

ARTICLE

Pyrene Derivate Functionalized with Acetylene for Organic Field Effect Transistors

Zuo-qin Liang^{a*}, Jie Zhou^a, Xiao-mei Wang^a, Xu-tang Tao^b

a. Jiangsu Key Laboratory for Environment Functional Materials, School of Chemistry, Biology and Material Engineering, Suzhou University of Science and Technology, Suzhou 215009, China

b. State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

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A new X-shaped compound (SiPy) functionalized with acetylene bonds in the 1-, 3-, 6-, and 8-positions of the pyrene core has been synthesized by Sonogashira coupling reactions. Its photophysical, thermal, and organic field effect transistor (OFET) properties as well as the film morphologies have been investigated. SiPy exhibits high stability which is evidenced by thermal gravimetric analysis. The atomic force microscopy images reveal that the morphology of thin films depends on the substrate temperature. The film OFET devices based on SiPy were constructed and exhibited *p*-type performances.

Key words: Pyrene, Acetylene, Organic field effect transistors, Carrier mobility, On/off ratio

I. INTRODUCTION

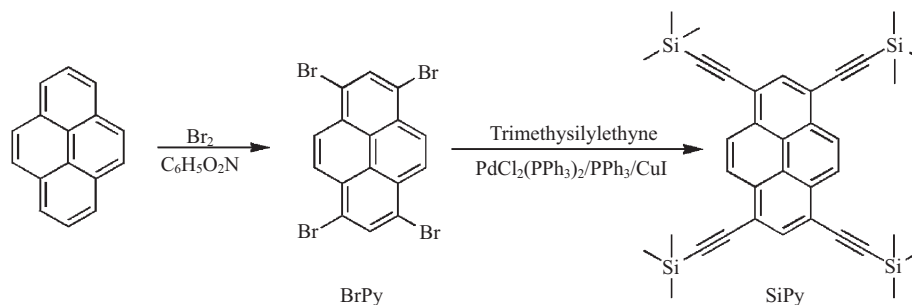
Recently, organic semiconductors have received significant attention for their utility in organic light emitting diodes [1], solar cells [2], and organic field effect transistors (OFETs) [3]. OFETs are easier to fabricate than traditional silicon based transistors which require severe processing techniques, and there also exists the likelihood of replacing amorphous silicon in applications such as identification tags, smart cards, and display drivers that are intended for short term use and large scale manufacture. The performance of OFETs is mainly determined by the carrier mobility in the organic semiconductor layers. It is generally believed that a good OFET material should have strong π - π interaction between neighboring molecules and can be readily sublimed to form polycrystalline film [4]. During the last few years, several organic compounds have been synthesized and used in OFETs [5]. Pentacene OFETs have received particular attention since they have shown high hole mobility over $1.0 \text{ cm}^2/(\text{V}\cdot\text{s})$ with on/off current ratio larger than 10^6 [6]. However, pentacene is only moderately stable to oxygen as a dense solid and is unstable under illumination [7]. Therefore, stability under ambient and operating conditions is also an important parameter for the organic semiconductors in the practical applications.

Pyrene derivatives have been studied intensively as organic chromophores [8] and as light emitting mate-

rials in organic light-emitting diodes [9] because of its high photoluminescence quantum yield, excellent thermal stability, and high charge carrier mobility. Their stability and mobility meet well with the requirement of OFET application. Furthermore, pyrene derivatives, possess rigidity, coplanar, and π -conjugated framework structure, and show a great propensity to form π -stacking and crystallization. Therefore, pyrene is a promising candidate for OFET applications. Liu *et al.* reported the first example of butterfly pyrene derivative functionalized with thienyl aromatic group. The OFET device using it as the active material afforded mobility of $3.7 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$ with an on/off ratio of 10^4 . And its crystal structures were investigated. The molecular displayed an inner flat, symmetric molecular geometry, while the peripheral thienyl units adopted twisted forms [10]. Subsequently, Ashizawa *et al.* developed a series of pyrene derivatives with peripheral thienyl groups, fabricated single-crystal transistors of these compounds, and directly compared the field-effect performance between the devices of the two isoforms of tetrathienylpyrene and those of the two isomers of dithienylpyrene [11]. The observation demonstrates that larger overlap integrals between the adjacent molecules favor the FET performances.

In this work, we employed pyrene as a core to synthesize a X-shaped compound 1,3,6,8-tetrakis-(trimethylsilanylethynyl)pyrene (SiPy) (Scheme 1). The introduction of acetylene bonds can extend the intramolecular π -conjugation, so as to improve the charge mobility of the material. In addition, the relative planar configuration of acetylene moieties along the molecule was reported to be important for the on-off switch stage [12]. Herein, we present the synthesis, photophys-

* Author to whom correspondence should be addressed. E-mail: zuoqinliang@mail.usts.edu.cn



Scheme 1 Synthetic route of pyrene (SiPy).

ical, and OFET properties of SiPy compound.

II. EXPERIMENTS

A. Chemicals and instruments

All reagents and materials used for the synthesis were commercially available. Dry toluene was freshly distilled over sodium prior to use. All other reagents were used as received. The ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C using a Bruker Avance 300 MHz spectrometer. Mass spectrum was determined with an AXIMA-CFR plus MALDI-TOF mass spectrometer. Thermal gravimetric analysis (TGA) measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min with a Perkin-Elmer Diamond thermogravimetric analyzer. UV-Vis absorption spectra were recorded on Varian Cary 50 spectrophotometer. Fluorescence measurements were carried out with a Hitachi F-4500 fluorescence spectrometer equipped with a 150 W Xe lamp. The atomic force microscopy (AFM) images were obtained by using a Digital Instruments (DI) Dimension 3100 operating in tapping mode.

OFET devices were fabricated in the top contact configuration. Gold electrodes were deposited using shadow masks with width-to-length ratio of ca. 60/1. Organic semiconductors were deposited at a rate of 0.1 Å/s under a pressure of about 5.0×10^{-4} Pa. OFET characteristics were obtained at room temperature in air on Keithley 4200 SCS.

B. Synthesis

To a stirred solution of pyrene (5.00 g, 24.7 mmol) in nitrobenzene (100 mL) was added Br_2 (17.5 g, 0.11 mol). After complete addition, the temperature was increased to 120 °C, maintained for 4 h, and then cooled to room temperature to yield a pale-green precipitate. The product was filtrated, washed by ethanol, and dried under vacuum, which was BrPy and used without further purification.

A three-necked flask was charged with BrPy (100 mg, 0.20 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (27.0 mg, 0.04 mmol), CuI

(15.0 mg, 0.08 mmol), PPh_3 (20.0 mg, 0.08 mmol), triethyl amine (10 mL) and toluene (1.5 mL). The flask was evacuated and flushed with N_2 , and the solvent was degassed. Under stirring, the mixture was heated at 60 °C and trimethylsilylethyne (114 mg, 1.16 mmol) was injected through a syringe. The mixture was then allowed to increase to 80 °C and maintained for 12 h. The solvent was evaporated under reduced pressure, and the crude product was purified by flash column chromatography using petroleum ether as eluent to afford an orange solid 80.0 mg. Yield: 70.2%.

III. RESULTS AND DISCUSSION

SiPy: ^1H NMR (CDCl_3 , 300 MHz) δ /ppm: 0.39 (s, 36H), 8.30 (s, 2H), 8.58 (s, 4H). ^{13}C NMR (CDCl_3 , 75.5 MHz) δ /ppm: 100.90, 102.33, 118.11, 122.99, 126.43, 131.47, 134.00. MALDI-TOF, m/z : 586.24 (calculated), 586.3 (found).

A. Photophysical and thermal properties

To investigate the photophysical properties, the absorption and photoluminescence (PL) spectra of SiPy in different polar solvents (2.5 $\mu\text{mol/L}$) and the thin film were measured, as shown in Fig.1. In toluene, SiPy shows two prominent absorption bands with maxima at about 317 and 439 nm. The first absorption band exhibits the characteristic vibronic pattern of the isolated pyrene group [13]. The second band should be ascribed to the intramolecular π - π^* transitions. When the solvent polarity changes from toluene to DMF, there are no significant changes in its absorption spectrum. For the thin film, the absorption spectrum of SiPy has lost vibronic structure and is slightly blue shifted with respect to the solution state absorption. The fluorescence spectrum of SiPy in toluene has three emission bands located at 441, 470, and 502 nm, as shown in Fig.1(b). Increasing the solvent polarity, the emission peaks remain almost unchanged. Differing from the absorption spectrum, the fluorescence spectrum of thin film is shifted to longer wavelength of about 583 nm. Compared to the spectrum in toluene, SiPy represents

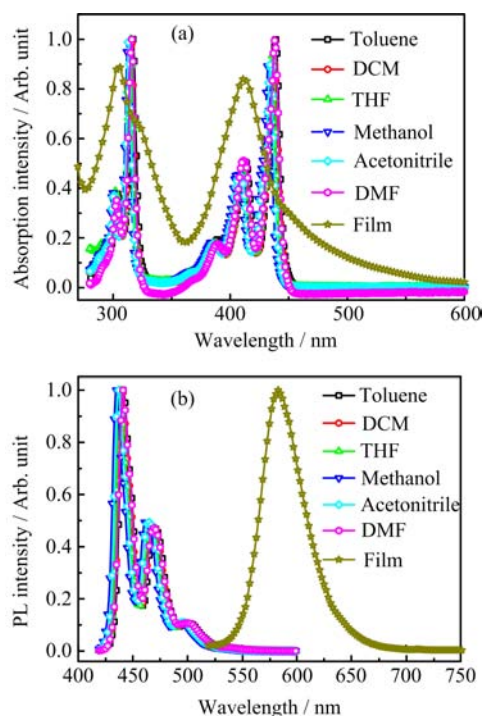


FIG. 1 (a) Normalized optical absorption and (b) PL emission spectra of SiPy in different polar solvents and thin film.

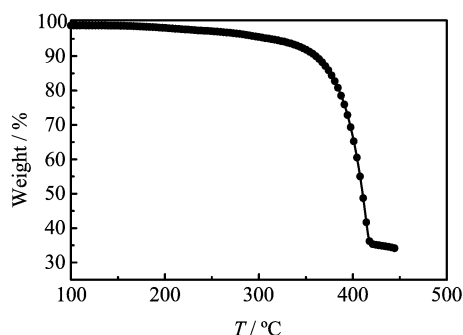


FIG. 2 TGA analysis for SiPy.

a 81 nm bathochromic shift, indicating strong intermolecular interactions in its solid state.

High thermal stability is prerequisite for organic materials in the practical applications of OFET. Therefore, the thermal property of SiPy was evaluated by TGA (Fig.2). The decomposition temperature of SiPy is 388 °C. The result of the TGA indicates that SiPy possesses excellent thermal stability.

B. OFET properties

The OFET behaviors of SiPy were studied using the top contact device structure on tetradecyltrichlorosilane (TDTS) modified SiO₂/Si substrates. All the devices show typical *p*-type channel OFET properties. The typical OFET output and transfer characteristics of SiPy

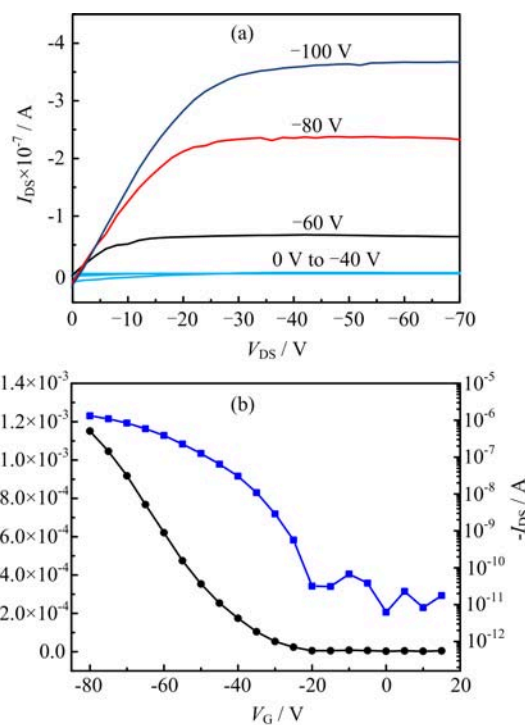


FIG. 3 OFET characteristics of SiPy on TDTS-pretreated substrate ($T_{\text{sub}}=80\text{ }^{\circ}\text{C}$): (a) output characteristic and (b) transfer characteristic.

TABLE I Performance of OFETs based on SiPy under different substrate temperature (T_{sub}).

$T_{\text{sub}}/^{\circ}\text{C}$	$\mu/(\text{cm}^2/(\text{V}\cdot\text{s}))$	$I_{\text{on}}/I_{\text{off}}$
50	7.4×10^{-4}	1.0×10^4
80	4.0×10^{-3}	7.0×10^5
100	1.5×10^{-3}	2.0×10^5

on TDTS-pretreated SiO₂/Si at 80 °C are presented in Fig.3. The *I*-*V* characteristics shows standard linear and saturation regions. The OFET performance obtained at different fabrication conditions is summarized in Table I. The hole mobility was extracted from the saturation regime of the transfer curve by using the classic equation describing OFET. With the increase of substrate temperature, the mobility of SiPy increases and a high mobility up to $4.0\times 10^{-3}\text{ cm}^2/(\text{V}\cdot\text{s})$ as well as on/off ratio over 10^5 are obtained at $T_{\text{sub}}=80\text{ }^{\circ}\text{C}$. On further increasing the substrate temperature to 100 °C, the mobility and on/off ratio decrease slightly.

To understand the effect of the substrate temperature-dependent mobility, the surface morphology of the film of SiPy was explored with AFM. Figure 4 exhibits the AFM images of the film of SiPy at different substrate temperature. AFM images show that the morphology of thin films strongly depends on the deposited temperature. At 50 °C, the thin film shows layer by layer growth and the morphology of the

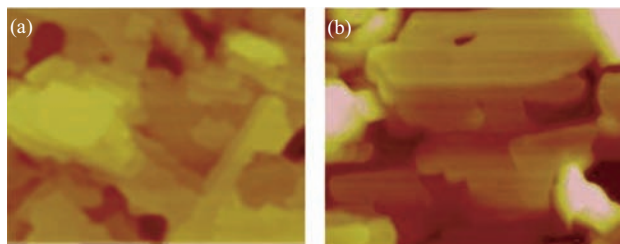


FIG. 4 AFM images of films deposited on TDTS-pretreated SiO₂/Si at (a) 50 °C and (b) 80 °C.

films is continuous and terrace-like step structures appear. When the deposited temperature was increased to 80 °C, morphology of films was improved. The size of the grains was substantially increased, which is the origin of the strong dependence of mobility to the substrate temperature. This variation tendency of thin film morphology along with the depositing condition is coincident with the OFET performance change.

IV. CONCLUSION

A new X-shaped compound containing a pyrene core and acetylene bonds has been successfully synthesized. The PL spectra reveal that there is strong intermolecular interaction in its thin film. TGA result suggests that SiPy has good thermal stability. AFM images show that the morphology of thin films depends on the deposition temperature. Mobility up to $4.0 \times 10^{-3} \text{ cm}^2/(\text{V}\cdot\text{s})$ and on/off ratio over 10^5 are achieved for SiPy at $T_{\text{sub}}=80 \text{ }^\circ\text{C}$ on the TDTS modified SiO₂/Si substrate. These results indicate that SiPy is a promising organic semiconductor for OFET.

V. ACKNOWLEDGMENTS

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