

Short communication

# Preparation of new semiconducting tetraphenylethynyl porphyrin derivatives and their high-performing organic field-effect transistors



Seung Hyun Chae<sup>a</sup>, Hyojeong Kim<sup>a</sup>, Jun Yeol Kim<sup>a</sup>, Sung-Jin Kim<sup>b</sup>, Youngmee Kim<sup>b</sup>, Suk Joong Lee<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Research Institute for Natural Sciences, Korea University, Seoul 136-701, South Korea

<sup>b</sup> Department of Chemistry and Nano Science Ewha Womans University, Seoul 120-750, South Korea

## ARTICLE INFO

## Article history:

Received 13 April 2016

Received in revised form 17 May 2016

Accepted 20 May 2016

Available online 1 June 2016

## Keywords:

Semiconductor

Porphyrin

Thin film

 $\pi$ - $\pi$  interaction

Field-effect transistor

## ABSTRACT

The design and synthesis of new solution processable semiconducting  $\pi$ -extended porphyrin derivatives **H2TPEP** and **ZnTPEP** were introduced and their use in the fabrication of high-performing thin film and single-crystal OFET devices were described. Due to strong  $\pi$ - $\pi$  interactions, new porphyrin derivatives showed high crystallinity in film state and displayed excellent electrical characteristics with high carrier mobilities of 0.15 cm<sup>2</sup>/Vs for **ZnTPEP** and 0.029 cm<sup>2</sup>/Vs for **H2TPEP** together with high on/off current ratios of  $>10^5$  and  $>10^4$ , respectively. When the devices were fabricated with their single crystals, **ZnTPEP** displayed excellent characteristic with a high mobility of 0.2 cm<sup>2</sup>/Vs and **H2TPEP** showed 0.3 cm<sup>2</sup>/Vs with high on/off current ratios of  $>10^4$  and  $>10^5$ , respectively. Remarkably, although Zn(II)-porphyrin based single-crystal device usually shows much higher mobility than the device made of free-based porphyrin single-crystal, the mobility of **H2TPEP** single-crystal device was significantly higher than that of the **ZnTPEP** one, because of effective crystalline packing with short layer distances found in the single-crystal prepared from **H2TPEP**.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Recently charge-transporting organic materials have been extensively studied owing to their potential applications in electronics and optoelectronics. The most important structural features of these materials are planarity and  $\pi$ -conjugation with strong possibilities to expedite the movement of charge, because the large overlap of  $\pi$ -orbitals between nearby molecules is expected to provide a large increase in the bandwidth and allow better charge transportation [1]. In addition, good charge-transporting materials should provide strong intermolecular interactions which significantly affect the performance of electronic devices such as organic field-effect transistors (OFETs) [2]. Therefore, there have been remarkable research endeavors on synthesizing highly  $\pi$ -conjugated planar molecules such as pentacene, oligothiophene, and perylene for use in the charge transport layers [3]. When these planar and  $\pi$ -conjugated molecules interact themselves in solid states,  $\pi$ - $\pi$  interactions would dominate in their packing and form well-ordered crystalline

systems with good charge-transporting properties [4]. Despite their structural advantages, the porphyrins have not been studied as much as other organic materials, because of their poor charge transport characteristics [5]. For the OFET with good performance, porphyrins ought to be structurally planar and display high crystallinity and close  $\pi$ - $\pi$  stacking distance in solid state, because the intermolecular arrangement and molecular packing in solid state are directly associated with the charge-transport performance. In this regards, porphyrins have been considered as one of the most important candidates for the use in charge-transport layers in OFETs, owing to their unique structural and photophysical properties [6]. Therefore, the preparation of  $\pi$ -extended planar porphyrins has become one of the most important requirements to fabricate the good performing OFETs [7].

In this study, we report the preparation of new  $\pi$ -extended tetrakis(4-hexylphenyl)ethynylporphyrin, **H2TPEP**, and its Zn(II)-metallated form, **ZnTPEP**, and the investigation of their charge-transport properties when they were used to fabricate thin-film and single-crystal based OFETs. Porphyrins were readily obtained via the Sonogashira coupling reaction of 4-iodohexylbenzene with corresponding tetraethynylporphyrins for **H2TPEP**, followed by metallation with Zn(II) for **ZnTPEP** [8]. The detailed synthetic route is described in Scheme 1. The resulting materials exhibited good

\* Corresponding author.

E-mail address: [slee1@korea.ac.kr](mailto:slee1@korea.ac.kr) (S.J. Lee).

film-forming properties and high solubilities in various solvents such as chloroform, dichloromethane, THF, and chlorobenzene at room temperature because of their four hexyl substituents

## 2. Experiment

### 2.1. Materials

*N*-butyllithium (*n*-BuLi), pyrrole, tetrabutylammonium fluoride (TBAF), 3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), triethylamine (TEA), copper iodide (CuI), bis(dibenzylideneacetone) palladium(0) (Pd(dba<sub>3</sub>)<sub>2</sub>), 4-iodo-1-hexylbenzene, Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, triphenyl arsine (AsPh<sub>3</sub>) and trifluoroacetic acid (TFA) and solvents (HPLC grade) were purchased from Aldrich and TCI, and used without further purification. All of the reactions for the porphyrin and manipulations were carried out under N<sub>2</sub> with standard inert-atmosphere and Schlenk techniques, unless otherwise noted. Solvents used in inert atmosphere reactions were dried using standard procedures. Flash column chromatography was carried out with 230–400 mesh silica-gel from Aldrich. All deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. **Scheme 1** shows the synthetic route and molecular structure of **H2TPEP** and **ZnTPEP** which were prepared by the modified literature procedures [8,9].

### 2.2. Instrumentation

<sup>1</sup>H NMR spectra were recorded on a Varian AS400 (399.937 MHz for <sup>1</sup>H and 100.573 MHz for <sup>13</sup>C) spectrometer. <sup>1</sup>H chemical shifts are referenced to the proton resonance resulting from protic residue in deuterated solvent and <sup>13</sup>C chemical shift recorded downfield in ppm relative to the carbon resonance of the deuterated solvents. Absorbance spectra were obtained using an HP 8453 spectrophotometer (photodiode array type) quartz cells and plates. Atomic force microscopy (AFM, Digital Instruments Multimode equipped with a nanoscope IIIa controller) operating in tapping mode with a silicon cantilever was used to characterize the surface morphologies of the samples. Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectra were obtained on a Bruker Daltonics LFP20 MALDI TOF Mass Spectrometer Industry-Academic Cooperation Foundation at Yonsei University, Seoul. Powder X-ray diffraction (XRD) measurements were recorded with a Rigaku D/MAX Ultima III using nickel-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) over a range of  $2^\circ < 2\theta < 40^\circ$  and X'celerator detector operating at 40 kV and 30 mA. The redox properties were examined by using cyclic voltammetry (Model: EA161eDAQ).

### 2.3. Synthesis

#### 2.3.1. 5,10,15,20-Tetrakis((4-hexylphenyl)ethynyl)porphyrin (H2TPEP)

A solution of **3** (130 mg, 0.320 mmol), 4-iodo-1-hexylbenzene (588.67 mg, 2.032 mmol), and TEA (100 mL) in THF (150 mL) was degassed with N<sub>2</sub> for 10 min. Pd(dba<sub>3</sub>)<sub>2</sub> (29.3 mg, 0.032 mmol) and AsPh<sub>3</sub> (157 mg, 0.514 mmol) were added into the mixture and then warmed-up to 50 °C under N<sub>2</sub> atmosphere. After 5 h, the reaction mixture was evaporated to dryness in vacuo to afford a solid residue which was purified by silica-gel column chromatography (methylenechloride (DCM)/hexane, 2:1 v/v) to afford pure **H2TPEP** as a purple solid (172.8 mg, 51.6% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 9.08 (s, 8H), 7.91 (d, <sup>3</sup>J<sub>H-H</sub> = 7.04 Hz, 8H), 7.37 (d, <sup>3</sup>J<sub>H-H</sub> = 7.83 Hz, 8H), 2.78 (t, <sup>3</sup>J<sub>H-H</sub> = 7.83 Hz, 8H), 1.74–1.84 (m, 8H), 1.39–1.54 (m, 24H), 0.96–1.02 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 144.0, 132.0, 129.0, 121.4, 102.0, 97.7, 91.1, 36.4, 32.1, 31.7, 29.4, 22.9, 14.4. MS (MALDI-TOF):  $m/z = 1048.0$  for M<sup>+</sup>; Calcd. 1047.46.

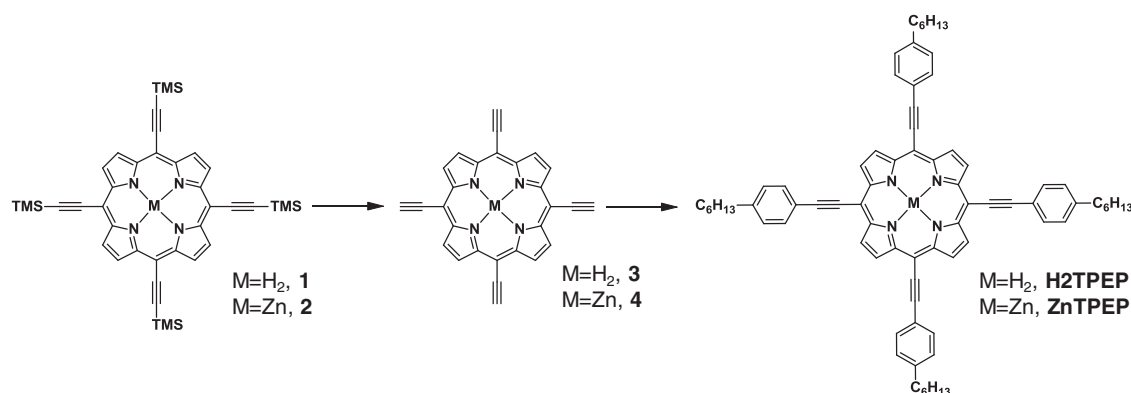
#### 2.3.2. [5,10,15,20-Tetrakis((4-hexylphenyl)ethynyl)porphyrinato]zinc (II) (ZnTPEP)

A solution of **4** (30 mg, 0.065 mmol), 4-iodo-1-hexylbenzene (118 mg, 0.41 mmol), and TEA (20 mL) in THF (30 mL) was degassed with N<sub>2</sub> for 10 min. Pd(dba<sub>3</sub>)<sub>2</sub> (6 mg, 0.0065 mmol) and AsPh<sub>3</sub> (32 mg, 0.104 mmol) were added into the mixture and then warmed-up to 50 °C under N<sub>2</sub> atmosphere. After 5 h, the reaction mixture was evaporated to dryness in vacuo to afford a solid residue which was purified by silica-gel column chromatography (DCM/hexane, 1:1 v/v) to afford pure **ZnTPEP** as a purple solid (60 mg, 83.1% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) 8.54 (s, 8H), 7.75 (d, <sup>3</sup>J<sub>H-H</sub> = 7.04 Hz, 8H), 7.24 (d, <sup>3</sup>J<sub>H-H</sub> = 7.83 Hz, 8H), 2.71 (t, <sup>3</sup>J<sub>H-H</sub> = 7.83 Hz, 8H), 1.71–1.81 (m, 8H), 1.39–1.54 (m, 24H), 0.98–1.06 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 149.4, 143.0, 131.8, 129.6, 128.6, 121.7, 101.7, 96.7, 91.3, 36.4, 32.2, 31.6, 29.6, 23.1, 14.5. MS (MALDI-TOF):  $m/z = 1111.4$  for M<sup>+</sup>; Calcd. 1110.82.

### 2.4. Single-crystal X-ray crystallography

Single crystals of **H2TPEP** and **ZnTPEP** were grown in air by careful layering a 1 mM toluene solution of the respective compounds over *n*-hexane inside a glass tube (5–8 mm in diameter). The tube was then capped and allowed to reach equilibrium under darkness. Single crystals formed at the interface of the two solvents over a period of 10–15 days and were mounted for XRD data collection immediately from solution using epoxy super glue.

The X-ray diffraction data were collected on a Bruker SMART APEX-II diffractometer for both **H2TPEP** and **ZnTPEP** equipped



**Scheme 1.** Synthesis of **H2TPEP** and **ZnTPEP**.

Download English Version:

<https://daneshyari.com/en/article/1440061>

Download Persian Version:

<https://daneshyari.com/article/1440061>

[Daneshyari.com](https://daneshyari.com)