

Synthesis and Characterization of *N*-Acyl-substituted PyrroloTTF Derivatives and Improved Air-stability of PyrroloTTF-based OFETs

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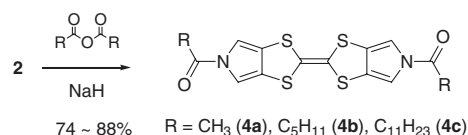
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As novel bis(pyrrolo[3,4-*d*])tetrathiafulvalene (PyTTF)-based organic semiconductors, *N*-acyl-substituted PyTTFs **4** were synthesized and evaluated. Their oxidation potentials determined by cyclic voltammetry were shifted cathodically by more than 0.35 V compared with the *N*-alkyl-PyTTFs **3**. In accordance with elevated oxidation potentials, their vapor-processed field-effect transistors showed improved air-stability with mobilities up to $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions.

Organic field-effect transistors (OFETs) have attracted current attention for potential applications to various electronic devices, such as flexible displays, inexpensive electronic papers, and radio-frequency-identification tags.¹ Recent development of new organic semiconductors and processing techniques have achieved high-performance OFETs with field-effect mobility (μ_{FET}) higher than $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in thin-film-transistor settings, making OFETs a viable alternative to the current amorphous-silicon-based FETs.² Among a wide variety of p-channel organic semiconductors so far developed, tetrathiafulvalene (TTF) derivatives have occupied an important position:³ one of the highest FET mobilities so far attained ($1.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was achieved by dithieno[3,4-*d*]tetrathiafulvalene (DT-TTF, **1**, Figure 1).⁴ We recently reported that *N*-alkyl-substituted bis(pyrrolo[3,4-*d*])tetrathiafulvalenes (R_2 -PyTTFs, **3**, Figure 1), highly soluble heteroaromatic-annulated TTF derivatives isoelectronic with DT-TTF, are useful as solution-processible organic semiconductors.⁵ Thus fabricated FET devices with their spin-coated thin films showed FET mobility as high as $0.017 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in air. Although their FET performances were relatively good for solution-processed OFETs without intensive optimizations in device fabrication, their sensitivity to ambient air was a severe drawback: shortly after exposure to air, off-current of the OFETs rose significantly. The poor stability in air is likely due to their low oxidation potentials ($E_{1/2} = -0.11 \text{ V}$ vs. Fc/Fc^+), in other words, the higher-lying energy level of the highest occupied molecular orbital (HOMO), which makes **3** susceptible to air oxidation.

In order to stabilize **2**-based organic semiconductors, we intended to introduce electron-withdrawing groups on the nitrogen atoms instead of rather electron-donating *N*-alkyl groups and synthesized *N*-acyl-substituted PyTTFs (**4**, Scheme 1). In this



Scheme 1. Synthesis of *N*-acyl-substituted PyTTFs **4**.

paper, we describe the synthesis of *N*-acyl-PyTTFs and the characteristics of FET devices using their vapor deposited thin films.

N-alkylation of the parent PyTTF (**2**) was easily done by a reaction of **2** with alkyl halide in the presence of sodium hydride.⁵⁻⁸ Thus, introduction of acyl substituents on **2** was first attempted under a similar condition using acyl chlorides. The reaction however, gave a complex mixture, and **4** could not be isolated. Instead, the use of acid anhydrides turned out to give **4** successfully in reasonable isolated yields (Scheme 1). Thus, *N*-acetyl- (**4a**), *n*-hexanoyl- (**4b**), and *n*-dodecanoyl-PyTTF (**4c**) were obtained. All new derivatives were fully characterized by spectroscopic and combustion analyses.

Unambiguous structural determination of *N*-*n*-hexanoyl derivative **4b** was achieved by single-crystal X-ray analysis. In the crystal structure, two crystallographically independent molecules exist (Figure S1). Although the conformations of *n*-C₅H₁₁ chains in two molecules are different, the central core parts of the molecules are similar to each other: the carbonyl moieties are in the same plane that the PyTTF part defined, indicating that the conjugation effectively extends to the *N*-acyl moieties (Figure 2).

Cyclic voltammograms of **4** showed two reversible oxidation couples typical for the TTF derivatives. (Figure S3) As expected, the oxidation peaks of **4** ($E_{1/2} = +0.25 \text{ V}$ vs. Fc/Fc^+) were shifted cathodically by more than 0.35 V compared with those of **3**, indicating a significant decrease of the energy level of the HOMO. The HOMO level of **4** estimated from the oxidation onset is ca 5.0 eV below the vacuum level, which is almost comparable with that of pentacene, known as a representative organic semiconductor.

In contrast to the highly soluble *N*-alkyl-PyTTFs **3**, the solubilities of **4** even with the long alkyl chains were very poor:

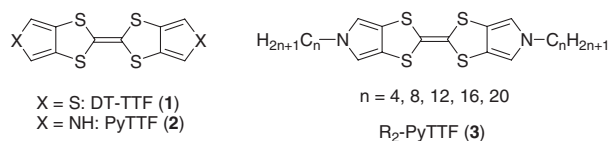


Figure 1. Structures of DT-TTF and Py-TTFs.

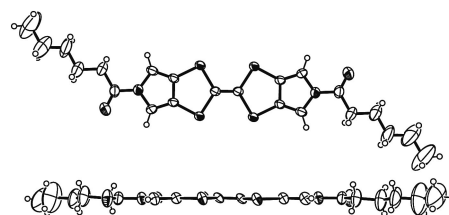


Figure 2. Molecular structure of **4b**.

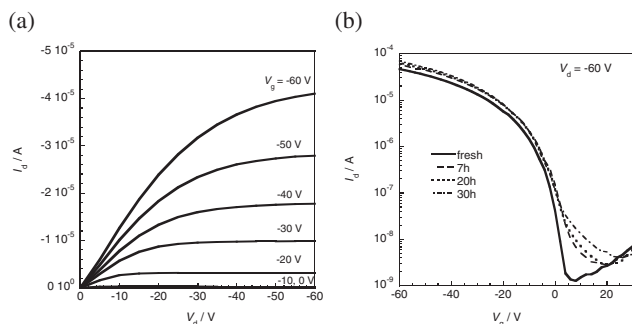


Figure 3. FET characteristics of **4b**-based OFET. (a) output characteristics and (b) transfer characteristics.

the solubility in toluene at rt was 0.01 g L^{-1} for **4b** and 0.002 g L^{-1} for **4c**, which were lower than those of **3** by more than two orders of magnitude. Although the reasons for the extremely low solubility of **4** are not clear, we speculate that incorporation of the carbonyl groups in the conjugation of PyTTF core and thus induced planar and rigid molecular structure confirmed by X-ray structural analysis account for it.

Poor solubility of **4** in organic solvents prevented the deposition of thin films by solution processes. Instead, physical vapor deposition of **4** gave homogeneous thin films with metallic luster on Si/SiO₂ substrates except for **4c**, which thermally decomposed during vapor deposition. The thin films consist of well-ordered polycrystalline grains as confirmed by the atomic force microscopy (AFM) images (Figure S4). Such morphology is a prerequisite for high-performance OFETs.

The XRD measurements of the thin films of **4a** and **4b** indicated that the films have crystalline order in the direction of the substrate normal (Figure S5). The calculated interlayer distances (*d*-spacings) are 17.0 \AA for **4a** and 22.6 \AA for **4b**. The *d*-spacing of **4b** is almost the same as the length of the crystallographic *c* axis in the bulk single crystal, which suggests that molecular arrangements in the thin film and in the bulk single crystal are similar to each other.

On top of the evaporated thin films, gold source and drain electrodes were thermally deposited through a shadow mask to define the channel of the transistors with a length (*L*) of 50 or $100 \mu\text{m}$ and width (*W*) of 1.5 mm , respectively. The OFET devices were evaluated under ambient conditions, and the **4a**- and **4b**-based devices showed normally-off FET characteristics (Figure 3). Extracted FET mobilities from the saturation regime are up to $0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **4a**-based devices and $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **4b**-based devices, respectively (Table S1).

As already mentioned, the **3**-based OFETs suffered from severe air-oxidation: the fresh devices showed typical normally-off FET characteristics. However, exposure to air for 2 h increased the off-current significantly, higher than that of the fresh device by a factor of more than two orders of magnitude (Figure S6). In contrast, the present **4**-based devices showed improved air-stability. As shown in Figure 3b, the devices showed typical normally-off FET responses even after exposure to ambient lab conditions for more than 9 h. This stabilization can be accounted for by the lowered HOMO energy level of **4** by introduction of the electron-withdrawing acyl groups on the PyTTF core.

In summary, we successfully synthesized *N*-acyl-PyTTFs **4** and evaluated the FET devices based on their vapor-deposited thin films. The electron-withdrawing acyl groups introduced brought about lower HOMO levels than those of *N*-alkyl-PyTTFs **3**, which contributes to stabilization of **4**-based FET devices under ambient conditions without decreasing the FET characteristics. These results indicate that the tuning of the energy level of HOMO is important in developing air-stable p-channel organic semiconductors and air-stable OFETs.

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- 7 Efficient synthetic route for the parent PyTTF (**2**) was established. See supporting Information.
- 8 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.