Digest Journal of Nanomaterials and Biostructures Vol. 14, No. 2, April – June 2019, p. 395 - 399

SYNTHESIS AND CHARACTERIZATION OF COPPER PERCHLORINATED PHTHALOCYANINE AS SEMICONDUCTOR MATERIAL FOR THIN FILM TRANSISTORS

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An organic semiconductor material copper perchlorinated phthalocyanine ($CuPcCl_{16}$) was synthesized and its optical, thermal and electrical properties were characterized. UV-Vis spectra showed that the two strong absorption peaks for Q band were 649 and 684 nm. The electrochemical characterization indicated that the $CuPcCl_{16}$ compound embody suitable lowest unoccupied molecular orbital level for electron injection. Thermal analysis showed the compound has excellent thermal stability with decomposition temperature above 260 ^{o}C. The $CuPcCl_{16}$-based OTFTs was fabricated by the physical vapor deposition technique and their electrical properties were investigated. The charge carrier field-effect mobility and threshold voltage of the OTFTs were 0.46×10^{-2} cm^2/V s and 30 V, respectively.

(Received December 7, 2018; Accepted May 7, 2019)

Keywords: Semiconductor, Phthalocyanines, Thin film transistors, Mobility

1. Introduction

Phthalocyanines (Pcs) are organic pigments with narrow HOMO-LUMO gaps, good environmental stabilities, and their characters can be tuned by the choice of central metal and the introduction of various substituents [1]. Thus, Pcs attract much attention and they have been studied for various applications. Metallophthalocyanines have been demonstrated to possess remarkable semiconducting properties [2, 3]. They have been widely studied as solar cells, optical limiters, and photoconductors [4].

Most of the unsubstituted phthalocyanines show the characteristics of p-type semiconductor while some metal hexadecafluorophthalocyanines ($MPcF_{16}$), such as $CuPcF_{16}$, exhibit air-stable n-type semiconducting behavior due to the strong electron-withdrawing effect of the -F substituent [5]. Li et al. [6] have reported $CuPcF_{16}$-based OTFTs by inserting the *p*-6p inducing layer with good electron mobility of 0.07 $cm^2/V\cdot s$. The introduction of strong electron-withdrawing group in p-type metal phthalocyanines ring may produce n-type semiconductors, allowing many n-type semiconductors designed in accordance with this approach.

So far, most organic semiconductor materials show p-type behavior, while n-type properties are found in only a few materials [7]. Meanwhile, the n-type organic semiconductor materials play important roles on p-n junction diodes, bipolar transistor and complementary CMOS circuit, etc [4]. Therefore, it is very important to develop the n-type organic semiconductor materials. In this paper, we introduce -Cl substituents on phthalocyanine ring and study the semiconductor properties of the compound.

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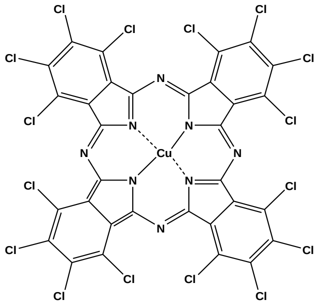

Fig. 1. Molecular structure of $CuPcCl_{16}$.

2. Experiment

For the synthesis of $CuPcCl_{16}$, Tetrachlorophthalonitrile (2.66 g), urea (3 g) and copper acetate dehydrate (0.55 g) were mixed then heated with ammonium molybdate (0.02 g) used as catalyst. The mixture was brought to 260°C in 2h. The heating was carried on for 5 h. The mixture was alternatively washed with 0.1 M H_2SO_4 and 0.1 M NaOH solution, until the washes were colorless. The product was then rinsed with hot water and dried. Three washes with DMF followed by three sublimations removed the last impurities and afforded (1.07 g, 38 %).

A dark blue precipitate formed and was suction filtered through a fine Teflon filter. The compound was recrystallized from sulfuric acid and isolated in 52.51 % yield. IR (KBr) 1607, 1509, 1490, 1490, 1459, 1370, 1320, 1276, 1154, 832 and 784 cm^{-1}. MS (TOF, Methanol) m/e 1128.32.

The $CuPcCl_{16}$-based OTFTs configuration is given in Fig. 2. The $CuPcCl_{16}$ compound was further purified by sublimation twice at a pressure of 10^{-5} Torr or lower. An n-doped Si with a thermally grown dry oxide layer as gate dielectric were used as substrate. Semiconducting thin films were prepared by vacuum deposition at above 300 °C at a rate of 2 Å/s under a pressure of 10^{-6} Torr, and the thickness of the resulting films was 45 nm. Devices were fabricated by depositing gold source and drain electrodes onto the organic semiconductor films through a shadow mask with channel width of 4000 μm and channel length of 200 μm. The electrical characteristics of organic thin film transistor devices were measured using two Keithley 2400 semiconductor parameter analyzers.

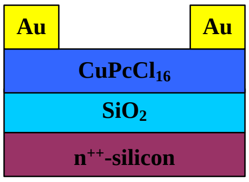

Fig. 2. The device configuration of $CuPcCl_{16}$-based thin film transistor.

3. Results and discussion

3.1. UV-vis absorption spectra

As unsubstituted CuPc, $CuPcCl_{16}$ is characterized by low solubility. Fig. 3 shows the UV-vis absorption spectra of 5×10^{-5} mol L^{-1} $CuPcCl_{16}$ solutions in dimethylformamide (DMF). The absorption spectra were measured by an EVOLUTION300 spectrometer. Absorption maxima for Q band are seen at 649 nm and 684 nm. The two strong absorption peaks indicate that $CuPcCl_{16}$ molecules aggregate in DMF solution [5, 8]. Maximum absorption peak is 673 nm for CuPc in DMF. Compared with CuPc, the maximum absorption peak of $CuPcCl_{16}$ show red shifted, which originates from the extension of the π-π conjugated system of the phthalocyanine ring caused by the the n-π^* transition due to the introduction of -Cl substituent. From Fig. 3, the optical gap energy can be obtained from the edge of absorption band [9, 10]. The absorption edge of

$CuPcCl_{16}$ in DMF is found around 719 nm, from which the optical band gap energy of $CuPcCl_{16}$, *Eg*, is estimated to be 1.73 eV.

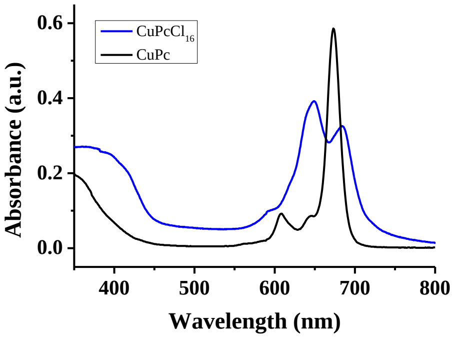

Fig. 3. The UV-vis spectra of $CuPcCl_{16}$ and CuPc in DMF solvent.

3.2. C-V curve

Solution cyclic voltammetry (CV) was employed to investigate the electrons transport ability and electrochemical properties of the $CuPcCl_{16}$ compound. The cyclic voltammogram (Fig. 4) were collected on a CHI760E electrochemistry workstation at room temperature in DMF measured against a saturated calomel electrode (SCE) with tetrabutylammonium perchlorate (Bu_4NClO_4, 0.10 M) as the supporting electrolyte. As shown in Fig. 4, the chemical oxidation and reduction peaks of E_{OX} = -0.68 V and E_{RE}= -1.35 V (versus standard calomel electrode, SCE) are observed. The reductive process started at -0.74 V. The energy level of the lowest unoccupied molecular orbital, E_{LUMO}, can be estimated from the reductive onset potential to be -4.00 eV [11, 12]. The low LUMO energy level is favorable for electron injection and transport; in other words, $CuPcCl_{16}$ should be a good electron transport material. The energy level of the highest occupied molecular orbital, E_{HOMO}, can be estimated by adding Eg from E_{LUMO} as determined by the electrochemistry. This leads to an estimation of E_{HOMO} to be -5.73 eV for $CuPcCl_{16}$.

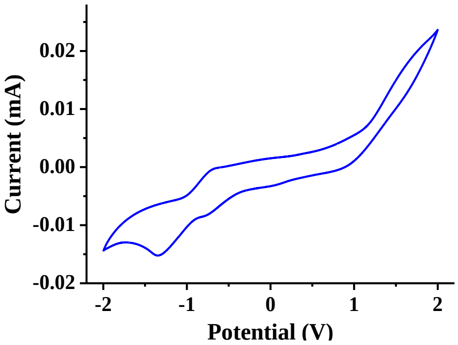

Fig. 4. Cyclic voltammogram of $CuPcCl_{16}$ in DMF.

3.3. Thermal properties

The thermal properties of $CuPcCl_{16}$ were characterized by thermogravimetric analysis (TGA) at a heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere. The TGA curve was measured by a TG 209 F3 thermo gravimetric analyzer. $CuPcCl_{16}$ is relative stable and the mass loss is less than 10% below 100 ^{o}C. TGA measurements indicate that $CuPcCl_{16}$ has high decomposition temperature of 260 °C (Td, correspond to a 10% mass loss, Fig. 5). $CuPcCl_{16}$ exhibits excellent thermal stability and so its semiconductor thin film can be prepared by thermal deposition technique.

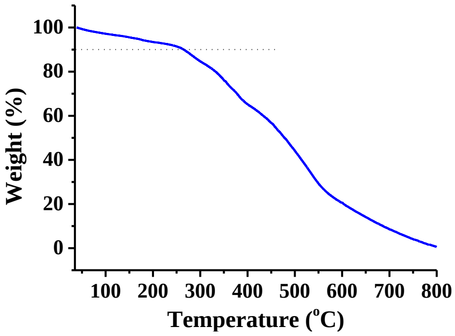

Fig. 5. TGA curves of $CuPcCl_{16}$.

3.4. Current-voltage characteristics

The output characteristic curves of the $CuPcCl_{16}$-based OTFTs are shown in Fig. 6 at different gate-source voltages (V_{GS}) from 0 to 100 V. When a positive bias of 100 V was applied to the gate and drain electrode, saturated drain current of about 2.56 μA in electron-accumulation mode was obtained. Fig. 7 shows the transfer characteristics of the $CuPcCl_{16}$-based OTFTs with different gate voltages at a fixed V_{DS} of 100 V. The field effect mobility was extracted from Fig. 7 in the saturation region ($V \geq (V_{GS} - V_T)$) based on

$$I_{DS} = \frac{W}{2L}\mu C_i (V_{GS} - V_T)^2 \tag{1}$$

where I_{DS} is the drain-source current, W and L are the width and length of the channel, respectively, μ is the field-effect mobility, V_{GS} is the gate voltage and V_T is the threshold Voltage. According to the electrical properties, *n*-type conductivity of the $CuPcCl_{16}$ semiconductor material was confirmed. The effect mobility of 0.46×10^{-2} cm^2/V s and the threshold Voltage of 30 V were extracted from the saturation region in Fig. 7.

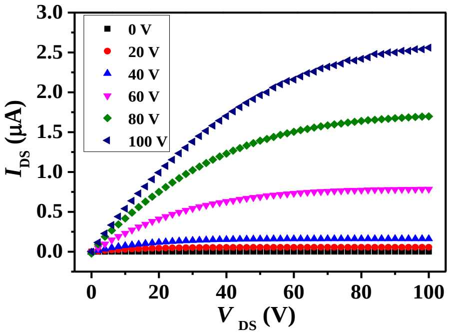

Fig. 6. Output characteristics of $CuPcCl_{16}$*-based OTFTs.*

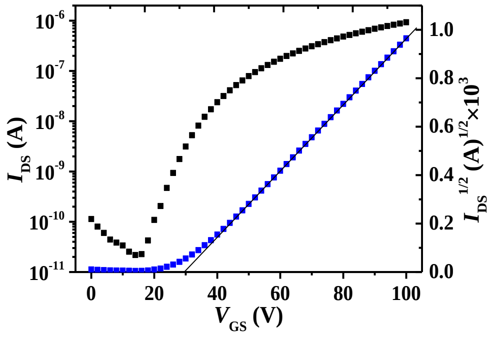

Fig. 7. Transfer characteristics of $CuPcCl_{16}$*-based OTFTs at a fixed* V_{DS} *(100 V).*

4. Conclusions

In summary, the $CuPcCl_{16}$ compound was synthesized with yield of 38 %. The compound showed n-type semiconductor properties due to the introduction of electron-withdrawing substituent (-Cl). The electronic property was studied by UV-vis absorption and cyclic voltammetry methods. The $CuPcCl_{16}$-based OTFTs was fabricated by the physical vapor deposition technique. The electrical properties of the OTFTs were investigated and n-type of conductivity was confirmed. And the charge carrier field-effect mobility of the OTFTs was 0.46×10^{-2} cm^2/V s. The stable $CuPcCl_{16}$ compound with high mobility will be a promising material for optical and electronic devices application.

Acknowledgements

The work has been partially supported by National Natural Science Foundation of China (no. 21401138) and Tianjin Project of Innovation Team of Colleges and Universities in Tianjin (TD13-502).

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