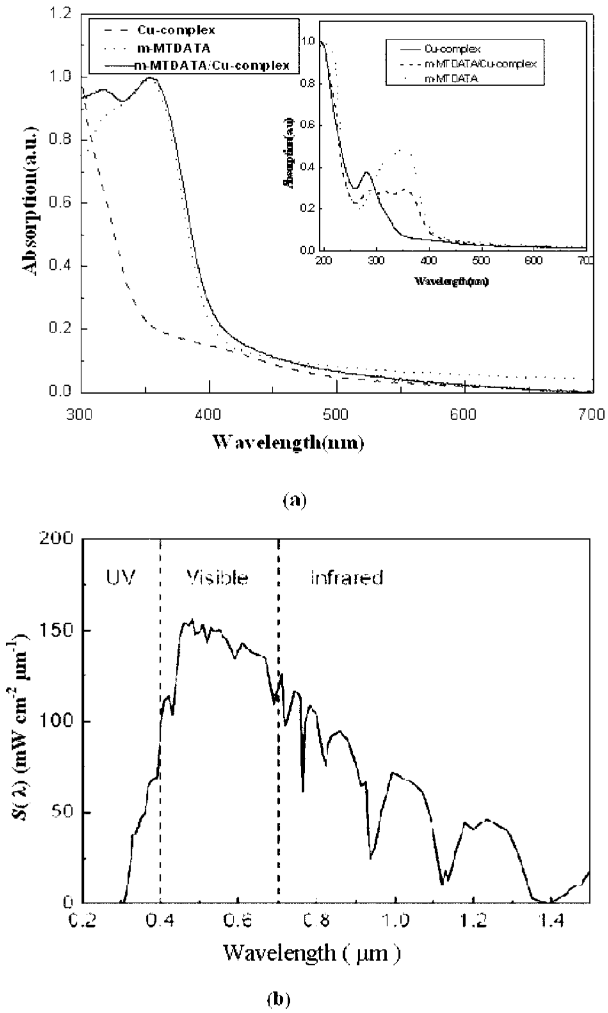
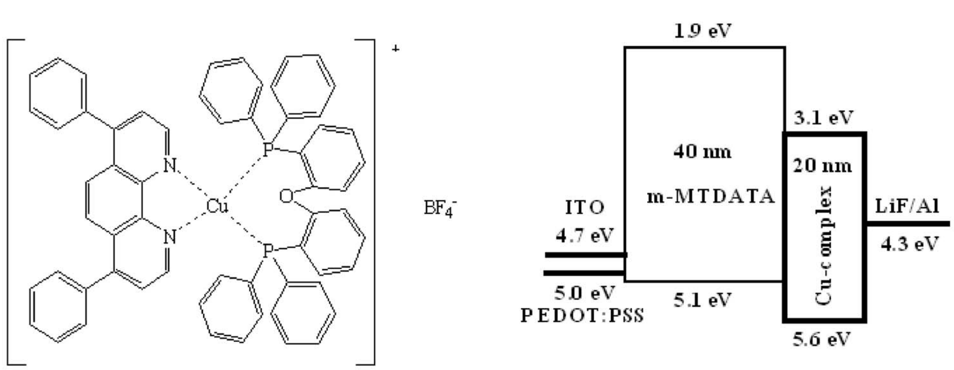


FIG. 1. (a) Absorption spectra of films of the m-MTDATA and the Cu complex as well as double films of m-MTDATA/Cu-complex, respectively. Inset: The 200–300 nm region containing absorption spectra of films of the m-MTDATA and the Cu complex as well as double films of m-MTDATA/Cu-complex, respectively. (b) The standard solar spectrum illuminating earth's surface (Ref. 18).

tional layers was monitored by quartz oscillators and controlled at a rate of 0.2–0.4 nm/s for the organics and LiF and 1.0 nm/s for the Al layer, respectively. The active area of the diodes was 2×5 mm^2. Absorption spectra of the organic films evaporated onto quartz glasses were measured with a Shimadzu UV-3000 spectrophotometer. Photocurrent response curves of the sensor were tested by a 40 μW/cm^2 Xe lamp. The dependence of UV intensity of the I_{sc} was also determined by the different illuminating intensities with 365 nm UV light. The dependence of I_{sc} on working temperature was determined by the tunable temperature equipment and other measurements were carried out at room temperature. All the devices were tested in air ambient.

m-MTDATA has been often used as a hole-injecting material in OLEDs due to its low ionization potential (5.1 eV) (Ref. 16) and its LUMO level was at 1.9 eV. The double-layer device based on m-MTDATA/Alq_3 (8-hydroxyquinoline aluminum) emits yellow electroluminescence easily from the interfacial exciplex,[16,17] and it is suitable to act as donor in PV diodes. The respective absorption spectra of m-MTDATA, Cu-complex, and m-MTDATA/Cu-complex film were determined to study the UV sensitivity of the sensor based on our Cu (I) complex. As indicated in Fig. 1(a), we can see that there is a broad absorption band at 300–420 nm in the spectra of double-layer film due to the addition of the corresponding absorption of two components, which also inosculates to the UV area of the solar spectrum illuminating to earth's surface,[18] as shown in Fig. 1(b). Although there is an absorption band from 200 to 300 nm assigned to the allowed (π-π^*) transition of the ligands[14,15] [see the inset in Fig. 1(a)], there is no disturbance to the UV-A sensor for that there is almost no UV radiation at the spectral region shorter than 300 nm in the solar spectrum reaching earth's surface. Figure 2(a) demonstrates the chemical structure of the Cu complex and the schematic energy level diagram of the sensor. PEDOT:PSS is benefited for improving the collecting hole[19] and the built-in potential can be increased.[20] So, an efficient sensor based on above two materials can be designed in which m-MTDATA and the Cu complex were used as the donor and the acceptor in that the LUMO and HOMO levels of the Cu complex are fairly higher than those of m-MTDATA, and UV sensor with the structure of ITO/PEDOT:PSS (80 nm)/m-MTDATA (40 nm)/Cu complex (20 nm)/LiF (1 nm)/Al (100 nm) was fabricated. Figure 3(a) shows the photocurrent response curve of the device, which is obviously coincident with the absorption band of the double films of m-MTDATA/Cu complex, and the responsive wavelength center locates at 365 nm, indicating that photogenerated excitons result in both m-MTDATA layer and Cu-complex layer. Comparing the photocurrent response spectrum with solar spectrum illuminating to earth's surface, fine matching relation was observed.



(a)Cu (DPEphos) ((Bphen)) BF4 (b) Schematic energy level diagram

FIG. 2. (a) Chemical structures of the Cu complex. (b) The schematic energy level diagrams.

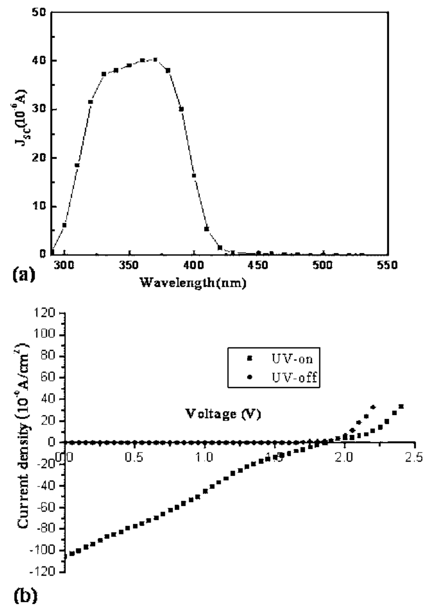


FIG. 3. (a) Photocurrent response curve of the sensor with the structure of ITO/PEDOT:PSS (80 nm)/m-MTDATA (40 nm)/Cu complex (20 nm)/LiF (1 nm)/Al (100 nm). (b) *I-V* characteristics of the sensor under dark (curve: UV off) and under illumination of 365 nm light with power of 1.7 mW/cm^2 (curve: UV on).

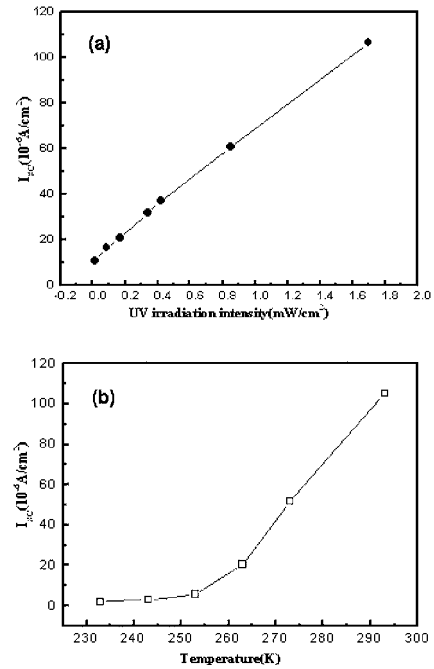


FIG. 4. (a) Dependence of I_{sc} of the UV sensor on the varying illuminating intensities. (b) The dependence of I_{SC} of the UV sensor on the lowering working temperature.

Figure 3(b) reveals the *I-V* characteristics of the UV sensor under dark (UV off) and under illumination of 365 nm UV light with power of 1.7 mW/cm^2 (UV on). A short circuit current (I_{SC}) of 105.3 μA/cm^2, an open circuit voltage (V_{oc}) of 1.86 V, a fill factor (FF) of 0.246, and a power conversion efficiency (η_e) of 2.83% were reached, respectively. Thus, we can conclude that the sensor provides remarkable electrical response while there is almost no signal under dark, indicating a low background signal. The dependence of the I_{sc} on the UV radiation intensity was measured, as shown in Fig. 4(a). There is a gradual decrease in I_{sc} as the UV radiation intensity gradually lowered which is almost a linear dependent relation of I_{sc} on the UV radiation intensity, indicating that I_{sc} is very sensitive to the UV illumination intensity. Even under an illumination intensity of 0.017 mW/cm^2, I_{sc} of 1.8 μA/cm^2 can still be clearly determined. We can conclude that the UV sensor based on PV diode presents high response sensitivity to UV-A band. The dependence of working temperature on the sensitivity of the sensor was also determined, the variation of I_{sc} with the lowering temperature as shown in Fig. 4(b). We can conclude that there are obviously responding performances to the temperature which was attributed to the lowering carrier mobility of the Cu complex and the electron-donor material.[21]

In conclusion, UV-A sensitized organic optical sensor based on the phosphorescent Cu (I) complex was constructed. It has a highly sensitivity to UV radiation zone at 300–420 nm while it has almost no response to the visible light. Under illumination of 365 nm UV light, a large short circuit current of 105.3 μA/cm^2 was achieved, and there is almost a linear dependent relation of the I_{SC} with the UV radiation intensity as well as a markedly variation of ISC with the working temperature was investigated. The favorable performances of the optical sensor would be attributed to the triplet nature of the phosphorescent Cu (I) complex and good electron accepting properties. The investigation on UV sensor based on the Cu (I) complex is expected to develop an application field of phosphorescent materials.

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