Digest Journal of Nanomaterials and Biostructures Vol. 13, No. 1, January - March 2018, p. 7 - 12

SYNTHESIS AND CHARACTERIZATION OF COBALT (II) PERFLUOROPHTHALOCYANINE

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Metal perfluorophthalocyanines compound $CoPcF_{16}$ was synthesized and characterized. The electron energy levels were studied by UV-vis absorption and cyclic voltammetry methods. The measurement results indicate that the $CoPcF_{16}$ compound embodies suitable lowest unoccupied molecular orbital (LUMO) level for electron injection. Thermal analysis shows that the compound has excellent thermal stability with decomposition temperature above 537 ^{o}C. The $CoPcF_{16}$ thin film was characterized by XRD and AFM. And the results show that $CoPcF_{16}$ molecules are almost perpendicular to the substrate. These results indicate that the $CoPcF_{16}$ compound is a good candidate for the application in Organic field-effect transistors (OFETs) as n-type semiconductor materials.

(Received July 6, 2017; Accepted January 3, 2018)

Keywords: Semiconductor, Phthalocyanines, Transistors

1. Introduction

Organic field-effect transistors (OFETs) have been widely studied due to their potential applications in flat-panel displays, complement circuits and sensors [1-3]. Organic semiconductor material is an important component of OFETs, which directly affects the mobility of organic devices. So far, most organic semiconductor materials show *p*-type behavior, while *n*-type properties are found in only a few materials [3, 4]. Meanwhile, the *n*-type organic semiconductor materials play important roles on p-n junction diodes, bipolar transistor and complementary CMOS circuit, etc. Therefore, it is very important to develop the *n*-type organic semiconductor materials.

Phthalocyanines (Pcs) have attracted much attention for many decades because they exhibit excellent photoelectrochemical properties [5, 6]. Phthalocyanine compounds are widely used as photoelectric materials for organic photoconductors, photovoltaic solar cells, organic field effect transistors, optical switches, optical storage, etc. Most of the unsubstituted phthalocyanines show the properties of *p*-type semiconductor while some metal perfluorophthalocyanines, such as $CuPcF_{16}$, exhibit *n*-type semiconducting behavior due to the strong electron-withdrawing effect of the -F substituent [7, 8].

Synthesis and characterization of copper hexadecafluorophthalocyanine ($CuPcF_{16}$) were reported in Ref. [7, 9]. And the electron mobility of the $CuPcF_{16}$/*p*-6p organic field effect

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transistors was 0.07cm^2/V s. The authors also investigated the synthesis and chemical properties of Tin (χ) Dichloride hexadecafluorophthalocyanine ($SnPcCl_2F_{16}$) and found the compound exhibited *n*-type semiconductor behaviors [6]. The fluorination of *p*-type metal phthalocyanines may produce *n*-type semiconductors, allowing many *n*-type semiconductors designed in accordance with this approach. In this paper, Cobalt (II) Perfluorophthalocyanines (shown in Fig. 1) was synthesized and its optical, electrochemical and thermal properties were characterized in detail.

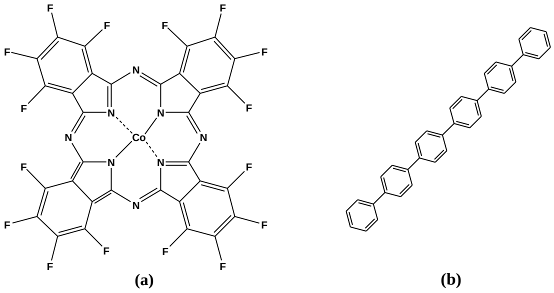

Fig. 1 Molecular structure of (a) $CoPcF_{16}$ and (b) p-6p

2. Experiment

The $CoPcF_{16}$ compound was synthesized using a procedure similar to that previously reported [6, 7, 9]. An equimolar 4:1 ratio mixture of 3, 4, 5, 6-tetrafluorophtalo-1, 2-dinitrile and Cobalt (Ⅱ) acetate was filled in a glass vessel and sealed under vacuum (1.33×10^{-3} Pa). After heating for 8 h at 200 ^{o}C the dark blue product was washed with ethanol and acetone to remove the soluble organic admixtures. The $CoPcF_{16}$ compound was recrystallized from sulfuric acid and isolated in 56.1% yield. IR (KBr) 1612, 1532, 1466, 1153, 843 and 756 cm^{-1}. MS (TOF, Methanol) m/e 860.101. The $CoPcF_{16}$ thin film was prepared with the $CoPcF_{16}$ compound and a rod-like conjugated oligomer *p*-6p (shown in Fig. 1) molecule. A 6nm thick film of *p*-6p was first deposited on a SiO_2 substrate at 180 ^{o}C, and then a 30 nm thick layer of $CoPcF_{16}$ was deposited on top of the *p*-6p surface by vacuum deposition.

3. Results and discussion

3.1. UV-vis and fluorescence spectra

Fig. 2 shows the UV-vis absorption spectra of 0.5×10^{-5} mol L^{-1} $CoPcF_{16}$ solutions in 1, 2-dichlorobenzene (DCB), tetrahydrofuran (THF), pyridine and dimethylformamide (DMF), respectively. The absorption spectra were measured by an EVOLUTION300 spectrometer. Absorption maxima for Q band are seen at 665 nm for $CoPcF_{16}$ dissolved in DCB and maximum absorption peak at 664 and 663 nm for $CoPcF_{16}$ solution in THF and pyridine, respectively. With the increase of the polarity of solvents, the Q band shift to a shorter wave length to some extent, which originates from the increasement of the transition energy gap in the π-π* transition system. In polar solvent DMF, the Q band has only absorption peak at about 630nm and blue shift. It is well known that the phthalocyanine compounds are blue-shifted by dimerization. Thus, $CoPcF_{16}$ aggregates in DMF solvent according to reference literature [7, 9, 10]. The absorption edge of

$CoPcF_{16}$ in DMF is found around 777nm, from which the optical band gap energies of $CoPcF_{16}$, *Eg*, is estimated to be 1.60 eV .

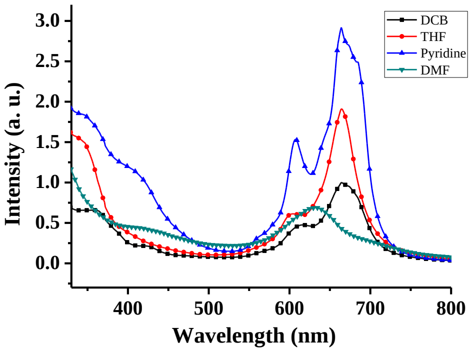

Fig. 2 The UV-vis spectra of $CoPcF_{16}$ in different solvents.

The fluorescences pectrums of $CoPcF_{16}$ in DMF was measured on a CARYE clipse fluorescence spectrophotometer, as shown in Fig. 3. The emission maxima are observed at 696 nm corresponding to the red light emission.

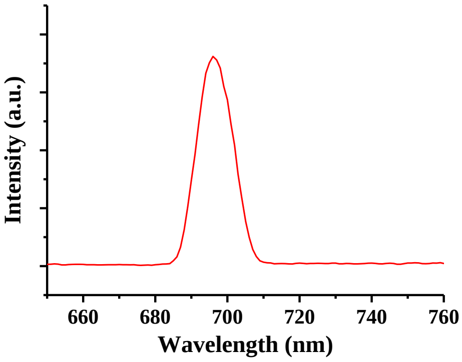

Fig. 3 Fluorescence emission spectra of $CoPcF_{16}$ in DFM.

3.2 C-V curve

The electrons transport ability and electrochemical properties of the $CoPcF_{16}$ were examined by solution cyclic voltammetry (CV). 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 $E_{OX} = -0.78$ V and $E_{RE}= -0.64$ V are observed for $CoPcF_{16}$. The reductive process started at -0.24 V. The energy level of the lowest unoccupied molecular orbital, E_{LUMO}, can be estimated from the reductive onset potential to be -4.50 eV [14, 15]. The low LUMO energy level is favorable for electron injection and transport; in other words, $CoPcF_{16}$ should be a good electron transport material. The energy level of the highest occupied molecular orbital, E_{HOMO}, can be calculated by adding Eg from E_{LUMO} as determined by the electrochemistry curve. This leads to an estimation of E_{HOMO} to be -6.10 eV for $CoPcF_{16}$.

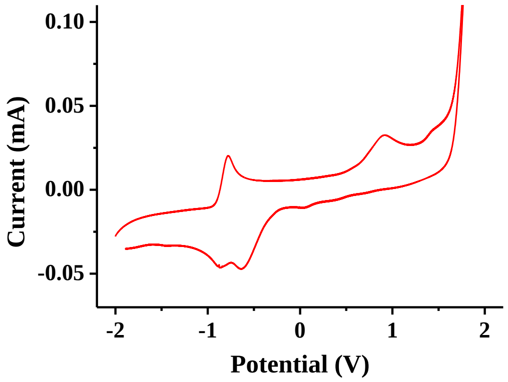

Fig. 4. Cyclic voltammogram of $CoPcF_{16}$ in DMF.

3.3. Thermal properties

The thermal stability of $CoPcF_{16}$ compound was tested by thermogravimetric analysis (TGA) at a heating rate of 10 ^{o}C min^{-1} under nitrogen atmosphere. The TGA curves were measured by a TG 209 F3 thermo gravimetric analyzer. As shown in Fig. 5, the $CoPcF_{16}$ possesses excellent thermal stability properties with high decomposition temperature (T_d) of 537 °C. (T_d, correspond to a 10% mass loss).

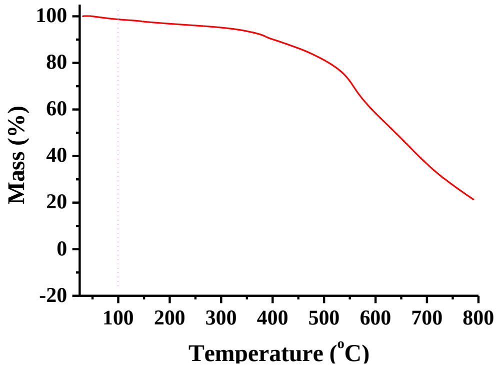

Fig. 5 TGA curves of $CoPcF_{16}$.

3.4 XRD of $CoPcF_{16}$ thin film

Fig. 6 shows the XRD pattern of the $CoPcF_{16}$ thin film. The X-ray diffraction was performed in a Rigaku D/max 2500 PC X-ray diffractometer with a Cu Kα radiation (λ = 1.54056 Å). The diffraction peaks of the $CoPcF_{16}$ thin film at 2θ = 6.21, corresponding to d_{200} spacing of 14.22 Å, are observed. The XRD pattern indicates that the $CoPcF_{16}$ molecules are approximately standing-up on the *p*-6p layer [16-18].

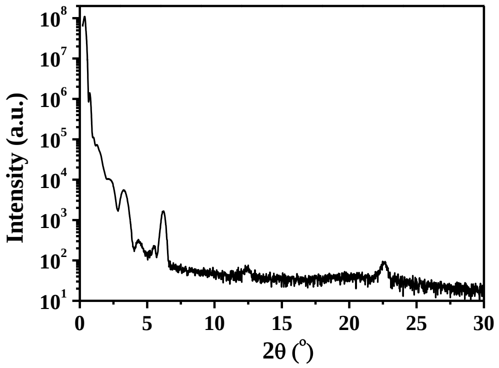

Fig. 6 X-ray diffraction spectra of the CoPcF$_{16}$ thin film.

3.5 AFM of CoPcF$_{16}$ Thin film

Atomic force microscopy (AFM) observations further investigated the morphology of the CoPcF$_{16}$ thin film, as shown in Figure 7. The CoPcF$_{16}$ molecules growth on the *p*-6P modified SiO$_2$ substrate displays island crystal domains and arranges upright on the substrate, which is in agreement with the X-ray diffraction measurements. The vertical arrangement of large π-conjugated phthalocyanine molecules is favorable for carrier transport [16].

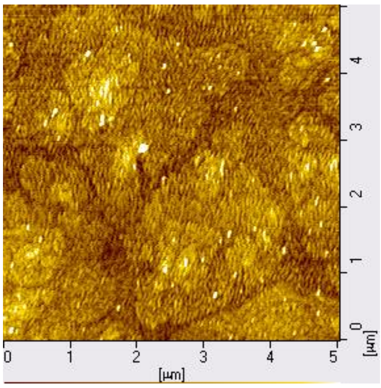

Fig. 7 AFM of the CoPcF$_{16}$ thin film

4. Conclusions

In summary, the CoPcF$_{16}$ compound was synthesized by the solid state reaction. The photoluminescence spectra of the CoPcF$_{16}$ compound exhibit a maximum peak at 696 nm. The LUMO level of the compound was -4.50 eV, which favor the electron injection. High decomposition temperature implies that the compound has excellent thermal stability.

The CoPcF$_{16}$ thin film was fabricated by vacuum thermal deposition and the CoPcF$_{16}$ molecules were approximately standing-up on the substrate, which facilitate the carrier transportation. These results show that the CoPcF$_{16}$ compound is good candidates for the application in OFETs as n-type semiconductor materials.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (no. 21401138), High School Science and Technology Fund Planning Project of Tianjin (no. 20130508) and National Key R＆D Program of China (no. 2016YFB0401303).

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