



Synthesis, characterization and air stable semiconductor properties of thiophene-condensed pyrene derivatives



Tetsuji Moriguchi^{a, *}, Makoto Higashi^a, Daisuke Yakeya^a, Venkataprasad Jalli^a, Akihiko Tsuge^a, Tatsuo Okauchi^a, Shuichi Nagamatsu^b, Wataru Takashima^c

^a Department of Applied Chemistry, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu 804-8550, Japan

^b Department of Computer Science and Electronics, Kyushu Institute of Technology, 680-4 Kawazu, Iizuka, Fukuoka 820-8502, Japan

^c Graduate School of Life Science and System Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu 808-0196, Japan

ARTICLE INFO

Article history:

Received 31 May 2016

Received in revised form

25 July 2016

Accepted 25 July 2016

Available online 27 July 2016

Keywords:

Thiophene condensed pyrene derivatives

Organic semiconducting material

Photo cyclization

π -Conjugated structure

X-ray analysis

Molecular packing

ABSTRACT

New and simple polyaromatic compounds containing two thiophene rings were prepared via photocyclization and their structural and photophysical properties were evaluated via ¹H NMR spectroscopy and X-ray crystallographic analysis. On the basis of X-ray analysis, it was determined that the molecular structure of the compound was highly strained and that they contain two hetero [4] helicene moieties. The compounds were investigated as active layer in p-type organic field-effect transistors (p-OFET) in top contact type devices. Notably, the compound containing two thiophene components exhibited very stable p-type semiconducting behavior in moist air.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, polycyclic aromatic hydrocarbons (PAHs) have been attracting great interest owing to their significant photochemical and electrical properties, and have found various applications in organic opto-electronic materials [1–5]. Planar PAHs such as pentacene, hexacene, pyrene, perylene are readily stacked in solution and crystalline state owing to π – π interactions, and are therefore widely used as components of new materials such as organic semiconductors [6,7]. In recent year, for example, Nuckolls and co-workers developed a novel approach to the synthesis of a phase-forming, distorted hexa-cata-hexa-benzocoronene derivative, whereby the decisive step was accomplished via photocyclization. The material formed columnar liquid-crystalline phases with high charge-carrier mobilities as determined in organic field-effect transistors (OFETs) [8].

On the other hand, the structural and physical properties of “strained” PAHs such as helicene, fullerene and bucky bowl, have

also been intensively studied in order to investigate the potential for their use as organic semiconductors with interesting properties compared to those of the various planar compounds [9]. Yamato *et al* reported the preparation, structural and opto-electrical properties of *t*-butylated pyrenes and their derivatives [10,11]. Lakshman *et al*, meanwhile, reported the preparation and structural properties of the highly strained 1,4-dimethylbenzo[*c*]phenanthrene [12]. There is a fjord region in the molecule, and the protons located in the fjord region showed strange ¹H NMR chemical shifts due to the strained structure.

For flexible electronics, OFETs are indispensable for the fabrication of electronic circuits on plastic substrates [8–10]. Typically, organic semiconducting materials that have large mobility also have a planar structure. However, their solubility is usually not good, and thus these compounds are not suitable for the synthesis of OFETs via wet processes such as spin-coating and drop-casting. Here, we report the synthesis, characterization and structural properties of highly twisted di-*t*-butylated polyaromatic compounds containing two thiophene rings. The compounds were prepared via oxidative photo-cyclization, and their structural and photophysical properties were evaluated via ¹H NMR, UV-Vis and X-ray crystallographic analysis. The p-type semiconducting

* Corresponding author.

E-mail address: moriguch@che.kyutech.ac.jp (T. Moriguchi).

properties of the new compounds were evaluated in top contact-type OFET devices, and their air and moisture stabilities were examined over 40 days.

2. Results and discussion

Reactions of pyrene-based bis Wittig reagent **1** (2,7-di-*t*-butylpyrene-4,9-bis(ethyldiethylphenyl)phosphonium dichloride) with thiophene carbaldehyde **2** (2-thiophenecarboxaldehyde **2a**, 5-methyl-2-thiophenecarboxaldehyde **2b**) successfully proceeded to give the diarylethenyl compounds **3** in excellent yields (>90%, Scheme 1). Subsequently, photo-cyclization of the diarylethenyl compounds **3** under irradiation from a high pressure Hg lamp in the presence of iodine as the oxidative reagent gave the desired products **4a** and **4b** in moderate yields.

^1H NMR spectra for the photo-cyclized products **4a** and **4b** showed downfield shifts of the protons located in the fjord regions which consist of three benzene rings and one thiophene ring. The shifting of these peaks is due to strong ring current effects. X-ray analyses of **4a** and **4b** were then performed to clarify the exact structures and packing orientations.^{7,8} The molecular structure of **4a** is shown in Fig. 1. The crystal packing is not side-by-side orientation but herringbone as shown in Fig. 2. In addition, in the crystal structure of the molecule **4a** oriented as a one-dimensional array column with an inclination of 45° . The shortest intermolecular distance for molecule **4a** between the π systems in the column is 3.477 Å.

The molecular structure of **4b** was also shown in Fig. 3. The molecules stacked as side by side orientation as shown in Fig. 4. In addition, in the crystal structure, the molecule **4b** oriented as a one-dimensional array column with an inclination of 0° . The shortest intermolecular distance between the π systems in the column is 3.623 Å for **4b**.

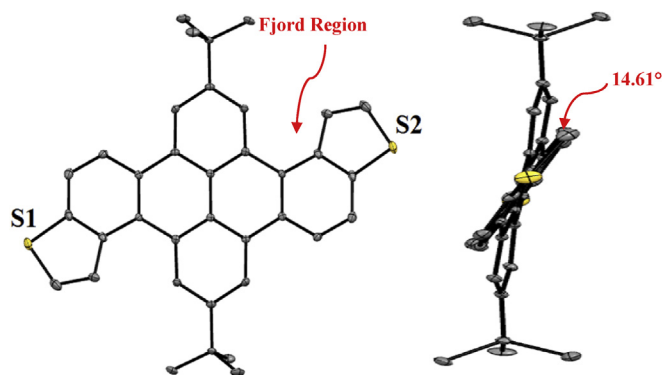
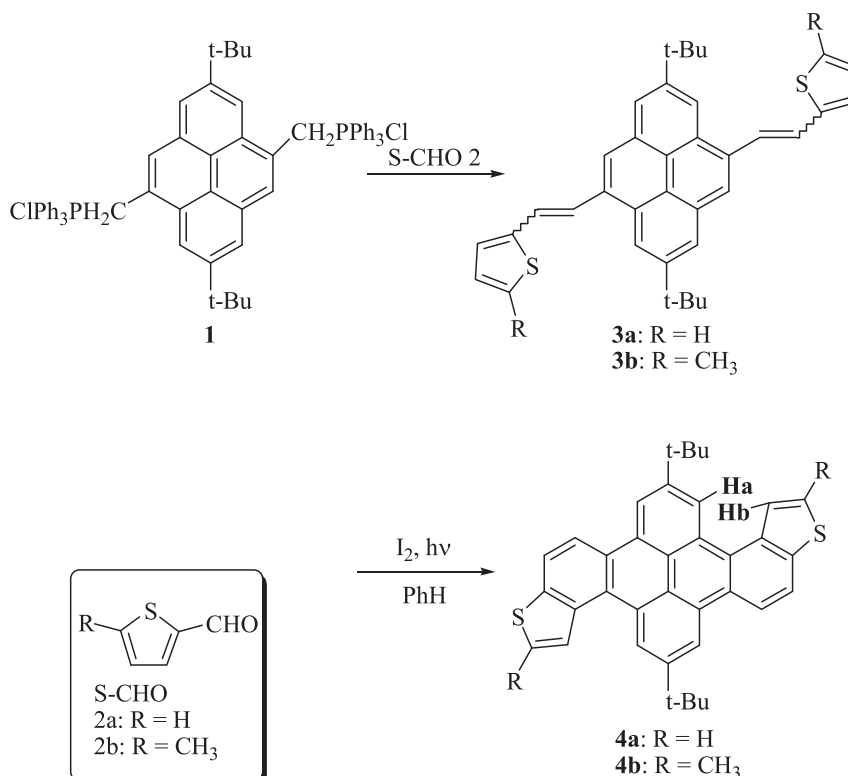


Fig. 1. Top (above) and side (below) views of the **4a** and thermal ellipsoids are drawn on 50% probability level.

The short values between the π systems suggest that these compounds should be suitable as the conducting layer in OFETs because the molecules may be easily stacked in a layer on a device by using vacuum sublimation. Therefore, a top contact-type electronic device was constructed according to the procedure we previously reported [13]. SiO_2 and Si were used as the insulating and gate layers, respectively, and gold sputtering was used to create the source and drain electrode.

Typical p-semiconducting properties ($I_{\text{Drain-Source}}-V_{\text{Drain-Source}}$ curve) of the top-contact-type device of **4b** are shown in Fig. 5 and Fig. 6. Hysteresis was not observed owing to the excellent hole transport properties in a vacuum and moist air. The hole mobility (μ) was on the order of 10^{-2} cm^2/Vs , and the threshold voltage V_{th} was -44 V. The hole mobility (μ) of **4a** was on the order of 10^{-3} cm^2/Vs , and the threshold voltage V_{th} was -45 V.

The differences between **4a** and **4b** were well explained by



Scheme 1. Synthesis of molecules **4a** and **4b**.

Download English Version:

<https://daneshyari.com/en/article/1407550>

Download Persian Version:

<https://daneshyari.com/article/1407550>

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