A new narrow bandgap polyfluorene copolymer containing 2,6-bis-(3-hexyl-thiophen-2-yl)-anthraquinone unit for solar cell applications

Jung Feng Lee [a], Steve Lien Chung Hsu [a,*], Po I. Lee [a], Hung Yi Chuang [a], Jen Sue Chen [a], Wei Yang Chou [b]

[a] Department of Materials Science and Engineering, Research Center for Energy Technology and Strategy, National Cheng-Kung University, Tainan 701-01, Taiwan, ROC
[b] Institute of Electro-Optical Science and Engineering, National Cheng-Kung University, Tainan 701-01, Taiwan, ROC

ARTICLE INFO

ABSTRACT

We have synthesized a new narrow bandgap alternating polyfluorene copolymer (PFTTDIONE) based on 2,7-dibromo-9,9-dioctylfluorene, 2,5-bis-(tributyl-stannyl)thiophene, and 2,6-bis-(5-bromo-3-hexyl-thiophen-2-yl)-anthraquinone (M1), via a Stille polymerization reaction. The optical properties, electrochemical properties, photovoltaic properties, hole mobility, and AFM morphology of the copolymers were investigated and discussed. The optical bandgap of PFTTDIONE is equal to the electrochemical bandgap (1.90 eV). PFTTDIONE exhibits an extended absorption band in the visible part of the spectrum with an absorption edge close to 650 nm. In order to investigate its photovoltaic properties, polymer solar cells (PSCs) devices based on PFTTDIONE were fabricated with a structure of ITO/PEDOT:PSS/ copolymer:PCBM/ LiF/Al under the illumination of AM 1.5 G, 100 mW/cm². The bulk heterojuction (BHJ) polymer solar cells were fabricated with the conjugated polymer as the electron donor and 6,6-phenyl C_{61}-butyric acid methyl ester (PCBM) as the electron acceptor. The power conversion efficiency (PCE) of the solar cells based on PFTTDIONE/PCBM (1:2) annealing at 110 °C for 20 min was 1.58% with an open-circuit voltage (V_{oc}) of 0.74 V, Fill Factor of 35.7%, and a short-circuit current (J_{sc}) of 5.99 mA/cm².

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Recently, polymer solar cells have attracted a lot of attention for new generation renewable energy sources, because of their advantages of light weight, low fabrication cost, flexibility, and easy manufacturing [1–6]. Regioregular poly(3-hexylthiophene) (P3HT) and poly[2-methoxy-5-(3,7-dimethyloctyloxy)-p-pheny-lenevinylene] (MDMO-PPV) have been extensively studied in the past decade, promoting the efficiencies up to 3~5% [7,8]. However, the intrinsic light absorption of P3HT and MDMO-PPV limits the photovoltaic performance. At present, many research-ers have designed and developed new low-band-gap polymers and have enhanced the efficiencies up to 6–7% [9,10].

Polyfluorenes (PFs) are well known for polymer-light-emitting-diode (PLED) applications, due to their pure blue and efficient electroluminescence, combined with their high carrier mobility and thermal stability [11–14]. However, the blue shifted absorption range of PFs is less suitable for solar cell applications. To extend the optical absorption to longer wavelengths, the bandgaps of PFs can be reduced through copolymerization of donor–acceptor–donor (D–A–D) units. A regular alternation of donor and acceptor groups should lead to the broadening of the valence and conduction bands, and thus reduce the bandgaps [15–18]. Intramolecular D–A–D systems typi-cally consist of electron donating groups, and electron acceptors

[19–22]. The incorporation of D–A–D moieties in the backbone of a conjugated polymer can widen the absorption spectrum. After photoexcitation, the charge separation occurs through transfer of electrons from the main chains of the polymer to PCBM. Electrons can transfer at the PCBM by hopping, and holes can transfer at the main chains of the polymer by hopping and delocalization. Therefore, conjugated polymers containing D–A–D moieties not only exhibit enhanced charge transfer ability, but also absorb light more effec-tively [23].

In this paper, we report the synthesis of a new D–A–D monomer followed by a Stille polymerization reaction [24] to prepare a new low bandgap copolymer with a dioctylfluorene monomer. In the D–A–D monomer, 2,6-bis-(5-bromo-3-hexyl-thiophen-2-yl)- anthra-quinone (M1), the donor is the electron rich 3-hexylthiophene, and the acceptor is the electron deficient anthraquinone. The optical properties, electrochemical properties, and hole mobility of the synthesized copolymer (PFTTDIONE) and the performance of the solar cells based on PFTTDIONE were evaluated.

2. Experimental

2.1. Materials

2,6-Dibromo-anthraquinone, 3-hexylthiophene-2-boronic acid pinacol ester, 2,7-dibromo-9,9-dioctylfluorene, and 2,5-bis-(tri-butylstannyl)thiophene were obtained from Aldrich Chemicals.

Tetrakis(triphenylphosphine) palladium (Pd(PPh$_3$)$_4$), aliquat 336, and N-bromosuccinimide (NBS) were purchased from Acros Organics. Toluene, chloroform, o-dichlorobenzene, and ammonium hydroxide were obtained from TEDIA. PEDOT:PSS was purchased form Baytron. 6,6-Phenyl C$_{61}$-butyric acid methyl ester (PCBM) was obtained from FEM Technology Inc. All reagents were used as received.

2.2. Measurements and characterization

Hydrogen nuclear magnetic resonance (^{1}H-NMR) spectra were collected on a Brucker Advance 400 spectrometer. Molecular weight determination was obtained using a Waters GPC 2414 in tetrahydrofuran (THF) via a calibration curve of polystyrene standards. Thermal stability was analyzed using a TA Instrument Thermogravimetric Analyzer (TGA) Model 2050 at a heating rate of 10 °C/min under nitrogen. The glass transition temperature (T_g) was determined on a TA Instruments Model 2920 Differential Scanning Calorimeter (DSC) at a heating rate of 10 °C/min under nitrogen. Ultraviolet–visible (UV/vis) absorption spectra were recorded on a Hitachi U-2001 spectrophotometer. The electrochemical measurements of the copolymer were carried out on a potentiostat/galvanostat Autolab PGSTAT30 with a platinum electrode at a scan rate of 50 mV/s against Ag/AgCl reference electrode with nitrogen-saturated solution of 0.1 M tetra-butylammonium hexafluorophosphate (TBAPF) in acetonitrile. The polymer film electrode was prepared by first dissolving the copolymers in o-dichlorobenzene, and then drop-casting a film onto a glassy carbon disk electrode. The electrode was allowed to dry for 30 min at room temperature. Surface morphology of thin films images were obtained using atomic force microscopy (AFM, Veeco, model: Innova). External quantum efficiency (EQE) was measured using a EQE instrument (ENLI, model: QE-R). The light intensity at each wavelength was calibrated using a silicon diode with NIM or NIST-Traceable certification. The thickness of the polymer films were measured with a KLA-Tencor/AS-IQ new

Alpha-Step Profilometer. Hole mobility was investigated by fitting dark J–V curves to the space-charge-limited current (SCLC) model with a device structure of ITO/PEDOT:PSS/PFTTDIONE/Au, where the SCLC is described by

$$J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ is the hole mobility, V is the voltage drop across the device, and L is the thickness of the active layer [25].
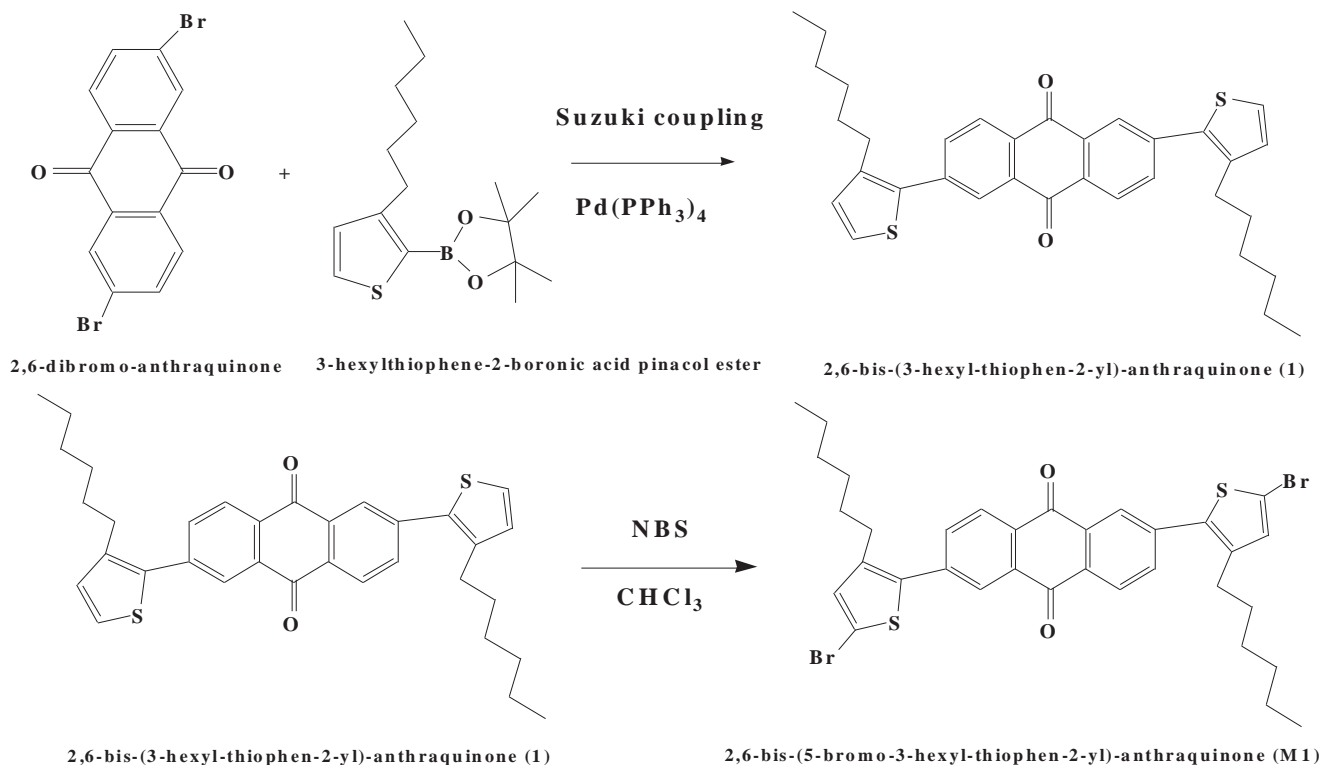
2.3. Synthesis

2.3.1. 2,6-bis-(3-hexyl-thiophen-2-yl)-anthraquinone (1)

The synthetic route is shown in Scheme 1. 3-hexylthiophene-2-boronic acid pinacol ester (1 g, 3.5 mmol) and 2,6-dibromo-anthraquinone (0.54 g, 1.5 mmol) were dissolved in 30 mL of toluene and purged under a nitrogen atmosphere for 30 min. Subsequently, Pd(PPh$_3$)$_4$ (10 mg, 0.0086 mmol), Aliquat 336 (several drops), and 2 M aqueous K$_2$CO$_3$ solution (20 mL) were added into a flask. The reaction mixture was stirred at 90 °C for 2 days. The precipitate was filtered and recrystallized from chloroform/methanol as a cosolvent. A bright yellow crystal was obtained, and the yield was 80%. ^{1}H-NMR (400 MHz, DMSO-d6, ppm):8.30 (d, 2H, J=8 Hz), 8.20 (d, 2H, J=1.2 Hz), 8.00 (q, 2H, J=8 Hz), 7.67 (d, 2H, J=5.2 Hz), 7.17 (d, 2H, J=5.2 Hz), 2.73 (t, 4H, J=7.6 Hz), 1.63 (m, 4H), 1.25 (m, 12H), 0.82 (t, 6H, J=6.4 Hz). Elemental analysis (%) calcd: C, 75.51; H, 6.71; S, 11.86; Found: C, 75.33; H, 6.62; S, 11.64.

2.3.2. 2,6-bis-(5-bromo-3-hexyl-thiophen-2-yl)-anthraquinone (M1)

The synthetic route is shown in Scheme 1. 2,6-bis-(3-hexyl-thiophen-2-yl)-anthraquinone (1) (0.7 g, 1.3 mmol) was dissolved in chloroform (60 mL) under nitrogen atmosphere, and then NBS (0.48 g, and 2.73 mmol) was added in one portion. The reaction mixture was stirred overnight at room temperature. The precipitate

Scheme 1. Synthesis of monomer.