



Organic field-effect transistors based on pyridine-terminated tetrathiafulvalene (TTF) derivatives



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ABSTRACT

We report two TTF-based small molecules (PY3 and PY4) in which pyridine acts as an electron withdrawing group for the construction of OFET to investigate the relationship between the FET characteristics and structures. While PY3 thin films demonstrated the highest mobilities up to $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, there was no OFET performance for PY4. Atomic force microscope (AFM) and X-ray diffraction (XRD) studies were conducted to gain insight into this dissimilarity. The no OFET performance of PY4 is mainly caused by its poor thin-film morphology and low crystallinity.

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1. Introduction

Organic field-effect transistors (OFETs) have drawn increasing attention on the grounds of potential applications in radio frequency identification tags (RFID), large-area electronic and sensors [1–4]. As a key part of organic field-effect transistors, substantial organic semiconductors have been explored [5–7]. Tetrathiafulvalene (TTF) and its derivatives have received a lot of interest in recent years on account of its unique electrical properties and synthetic versatility [8,9]. And recently, it has been shown that TTF derivatives are very promising materials for the preparation of OFETs owing to their processability and high devices performance [10–12]. In fact, OFETs based on TTF derivatives have been investigated and the corresponding single-crystal and thin-film transistors exhibit high mobilities of up to 10 and $0.98 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively [13,14]. However, the strong electron-donating property of TTF derivatives leads to easy doping of their thin films by oxygen and water, resulting in high off-state conductivity (low on/off ratio) and poor OFET performances in thin films. To enhance the air stability, decrease of the electron donating property is necessary. Electron deficient nitrogen heterocycles

such as pyridine and pyrazine are expected to further reduce the electron-donating property [9,15,16]. Several fused benzene rings and pyrazine groups have been connected to the TTF core to improve the air stability of the device and decrease the electron-donating properties [16,17]. However, to our knowledge, there is no report on OFETs based on such molecules that the TTF core is directly linked to the pyridine group. Herein, we present two TTF-based small molecules, **PY3** and **PY4** (see Fig. 1) in which pyridine acts as an electron withdrawing group. We have now fabricated the OFET devices of TTF-py derivatives **PY3** and **PY4**, and have investigated the relationship between the FET characteristics and structures. While **PY3** thin films demonstrated the highest mobility of up to $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, there was no OFET performance for **PY4**. Atomic force microscope (AFM) and small angle X-ray diffraction (SAXRD) studies were conducted to gain insight into this dissimilarity.

2. Experiment

2.1. Materials and methods

Compounds **PY3** and **PY4** were prepared according to the reported methods [18]. 4-(3'-pyridyl)-1,3-dithiol-2-one **1** (1.0 g, 5.1 mmol) was added to a mixture of $\text{P}(\text{OEt})_3$ (10 mL) in toluene (10 mL) under an Aron atmosphere. The resulting mixture was refluxed for 10 h. After cooling to room temperature, the red precipitate was filtered off, washed with methanol (3 mL \times 5 mL).

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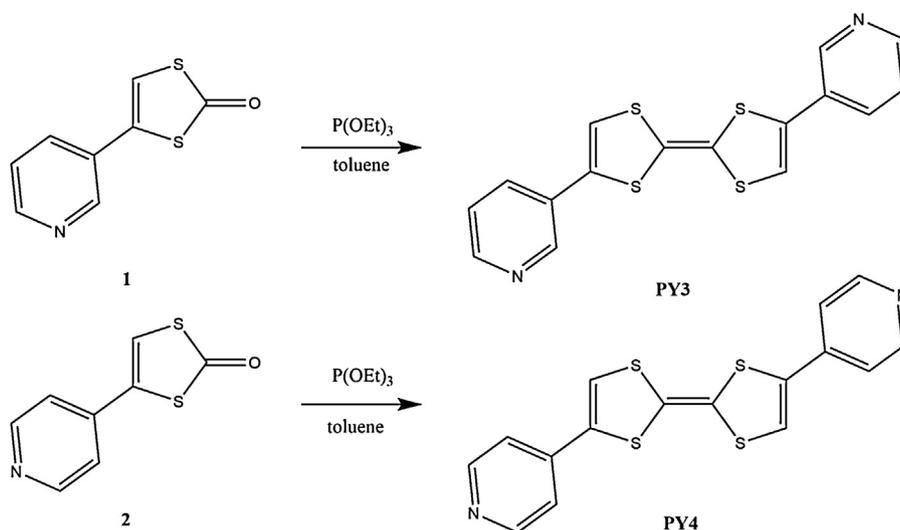


Fig. 1. Synthesis routes of PY3 and PY4.

The crude product was recrystallized through CH_2Cl_2 /hexane to give **PY3** (420 mg, 46% yield) as a red powder. ^1H NMR (500 MHz, CDCl_3): δ = 8.73 (d, 2H), 8.57 (d, 2H), 7.73 (t, 2H), 7.34 (m, 2H), 6.66 (s, 2H); MS: m/z = 358; Elemental Anal. Calc. for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{S}_4$ (%): C, 53.60; H, 2.81; N, 7.81. Found: C, 53.70; H, 2.89; N, 7.72.

PY4 was obtained by following a similar procedure as that for compound **PY3** (456 mg, 50% yield) by starting from compound 4-(4'-pyridyl)-1,3-dithiol-2-one **2** (1.0 g, 5.1 mmol). ^1H NMR (500 MHz, CDCl_3): δ = 8.67 (d, 2H), 8.62 (d, 2H), 7.31 (t, 2H), 7.16 (m, 2H), 6.86 (s, 2H); MS: m/z = 358; Elemental Anal. Calc. for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{S}_4$ (%): C, 53.60; H, 2.81; N, 7.81. Found: C, 53.71; H, 2.86; N, 7.73.

2.2. Optical properties

UV-vis absorption spectra of **PY3** and **PY4** were measured as thin films deposited on quartz slides in order to understand optical properties. As shown in Fig. 2, **PY3** and **PY4** films show a strong absorption band below 250 nm but a moderately intense absorption band in the range of 400–600 nm. **PY3** and **PY4** films exhibit long-wavelength absorption maxima at 457 nm and 477 nm, respectively. It can be seen that the different N position of **PY3** and **PY4** leads to dissimilar optical properties, with **PY3** having a band gap of around 2.1 eV and **PY4** having a little bit narrower band gap of around 2.0 eV, estimated from the absorption edges. **PY3** and **PY4** in solution exhibit long-wavelength absorption maxima at 406 nm and 432 nm, respectively [18]. Compared with their

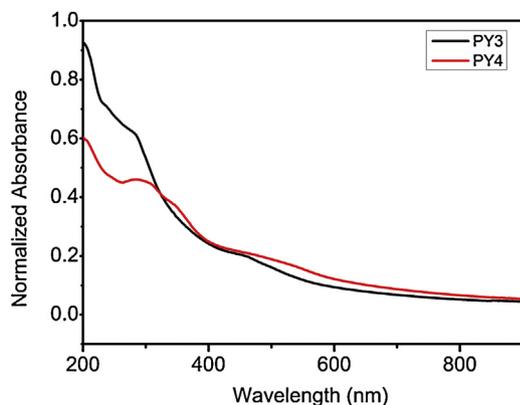


Fig. 2. UV-vis absorption spectra of PY3 and PY4 in films.

counterpart in solution, absorption peaks of thin films are red-shift, indicating intermolecular interactions.

2.3. OFET device properties and characterization

Bottom-gate/Top contact (BGTC) OFET devices were fabricated to investigate the charge transport properties of two new small molecules. **PY3** and **PY4** were deposited on top of bare and octadecyltrimethoxysilane (OTS)-modified SiO_2/Si substrates at various temperatures by thermal evaporation. The gold source/drain electrodes with a thickness of 30 nm were adopted and deposited on the semiconductor layer by thermal evaporation through a shadow mask. Both the thin-film devices were fabricated and measured in air, and average charge carrier mobilities and threshold voltages were calculated from the transfer characteristics in the saturation regime. Some representative transfer and output curves are displayed in Fig. 3 and OFET devices characteristics are collected and summarized in Table 1. FET devices based on PY3-OTS films showed that the mobility was improved with the increase of deposition temperature and reached maximum mobility of $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with on/off ratios of 10^5 upon deposition temperature at 100°C . In addition, with the increase of deposition temperature, absolute value of threshold voltage (V_T) shows a decline. However, PY3-Bare films showed relatively backward performance with maximum mobility of $6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The cause of this falling mobility may attribute to charge traps which can be greatly reduced by OTS. By contrast, the thin films of PY4 exhibited no OFET performance with or without modification of SiO_2/Si substrates.

2.4. Thin film morphology and crystallinity

In order to demonstrate the impact of deposition temperature on microstructure of small molecules surface and explain the great discrepancy of charge-transport behavior between **PY3** and **PY4** films deposited on bare and OTS-treated SiO_2/Si substrates, we utilized atomic force microscopy (AFM) to investigate film morphologies. Optical images of **PY3** films are shown in Fig. 4, and AFM images of **PY3** films are shown in Fig. S1.

As shown in Fig. 4 and Fig. S1, compared with PY3-Bare-RT films, PY3-OTS-RT films showed good crystallinity with small domains. With the increase of substrate temperature, PY3-OTS films appeared more crystalline with large and obvious domains. When the films were deposited at 100°C , rod-like grains were the

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