SYNTHESIS, CHARACTERIZATION OF COPPER PERFLUOROPHTHALOCYANINE (F_{16}CuPc) AND ITS APPLICATION IN ORGANIC THIN-FILM TRANSISTORS

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A stable n-type semiconductor material, F_{16}CuPc, was synthesized with liquid-phase synthesis and its optical, thermal and electrical properties were characterized. The electron energy levels were studied with UV–vis absorption and cyclic voltammetry. The F_{16}CuPc compound embodied a suitable lowest unoccupied molecular orbital (LUMO) level for electron injection. The thermal analysis showed that the compound had an excellent thermal stability with a decomposition temperature above 498 °C. F_{16}CuPc-based organic thin-film transistors (OTFTs) were fabricated with the physical-vapor-deposition technique. The charge-carrier field-effect mobility (μ), on-off current ratio (I_{on}/I_{off}) and threshold voltage (V_T) were 0.02 cm^2/V s, 10^5 and 11 V, respectively.

Keywords: organic semiconductors, thin-film transistors, thermal properties, phthalocyanines

1 INTRODUCTION

Organic thin-film transistors (OTFTs) employing organic semiconductors as the active layer have been widely studied because of their potential application in displays, logic circuits and sensors.1–3 The performance of p-type pentacene-based thin-film transistors has reached the level of a-Si devices.3,4 Compared with the p-type semiconductor materials, the mobility of the n-type materials with a high thermal stability is relatively low. However, the n-type semiconductor materials are essential for the fabrications of organic complementary circuits, p-n junction diodes and bipolar transistors. Therefore, the synthesis of high-performance and stable n-type organic semiconductors has been one of the research hotspots in the organic-optoelectronics field.

Phthalocyanines (Pc) show a long-standing record of interest in both the basic research and applications regarding their electrical and photoelectrical properties.5 Phthalocyanines have a great application potential in the areas related to semiconductors, chemical sensors, nonlinear optics, display devices, information-storage systems and others.6 While unsubstituted phthalocyanines exhibit the p-type behavior due to the doping with electron-accepting molecules, thin films of some metal hexadecafluorophthalocyanines exhibit the n-type behavior.

A metal hexadecafluorophthalocyanine is a kind of an n-type semiconductor material with stable air and high mobility.7 Although the synthesis of fluorinated metal phthalocyanines was reported a long time ago, an interest in the study of the properties of these compounds is rekindled. F_{16}CuPc was prepared with solid-phase synthesis with a maximum yield of 44 %.7 X. Yan et al.3 employed an organic heterojunction buffer layer to decrease the contact resistance of the organic/metal interface and the electron field-effect mobility of OTFTs was 7.6 × 10^{-2} cm^2/V s. N. Zhang et al.8 reported on F_{16}CuPc-based transparent OTFTs based on Ag/LiF bilayer transparent S/D electrodes with a good electron mobility of 1.31 × 10^{-2} cm^2/V s.
In this paper, a copper hexadecafluorophthalocyanine (F\textsubscript{16}CuPc, shown in Figure 1) was synthesized with liquid-phase synthesis and its optical, thermal and electrical properties were characterized. The F\textsubscript{16}CuPc-based thin-film transistors were fabricated with vapor-deposition techniques and their electrical characteristics were investigated.

2 EXPERIMENTAL PART

For the synthesis of F\textsubscript{16}CuPc, tetrafluorophthalonitrile and copper (II) acetate with a molar ratio of 5:1 were mixed in an N-methyl pyrrolidone solvent under nitrogen. The mixture was refluxed for 24 h, cooled to room temperature and suction filtered. Then petroleum ether was added to the blue filtrate that was then submerged into an ice bath. A dark blue precipitate formed and was suction filtered through a fine Teflon filter. The F\textsubscript{16}CuPc compound was recrystallized from sulfuric acid and isolated in a 52.51 % yield. The IR (KBr) spectrum of F\textsubscript{16}CuPc is shown in Figure 2. The main absorption peaks are (1615, 1527, 1490, 1459, 1318, 1275, 1151, 964, 840 and 754) cm\textsuperscript{-1}. MS (TOF, Methanol) m/e 862.86. The F\textsubscript{16}CuPc-based OTFT configuration is given in Figure 3. A 30-nm layer of F\textsubscript{16}CuPc was deposited on top of the SiO\textsubscript{2} substrate with vacuum deposition. The organic film was deposited in vacuum (10\textsuperscript{-4}–10\textsuperscript{-5} Pa) at a rate of 0.50 nm min\textsuperscript{-1}. An Au source and drain electrodes with a thickness of 30 nm were prepared using thermal deposition with a shadow-mask-defining channel width (W) and length (L) of 6000 μm and 200 μm, respectively. The output and transfer characteristics of the transistors were measured with two Keithley 2400 source-measurement units under ambient conditions at room temperature.

3 RESULTS AND DISCUSSION

3.1 UV–vis and fluorescence spectra

Figure 4 shows the UV–vis absorption spectra of 1 × 10\textsuperscript{-6} mol·L\textsuperscript{-1} F\textsubscript{16}CuPc solutions in tetrahydrofuran (THF), pyridine and dimethylformamide (DMF), respectively. The absorption spectra were measured with an EVOLUTION300 spectrometer. The absorption maxima for the Q-band are seen at 683 nm with a shoulder peak at 651 nm for the F\textsubscript{16}CuPc dissolved in pyridine and at 680 and 686 nm for the F\textsubscript{16}CuPc solution in THF and DMF. And with the increase of the polarity of the solvents, the ground state is more stable than the excited

Figure 1: Molecular structure of F\textsubscript{16}CuPc

Figure 2: IR spectrum of the F\textsubscript{16}CuPc

Figure 3: Configuration of F\textsubscript{16}CuPc-based thin-film transistors

Figure 4: UV–vis spectra of F\textsubscript{16}CuPc in different solvents
In the state of the π−π* transition system, the transition energy gap increases, inducing a Q-band shift to a shorter wavelength to some extent. In Figure 4, the optical-gap energy can be obtained from the edge of the absorption band. The absorption edge of the F16CuPc in DMF is found at around 770 nm, from which the optical-band-gap energy of F16CuPc, Eg, is estimated to be 1.61 eV.

The fluorescence spectrum of 1 × 10⁻⁶ mol·L⁻¹ F16CuPc solution in 1, 2-dichlorobenzene (DCB) was measured on a CARY Eclipse fluorescence spectrophotometer, as shown in Figure 5. The emission maxima are observed at 712 nm corresponding to the red-light emission.

3.2 Thermal properties

The thermal properties of F16CuPc were characterized with a thermogravimetric analysis (TGA) at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. The TGA curve was obtained with a TG 209 F3 thermogravimetric analyzer. F16CuPc is relatively stable and the mass loss is less than 10 % below 100 °C. The TGA measurements indicate that the F16CuPc compound has a high decomposition temperature of 498 °C (T₅₀ corresponding to a 10-% mass loss, Figure 6). F16CuPc exhibits an excellent thermal stability and so its semiconductor thin film can be prepared with the thermal-deposition technique.

3.3 C-V curve

The electron-transport ability and electrochemical properties of F16CuPc were examined with solution cyclic voltammetry (CV). The cyclic voltammogram (Figure 7) was obtained on a CHI760E electrochemistry workstation at room temperature in DMF, measured against a saturated calomel electrode (SCE) with tetrabutylammonium perchlorate (Bu₄NClO₄, 0.10 M) as the supporting electrolyte. In Figure 7, the chemical-oxidation and reduction peaks of E° = –0.78 V and E°R = –0.64 V are observed for F16CuPc. The reductive process started at –0.29 V. The energy level of the lowest unoccupied molecular orbital, E_LUMO, is estimated from the reductive onset potential to be –4.45 eV.10,11 The low LUMO energy level is favorable for electron injection and transport; in other words, F16CuPc should be a good electron-transport material. The energy level of the highest occupied molecular orbital, E_HOMO, can be calculated by adding E_g from E_LUMO as determined by the electrochemistry curve. This leads to an estimation of E_HOMO to be –6.06 eV for F16CuPc.

3.4 Current-voltage characteristics

Typical output characteristic curves of the F16CuPc-based OTFTs are shown in Figure 8 at different gate-source voltages (V_GS) from 0 to 50 V. Positive voltage signals imply an electron-accumulated process in these OTFTs. With an increase in V_GS, the linear region and the saturation region can be observed. For a lower V_DS ranging from 0 V to 20 V, I_DS is almost linearly increased with the increasing V_DS. In contrast, for a higher V_DS, I_DS tends to saturate.

Figure 5: Fluorescence-emission spectrum of F16CuPc in DCB

Figure 6: TGA curve of F16CuPc

Figure 7: Cyclic voltammogram of F16CuPc in DMF
Figure 9 shows typical transfer characteristics of the F16CuPc-based OTFTs with different gate voltages at a fixed $V_{DS}$ of 50 V. The field-effect mobility was extracted from the saturation region ($V_{GS} - V_T$) based on the following formula:\(^3\)

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

Here, $I_{DS}$ is the drain-source current, $W$ and $L$ are the width and length of the channel, respectively, $\mu$ is the field-effect mobility, $V_{GS}$ is the gate voltage and $V_T$ is the threshold voltage. The capacitance per unit area of the insulator ($C_i$) is 8 nF/cm\(^2\). When a positive $I_{DS}$ is observed upon the application of positive $V_{GS}$ and $V_{DS}$, the semiconductor is of the n-type since the electrons are mobile. According to the electrical properties, the n-type conductivity of the F16CuPc semiconductor material was confirmed. A field-effect mobility ($\mu$) of 0.02 cm\(^2\)/Vs, on-off current ratio ($I_{on}/I_{off}$) of 10\(^5\) and threshold voltage ($V_T$) of 11 V were extracted from the saturation region in Figure 9.

4 CONCLUSIONS

In summary, an n-type semiconductor material, F16CuPc, was synthesized and characterized. The F16CuPc compound has a high $T_d$, above 498 °C, showing that it has a good thermal stability. The LUMO level of F16CuPc is $-4.45$ eV, which is beneficial to the electron transportation. F16CuPc-based OTFTs were fabricated using the physical-vapor-deposition technique and their electronic properties were demonstrated. The field-effect mobility, on-off current ratio and threshold voltage of the OTFTs were 0.02 cm\(^2\)/Vs, 10\(^5\) and 11 V, respectively. Therefore, F16CuPc is a good n-type semiconductor material and can be used in organic electronic devices such as organic field-effect transistors.

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5 REFERENCES

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