A novel Cu(I) complex based organic ultraviolet optical sensor[*]

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A novel Cu(I) complex with the formula of [Cu(DPEphos)(Dicnq)]BF_4 (CuDD) was synthesized and characterized by X-ray single crystal diffraction method, in which DPEphos and Dicnq denote bis[2-(diphenylphosphino)phenyl]ether and 6,7-Dicyanodipyrido[2,2-d:2',3'-f] quinoxaline, respectively. Organic ultraviolet optical sensor based on photovoltaic diode is fabricated by using CuDD as an electron acceptor and 4,4',4"-tris-(2-methylphenyl phenylamino) triphenylamine (m-MTDATA) as an electron donor. The sensor is sensitive to UV light band from 300 to 400 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, an open circuit voltage of 1.47 V, a short circuit current of 38.9 mA/cm^2, a fill factor of 0.24, and a power conversion efficiency of 0.8 % are achieved. In addition, the dependence of ultraviolet responsive sensitivity of the sensor on working temperature is also discussed.

Ultraviolet (UV) optical sensor is a kind of photovoltaic (PV) diodes which is sensitive to UV zone from 200-400 nm while it has no response to the visible light[1]. Therefore, it can detect the existence and intensity of ultraviolet light so as to prevent the people from its harm. Conventionally, inorganic semiconductors with wide band gap, such as SiC, III-nitrides, diamond, ZnO or ZnSe are widely used in ultraviolet optical sensor[2-6]. A less conventional, but promising type of photoactive material for ultraviolet optical sensor is the organic semiconductor, both small molecule weight organic compounds and conjugated polymers. Compared with those inorganic semiconductors, organic thin films can be processed from solution or by using simple and relatively inexpensive deposition techniques. They are intrinsically compatible with flexible substrates such as stainless steel foils and plastic, allowing roll-to-roll fabrication of large-scale devices. The material cost of the organic materials is far lower than their inorganic counterparts. The UV-sensitized organic PV diodes with fluorescent materials and phosphorescent materials have been demonstrated[7,8]. Owing to the longer lifetime of the excited state and the exciton diffusing length of phosphorescent materials than those fluorescent materials, PV efficiency would be increased. Recently, Cu(I) complexes as a new class of electrophosphorescent materials have attracted much attention due to their advantages including abundant resource, low cost and nontoxic property compared with noble metal complexes, e.g., Re(I), Os(II), Ir(III), Pt(II) and Rh(I). Up to date, highly efficient green, white and yellow organic light-emitting diodes (OLEDs) based on Cu (I) complexes have been acquired[9-11]. However, organic UV sensor based on Cu(I) complexes was scarcely reported. Herein, we report a phosphorescent Cu (I) complex for application in UV optical sensor along with its synthesis and characterization.

Organic ligand Dicnq and Cu(I) complex (CuDD) were prepared according to literatures[11,12] and the purity was verified by elemental analysis. Single crystals of suitable for X-ray crystallograpic analysis were grown by slow evaporation of solutions in CH_2Cl_2/ethanol at room temperature. Diffraction data were collected with a Siemens SMART CCD diffractometer using monochromated Mo-Ka (l = 0.71069 Å) radiation at 293 K in the range of 1.58° < q < 28.61°. Empirical absorption correction (w scan) was applied. The

structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 software[13]. All non-hydrogen atoms were refined anisotropically.

UV optical sensor based on photovoltaic effect was constructed with the structure of ITO/ PEDOT: PSS (70 nm)/ m-MTDATA (10-60 nm)/CuDD (10-50 nm)/LiF (1 nm)/Al (100 nm), in which CuDD was used as an electron acceptor and m-MTDATA as an electron donor. PEDOT: PSS has been reported to facilitate hole injection and to increase the built-in potential[14]. m-MTDATA has been often used as a hole-injecting material in OLEDs and as donor in PV diodes due to its low ionization potential (5.1 eV) and its LUMO level was at 1.9 eV[15]. LiF is used as electron injector in combination with an aluminum cathode. Except the Cu complex synthesized in our laboratory, all materials were commercially available without further purification. 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 2 hours. 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 functional layers was monitored by quartz oscillators and controlled at a rate of 0. 2–0.4 nm/s for the organic compounds 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 short circuit current (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.

Major crystallographic data are summarized in Tab.1. Chemical structure and ORTEP plot of CuDD are presented in Fig.1. The X-ray crystallographic study on CuDD reveals a distorted tetrahedral coordination environment about Cu (I) with P-Cu-P and N-Cu-N bond angles of 113.53(11)° and

80.5(3)°, respectively. At the same time, the structures reveal that there does not exist distinct remarkably on average bond distances of Cu-P [Cu-P(1) = 2.249(3) and Cu-P(2) = 2.238(3) Å] and Cu-N [Cu-N(1) = 2.088(7) and Cu-N(2) = 2.041(8) Å] in CuDD compared with other Cu (I) complexes reported[16]. It can be noted that the DPEphos ligand is bound to the metal only through its pair of P donor atoms, the ether O atom being at a non-bonding distance (3.1 Å) from the Cu (I) center.
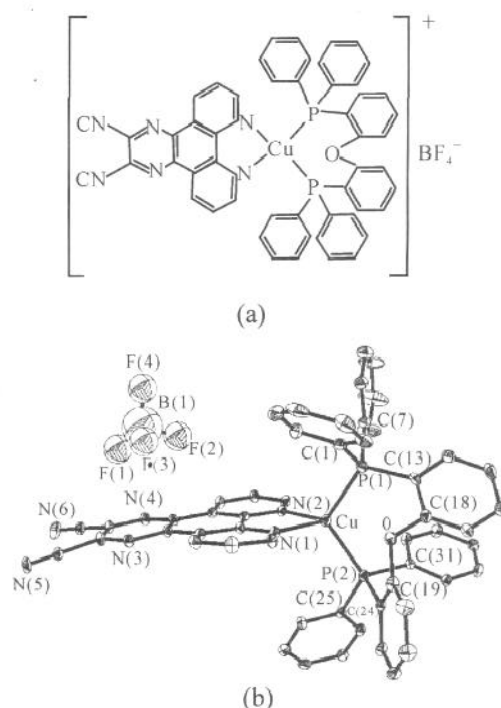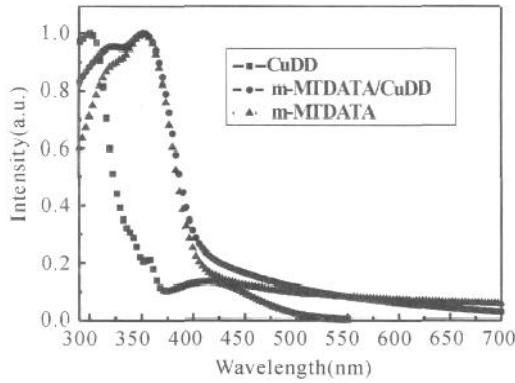

Fig.1 Chemical structure and perspective drawing of Cu (I) complex.

Our group obtained highly efficient and color-tuning electrophosphorescent devices based on CuDD[10]. During the process of fabricating OLEDs by utilizing CuDD as emitter, we found that the absorption of CuDD and host material (m-MTDATA) in visible light is so weak that it has to be omitted and they could be used to architect UV sensor. The respective electronic absorption spectra of m-MTDATA, CuDD and m-MTDATA/CuDD film were determined to study the UV sensitivity of the sensor based on our Cu complex. As indicated in Fig.2, there is an intense broad absorption band at 300–400 nm in the spectra of double-layer film due to the combination of the corresponding absorption of two components. Fig.3 illustrates the structure (schematic energy level diagram) of the sensor and Fig.4 plots the photocurrent response curve of the device with the structure of ITO/ PEDOT:PSS (70 nm)/ m-MTDATA (30 nm) /CuDD (20 nm)/ LiF (1 nm)/Al (100 nm), which is obviously coincident with
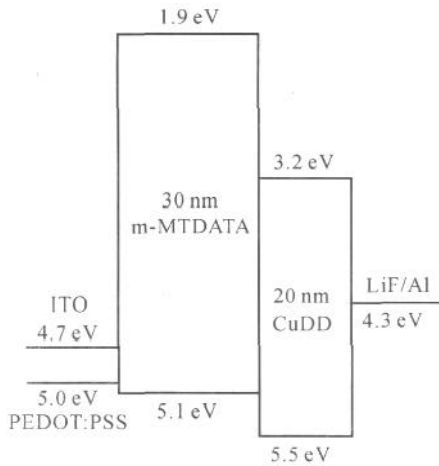
Tab.1 Crystallographic data for CuDD at 293 K

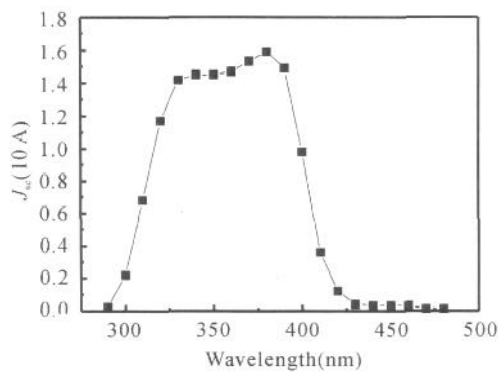|	CuDD		
Molecular formula	$C_{52}H_{34}BCuF_4N_6OP_2$	CCDC numbers	280518
Molecular mass	971.14	Space group	P-1
a/Å	12.779(5)	α/°	68.630(5)
b/Å	13.979(5)	β/°	78.501(5)
c/Å	17.970(5)	γ/°	77.526(5)
V/Å^3, Z	2893.0(17),2	μ/mm^{-1}	0.561
λ/Å	0.71069	ρ/g cm^{-3}	1.115
R$_1$	0.1036	wR$_2$	0.2587

the absorption band of the double films of m-MTDATA/Cu (I) complex, and the responsive wavelength center locates at 365 nm, indicating that photogenerated excitons result in both m-MTDATA layer and CuDD layer.

Fig.2 Absorption spectra of the m-MTDATA and the Cu (I) complex as well as double films of m-MTDATA/Cu (I) complex, respectively.
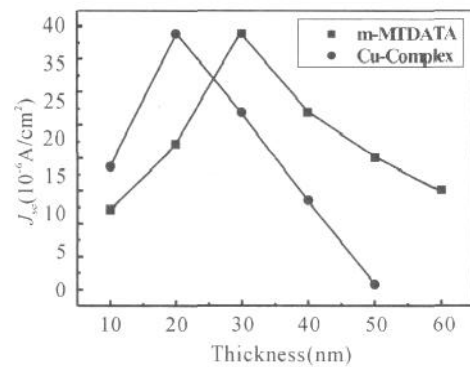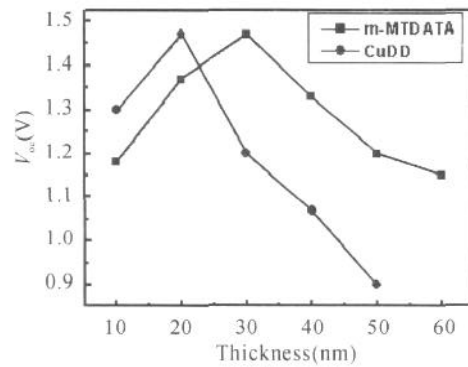

Fig.3 The schematic energy level diagram of UV sensor.

Fig.4 Photocurrent response curve of the UV sensor with the structure of ITO/ PEDOT: PSS (70 nm)/ m-MTDATA (30 nm) /CuDD (20 nm)/LiF (1 nm)/Al (100 nm).

A series of UV optical sensors with various thicknesses of m-MTDATA and Cu complex layers were fabricated to achieve the best sensor. When the thickness of PEDOT:PSS was fixed at 70 nm, the short circuit current (I_{sc}) and the open circuit voltage (V_{oc}) with different thickness of m-MTDATA layer with 10 nm Cu complex layer and with different thickness of Cu complex with 10 nm m-MTDATA were determined (Fig.5). The results reveal that UV optical sensor demonstrates the best performance when the thicknesses of Cu complex and m-MTDATA layers are 20 nm and 30 nm, respectively. Fig.6 reveals the *I-V* characteristics of the UV optical sensor with the structure of ITO/PEDOT: PSS (70 nm)/m-MTDATA (30 nm) /CuDD (20 nm)/LiF (1 nm)/Al (100 nm) under dark (UV off) and under illumination of 365 nm UV light with power of 1.7 mW/cm² (UV on). An I_{sc} of 38.9 μA/cm², a V_{oc} of 1.47 V, a fill factor (*FF*) of 0.24, and a power conversion efficiency (h_e) of 0.8 % were obtained, respectively. Thus, we can conclude that the sensor provides remarkable electrical response while there is almost no signal under dark, indicating this diode can accurately detect the UV radiation. There are several factors to be responsible for such a modest performance. Firstly, the developed Cu (I) complex possesses highly rigid structure which can facilitate the carrier injection, and consequently, leads to efficient ex-
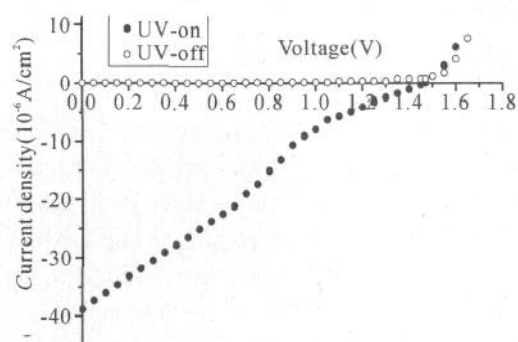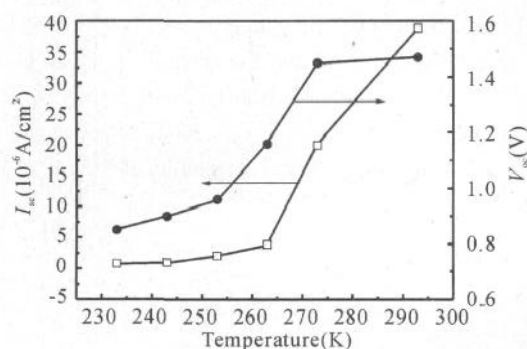

(a)

(b)

Fig.5 The dependence of PV performance on film thickness of CuDD and m-MTDATA.

citon formation. Secondly, for the Cu complex, the highest occupied molecular orbital (HOMO) level was estimated to lie at 5.5 eV and the LUMO level was calculated to be 3.2 eV, as displayed in Fig.3 . So, the difference between the HOMO level (5.5 eV) of acceptor (CuDD) and LUMO level (1.9 eV) of donor (m-MTDATA) is sufficiently large to overcome the exciton binding energy, so the dissociation of the strongly bound exciton occurring at a Cu complex-m-MTDATA interface is energetically favorable. This can contribute to high performance of UV optical sensor. Furthermore, the long excited lifetime of phosphorescent Cu complex (4.26 μs) can result in longer exciton diffusing length, which can be also helpful to high UV optical sensor performance . In addition, the variation of I_{sc} and V_{oc} with different working temperature was also studied. As shown in Fig.7, the performance of UV optical sensor has a strong

dependence on working temperature. With the decreasing of the working temperature, I_{sc} and V_{oc} are both gradually lowered attributed to the lowering carrier mobility of the Cu complex and the electron-donor material.

In summary, we demonstrate a phosphorescent Cu complex for application in UV optical sensor as an electron acceptor along with its synthesis and characterization. The UV optical sensor with the structure of ITO/PEDOT: PSS (70 nm)/m-MTDATA (30 nm) /CuDD (20 nm)/LiF (1 nm)/Al (100 nm) exhibits the best performance. Under illumination of 365 nm UV light with power of 1.7 mW/cm² (UV on), I_{sc} of 38.9 ì A/cm², V_{oc} of 1.47 V, *FF* of 0.24, and h_e of 0.8% were achieved, respectively. The optical sensor performances have a strong dependence on the working temperature. With the decreasing of working temperature, I_{sc} and V_{oc} are both gradually lowered attributed to the lowering carrier mobility of the Cu complex and the electron-donor material. The successful application of phosphorescent CuDD in UV optical sensor suggests that CuDD can be utilized as a bifunctional material, thus providing the roadmaps for developing phosphorescent materials and their application in optoelectronic devices.

Fig.6 I-*V* characteristics of the sensor under dark (curve: UV off) and under illumination of 365 nm light with power of 1.7 mW/cm² (curve: UV on).

Fig.7 Dependence of I_{sc} of the UV sensor on the lowering working temperature.

The highest occupied molecular orbital (HOMO) energy level of CuDD was determined to be 5.5 eV, by cyclic voltammetry. The lowest unoccupied molecular orbital (LUMO) energy level was calculated to be 3.2 eV according to the absorption band edge of CuDD. The excited-state lifetime of CuDD was determined by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed Nd:YAG laser with a THG 355 nm output.

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