



Functionalized soluble triethylsilylethynyl anthradithiophenes (TESADTs) for organic electronic devices



Hsien-Cheng Yu ^{a,1}, Guhyun Kwon ^{b,1}, Sureshraj Vegeraju ^{a,1}, Chi-Wen Chao ^c, Long-Huan Li ^a, Jen-Shyang Ni ^a, Peng-Yi Huang ^a, Shueh Lin Yau ^a, Yu-Chiang Chao ^{c,*}, Choongik Kim ^{b,**}, Ming-Chou Chen ^{a,***}

^a Department of Chemistry, National Central University, Jhong-Li 32054, Taiwan, ROC

^b Department of Chemical and Biomolecular Engineering, Sogang University, 1 Shinsoo-dong, Mapo-gu, Seoul 121742, South Korea

^c Department of Physics and Center for Nanotechnology, Chung Yuan Christian University, Chung-Li 32023, Taiwan, ROC

ARTICLE INFO

Article history:

Received 6 October 2015

Received in revised form

1 December 2015

Accepted 12 December 2015

Available online 21 December 2015

Keywords:

Organic thin-film transistor

Organic photovoltaics

Organic semiconductor

Solution process

Anthradithiophene

Solution shearing

ABSTRACT

Four new solution-processable triethylsilylethynyl anthradithiophene-(TESADT) based organic semiconductors, end-capped with phenyl (DP-; **1**), thien-2-yl (DT-; **2**), thienothien-2-yl (DTT-; **3**), and perfluorophenyl (DFP-; **4**) groups have been synthesized, characterized, and incorporated in organic thin-film transistors (OTFTs) and organic photovoltaics (OPVs). For the fabrication of solution-processed OTFT, thin films of all four compounds have been fabricated via a solution process of solution-shearing (SS), droplet-pinned crystallization (DPC), and drop-casting (DC). Among various solution-processing methods, solution-shearing produced TFTs the highest electrical performance. Thin films of compound **1** formed via the SS method exhibited p-channel characteristics, with hole mobilities as high as $\sim 0.034 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The film morphologies and microstructures of these compounds have been characterized by atomic force microscopy and X-ray diffraction to rationalize device performance trends. Furthermore, DP-TESADT (**1**) and DFP-TESADT (**4**) has been employed for the fabrication of OPVs. Especially, pseudo-bilayer polymer solar cells based on an underlayer of poly(3-hexylthiophene) (P3HT) doped with 2.4% DP-TESADT and 9.1% DFP-TESADT and an upper layer of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) achieved power conversion efficiency up to 2.1%.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Solution-processable organic semiconductors have attracted extensive research attention as active layers of organic thin-film transistors (OTFTs) and organic photovoltaics (OPVs) for disposable, inexpensive, large-area electronics, such as electronic papers, sensors, and smart textiles [1–18]. Among the well-developed organic semiconductor classes, pentacene (PEN) [19–24], anthradithiophene (ADT) [25–29], and fused-thiophene derivatives [30–38] are archetypical small-molecule semiconductors. However, these small molecules are not very soluble in common solvents,

which limits their applicability in many high-throughput coating and printing processes. Furthermore, pentacene suffers from oxidative instability by photooxidation at the C-6/C-13 positions [19–24]. There have been a number of reports addressing the limitations of small molecule organic semiconductors by pursuing solution-processable compounds with enhanced oxidative stability. Pentacene **A** [39,40] and ADT derivatives **B** – **D** [41–45] after introducing substituents at the pentacene C-6/C-13 positions have proven to be effective at enhancing the stability of the pentacene framework, as well as greatly improving carrier mobility in OTFTs. For example, triisopropylsilylethynyl (TIPS)-substituted pentacene (TIPS-PEN; **A**) exhibits enhanced electrical performance with a carrier mobility of $>1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ [42,46]. Similar approaches have been investigated for ADT derivatives, and a solution processable p-channel triethylsilylethynyl ADT derivative (TES-ADT; **B**) with a mobility as high as $1.0 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was reported by Jackson et al. [47,48] Meanwhile, Tykwinski et al. reported ADT derivatives with a mobility of $1.0 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (*syn*-ADT; **C**) [49] and with relatively low

* Corresponding author.

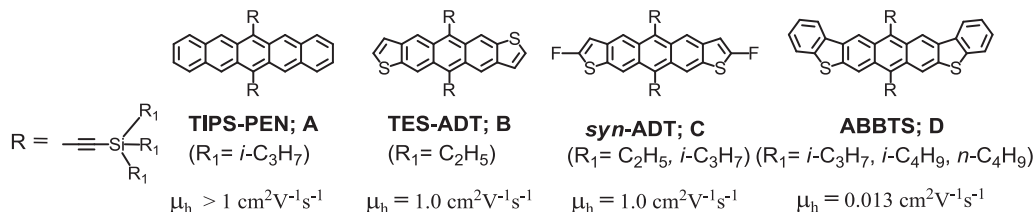
** Corresponding author.

*** Corresponding author.

E-mail addresses: ycchao@cycu.edu.tw (Y.-C. Chao), choongik@sogang.ac.kr (C. Kim), mcchen@ncu.edu.tw (M.-C. Chen).

¹ These authors contributed equally to this work.

carrier mobility of $0.013 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (**ABBTS; D**) [50] from solution-processed thin films. All of these studies demonstrated that trialkylsilyl-ethynyl substituents on the **PEN/ADT** cores significantly influence solid state electrical performance [51–53].



More conjugated groups (e.g. phenyl or thiophenyl) connected to the ADT core are expected to further enhance self-assembly of the aromatic moieties into closely π -stacked arrays, therefore improving intermolecular orbital overlap and the resulting device performance. To prove this postulation, four solution-processable **TESADT** derivatives, end-capped with phenyl (**DP-TESADT; 1**), thien-2-yl (**DT-TESADT; 2**), thienothien-2-yl (**DTT-TESADT; 3**), and perfluorophenyl (**DFF-TESADT; 4**) groups were synthesized, characterized, and incorporated in OTFTs and OPVs. From the film morphologies/microstructures of these four compounds, it will be clearly seen that the end-capped substituents did strongly affect the intermolecular stacking of these new derivatives (*vide infra*). For solution-processable organic semiconductors, various methods, including spin-coating (SC), drop-casting (DC), solution-shearing (SS), and droplet-pinned crystallization (DPC), have been reported to enhance electrical performance of the resulting devices [54–57]. In particular, the SS and DPC methods have been demonstrated to be effective to form highly crystalline films for several organic semiconductors with high electrical performance, as reported by Bao et al. [58,59]. In this study, four new solution-processable semiconductors were developed and employed as an active component with three different solution processing methods of SS, DPC, and DC in a top-contact/bottom-gate OTFT, and the resulting device characteristics were investigated. The morphology and microstructure of the semiconducting films relating to the film growth conditions were investigated to correlate these properties with device performance. In particular, thin films of compound **1** formed via the SS method exhibited decent p-channel characteristics in OTFTs, with hole mobilities as high as $0.034 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and a current on/off ratio of 3×10^6 . Furthermore, newly developed compound has been employed for the fabrication of OPVs – bulk heterojunction and pseudo-bilayer polymer solar cells. For bulk heterojunction solar cells, the power conversion efficiency (PCE) of 1.53% was obtained with open-circuit voltages (V_{oc}) of 0.78 V. For Pseudo-bilayer polymer solar cells comprising an underlayer of poly(3-hexylthiophene) (P3HT) doped with compound **1** and an upper layer of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), the power conversion efficiency up to 2.1% was achieved.

2. Experimental section

2.1. Materials and methods

All chemicals and solvents were of reagent grade and were obtained from Aldrich, Arco, or TCI Chemical Co. Solvents for the reactions (toluene, benzene, ether, and THF) and were distilled under N_2 from sodium/benzophenone ketyl, while the halogenated solvents were distilled from CaH_2 . ^1H and ^{13}C . NMR spectra were recorded on Bruker 500 and 300 MHz instruments. Chemical shifts for ^1H and ^{13}C spectra were referenced to solvent peaks. ^{19}F NMR

spectra were referenced to external CFCl_3 . Differential scanning calorimetry (DSC) was carried out on a Mettler DSC 822 instrument, and calibrated with a pure indium sample at a scan rate of 10 K/min. Thermogravimetric analysis (TGA) was performed on a Perkin

Elmer TGA-7 thermal analysis system using dry N_2 as a carrier gas at a flow rate of 40 mL/min. The UV–Vis absorption and fluorescence spectra were obtained using JASCO V-530 and Hitachi F-4500 spectrometers, respectively, and all spectra were measured in a specified solvent at room temperature. Differential pulse voltammetry experiments were performed with a CH Instruments model CHI621C Electrochemical Analyzer. All measurements were carried out at a specified temperature with a conventional three-electrode configuration consisting of a Pt disk working electrode, an auxiliary Pt wire electrode, and a non-aqueous Ag reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) in the specified dry solvent. All potentials reported here are referenced to an Fc^+/Fc internal standard (at +0.6 V) [38]. Elemental analyses were performed on a Heraeus CHN–O–Rapid elemental analyzer. Mass spectrometric data were obtained with a JMS-700 HRMS instrument. Prime grade silicon wafers ($n^{++}\text{-Si}$) with $\sim 300 \text{ nm}$ ($\pm 5\%$) thermally grown oxide (Taewon Scientific Co.) were used as device substrates. The reagents **TESADT** [47,60,61] and **TT** [62] were prepared according to procedures reported in the literature.

2.2. Synthesis of Di-2,8-aryl-5,11-Bis(4-triethylsilylethynyl)anthradithiophenes (**DAr-TESADT; 1–4**)

Under nitrogen at $-78 \text{ }^\circ\text{C}$, lithium diisopropylamide (LDA) (2.0 M, 1.44 mL, 2.88 mmol) was added to a 40 mL THF solution of 4-triethylsilylanthradithiophene (**TESADT**, 0.40 g, 0.72 mmol) and the mixture was stirred at this temperature for 1 h. Tri-*n*-butylstannyl chloride (0.94 mL, 2.88 mmol) in a 20 mL THF was then added into the mixture and stirred for 3 h at room temperature. THF was next removed under vacuum, and a 20 mL toluene solution of dry bromobenzene (0.24 g, 1.5 mmol) as well as a 20 mL toluene solution of tetrakis(triphenylphosphine) palladium (50 mg, 0.043 mmol) were added to this, and the resulting mixture was refluxed for 24 h. Water was added to quench the reaction and the product was extracted with CH_2Cl_2 and evaporated, which was then purified by column chromatography using hexanes as eluent and recrystallized from diethyl ether, giving a purple solid **DP-TESADT (1)**; 280 mg) in a yield of 55%. ^1H NMR (300 MHz, CDCl_3): δ 9.09 (s, 2H), 9.03 (s, 2H), 7.82 (d, $J = 7.5 \text{ Hz}$, 4H), 7.69 (s, 2H), 7.51–7.40 (m, 2H), 1.27 (t, $J = 5.1 \text{ Hz}$, 18H), 0.93 (t, $J = 7.5 \text{ Hz}$, 12H). HRMS (m/z , FAB^+) calcd for $\text{C}_{46}\text{H}_{46}\text{S}_2\text{Si}_2$: 718.2579; found: 718.2571.

DT-TESADT (2), **DTT-TESADT (3)**, and **DFF-TESADT (4)** were prepared via a similar procedure, except for using the corresponding aryl bromide, i.e. thiophenyl bromide, thienothiophenyl bromide, and pentafluorophenyl bromide, in the coupling reaction.

2.2.1. DT-TESADT (2)

The title compound was obtained as a purple solid (synthetic yield = 57%).

Download English Version:

<https://daneshyari.com/en/article/175628>

Download Persian Version:

<https://daneshyari.com/article/175628>

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