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Synthesis, spectral characterization of $CuPcF_{16}$ and its application in organic thin film transistors using *p*-6p as inducing layer

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ABSTRACT

An air-stable *n*-channel semiconductor material, CuPcF₁₆, was synthesized in a slightly modified procedure and characterized by infrared (IR), X-ray diffraction (XRD), UV–vis and fluorescence spectra. CuPcF₁₆ showed a monomer characteristic in THF and pyridine while exhibited an aggregation property in DMF. The CuPcF₁₆/*p*-6p (CuPcF₁₆ on *p*-6p) organic thin film transistors (OTFTs) using CuPcF₁₆ 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), I_{on}/I_{off} and threshold voltage (V_T) of the CuPcF₁₆/*p*-6p OTFTs were 0.07 cm²/V s, 10⁵ and 5.28 V, respectively. The charge mobility of the OTFTs was two or even three times higher than that of the conventional single layer CuPcF₁₆-based OTFTs. The improved performance was attributed to the introduction of *p*-6p to form a highly oriented and continuous film of CuPcF₁₆ with the molecular π - π conjugated direction parallel to the substrate.

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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]. For these organic electronics, a highly oriented and continuous organic thin film is an ideal active layer to improve the device performance. However, their thin films are normally composed of needle-like crystals with random orientations, which will induce more grain boundaries. The high defect concentration in grain boundaries of multi-crystal thin films usually leads to poor carrier transport, especially for phthalocyanine compounds [5–7].

In this paper, we synthesized CuPcF₁₆ in a slightly modified procedure and went on investigating its spectral characterization. Especially we employed *p*-6p as an inducing layer to fabricate high-quality CuPcF₁₆/*p*-6p thin film using the vapor deposition techniques. The morphology and structure of the thin film was examined by the XRD and the SEM. Furthermore, we fabricated CuPcF₁₆/*p*-6p OTFTs and measured their electrical characteristics to illustrate the significant role of *p*-6p in the improvement of device performance.

2. Experiment

The synthesis of CuPcF₁₆: Sublimed tetrafluorophthalonitrie and anhydrous copper (I) chloride in an equimolar 4:1 ratio was 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 $(1.33 \times 10^{-3} \text{ Pa})$. 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. Compared with the synthesis process reported in the previous literature [8], the reaction time was extended from 7 to 8 h and the reaction temperature was elevated from 220 to 240 °C. Meanwhile, the reaction ampoule contained less water, which would affect the reaction yield through three times exchange with nitrogen and vacuum. The resulting purple crystals with higher yield of 52.0% after concentrated sulfuric acid purification were identified as copper hexadecafluorophthalocyanine having the X-ray diffraction maxima peak (2 θ) of 6.1° IR (KBr): 1637 w, 1617 w, 1526 m, 1506 w, 1489 s, 1460 m, 1337 s, 1320 m, 1272 m, 1152 s, 1073 w, 963 s, 945 w, 839 m, 767 w, 749 m, 656 w, 603 m, and 497 w cm $^{-1}$.

The CuPcF₁₆/*p*-6p OTFTs configuration is given in Fig. 1. The device was prepared with an air-stable n-type semiconductor CuPcF₁₆ and a rod-like conjugated oligomer *p*-6p molecule. Their molecular structures are also given in Fig. 1. CuPcF₁₆ and *p*-6p were purified twice by thermal gradient sublimation prior to processing. A 6 nm thick film of *p*-6p was first deposited on a SiO₂ substrate at 180 °C, and then a 30 nm thick layer of CuPcF₁₆ was deposited on top of the *p*-6p surface by vacuum deposition.

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Fig. 1. Device configuration and molecular structures used in the study.

The CuPcF₁₆/SiO₂ films were fabricated under the same conditions without introducing the *p*-6p organic layer. All organic films were deposited in vacuum $(10^{-4}-10^{-5} \text{ Pa})$ at a rate of 0.50 nm min⁻¹. Finally, a 30 nm Au film acting as source and drain electrodes was deposited by thermal evaporation through 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.

3. Results and discussion

3.1. UV-vis and fluorescence spectra

Fig. 2 shows the UV-vis absorption spectra of 2.2×10^{-5} mol L⁻¹ CuPcF₁₆ solutions in THF, Pyridine and DMF, respectively. The absorption spectra were measured by an EVOLUTION 300 spectrometer. Absorption maxima for Q band are seen at 677 nm with shoulders at 646 and 610 nm for CuPcF₁₆ dissolved in THF and at 679, 647 and 611 nm for CuPcF₁₆ solution in pyridine. The absence of aggregation effects indicates monomer behavior of CuPcF₁₆ in THF and pyridine [9]. And with the polarity of solvents increasing, the stability of the excited state is higher than the ground state in the $\pi \rightarrow \pi^*$ transition system, so the transition energy gap decreases, which will induce the Q band shift to a longer wavelength to some extent. The spectra of CuPcF₁₆ dissolved in DMF differs from the spectrums of this compound in pyridine and THF solvents since it shows two strong absorption peaks at 646 and 676 nm. It demonstrates that CuPcF₁₆ aggregates in DMF solvent according to reference literature [9]. Fig. 3 shows the UV-vis absorption curves of different concentrations of CuPcF₁₆ in DMF. In the low concentration region, there are two strong absorption peaks at 676 and 606 nm for Q band. With the concentration of CuPcF₁₆ increasing, a new absorption peak at



Fig. 2. UV-vis spectra of $CuPcF_{16}$ dissolved in THF (dotted line), pyridine (dashed line) and DMF (solid line).



Fig. 3. UV-vis absorption of different concentration CuPcF₁₆ solution in DMF.

646 nm appears and the absorption intensity grows while the intensity of absorption peak at 606 nm declines and even disappears. It is a typical UV–vis absorption pattern for aggregation behavior. The higher the concentration, the more easily it aggregates in DMF.

The fluorescence spectrums of CuPcF₁₆ in THF, pyridine and N-methyl pyrrolidone were measured on a CARY Eclipse fluorescence spectrophotometer, as shown in Fig. 4. The emission maxima are observed at 398, 416 and 435 nm corresponding to the purple light emission. The red-shifted emission peak may be caused by the solvent effect that the excited state in the $\pi \rightarrow \pi^*$ transition system becomes more stable with the increase of these solvents polarity leading to the Q band shift to a longer wavelength.

3.2. XRD of the CuPcF₁₆/SiO₂ and CuPcF₁₆/p-6p films

Fig. 5 shows the XRD spectra of the CuPcF₁₆/SiO₂ and CuPcF₁₆/ *p*-6p thin films. The X-ray diffraction was performed in a Rigaku D/max 2500 PC X-ray diffractometer with a Cu K α radiation (λ =1.54056 Å). The *d*₂₀₀ spacing of the CuPcF₁₆/SiO₂ film is 14.92 Å. The XRD pattern indicates that CuPcF₁₆ molecules are



Fig. 4. Fluorescence emission spectra of CuPcF₁₆ dissolved in THF (dotted line), pyridine (dashed line) and N-methyl pyrrolidone (solid line).



Fig. 5. X-ray diffraction spectra of CuPcF₁₆/SiO₂ and *p*-6p/CuPcF₁₆ thin films.

grown upright on the SiO₂ substrate with the metastable α -phase [5,6,10,11]. For CuPcF₁₆/p-6p film, d_{200} =14.78 Å, which has a slight deviation from the diffraction peak of CuPcF₁₆/SiO₂ thin film. It possibly originates from the difference between the molecule–substrate interaction and intermolecular interaction [5,10,12]. These results also demonstrate that the CuPcF₁₆ molecules are approximately standing-up on the *p*-6p layer.

3.3. SEM of the CuPcF₁₆/SiO₂ and CuPcF₁₆/p-6p films

Fig. 6 shows the SEM of CuPcF₁₆/SiO₂ and CuPcF₁₆/*p*-6p thin films. The SEM images were obtained by a FEI Nanosem 430 electron microscopy instrument. The surface image of CuPcF₁₆/SiO₂ thin film is shown in Fig. 6a. The CuPcF₁₆ growth on the SiO₂ substrate displays worm crystal grain morphology and arranges on the substrate disorderly, lacking continuity. Compared with the image of the CuPcF₁₆/SiO₂ film, the CuPcF₁₆/*p*-6p thin film in Fig. 6b shows better connectivity and fewer grain boundaries and traps in the CuPcF₁₆ bulk. The image shows a strip grain pattern of CuPcF₁₆/*p*-6p film. It implies that the π - π interaction direction of





Fig. 6. (a) SEM of CuPcF₁₆/SiO₂ thin films and (b) SEM of *p*-6*p*/CuPcF₁₆ thin films.

the CuPcF₁₆ molecules is parallel to the p-6p layer, which will facilitate the carrier transportation.

Because of the liquid–crystal-like behavior of the *p*-6p monolayer film and the good coalescence behavior of the *p*-6p crystal domains [13,14], a highly-ordered large-sized and continuous *p*-6p ultrathin film can be fabricated on a SiO₂ substrate. The *p*-6p ultrathin film can supply a high quality substrate (the inducing layer) for the growth of phthalocyanine molecules. Dish-like CuPcF₁₆ molecules can be oriented after the employment of the *p*-6p inducing layer, which likely result from the geometrical channel of the surface of the inducing layer and the domain diffusion direction of phthalocyanine molecules on the surface of the inducing layer [15].

3.4. Current-voltage characteristics

Typical output characteristic curves of the CuPcF₁₆/*p*-6p OTFTs are shown in Fig. 7 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_D , the linear region and the saturation region can be observed. For lower V_{DS} from 0 to 10 V, I_D is almost linearly increased with increasing V_{DS} . In contrast, for higher V_{DS} above 10 V, I_D tends to saturate. Fig. 8 shows the typical transfer characteristics of the CuPcF₁₆/*p*-6p OTFTs with different gate voltages at a fixed V_D of 50 V. The field effect mobility were extracted from Fig. 8 in the saturation region



Fig. 7. Output characteristics of CuPcF₁₆/p-6p at varied V_G from 0 to 50 V (at a step of 10 V).



Fig. 8. Transfer characteristics of $CuPcF_{16}/p$ -6p OTFTs at fixed V_D (50 V).

 $(V_D \ge (V_G - V_T))$ based on the following:

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

where I_{DS} is the drain–source current, W and L are the width and the length of the channel, respectively, μ is the field-effect mobility, V_G 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.

From the transfer characteristics, we extract a mobility μ of 0.07 cm²/V s, threshold voltage V_T of 5.28 V and on–off current ratio I_{on}/I_{off} of 10⁵ for CuPcF₁₆/*p*-6p transistors. The mobility was

two or even three times higher than the single $CuPcF_{16}$ layer OTFTs devices without *p*-6p as the inducing layer [16,17]. The field effect mobility of $CuPcF_{16}/p$ -6p thin film transistor has been greatly improved due to the introduction of *p*-6p layer having induced the formation of a high quality $CuPcF_{16}$ thin film.

4. Conclusion

In summary, highly oriented organic thin film of CuPcF₁₆ with the molecular π - π conjugated direction parallel to the substrate was fabricated. By applying this film-forming technique, the performance of the *n*-channel CuPcF₁₆/*p*-6p OTFTs is greatly improved. Employing *p*-6p as an inducing layer is an effective and a simple method to fabricate the high performance OTFTs for practical application.

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References

- [1] B. Tamara, P. Vladimir, H. Aseel, Surf. Sci. 602 (2008) 2368.
- [2] S. Tang, C. Shao, Y. Liu, S. Li, R. Mu, J. Phys. Chem. Solids 68 (2007) 2337.
- [3] R.C. Cherian, C.S. Menon, J. Phys. Chem. Solids 69 (2008) 2858.
- [4] J. Shi, H. Wang, D. Song, H. Tian, Y. Geng, D. Yan, Adv. Funct. Mater. 17 (2007) 397.
- [5] H. Wang, F. Zhu, J. Yang, Y. Geng, D. Yan, Adv. Mater. 19 (2007) 2168.
- [6] Z. Bao, A.J. Lovinger, A. Dodabalapur, Adv. Mater. 9 (1997) 42.
- [7] J. Zhang, H. Wang, D. Yan, Appl. Phys. Lett. 84 (2004) 142.
- [8] E. Kol'tsov, T. Basova, P. Semyannikov, I. Igumenov, Mater. Chem. Phys. 86 (2004) 222–227.
- [9] M. Handa, A. Suzuki, S. Shoji, K. Kasuga, K. Sogabe, Inorg. Chim. Acta 230 (1995) 41.
- [10] H. Wang, J. Wang, H. Huang, X. Yan, D. Yan, Org. Electron. 7 (2006) 369.
- [11] Z. Bao, A.J. Lovinger, J. Brown, J. Am. Chem. Soc. 120 (1998) 207.
- [12] T. Wang, D. Ebeling, J. Yang, C. Du, L. Chi, H. Fuchs, D. Yan, J. Phys. Chem. B 113 (2009) 2333.
- [13] J. Yang, T. Wang, H. Wang, F. Zhu, G. Li, D. Yan, J. Phys. Chem. B 112 (2008) 7816.
- [14] J. Yang, T. Wang, H. Wang, F. Zhu, G. Li, D. Yan, J. Phys. Chem. B 112 (2008) 7821.
- [15] J. Yang, T. Wang, H. Wang, F. Zhu, G. Li, D. Yan, J. Phys. Chem. B 112 (2008) 3132.
- [16] W. Gu, X. Li, H. Zhang, B. Wei, J. Zhang, J. Wang, Thin Solid Films 519 (2010) 439.
- [17] J. Shi, H. Wang, D. Song, H. Tian, Y. Geng, D. Yan, Thin Solid Films 516 (2008) 3270.