UDK 621.315.5:621.382.3:620.1 ISSN 1580-2949
Original scientific article/Izvirni znanstveni članek MTAEC9, 53(6)827(2019)

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

SINTEZA IN KARAKTERIZACIJA BAKROVEGA PERFLUOROFTALOCIANINA ($F_{16}CuPc$) IN NJEGOVA UPORABA V ORGANSKIH TANKOPLASTNIH TRANZISTORJIH

Guangjing Zhang[1,2], Feng Ma[1*], Luzhen Wang[1], Bo Sun[1], Jiongpeng Zhao[1], Fude Liu[1]

[1]School of Chemistry and Chemical Engineering, Tianjin University of Technology, 300384 Tianjin, China
[2]Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, 300384 Tianjin, China

Prejem rokopisa – received: 2018-12-06; sprejem za objavo – accepted for publication: 2019-06-27

doi:10.17222/mit.2018.260

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

Avtorji članka so v tekoči fazi sintetizirali stabilni n-tip polprevodniškega materiala na osnovi $F_{16}CuPc$ in tako določili njegove optične, termične in električne lastnosti. Energijske nivoje elektronov so študirali z UV–vis absorpcijo in ciklično voltametrijo. $F_{16}CuPc$ je spojina z najnižjim nezasedenim molekularno-orbitalnim (LUMO) nivojem za zasedbo elektrona. Termična analiza je pokazala da ima spojina odlično termično stabilnost s temperaturo razpada nad 498 °C. Organski tankoplastni tranzistor na osnovi $F_{16}CuPc$ (OTFTs) so izdelali s tehniko depozicije (odlaganja) iz parne faze. Ugotovili so, da je učinek poljske mobilnosti nosilcev naboja (μ) 0,02 cm^2/Vs, razmerje vklop-izklop toka (I_{on}/I_{off}) 10^5 in vršna napetost (V_T) 11 V.

Ključne besede: organski polprevodniki, tankoplastni tranzistorji, termične lastnosti, ftalocianini

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.

*Corresponding author's e-mail:
mafontune@sina.com.cn (Feng Ma)

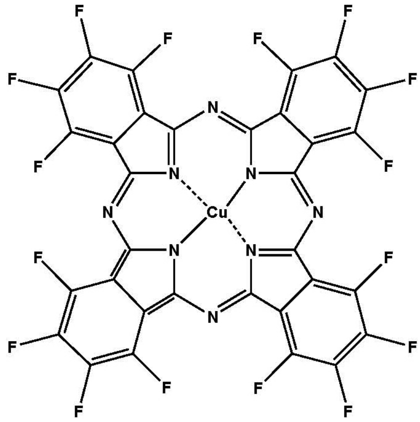

Figure 1: Molecular structure of $F_{16}CuPc$

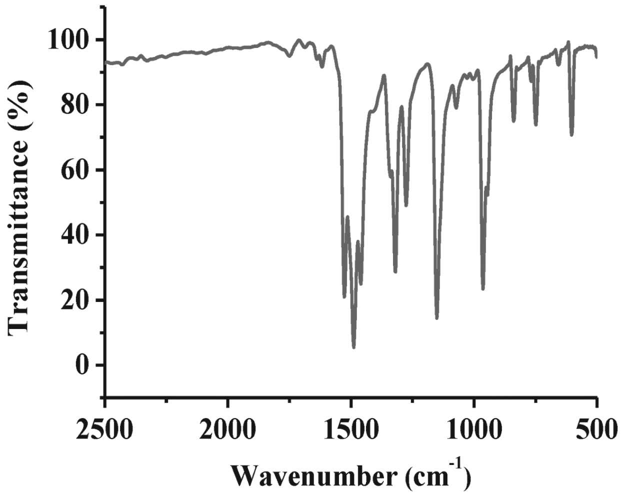

Figure 2: IR spectrum of the $F_{16}CuPc$

In this paper, a copper hexadecafluorophthalocyanine ($F_{16}CuPc$, shown in **Figure 1**) was synthesized with liquid-phase synthesis and its optical, thermal and electrical properties were characterized. The $F_{16}CuPc$-based thin-film transistors were fabricated with vapor-deposition techniques and their electrical characteristics were investigated.

2 EXPERIMENTAL PART

For the synthesis of $F_{16}CuPc$, tetrafluorophthalo nitrile and copper (I1) 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 $F_{16}CuPc$ compound was recrystallized from sulfuric acid and isolated in a 52.51 % yield. The IR (KBr) spectrum of $F_{16}CuPc$ is shown in **Figure 2**. The main absorption peaks are (1615, 1527, 1490, 1459, 1318, 1275, 1151, 964, 840 and 754) cm^{-1}. MS (TOF, Methanol) m/e 862.86. The $F_{16}CuPc$-based OTFT configuration is given in **Figure 3**. A 30-nm layer of $F_{16}CuPc$ was deposited on top of the SiO_2 substrate with vacuum deposition. The organic film was deposited in vacuum (10^{-4}–10^{-5} Pa) at a rate of 0.50 nm min^{-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^{-6} mol·L^{-1} $F_{16}CuPc$ 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 $F_{16}CuPc$ dissolved in ptridine and at 680 and 686 nm for the $F_{16}CuPc$ solution in THF and DMF. And with the increase of the polarity of the solvents, the ground state is more stable than the excited

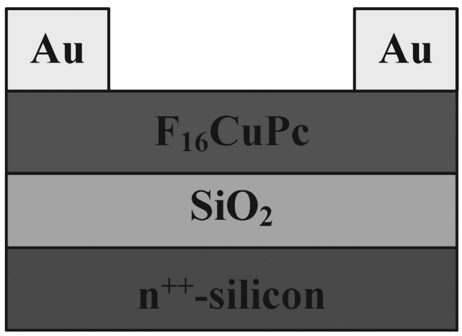

Figure 3: Configuration of $F_{16}CuPc$-based thin-film transistors

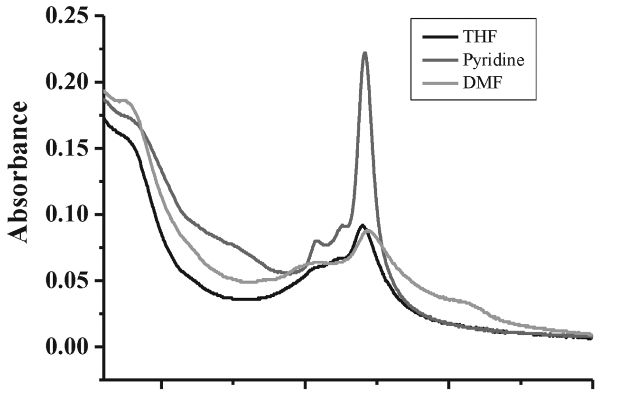

Figure 4: UV–vis spectra of $F_{16}CuPc$ in different solvents

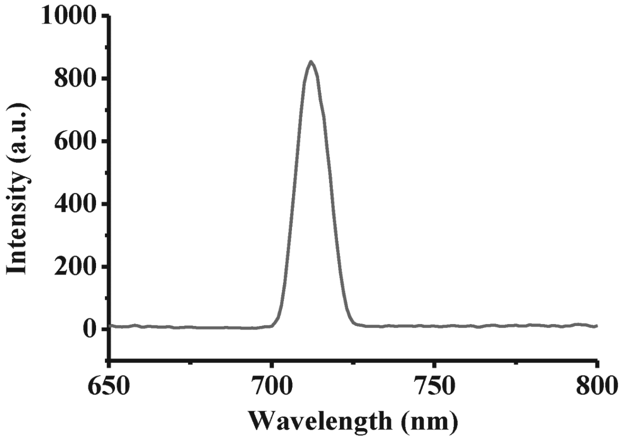

Figure 5: Fluorescence-emission spectrum of $F_{16}CuPc$ in DCB

state in the π–π* transition system, so the transition energy gap increases, inducing a Q-band shift to a shorter wave length to some extent. In **Figure 4**, the optical-gap energy can be obtained from the edge of the absorption band.[9] The absorption edge of the $F_{16}CuPc$ in DMF is found at around 770 nm, from which the optical-band-gap energy of $F_{16}CuPc$, Eg, is estimated to be 1.61 eV.

The fluorescence spectrum of 1 × 10^{-6} mol·L^{-1} $F_{16}CuPc$ 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 $F_{16}CuPc$ 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. $F_{16}CuPc$ is relatively stable and the mass loss is less than 10 % below 100 °C. The TGA measurements indicate that the $F_{16}CuPc$ compound has a high decomposition temperature of 498 °C (T_d, corresponding to a 10-% mass loss, **Figure 6**). $F_{16}CuPc$ 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 $F_{16}CuPc$ 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 (Bu_4NClO_4, 0.10 M) as the supporting electrolyte. In **Figure 7**, the chemical-oxidation and reduction peaks of E_{OX} = –0.78 V and E_{RE}= –0.64 V are observed for $F_{16}CuPc$. 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, $F_{16}CuPc$ 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 $F_{16}CuPc$.

3.4 Current-voltage characteristics

Typical output characteristic curves of the $F_{16}CuPc$-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_{DS}, 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.

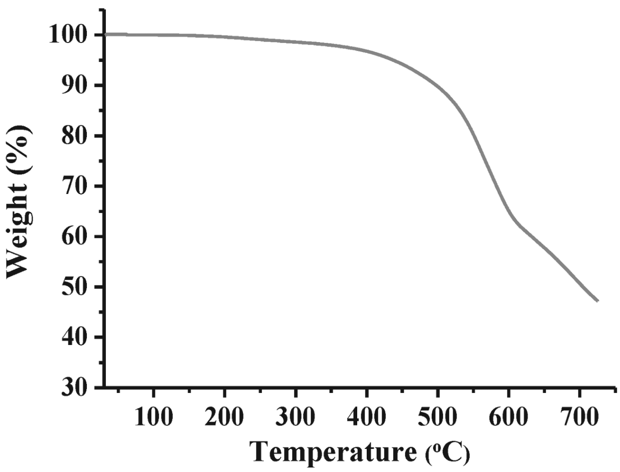

Figure 6: TGA curve of $F_{16}CuPc$

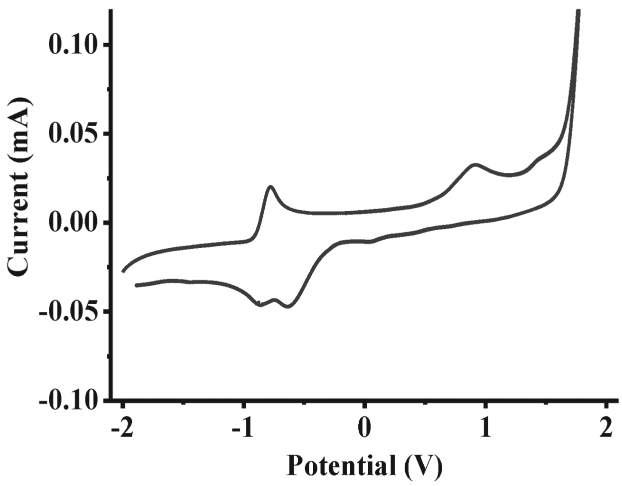

Figure 7: Cyclic voltammogram of $F_{16}CuPc$ in DMF

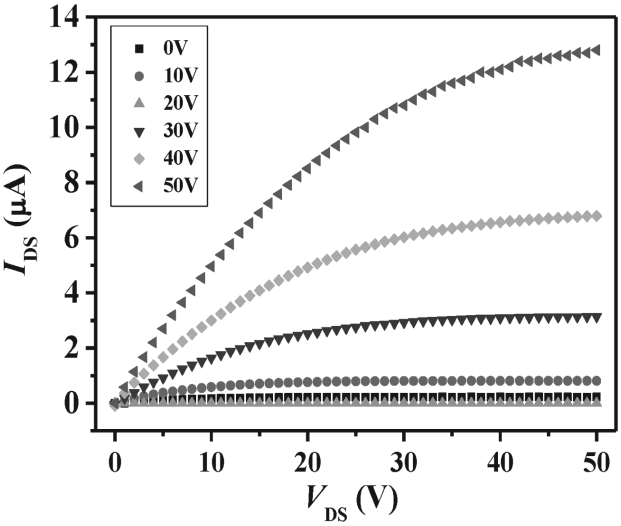

Figure 8: Output characteristics of $F_{16}CuPc$-based OTFTs

Figure 9 shows typical transfer characteristics of the $F_{16}CuPc$-based OTFTs with different gate voltages at a fixed V_{DS} of 50 V. The field-effect mobility was extracted from the saturation region ($V \geq (V_{GS} - V_T)$) based on the following formula:[3]

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

Here, 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 (Ci) 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 $F_{16}CuPc$ semiconductor material was confirmed. A field-effect mobility (μ) of 0.02 cm^2/V s, on-off current ratio (I_{on}/I_{off}) of 10^5 and threshold voltage

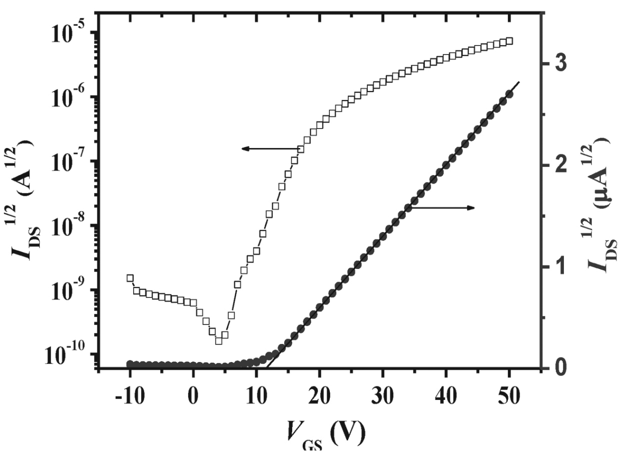

Figure 9: Transfer characteristics of $F_{16}CuPc$-based OTFTs at a fixed V_{DS} (50 V)

(V_T) of 11 V were extracted from the saturation region in **Figure 9**.

4 CONCLUSIONS

In summary, an n-type semiconductor material, $F_{16}CuPc$, was synthesized and characterized. The $F_{16}CuPc$ compound has a high T_d, above 498 °C, showing that it has a good thermal stability. The LUMO level of $F_{16}CuPc$ is –4.45 eV, which is beneficial to the electron transportation. $F_{16}CuPc$-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/V s, 10^5 and 11 V, respectively. Therefore, $F_{16}CuPc$ is a good n-type semiconductor material and can be used in organic electronic devices such as organic field-effect transistors.

Acknowledgements

The authors are grateful to the Donghang Yan Research Group at the Changchun Institute of Applied Chemistry of the Chinese Academy of Sciences for the help with the fabrication of devices. The work was partially supported by the National Natural Science Foundation of China (no. 21401138) and the Tianjin Project of the Innovation Team of Colleges and Universities in Tianjin (TD13–502).

5 REFERENCES

[1] H. E. A. Huitema, G. H. Gelinck, J. B. P. H. Van Der Putten, K. E. Kuijk, C. M. Hart, E. Cantatore, D. M. De Leeuw, Active-Matrix Displays Driven by Solution-Processed Polymeric Transistors, Adv. Mater., 14 (**2002**) 17, 1201–1204

[2] B. Crone, A. Dodabalapur, Y.-Y. Lin, R. W. Filas, Z. Bao, A. Laduca, R. Sarpeshkar, H. E. Katz, W. Li, Large-scale complementary integrated circuits based on organic transistors, Nature, 403 (**2000**), 521–523, doi:10.1038/35000530

[3] X. Yan, J. Wang, H. Wang, H. Wang, D. Yan, Improved n-type organic transistors by introducing organic heterojunction buffer layer under source/drain electrodes, App. Phys. Lett., 89 (**2006**) 5, 053510, doi:10.1063/1.2227714

[4] T. N. Jackson, Y. Y. Lin, D. J. Gundlach, H. Klauk, Organic thin-film transistors for organic light-emitting flat-panel display backplanes, IEEE J. Sel. Top. Quantum Electron., 4 (**1998**) 1, 100–104, doi:10.1109/2944.669475

[5] H. Brinkmann, C. Kelting, S. Makarov, O. Tsaryova, G. Schnurpfeil, D. Wöhrle, D. Schlettwein, Fluorinated phthalocyanines as molecular semiconductor thin films, Phys. Stat. Sol. (a), 205 (**2008**) 3, 409–420, doi:10.1002/pssa.200723391

[6] E. Kol'tsov, T. Basova, P. Semyannikov, I. Igumenov, Synthesis and investigations of copper hexadecafluorophthalocyanine $CuPcF_{16}$, Mater. Chem. Phys., 86 (**2004**) 1, 222–227, doi:10.1016/j.matchemphys.2004.03.007

[7] T. Wang, D. Ebeling, J. Yang, C. Du, L. Chi, H. Fuchs, D. Yan, Weak Epitaxy Growth of Copper Hexadecafluorophthalocyanine ($F_{16}CuPc$) on p-Sexiphenyl Monolayer Film, J. Phys. Chem. B, 113 (**2009**) 8, 2333–2337, doi:10.1021/jp8080639

[8] N. Zhang, J. Lin, J. S. Luo, Y. T. Li, Z. H. Gan, Y. Fan, X. Y. Liu, N-channel transparent organic thin-film transistors with Ag/LiF

bilayer transparent source-drain electrodes fabricated by thermal evaporation, Appl. Phys. Express, 7 (**2014**) 2, 021610, doi:10.7567/apex.7.021601

[9] H. Jin, X. Li, T. Tan, S. Wang, Y. Xiao, J. Tian, Electrochromic properties of novel chalcones containing triphenylamine moiety, Dyes and Pigments, 106 (**2014**), 154–160, doi:10.1016/j.dyepig.2014.02.018

[10] J. Yang, T. Wang, H. Wang, F. Zhu, G. Li, D. Yan, Ultrathin-Film Growth of *para*-Sexiphenyl (I): Submonolayer Thin-Film Growth as a Function of the Substrate Temperature, J. Phys. Chem. B, 112 (**2008**) 26, 7816–7820, doi:10.1021/jp711455u

[11] J. Yang, T. Wang, H. Wang, F. Zhu, G. Li, D. Yan, Ultrathin-Film Growth of para-Sexiphenyl (II): Formation of Large-Size Domain and Continuous Thin Film, J. Phys. Chem. B, 112 (**2008**) 26, 7821–7825, doi:10.1021/jp711457p