

Synthesis, spectral characterization of VOPcF₁₆ and its application in organic thin film transistors using *p*-6p as inducing layer

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A stable n-type semiconductor material, VOPcF₁₆, was synthesized and characterized by infrared (IR), UV-vis and fluorescence spectra. VOPcF₁₆ showed a monomer characteristic in DCB while exhibited an aggregation property in THF. The VOPcF₁₆/*p*-6p (VOPcF₁₆ on *p*-6p) organic thin film transistors (OTFTs) using VOPcF₁₆ as an active layer and *p*-6p as an inducing layer was fabricated by the physical vapor deposition technique. Charge carrier field-effect mobility (μ) and threshold voltage (V_T) of the VOPcF₁₆/*p*-6p OTFTs were $4.5 \times 10^{-4} \text{ cm}^2/\text{V s}$ and 23 V, respectively.

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1. Introduction

Metal hexadecafluorophthalocyanine, such as CuPcF₁₆, is currently receiving a great deal of attention as one of the few molecules that exhibit air-stable n-channel semiconducting behavior [1]. Such properties result in a number of studies aiming at different applications like organic solar cell, OTFTs, gas sensors and rectifying junction [2–4].

Synthesis and characterization of copper hexadecafluorophthalocyanine were reported in Ref. [5]. Schlettwein et al. consider a possibility of epitaxial growth of ZnPcF₁₆ films on NaCl, KCl and KBr surfaces by organic molecular beam deposition (OMBD) technique [5, 6]. It was shown that ZnPcF₁₆ film structure depends not only on substrate materials but also on film thickness and substrate temperature [5, 7]. The electrical properties of ZnPcF₁₆ films were investigated and n-type of conductivity was confirmed in Ref. [8]. Employing para-hexaphenyl (*p*-6p, shown in Fig. 1) as an inducing layer is an effective and a simple method to fabricate the high performance of OTFTs for practical application [9, 10].

In this paper, vanadyl hexadecafluorophthalocyanine (VOPcF₁₆, shown in Fig. 1) was synthesized and its spectral properties were studied. Especially we employed *p*-6p as an inducing layer to fabricate VOPcF₁₆-based thin film transistors using the vapor deposition techniques and measured their electrical characteristics.

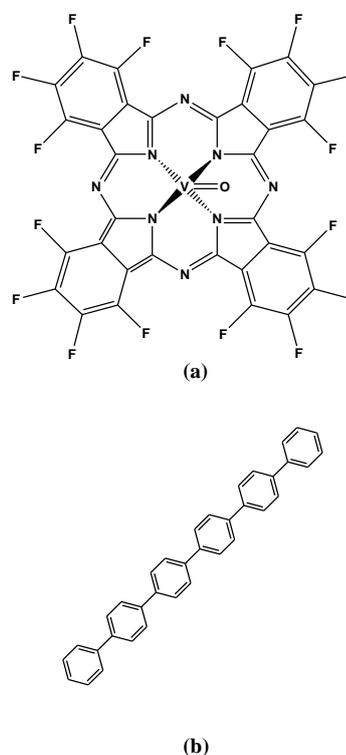


Fig. 1. Molecular structure of (a) VOPcF₁₆ and (b) *p*-6p.

2. Experiment

For the synthesis of VOPcF₁₆, sublimed tetrafluorophthalonitric and Vanadium pentoxide in an equimolar 4:1 ratio were intensively mixed in a mortar. The mixture was filled in a glass vessel, three times flushed with nitrogen and vacuum and finally the glass ampoule was sealed under vacuum (1.33×10^{-3} Pa). After heating for 8 h at 240 °C the blue product was isolated and washed with ethanol and acetone to remove the soluble organic admixture. The resulting purple deposit with yield of 14.9% after purification by concentrated sulfuric acid was identified as vanadyl hexadecafluorophthalocyanine. IR (KBr) 1630, 1530, 752, 1147, and 839 cm⁻¹. MS (TOF, Methanol) *m/e* 966.685. The VOPcF₁₆/*p*-6p OTFTs configuration is given in Fig. 2. The device was prepared with an air-stable n-type semiconductor VOPcF₁₆ and a rod-like conjugated oligomer *p*-6p molecule. VOPcF₁₆ and *p*-6p were purified twice by thermal gradient sublimation prior to processing. A 6nm thick film of *p*-6p was first deposited on a SiO₂ substrate at 180 °C, and then a 30 nm thick layer of VOPcF₁₆ was deposited on top of the *p*-6p surface by vacuum deposition.

All organic films were deposited in vacuum (10^{-4} - 10^{-5} Pa) at a rate of 0.50 nm min⁻¹. Finally, Au source and drain electrodes with 30 nm thickness were prepared by 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 236 source-measurement units under ambient conditions at room temperature.

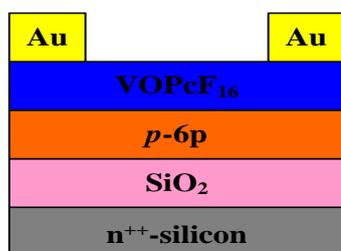


Fig. 2. The device configurations of VOPcF₁₆/*p*-6p thin film transistors.

3. Results and discussion

3.1. UV-vis and fluorescence spectra

Fig. 3 shows the UV-vis absorption spectra of 5×10^{-5} mol L⁻¹ VOPcF₁₆ 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 710 nm with shoulders at 644 and 679 nm for VOPcF₁₆ dissolved in DCB and at 690, 645 and 643 nm for VOPcF₁₆ solution in

THF, Pyridine and DMF. The absence of aggregation effects indicates monomer behavior of VOPcF₁₆ in DCB [11]. And with the increase of the polarity of solvents, the ground state is more stable than the excited state in the π - π^* transition system, so the transition energy gap increases, which will induce the Q band shift to a shorter wave length to some extent. The spectrum of VOPcF₁₆ dissolved in THF differs from the spectrums of this compound in DCB solvents since it shows two strong absorption peaks at 640 and 690 nm. It demonstrates that VOPcF₁₆ aggregates in THF solvent according to reference literature [11].

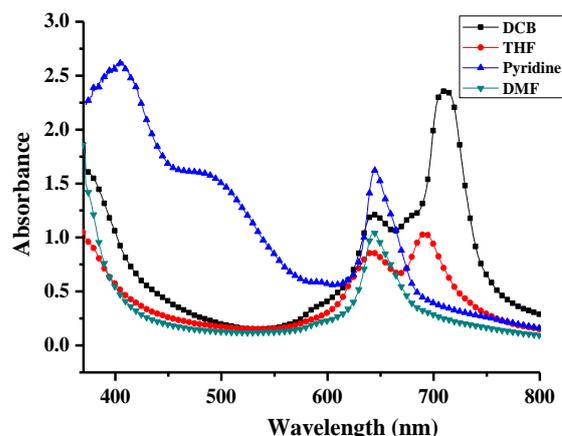


Fig. 3. The UV-vis spectra of VOPcF₁₆ in different solvents.

The fluorescence spectrum of VOPcF₁₆ in DCB was measured on a CARY Eclipse fluorescence spectrophotometer, as shown in Fig. 4. The emission maxima are observed at 689 nm corresponding to the red light emission.

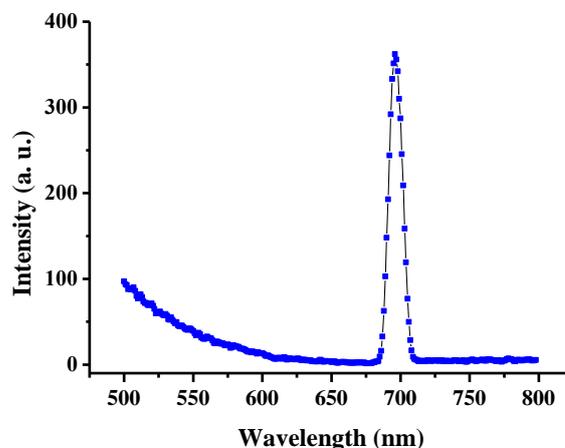


Fig. 4. Fluorescence emission spectrum of VOPcF₁₆ in DCB

3.2. Thermal properties

The thermal properties of VOPcF₁₆ were characterized by thermogravimetric analysis (TGA) at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The TGA curve was measured by a TG 209 F3 thermo gravimetric analyzer. VOPcF₁₆ is relative stable and the mass loss is less than 10% below 100 °C. TGA measurements indicate that VOPcF₁₆ compound has high decomposition temperature of 467 °C (Td, correspond to a 10% mass loss, Fig. 5). VOPcF₁₆ exhibits excellent thermal stability and so its semiconductor thin film can be prepared by thermal deposition technique.

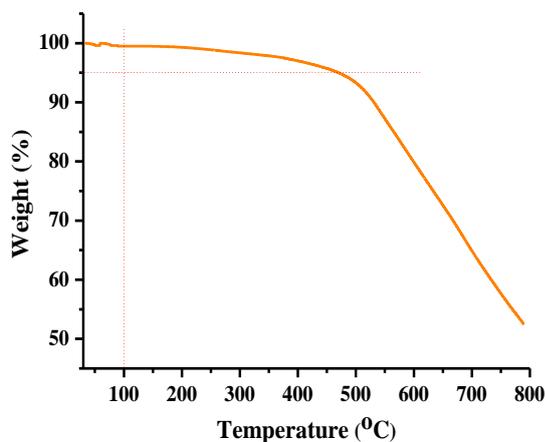


Fig. 5. TGA curve of VOPcF₁₆

3.3. Current-voltage characteristics

Typical output characteristic curves of the VOPcF₁₆/p-6p OTFTs are shown in Fig. 6 at different gate-source voltages (V_G) from 0 to 50 V. The positive voltage signals imply an electron-accumulated process in these OTFTs. With the increase of V_{DS} , the linear region and the saturation region can be observed. For lower V_{DS} from 0 to 10 V, I_{DS} is almost linearly increased with increasing V_{DS} . In contrast, for higher V_{DS} above 15 V, I_{DS} tends to saturate.

Fig. 7 shows the typical transfer characteristics of the VOPcF₁₆/p-6p OTFTs with different gate voltages at a fixed V_{DS} of 50 V. The field effect mobility was extracted from Fig. 7 in the saturation region ($V \geq (V_{GS} - V_T)$) based on

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

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. The capacitance per unit area of the insulator (C_i) is 8 nF/cm². When a positive I_{DS} is observed upon the application of positive V_{GS} and V_{DS} , the semiconductor is n-type since the electrons are mobile.

According to the electrical properties, n-type conductivity of the VOPcF₁₆ semiconductor material was confirmed. The field effect mobility of 4.5×10^{-4} cm²/V s and the threshold Voltage of 23 V were extracted from the saturation region in Fig. 7.

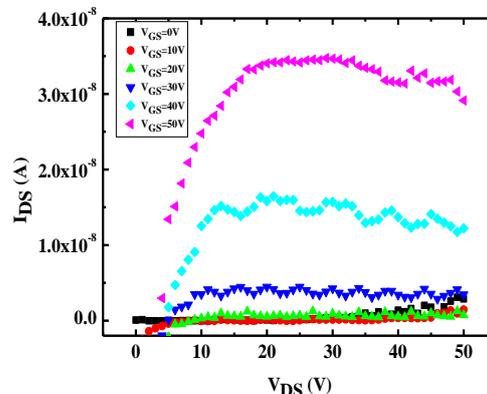


Fig. 6. Output characteristics of VOPcF₁₆/p-6p OTFTs

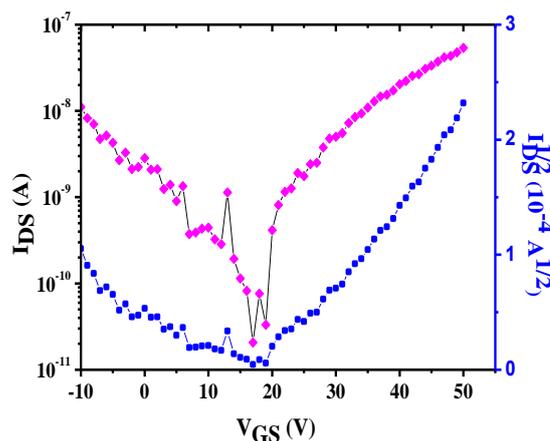


Fig. 7. Transfer characteristics of VOPcF₁₆/p-6p OTFTs at a fixed V_{DS} (50 V)

4. Conclusion

In summary, an n-type semiconductor material, VOPcF₁₆, was synthesized and characterized by infrared (IR), MS, UV-vis and fluorescence spectra. The VOPcF₁₆-based OTFTs was fabricated by the physical vapor deposition technique and measured by Keithley 236 source units. The measurement results show the VOPcF₁₆ material having n type characteristics of conductivity.

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