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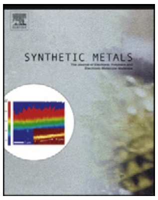

Organic field effect transistors based on 5,10,15,20-tetrakis(4-pentyloxyphenyl)porphyrin single crystal

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ABSTRACT

Diffusion of methanol into the chloroform solution of metal free 5,10,15,20-tetrakis(4-pentyloxyphenyl)porphyrin H_2TPOPP yields large single crystals with length as long as 1.5 mm, which allow the fabrication of single crystal-based organic field effect transistors (OFETs). These single crystal-based devices were revealed to exhibit relatively good OFET performance with the carrier mobility for hole of 0.0018 $cm^2 V^{-1} s^{-1}$ and current modulation of 10^4. In addition to confirming the tetrappyrole nature, single crystal X-ray diffraction analysis also reveals the planar two-dimensional supramolecular structures formed via porphyrin molecules in the head-to-tail manner through C–H···O interaction between oxygen atom and pyrrole hydrogen atom as well as p(O)–π(phenyl) interaction between the meso-attached phenyloxy groups of neighboring porphyrin molecules in the single crystal. This results in effective intermolecular interaction due to the significant participation of phenyloxy groups to the HOMO of the central porphyrin core as revealed by density functional theory (DFT) analysis and in turn is responsible for the relatively good OFET performance in terms of carrier mobility for hole in the direction parallel to the aromatic porphyrin ring. Density functional theory (DFT) calculation also reproduces the experimentally revealed carrier mobility for hole in the single crystal of H_2TPOPP. The present work, representing our continuous efforts in understanding the relationship between molecular structure, crystal packing, and OFET performance of tetrapyrrole organic semiconductors, will be helpful for attracting further research interest over the semiconducting properties of tetra(aryl)porphyrin compounds for OFET applications.

1. Introduction

Organic semiconductors have attracted significant research interest since 1986 when they were first constructed into field effect transistors (OFETs) as active layers [1]. Great industrial interests for these OFETs come from their potential applications in low-cost electronic circuits such as large area and flexible displayer, active-matrix electronic-paper, and smart cards and price tags [2–11]. Despite that the performance of organic semiconductor-based FETs achieved thus far can still not completely compete with the widely utilized inorganic analogues, significant progress has been made in the past two decades in this field. In addition to paying great efforts in continuously searching for novel organic semiconductors with good OFET performance, understanding the relationship between molecular structure, crystal packing, and device performance still remains a great challenge for chemists and material scientists.

Among various organic semiconductors, artificial phthalocyanine derivatives have been the focus of the most intensively studied small molecule organic semiconductor [12–19]. In good contrast, porphyrins as another species of the most important tetrapyrrole derivatives have been relatively less investigated for their semiconducting properties. Despite the investigation over the semiconductor properties of some peripherally substituted porphyrin compounds via indirect pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC) as early as in 1991 [20], fabrication of OFET devices from porphyrin compounds still remains rare, limited to very few scaffolds such as 2,3,7,8,12,13,17,18-octaethyl-porphyrin and tetrabenzoporphyrin derivatives with planar molecular structure. In 2003, Noh et al. fabricated the epitaxially grown crystalline film of 2,3,7,8,12,13,17,18-octaethyl-porphyrinato platinum PtOEP into OFETs [21]. Later, Minari et al. fabricated a series of 2,3,7,8,12,13,17,18-octaethyl-porphyrinato metal complexes MOEP (M = Co, Cu, Zn, Pd) into single crystal-based

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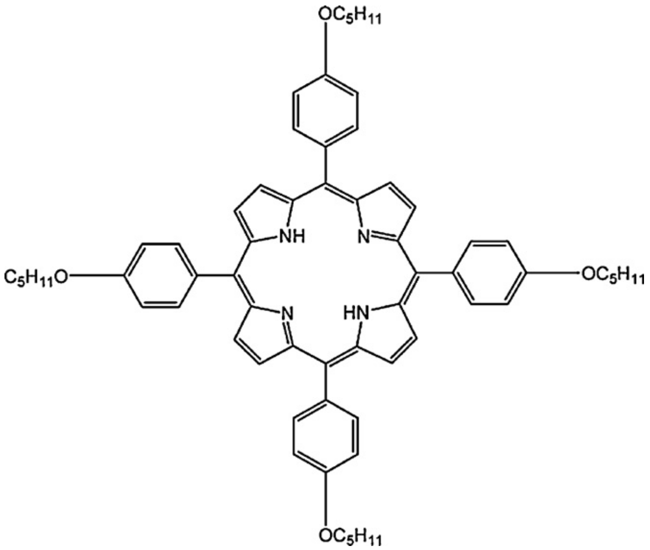

Scheme 1. Schematic molecular structure of metal free tetrakis(4-pentyloxyphenyl)porphyrin H_2TPOPP.

OFET devices, with the largest carrier mobility of 0.20 $cm^2\,V^{-1}\,s^{-1}$ obtained from CoOEP single crystal [22]. Since 2004, several groups have studied the performance of OFET devices fabricated from tetrabenzoporphyrin derivatives MTBP (M = 2H, Ni, Cu) using a soluble precursor method [23–29]. Until 2008, Che et al. fabricated OFETs from a series of porphyrinato platinum complexes and tried to establish correlation between the peripheral substituents, film structure, and charge mobility [30]. It is worth noting that the carrier mobility for hole recorded for the porphyrin-based OFET devices is about in the range of 10^{-6} to 10^{-1} $cm^2\,V^{-1}\,s^{-1}$. Surprisingly, the device fabricated from the spin coating film of metal free 5,10,15,20-tetra(phenyl)porphyrin, H_2TPP, was revealed to exhibit carrier mobility for hole as high as 0.007 $cm^2\,V^{-1}\,s^{-1}$ [31]. To the best of our knowledge, this is the sole report on the tetra(aryl)porphyrin-based OFETs. Despite the lack of any information about the molecular structure and packing in their spin coating film, it appears that the four bulky aryl groups attached at the meso positions of porphyrin ring with a large dihedral angle with respect to the central conjugated porphyrin ring in tetra(phenyl)porphyrins does not prevent effective π–π interaction between neighboring H_2TPP molecules according to Checcoli et al.

To get insight into the semiconducting nature of tetra(aryl)porphyrin derivatives, in the present paper, we describe the fabrication of OFETs from single crystals of metal free 5,10,15,20-tetrakis(4-pentyloxyphenyl)porphyrin H_2TPOPP (Scheme 1). These single crystal-based devices were revealed to exhibit relatively high carrier mobility for hole of 1.8×10^{-3} $cm^2\,V^{-1}\,s^{-1}$ in the direction parallel to the aromatic porphyrin ring. Single crystal X-ray diffraction analysis reveals that metal free porphyrin molecules form a two-dimensional planar supramolecular structure in a head-to-tail manner along the *b*-axis direction through C–H···O interaction between oxygen atom and pyrrole hydrogen atom as well as p(O)–π(phenyl) interaction between the meso-attached phenyloxy groups of neighboring porphyrin molecules in the single crystal. This results in effective intermolecular interaction between neighboring porphyrin molecules due to the significant participation of meso-attached phenyloxy substituents to the HOMO of central porphyrin core as verified by the DFT analysis, in the direction parallel to the conjugated porphryin ring, and in turn is responsible for the relatively higher carrier mobility for hole in the single crystal. Density functional theory (DFT) calculation also reproduces the experimentally revealed charge transport property of this compound in terms of carrier mobility for hole in single crystals. The present work, representing our continuous efforts in understanding the relationship between molecular structure, crystal packing, and OFET performance of tetrapyrrole organic semiconductors [16–19,32,33], will be helpful for attracting further research interests over the semiconducting properties of porphyrin derivatives, in particular tetra(aryl)porphyrin compounds for OFET applications.

Table 1
Crystallographic data for H_2TPOPP.

	Compound
Formula	$C_{64}H_{70}O_4N_4$
M_r	959.24
Crystal size [mm^3]	0.20 × 0.15 × 0.10
Crystal system	Monoclinic
Space group	$P2_1/c$
a [Å]	14.27(3)
b [Å]	16.52(3)
c [Å]	12.43(2)
α [°]	90.00
β [°]	93.58(3)
γ [°]	90.00
V [$Å^3$]	2924(9)
Z	2
$F(000)$	1028
ρ_{calcd} [$mg\,m^{-3}$]	1.090
μ [mm^{-1}]	0.068
θ range [°]	1.89 to 25.00
Total no. of reflns.	21326
No. of indep. reflns.	4409 (R_{int} = 0.0320)
Parameters	290
$R1$ [$I > 2\sigma(I)$]	0.0706
$wR2$ [$I > 2\sigma(I)$]	0.2059
Goodness of fit	1.077

2. Experimental

2.1. Materials

All reagents and solvents were used as received. The metal free porphyrin H_2TPOPP was prepared according to the published procedure [34]. Single crystals of this compound were obtained by diffusion of methanol into the chloroform solution of H_2TPOPP.

2.2. X-ray crystallographic analyses of H_2TPOPP

Crystal data and details of data collection and structure refinement are given in Table 1. Data were collected on a Bruker SMART CCD diffractometer with an Mo K_α sealed tube (λ = 0.71073 Å) at 293 K, using a ω scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 45 frames. Final unit cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections, and determining lattice constants, SAINT-PLUS was used for integration of intensity of reflections and scaling, SADABS was used for absorption correction [35], and SHELXL was used for space group and structure determination, refinements, graphics, and structure reporting [36]. CCDC-715535 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.