



Short communication

Organic field-effect transistors based on semiconducting porphyrin single crystals

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ABSTRACT

Porphyrin offers a variety of optical, electrochemical, and catalytic properties from the central metal and structural modifications. However, porphyrins have been relatively less investigated for their semiconducting properties. In this work, we report on the design and synthesis of new solution processable semiconducting porphyrins **2TBPH** and **2TBPZ**. They contain two 5-hexylthiophen-2-yl ethynyl phenyl arms and produce smooth films and high quality single-crystals. The single-crystal field effect transistors from **2TBTZ** show a maximum field effect mobility of $\sim 0.36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a high current on/off ratio of 2×10^3 . Remarkably, the mobilities of single-crystal devices are two orders higher than those of thin-film based transistor devices.

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1. Introduction

Organic field-effect transistors (OFETs) are one of the most promising electronic devices when they are fabricated from either well-defined single crystals (SCs) or well-ordered thin films as the charge-transporting layers [1–3]. In particular, soluble organic semiconductors are attracting much attention for the development of low-cost, large-scale, and practical devices [4,5]. Among them, porphyrin derivatives are of much interest due to their unique properties in photonics and electronics [6]. Since wide range of properties can be expected by derivatizing with various metals and substituents in a large and flat conjugated macrocyclic ring, porphyrins have often found in the use of solar energy conversion, electron transfer, and artificial photosynthesis [7], but they have been relatively less exploited as building blocks for the fabrication of OFET devices [8]. Despite the investigation over the semiconductor properties of some peripherally substituted porphyrin derivatives *via* indirect pulse-radiolysis time-resolved microwave conductivity technique has been reported as early as in 1991 [9], fabrication of OFET devices from porphyrin derivatives still remains as a new territory [10].

Most of the organic semiconductors are based on the structural advantages of building blocks such as planarity and π -conjugation which would be beneficial for their packing and interactions for well-ordered crystalline arrangements. On this account,

porphyrin-based building blocks would be beneficial for field effect transistors, if one can make a profit on their constitutional uniqueness. Depending on the modification of framework, porphyrins could generate multiple inter- and/or intra-interactions such as π - π stacking, electrostatic interactions, hydrogen bonding, and even metal–ligand coordination [11]. Consequently, well-defined crystalline nano- and micron-sized structures such as fibers, rods, ribbons, plates, sheets, cubes, wheels, rings, and grids are able to be successfully assembled utilizing above mentioned interactions [6,12].

Although porphyrins have great potentials as organic semiconducting materials, the performance in OFET devices show relatively low carrier mobility ranged from 10^{-6} to $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ comparing with their inorganic analogues [8,13]. Therefore, the structural modification on porphyrin peripheries is highly demanded to obtain well-ordered and highly packed crystalline systems.

Herein, we report on new π -extended porphyrin derivatives **2TBPH** and **2TBPZ** and their unique electrical properties in OFET devices along with single-crystal objects.

2. Experiment

2.1. Materials

All commercially available starting materials and solvents were purchased from Aldrich, TCI, and Acros Co. and used without further purification. All of the reactions and manipulations were carried out under N_2 with standard inert-atmosphere and Schlenk techniques unless otherwise noted. Solvents used in

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inert-atmosphere reactions were dried using standard procedures. Flash column chromatography was carried out with 230–400 mesh silica-gel from Aldrich using wet-packing method. All deuterated solvents were purchased from Sigma–Aldrich. The porphyrin precursors of 4-((5-hexylthiophen-2-yl)ethynyl)benzaldehyde (**1**) [14] and 2,2'-(heptane-1,1-diyl)bis(1H-pyrrole) (**2**) [15] were prepared according to the modified literature procedures.

2.2. Synthesis

2.2.1. 5,15-Bis(4-((5-hexylthiophene-2-yl)ethynyl)phenyl)-10,20-di(*n*-hexyl)porphyrin (2TBPH)

A solution of **1** (2.96 g, 10 mmol) and **2** (2.3 g, 10 mmol) in 300 mL chloroform was allowed to stir for 3 h in the presence of trifluoroacetic acid (1 mL) at room temperature under N₂, and then *p*-chloranil (2.9 g, 12 mmol) was added and kept for another 4 h. The reaction mixture was then quenched by adding triethylamine (1.5 mL) and evaporated to dryness. The residue was purified by column chromatography on silica-gel with CH₂Cl₂/hexane (1:1, v/v) as an eluent and recrystallized in methanol to afford 0.8 g of purple solid **2TBPH**: yield 16%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.39 (d, *J* = 4.8 Hz, 4H), 8.84 (d, *J* = 4.8 Hz, 4H), 8.14 (d, *J* = 8.2 Hz, 4H), 7.88 (d, *J* = 8.2 Hz, 4H), 7.25 (d, *J* = 3.2 Hz, 2H), 6.75 (d, *J* = 3.2 Hz, 2H), 4.90 (t, 4H), 2.86 (t, 4H), 2.44–2.52 (m, 4H), 1.69–1.84 (m, 8H), 1.32–1.54 (m, 20H), 0.92 (t, 12H), –2.69 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 148.68, 142.61, 142.25, 134.43, 132.20, 129.67, 129.51, 124.34, 122.54, 122.38, 120.50, 120.08, 119.24, 118.14, 92.38, 84.30, 38.89, 38.73, 31.90, 31.58, 30.30, 30.26, 30.22, 28.76, 22.75, 22.72, 22.61, 14.18, 14.12. MS (MALDI-TOF) *m/z*: calcd C₆₈H₇₄N₄S₂ [M⁺] 1011.47; found 1012.50.

2.2.2. [5,15-Bis(4-((5-hexylthiophene-2-yl)ethynyl)phenyl)-10,20-di(*n*-hexyl)porphyrinato]zinc(II) (2TBPZ)

A solution of Zn(OAc)₂ (182 mg, 1 mmol) in 10 mL methanol was added to a solution of **2TBPH** (400 mg, 0.4 mmol) in 50 mL chloroform. The resulting mixture was refluxed for 2 h. After removal of solvent, the residue was purified by silica-gel column chromatography with CH₂Cl₂/hexane (1:1, v/v) as an eluent and recrystallized in methanol to afford 330 mg of purple solid **2TBPZ** (yield 73%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.38 (d, *J* = 4.8 Hz, 4H), 8.86 (d, *J* = 4.8 Hz, 4H), 8.12 (d, *J* = 8.2 Hz, 4H), 7.89 (d, *J* = 8.2 Hz, 4H), 7.25 (d, *J* = 3.2 Hz, 2H), 6.76 (d, *J* = 3.2 Hz, 2H), 4.78 (t, 4H), 2.86 (t, *J* = 8.0 Hz, 4H), 2.44–2.51 (m, 4H), 1.70–1.84 (m, 8H), 1.32–1.54 (m, 20H), 0.94 (t, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 150.06, 148.84, 148.61, 142.99, 134.44, 132.18, 131.86, 129.46, 128.76, 124.33, 122.26, 120.95, 120.58, 119.01, 92.48, 84.17, 62.63, 38.99, 35.60, 31.92, 31.56, 30.40, 30.31, 28.78, 22.75, 22.61, 14.18, 14.12. MS (MALDI-TOF) *m/z*: calcd C₆₈H₇₂N₄S₂Zn [M⁺] 1072.45; found 1073.91.

2.3. Instrumentation

¹H NMR spectra were recorded on a Varian AS400 (399.937 MHz for ¹H and 100.573 MHz for ¹³C) spectrometer. ¹H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and ¹³C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. MALDI-TOF analysis was performed on a Voyager-DE STR MALDI-TOF mass spectrometer. Thermal properties were studied under nitrogen atmosphere on a Mettler DSC 821e and Mettler TGA 50. The X-ray diffraction experiment was performed using a Bruker SMART APEX diffractometer equipped with a monochromator in the Mo Kα (*k* = 0.71073 Å) incident beam. The measurements were obtained in a scanning interval of 2θ between 1° and 60°.

All scanning electron microscopy (SEM) images were obtained using a Jeol JSM-7500F. The redox properties of the molecules were examined by using cyclic voltammetry (Model: EA161 eDAQ). Thin films were prepared on a platinum plate using chloroform as a solvent. The employed electrolyte solution was 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in a freshly dried dichloromethane (DCM). The Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were utilized as reference and counter electrodes, respectively. The scan rate was at 50 mV/s. Absorption and emission spectra were obtained using an HP-8453 spectrophotometer (photodiode array type) and Hitachi F-7000 fluorescence spectrophotometer using quartz cells, respectively.

2.4. OFET fabrication

Bottom gate top contact OFET devices were consisted of heavily *n*-type doped <100> silica as a gate electrode and 300 nm thick thermally grown SiO₂ as a gate insulator. The source and drain electrodes (120 nm Au) were deposited by thermal evaporation through a shadow mask. The resulting wafers were washed with acetone, isopropanol, followed by ultraviolet-ozone exposure for further cleaning. The silicon oxide layer was treated with *n*-octyltrichlorosilane (OTS) by immersing freshly cleaned wafers in an 8 mmol/L solution of OTS in anhydrous toluene for 30 min, followed by sonication in toluene and isopropanol, consecutively. The thin-film transistors were fabricated by directly spin-coating a 1% solution of porphyrins onto the dielectric substrate at 1600 rpm. The single-crystal FET devices were fabricated by growing porphyrin crystals directly on the top of OTS-treated wafers before depositing the source and drain electrodes. The device performance was evaluated in air using Keithley 4200-SCS semiconductor characterization system under ambient conditions.

3. Results and discussion

3.1. DFT calculation

To determine the minimum energy conformations for **2TBPH** and **2TBPZ**, the density functional theory (DFT) model incorporated into the Spartan program ('10) was employed [16]. The optimized geometrical structures of two molecules are illustrated in Fig. 1. The shapes and geometries of two molecules are expected to be quite similar. The porphyrin cores were nearly planar. However, two phenyl rings at 5,15-position were twisted with an angle of ~75.0° to the porphyrin framework. Meanwhile, thiophenes and phenyls were aligned in a planar fashion (Scheme 1).

3.2. Optical and photoluminescence (PL) properties

The solution samples of **2TBPH** and **2TBPZ** were prepared in DCM with a concentration of 1 × 10⁻⁶ M, and the thin film samples were fabricated by spin-coating with 1 wt% solutions. The UV–vis absorption and photoluminescence (PL) spectra of both solution and film of **2TBPH** and **2TBPZ** show that these compounds generate densely packed aggregates in the solid state (Fig. 2). The absorption spectra reveal slight red-shift by 8 nm upon the film formation in **2TBPH**, but a slight blue-shift is observed in case of the film formation of **2TBPZ**. These spectral shifts are unequivocal evidence of effective intermolecular interactions. For example, the solution sample of **2TBPH** exhibits Sorét-bands at 422 nm with multiple Q-bands in wavelength range from 520 to 655 nm. The film samples on quartz glass plates show a broadened and slightly red-shifted Sorét-band at 430 nm and red-shifted multiple Q-bands in wavelength range from 526 to 660 nm. The PL spectrum of the film obtained from **2TBPH** shows two well-isolated bands at 666 and 734 nm, while two bands at 660 and 725 nm are observed

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