Dyes and Pigments 120 (2015) 126–135

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

New D-A-D-A-D push–pull organic semiconductors with different benzo[1,2-b:4, 5-b′] dithiophene cores for solution processed bulk heterojunction solar cells

Kwangseok Do [a, 1], Nara Cho [a, 1], S.A. Siddiqui [c], Surya Prakash Singh [b], Ganesh D. Sharma [c, *], Jaejung Ko [a, **]

[a] *Department of Materials Chemistry, Korea University, 2511 Sejong-Ro, Sejong 339-700, Republic of Korea*
[b] *Inorganic & Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad 500607, India*
[c] *R & D Center for Engineering and Science, JEC Group of Colleges, Jaipur Engineering College Campus, Kukas, Jaipur, Raj., India*

ARTICLE INFO

Article history:
Received 16 February 2015
Received in revised form
6 April 2015
Accepted 8 April 2015
Available online 18 April 2015

Keywords:
Push–pull organic semiconductors
Bulk heterojunction organic solar cells
Power conversion efficiency
Solvent additives
Small molecules
Solution process

ABSTRACT

The synthesis and characterization of two D–A–D–A–D push–pull organic semiconductors based on either bis- (2-ethylhexyloxy) benzo [1,2-*b*:4,5-*b*′] dithiophene or bis- (triisopropylsilylethynyl) benzodithiophene electron rich core are described. The optical and electrochemical properties of these compounds indicate that these materials can absorb sunlight over a wide spectral range from 350 to 700 nm and exhibit suitable energy levels for efficient exciton dissociation. These small molecules were used as donor coupled with phenyl-C_{71}-butyric acid methyl ester acceptor for the fabrication of solution processed small molecule bulk heterojunction solar cells. The rigid and -conjugation of the silylacetylene substituted analog π-extended compared to the hexyloxy substituted analog facilitates intermolecular packing interactions of small π–π charge transfer and intermolecular molecule which induce a deep HOMO level, producing a high open circuit voltage of ~0.98 V. The achieved PCE was 5.69% when the active layer hexyloxy analog: phenyl-C_{71}-butyric acid methyl ester was processed with optimized 1-chloronaphathalene additive.

1. Introduction

Organic solar cells based on a solution processed bulk heterojunction (BHJ) active layer have been fabricated using inexpensive manufacturing processes such as roll-to-roll coating and achieving power conversion efficiencies (PCEs) that exceed 10% [1]. Significant research efforts have focused on BHJ organic solar cells (OSC) based on low bandgap polymer/fullerene blends [2] and on low bandgap semiconducting polymers composed of thieno [3,4-*b*] thiophene and benzodithiophene (poly(thieno[3,4-*b*]thiophene-alt-benzodi-thiophene) (PTB) BHJ OSCs fabricated using these materials with $PC_{60}BM$ or $PC_{70}BM$ have achieved remarkable PCEs of up to 9.2% [2d]. These low band gap polymers have potential applications in next generation solar cells and can be a viable alternative to inorganic solar cells and dye sensitized solar cells. However, polymer based materials can suffer from poor reproducibility of the weight average molecular weight, high polydispersity, and difficulties in purification.

Compared to conjugated polymers, small molecules can avoid the inherent batch-to-batch variations of physical properties because of their well defined chemical structure, therefore providing higher reproducibility [3]. OSC based on vacuum processed small molecule have achieved PCE of up to 12% using tandem structures [4]. Solution processed small molecules with different structures have been designed in recent years and applied as donors for the BHJ organic solar cells [5]. Some of these small molecules have shown PCEs comparable to those of conjugated polymers [6–8]. Recently, Liu et al. successfully demonstrated high-efficiency solution-processed single junction (PCE = 8.02%) and double junction tandem (PCE = 10.1%) OSCs based on a 2-D conjugated small molecule [9].

To improve the PCE of organic solar cells based on small molecule donors along with fullerene derivatives as acceptors, we have recently reported various organic semiconductors having

---

[*] Corresponding author.
[**] Corresponding author. Tel.: +82 44 860 1337; fax: +82 44 860 1331.
E-mail addresses: gdsharma273@gmail.com, sharmagd_in@yahoo.com (G.D. Sharma), jko@korea.ac.kr (J. Ko).
[1] Tel.: +82 44 860 1337; fax: +82 44 860 1331.

http://dx.doi.org/10.1016/j.dyepig.2015.04.012
0143-7208/© 2015 Elsevier Ltd. All rights reserved.

push–pull molecular skeletons composed of electron donating (D) groups bridged with electron accepting (A) groups via π-conjugated motifs, i.e. D–π–A for solution processed small molecule organic solar cells [10]. Among the various donor units used in the D–A copolymers, benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) is one of the most promising electron-donor units for applications in high-performance polymer semiconductors. Its large planar π-conjugated structure promotes facile π–π stacking and improves hole mobility [11]. Very recently, Chen et al. have reported highly efficient semiconducting small molecules containing a benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) unit, affording OSCs with PCEs of 8.02% and high fill factor (FF) [6c]. These molecular frameworks with BDT units exhibited a remarkable photovoltaic performance in PSCs and small molecule solar cells (SMOSCs) [12]. Therefore, we aimed to develop efficient small molecule organic semiconductors based on the BDT derivative, 3,6-bis(triisopropylsilylethynyl)-benzo[1,2-*b*:4,5-*b*′]dithiophene (TIPSBDT) [13], which is quite similar to the soluble and cystallizable 6,13-bis(triisopropylsilyl-ethynyl) anthracene (TIPSAnt) reported previously for use in SMOSCs [14]. We expect that the TIPS motif might extend π-conjugation and induce a rigid structure, producing a more electron rich BDT core that would facilitate the intermolecular charge transfer as well as molecular self networking. Recently, we have synthesized a series of A–D–A small molecules with TIPSBDT donor core and different acceptors indicating hexyl cyanoacetate, 3-ethylrhodanine, and 3-ethyl-2,4-thiazolidinedione, linked via an alkyl-substituted terthiophene π-conjugation bridge and applied as donors for SMOSCs and achieved a PCE of 5.48% [15].

In continuation to our research work on SMOSCs, herein, we report the synthesis, optical and electrochemical properties of two new planar small molecules **1** and **2** consisting of different donor core bis-(2-ethylhexyloxy) benzo [1,2-*b*:4,5-*b*′] dithiophene (OEtHxBDT) and bis-(triisopropylsilylethynyl) benzodithiophene) (TIPSBDT), respectively as a donor cores unit and same fluoro-benzothiadiazole ($FBTTh_2$) as the acceptor units. Due to their D–A–D–A–D structure, both of these small molecules exhibit efficient charge separation. These small molecules were used as the donor component along with the $PC_{71}BM$ as the acceptor for the fabrication of solution processed BHJ solar cells. The device based on **2**:$PC_{71}BM$ exhibits a high V_{oc} of ~0.98 V, that is attributed the deeper HOMO level of **2**. Moreover, the processing with additive 1-chloronaphthalene (CN) significantly affected the performance of devices based on **1**–**2**:$PC_{71}BM$, achieving a remarkable enhancement in short circuit current and fill factor. The device based on **2**:$PC_{71}BM$ (1:2 w/w) processed with CN additive exhibits a high PCE of 5.69%.

2. Experimental section

2.1. General methods

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma–Aldrich. (4,8-Bis(2-ethylhexyloxy) benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl)bis(trimethylstannane) (1) [16], 2,6-bis(trimethyltin)-4,8-bis(triisopropylsilylethynyl)-benzo[1,2-*b*:4,5-*b*′]dithiophene (2) [15] and 4-bromo-5-fluoro-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (3) [17] were synthesized using a modified procedure of previous references.

2.2. Spectroscopic measurements

^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer. Elemental analyses were performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. The absorption and photoluminescence spectra were recorded on a Perkin–Elmer Lambda 2S UV–Visible spectrometer and a Perkin LS fluorescence spectrometer, respectively. FT-IR spectra were obtained with a Nicolet Nexus 6700 spectrometer.

2.3. Electrochemical measurements

Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical System, Inc.). A three electrode system was used and consisted of non-aqueous reference electrode (0.1 M Ag/Ag^+ acetonitrile solution; MF-2062, Bioanalytical System, Inc.), platinum working electrode (MF-2013, Bioanalytical System, Inc.), and a platinum wire (diam. 1.0 mm, 99.9% trace metals basis, Sigma–Aldrich) as counter electrode. Redox potential of these materials was measured in CH_2Cl_2 with 0.1 M $(n\text{-}C_4H_9)_4N\text{-}PF_6$ with a scan rate between 50 mVs^{-1}(vs. Fc/Fc^+).

2.4. Synthesis of materials

2.4.1. (4,8-Bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl)bis(6-fluoro-4-(5′ hexyl-[2,2′-bithiophen]-5-yl)benzo[c][1,2,5] thiadiazole) (FBT-OEtHxBDT) (1)

Under N_2 atmosphere, a mixture of (4,8-bis(2-ethylhexyloxy) benzo[1,2-*b*:4,5-*b*′]dithiophene-2,6-diyl)bis(trimethylstannane) (**1**) (0.24 g, 0.311 mmol), 4-bromo-5-fluoro-7-(5′-hexyl-[2,2′-bithiophene]-5-yl)benzo[*c*][1,2,5]thiadiazole (**3**) (0.374 g, 0.777 mmol), and $Pd(PPh_3)_4$ (0.036 g, 0.031 mmol) in anhydrous toluene (80 mL) was stirred at 110 °C for 24 h. The mixture was cooled down to room temperature. Water was added and the resulting solution was extracted three times with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (dichloromethane/hexane = 1:2) in 56% yield. T_g = 138 °C (Figure S1, supplementary information). FTIR (KBr, cm^{-1}): 2800–3250 (C–H), 1628, 1580, 1556, 1532, 1492, 1428, 1396, 1300 (C–O), 1276–1244 (aromatic amine, C–N), 1204, 1132, 1092, 1020, 860, 812. (Figure S2, supplementary information). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (s, 2H), 8.06 (t, 4H, *J* = 5.4 Hz), 7.47 (d, 2H, *J* = 5.4 Hz), 7.18 (t, 2H, *J* = 3.6 Hz), 7.11 (t, 2H, *J* = 3.0 Hz), 4.28 (d, 4H, *J* = 5.4 Hz), 2.81 (t, 4H, *J* = 6.9 Hz), 1.85 (br m, 2H), 1.56 (br m, 8H), 1.31 (br m, 24H), 0.89 (m, 18H). Mass: m/Z = 1246.34 [M^+]. Calcd. $C_{66}H_{72}F_2N_4O_2S_8$: C, 63.53; H, 5.82; N, 4.49. Found: C, 63.22; H, 5.70; N, 4.37.

2.4.2. 4,8-Bis(triisopropylsilylethynyl)-benzo[1,2-b:4,5-b′] dithiophene-2,6-diyl)bis(6-fluoro-4-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole) (FBT-TIPSBDT) (2)

The product was obtained in 64% yield and was synthesized according to the procedure as described above for synthesis of **FBT-OEtHx**. T_g = 132 °C (Figure S1, supplementary information). FTIR (KBr, cm^{-1}): 2800–3250 (C–H), 2244 (C≡C), 1628, 1580, 1540, 1524, 1492, 1420, 1372, 1348, 1284–1244 (aromatic amine, C–N), 1132, 1100, 1052, 1020, 900, 860, 684. (Figure S2, supplementary information). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.98 (s, 2H), 8.94 (d, 4H, *J* = 6.3 Hz), 8.18 (s, 2H), 8.13 (d, 2H, *J* = 3.6 Hz), 7.69 (d, 2H, *J* = 3.6 Hz), 2.83 (t, 4H, *J* = 6.9 Hz), 1.55 (br m, 10H), 1.38 br (m, 12H), 0.95 (br m, 42H). Mass: m/Z = 1350.37 [M^+]. Calcd. $C_{72}H_{80}F_2N_4S_8Si_2$: C, 63.96; H, 5.96; N, 4.14. Found: C, 63.74; H, 5.85; N, 4.02.

2.5. Device fabrication and characterization

The BHJ films were prepared under optimized conditions according to the following procedure: The indium tin oxide (ITO)-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried