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APPLICATION OF ASYMMETRICAL ZINC PHTHALOCYANINES: ORGANIC FIELD EFFECT TRANSISTORS

Gülenay Tunç(✉)[1],Betül Canımkurbey[2,3] Ayşe Gül Gürek[1]

[1]Department of Chemistry, Gebze Technical University, 41400, Gebze, Kocaeli, Turkey.
[2]S. Şerefeddin Health Services Vocational School, Amasya University, Amasya, 05100, Turkey
[3]Central Research Laboratory, Amasya University, 05100, Amasya, Turkey

[1]ORCID: 0000-0002-9208-4090
[2,3]ORCID: 0000-0002-5938-0509
[4]ORCID: 0000-0001-9341-5843

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(✉) Corresponding author: gtunc@gtu.edu.tr

ABSTRACT

Asymmetric zinc phthalocyanine (GT4), consisting of a carboxyl function attached to the Pc ring as an anchor group, was prepared according to the procedure we described previously. The structure of this molecule was elucidated by spectroscopic methods (FT -IR, MALDI-MS, UV-VIS). In this study, asymmetric Zn (II) Pc bearing a carboxylic acid group and three hexylthio groups at the peripheral positions were synthesized, and the influence of the COOH group and the positions of the hexylthio groups on the OFET performance was investigated.

Keywords: Phthalocyanine, thin film, ambipolar, OFET, carboxylic acid.

ÖZET

Ftalosiyanin halkasına bağlayıcı grup olarak karboksilik asit fonksiyonlandırılmış asimetrik çinko ftalosiyanin (GT4) molekülü daha önce belirtilen prosedürlerimize uygun olarak hazırlanmış ve molekül yapısı spektroskopik yöntemler (FT-IR, MALDI-MS, UV-VIS) kullanılarak aydınlatılmıştır.

Bu çalışmada peripheral pozisyonda hekziltiya ve karboksilik asit grubu içeren ftalosiyanin molekülünün sentezi ve bu grupların OFET performansı üzerine etkileri araştırılmıştır.

Anahtar Kelimeler: Ftalosiyanin, ince film, OFET, karboksilik asit.

1. INTRODUCTION

In recent years, organic field-effect transistors (OFETs) have received increasing attention due to their potential applications [1], focusing on the low-cost deposition of materials with large-area properties on both solid and flexible substrates for diverse applications used in displays and integrated microelectronics [2]. OFETs have several excellent properties that silicon transistors do not, most notably their flexibility. Because OFETs can be fabricated at or near room temperature, they enable the fabrication of integrated circuits on plastic or other flexible substrates that would otherwise not withstand the high temperature conditions of inorganic-based devices [3]. To achieve good OFET performance, organic semiconductors, as the most important component of OFET devices, should have the following properties: a large conjugated pi system, sufficient chemical purity, good film-forming properties, and good intermolecular electronic overlap. In general, organic oligomers, polymers and some small molecules with conjugated electronic structures are among the most studied organic semiconductors for OFET applications [4].

Phthalocyanines and their derivatives have become more important in recent years with developing technology. They are also popular in scientific research due to the discovery of their application as semiconductors. Phthalocyanines (Pcs) exhibit excellent thermal and chemical stability. These aromatic molecules have very high molar absorption coefficients in the red/near-infrared (IR) region of the solar spectrum. Moreover, they have corresponding applications in various technological fields, including organic field-effect transistors, photovoltaic solar cells, liquid crystals, photodynamic therapy, chemical sensors, catalysts, and nonlinear optics, since they have a large overlap with the visible spectrum [5-7]. This versatility of use demonstrates the importance of phthalocyanine derivatives.

Organic semiconductors are of great interest because of their growing performance in optical and electronic devices [8]. One of them also organic field effect transistors. Organic field effect transistors (OFETs) are widely used in many technological applications due to their unique properties such as mechanical flexibility, light weight, transparency and low cost [9]. In this study, asymmetric Zn(II) Pc bearing one carboxylic acid group and four hexylthio groups at the peripheral positions were designed and synthesized. We investigated the influence of the carboxylic acid (COOH) group and the positions of the hexylthio groups on the OFET performance.

2. MATERIAL AND METHODS

All solvents and chemicals were of reagent grade and were purchased from Sigma Aldrich Chemical Co. and Merck.

Absorption spectra were recorded at room temperature on a Shimadzu UV-2600 UV-vis spectrometer using a 1 cm path length quartz cuvette between maximum range 300 and 1400 nm. Solutions were prepared in spectro-grade solvents. OFET characterization was performed using a semiconductor parameter analyzer (Keithley 4200).

2.1. Synthesis

The synthesis of 4-(hexylsulfanyl)-phthalonitrile (PN1) [10] and 3,4-dicyanobenzoic acid (PN2) [11] was carried out according to the literature. The synthesis of 2,9(10),16(17) tri(hexylsulfanyl)-23(24)-(carboxy) zinc(II)phthalocyanine (GT4) was shown in Scheme 1. All the synthesis data were reported in our previous study [12]

2.2. Device Fabrication

Before it was prepared 15% wt. PVA- solution of pure water (average molecular weight ~30). This solution was mixed at 110 ºC during the day. At the same time, the ITO substrate was purified in pure water, acetone or ethanol. After the purification process, the PVA solution was spin coated onto the ITO substrate. The PVA films were annealed in a glove box at 60 ºC for one day. ZnPc was also spin-coated as the active layer and annealed at 50 ºC for 30 minutes. Then, silver (Ag) was deposited on the ZnPc film as a source-drain electrode (Figure 1). Keithley 4200 semiconductor characterization instrument was used for transistor characterization.

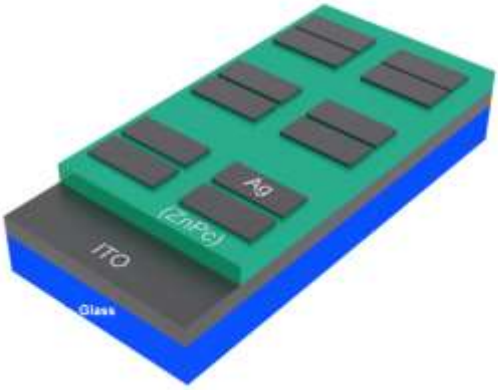
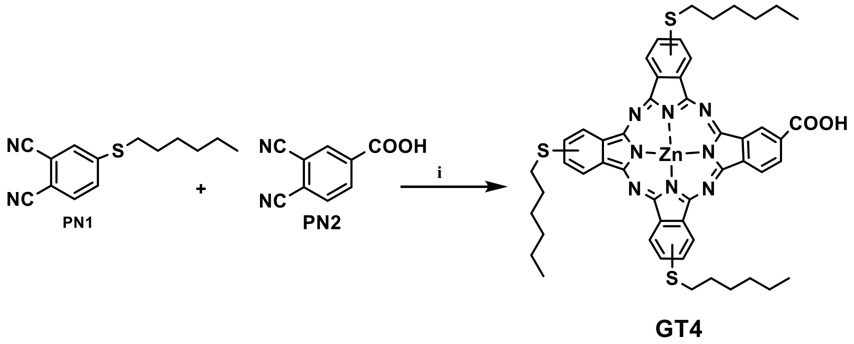


Figure 1. Basic OFET structure.

3. RESULTS AND DISCUSSION

Phthalocyanine GT4 [12] was prepared according to the procedure we described previously. The synthetic route of phthalocyanine GT4 was shown in Scheme 1. Phthalocyanine GT4 (Scheme 1) was prepared by cyclotetramerization reaction of 4-(hexylsulfanyl)phthalonitrile (PN1) and 3,4-dicyanobenzoic acid (PN2) in a ratio of 9:1 in the presence of zinc chloride (ZnCl2) and heated under reflux in DMF (dimethylformamide) to 18% yield. The desired Pc was separated chromatographically from the reaction mixture.



Scheme 1. The synthetic pathway of GT4 (i) ZnCl2, DMF (dimethylformamide), (1,8-diazabicyclo [5.4.0] undec-7-ene) (DBU),160 °C.

The synthesized phthalocyanine derivative (GT4) was fully characterized by spectroscopic techniques such as NMR, FT -IR, mass spectrometry (MS), electronic absorption spectroscopy. The GT4 molecule showed high solubility in common organic solvents including acetone, THF, chloroform, DMSO, DMF and DCM. In the FT -IR spectra of GT4, the presence of the characteristic broad stretching vibration of carboxylic acid- OH at about 3300 cm-1 and the peak of C=O at about 1710 cm-1 observed that the formation of Pc derivatives took place. The peaks of molecular ions at m/z 971.542 [M]+ of the molecule correspond to the expected molecular structures. 1H NMR spectra were recorded in d8-THF and showed broad chemical shifts, possibly due to self-aggregation at NMR concentration. However, the integrated intensities of the signals correspond to the number of hydrogen atoms in the molecule. The UV-vis absorption spectra of the Pc molecule were carried out in dilute THF solutions (1×10-5 M) and shown in Figure 1, the characteristic Q bands were observed at 684 nm and the B band at 354 nm.

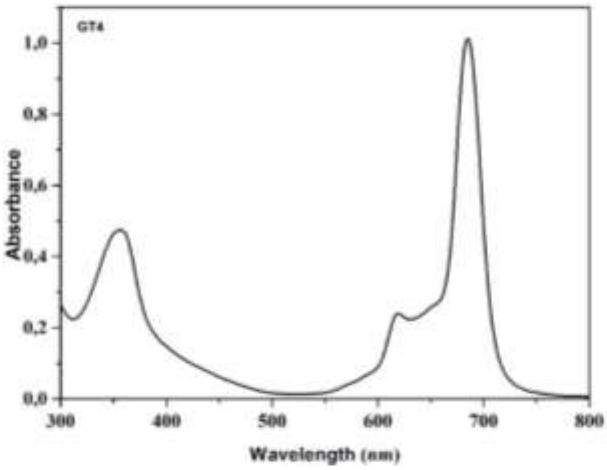


Fig. 1 Absorption spectra of **GT4** in THF (1×10^{-5} M).

Figure 2 shows the output characteristic (a) and the transfer characteristic of phthalocyanine-based OFETs. The ON /OFF ratio of the OFET is about 104.

Table 1. Parameter of fabricated OFETs

Sample	Mobility (cm^2/Vs)	On/Off Ratio	V_{Th}(V)
GT4	$4,8\times10^{-2}$ cm^2/Vs	~10^4	-5V

The threshold voltage is around -5 V. Mobility (μ_{FET}) values of devices are measured by using equation below:

$$\mathbf{I_{DS} = \mu_{FET}\left(\frac{WC_i}{2L}\right)(V_{GS} - V_{Th})^2}$$

where L and W are the length and width of the channels respectively, V_{Th} is the threshold voltage and C_i are the capacitance per unit area. As shown in the Table, the mobility calculated ~ $4,8\times10^{-2}$ cm^2/Vs.

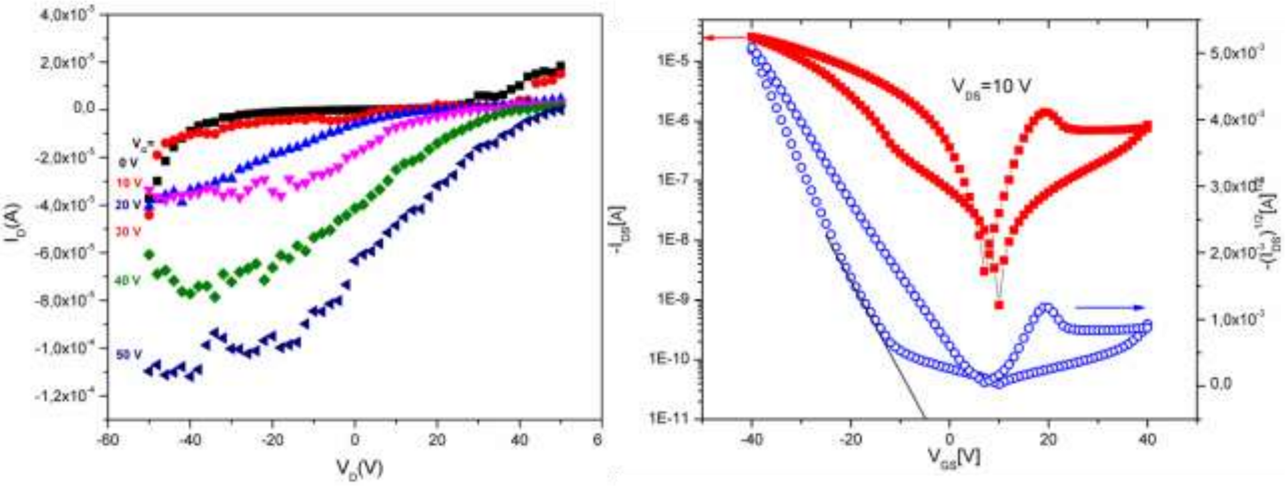


Figure 2. a) Output characteristic and **b)** Transfer characteristic of OFET

4. CONCLUSIONS

In summary, an asymmetric zinc phthalocyanine (GT4) consisting of a carboxyl function attached to the Pc ring as an anchor group was developed. The asymmetric Zn (II) Pcs bearing a carboxylic acid group and four hexylthio groups at the peripheral positions were investigated for the influence of the COOH group and the positions of the hexylthio groups on the OFET performance. We observed that the increased mobility (4.8×10-2 cm2/Vs) according to the studies in the literature.[13].

Conflicts of interest

The authors declare that there are no potential conflicts of interest relevant to this article.

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